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PREFACE

In investigating the highly different phenomena in nature, scientists have always tried to find some fundamental principles that can explain the variety from a basic unity. Today they have not only shown that all the various kinds of matter are built up from a rather limited number of atoms, but also that these atoms are constituted of a few basic elements of building blocks. It seems possible to understand the innermost structure of matter and its behavior in terms of a few elementary particles: electrons, protons, neutrons, photons, etc., and their interactions. Since these particles obey not the laws of classical physics but the rules of modern quantum theory of wave mechanics established in 1925, there has developed a new field of "quantum science" which deals with the explanation of nature on this ground.

Quantum chemistry deals particularly with the electronic structure of atoms, molecules, and crystalline matter and describes it in terms of electronic wave patterns. It uses physical and chemical insight, sophisticated mathematics, and high-speed computers to solve the wave equations and achieve its results. Its goals are great, but perhaps the new field can better boast of its conceptual framework than of its numerical accomplishments. It provides a unification of the natural sciences that was previously inconceivable, and the modern development of cellular biology shows that the life sciences are now, in turn, using the same basis. "Quantum biology" is a new field which describes the life processes and the functioning of the cell on a molecular and submolecular level.

Quantum chemistry is hence a rapidly developing field which falls between the historically established areas of mathematics, physics, chemistry, and biology. As a result there is a wide diversity of backgrounds among those interested in quantum chemistry. Since the results of the research are reported in periodicals of many different types, it has become increasingly difficult for both the expert and the nonexpert to follow the rapid development in this new borderline area.

The purpose of this serial publication is to try to present a survey of the current development of quantum chemistry as it is seen by a number of the internationally leading research workers in various countries. The authors have been invited to give their personal points of view of the subject freely and without severe space limitations. No attempts have been made to avoid overlap—on the contrary, it has seemed desirable to have certain important research areas reviewed from different points of view. The response from the authors has been so encouraging that a fifteenth volume is now being prepared.

The Editor would like to thank the authors for their contributions which give an interesting picture of the current status of selected parts of quantum chemistry. The topics in this volume cover studies of the concept of atoms in molecules using modern catastrophe theory, over treatments of symmetry properties of reduced density matrices, and applications of group theoretical techniques to the many-electron problem, to the importance of Feshbach resonances in chemical reactions. Some of the articles emphasize studies in fundamental quantum theory and quantum statistics, and others applications to comparatively complicated systems.

It is our hope that the collection of surveys of various parts of quantum chemistry and its advances presented here will prove to be valuable and stimulating, not only to the active research workers but also to the scientists in neighboring fields of physics, chemistry, and biology who are turning to the elementary particles and their behavior to explain the details and innermost structure of their experimental phenomena.

PER-OLOV LÖWDIN

Symmetry Properties of Reduced Density Matrices

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I. Introduction

It is known (Coleman, 1963, 1965; Coulson, 1960; Davidson, 1976; Mestechkin, 1977) that using the approach of reduced density matrices (RDM) offers certain advantages over the usual language of wave functions, at least in calculating the averages of the physical relevant operators (see also Löwdin, 1955). First we define the transition RDM. Assume we are given two functions $\Psi_1 = \Psi_1(x_1, \ldots, x_N)$ and $\Psi_2 = \Psi_2(x_1, \ldots, x_N)$ normalized, e.g., to unity. Then the transition RDM of pth order (or p matrix) is defined as an integral operation with the kernel

$$\begin{aligned} D^p_{\Psi_1\Psi_2}&(x_1, \ldots, x_p; x_1', \ldots, x_p') \\ &= \int \Psi_1(x_1, \ldots, x_N)\Psi_2(x_1', \ldots, x_p', x_{p+1}, \ldots, x_N) \\ &\quad \times dx_{p+1} \ldots dx_N. \end{aligned} \tag{1}$$

In particular, if $\Psi_1 = \Psi_2 = \Psi$, Eq. (1) defines the RDM of pth order D^p_Ψ.

In general, the wave function Ψ that describes the state of a certain quantum mechanical system exactly or approximately possesses some symmetry properties, i.e., there exists a set of operators $\{\Lambda_i\}_1^m$ in the case of a continuous symmetry group and a set of elements $\{g_k\}_1^l$ generating the group G (a discrete case) such that

$$[P_\Psi, \Lambda_i] = 0, \quad i = 1, \ldots, m; \qquad [P_\Psi, g_k] = 0, \quad k = 1, \ldots; l;$$

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where $P_\Psi = |\Psi\rangle\langle\Psi|$. Then if $\{|\lambda_p^{(i)}\rangle\}$ is a complete orthonormalized set of eigenfunctions of the operator Λ_t, or $\{e_{rS}^{\alpha}; \alpha; r, S = 1, \ldots, f^\alpha\}$ (f^α is the dimension of the irreducible representation α) is the basis of primitive orthogonal idempotents of the group algebra of the group G, then the projector P_Ψ is decomposed into a direct sum of matrices $P_\Psi^{(\lambda_t^{(i)})}$ or $P_\Psi^{\alpha r}$:

$$P_\Psi = P_\Psi^{(\lambda_1^{(i)})} \oplus P_\Psi^{(\lambda_2^{(i)})} \oplus \cdots; \tag{2a}$$

$$P_\Psi = \sum_\alpha \sum_{r=1}^{f^\alpha} {}^{\oplus} P_\Psi^{\alpha r}. \tag{2b}$$

In the case when there exists a subset $\{\tilde{\Lambda}_t\} = \{\Lambda_t\}$ of mutually commutative operators, the structure of expansions (2a) and (2b) is markedly simplified.

In the RDM approach there naturally arises the problem of finding the integral of motion and discrete symmetries for the density matrix D_Ψ^p and their relation with the motion integrals for the wave function Ψ. This problem up to now has not been solved completely, which is natural. This problem is more general and profound than the so-called N-representability problem (Coleman, 1963), which consists of finding a complete set of characteristics of RDM arising from the contraction of either antisymmetric or symmetric wave functions. A more complex problem is to find the symmetry properties of the transition density matrices from the known symmetry properties of the wave functions that determine it. The RDM symmetry problems have been investigated in the articles by Bingel, Klein, Kutzelnigg, Löwdin, McWeeny, Mestechkin, Harriman, and others.

The known RDM symmetry allows one to simplify the calculation of matrix elements, to quasi-diagonalize a secular problem. Note that problems of the RDM symmetry properties were greatly simplified, since in most cases of calculating the matrix elements of the density matrix only its completely symmetric component. However, it is not always the case. For example, according to Kutzelnigg (McWeeny, 1969) the above statement depends also on the state and if the state is degenerated, then the RDM have significantly lower symmetry than the operator. So in general, the eigenfunctions of RDM possess mixed symmetry. It is important to note that the symmetry can be recovered in two ways: either by assembly averaging over all densities of a complete set of degenerated states or by averaging the density for a certain state over the whole symmetry group of a system. These procedures are absolutely equivalent and give the invariant part of RDM. It is only uncertain as to what procedure is the most useful. As McWeeny remarks (1969), however, the assembly averaging is more useful in applications and in proofs of general statements concerning the RDM properties of the degenerated states.

This review is devoted to the symmetry properties of RDM and their eigenfunctions, and to obtaining RDM-1 and RDM-2 for the projected wave functions. The main purpose of this article is to propose a unified rigorous approach to the study of the symmetry properties of RDM.

II. Spin Symmetry of Reduced Fermion Density Matrices

1.1. We consider the spin symmetry of the 1-matrix. $D^1{}_{\Psi_1\Psi_2}(x_1;\, x_1')$ $[x = (\mathbf{r},\, S)]$ can be formally represented as a matrix element of the operator $O_1 = O_1(x_i)$ acting only upon the variables $x_1 = (r_1,\, S_1)$:

$$\begin{aligned} D^1_{\Psi_1\Psi_2}(x_1;\, x_1') &= \langle \Psi_2 | O_1 | \Psi_1 \rangle \\ &= \int \Psi_2(y_1', y_2, \ldots, y_N) \\ &\quad \times O_1 \Psi_1(y_1, \ldots, y_N)\, dy_1 \cdots dy_N\, dy_1' . \end{aligned} \tag{1}$$

The operator $O_1(x_1)$ evidently replaces y_1 in Ψ_1 by x_1 and y_1 in $\bar{\Psi}_2$ by x_1', removing simultaneously integration over y_1. This operator can be formally represented as an integral operator with the delta-functional kernal (McWeeny, 1959, 1960; McWeeny and Mizuno, 1961)

$$O_1(x_1; x_1' | y_1; y_1') = \delta(x_1 - y_1)\, \overline{\delta(x_1' - y_1')}.$$

Then

$$\begin{aligned} O_1 \Psi(y_1, y_2, \ldots, y_N) &= \int O_1(x_1; x_1' | y_1; y_1') \Psi(y_1, y_2, \ldots, y_N) y_1 \\ &= \overline{\delta(x_1' - y_1')} \Psi(x_1, y_2, \ldots, y_N). \end{aligned}$$

The operator O_1 is factorized by the space and spin components

$$O_1 = O_1^R O_1^S. \tag{2}$$

Accordingly the kernel of this integral operator is also factorized:

$$\begin{aligned} O_1(x_1;\, x_1' | y_1;\, y_1') &= O_1^R(\mathbf{R}_1;\, \mathbf{R}_1' | \mathbf{r}_1;\, \mathbf{r}_1') O_1^S(S_1;\, S_1' | S_1;\, S_1'), \\ O_1^R(\mathbf{R}_1;\, \mathbf{R}_1' | \mathbf{r}_1;\, \mathbf{r}_1') &= \delta(\mathbf{R}_1 - \mathbf{r}_1)\, \overline{\delta(\mathbf{R}_1^! - \mathbf{r}_1')}, \\ O_1^S(S_1;\, S_1^1 | s_1;\, s_1') &= \delta(S_1 - s_1)\, \overline{\delta(S_1' - s_1')}\, ; \\ &\quad \times (\mathbf{R},\, S), \qquad y = (r,\, s). \end{aligned}$$

We express the spin operator O_1^S through the spin functions. Since any function of N independent variables can be represented in the form

$$\Psi(x_1, \ldots, x_N) = \Psi_\alpha(\mathbf{r}_1, x_2, \ldots, x_N)\alpha(S_1) + \Psi_\beta(\mathbf{r}_1, x_2, \ldots, x_N)\beta(S_1)$$

and

$$\begin{aligned} (\alpha\bar{\alpha})\Psi &= \alpha[\Psi_\alpha(\alpha|\alpha) + \Psi_\beta(\alpha|\beta)] = \Psi_\alpha \alpha, \\ (\beta\bar{\beta})\Psi &= \beta[\Psi_\alpha(\beta|\alpha) + \Psi_\beta(\beta|\beta)] = \Psi_\beta \beta, \end{aligned}$$

it follows that

$$\delta(S - s) = \alpha(S)\bar{\alpha}(s) + \beta(S)\bar{\beta}(s),$$

since $\alpha\bar{\alpha}$ and $\beta\bar{\beta}$ are the projection operators on the spin space formally written as the integral operators. Thus, the spin operator O_1^S can be written in the form

$$\begin{aligned} O_1^S(S_1;\, S_1'|s_1;\, s_1') = {} & \alpha(S_1)\bar{\alpha}(S_1')\bar{\alpha}(s_1)\alpha(s_1') + \alpha(S_1')\bar{\beta}(S_1')\bar{\alpha}(s_1)\beta(s_1') \\ & + \beta(S_1)\bar{\alpha}(S_1')\bar{\beta}(s_1)\alpha(s_1') + \beta(S_1)\bar{\beta}(S_1')\bar{\beta}(s_1)\beta(s_2'). \end{aligned} \tag{3}$$

Taking into account (2) and substituting (3) into (1), we obtain finally

$$\begin{aligned} D^1_{\Psi_1\Psi_2}(X_1;\, X_1') = {} & {}_1P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_1')\alpha(S_1)\bar{\alpha}(S_1') \\ & + {}_2P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_1')\alpha(S_1)\bar{\beta}(S_1') \\ & + {}_3P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_1')\beta(S_1)\bar{\alpha}(S_1') \\ & + {}_4P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_1')\beta(S_1)\bar{\beta}(S_1'), \end{aligned} \tag{4}$$

where

$$\begin{aligned} {}_1P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_1') = {} & \int \bar{\Psi}_2(x_1',\, x_2,\, \ldots,\, x_N)O_1^R\alpha(S_1')\bar{\alpha}(S_1)\Psi_1 \\ & \times (x_1,\, x_2,\, \ldots,\, x_N)\, dx_1'\, dx_1 \ldots dx_N; \\ {}_2P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_1') = {} & \int \bar{\Psi}_2(x_1',\, x_2,\, \ldots,\, x_N)O_1^R\beta(S_1')\bar{\alpha}(S_1)\Psi_1 \\ & \times (x_1,\, x_2,\, \ldots,\, x_N)\, dx_1'\, dx_1 \ldots dx_N; \\ {}_3P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_1') = {} & \int \bar{\Psi}_2(x_1',\, x_2,\, \ldots,\, x_N)O_1^R\alpha(S_1')\bar{\beta}(S_1)\bar{\Psi}_1 \\ & \times (x_1,\, x_2,\, \ldots,\, x_N)\, dx_1'\, dx_1 \ldots dx_N; \\ {}_4P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_1') = {} & \int \bar{\Psi}_2(x_1',\, x_2,\, \ldots,\, x_N)O_1^R\beta(S_1')\bar{\beta}(S_1)\Psi_1 \\ & \times (x_1,\, x_2,\, \ldots,\, x_N)\, dx_1'\, dx_1 \ldots dx_N. \end{aligned}$$

The functions ${}_1P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_2')$ and ${}_4P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_1')$ with $\mathbf{R}_1 = \mathbf{R}_1'$ have a simple physical interpretation, e.g.,

$${}_1P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1)\, d\mathbf{R}_1 = {}_1P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\, \mathbf{R}_1)\, d\mathbf{R}_1$$

is a probability of finding a particle in the volume $d\mathbf{R}_1$ near the point $\mathbf{R}_1$ with the spin α. ${}_4P^1{}_{\Psi_1\Psi_2}(\mathbf{R})$ has a similar meaning (McWeeny and Sutcliffe, 1969).

1.2.1. We now turn to considering the spin operators. Obviously the unit operator I has the form

$$I = \alpha\bar{\alpha} + \beta\bar{\beta}.$$

We define the following spin operators

$$S_0 = \tfrac{1}{2}(\alpha\bar{\alpha} - \beta\bar{\beta}),\ S_+ = \alpha\bar{\beta},\ S_- = \beta\bar{\alpha}.$$

These operators are irreducible tensor operators of the Ith rank (McWeeny, 1955, 1959; McWeeny and Mizuno, 1961). Then

$$\begin{aligned}
{}_1P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\mathbf{R}_1') &= \tfrac{1}{2}\,{}_0V^{(0)}{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\mathbf{R}_1') + {}_0V^{(1)}{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\mathbf{R}_1'),\\
{}_2P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\mathbf{R}_1') &= {}_1V^{(1)}{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\mathbf{R}_1'),\\
{}_3P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\mathbf{R}_1') &= {}_{-1}V^{(1)}{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\mathbf{R}_1'),\\
{}_4P^1{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\mathbf{R}_1) &= \tfrac{1}{2}\,{}_0V^{(0)}{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\mathbf{R}_1) - {}_0V^{(1)}{}_{\Psi_1\Psi_2}(\mathbf{R}_1;\mathbf{R}_1')
\end{aligned}$$

where

$$\begin{aligned}
{}_0V^{(0)}{}_{\Psi_1\Psi_2} &= \langle\Psi_2|O_1^R I|\Psi_1\rangle,\\
{}_kV^{(1)}{}_{\Psi_1\Psi_2} &= \langle\Psi_2|O_1^R S_k^1|\Psi_1\rangle,\\
k &= 0 \pm 1.
\end{aligned}$$

1.2.2. Assume Ψ_1 and Ψ_2 are the eigenfunctions of the operators $\mathbf{S}^2$ and S_z, i.e.,

$$\begin{aligned}
\mathbf{S}^2\Psi_1 &= S_1(S_1 + 1)\Psi_1,\\
\mathbf{S}^2\Psi_2 &= S_2(S_2 + 1)\Psi_2,\\
S_z\Psi_1 &= M_1\Psi_{1_0},\\
S_z\Psi_2 &= M_2\Psi_2.
\end{aligned}$$

Then, according to the Wigner–Eckart theorem (Kaplan, 1969; Warshalovich *et al.*, 1975) we have

$${}_0V^{(0)}_{\Psi_1\Psi_2} = (-1)^{S_2-M_2}\begin{pmatrix} S_2 & 0 & S_1\\ -M_2 & 0 & M_1\end{pmatrix}\langle\Psi_2\|O_1^R I^{(0)}\|\Psi_1\rangle, \tag{5a}$$

$${}_kV^{(1)}_{\Psi_1\Psi_2} = (-1)^{S_2-M_2}\begin{pmatrix} S_2 & 1 & S_1\\ -M_2 & k & M_1\end{pmatrix}\langle\Psi_2\|O_1^R S^{(1)}\|\Psi_1\rangle \tag{5b}$$

Taking into account that

$$\begin{pmatrix} S_2 & 0 & S_1\\ -M_2 & 0 & M_1\end{pmatrix} = (2S_1 + 1)^{-1/2}\delta_{S_1S_2}\delta_{M_1-M_2},$$

we obtain

$$V^{(0)}_{\Psi_1\Psi_2} = (-1)^{S_1-M_1}(2S_1 + 1)^{-1/2}\delta_{S_1S_2}\delta_{M_1-M_2}\langle\Psi_2\|O_1^R I^{(0)}\|I_1\rangle.$$

From the triangle rule for $3j$-symbols it follows that at the given S_1, S_2 takes values $S_2 = S_1$, $S_1 \pm 1$. Let us consider each of these cases (McWeeny, 1955, 1959, 1960)

(*i*) $S_1 = S_2 = S$.

We first introduce the following notations:

$$P^1_{\Psi_1\Psi_2}(\mathbf{R}_1; \mathbf{R}_1') = \int_{S_1=S_1'} D^1_{\Psi_1\Psi_2}(X_1; X_1')dS_1 = {}_1P^1_{\Psi_1\Psi_2} + {}_4P^1_{\Psi_1\Psi_2} = V_{\Psi_1\Psi_2}$$

is the spinless transition density matrix;

$$\begin{aligned} Q^1_{\Psi_1\Psi_2}(\mathbf{R}_1; \mathbf{R}_1') &= \int_{S_1=S_1'} S_0(1)D^1_{\Psi_1\Psi_2}(X_1; X_1')dS_1 \\ &= \tfrac{1}{2}[{}_1P^1_{\Psi_1\Psi_2} - {}_4P^1_{\Psi_1\Psi_2}] = {}_0V^{(1)}_{\Psi_1\Psi_2} \end{aligned}$$

is the spin transition density matrix.

$${}_1P^1_{\Psi_1\Psi_2} = (-1)^{S-M_2}\left\{\frac{1}{2(2S+1)^{1/2}}P^1_{\Psi_1\Psi_2} + \frac{M_2}{[S(S+1)]^{1/2}}Q^1_{\Psi_1\Psi_2}\right\}\delta_{M_1-M_2};$$

$${}_2P^1_{\Psi_1\Psi_2} = (-1)^{S-M_2}\delta_{M_1,-M_2+1}\left[\frac{(S+M_1)(S-M_1+1)}{2S(S+1)}\right]^{1/2}Q^1_{\Psi_1\Psi_2};$$

$${}_3P^1_{\Psi_1\Psi_2} = (-1)^{S-M_2}\delta_{M_1,-M_2-1}\left[\frac{(S-M_1-1)(S+M_1+1)}{2S(S+1)}\right]^{1/2}Q^1_{\Psi_1\Psi_2};$$

$${}_4P^1_{\Psi_1\Psi_2} = (-1)^{S-M_2}\delta_{M_1-M_2}\left\{\frac{1}{2(2S+1)^{1/2}}P^1_{\Psi_1\Psi_2} - \frac{M_1}{[S(S+1)]^{1/2}}Q^1_{\Psi_1\Psi_2}\right\};$$

(*ii*) $S_1 = S_2 + 1$.

$$\begin{aligned} {}_1P^1_{\Psi_1\Psi_2} &= (-1)^{S_2-M_2}\delta_{M_1,-M_2} \\ &\times\left\{\frac{1}{2(2S+1)^{1/2}}P^1_{\Psi_1\Psi_2} + \left[\frac{(S_1-M_1+1)(S_1+M_1+1)}{(2S_1+1)(S_1+1)}\right]^{1/2}Q^1_{\Psi_1\Psi_2}\right\}, \end{aligned}$$

$${}_2P^1_{\Psi_1\Psi_2} = (-1)^{S_2-M_2}\delta_{M_1,-M_2+1}\left[\frac{(S_1+M_1)(S_1+M_1+1)}{(2S_1+1)(2S_1+2)}\right]^{1/2}Q^1_{\Psi_1\Psi_2},$$

$${}_3P^1_{\Psi_1\Psi_2} = (-1)^{S_2-M_2}\delta_{M_1,-M_2-1}\left[\frac{(S_1-M_1)(S_1-M_1+1)}{(2S_1+1)(2S_1+2)}\right]^{1/2}Q^1_{\Psi_1\Psi_2},$$

$$\begin{aligned} {}_4P^1_{\Psi_1\Psi_2} &= (-1)^{S_2-M_2}\delta_{M_1-M_2} \\ &\times\left\{\frac{1}{2(2S_1+1)^{1/2}}P^1_{\Psi_1\Psi_2} - \left[\frac{(S_1-M_1+1)(S_1+M_1+1)}{(2S_1+1)(S_1+1)}\right]^{1/2}Q^1_{\Psi_1\Psi_2}\right\}; \end{aligned}$$

(*iii*) $S_1 = S_2 - 1$.

$$
\begin{aligned}
{}_1P^1_{\Psi_1\Psi_2} &= (-1)^{S_2-M_2}\delta_{M_1,-M_2} \\
&\quad \times \left\{ \frac{1}{2(2S_1+1)^{1/2}}\, P^1_{\Psi_1\Psi_2} - \left[\frac{(S_1-M_1)(S_1+M_1)}{S_1(2S_1+1)}\right]^{1/2} Q^1_{\Psi_1\Psi_2} \right\}, \\
{}_2P^1_{\Psi_1\Psi_2} &= (-1)^{S_2-M_2}\delta_{M_1,-M_2+1} \left[\frac{(S_1-M_1)(S_1-M_1+1)}{2S_1(2S_1+1)}\right]^{1/2} Q^1_{\Psi_1\Psi_2}, \\
{}_3P^1_{\Psi_1\Psi_2} &= (-1)^{S_2-M_2}\delta_{M_1,-M_2+1} \left[\frac{(S_1+M_1+1)(S_1+M_1)}{2S_1(2S_1+1)}\right]^{1/2} Q^1_{\Psi_1\Psi_2}, \\
{}_4P^1_{\Psi_1\Psi_2} &= (-1)^{S_2-M_2}\delta_{M_1,-M_2} \\
&\quad \times \left\{ \frac{1}{2(2S_1+1)^{1/2}}\, P^1_{\Psi_1\Psi_2} + \left[\frac{(S_1-M_1)(S_1+M_1)}{S_1(2S_1+1)}\right]^{1/2} Q^1_{\Psi_1\Psi_2} \right\}.
\end{aligned}
$$

1.2.3. Let $\Psi_1 = \Psi_2 = \Psi$, i.e., we investigate the spin symmetry of the I-matrix. Then

$$
{}_{1,4}P^1_\Psi = (-1)^{S-M} \left\{ \frac{1}{2(2S+1)^{1/2}}\, P^1_\Psi \pm \frac{M}{[S(S+1)^{1/2}}\, Q^1_\Psi \right\}
$$

and

$$
\begin{aligned}
D^1_\Psi(X_1; X_1') = (-1)^{S-M} \Bigg\{ & \frac{1}{2(2S+1)^{1/2}}\, P^1_\Psi(\mathbf{R}_1; \mathbf{R}_1') \Big[\bar{\alpha}(S_1)\alpha(S_1') \\
& + \beta(S_1)\bar{\beta}(S_1') + \frac{M}{[S(S+1)]^{1/2}}\, Q^1_\Psi(\mathbf{R}_1; \mathbf{R}_1') \\
& \times \Big[\alpha(S_1)\bar{\alpha}(S_1') - \beta(S_1)\bar{\beta}(S_1') \Big]\Big] \Bigg\}.
\end{aligned} \tag{7}
$$

If $M = 0$, then

$$
D^1_\Psi(X_1; X_1') = \frac{(-1)^S}{2(2S+1)^{1/2}}\, P^1_\Psi(\mathbf{R}_1; \mathbf{R}_1')[\alpha(S_1)\alpha(S_1') + \beta(S_1)\beta(S_1')]. \tag{8}
$$

Following McWeeny (1960) we rewrite (5b) in the form

$$
{}_mV^{(1)}_{\Psi_1\Psi_2}(k_1k_2|\mathbf{R}_1; \mathbf{R}_1') = (-1)^{S_2-M_2} \begin{pmatrix} S_2 & 1 & S_1 \\ -M_2 & k & M_1 \end{pmatrix} V^{1(0)}_{\Psi_1\Psi_2}(S_1; S_2|\mathbf{R}_1; \mathbf{R}_1'), \tag{9}
$$

where we introduce an explicit dependence ${}_kV^{(1)}_{\Psi_1\Psi_2}$ on $k_1 = (S_1, M_1)$ and $k_2 = (S_2, M_2)$. In order to determine the function in the right-hand side of the relation (9) we define "standard" state with $\bar{k}_1 = (S_1, S_1)$ and $\bar{k}_2 = (S_2, S_2)$, and $\bar{m} = S_2 - S_1$.

Then

$$ {}_{m}V^{(1)}_{\psi_1\psi_2}(k_1k_2|\mathbf{R}_1; \mathbf{R}'_1) = C_1(S_1M_1; S_2M_2)V^{1(S\dagger)}_{\psi_1\psi_2}(\bar{k}_1\bar{k}_2|\mathbf{R}_1; \mathbf{R}'_1). $$

So, the expression (9) can be rewritten in the form

$$ {}_{m}V^{(1)}_{\psi_1\psi_2}(k_1k_2|\mathbf{R}_1; \mathbf{R}'_1) = C_1(S_1M_1; S_2M_2)V^{1(S\dagger)}_{\psi_1\psi_2}(\bar{k}_1\bar{k}_2|\mathbf{R}_1; \mathbf{R}'_1), \tag{10} $$

where C_1 is a "normalized" $3j$-symbol

$$ C_1(S_1M_1; S_2M_2) = (-1)^{S_2-M_2}\begin{pmatrix} S_2 & 1 & S_1 \\ -M_2 & m & M_1 \end{pmatrix} \Big/ \begin{pmatrix} S_2 & 1 & S_1 \\ -S_2 & \bar{m} & S_1 \end{pmatrix}. $$

All nonvanishing coefficients $C_1(S_1M_1; S_2M_2)$ are given in Table I.

From (5a) it follows that the transition spinless density matrix $P^1_{\psi_1\psi_2} = \delta_{S_1S_2}\delta_{M_1M_2}P^{1(0)}_{\psi_1\psi_2}$, $P^{1(0)}_{\psi_1\psi_2}$ is independent of the spin projections M_1 and M_2.

1A.3. We consider the spin density matrix $Q^1_{\psi_1\psi_2}$ in more detail (6). In essence, it determines the density excess of electrons with upward spin as compared with the density of electrons with downward spin. The average value of the z-component of the spin moment in the state $k_1 = k_2 = (S, M)$ is equal to

$$ \langle k_1|S_0|k_1\rangle = \int Q^1_{k_1}(R_1; R_1)\,dR_1 = M. $$

Therefore the term "spin density" is justified.

The function

$$ \tilde{Q}_{\Psi_1}(\mathbf{R}_1) = M^{-1}Q^1_{\Psi_1,\Psi_1}(\mathbf{R}_1; \mathbf{R}_2) $$

is called a normalized spin density. A normalized spin density was first introduced by McConnell (1958). He obtained a general formula connecting the proton hyperfine splitting with the spin density and showed that the observed splittings depend mostly on diagonal elements of the spin density matrix and these splittings, in fact, can be used for the evaluation of the diagonal elements.

2.1. By analogy with the previous case we consider the second-order density matrix. The spin expansion of the density matrix is performed by means of the operator represented as a product of two multipliers, each of which is taken from the following sets: (*i*) $I(1)$, $S_+(1)$, $S_-(1)$, $S_0(1)$; (*ii*) $I(2)$, $S_+(2)$, $S_-(2)$, $S_0(2)$.

Since in the following we shall use the Wigner–Eckart theorem, we express these pair spin operators through the irreducible tensors. From nine components of the second-rank tensor $S_\alpha(1)S_\beta(2)$ (d, $\beta = \pm, 0$) we obtain the irreducible tensors of 0, 1, 2, ranks, namely, by analogy with (McWeeny, 1965):

TABLE I

Coefficients C_1

	$m = M_2 - M_1$		
S_2	1	0	-1
S_1	$-\left[\frac{(S_2 - M_2)(S_2 - M_2 + 1)}{2}\right]^{1/2} \frac{1}{S_2}$	$\frac{M_2^{1/2}}{S_2}$	$\left[\frac{(S_2 + M_2 + 1)(S_2 - M_2)}{2}\right]^{1/2} \frac{1}{S_2}$
$S_1 + 1$	$\left[\frac{(S_2 + M_2 - 1)(S_2 + M_2)}{2S_2(2S_2 - 1)}\right]^{1/2}$	$\left[\frac{(S_2 + M_2)(S_2 - M_2)}{S_2(2S_2 - 1)}\right]^{1/2}$	$\left[\frac{(S_2 - M_2 - 1)(S_2 - M_2)}{2S_2(2S_2 - 1)}\right]^{1/2}$
$S_1 - 1$	$\left[\frac{(S_2 - M_2 + 1)(S_2 - M_2 + 2)}{(2S_2 + 1)(2S_2 + 2)}\right]^{1/2}$	$-\left[\frac{(S_2 + M_2 + 1)(S_2 - M_2 + 1)}{(S_2 + 1)(2S_2 + 1)}\right]^{1/2}$	$\left[\frac{(S_2 + M_2 + 2)(S_2 + M_2 + 4)}{2(2S_2 + 1)(S_2 + 1)}\right]^{1/2}$

$$
\begin{aligned}
T_{0}^{(0)} &= (1/\sqrt{3})\{S_{+}(1)S_{-}(2) + S_{-}(1)S_{+}(2) - S_{0}(1)S_{0}(2)\},\\
T_{+1}^{(1)} &= (1/\sqrt{2})\{S_{+}(1)S_{0}(2) - S_{0}(1)S_{+}(2)\},\\
T_{0}^{(1)} &= (1/\sqrt{2})\{S_{+}(1)S_{0}(2) - S_{-}(1)S_{+}(2)\},\\
T_{-1}^{(1)} &= (1/\sqrt{2})\{S_{0}(1)S_{-}(2) - S_{-}(1)S_{0}(2)\},\\
T_{+2}^{(2)} &= S_{+}(1)S_{+}(2),\\
T_{+1}^{(2)} &= (1/\sqrt{2})\{S_{+}(1)S_{0}(2) + S_{0}(1)S_{+}(2)\},\\
T_{0}^{(2)} &= (1/\sqrt{2})\{S_{+}(1)S_{-}(2) + 2S_{0}(1)S_{0}(2) + S_{-}(1)S_{+}(2)\},\\
T_{-1}^{(2)} &= (1/\sqrt{2})\{S_{-}(1)S_{0}(2) + S_{0}(1)S_{-}(2)\},\\
T_{-2}^{(2)} &= S_{-}(1)S_{-}(2).
\end{aligned}
$$

Then the spin decomposition of the transition reduced density matrix of second order corresponding to the functions Ψ_1 and Ψ_2 takes the form:

$$
\begin{aligned}
&D^{2}_{\Psi_1\Psi_2}(\mathbf{r}_1, \mathbf{r}_2, S_1, S_2|\mathbf{r}'_1, \mathbf{r}'_2, S'_1, S_2)\\
&\quad = + P^{2}_{1}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\alpha(S_1)\bar{\alpha}(S'_1)\alpha(S_2)\bar{\alpha}(S'_2)\\
&\qquad + P^{2}_{2}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\alpha(S_1)\alpha(S_2)\bar{\alpha}(S'_1)\bar{\beta}(S'_2)\\
&\qquad + P^{2}_{3}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\alpha(S_1)\alpha(S_2)\bar{\beta}(S'_1)\bar{\alpha}(S'_2)\\
&\qquad + P^{2}_{4}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\alpha(S_1)\alpha(S_2)\bar{\beta}(S'_1)\bar{\beta}(S'_2)\\
&\qquad + P^{2}_{5}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\alpha(S_1)\beta(S_2)\bar{\alpha}(S'_1)\bar{\alpha}(S'_2)\\
&\qquad + P^{2}_{6}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\alpha(S_1)\beta(S_2)\bar{\alpha}(S'_1)\bar{\beta}(S'_2)\\
&\qquad + P^{2}_{7}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\alpha(S_1)\beta(S_2)\bar{\beta}(S'_1)\bar{\alpha}(S'_2)\\
&\qquad + P^{2}_{8}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\alpha(S_1)\beta(S_2)\bar{\beta}(S'_1)\bar{\beta}(S'_2)\\
&\qquad + P^{2}_{9}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\beta(S_1)\alpha(S_2)\bar{\alpha}(S'_1)\bar{\alpha}(S'_2)\\
&\qquad + P^{2}_{10}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\beta(S_1)\alpha(S_2)\bar{\alpha}(S'_1)\bar{\beta}(S'_2)\\
&\qquad + P^{2}_{11}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\beta(S_1)\alpha(S_2)\bar{\beta}(S'_1)\bar{\alpha}(S'_2)\\
&\qquad + P^{2}_{12}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\beta(S_1)\alpha(S_2)\bar{\beta}(S'_1)\bar{\beta}(S'_2)\\
&\qquad + P^{2}_{13}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\beta(S_1)\beta(S_2)\bar{\alpha}(S'_1)\bar{\alpha}(S'_2)\\
&\qquad + P^{2}_{14}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\beta(S_1)\beta(S_2)\bar{\alpha}(S'_1)\bar{\beta}(S'_2)\\
&\qquad + P^{2}_{15}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\beta(S_1)\beta(S_2)\bar{\beta}(S'_1)\bar{\alpha}(S'_2)\\
&\qquad + P^{2}_{16}(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)\beta(S_1)\beta(S_2)\bar{\beta}(S'_1)\bar{\beta}(S'_2),
\end{aligned}
$$

where

$$\begin{aligned}
P^2_1 &= \tfrac{1}{4}U_0 + \tfrac{1}{2}[X_{0(1)} + X_{0(2)}] + (1/\sqrt{3})(\sqrt{2}W^{(2)}_0 - Y^{(0)}_0),\\
P^2_2 &= \tfrac{1}{2}X_{+(2)} + (1/\sqrt{2})(W^{(2)}_{+1} - V^{(1)}_{+1}),\\
P^2_3 &= \tfrac{1}{2}X_{+(1)} + (1/\sqrt{2})(W^{(2)}_{+1} + V^{(1)}_{+1}), \qquad P^2_4 = W^{(2)}_{+2},\\
P^2_5 &= \tfrac{1}{2}X_{-(2)} + (1/\sqrt{2})(W^{(2)}_{-1} + V^{(1)}_{-1}),\\
P^2_6 &= \tfrac{1}{4}U_0 + \tfrac{1}{2}[X_{0(1)} - X_{0(2)}] - (1/\sqrt{3})(\sqrt{2}W^{(2)}_0 - Y^{(0)}_0),\\
P^2_7 &= (1/\sqrt{3})Y^{(0)}_0 + (1/\sqrt{6})W^{(2)} + (1/\sqrt{2})V^{(1)}_0,\\
P^2_8 &= \tfrac{1}{2}X_{+(1)} - (1/\sqrt{2})(W^{(2)}_{+1} + V^{(1)}_{+1}),\\
P^2_9 &= \tfrac{1}{2}X_{-(1)} + (1/\sqrt{2})(W^{(2)}_{-1} - V^{(1)}_{-1}),\\
P^2_{10} &= (1/\sqrt{3})Y^{(0)}_0 + (1/\sqrt{6})W^{(2)}_0 - (1/\sqrt{2})V^{(1)}_0,\\
P^2_{11} &= \tfrac{1}{4}U_0 + \tfrac{1}{2}[X_{0(2)} - X_{0(1)}] - (1/\sqrt{3})(\sqrt{2}W^{(2)}_0 - Y^{(0)}_0),\\
P^2_{12} &= \tfrac{1}{2}X_{+(2)} - (1/\sqrt{2})(W^{(2)}_{+1} - V^{(1)}_{+1}), \qquad P^2_{13} = W^{(2)}_{-2},\\
P^2_{14} &= \tfrac{1}{2}X_{-(2)} - (1/\sqrt{2})(W^{(2)}_{-1} - V^{(1)}_{-1}),\\
P^2_{15} &= \tfrac{1}{2}X_{-(2)} - (1/\sqrt{2})(W^{(2)}_{-1} + V^{(1)}_{-1}),\\
P^2_{16} &= \tfrac{1}{4}U_0 - \tfrac{1}{2}[X_{0(1)} + X_{0(2)}] + (1/\sqrt{3})(\sqrt{2}W^{(2)}_0 - Y^{(0)}_0),
\end{aligned}$$

with the following notations

$$\begin{aligned}
U_0 &= \langle \Psi_2 | O^R_2 I(1) I(2) | \Psi_1 \rangle;\\
Y^{(0)}_0 &= \langle \Psi_2 | O^R_2 T^{(0)}_0 | \Psi_1 \rangle;\\
X_{i(k)} &= \langle \Psi_2 | O^R_2 S_{i(k)} | \Psi_1 \rangle; \qquad k = 1, 2; \quad i = \pm 1, 0;\\
V^{(1)}_m &= \langle \Psi_2 | O^R_2 T^{(1)}_m | \Psi_1 \rangle, \qquad m = \pm 1, 0;\\
W^{(2)}_n &= \langle \Psi_2 | O^R_2 T^{(2)}_n | \Psi_1 \rangle, \qquad n = \pm 2, \pm 1, 0.
\end{aligned}$$

The functions $U_0, \ldots, W^{(2)}_{-2}$ are not independent. They satisfy certain relations that follow from the antisymmetry of the 2-matrix on each pair of variables, namely[1]

$$\begin{aligned}
P^2_1(2, 1; 1', 2') &= -\, P^2_1(1, 2; 1', 2') = P^2_1(1, 2; 2', 1'),\\
P^2_2(1, 2; 2', 1') &= -\, P^2_3(1, 2; 1', 2'),\\
P^2_4(2, 1; 1', 2') &= -\, P^2_4(1, 2; 1', 2') = P^2_4(1, 2; 2', 1'),\\
P^2_5(2, 1; 1', 2') &= -\, P^2_9(1, 2; 1', 2'),
\end{aligned}$$

---

[1] For brevity, owing to uniqueness the coordinate vectors are omitted and only the corresponding indices are given.

$$\begin{aligned}
P^2_6(2, 1; 1', 2') &= -\ P^2_{10}(1, 2; 1', 2'),\\
P^2_5(1, 2; 2', 1) &= -\ P^2_5(1, 2; 1', 2'),\\
P^2_7(2, 1; 1', 2') &= -\ P^2_{11}(1, 2; 1', 2'),\\
P^2_6(1, 2; 2', 1) &= -\ P^2_7(1, 2; 1', 2'),\\
P^2_8(2, 1; 1', 2') &= -\ P^2_{12}(1, 2; 1', 2'),\\
P^2_8(1, 2; 2', 1) &= -\ P^2_8(1, 2; 1', 2'),\\
P^2_9(1, 2; 2', 1') &= -\ P^2_9(1, 2; 1', 2'),\\
P^2_{10}(1, 2; 2', 1) &= -\ P^2_{11}(1, 2; 1', 2'),\\
P^2_{12}(1, 2; 2', 1) &= -\ P^2_{12}(1, 2; 1', 2'),\\
P^2_{13}(2, 1; 1', 2') &= -\ P^2_{13}(1, 2; 1', 2') = P^2_{13}(1, 2; 2', 1'),\\
P^2_{14}(2, 1; 1', 2') &= -\ P^2_{14}(1, 2; 1', 2'),\\
P^2_{14}(1, 2; 2', 1) &= -\ P^2_{15}(1, 2; 1', 2'),\\
P^2_{15}(2, 1; 1', 2') &= -\ P^2_{15}(1, 2; 1', 2'),\\
P^2_{16}(2, 1; 1', 2') &= -\ P^2_{16}(1, 2; 1', 2') = P^2_{16}(1, 2; 1', 2').
\end{aligned}$$

The 2-matrix diagonal elements have a simple physical meaning. The term $P^2_1(1, 2; 1, 2)$ contributes to the function D^2 from two electrons at the points $\mathbf{r}_1$ and $\mathbf{r}_2$ when both of them have the spin α; similarly $P^2_6(1, 2; 1, 2)$ contributes from electrons at the points $\mathbf{r}_1$ and $\mathbf{r}_2$ with the spin α and β, respectively. Hence, the components $P^2_1(1, 2; 1, 2)$, $P^2_6(1, 2; 1, 2)$, $P^2_{11}(1, 2; 1, 2)$ and $P^2_{16}(1, 2; 1, 2)$ have a probable character, namely, they determine the probability of simultaneously finding the electrons with the spins $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, $\beta\beta$, respectively, at the two points $\mathbf{r}_1$ and $\mathbf{r}_2$.

2.2.1. Assume the functions Ψ_1 and Ψ_2 are eigenfunctions of the total spin operator $\mathbf{S}^2$ and the spin projection S_z with the eigenvalues S_1, M_1, S_2, M_2, respectively.

Then, according to the Wigner–Eckart theorem we have

$$\begin{aligned}
U_0 &= (-1)^{S_2-M_2}(2S_1 + 1)^{-1/2}\delta_{S_1S_2}\delta_{M_1-M_2}\langle\Psi_2\|O^R_2\|\Psi_1\rangle,\\
Y^{(0)}_0 &= (-1)^{S_2-M_2}(2S_1 + 1)^{-1/2}\delta_{S_1S_2}\delta_{M_1-M_2}\langle\Psi_2\|O^R_2T^{(0)}\|\Psi_1\rangle,\\
X_{i(k)} &= (-1)^{S_2-M_2}\begin{pmatrix} S_2 & 1 & S_1\\ -M_2 & i & M_1\end{pmatrix}\langle\Psi_2\|O^R_2S^1(k)\|\Psi_1\rangle,
\end{aligned}$$

$$V_m^{(1)} = (-1)^{S_2-M_2}\begin{pmatrix} S_2 & 1 & S_1 \\ -M_2 & m & M_1 \end{pmatrix}\langle\Psi_2\|O_2^R T^{(1)}\|\Psi_1\rangle,$$

$$W_n^{(2)} = (-1)^{S_2-M_2}\begin{pmatrix} S_2 & 2 & S_1 \\ -M_2 & n & M_1 \end{pmatrix}\langle\Psi_2\|O_2^R T^{(2)}\|\Psi_1\rangle,$$

2.2.2. Consider some components of the 2-matrix D_Ψ^2. In calculating the matrix elements of two-electron operators whose spin part depends only on the spin of one electron there appears the so-called "spin–orbital coupling function," which is defined as follows (McWeeny and Sutcliffe, 1969):

$$D_{\mathrm{SL}}^2(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2')_m = \int_{\substack{S_1'=S_1 \\ S_2'=S_2}} S_m(1)D^2{}_{\Psi_1\Psi_2}(x_1, x_2; x_1', x_2')\, dS_1\, dS_2. \tag{12}$$

If Ψ_1 and Ψ_2 are the eigenfunctions $\mathbf{S}^2$ and S_z with the corresponding values (S_1, M_1) and (S_2, M_2), then introducing a "standard state" similar to that in Section II.I we have

$$\begin{aligned} &D_{\mathrm{SL}}^2(S_1, S_2; M_1, M_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2')_m \\ &\quad = C_1(S_1, M_1; S_2, M_2)D_{\mathrm{SL}}^2(S_1, S_2; S_1, S_2)|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2')_m \end{aligned}$$

The reason for this name of the term D_{SL}^2 will be explained in what follows (Section III). The function D_{SL}^2 has a very interesting physical interpretation. Substituting $m = 0$ into (12) and taking into account (II) we easily obtain[2]

$$D_{\mathrm{SL}}^2(\Psi_1, \Psi_2|\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2') = \tfrac{1}{2}[P_1^2(\alpha\alpha) + P_6^2(\alpha\beta) - P_n^2(\beta\alpha) - P_k^2(\beta\beta)]$$

i.e., D_{SL}^2 (its diagonal element) determines the abundance of the probability of finding the electron with the spin α at the point $\mathbf{r}_1$ as compared with the same probability for the spin β for the second electron at the point $\mathbf{r}_2$. Therefore, this component is just called "conditional" function also (McWeeny and Sutcliffe, 1969).

Similarly in calculating the matrix elements of two-particle operators with a spin–spin interaction, a "spin–spin function" appears:

$$D_{\mathrm{SS}}^2(\Psi_1, \Psi_2|r_1, r_2; r_1', r_2')_m^{(k)} = \int_{\substack{S_1'=S_1 \\ S_2'=S_2}} T_m^{(k)} D_{\Psi_1\Psi_2}^2(x_1, x_2; x_1', x_2')\, dS_1\, dS_2. \tag{13}$$

---

[2] In the argument P_1^2 the spin variables $\sigma(S_1)\bar{\sigma}(S_2)\sigma(S_1')\sigma(S_2')$ are indicated by $(\sigma\sigma)$. With the above variables P_1^2 enters (11) as a multiplier.

Then in the standard notation

$$D^2_{\mathrm{SS}}(S_1S_2;\, M_1M_2|\mathbf{r}_2,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')^{(k)}_m$$
$$= C_2(S_1M_1;\, S_2M_2)D^2_{\mathrm{SS}}(S_1S_2,\, S_1S_2|\mathbf{r}_1,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')^{(k)}_m,$$

where the values of $C_2(S_1M_1;\, S_2M_2)$ are given in Table II. The physical interpretation of this function is of some interest. The irreducible tensor operator $T^{(0)}_0$ of the zeroth rank has the form $T^{(0)}_0 = (1/\sqrt{3})[\mathbf{S}(1)\mathbf{S}(2) - 3S_0(1)S_0(2)]$. Then in the case $\Psi_1 = \Psi_2 = |SM\rangle$ we have

$$\langle SM|\sum_{ij}{}' S(ij)|SM\rangle = -\sqrt{3}\int D^2_{\mathrm{SS}}(SM|\mathbf{r}_1\mathbf{r}_2)^{(0)}_0 d\mathbf{r}_1\, d\mathbf{r}_2, \tag{14}$$

where $S(ij) = S_{i0}S_{j0} - \frac{1}{3}\mathbf{S}(i)\mathbf{S}(j)$.

The left-hand side of formula (14) is the average of the operator of an anisotropy of the electron spin pair, which is summarized over all different pairs in the state $|SM\rangle$ and, consequently, is equal to $\frac{1}{2}[M^2 - \frac{1}{3}S(S+1)]$. The right-hand side represents a diagonal element of the spin–spin coupling function, which is integrated over all positions of two elements of the volume and, thereby, defines the density of the anisotropy of the spin–spin coupling (McWeeny, 1961).

2.3. Consider the case $\Psi = \Psi_1 = \Psi_2 = |SM\rangle$ in detail. Since Ψ is the eigenfunction of S_z, because of the orthogonality of the spin functions with different projections on the axis z we have

$$X_{i(k)} = 0,\ i = \pm,\ k = 1, 2;\ V^{(1)}_m = 0,\ m \equiv \pm 1;\ W^{(2)}_n = 0,\ n = \pm 2, \pm 1.$$

Therefore, $P^2_2 = P^2_3 = P^2_4 = P^2_5 = P^2_8 = P^2_9 = P^2_{12} = P^2_{13} = P^2_{14} = P^2_{15} = 0$ in the expansion (11) D^2_Ψ only 6 components with spins $\alpha\bar\alpha\alpha\bar\alpha$, $\alpha\bar\alpha\beta\bar\beta$, $\alpha\bar\beta\beta\bar\alpha$, $\beta\bar\alpha\alpha\bar\beta$, $\beta\bar\beta\alpha\bar\alpha$, and $\beta\bar\beta\beta\bar\beta$ out of 16 do not vanish. Since the density matrix is antisymmetric, all the coordinate parts with the spin components $\alpha\bar\alpha\beta\bar\beta$, $\alpha\bar\beta\beta\bar\alpha$, $\beta\bar\alpha\alpha\beta$, and $\beta\bar\beta\alpha\bar\alpha$ can be expressed by one of them, say, P^2_6. Thus, we finally obtain

$$\begin{aligned} &D^2_\Psi(\mathbf{r}_1,\, \mathbf{r}_2;\, S_1,\, S_2|\mathbf{r}_1',\, \mathbf{r}_2';\, S_1',\, S_2') \\ &\quad = +\, P^2_1(\Psi|\mathbf{r}_1,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')\alpha(S_1)\alpha(S_2)\bar\alpha(S_1')\bar\alpha(S_2') \\ &\quad\quad + (1 - P_{12})P^2_6(\Psi|\mathbf{r}_1,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')\alpha(S_1)\beta(S_2)\bar\alpha(S_1')\bar\beta(S_2')(1 - P_{1'2'}) \\ &\quad\quad + P^2_{16}(\Psi|\mathbf{r}_1,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')\beta(S_1)\beta(S_2)\bar\beta(S_1')\bar\beta(S_2') \end{aligned} \tag{15}$$

or

$$\begin{aligned} D^2_\Psi(\mathbf{r}_1,\, \mathbf{r}_2;\, S_1,\, S_2|\mathbf{r}_1',\, \mathbf{r}_2';\, S_1',\, S_2') &= R(\mathbf{r}_1,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')I(1)I(2) \\ &\quad + Q_1(\mathbf{r}_1,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')I(1)S_0(2) + Q_2(\mathbf{r}_1,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')S_0(1)I(2) \\ &\quad + 3Q^{(1)}_a(\mathbf{r}_1,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')S_0(1)S_0(2) \\ &\quad + \tfrac{1}{2}Q^{(2)}_a(\mathbf{r}_1,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')[S_+(1)S_-(2) + S_-(1)S_+(2)] \\ &\quad + Q(\mathbf{r}_1,\, \mathbf{r}_2;\, \mathbf{r}_1',\, \mathbf{r}_2')[S_+(1)S_-(2) - S_-(1)S_+(2)], \end{aligned} \tag{16}$$

TABLE II

COEFFICIENTS C_2

S_2	$m = M_1 - M_2$	$C_2(S_1M_1;\ S_2M_2)$	
$S_1 + 2$	± 2	$[(S_2 \pm M_2 - 3)(S_2 \pm M_2 - 2)(S_2 \pm M_2 - 1)(S_2 \pm M_2)]^{1/2}$	$\times\ [(2S_2 - 3)(2S_2 - 2)(2S_2 - 1)2S_2]^{-1/2}$
	± 1	$[2(S_2 \pm M_2 - 2)(S_2 \pm M_2 - 1)(S_2 \pm M_2)(S_2 \mp M_2)]^{1/2}$	
	0	$[3(S_2 + M_2 - 1)(S_2 + M_2)(S_2 - M_2 - 1)(S_2 - M_2)]^{1/2}$	
$S_1 + 1$	± 2	$\mp [(S_2 \pm M_2 - 2)(S_2 \pm M_2 - 1)(S_2 \pm M_2)(S_2 \mp M_2 + 1)]^{1/2}$	$\times\ [2S_2(2S_2 - 1)]^{-1}$
	± 1	$\mp(S_2 \mp 2M_2 + 1)[(S_2 \pm M_2 - 1)(S_2 \pm M_2)]^{1/2}$	
	0	$M_2[6(S_2 + M_2)(S_2 - M_2)]^{1/2}$	
S_1	± 2	$[3(S_2 \pm M_2)(S_2 \pm M_2 - 1)(S_2 \mp M_2 + 1)(S_2 \mp M_2 + 2)]^{1/2}$	$\times\ [\sqrt{2}S_2(2S_2 - 1)]^{-1}$
	± 1	$(1 \mp 2M_2)[3(S_2 \pm M_2)(S_2 \mp M_2 + 1)]^{1/2}$	
	0	$\sqrt{2}[3M_2^2 - S_2(S_2 + 1)]$	
$S_1 - 1$	± 2	$\mp [(S_2 \pm M_2)(S_2 \mp M_2 - 1)(S_2 \mp M_2 + 2)(S_2 \mp M_2 + 3)]^{1/2}$	$\times\ [2(S_2 + 1)(2S_2 + 1)]^{-1}$
	± 1	$\pm (S_2 \pm M_2)[(S_2 \mp M_2 + 1)(S_2 \mp M_2 + 2)]^{1/2}$	
	0	$- M_2[6(S_2 + M_2 + 1)(S_2 - M_2 + 1)]^{1/2}$	
$S_1 - 2$	± 2	$[(S_2 \mp M_2 + 1)(S_2 \mp M_2 + 2)(S_2 \mp M_2 + 3)(S_2 \mp M_2 + 4)]^{1/2}$	$\times\ [(2S_2 + 1)(2S_2 + 2)(2S_2 + 3)(2S_2 + 4)]^{-1/2}$
	± 1	$- [2(S_2 \pm M_2 + 1)(S_2 \mp M_2 + 1)(S_2 \mp M_2 + 2)(S_2 \mp M_2 + 3)]^{1/2}$	
	0	$[6(S_2 + M_2 + 1)(S_2 + M_2 + 2)(S_2 - M_2 + 1)(S_2 - M_2 + 2)]^{1/2}$	

where

$$\begin{aligned} R &= \tfrac{1}{2}(P_1^2 + P_{16}^2) - \tfrac{1}{4}(P_6^2 P_{1'2'} + P_{12} P_6^2), \\ Q_1 &= \tfrac{1}{2}(P_1^2 - P_{16}^2) - \tfrac{1}{2}(P_6^2 - P_{12} P_6^2 P_{1'2'}^2), \\ Q_2 &= \tfrac{1}{2}(P_1^2 - P_{16}^2) + \tfrac{1}{2}(P_6^2 - P_{12} P_6^2 P_{1'2'}), \\ Q_a^{(1)} &= P_1^2 + P_{16}^2 - P_6^2 - P_{12} P_6^2 P_{1'2'}, \\ Q_a^{(2)} &= -P_6^2 P_{1'2'} - P_{12} P_6^2, \qquad Q_a = -\tfrac{1}{2}(P_6^2 P_{1'2'} + P_{12} P_6^2). \end{aligned} \tag{17}$$

The above formulas give a complete solution of the 2-matrix spin decomposition problem. The following should be noted. Sometimes it is convenient to choose spin functions in another way, i.e., to pass to an equivalent set of irreducible tensor operators. In particular, one such way was proposed by Kutzelnigg. Let us introduce four possible types of spin functions (Kutzelnigg, 1963, 1964):

$$\begin{aligned} a(1,2) &= \alpha(1)\alpha(2), & c(1,2) &= (1/\sqrt{2})[\alpha(1)\beta(2) + \beta(1)\alpha(2)], \\ b(1,2) &= \beta(1)\beta(2), & d(1,2) &= (1/\sqrt{2})[\alpha(1)\beta(2) - \beta(1)\alpha(2)]. \end{aligned} \tag{18}$$

Then formula (15) for D_Ψ^2 will be rewritten as follows:

$$\begin{aligned} D_\Psi^2 = {} & P_{2\Psi}^{aa} a(1,2)\bar{a}(1',2') + P_{2\Psi}^{bb} b(1,2)\bar{b}(1',2') \\ & + P_{2\Psi}^{cc} c(1,2)\bar{c}(1',2') + P_{2\Psi}^{dd} d(1,2)\bar{d}(1',2') \\ & + P_{2\Psi}^{cd} c(1,2)\bar{d}(1',2') + P_{2\Psi}^{dc} d(1,2)\bar{c}(1',2'). \end{aligned} \tag{19}$$

with

$$\begin{aligned} P_2^{cc} &= \tfrac{1}{2}[P_6^2 - P_6^2 P_{1'2'} - P_{12} P_6^2 + P_{12} P_6^2 P_{1'2'}], \\ P_2^{dd} &= \tfrac{1}{2}[P_6^2 + P_6^2 P_{1'2'} + P_{12} P_6^2 + P_{12} P_6^2 P_{1'2'}], \\ P_2^{cd} &= \tfrac{1}{2}[P_6^2 + P_6^2 P_{1'2'} - P_{12} P_6^2 - P_{12} P_6^2 P_{1'2'}], \\ P_2^{dc} &= \tfrac{1}{2}[P_6^2 + P_6^2 P_{1'2'} + P_{12} P_6^2 - P_{12} P_6^2 P_{1'2'}]. \end{aligned} \tag{20}$$

At $M = 0$, $P_6^2 = P_{11}^2$ and $P_7^2 = P_{10}^2$, i.e., $P_{2\Psi}^{cd} = P_{2\Psi}^{dc} = 0$ and $P_{2\Psi}^{aa} = P_{2\Psi}^{bb}$. Note that the interesting applications of the factorization of D_Ψ^2 with $M = 0$ were obtained by Wienhold and Wilson (1967).

Finally, if $S = M = 0$, then because of the triangle rule for $3j$-symbols $W_0^{(2)} = Y_0^{(0)} = 0$ and

$$P_{2\Psi}^{aa} = P_{2\Psi}^{bb} = P_{2\Psi}^{cc}, \qquad D_\Psi^2 = P_{\mathrm{t}}(a\bar{a} + b\bar{b} + c\bar{c}) + P_{\mathrm{s}} d\bar{d}. \tag{21}$$

Kutzelnigg's choice (21) is of interest. The coordinate parts of the 2-matrix D_Ψ^2 are the singlet P_{s}^2 and the triplet P_{t}^2 spinless density matrices:

$$\begin{aligned} P_{\mathrm{s}}^2(1,2;1',2') &= \tfrac{1}{2}[\tilde{U}_0(1,2;1',2') + \tilde{U}_0(2,1;1',2')], \\ P_{\mathrm{t}}^2(1,2;1'\,2') &= \tfrac{1}{2}[\tilde{U}_0(1,2;1',2') - \tilde{U}_0(2,1;1',2')], \end{aligned}$$

where

$$\tilde{U}_0 = P_6^2 + P_{12}P_6^2P_{1'2'}.$$

Hence there directly follows the symmetry of P_s^2 and the antisymmetry of P_t^2 relative to the permutations P_{12} and $P_{1'2'}$.

We have considered the spin symmetry of RDM. The applications of the spin symmetry in calculating the matrix elements of the physical operators will be given in Section III. The spin decomposition of the 2-matrix is used for an investigation of the Fermi and Coulomb correlations (McWeeny, 1961; McWeeny and Sutcliffe, 1969), the intermolecular interactions (Dacre and McWeeny, 1970), in constructing the chemical bonding theory (Davidson, 1972, 1976), etc. The 1-matrix or any of its spin component, e.g., the spin density, can be considered as a kernel of a certain integral operator and, therefore, it can be expanded in a complete set of orbitals, e.g., atomic ones. The diagonal and nondiagonal elements of coefficient matrix are called orbital and overlap populations for the whole 1-matrix (McWeeny and Sutcliffe, 1969) and orbital and overlap spin populations (McWeeny, 1960; McWeeny and Sutcliffe, 1969) for the spin density, which allows one to construct the chemical bonding theory although these populations in a general case depend on a chosen orbital basis, and only a complete set of the coefficient matrices for all possible choices of one-particle basis of functions is meaningful (see also Bingel, 1961).

III. Orbital Symmetry

1. It is known that when considering many electron systems and neglecting spin–orbital interaction and other higher relativistic corrections in the Schrödinger equation, a complete orbital moment L of the system and its projection M_L are the good quantum numbers. Therefore the study of the RDM orbital symmetry (Garrod, 1968) seems to be necessary.

As in the previous part we consider subsequently the orbital symmetry of the 1- and 2-matrices.

2.1. In order to study the orbital dependence of RDM, we consider the angular component of the spatial δ-operator whose matrix elements are just the transition RDM

$$O_1^R(\mathbf{R}_1; \mathbf{R}_1' | \mathbf{r}_1; \mathbf{r}_1') = \delta(\mathbf{R}_1 - \mathbf{r}_1)\, \overline{\delta(\mathbf{R}_1' - r_1)}.$$

Introducing the spherical coordinates, we have

$$\delta(\mathbf{R}_1 - \mathbf{r}_1)\, \overline{\delta(\mathbf{R}_1' - \mathbf{r}_1')} = \frac{\delta(R_1 - r_1)\, \delta(R_1' - r_1')}{(R_1R_1')^2}\, \delta(\Omega_1 - \omega_1)\, \delta(\Omega_1' - \omega_1'),$$

where

$$\mathbf{R} = (R, \Omega), \qquad \mathbf{r} = (r, \omega).$$

Let us define dipolar spherical harmonics (Warshalovich *et al.*, 1975) as an irreducible tensor product of two spherical functions of different arguments:

$$\{Y_{l_1}(\Omega_1) \otimes Y_{l_2}(\Omega_2)\}_{LM} = \sum_{m_1 m_2} (-1)^{l_1 - l_2 + M}(2L+1)^{1/2} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_2).$$

Then the completeness condition for dipolar spherical harmonics takes the form

$$\delta(\Omega_1 - \omega_1)\, \delta(\Omega_1' - \omega_1') = \sum_{l_1 l_2 LM} \{Y_{l_1}(\Omega_1) \otimes Y_{l_2}(\Omega_1')\}_{LM} \{Y_{l_1}(\omega_1) \otimes Y_{l_2}(\omega_1')\}_{LM},$$

Thus, the orbital expansion of the 1-matrix is defined by the formula

$$D^1_{\Psi_1\Psi_2}(X_1; X_1') = \sum_{l_1 l_2 LM} D^1_{\Psi_1\Psi_2}(R_1 S_1; R_1' S_1' | l_1 l_2 LM) \{Y_{l_1}(\Omega_1) \otimes Y_{l_2}(\Omega_1')\}_{LM}, \quad (1)$$

where

$$\begin{aligned} &D^1_{\Psi_1\Psi_2}(R_1 S_1; R_1' S_1' | l_1 l_2 LM) \\ &\quad = \int dx_1'\, dx_1 \cdots dx_N\, \Psi_1(x_1 \cdots x_N) \frac{\delta(R_1 - r_1)\, \delta(R_1' - r_1')}{(R_1 R_1')^2} \\ &\quad \times \{Y_{l_1}(\omega_1) \otimes Y_{l_2}(\omega_1')\}_{LM} D_1^S \Psi_2(x_1' x_2 \cdots x_N). \end{aligned}$$

So in (1) we expressed the angular part of the 1-matrix by irreducible two-particle angular tensor operators. This allows one to simplify the calculation of the matrix elements via the Wigner–Eckart theorem.

The diagonal part of the 1-matrix $D^1_{\Psi_1\Psi_2}$ has the form

$$\begin{aligned} D^1_{\Psi_1\Psi_2}(X) = &\sum_{l_1 l_2 LM} D^1_{\Psi_1\Psi_2}(RS | l_1 l_2 LM)(-1)^{l_1 - l_2} \\ &\times \left[\frac{(2l_1+1)(2l_2+1)}{4\pi}\right]^{1/2} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} Y_{LM}(\Omega). \end{aligned} \quad (2)$$

2.2. Let Ψ_1 and Ψ_2 be eigenfunctions L^2 and L_z:

$$\Psi_1 = |L_1 M_1\rangle, \qquad \Psi_2 = |L_2 M_2\rangle. \quad (3)$$

Then according to the Wigner–Eckart theorem

$$D^1_{\Psi_1\Psi_2}(R_1 S_1; R_1' S_1' | l_1 l_2 LM) = (-1)^{L_2 - M_2} \begin{pmatrix} L_2 & L & L_1 \\ -M_2 & M & M \end{pmatrix} \langle L_2 \| L \| L_1 \rangle_{l_1 l_2}$$

and

$$\begin{aligned} D^1_{\Psi_1\Psi_2}(X_1;\, X_1') &= \sum_{l_1 l_2 L} (-1)^{L_2-M_2} \begin{pmatrix} L_2 & L & L_1 \\ -M_2 & M_1 - M_2 & M_1 \end{pmatrix} \\ &\quad \times \langle L_2 \| L \| L_1 \rangle_{l_1 l_2} \{ Y_{l_1}(\Omega_1) \otimes Y_{l_2}(\Omega_1') \}_{L, M_1 - M_2}. \end{aligned} \tag{4}$$

Up to now we have assumed that the Hamiltonian H of the electron system commutes with $\mathbf{L}^2$ and L_z. Moreover, H is known to be invariant with respect to the inversion i of all electron coordinates. Therefore the solution Ψ of the Schrödinger equation with the Hamiltonian H should possess a certain parity p $(= \pm)$ depending on the change of sign of Ψ for the inversion i. It is not difficult to show (Bingel, 1962) that the application of i to (2) leads to the relation

$$p_1 p_2 = (-1)^L. \tag{5}$$

where p_1 and p_2 are the parities Ψ_1 and Ψ_2, respectively. Under the condition (3) the summation over L in (4) contains a finite number of terms and obeys the triangle condition $|L_1 - L_2| \leq L \leq L_1 + L_2$. Moreover, from (5) it follows that possible values of L are limited by the series $L = L_1 + L_2$, $L_1 + L_2 - 2, \ldots$, if Ψ_1 and Ψ_2 have identical parities, and by the series $L = L_1 + L_2 - 1, L_1 + L_2 - 3, \ldots$, if the parities of Ψ_1 and Ψ_1 are different.

As in the case of spin symmetry of the transition RDM we may define the standard states with $M_1 = L_1$ and $M_2 = L_2$ and introduce the coupling coefficients that are the relation of the $3j$-symbol (Bingel, 1962).

2.3 Let $\Psi = \Psi_1 = \Psi_2 = |L_0 M_0\rangle$. Then

$$\begin{aligned} D^1_{L_0 M_0}(X_1;\, X_1') &= \sum_{l_1 l_2 L} (-1)^{L_0 - M_0} \begin{pmatrix} L_0 & L & L_0 \\ -M_0 & 0 & M_0 \end{pmatrix} \langle L_0 \| L \| L_0 \rangle_{l_1 l_2} \\ &\quad \times \{ Y_{l_1}(\Omega_1) \otimes Y_{l_2}(\Omega_1') \}_{L_0}. \end{aligned}$$

From the triangle law it follows that $L = 0$ and consequently $l_1 = l_2$. Thus,

$$\begin{aligned} D^1_{L_0 M_0}(X_1;\, X_1') &= \sum_{lm} (-1)^{L_0 - M_0} D^1_{L_0 M_0}(R_1 S_1;\, R_1' S_1' | l)(-1)^{l-m}(2l + 1)^{1/2} Y_{lm}(\Omega_1) \bar{Y}_{lm}(\Omega_1'). \end{aligned} \tag{6}$$

So we have considered the orbital expansion of the 1-matrix. In the same way one may study, if necessary, the orbital symmetry of a spinless matrix and a matrix of spin density.

3. In the case of the 2-matrices we act similarly. Firstly we introduce the four-polar spherical harmonics

$$\{\{Y_{l_1}(\Omega_1) \otimes Y_{l_2}(\Omega_1')\}_{\lambda_1} \otimes \{Y_{l_3}(\Omega_2) \otimes Y_{l_4}(\Omega_2')\}_{\lambda_2}\}_{LM}.$$

The angular part of the δ-operator

$$\begin{aligned} &O_2^R(\mathbf{R}_1, \mathbf{R}_2; \mathbf{R}_1', \mathbf{R}_2' | \mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2') \\ &\quad = \delta(\mathbf{R}_1 - \mathbf{r}_1)\, \delta(\mathbf{R}_1' - \mathbf{r}_1)\, \delta(\mathbf{R}_2 - \mathbf{r}_2)\, \delta(\mathbf{R}_2' - \mathbf{r}_2') \end{aligned}$$

is represented as

$$\begin{aligned} &\delta(\Omega_1 - \omega_1)\, \delta(\Omega_1' - \omega_1')\, \delta(\Omega_2 - \omega_2)\, \delta(\Omega_2' - \omega_2') \\ &\quad = \sum_{l_1 l_2} \sum_{l_3 l_4} \sum_{\lambda_1 \lambda_2} \sum_{LM} \{\{Y_{l_1}(\Omega_1) \otimes Y_{l_2}(\Omega_1')\} \\ &\quad \otimes \{Y_{l_3}(\Omega_2) \otimes Y_{l_4}(\Omega_2')\}_{\lambda_2}\}_{LM} \\ &\quad \times \{\{Y_{l_1}(\omega_1) \otimes Y_{l_2}(\omega_1')\}_{\lambda_1} \otimes \{Y_{l_3}(\omega_2) \otimes Y_{l_4}(\omega_2')\}_{\lambda_2}\}_{LM}, \end{aligned}$$

the condition of the completeness of these spherical harmonics.

Then

$$\begin{aligned} &D^2_{\Psi_1 \Psi_2}(X_1, X_2; X_1', X_2') \\ &\quad = \sum_{l_1 l_2 l_3 l_4} \sum_{\lambda_1 \lambda_2 LM} D^2_{\Psi_1 \Psi_2}(R_1 S_1, R_2 S_2; R_1' S_1', R_2' S_2' | l_1 l_2 l_3 l_4 \lambda_1 \lambda_2 LM) \\ &\quad \times \{\{Y_{l_1}(\Omega_1) \otimes Y_{l_2}(\Omega_1')\}_{\lambda_1} \otimes \{Y_{l_3}(\Omega_2) \otimes Y_{l_4}(\Omega_2')\}_{\lambda_2}\}_{LM}, \end{aligned} \tag{7}$$

where

$$\begin{aligned} &D^2_{\Psi_1 \Psi_2}(R_1 S_1, R_2 S_2; R_1' S_1', R_2' S_2' | l_1 l_2 l_3 l_4 \lambda_1 \lambda_2 LM) \\ &\quad = \int dx_1'\, dx_2'\, dx_1 \cdots dx_N \Psi_1(x_1 \cdots x_N) \\ &\quad \times \frac{\delta(R_1 - r_1)\, \delta(R_2 - r_2)\, \delta(R_1' - r_1')\, \delta(R_2' - r_2')}{(R_1 R_2 R_1' R_2')^2}\, O_2^S \\ &\quad \times \{\{Y_{l_1}(\omega_1) \otimes Y_{l_2}(\omega_1')\}_{\lambda_1} \otimes \{Y_{l_3}(\omega_2) \otimes Y_{l_4}(\omega_2')\}_{\lambda_2}\}_{LM}\, \bar{\Psi}_2(x_1' x_2' x_3 \cdots x_N). \end{aligned}$$

The diagonal component $D^2_{\Psi_1 \Psi_2}$ has the form

$$\begin{aligned} &D^2_{\Psi_1 \Psi_2}(X_1; X_2) \\ &\quad = \frac{1}{4\pi} \sum_{l_1 l_2 l_3 l_4} \sum_{\lambda_1 \lambda_2 LM} D^2_{\Psi_1 \Psi_2}(R_1 S_1; R_2 S_2 | l_1 l_2 l_3 l_4 \lambda_1 \lambda_2 LM) \\ &\quad \times (-1)^{l_1 + l_3 - l_2 - l_4} [(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)(2l_4 + 1)]^{1/2} \begin{pmatrix} l_1 & l_2 & \lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \\ &\quad \times \begin{pmatrix} l_3 & l_4 & \lambda_2 \\ 0 & 0 & 0 \end{pmatrix} \{Y_{\lambda_1}(\Omega_1) \otimes Y_{\lambda_2}(\Omega_2)\}_{LM}. \end{aligned}$$

If Ψ_1 and Ψ_2 are the eigenfunctions of $\mathbf{L}^2$ and L_z then

$$\begin{aligned} &D^2_{\Psi_1 \Psi_2}(R_1 S_1, R_2 S_2; R_1' S_1', R_2' S_2' | l_1 l_2 l_3 l_4 \lambda_1 \lambda_2 LM) \\ &\quad = (-1)^{L_2 - M_2} \begin{pmatrix} L_2 & L & L_1 \\ -M_2 & M & M_1 \end{pmatrix} \langle L_2 \| L \| L_1 \rangle^{(l_3 l_4)\lambda_2}_{(l_1 l_2)\lambda_1}. \end{aligned}$$

Assume $\Psi_1 = \Psi_2 = |L_0M_0\rangle$. Then

$$\begin{aligned}
&D^2_{L_0M_0}(X_1X_2;\, X'_1X'_2)\\
&\quad = \sum_{l_1l_2l_3l_4}\sum_{\lambda m}\sum_{\substack{m_1m_2\\ m_3m_4}}\\
&\qquad \times D^2_{L_0M_0}(R_1S_1,\, R_2S_2;\, R'_1S'_1,\, R'_2S_2|l_1l_2l_3l_4\lambda)(-1)^{l_1-l_2+l_3-l_4+\lambda-m}\\
&\qquad \times \begin{pmatrix} l_1 & l_2 & \lambda \\ m_1 & m_2 & -m \end{pmatrix}\begin{pmatrix} l_3 & l_4 & \lambda \\ m_3 & m_4 & m \end{pmatrix}\\
&\qquad \times (2\lambda + 1)^{1/2} Y_{l_1m_1}(\Omega_1)\bar{Y}_{l_2m_2}(\Omega'_1)Y_{l_3m_3}(\Omega_2)Y_{l_4m_4}(\Omega'_2). \qquad (8)
\end{aligned}$$

Thus we have examined the orbital symmetry of the 1- and 2-matrices corresponding to arbitrary wave functions both exact and approximated. Therefore in Section III,4 we use the above formulas, as an illustration, for the approximated Slater wave functions of atomic systems.

4.1. It is known (see, e.g., Kaplan, 1969), that in the LS-coupling approximation an antisymmetric function may be represented in the form of a linear combination of products of a coordinate part by a spin one

$$\Psi^{[1^N]}_{[\lambda]}(x_1 \cdots x_N) = (f^{[\lambda]})^{-1/2} \sum_{r=1}^{f^{[\lambda]}} \Phi^{[\lambda]}_{rr}(\mathbf{r}'_1 \cdots \mathbf{r}_N)\Omega^{[\tilde{\lambda}]}_{\tilde{r}\tilde{r}}(S_1 \cdots S_N), \qquad (9)$$

where

$$\Phi^{[\lambda]}_r = e^{[\lambda]}_{rr}\Phi_0 = (f^{[\lambda]}/N!)^{1/2} \qquad (10)$$

$$\Phi_0 = \varphi_1(\mathbf{r}_1)\ \varphi_2(\mathbf{r}_2) \cdots \varphi_N(\mathbf{r}_N). \qquad (11)$$

Since in what follows we shall use the theory of nonstandard representation of a symmetric group (Kaplan, 1969), to simplify the notation we define RDM in a form somewhat different from the traditional one:

$$\begin{aligned}
&D^m_{\Psi^{[1^N]}_{1[\lambda_1]}\Psi^{[1^N]}_{2[\lambda_2]}}(x_1 \cdots x_m;\, x'_1 \cdots x'_m)\\
&\quad = \int dx_{m+1} \cdots dx_N\ \Psi^{[1^N]}_{1[\lambda_1]}(x_N, \ldots, x_2, x_1)\ \bar{\Psi}^{[1^N]}_{2[\lambda_2]}\\
&\quad = \times\ (x_N, \ldots, x_{m+1}, x'_m, \ldots, x'_1)\\
&\quad = (f^{[\lambda_1]}f^{[\lambda_2]})^{-1/2} \sum_{r=1}^{f^{[\lambda_1]}}\sum_{t=1}^{f^{[\lambda_2]}} D^m_R(\Phi^{[\lambda_1]}_{rr};\, \Phi^{[\lambda_2]}_{tt})\, D^m_S(\Omega^{[\tilde{\lambda}_1]}_{\tilde{r}\tilde{r}};\, \Omega^{[\tilde{\lambda}_2]}_{\tilde{t}\tilde{t}}), \qquad (12)
\end{aligned}$$

where

$$\begin{aligned}
&D^m_R(\Phi^{[\lambda_1]}_{rr};\, \Phi^{[\lambda_2]}_{tt}\,|\mathbf{r}_1 \cdots \mathbf{r}_m;\, \mathbf{r}'_1 \cdots \mathbf{r}_m)\\
&\quad = \int d\mathbf{r}_{m+1} \cdots d\mathbf{r}_N\, \Phi^{[\lambda_1]}_{rr}(\mathbf{r}_N \cdots \mathbf{r}_1)\, \bar{\Phi}^{[\lambda_2]}_{tt}(\mathbf{r}_N \cdots \mathbf{r}_{m+1}\mathbf{r}'_m \cdots \mathbf{r}'_1);
\end{aligned}$$

$$\begin{aligned}
&D^m_S(\Omega^{[\tilde{\lambda}_1]}_{\tilde{r}\tilde{r}};\, \Omega^{[\tilde{\lambda}_2]}_{\tilde{t}\tilde{t}}\,|S_1 \cdots S_m;\, S'_1 \cdots S'_m)\\
&\quad = \int \Omega^{[\lambda_1]}_{\tilde{r}\tilde{r}}(S_N \cdots S_1)\, \bar{\Omega}^{[\tilde{\lambda}_2]}_{\tilde{t}\tilde{t}}(S_N \cdots S_{m+1}S'_m \cdots S'_1)\, dS_{m+1} \cdots dS_N.
\end{aligned}$$

TABLE III

PERMITTED TERMS OF CONFIGURATION OF EQUIVALENT ELECTRONS

$S^n p^m$	Young scheme	Orbital moment	Spin S	Multiplicity M	Term
S^2	[2]	0	0	1	^1S
p^2	[1^2]	1	1	3	^3P
	[2]	0, 2	0	1	^1S, ^1D
p^3	[1^3]	0	$\frac{3}{2}$	4	^4S
	[21]	1, 2	$\frac{1}{2}$	2	^2P, ^2D
p^4	[21^2]	1	1	3	^3P
	[2^2]	0, 2	0	1	^1S, ^1D
p^5	[$2^2 1$]	1	$\frac{1}{2}$	2	^2P
p^6	[2^3]	0	0	1	^1S
Sp	[1^2]	1	1	3	^3P
	[2]	1	0	1	^1P
Sp^2	[21]	0, 1, 2	$\frac{1}{2}$	2	^2S, ^2P, ^2D
	[1^3]	1	$\frac{3}{2}$	4	^4P
Sp^3	[2^2]	0, 1, 2	0	1	^1S, ^1P, ^1D
	[25^2]	0, 1, 2	1	3	^3S, ^3P, ^3D
	[2^4]	0	2	5	^5S
Sp^4	[21]	0, 1, 2	$\frac{1}{2}$	2	^2S, ^2P, ^2D
	[21^3]	1	$\frac{3}{2}$	4	^4P
Sp^5	[2^3]	1	0	1	^1P
	[$2^2 1^2$]	1	1	3	^3P
Sp^6	[$2^3 1$]	0	$\frac{1}{2}$	2	^2S
S^2p	[21]	1	$\frac{1}{2}$	2	^2P
S^2p^2	[2^2]	0, 1, 2	0	1	^1S, ^1P, ^1D
	[21^2]	1	1	3	^3P
S^2p^3	[$2^2 1$]	0, 1, 2	$\frac{1}{2}$	2	^2S, ^2P, ^2D
	[21^3]	0	$\frac{3}{2}$	4	^4S
S^2p^4	[2^3]	0, 1, 2	0	1	^1S, ^1P, ^1D
	[$2^2 1^2$]	1	1	3	^3P
S^2p^5	[$2^3 1$]	1	$\frac{1}{2}$	2	^2P
S^2p^6	[2^4]	0	0	1	^1S

Then taking into account formulas (10)–(11) we have

$$\begin{aligned} &D_R^m(\Phi_{rr}^{[\lambda_1]}; \Phi_{tt}^{[\lambda_2]}) \\ &\quad = \frac{(f^{[\lambda_1]} f^{[\lambda_2]})^{1/2}}{N!} \sum_{P \in S_N} \sum_{P' \in S_N} [P]_{rr}^{[\lambda_1]} [P'^{-1}]_{tt}^{[\lambda_2]} D^m_{\Phi_0^{(1)} \Phi_0^{(2)}}[P|P']; \\ &D^m_{\Phi_0^{(1)} \Phi_0^{(2)}}[P|P'](\mathbf{r}_1 \cdots \mathbf{r}_m; \mathbf{r}'_1 \cdots \mathbf{r}'_m) \\ &\quad = \int d\mathbf{r}_{m+1} \cdots d\mathbf{r}_N \, \varphi_{P(1)}(\mathbf{r}_N) \cdots \varphi_{P(N)}(\mathbf{r}_1) \, \bar{\psi}_{P'(1)}(\mathbf{r}_N) \\ &\qquad \cdots \bar{\varphi}_{P'(n)}(\mathbf{r}_{m+1}) \, \psi_{P'(n+1)}(\mathbf{r}_m) \cdots \bar{\psi}_{P'(N)}(\mathbf{r}'_1), \qquad n + m = N \end{aligned} \tag{13}$$

4.2. In Section IV we shall find the expression for $D^m_R(\Phi^{[\lambda_1]}_{rr}\,;\,\Phi^{[\lambda_2]}_{tt})$ through the transformation matrices and coefficients of outer products of a symmetric group (Kaplan, 1969). But now following W. A. Bingel (1962), in Table III we write down, using the reduction (Kaplan, 1969, p. 176)

$$\begin{tikzcd} U^{[\lambda]}_{2l+1} \arrow[r, leftrightarrow] \arrow[d, phantom, "\cup"] & U^{(\tilde{\lambda})}_{2} \arrow[d, phantom, "\cup"] \\ SO_L(3) \arrow[r, leftrightarrow] & SO_S(3) \end{tikzcd}$$

the permitted terms of the configuration of equivalent electrons $S^n p^m$.

4.3. Since we need at least the 2-matrices, we consider the reduction $S_N = S_{N-2} \times S_2$ for the configuration $S^n p^m$ using the Littlewood rule (Littlewood, 1958, p. 128):

(*i*) $[1]\otimes[1^2] = [1^3] \dotplus [21]$, $[1^2]\otimes[1] = [1^3] \dotplus [21]$

$[2]\otimes[1] = [21] \dotplus [3]$, $[1]\otimes[2] = [21] \dotplus [3]$;

(*ii*) $[21]\otimes[1] = [31] \dotplus [2^2] \dotplus [21^2]$, $[1^3]\otimes[1] = [21^2] \dotplus [1^4]$,

$[2]\otimes[1^2] = [21^2] \dotplus [31]$, $[2]\otimes[2] = [2^2] \dotplus [4] \dotplus [31]$,

$[1^2]\otimes[2] = [31] \dotplus [21^2]$, $[1^2]\otimes[1^2] = [2^2] \dotplus [21^2] \dotplus [1^4]$;

(*iii*) $[2^2]\otimes[1] = [2^21] \dotplus [32]$, $[21^2]\otimes[1] = [31^2] \dotplus [21^3] \dotplus [2^21]$,

$[1^4]\otimes[1] = [21^3] \dotplus [1^5]$, $[21]\otimes[1^2] = [32] \dotplus [31^2] \dotplus [2^21] \dotplus [21^3]$,

$[21]\otimes[2] = [41] \dotplus [32] \dotplus [2^21]$, $[1^3]\otimes[1^2] = [1^5] \dotplus [21^3] \dotplus [2^21]$,

$[1^3]\otimes[2] = [31^2] \dotplus [21^3]$;

(*iv*) $[2^21]\otimes[1] = [2^3] \dotplus [2^21^2]$, $[21^3]\otimes[1] = [31^3] \dotplus [2^21^2] \dotplus [21^4]$,

$[1^5]\otimes[1] = [1^6] \dotplus [21^4]$, $[2^2]\otimes[1^2] = [32] \dotplus [2^21^2] \dotplus [321]$,

$[21^2]\otimes[1^2] = [2^3] \dotplus [21^4] \dotplus [321] \dotplus [31^3]$,

$[21^2]\otimes[2] = [41^2] \dotplus [321] \dotplus [31^3]$,

$[1^4]\otimes[1^2] = [1^6] \dotplus [2^21^2] \dotplus [21^4]$;

(*v*) $[2^3]\otimes[1] = [32^2] \dotplus [2^31]$; $[2^21^2]\otimes[1] = [321^2] \dotplus [2^31] \dotplus [2^21^3]$,

$[2^21]\otimes[1^2] = [3^21] \dotplus [32^2] \dotplus [321^2] \dotplus [2^31]$,

$[2^21]\otimes[2] = [421] \dotplus [32^2] \dotplus [321^2] \dotplus [2^31]$,

$[21^3]\otimes[1^2] = [321^2] \dotplus [31^4] \dotplus [2^31] \dotplus [21^5] \dotplus [2^21^3]$,

$[21^3]\otimes[2] = [41^3] \dotplus [321^2] \dotplus [31^4] \dotplus [2^21^3]$;

(*vi*) $[2^31]\otimes[1] = [2^4] \dotplus [2^31^2] \dotplus [32^21]$,

$[2^21^2]\otimes[1^2] = [3^22^2] \dotplus [2^4] \dotplus [321^3] \dotplus [32^21] \dotplus [2^21^4]$.

4.4. As an example, the nonzero coordinate densities of a diagonal part of the 1-matrix of possible values of the orbital moment L for the configurations p and p^2 are the following:

(*i*) p(10) $a_{00} = 5/(6\sqrt{\pi})$, $a_{20} = \frac{1}{3}(5/\pi)^{1/2}$

(*ii*) $p^2[1^2](10, 11)$

$a_{00} = 5/(12\sqrt{\pi})$, $a_{20} = \frac{1}{6}(5/\pi)^{1/2}$, $a_{21} = -\frac{5}{2}(5/3\pi)^{1/2}$, $a_{22} = \frac{5}{4}(10/3\pi)^{1/2}$;

(*iii*) $p^2[2](10, 10)$ $a_{00} = 5/(3\sqrt{\pi})$, $a_{20} = \frac{2}{3}(5/\pi)^{1/2}$;

(*iv*) $p^2[2](10, 11)$

$a_{00} = 5/(12\sqrt{\pi})$, $a_{20} = \frac{1}{3}(5/\pi)^{1/2}$, $a_{21} = \frac{5}{2}(5/3\pi)^{1/2}$, $a_{22} = \frac{5}{4}(10/3\pi)^{1/2}$;

(*v*) $p^2[2](11, 11)$ $a_{22} = 5(10/3\pi)^{1/2}$,

$$|\varphi(r)|a_{LM} = \sum_{\substack{l_1 l_2 \\ m_1 m_2}} D^1_\psi(r|l_1 l_2 LM)(-1)^{l_1 - l_2} \left[\frac{(2l_1 + 1)(2l_2 + 1)(2L + 1)}{4\pi}\right]^{1/2}$$
$$\times \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}.$$

5.1. In this paragraph we consider some applications the LS-symmetry of RDM in the calculations of the matrix elements of effective operators. When considering electron-spin and nuclear-magnetic resonances, an effective spin Hamiltonian is usually introduced. Thus a difficult (sometimes analytically unsolvable), multiparticle problem is replaced by a rather simple equivalent spin problem.

We shall discuss briefly how the spin Hamiltonian (Bethe and Salpeter, 1957; Löwdin, 1964) is obtained via the perturbation theory. Let $H = H_0 + H', H' = H_{\text{ext}} + H_{\text{SL}} + H_{\text{SS}} + H_{Z} + H_{N'}$, where H_0 is the molecular Hamiltonian without spin and field variables, H' is the perturbation that involves the medium effect (H_{ext}), the spin–orbital coupling (H_{SL}), the electron spin–spin interaction (H_{SS}), the electron-Zeeman term (H_Z), and different nuclear bonds. Notice that a detailed discussion of these terms was given by McWeeny (1965).

Let Φ_k be the electron and ϑ_λ the spin-nuclear wave functions. Then the total wave function of electrons and nuclear spins may be written in the form $\Psi = \sum_{k\lambda} c_{k\lambda}\Phi_k\vartheta_\lambda = \sum_{k\lambda} c_{k\lambda}|k\lambda\rangle$, the eigenvalues and the coefficients $c_{k\lambda}$ resulting from the Schrödinger equation written in the matrix form[3]:

$$H_c = E_c \quad \text{where} \quad H = \|\langle k\lambda|H|k'\lambda'\rangle\|. \tag{14}$$

We divide all the energy levels into two types. The unperturbed states $|k_a\lambda\rangle$ with the energy E_a form the group A. The remaining one

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[3] The ket-vectors $|k\lambda\rangle$ are assumed to form a complete set.

form the group B. This induces the following partition of the matrices H:

$$H^{AA} = \|\langle k_a\lambda|H|k'_a\lambda'\rangle\|, \quad H^{AB} = H^{BA+} = \|\langle k_a\lambda|H|k'_b\lambda'\rangle\|, \quad H^{BB} = \|\langle k_b\lambda|H|k'_b\lambda'\rangle\|.$$

Then the secular problem (14) is reduced to the following one:

$$H^{AA}_{\text{eff}}A = EA, \tag{15}$$

where

$$H^{AA}_{\text{eff}} = H^{AA} + H^{AB}(E - H^{BB})^{-1}H^{BA} \tag{16}$$

which refers to a less set of states belonging to the set A. Let us denote the matrix elements (16) through $\langle k'_a\lambda'|H^{AA}_{\text{eff}}|k_a\lambda\rangle$ and according to the perturbation theory (up to the second order) we have

$$\begin{aligned}\langle k'_a\lambda'|H^{AA}_{\text{eff}}|k_a\lambda\rangle &= E_a\delta_{k_a,k'_a}\delta_{\lambda\lambda'} + \langle k'_a\lambda'|H'|k_a\lambda\rangle \\ &\quad + \sum_{k''_b\lambda''} \frac{\langle k'_a\lambda'|H'|k''_b\lambda''\rangle\ \langle k''_b\lambda''|H'|k_a\lambda\rangle}{E_a - E_b}.\end{aligned} \tag{17}$$

Putting $E_a = 0$, we define the effective spin operators $H^{(1)}_{\text{spin}}$ and $H^{(2)}_{\text{spin}}$ containing the operators of nuclear and electron spins as follows:

$$\langle k'_a\lambda'|H'|k_a\lambda\rangle = \langle M'_a\lambda'|H^{(1)}_{\text{spin}}|M_a\lambda\rangle, \tag{18}$$

$$\sum_{k''_b\lambda''} \frac{\langle k'_a\lambda'|H'|k''_b\lambda''\rangle\ \langle k''_b\lambda''|H'|k_a\lambda\rangle}{E_a - E_b} = \langle M'_a\lambda'|H^{(2)}_{\text{spin}}|M_a\lambda\rangle. \tag{19}$$

Then a total spin Hamiltonian in this approach is the following

$$H_{\text{spin}} = H^{(1)}_{\text{spin}} + H^{(2)}_{\text{spin}} \tag{20}$$

and the secular problem (15) is rewritten as

$$H_{\text{spin}}A = EA. \tag{21}$$

Thus, the problem of finding the eigenvectors and eigenvalues (14) is reduced (in the present approximation) to a completely equivalent spin secular problem (21). Thus the problem is reduced to the construction of an equivalent spin operator for any term of the perturbation Hamiltonian H' using the formulas (18) and (19).

5.2. Consider the electron-nuclear contraction Hamiltonian (McWeeny, 1965):

$$H^{\text{cont}}_N = \tfrac{8}{3}\pi_g\beta \sum_n g_n\beta_n \sum_{im} (-1)^m\delta(\mathbf{r}_{ni})S_{-m}(i)I_m(n). \tag{22}$$

Then

$$\begin{aligned}&\langle k'_a\lambda'|H^{\text{cont}}_N|k_a\lambda\rangle \\ &\quad = \tfrac{8}{3}\pi_g\beta \sum_n g_n\beta_n \sum_m (-1)^m \int_{\mathbf{r}_1=\mathbf{r}'_1} \delta(\mathbf{r}_{n_1})D^1_a(\mathbf{r}_1;\mathbf{r}'_1) \\ &\quad\quad \times d\mathbf{r}_1\ \langle M'_a|S_{-m}|M_a\rangle\langle\lambda'|I_m|\lambda\rangle \\ &\quad = \langle M'_a\lambda'|\tfrac{8}{3}\pi_g\beta \sum_n g_n\beta_nD^1_a(\mathbf{r}_n)\mathbf{SI}(n)|M_a\lambda\rangle,\end{aligned}$$

$$D_a^1(\mathbf{r}_n) = \int_{\mathbf{r}_1=\mathbf{r}_1'} \delta(\mathbf{r}_{n_1}) D_a^1(\mathbf{r}_1; \mathbf{r}_1')\, d\mathbf{r}_1.$$

Hence

$$H_{\text{spin}}^{(1)}(\text{cont}) = \sum_n hA_n^{(\text{cont})}\mathbf{I}(n)\mathbf{S},$$

where

$$A_n^{(\text{cont})} = \frac{8\pi g g_n \beta\beta_n}{3h} D_a^1(\mathbf{r}_n)$$

is the contract coupling constant. It depends, obviously, on the spin density calculated in the kernel n. It is clear that $A_n^{(\text{cont})}$ is isotropic since it does not depend on the molecule orientation.

5.3. The dipole–dipole term of the nuclear Hamiltonian is defined as follows (McWeeny, 1965):

$$H_N^{\text{dip}} = 3g\beta \sum_n g_n\beta_n \sum_{mi} (-1)^m r_{ni}^{-5}[\mathbf{r}_{ni} \times \mathbf{r}_{ni}]_{-m}^{(2)} [\mathbf{S}(i) \times \mathbf{I}(n)]_m^{(2)}. \quad (23)$$

It is not difficult to show that

$$\begin{aligned} r_{ni}^{-5}[\mathbf{r}_{ni} \times \mathbf{r}_{ni}]_{-m}^{(2)} &= \frac{16\pi^2\sqrt{5}}{3(\mathbf{r}_i^2 - \mathbf{r}_n^2)} \sum_{l=0}^{\infty} \sum_{m=-l} \bar{Y}_m^l(\Omega_n) \sum_{\mu\nu} (-1)^m \begin{pmatrix} 1 & 1 & 2 \\ \mu & \nu & m \end{pmatrix} \\ &\times \left(\frac{r_n^l}{r_i^{2l+1}}\right) Y_\mu^1(\Omega_{ni}) Y_\nu^1(\Omega_{ni}) Y_m^l(\Omega_i), \qquad (r_n < r_i); \end{aligned}$$

$$[\mathbf{S}(i) \times \mathbf{I}(n)]_m^{(2)} = \sum_{\mu\nu} (-1)^m \begin{pmatrix} 1 & 1 & 2 \\ \mu & \nu & -m \end{pmatrix} \sqrt{5} S_\mu(i) I_\nu(n).$$

Then

$$H_{\text{spin}}^{(1)}(\text{dip}) = \sum_{n\mu\nu} hA_{n\mu\nu}^{(\text{dip})}(\mathbf{r}_n) I_\nu(n) S_\mu,$$

where

$$\begin{aligned} A_{n\mu\nu}^{(\text{dip})} &= \frac{3g\beta g_n\beta_n}{h} \sum_{l=0}^{\infty} \sum_{m_1=-l}^{l} \sum_{\mu_1\nu_1} \sum_{m=-2}^{2} \frac{16\pi^2\sqrt{5}}{3} \begin{pmatrix} 1 & 1 & 2 \\ \mu_1 & \nu_1 & m \end{pmatrix} r_{n\langle}^l \bar{Y}_{m_1}^l(\Omega_n) \\ &\times \int \frac{Y_{\mu_1}^1(\Omega_{n_1}) Y_{\nu_1}^1(\Omega_{n_1}) Y_{m_1}^l(\Omega_1)}{(\mathbf{r}_{1\rangle}^2 - \mathbf{r}_{n\langle}^2)\mathbf{r}_{1\rangle}^{2l+1}} \begin{pmatrix} 1 & 1 & 2 \\ \mu & \nu & -m \end{pmatrix} D_a^1(\mathbf{r}_1)\, d\mathbf{r}_1. \end{aligned}$$

Thus $H^{(1)}_{\text{spin}}(\text{dip})$ is reduced to the consideration of orbital symmetry of the component ${}_{\mu}V^{(1)}_{a}$ of the I-matrix D^{1}_{a}.

5.4. Consider the Hamiltonian of the electron spin–spin coupling (McWeeny, 1965):

$$H_{\text{SS}} = -\tfrac{3}{2}g^2\beta^2 \sum_{ij} \sum_{m} (-1)^m r_{ij}^{-5}[\mathbf{r}_{ij} \times \mathbf{r}_{ij}]^{(2)}_{-m}[\mathbf{S}(i) \times \mathbf{S}(j)]^{(2)}_{m}. \tag{24}$$

Then

$$H^{1}_{\text{spin}}(\text{spin–spin}) = \sum_{\alpha\beta} hD_{\alpha\beta}S_{\alpha}(1)S_{\beta}(2), \tag{25}$$

where

$$D_{\alpha\beta} = \frac{8g^2\beta^2\pi^2\sqrt{5}}{h}\sum_{l=0}^{\infty}\sum_{m_1=-l}^{l}\sum_{\mu_1\nu_1}\sum_{m=-2}^{2}\begin{pmatrix}1 & 1 & 2\\ \mu_1 & \nu_1 & m\end{pmatrix}\begin{pmatrix}1 & 1 & 2\\ \mu & \nu & -m\end{pmatrix}$$

$$\times \int \frac{\bar{Y}^{l}_{m}(\Omega_1)\bar{Y}^{l}_{m}(\Omega_2)Y^{1}_{\mu_1}(\Omega_{12})Y^{1}_{\nu_1}(\Omega_{12})}{(r^2_{1\langle} - r^2_{2\rangle})r^{2l+1}_{2\rangle}} r^{l}_{1\langle}D^{2}_{\text{SS}}(a|\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2.$$

In a general case this coupling is anisotropic. Then we may define the principal axes (X, Y, Z) of the tensor $D_{\alpha\beta}$ and the expressions (25) take the following form:

$$H^{(1)}_{\text{spin}}(\text{spin–spin}) = h\{D[S^2_0 - \tfrac{1}{3}S(S+1)] + E(S^2_X - S^2_Y)\},$$

$$D = \tfrac{3}{2}D_{zz}, \qquad E = \tfrac{1}{2}(D_{XX} - D_{YY}).$$

Hence, the Hamiltonian of the electron spin–spin coupling responsible for the decomposition (in the zero approximation over a field) of Zeeman levels is expressed by the coupling anisotropy or of the "spin–spin coupling" introduced in Section II.

Thus concerning the applications of RDM to the effective Hamiltonian theory, we have considered only the Hamiltonians of electron-nuclear contact coupling, electron-nuclear dipole coupling, and electron spin–spin coupling. In general, we would like to note the following: All the system characteristics appearing in the writing of the spin Hamiltonian can be evidently expressed by no less than 2-matrices and are reduced to the LS-expansion of the 1- and 2-matrices and to the quantum theory method of the angular momentum (Warshalovich *et al.*, 1975; Yucis and Savukinas, 1972).

6. The orthonormalized N-electron spin functions transformed according to the Young scheme $[\lambda] = [2^p 1^{N-2p}](S = \frac{1}{2}N - p, M = N - 2p + 1)$ are known to be constructed from the spin $(N - 1)$-electron functions according to the following branching rule (Bingel, 1960; Kotani *et al.*, 1955):

$$\begin{aligned}
\Omega^N_{S,M;k} &= -\left[\frac{S - M + 1}{2(S + 1)}\right]^{1/2} \Omega^{N-1}_{S+1/2;M-1/2;k}\alpha(N) \\
&\quad + \left[\frac{S + M + 1}{2(S + 1)}\right]^{1/2} \Omega^{N-1}_{S+1/2,M+1/2;k}\beta(N) \\
&\qquad (k = 1, 2, \ldots, f^{N-1}_{S+1/2}); \\
\Omega^N_{S,M;k} &= \left[\frac{S + M}{2S}\right]^{1/2} \Omega^{N-1}_{S-1/2,M-1/2;h}\alpha(N) \\
&\quad + \left[\frac{S - M}{2S}\right]^{1/2} \Omega^{N-1}_{S-1/2,M+1/2;h}\beta(N) \\
&(k = f^{N-1}_{S+1/2} + h, \quad h = 1, 2, \ldots, f^{N-1}_{S-1/2}), \\
&f^N_S = (N/2^N + S) - (N/2^N + S + 1).
\end{aligned} \tag{26}$$

We shall not give the 2-matrices $D^2_S(\Omega^N_{S_1,M_1;k_1}; \Omega^N_{S_2,M_2;k_2})$ in full, since this is a rather trivial procedure. Here are some examples for the case $k_1, k_2 \in \{1, \ldots, f^{N-1}_{S+1/2}\}(S = S_1 = S_2)$:

(*i*) $M = M_1 = M_2$

$$\begin{aligned}
D^2_S = &\frac{(S - M + 1)(S - M + 2)}{(2S + 2)(2S + 3)} \\
&\times \delta_{k_1k_2}\alpha(S_{N-1})\alpha(S_N)\bar{\alpha}(S'_{N-1})\bar{\alpha}(S'_N) \\
&+ \frac{(S - M + 1)(S + M + 1)}{(2S + 2)(2S + 3)}\delta_{k_1k_2} \\
&\times [\beta(S_{N-1})\alpha(S_N) + \alpha(S_{N-1})\beta(S_N)][\bar{\beta}(S'_{N-1})\bar{\alpha}(S'_N) \\
&+ \bar{\alpha}(S'_{N-1})\bar{\beta}(S'_N)] \\
&+ \frac{(S + M + 1)(S + M + 2)}{(2S + 2)(2S + 3)} \\
&\times \delta_{k_1k_2}\beta(S_{N-1})\beta(S_N)\bar{\beta}(S'_{N-1})\bar{\beta}(S'_N);
\end{aligned}$$

(*ii*) $M_1 - 1 = M_2 = M - 1$

$$\begin{aligned}
D^2_S = {} & -\frac{S - M + 2}{(2S + 2)(2S + 3)}[(S - M + 1)(S + M)]^{1/2} \\
& \times \delta_{k_1k_2}\alpha(S_{N-1})\alpha(S_N)[\bar{\beta}(S'_{N-1})\bar{\alpha}(S'_N) \\
& + \bar{\alpha}(S'_{N-1})\bar{\beta}(S'_N)] - \frac{S + M + 1}{(2S + 2)(2S + 3)} \\
& \times [(S - M + 1)(S + M)]^{1/2} \\
& \times \delta_{k_1k_2}[\beta(S_{N-1})\alpha(S_N) \\
& + \alpha(S_{N-1})\beta(S_N)]\bar{\beta}(S'_{N-1})\bar{\beta}(S'_N);
\end{aligned}$$

(*iii*) $M_1 = M, \quad M_2 = M - 2$

$$\begin{aligned}
D^2_S = {} & \frac{[(S - M + 1)(S - M + 2)(S + M - 1)(S + M)]^{1/2}}{(2S + 2)(2S + 3)} \\
& \times \delta_{k_1k_2}\alpha(S_{N-1})\alpha(S_N)\bar{\beta}(S'_{N-1})\bar{\beta}(S'_N);
\end{aligned}$$

(*iv*) $M_1 = M, \quad M_2 = M + 1$

$$\begin{aligned}
D^2_S = {} & -\frac{S - M + 1}{(2S + 2)(2S + 3)}[(S + M + 1)(S - M)]^{1/2} \\
& \times \delta_{k_1k_2}[\beta(S_{N-1})\alpha(S_N) + \alpha(S_{N-1})\beta(S_N)] \\
& \times \bar{\alpha}(S'_{N-1})\bar{\alpha}(S'_N) - \frac{S + M + 2}{(2S + 2)(2S + 3)} \\
& \times [(S + M + 1)(S - M)]^{1/2}\,\delta_{k_1k_2}\beta(S_{N-1})\beta(S_N) \\
& \times [\bar{\beta}(S'_{N-1})\bar{\alpha}(S'_N) + \bar{\alpha}(S'_{N-1})\bar{\beta}(S'_N)];
\end{aligned}$$

(*v*) $M_1 = M, \quad M_2 = M + 2$

$$\begin{aligned}
D^2_S = {} & \frac{[(S - M - 1)(S - M)(S + M + 1)(S + M + 2)]^{1/2}}{(2S + 2)(2S + 3)} \\
& \times \delta_{k_1k_2}\beta(S_{N-1})\beta(S_N)\bar{\alpha}(S'_{N-1})\bar{\alpha}(S'_N).
\end{aligned}$$

The branching rules (26) allow one to solve completely the problem of spin-orbital expansion of wave functions of the type (9) in the LS-coupling.

Thus, we have considered the LS-symmetry of the 1- and 2-matrices. The *J*-symmetry of RDM may be considered in a similar way though it had been little investigated to date (Hunter, 1971), but the *J*-expansions of 1- and 2-matrices would allow one to simplify considerably the calculations of the matrix elements of the operators and to construct the theory of effective operators in the *jj*-coupling.

IV. Permutational Symmetry Properties

1. As we have already emphasized, the RDM offer considerable advantages in considering the quantum mechanical systems. The 1- and 2-matrices, e.g., contain complete information concerning calculations of matrix elements of one- and two-particle operators. So called "spinfree" RDM (Kaplan, 1963; Poshusta and Matsen, 1966; Poshusta, 1967; Klein, 1969, 1970, 1974a) offer an additional economy in calculations of spinless operators. The spinfree RDM are the generalization of the common boson and fermion RDM from the viewpoint of permutational symmetry. Consequently, the variety of problems arising in the theory of the usual RDM is extended; in particular, this concerns the variety of the transition RDM, the transition not only between different wave functions, but also between different Young schemes, as well as the N-representability problem whose solution for spinfree RDM is especially far from being the final one.

2. Let U be the Hilbert space over the field of complex numbers C. The elements U will be called the ket-vectors or simply kets. In essence, U represents the space of all one-particle states. Assume $U_N = \otimes^N U$ is the N-multiple tensor product of U-space. If U^+ is a dual space to U, i.e., the set of all linear mappings of in U, then similarly $U^N = \otimes^N U^+$.

Let $U_N^N = U_N \otimes U^N$ be the space of tensors of the type (N, N), i.e., the tensors that transform covariantly and contravariantly in N indices relative to the transformations of U-space. If $\{|i_k\rangle\}_k$ is the basis of U-space then $\{|I(N)\rangle\langle y(N)|\}_{Ij}$, where $|I(N)\rangle = |i_1\rangle|i_2\rangle \cdots |i_N\rangle$, $\langle j(N)| = \langle j_N|\langle j_{N-1}| \cdots \langle j_1|$ is the natural basis of U_N^N.

It is obvious that any element $|U\rangle\langle U| \in U_N^N$ may be expanded in this basis

$$|U\rangle\langle V| = \sum_{I(N)} \sum_{j(N)} |I(N)\rangle\langle j(N)|\langle I(N)|U\rangle\langle V|j(N)\rangle.$$

Let $|U\rangle\langle V|$ and $|W\rangle\langle X|$ be the elements of U_N^N. Then the composition law is naturally given on

$$(|U\rangle\langle V|)(|W\rangle\langle X|) \equiv |U\rangle\langle V|W\rangle\langle X| \equiv |U\rangle\langle X|\langle V|W\rangle.$$

It is clear $|U\rangle\langle V|$ is the idempotent provided that $\langle U|U\rangle = 1$. It is obvious that the N-particle density matrices are the (N, N)-type tensors. Furthermore, the set of all N-particle density matrices that correspond to pure and mixed states form a convex subset in U_N^N. And finally, the transition density matrices are also the tensors of (N, N)-type.

Let us define the reduction of tensors of the (N, N)-type (Poshusta and Matsen, 1966), which is a particular case of contraction. Let

$$|I(N)\rangle = |i\rangle|i_2\rangle \cdots |i_n\rangle = |i(n)\rangle|i(m)\rangle,$$

$$|j(N)\rangle = |j_1\rangle|j_2\rangle \cdots |j_n\rangle \cdots |j_N\rangle = |j(n)\rangle|j(m)\rangle \qquad (n + m = N).$$

Then according to the definition

$$\mathrm{Tr}^{(m)}|I(N)\rangle\langle j(N)| \equiv |i(n)\rangle\langle j(n)|\langle j(m)i(m)\rangle.$$

Then for any $X \in U_N^N$

$$\mathrm{Tr}^{(m)}X = \sum_{I(n)}\sum_{j(n)} \mathrm{Tr}^{(m)}(|I(N)\rangle\langle I(N)|X|j(N)\rangle\langle j(N)|)$$

$$= \sum_{I(n)}\sum_{j(n)} |i(n)\rangle\langle I(N)|X|j(n)j(m)\rangle\langle j(m)|i(m)\rangle\langle j(n)|.$$

It is obvious that $\mathrm{Tr}^{(m)}$: $U_N^N \to U_n^n$.

3. Let S_N be the symmetric group, i.e., the group of all $N!$ permutations of N symbols.

Let us consider now the group algebra R_N. The algebra is semisimple and there is an expansion $R_N = \Sigma_{[\lambda]}^{\oplus} R_N e^{[\lambda]}$ in the direct sum of invariant subalgebras of the algebra R_N and

$$e^{(\lambda)} = \frac{f^{[\lambda]}}{N!} \sum_{P \in S_N} \chi^{[\lambda]}(P^{-1})P,$$

where $f^{[\lambda]}$ is the dimension of the irreducible representation (irr) corresponding to the Young scheme $[\lambda]$ (which equals the number of standard Young tableau for the given scheme $[\lambda]$), $\chi^{[\lambda]}(P)$ is the character of the element $P \in S_N$ in $[\lambda]$.

The metric basis R_N forms the primitive orthogonal idempotents $\{e_{rs}^{[\lambda]}\}$ satisfying the relation: $e_{rs}^{[\lambda_1]} e_{tu}^{[\lambda_2]} = \delta^{[\lambda_1][\lambda_2]} \delta_{st} e_{ru}^{[\lambda_1]}$. In particular, as a basis R_N we may take the complete set of semi-normal idempotents.

There is a connection between the given basis of the group algebra and its regular basis

$$e_{rs}^{[\lambda]} = \frac{f^{[\lambda]}}{N!} \sum_{P \in S_N} [P^{-1}]_{sr}^{[\lambda]} P, \qquad P = \sum_{[\lambda]} \sum_{r,s=1}^{f^{[\lambda]}} [P]_{rs}^{[\lambda]} e_{rs}^{[\lambda]},$$

where $[P]_{rs}^{[\lambda]}$ is the (r, s)th matrix element of $P \in S_N$ in irr $[\lambda]$.

The expansion of R_N in a direct sum of invariant subalgebras induces the expansion of U_N^N:

$$U_N^N = \sum_{[\lambda_1][\lambda_2]}^{\oplus} U_{[\lambda_1][\lambda_2]}^N \qquad \text{where} \quad U_{[\lambda_1][\lambda_2]}^N \equiv e^{[\lambda_1]} U_N^N e^{[\lambda_2]\dagger}$$

or the subexpansion over

$$U^{N}_{[\lambda_1]r,[\lambda_2]t} \equiv e^{[\lambda_1]}_{rr}\, U^{N}_{N} e^{[\lambda_2]\dagger}_{tt}$$

due to $e^{[\lambda]}_{rs} R_N = e^{[\lambda]}_{r\sigma} R_N$.

Finally, we introduce two more notations:

$$U^{N\to n}_{[\lambda_1][\lambda_2]} \equiv \mathrm{Tr}^{(m)}(e^{[\lambda_1]} U^{N}_{N} e^{[\lambda_2]\dagger}),$$

$$U^{N\to n}_{[\lambda_1]r,[\lambda_2]t} \equiv \mathrm{Tr}^{(m)}(e^{[\lambda_1]}_{rr}\, U^{N}_{N} e^{[\lambda_2]\dagger}_{tt}).$$

4.1. Let $|U\rangle$ and $|V\rangle$ be arbitrary elements of U_N. Then the RDM of the nth order $(n < N)$ corresponding to the kets $|U\rangle$ and $|V\rangle$ is defined as

$$D^{n}_{UV} \equiv \mathrm{Tr}^{(m)}(|U\rangle\,\langle V|) \qquad (n + m = N)$$

Let us consider the kets $|U\rangle = |u_1\rangle|u_2\rangle \cdots |u_N\rangle$ and $|V\rangle = |v_1\rangle|v_2\rangle \cdots |v_N\rangle$. Then according to the definition

$$\begin{aligned} D^{n}_{UV}([\lambda_1]rs;\, [\lambda_2]tu &= \mathrm{Tr}^{(m)}(e^{[\lambda_1]}_{rs}\,|U\rangle\langle V| e^{[\lambda_2]\dagger}_{tu}) \\ &= \frac{f[\lambda_1]\, f[\lambda_2]}{(N!)^2} \sum_{P\in S_N} [P^{-1}]^{[\lambda_1]}_{sr} \sum_{P'\in S_N} [P^{1}]^{[\lambda_2]}_{ut} D^{n}_{UV}[P|P^{1}], \end{aligned}$$

where $D^{n}_{UV}[P|P'] = \mathrm{Tr}^{(m)}(P|U\rangle\langle V|P')$ are primitive RDM. They satisfy the following relation (Poshusta and Matsen, 1966):

$$D^{n}_{UV}[P|P'] = D^{n}_{UV}[\pi P|P'\pi^{-1}] \tag{7}$$

for any $\pi \in S_m$ of the group of permutations of $n + 1, n + 2, \ldots, N$ particles.

In what follows in order to use this property we expand S_N in left cosets on the subgroup S_m: $S_N = \cup_c P_c S_m$.

Then

$$\begin{aligned} &\sum_{P\in S_N} [P^{-1}]^{[\lambda_1]}_{sr} \sum_{P'\in S_N} [P']^{[\lambda_2]}_{ut} D^{n}_{UV}[P|P'] \\ &\quad = \bigcup_{c} \bigcup_{c'} \sum_{\pi\in S_m} \sum_{\pi'\in S_m} [P_c^{-1}\pi^{-1}]^{[\lambda_1]}_{sr} [P'_{c'}\pi]^{[\lambda_2]}_{ut} D^{n}_{UV}[\pi P_c|P'_{c'}\pi'] \\ &\quad = \bigcup_{c} \bigcup_{c'} \sum_{s=1}^{f^{[\lambda_1]}} \sum_{W=1}^{f^{[\lambda_2]}} [P_c^{-1}]^{[\lambda_1]}_{sv} [P'_{c'}]^{[\lambda_2]}_{uw} \sum_{\pi\in S_m} \sum_{\pi'\in S_m} [\pi^{-1}]^{[\lambda_1]}_{sr} [\pi']^{[\lambda_2]}_{ut} \\ &\qquad \times D^{n}_{UV}[\pi P_c|P'_{c'}\pi']. \end{aligned}$$

By means of substitution $\pi' = \tau\pi^{-1}$ and taking into account (7) we have

$$\begin{aligned} &\sum_{\pi\in S_m} \sum_{\pi'\in S'_m} [\pi^{-1}]^{[\lambda_1]}_{v} [\pi']^{[\lambda_2]}_{wt} D^{n}_{UV}[\pi P_c|P'_{c'}\pi'] \\ &\qquad = \sum_{z=1}^{f^{[\lambda_2]}} \sum_{\tau\in S_m} [\tau]^{[\lambda_2]}_{wz} D^{n}_{UV}]P_c|P'_{c'}\tau] \sum_{\pi\in S_m} [\pi^{-1}]^{[\lambda_1]}_{vr} [\pi^{-1}]^{[\lambda_2]}_{zt}. \end{aligned}$$

To calculate the last sum we consider the reduction $S_N \supset S_n \times S_m$. Then

$$[\lambda] = \sum_{[\lambda_1][\lambda_2]} ([\lambda_1] \otimes [\lambda_2] \rightarrow [\lambda])[\lambda_1] \otimes [\lambda_2],$$

where $[\lambda]$, $[\lambda_1]$, $[\lambda_2]$ are the Young schemes corresponding to the symmetry groups S_N, S_n, S_m, respectively; $\otimes$ denotes an outer direct product of groups.

The possible Young schemes $[\lambda_1]$ and $[\lambda_2]$ into which the scheme $[\lambda]$ breaks in reduction $S_N \supset S_n \times S_m$ are usually found by means of the Littlewood theorem (Littlewood, 1958). Next, we shall denote by A a nonstandard representation based on this reduction. Let $\langle r|(r)^A\rangle^{[\lambda]}$ be the element of the transformation matrix (Kaplan, 1974) that connects the standard and nonstandard representation for the given Young scheme $[\lambda]$. Then

$$[\pi]_{rt}^{[\lambda]} = \sum_{(r)^A(t)^A} \langle r|(r)^A\rangle^{[\lambda]}\langle (r)^A|\pi|(t)^A\rangle^{[\lambda]}\langle (t)^A|t\rangle^{[\lambda]}.$$

Taking into account $\pi \in S_m$ we obtain

$$[\pi]_{rt}^{[\lambda]} = \sum_{(r)^A(t)^A} \langle r|(r)^A\rangle^{[\lambda]}\langle (r)^A|\pi|(t)^A\rangle^{[\lambda]}\langle (t)^A|t\rangle^{[\lambda]}.$$

since for the reduction $A(r)^A = (r_1, r_2)$. Thus

$$\begin{aligned}
&\sum_{\pi\in S_m} [\pi^{-1}]_{vr}^{[\lambda_1]} [\pi^{-1}]_{zt}^{[\lambda_2]} \\
&\quad = \sum_{v_1v_2} \sum_{[\lambda_1^1][\lambda_1^2]} \langle v|[\lambda_1^1]v_1[\lambda_1^2]v_2\rangle^{[\lambda_1]} \\
&\qquad \times \sum_{r_1r_2} \langle [\lambda_1^1]r_1[\lambda_1^2]r_2|r\rangle^{[\lambda_1]} \sum_{z_1z_2} \sum_{[\lambda_1^1][\lambda_2^2]} \langle z|[\lambda_2^1]z_1[\lambda_2^2]z_2\rangle^{[\lambda_2]} \\
&\qquad \times \sum_{t_1t_2} \langle [\lambda_2^1]t_1[\lambda_2^2]t_2|t\rangle^{[\lambda_2]} \delta_{v_1r_1}^{[\lambda_1^1]} \delta_{z_1t_1}^{[\lambda_2^1]} ([\lambda_1^1] \otimes [\lambda_1^2] \rightarrow [\lambda_1]) \\
&\qquad \times ([\lambda_2^1] \otimes [\lambda_2^2] \rightarrow [\lambda_2]) \sum_{\pi\in S_m} \langle v_2|\pi|r_2\rangle^{[\lambda_1^2]}\langle z_2|\pi|t_2\rangle^{[\lambda_2^2]}.
\end{aligned}$$

Taking into account the orthogonality relations for the real irr and for the elements of the transformation matrix (Kaplan, 1974), we obtain the following expression (Kryachko, 1976):

$$\begin{aligned}
&D_{UV}^{n}([\lambda_1]rs; [\lambda_2]tu) \\
&\quad = \frac{f^{[\lambda_1]}f^{[\lambda_2]}}{(N!)^2} \bigcup_{c} \bigcup_{c'} \sum_{v=1}^{f^{[\lambda_1]}} \sum_{W=1}^{f^{[\lambda_2]}} [P_c^{-1}]_{sv}^{[\lambda_1]} \\
&\qquad \times [P'_{c'}]_{uw}^{[\lambda_2]} \sum_{W_2} \sum_{\substack{v_1z_1\\ v_2r_2}} \sum_{[\lambda_1^1][\lambda_2^1]} \sum_{[\lambda^2]} \frac{m!}{f^{[\lambda^2]}} \langle W|[\lambda_2^1]z_1[\lambda_2^2]W_2\rangle^{[\lambda_2]} \\
&\qquad \times \langle [\lambda_2^1]z_1[\lambda^2]r_2|t\rangle^{[\lambda_2]}\langle [\lambda_1^1]v_1[\lambda^2]r_2|r\rangle^{[\lambda_1]} \\
&\qquad \times \langle v|[\lambda_1^1]v_1[\lambda^2]v_2\rangle^{[\lambda_1]}([\lambda_1^1] \otimes [\lambda^2] \rightarrow [\lambda_1])([\lambda_2^1] \otimes [\lambda_2] \rightarrow [\lambda^2]) \\
&\qquad \times \sum_{\tau\in S_m} \langle W_2|\tau|v_2\rangle^{[\lambda^2]} D_{UV}^{n}[P_c|P'_{c'}\tau]. \qquad (8)
\end{aligned}$$

Thus, from (8) it follows that the reduced transition density matrices exist not only between various kets but also between different Young schemes.

4.2. To consider the RDM in some particular cases it is convenient to use the following formula (Kryachko, 1976):

$$
\begin{aligned}
&D^n_{UV}([\lambda_1]rs;\,[\lambda_2]tu)\\
&\quad= \frac{f^{[\lambda_1]}f^{[\lambda_2]}}{(N!]^2} \bigcup_c \sum_{P\in S_N} \sum_{v=1}^{f^{[\lambda_1]}} \sum_{z=1}^{f^{[\lambda_2]}} [P_c^{-1}]^{[\lambda_1]}_{sv}\\
&\qquad\times [P]^{[\lambda_2]}_{uz}\, D^n_{UV}[P_c|P] \sum_{v_1z_1} \sum_{v_2r_2} \sum_{[\lambda^1_1][\lambda^1_2]} \sum_{[\lambda^2]} \frac{m!}{f^{[\lambda_2]}}\\
&\qquad\times \langle v|[\lambda^1_1]v_1[\lambda_2]v_2\rangle^{[\lambda_1]}\\
&\qquad\times \langle[\lambda^1_1]v_1[\lambda^2]r_2|r\rangle^{[\lambda_1]}\langle z|[\lambda^1_2]z_1[\lambda^2]v_2\rangle^{[\lambda_2]}\\
&\qquad\times \langle[\lambda^1_2]z_1[\lambda^2]r_2|t\rangle^{[\lambda_2]}\\
&\qquad\times ([\lambda^1_1]\otimes[\lambda^2]\to[\lambda_1])([\lambda^1_2]\otimes[\lambda^2]\to[\lambda_2]).
\end{aligned}
\tag{9}
$$

Because of the factors $([\lambda^1_1]\otimes[\lambda^2]\to[\lambda_1])([\lambda^1_2]\otimes[\lambda^2]\to[\lambda_2])$ in the formulas (8), (9) there follow selection rules for the RDM of transitions between kets that are transformed on irr's $[\lambda_1]$ and $[\lambda_2]$. For example, $D^n_{UV}([1^N];\,[N]) \equiv 0$ for $n = N-2, N-3, \ldots, 1$ (for any $|U\rangle$ and $|V\rangle$ from U_N), i.e., the mixture of boson and fermion Nth kets ($N \geq 4$) does not make the contribution to the 2-matrix.

In particular, if $|U\rangle = |V\rangle$ and $|U\rangle$ does not contain repetitive one-particle kets, i.e., invariant (Poshusta, 1967) (see §2.5) $|U\rangle$ is equal to $\{k\} = \{1, 1, \ldots, 1\}$, then the formula (8) is simplified:

$$
\begin{aligned}
&D^n_{UU}([\lambda_1]rs;\,[\lambda_2]tu)\\
&\quad= \frac{f^{[\lambda_1]}f^{[\lambda_2]}}{(N!)^2} \bigcup_c \sum_{v=1}^{f^{[\lambda_1]}} \sum_{W=1}^{f^{[\lambda_2]}} [P_c^{-1}]^{[\lambda_1]}_{sv}[P_c]^{[\lambda_2]}_{uW}\\
&\qquad\times \sum_{\substack{v_1z_1\\ v_2v_2}} \sum_{[\lambda^1_1][\lambda^1_2]} \sum_{[\lambda^2]} \frac{m!}{f^{[\lambda^2]}} \langle W|[\lambda^1_2]z_1[\lambda^2]v_2\rangle^{[\lambda_2]}\\
&\qquad\times \langle[\lambda^1_2]z_1[\lambda_2]v_2|t\rangle^{[\lambda_2]}\langle[\lambda^1_1]v_1[\lambda^2]v_2|t\rangle^{[\lambda_1]}\\
&\qquad\times \langle v|[\lambda^1_1]v_1[\lambda^2]v_2\rangle^{[\lambda_1]}\\
&\qquad\times ([\lambda^1_1]\otimes[\lambda^2]\to[\lambda_1])([\lambda^1_2]\otimes[\lambda^2]\to[\lambda_2])D^n_{UU}[P_c|P_c].
\end{aligned}
\tag{10}
$$

Now we consider the following example. Let

$$|U\rangle = |V\rangle = |u_1\rangle|u_2\rangle|u_3\rangle|u_4\rangle$$

and the invariant is equal to $\{1, 1, 1, 1\}$. We assume also that $[\lambda_1] = [2^2]$ and $[\lambda_2] = [21^2]$, and $r = s = t = u = 1$ in the formula (10). Then

$$S_4 = S_2 \cup (13)S_2 \cup (23)S_2 \cup (14)S_2 \cup (24)S_2 \cup (12)S_2 \cup (123)S_2 \cup (124)S_2 \cup (132)S_2 \cup (142)S_2 \cup (1324)S_2 \cup (1423)S_2.$$

In this case the transformation matrices have the form (Kaplan, 1974):

$$[\lambda_1^1]\text{:}\quad [2]\quad [2];\qquad [\lambda_1^2]\text{:}\quad [2]\quad [1^2]$$

$$\langle r|[\lambda_1^1][\lambda_1^2]\rangle^{[2^2]} = \begin{array}{c|cc|} r_1 & 0 & -1 \\ r_2 & 1 & 0 \end{array}\,.$$

$$\begin{array}{llll} [\lambda_2^1]\text{:} & [2] & [1^2] & [1^2] \\ [\lambda_2^2]\text{:} & [1^2] & [2] & [1^2] \end{array}$$

$$\langle r|[\lambda_2^1][\lambda_2^2]\rangle^{[21^2]} = \begin{array}{cccc} r_1 & 1 & 0 & 0 \\ r_2 & 0 & \frac{\sqrt{3}}{3} & -\frac{\sqrt{6}}{3} \\ r_3 & 0 & \frac{\sqrt{6}}{3} & \frac{\sqrt{3}}{3} \end{array}$$

Thus we have

$$\begin{aligned} &D^2_{UU}([2^2]_{11};\, [21^2]_{11}) \\ &= \tfrac{1}{12}\{|u_1\rangle|u_2\rangle\langle u_2|\langle u_1| + |u_2\rangle|u_1\rangle\langle u_1|\langle u_2| \\ &\quad + \tfrac{1}{4}[|u_3\rangle|u_2\rangle\langle u_2|\langle u_3| + |u_2\rangle|u_3\rangle\langle u_3|\langle u_2| + |u_1\rangle|u_3\rangle\langle u_3|\langle u_1| \\ &\quad + |u_4\rangle|u_2\rangle\langle u_2|\langle u_4| + |u_2\rangle|u_4\rangle\langle u_4|\langle u_2| + |u_1\rangle|u_4\rangle\langle u_4|\langle u_1| \\ &\quad + |u_4\rangle|u_1\rangle\langle u_1|\langle u_4| + |u_3\rangle|u_1\rangle\langle u_1|\langle u_3|]\}. \end{aligned}$$

From this there follows

$$\begin{aligned} &e^{[1^2]}D^2_{UU}([2^2]11;\, [21^2]11)e^{[1^2]} \\ &= + \tfrac{1}{36}\{|u_1\rangle|u_2\rangle\langle u_2|\langle u_1| - |u_2\rangle|u_1\rangle\langle u_2|\langle u_1| - |u_1\rangle|u_2\rangle\langle u_1|\langle u_2| \\ &\quad + |u_2\rangle|u_1\rangle\langle u_1|\langle u_2| + \tfrac{1}{4}[(|u_3\rangle|u_2\rangle\langle u_2|\langle u_3| - |u_2\rangle|u_3\rangle\langle u_2|\langle u_3| \\ &\quad - |u_3\rangle|u_2\rangle\langle u_3|\langle u_2| + |u_2\rangle|u_3\rangle\langle u_3|\langle u_2|) + (|u_1\rangle|u_3\rangle\langle u_3|\langle u_1| \\ &\quad - |u_3\rangle|u_1\rangle\langle u_3|\langle u_1| - |u_1\rangle|u_3\rangle\langle u_1|\langle u_3| + |u_3\rangle|u_1\rangle\langle u_1|\langle u_3|) \\ &\quad + (|u_4\rangle|u_2\rangle\langle u_2|\langle u_4| - |u_2\rangle|u_4\rangle\langle u_2|\langle u_4| - |u_4\rangle|u_2\rangle\langle u_4|\langle u_2| \\ &\quad + |u_2\rangle|u_4\rangle\langle u_4|\langle u_2|) + (|u_1\rangle|u_4\rangle\langle u_4|\langle u_1| - |u_4\rangle|u_1\rangle\langle u_4|\langle u_1| \\ &\quad - |u_1\rangle|u_4\rangle\langle u_1|\langle u_4| + |u_4\rangle|u_1\rangle\langle u_1|\langle u_4|)]\}, \end{aligned}$$

i.e.,

$$U^{u\to 2}_{[2^2][21^2]} \cap U^{2}_{[1^2][1^2]} \neq \emptyset$$ [4]

---

[4] This relation proves that the illustration of Theorem 1 of Klein and Kramling (1970), via contraction of $U^{[4]}_{[2^2][21^2]}$, omits the term $U^2_{[1^2][1^2]}$, which can also be seen by correctly applying the theorem.

4.3. Let us consider the case $[\lambda_1] = [\lambda_2]$ and $r = t$. We define the "completely averaged" (in irr $[\lambda]$) RDM (Poshusta and Matsen, 1966):

$$\langle D^n_{UV}([\lambda]s;[\lambda]u)\rangle \equiv \frac{1}{f^{[\lambda]}} \sum_{r=1}^{f^{[\lambda]}} D^n_{UV}([\lambda_1]rs;[\lambda]ru).$$

Then (Kryachko, 1977)

$$\langle D^n_{UV}([\lambda]s;[\lambda]u)\rangle = \frac{f^{[\lambda]}m!}{(N!)^2} \bigcup_c \sum_{P\in S_N} [P'_c P]_{us} D^n_{UV}[P|P'_c]$$

or (Poshusta and Matsen, 1966)

$$\langle D^n_{UV}([\lambda]s;[\lambda]u)\rangle = \sum_{i(n)} \sum_{j(n)} D^n_{UV}[i(n)|j(n)]_{su} |u_{i(n)}\rangle\langle v_{j(n)}|,$$

where each index of a summation i_k, j_l takes the values from 1 to N and $i_k \neq i_l (k \neq l)$,

$$D^n_{UV}[i(n)|j(n)]_{su} = \frac{f^{[\lambda]}m!}{(N!)^2} \sum_{i(m)} \left[\begin{pmatrix} i(n) & i(m) \\ j(n) & j(m) \end{pmatrix}\right]^{[\lambda]}_{us} \langle v_{j(m)}|u_{i(m)}\rangle,$$

and two indices from $i(m)$ in the sum are not equal to each other and are not equal to any index from $i(n)$.

Now we assume $|U\rangle = |V\rangle = |u_1\rangle|u_2\rangle \ldots |u_N\rangle$ and the kets $|u_i\rangle$ are orthonormalized. Then it is easily seen that

$$\langle D^1_{UU}([\lambda]s;[\lambda]s)\rangle = \frac{f^{[\lambda]}}{N!} \frac{1}{N} \sum_{i=1}^{N} |u_i\rangle\langle u_i|,$$

$$\begin{aligned}\langle D^2_{UU}([\lambda]s;[\lambda]t)\rangle &= \frac{f^{[\lambda]}}{N!} \frac{1}{N(N-1)} \sum_{i\neq j} \{|u_i\rangle|u_j\rangle\langle u_j|\langle u_i|\delta_{st} \\ &\quad + \left[\begin{pmatrix} i & j \\ j & i \end{pmatrix}\right]^{[\lambda]} |u_i\rangle|u_j\rangle\langle u_i|\langle u_j|\},\end{aligned}$$

$$\langle D^n_{UU}([\lambda]^s;[\lambda]t)\rangle = \frac{f^{[\lambda]}m!}{(N!)^2} \sum_{P\in S_N} \sum_{i(n)} [P]^{[\lambda]}_{st} |u_{i(n)}\rangle\langle u_{pi(n)}|.$$

The first formula shows that the "averaged" 1-matrix for the function $e^{[\lambda]}_{rs}|u(N)\rangle$ has the same (with an accuracy of a multiplier) form as for the Slater determinant. Finally, it is obvious that

$$D^n_{UU}([\lambda]) = \frac{1}{f^{[\lambda]}} \sum_{s=1}^{f^{[\lambda]}} \langle D^1_{UU}([\lambda]s;[\lambda]s)\rangle$$

is the nth-order immanent corresponding to the Young scheme $[\lambda]$ of the first-order density matrix $D^1_{UU'}([\lambda])$, namely (in notations of Littlewood, 1958):

$$D^n_{UU'}([\lambda]) = |\{D^1_{UU'}([\lambda])\}_{st}|^{[\lambda]}$$

i.e., gives the generalization of the formula for the nth-order density matrix by the first-order density matrix for the Fock–Dirack density matrix, providing the usual multiplication of the immanent elements should be considered as a tensor product.

4.4. Let us consider again the structure on U^N_N induced by the expansion of U^N_N in irreducible tensor components, each of which is transformed according to a certain irr of S_N.

We define the superoperation (Klein and Kramling, 1970) on U^N_N for each element $a = \Sigma_{P\in S_N}\alpha_P, P \in R_N$

$$a \circ X = \sum_{P\in S_N} \alpha_p PXP^{-1}, \qquad X \in U^N_N.$$

Then (Klein and Kramling, 1970) the set $\{T^{[\lambda]}_s;\ s = 1, \ldots, f^{[\lambda]}\}$ is an irreducible tensor set that is transformed on irr $[\lambda]$ of S_N if and only if for any $P \in S_N$

$$P \circ T^{[\lambda]}_s = \sum_{t=1}^{f^{[\lambda]}} [P]^{[\lambda]}_{ts} T^{[\lambda]}_t.$$

The superoperation induces the expansion of U^N_N in a direct sum of irreducible tensor algebras:

$$U^N_N = \sum_{[\lambda]}{}^{\otimes}\ U^{[\lambda]}_N \qquad \text{where} \quad U^{[\lambda]}_N \equiv e^{[\lambda]} \circ U^N_N.$$

Let $X \in U^N_N$. Then

$$e^{[\lambda_0]} \circ e^{[\lambda_1]}_{sr} X e^{[\lambda_2]}_{tw}$$
$$= \frac{f^{[\lambda_0]}}{N!} \sum_{u=1}^{f^{[\lambda_1]}} \sum^{f^{[\lambda_2]}} \Lambda([\lambda_0]; [\lambda_1]ur[\lambda_2]vw) e^{[\lambda_1]}_{ur} X e^{[\lambda_2]}_{vw},$$

where

$$\Lambda([\lambda_0]; [\lambda_1]ur, [\lambda_2]vw) = \sum_{P\in S_N} \chi^{[\lambda_0]}(P^{-1})[P]^{[\lambda_1]}_{ur}[P]^{[\lambda_2]}_{vw}$$

characterizes the multiplicity of irr $[\lambda_0]$ entering the inner direct product of irr's $[\lambda_1]$ and $[\lambda_2]$. Notice that so far there is no sufficiently simple method to define the expansion on irreducible components of the inner direct product of two Young schemes. Thus we have proved the following theorem.

THEOREM I

$$e^{[\lambda_0]} \circ U^N_{[\lambda_1][\lambda_2]} \subseteq \delta([\lambda_1] \times [\lambda_2], [\lambda_0]) U^N_{[\lambda_1][\lambda_2]},$$

where $\delta([\lambda_1] \times [\lambda_2], [\lambda_0])$ is distinct from zero if $[\lambda_0]$ enters (with the nonzeroth multiplicity) in the inner direct product $[\lambda_1] \times [\lambda_2]$. In particular, for any $X \in U^N_N$

$$e^{[N]} \circ e^{[\lambda]}_{rr} X e^{[\lambda]}_{rr} = \frac{N!}{f^{[\lambda]}} \sum_{s=1}^{f^{[\lambda]}} e^{[\lambda]}_{ss} X e^{[\lambda]}_{ss},$$

$$e^{[1^N]} \circ e^{[\tilde{\lambda}]}_{rr} X e^{[\lambda]}_{rr} = \frac{N!}{f^{[\lambda]}} \sum_{s=1}^{f^{[\lambda]}} e^{[\tilde{\lambda}]}_{ss} X e^{[\lambda]}_{ss},$$

where $[\lambda]$ is the Young scheme conjugated to $[\lambda]$.

THEOREM II. For any $U \in U_N$

$$D^n_{UU}([\lambda]) \in U^n_{[n]} \cap U^{N \to n}_{[\lambda][\lambda]} .$$

Proof. It is obvious that

$$\begin{aligned} D^n_{UU}([\lambda]) &= \left(\frac{1}{f^{[\lambda]}}\right)^2 \sum_{s=1}^{f^{[\lambda]}} \sum_{r=1}^{f^{[\lambda]}} D^n_{UU}([\lambda]rs ; [\lambda]rs) \\ &= \left(\frac{1}{f^{[\lambda]}}\right)^2 \sum_{s=1}^{f^{[\lambda]}} \sum_{r=1}^{f^{[\lambda]}} \mathrm{Tr}^{(m)}(e^{[\lambda]}_{rs}|U\rangle \langle U|e^{[3\lambda]^\dagger}_{rs}). \end{aligned}$$

Then for any $P \in S_k$

$$P e^{[\lambda]}_{rs}|U\rangle \langle U|e^{[\lambda]}_{rs} P^{-1} = \sum_{t=1}^{f^{[\lambda]}} \sum_{u=1}^{f^{[\lambda]}} [P]^{[\lambda]}_{tr} [P^{-1}]^{[\lambda]}_{ru} e^{[\lambda]}_{ts}|U\rangle \langle U|e^{[\lambda]}_{us}.$$

So we have

$$\begin{aligned} P D^n_{UU}([\lambda]) P^{-1} &= \left(\frac{1}{f^{[\lambda]}}\right)^2 \sum_{r,s,t=1}^{f^{[\lambda]}} [P]^{[\lambda]}_{tr} [P^{-1}]^{[\lambda]}_{ru} \, \mathrm{Tr}^{(m)}(e^{[\lambda]}_{ts}|U\rangle \langle U|e^{[\lambda]}_{us}) \\ &= \left(\frac{1}{f^{[\lambda]}}\right)^2 \sum_{s,t,u=1}^{f^{[\lambda]}} [PP^{-1}]^{[\lambda]}_{tu} \, \mathrm{Tr}^{(m)}(e^{[\lambda]}_{ts}|U\rangle \langle U|e^{[\lambda]}_{us}) \\ &= \left(\frac{1}{f^{[\lambda]}}\right)^2 \sum_{s,t=1}^{f^{[\lambda]}} \mathrm{Tr}^{(m)}(e^{[\lambda]}_{ts}|U\rangle \langle U|e^{[\lambda]}_{ts}| = D^n_{UU}([\lambda]). \end{aligned}$$

Q.E.D.

5. In this section we consider some necessary conditions of the N, $[\lambda_1]$, $[\lambda_2]$-derivability problem, which is a natural generalization of the N-representability problem (Coleman, 1963) on more general Young schemes.

Assume that $X \in U_n^n \cdot X$ is said to be derivable if there is an element $Y \in U_N^N$ $(n < N)$ such that

$$X = \mathrm{Tr}^{(m)}(e_{rr}^{[\lambda_1]} Y e_{tt}^{[\lambda_2]}).$$

It is obvious that X is N, $[\lambda_1)r$, $[\lambda_2]t$-derivable if

$$X \in U_{[\lambda_1]n[\lambda_2]t}^{N-n}$$

5.1. Considering the N, $[\lambda_1]$, $[\lambda_2]$-derivability problem, we restrict ourselves to the Young schemes of the form $[2^{p_1 N-2p}]$, which corresponds to the spin-free formulation of quantum mechanics of molecules and is of special interest for finding the eigenvalues of spinless electronic operators. The most convenient representation for considering the N, $[\lambda_1]$, $[\lambda_2]$-derivability problem is the seminormal representation of the symmetric group S_N (Rutherford, 1948). Let r be the standard Young tableau, and P_r and N_r be the permutation sets in the rows and columns of this Young tableau. Then $E_r = P_r N_r$ is the Young idempotent of the tableau r. Now we define a set of seminormal idempotents. Let $E_r^{(n)}$ be the Young idempotent that corresponds to the standard Young tableau of n squares obtained by separating the squares with the symbols $n + 1$, $n + 2, \ldots, N$ from the tableau. Then the seminormal idempotents $e_r^{(n)}$ are defined recurrently:

$$e_r \equiv \frac{n}{\theta_r} e_r^{(N-1)} E_r e_r^{(N-1)}$$

$$\vdots$$

$$e^{[1]} \equiv \varepsilon,$$

where ε is the unit of the algebra R_N. We have found the necessary conditions for the N, $[\lambda_1]$, $[\lambda_2]$-derivability problem in the work of Kryachko (1976). They have been proved on the basis of the properties of the seminormal idempotents of algebra R_N (Young, 1900, 1902, 1927; Yamanouchi, 1937; Thrall, 1941; Rutherford, 1948). There follows

THEOREM III

$$\mathrm{Tr}^{(m)}(e_r^{[\lambda_1]} U_N^N e_s^{[\lambda_2]+}) \subseteq e_r^{(N-m)[\lambda_1]} U_N^N e_s^{(N-m)[\lambda_2]+}.$$

6. Now we turn to the consideration of sufficient conditions of the N, $[\lambda_1]$, $[\lambda_2]$-derivability problem using primitive orthogonal minimal idempotents:

$$E_r^{[\lambda]} = P_r^{[\lambda]} N_r^{[\lambda]}.$$

We are interested in the Young schemes of the form $[2^{P_1 N-2p}]$ as in the previous section and divide, as before, our proof into four points depending on the place of symbol N in the Young tableau $|[\lambda_1]r\rangle$ and $|[\lambda_2]S\rangle$.

6.1. Assume that

$$E_r^{[\lambda_1]} = P_r^{(N-1)[\lambda_1]} N_r^{(N-1)[\lambda_1]}[1 - (Na_1) - \cdots - (Na_k)].$$

$$E_s^{[\lambda_2]} = P_s^{(N-1)[\lambda_2]} N_s^{(N-1)(\lambda_2)}[1 - (Nc_1) - \cdots - (Nc_m)].$$

Then

$$\begin{aligned}
&P_r^{(N-1)[\lambda_1]} N_r^{(N-1)[\lambda_1]} |i(N-1)\rangle \langle j(N-1)| N_s^{(N-1)[\lambda_2]} P_s^{(N-1)[\lambda_2]} \\
&\quad = \mathrm{Tr}^{(1)}\{E_r^{[\lambda_1]} |i(N)\rangle \langle j(N)| E_s^{[\lambda_2]\dagger}\} \\
&\quad = \sum_{u=1}^{k} \mathrm{Tr}^{(1)}\{P_r^{(N-1)[\lambda_1]} N_r^{(N-1)[\lambda_1]} (Na_u) |i(N)\rangle \langle j(N)| N_s^{(N-1)[\lambda_2]} P_s^{(N-1)[\lambda_2]}\} \\
&\qquad + \sum_{v=1}^{m} \mathrm{Tr}^{(1)}\{P_r^{(N-1)[\lambda_1]} N_r^{(N-1)[\lambda_1]} |i(N)\rangle \langle j(N)| (Nc_r) N_s^{(N-1)[\lambda_2]} P_s^{(N-1)[\lambda_2]}\} \\
&\qquad - \sum_{r=1}^{m} \sum_{u=1}^{k} \mathrm{Tr}^{(1)}\{P_r^{(N-1)[\lambda_1]} N_r^{(N-1)[\lambda_1]} (Na_u) |i(N)\rangle \\
&\qquad \times \langle j(N)| (Nc_r) N_s^{(N-1)[\lambda_2]} P_s^{(N-1)[\lambda_2]}\}.
\end{aligned} \tag{11}$$

The ket $|i(N)\rangle$ contains one-particle kets $|i_1\rangle, |i_2\rangle, \ldots, |i_k\rangle$ each $k_1, \ldots, k_k$ time. Then it indicates (Poshusta and Matsen, 1966) that the ket $|i(N)\rangle$ has the invariant $\{k\}_i = \{k_1, k_2, \ldots, k_k\}$ (numbers k_i are situated in nonincreasing order). Then $E_r^{[\lambda]}|i(N)\rangle \neq 0$ if $[\lambda] \geq \{k\}_i$ in the sense of usual ordering of the Young schemes (Rutherford, 1948).

Let us consider the ket $|i(N-1)\rangle$ and $|i(N)\rangle = |i(N-1)\rangle\, |h\rangle$. Then $\{k\}_i$ and $\{k\}_{ih}$ are invariants of $|i(N-1)\rangle$, $i(N)$, respectively. In this case[5] $[\lambda_1]_r \geq \{k\}_{N-1}$. For $[\lambda_1]_r \geq \{k\}_{ik}$ (similarly to $[\lambda_2]_s \geq \{k\}_{jh}$) we can choose an h that is not equal to any one-particle ket from $|i(N-1)\rangle$ and $|j(N-1)\rangle$. Then in (11) the second and the third right-hand terms vanish. Further expanding (Na_u) in the Young idempotents and taking into account the left $E_r^{(N-1)[\lambda_1]} = E_r^{[\lambda]}$, expanding only in the Young idempotents $E_r^{[\lambda_0]}$ where $[\lambda_0] \in \{[\lambda_+]\}$, we obtain the sum only on those Young schemes $[\lambda_0]$ for which $[\lambda_0] \in \{[\lambda_+]\}$—the corrollary of Theorem 10b (Rutherford, 1948); similarly to $[\lambda_2]$.

Using the same considerations for all the possible positions of the symbol N in the Young schemes $[\lambda_1]$ and $[\lambda_2]$, and Theorem 10b (Rutherford, 1948), we have finally:

THEOREM IV

$$U_{[\lambda_1][\lambda_2]}^{N-1} \subseteq \sum_{[\lambda_1\dagger]} \sum_{[\lambda_2\dagger]}^{\oplus} U_{[\lambda_1\dagger][\lambda_2\dagger]}^{N\to N-1}.$$

---

[5] $[\lambda_-]_r$ denotes the Young tableau obtained by separation of symbol N from the Young tableau $|[\lambda]_r\rangle$. Similarly, $[\lambda_+]$ denotes all the standard Young schemes obtained by an addition in any way of one square to the standard scheme $[\lambda_-]$.

Consequently, by induction it is easy to derive a general statement. Thus, we have found the sufficient condition for the N, $[\lambda_1]$, $[\lambda_2]$-derivability problem for any Pauli-allowed Young schemes $[\lambda_1]$ and $[\lambda_2]$.

7. In this section we shall, in principle, follow the paper by Poshusta and Matsen (1966). This section deals with the correlation. However, we will not dwell upon this matter in detail, moreover, we will try to give a strong mathematical definition (and it obviously exists) of the correlation notation. It is clear intuitively what this term means. It roughly means the consideration of corrections, the introduction of some specifications arising when comparing the results of the model under study and the properties that the system should possess but are not taken into account by the present model, with the experimental data.

We discuss the permutation correlation, i.e., we restrict ourselves to the consideration of the probability of coinciding pairs of particles. Further, we find that the coincidence probability of two particles depends on the permutation symmetry, namely: when $[\lambda]$ changes from $[1^N]$ to $[N]$[6] the coincidence probability increases from zero to the maximal value. Just this effect is called the permutation correlation.

Let us consider the two-particle operator

$$\rho = \sum_{i<j} \rho_{ij}$$

where ρ_{ij} is the operator of the coincidence of the ith and jth particles [in the Schrödinger representation $\rho_{ij} = \delta(\mathbf{r}_{ij})$]. Now we calculate the average value of this operator in the averaged state $\|[\lambda]s\rangle$

$$\begin{aligned}\langle \rho\rangle_{[\lambda]s} &= \frac{N(N-1)}{2}\,\mathrm{Tr}^{(2)}(\rho_{12}\langle D^2_{UU}([\lambda]s;\,[\lambda]s)\rangle) \\ &= \mathrm{Tr}^{(2)}\,\frac{f^{[\lambda]}}{2N!}\sum_{i\neq j}\Big\{\rho_{12}|u_i\rangle|u_j\rangle\langle u_j|\langle u_i| \\ &\quad + \left[\begin{pmatrix} i & j \\ j & i\end{pmatrix}\right]^{[\lambda]}_{ss}\rho_{12}|u_i\rangle|u_j\rangle\langle u_i|\langle u_j|\Big\}.\end{aligned}$$

Assume that

$$\langle u_i|\langle u_j|\rho_{12}|u_i\rangle|u_j\rangle \equiv \langle u_j|\langle u_i|\rho_{12}|u_i\rangle|u_j\rangle \equiv R_{ij}.$$

Then

$$\begin{aligned}\langle \rho\rangle_{[\lambda]s} &= \frac{f^{[\lambda]}}{2N!}\sum_{i\neq j}\left(1 + \left[\begin{pmatrix} i & j \\ j & i\end{pmatrix}\right]^{[\lambda]}_{ss}\right)R_{ij} \\ &= \frac{f^{[\lambda]}}{N!}\sum_{ij}\left\{1 + \left[\begin{pmatrix} i & j \\ j & i\end{pmatrix}\right]^{[\lambda]}_{ss}\right\}R_{ij}.\end{aligned}$$

---

[6] The possible Young schemes have no more than two columns.

Now we calculate

$$\langle \rho \rangle_{[\lambda]} \equiv \frac{1}{f^{[\lambda]}} \sum_{s=1}^{f^{[\lambda]}} \langle \rho \rangle_{[\lambda]s} = \frac{1}{N!}(1 + \chi_2^{[\lambda]})\bar{R},$$

where

$$\bar{R} \equiv \sum_{ij} R_{ij}, \; \chi_2^{[\lambda\,2]} \equiv \sum_{ij} \chi^{[\lambda]}\left(\begin{pmatrix} i & j \\ j & i \end{pmatrix}\right).$$

So we have (Klein, 1974a) in the case $[\lambda] = [2^p 1^{N-2p}]$

$$\chi_2^{[\lambda]} = f^{[\lambda]} \binom{N}{2}^{-1} \left[p^2 - p(N + 1) + \frac{N(N - 1)}{2}\right]$$

In particular, for $[\lambda] = [1^N] \langle \rho \rangle_{[1^N]} = 0$ and $[\lambda] = [2^p]$

$$\langle \rho \rangle_{[2p]} = \frac{1}{N!}(1 + 2f^{[\lambda]}\bar{R}.$$

Thus, for the antisymmetric state the coincidence probability of pairs of particles is equal to zero and for the Young scheme $[2^p]$ it takes the largest (with a given $N = 2p$) value.

V. *G*-Symmetry

1. In this section we consider the G-symmetry of RDM. Under G we mean any discrete group, in particular, a point one. A point symmetry appears in the problems in which a given effective Hamiltonian suggesting a rigid nuclear frame commutes with a point group.

Let U_N^N be the space of tensors of the type (N, N). Assume that $[G]^N$ is the N-multiple inner direct product (Klein, 1974b):

$$[G]^N \equiv G \boxtimes G \boxtimes \cdots \boxtimes G \equiv \boxtimes^N G,$$

i.e., the set of elements of the form $(g, g, \ldots, g)$ with the product rule of corresponding components $(g \in G)$. As a basis of the group algebra $R([G]^N)$ we may take a set of primitive orthogonal idempotents

$$\{e_{rs}^{\alpha(N)}; \alpha; r, s = 1, \ldots, f^\alpha\},$$

where

$$e_{rs}^{\alpha(N)} = \frac{f^\alpha}{[G:1]} \sum_{g \in G} [g^{-1}]_{sr}^{\alpha}(g, g, \ldots, g);$$

f^α is the dimension of the αth irr of G, $[G:1]$ is the order of G. The action of G is given *a priori* on the space U of one-particle kets. Hence we know how $[G]^N$ and also by a linearity $R([G]^N)$ act on U_N^N. Then U_N^N is expanded into a direct sum of subspaces

$$U_N^N = \sum_{\alpha\beta}^{\oplus} \sum_{r=1}^{f^\alpha}{}^{\oplus} \sum_{t=1}^{f^\beta}{}^{\oplus} e_{rr}^{\alpha(N)} U_N^N e_{tt}^{\beta(N)\dagger}.$$

Now we introduce the following notation

$$U_{\alpha\beta}^{N\to n} \equiv \mathrm{Tr}^{(m)}(e^{\alpha(N)} U_N^N e^{\beta(N)\dagger}),$$

where $\{e^{\alpha(N)}\}$ are the principal idempotents of the group algebra $R([G]^N)$

$$e^{\alpha(N)} = \frac{f^\alpha}{[G:1]} \sum_{g\in G} \chi^\alpha(g^{-1})g.$$

2.1. Let us consider the kets $|U\rangle = |u_1\rangle|u_2\rangle \ldots |u_N\rangle$ and $|V\rangle = |v_1\rangle|v_2\rangle \ldots |v_N\rangle$. Then by definition

$$\begin{aligned} D_{UV}^n(\alpha rs; \beta tu) &\equiv \mathrm{Tr}^{(m)}(e_{rs}^{\alpha(N)}|U\rangle\langle V|e_{tu}^{\beta(N)\dagger}) \\ &= \frac{f^\alpha f^\beta}{[G:1]^2} \sum_{g\in G} [g^{-1}]_{sr}^\alpha \sum_{n\in G} [n^{-1}]_{ut}^\beta (g \times \cdots \times g)_n |U(N)\rangle \\ &\quad \times \langle V(N)|(h \times \cdots h)_n \times \langle v_{n+1}|hg|u_{n+1}\rangle \cdots \langle v_N|hg|u_N\rangle \\ &\quad \times (n + m = N). \end{aligned}$$

We assume now that in U there is a one-particle basis $\{|x_k^{(\alpha)}\rangle : \alpha; k = 1, \ldots, f^\alpha\}$ that is adapted on G. It is clear that this assumption is not essential when the RDM-symmetry is discussed but the calculations are simplified. Next we consider in more detail the concept of adaptation on symmetry (Klein and Cantu, 1974; Klein, 1974a). Then

$$|u_k\rangle = \sum_\alpha \sum_{l=1}^{f^\alpha} U_{kl}^{(\alpha)} |x_l^{(\alpha)}\rangle,$$

$$|v_k\rangle = \sum_\alpha \sum_{l=1}^{f^\alpha} V_{kl}^{(\alpha)} |x_l^{(\alpha)}\rangle;$$

where $|x_k^{(\alpha)}\rangle$ is transformed under the action of G as follows

$$g|x_k^{(\alpha)}\rangle = \sum_{m=1}^{f^{(\alpha)}} [g]_{km}^\alpha |x_m^{(\alpha)}\rangle, \qquad g \in G.$$

Introducing the idempotent basis for the group algebra $R([G]^n)$ according to the formula

$$(g \times \cdots \times g)_n = \sum_\alpha \sum_{v,w=1}^{f^\alpha} [g]_{vw}^\alpha e_{vw}^{\alpha(n)}$$

we finally obtain

$$
\begin{aligned}
D^{n}_{UV}(\alpha rs;\beta tu) = {} & \frac{f^{\alpha}f^{\beta}}{[G:1]^2} \sum_{m=n+1}^{N} \sum_{\alpha_m} \sum_{l_m,k_m,n_m=1}^{f^{\alpha_m}} V^{(\alpha_{n+1})\dagger}_{l_{n+1}n+1} \cdots U^{(\alpha_N)}_{Nk} \\
& \times \sum_{g\in G} [g^{-1}]^{\alpha}_{sr} \sum_{\gamma} \sum_{V_1W_1=1}^{f^{\gamma}} [g]^{\gamma}_{V_1W_1}[g]^{\alpha_{n+1}}_{n n+1} \cdots [g]^{\alpha_N}_{n_N l_N} \\
& \times \sum_{h\in G} [h^{-1}]^{\beta}_{ut} \sum_{\delta} \sum_{V_2W_2=1}^{f^{\gamma}} \overline{[h]}^{\delta}_{V_2W_2}\overline{[h]}^{\alpha_{n+1}}_{k_{n+1}n_{n+1}} \cdots \overline{[h]}^{\alpha_N}_{K_N n_N} \\
& \times e^{\gamma(n)}_{V_1W_1}|U(n)\rangle\ \langle V(n)|e^{\delta(n)\dagger}_{V_2W_2}. \qquad (1)
\end{aligned}
$$

Thus the following theorem is proved:

THEOREM I

$$
\begin{aligned}
U^{N\to n}_{\alpha\beta} \le \sum_{\gamma\delta}{}^{\oplus} \Bigg[& \sum_{\mu_1,\dots,\mu_m} \delta(\gamma \boxtimes \mu_1 \boxtimes \cdots \boxtimes \mu_m;\alpha) \\
& \times \delta(\delta \boxtimes \mu_1 \boxtimes \cdots \boxtimes \mu_m i\ \beta)\Bigg] U^{n}_{\gamma\delta}. \qquad (2)
\end{aligned}
$$

Introducing the notation

$$\mu_1 \boxtimes \mu_2 \boxtimes \cdots \boxtimes \mu_m = \mu, \qquad (3)$$

we have in a briefer form

$$U^{N\to n}_{\alpha\beta} \subseteq \sum_{\gamma\delta}{}^{\oplus} \Big[\sum_{\mu}{}' \delta(\gamma \boxtimes \mu;\alpha)\delta(\delta \boxtimes \mu;\beta) \Big] U^{n}_{\gamma\delta},$$

where the prime in the sum over μ denotes the summation only over μ from (3). Hence by analogy with the previous part the selection rules follow. However they cannot be formulated in a general form for an arbitrary group G since up to now the problem of the decomposition of the inner group products has not been solved. By analogy with the N, $[\lambda_1)$, $[\lambda_2]$-derivability we may introduce the N, α, β-derivability for G. Then Theorem I represents the necessary condition of the N, α, β-derivability.

2.2. Equation (1) represents the nth matrix of the transition density for arbitrary kets $|U\rangle$ and $|V\rangle$. Since the kets adapted on symmetry play an essential role in the solution of the Schrödinger equation with the Hamiltonian that commutes with G, it is interesting to consider special cases of G-adaptation of the kets $|U\rangle$ and $|V\rangle$. And now we introduce the following definitions (Klein and Cantu, 1974; Klein, 1974a):

Definition I. The ket $|U\rangle$ is called strongly adapted on symmetry if it is transformed over the rth line of the αth irr of the group G.

Definition II. The ket $|U\rangle$ is called a weakly adapted on G-symmetry if it is not strongly adapted but is transformed only over the αth irr of G.

In a general case we may introduce either the notation of the degree of the G-adaptation or consider a maximal Abelian subgroup such that the given representation α, in general reducible, is induced by a one-dimensional representation of the group G_0.

Let

$$|X\rangle = |x_{k_1}^{(\alpha_1)}\rangle \cdots |x_{k_N}^{(\alpha_N)}\rangle,$$
$$|Y\rangle = |x_{l_1}^{(\beta_1)}\rangle \cdots |x_{l_N}^{(\beta_N)}\rangle.$$

Then

$$\begin{aligned} D_{XY}^{n}(\alpha rs;\beta tu) = {} & \frac{f^\alpha f^\beta}{[G:1]^2} \sum_{g\in G} [g^{-1}]_{sr}^{\alpha} \sum_{r=1}^{n} \sum_{n_r=1}^{f^{\alpha_n}} [g]_{k_1n_1}^{\alpha_1} \\ & \times [g]_{k_2n_2}^{\alpha_2} \cdots [g]_{k_nn_n}^{\alpha_n} \sum_{h\in G} [h^{-1}]_{ut}^{\beta} \sum_{s=1}^{n} \sum_{m_s=1}^{f^{\beta_s}} [h]_{m_1l_1}^{\beta_1} \cdots [h]_{m_nl_n}^{\beta_n} \\ & \times \sum_{p_1=1}^{f^{\alpha_{n+1}}} \cdots \sum_{p_m=1}^{f^{\alpha_N}} [\bar{n}]_{p_1l_n+2}^{\alpha_{n+1}} [g]_{l_{n+1}p_1}^{\alpha_{n+1}} \cdots \\ & \times [g]_{l_Np_m}^{\alpha_N} \times [g]_{l_Np_m}^{\alpha_N} \\ & \times \delta_{\alpha_{n+1},\beta_{n\to1}} \cdots \delta_{\alpha_N,\beta_N} |x_{k_1}^{(\alpha_1)}\rangle \cdots |x_{k_n}^{(\alpha_n)}\rangle \langle x_{l_n}^{(\beta_n)}| \cdots \langle x_{l_1}^{(\beta_1)}|. \end{aligned}$$

3. As in the previous part we may introduce a superoperation (Klein and Kramling, 1970; Klein, 1970). Namely,

$$g_0X = gXg^{-1}, \qquad g\in G, \qquad X\in U_N^N.$$

Then a notion of an irreducible tensor operator with respect to G is introduced analogously to the superoperation for S_N and the following expansion takes place:

$$U_N^N \equiv \sum_{\alpha} \sum_{r=1}^{f\alpha}{}^{\oplus} e_{rr}^{\alpha} \circ U_N^N = \sum_{\alpha r} U_{\alpha(r)}^{N}.$$

Since

$$\begin{aligned} & e_{vw}^{\gamma} \circ e_{r}^{\alpha} |U\rangle\langle V| e_{tu}^{\beta\dagger} \\ & \quad = \frac{f^\gamma}{[G:1]} \sum_{g\in G} [g^{-1}]_{vw}^{\gamma} \sum_{p=1}^{f\alpha} \sum_{g=1}^{f^\beta} [g]_{pr}^{\alpha} [\bar{g}]_{tg}^{\beta} e_{ps}^{\alpha} |U\rangle\langle V| e_{qu}^{\beta\dagger}, \end{aligned}$$

THEOREM II

$$U_{\alpha\beta}^{N} \subseteq \sum_{\gamma}{}^{\oplus} \delta(\alpha \boxtimes \bar{\beta};\gamma) U_{\gamma}^{N}.$$

Using successively Theorems I and II we have

$$\begin{aligned} U^{N\to n}_{\alpha\beta} &\subseteq \sum_{\gamma\delta}{}^{\oplus} \left[\sum_{\mu}{}' \ \delta(\gamma \boxtimes \mu; \alpha)\delta(\delta \boxtimes \mu; \beta) \right] U^{n}_{\gamma\delta} \\ &\subseteq \sum_{\gamma\delta} \sum_{\mu}{}' \sum_{\text{æ}} \delta(\gamma \boxtimes \mu; \alpha)\delta(\delta \boxtimes \mu; \beta)\delta(\gamma \boxtimes \bar{\delta}; \text{æ}) U^{n}_{\text{æ}}. \end{aligned}$$

So the following statement is valid:

THEOREM III

$$U^{N\to n}_{\alpha\beta} \subseteq \sum_{\text{æ}} \left[\sum_{\gamma\delta} \sum_{\mu}{}' \ \delta(\gamma \boxtimes \mu; \beta)\delta(\delta \boxtimes \mu; \beta)\delta(\gamma \boxtimes \bar{\delta}; \text{æ}) \right] U^{n}_{\text{æ}}.$$

4. Let X be the operator that commutes with the group G, and D be the density matrix. Then

$$\begin{aligned} \langle X \rangle_D = \mathrm{Sp}(XD) &= \frac{1}{[G:1]} \sum_{g\in G} \mathrm{Sp}(gXg^{-1}D) \\ &= \frac{1}{[G:1]} \sum_{g\in G} \mathrm{Sp}(Xg^{-1}Dg) = \mathrm{Sp}(XD_0). \end{aligned}$$

where

$$D_0 = \frac{1}{[G:1]} \sum_{g\in G} gDg^{-1} = e^{\tau} \circ D,$$

τ is a single representation of the group G.

Thus the calculation of averages of operators commuting with the group G is reduced to taking the trace of not all of the density matrix D but only its symmetric components D_0. Hence only the last component in similar calculations is physically meaningful. Following the articles by Klein and Cantu (1974), we may introduce the equivalence equation on a set of density matrices:

$$D_1 \sim D_2 \Leftrightarrow e^{\tau} \circ D_1 = e^{\tau} \circ D_2.$$

Then all the set of density matrices is partitioned into the equivalence classes. The density matrix is not likely to be reduced uniquely in its symmetric component. This follows from the fact that $\delta(\alpha \boxtimes \bar{\beta}; \tau) \neq 0$ only at $\beta = \alpha$, i.e.,

$$\sum_{\alpha} U^{N}_{\alpha\alpha} \subseteq U^{N}_{\tau}.$$

Finally, one may see the behavior of the equivalence classes in reduction from the following formulas:

$$(i) \qquad \sum_{\gamma} \sum_{\mu}{}' \ U^{N\to n}_{\gamma \boxtimes \mu:\alpha/\gamma \boxtimes \mu:\beta} \subseteq U^{n}_{0};$$

$$(ii)\quad U_{\alpha\alpha}^{N\to n} \subseteq \sum_{\ae} \left[\sum_{\gamma\delta} \sum_{\mu}{}' \; \delta(\gamma \boxtimes \mu; \alpha)\delta(\delta \boxtimes \mu; \alpha)\delta(\gamma \boxtimes \bar{\delta}; \ae) \right] U_{\ae}^{n}.$$

VI. Symmetry Properties of Natural Orbitals and Geminals

Up to now we have considered the RDM symmetry. In this part we investigate the symmetry of eigenfunctions of 1- and 2-matrices. This problem is far from being solved completely.

1. First, we consider the spin symmetry of natural orbital (norbs) and geminals (nags). From Section II it follows that the 1-matrix for the wave function $\Psi = |SM\rangle$ has the following form:

$$\begin{aligned} D_{\Psi}^{1}(x; x') = (-1)^{S-M} \bigg\{ & \frac{1}{2(2S+1)^{1/2}} P_{\Psi}^{1}(\mathbf{r}_1; \mathbf{r}_1')[\alpha(S_1)\bar{\alpha}(S_1') + \beta(S_1)\bar{\beta}(S_1')] \\ & + \frac{M}{[S(S+1)]^{1/2}} D_{\Psi}^{1}(\mathbf{r}_1; \mathbf{r}_1')[\alpha(S_1)\bar{\alpha}(S_1') - \beta(S_1)\bar{\beta}(S_1')] \bigg\}. \end{aligned}$$

"Free" spin functions of the form seem to be eigenfunctions of the 1-matrix D_{Ψ}^{1}. However this set of natural spin orbitals is not the complete set adapted with respect to the group of spin rotations since with the reflection $\alpha \to \beta$ $\varphi_i\alpha \to \varphi_i\beta$, which in a general case is not a natural spin orbital of D_{Ψ}^{1} (Kutzelnigg and Smith, 1964a,b, 1968; Bingel and Kutzelnigg, 1968, 1970). This is due to the fact that φ_i are the eigenfunctions of ${}_1P_{\Psi}^{1}$ and φ_j' are the eigenfunctions of ${}_4P_{\Psi}^{1}$. For the natural spin orbitals to be symmetrically adapted to rotations in the spin space we introduce a 1-matrix $\tilde{D}_{\Psi}^{1}$ that is invariant with respect to spin rotations and is the "best" in the trace or Frobenius metric:

$$\operatorname{Tr}(\tilde{D}_{\Psi}^{1} D_{\Psi}^{1}) = \max.$$

Then

$$\tilde{D}_{\Psi}^{1}(x; x') = (-1)^{S-M} \frac{1}{2(2S+1)^{1/2}} P_{\Psi}^{1}(\mathbf{r}_1; \mathbf{r}_1')]\alpha(S_1)\bar{\alpha}(S_1') + \beta(S_1)\bar{\beta}(S_1')].$$

i.e., $\tilde{D}_{\Psi}^{1}$ is simply an invariant part of the matrix D_{Ψ}^{1} relative to rotations in the spin space. We shall call the eigenfunctions of $\tilde{D}_{\Psi}^{1}$ spin-adapted natural spin orbitals that are norbs of the spinless operator P_{Ψ}^{1} with α- or β-factors. In the case of the degeneracy ($M \neq 0$) the usual natural spin orbitals have different orbital factors for the states with different M. The last remark is not physically satisfied due to the arbitrariness of the quantization direction and therefore is not a dependence of the space component on the choice of the quantization axis.

2. Now we turn to the consideration of the spin symmetry of natural spin geminals. If $\Psi = |SM\rangle$, then D^2_Ψ has the following form [Section II, Eq. (19)]:

$$\mathrm{D}^2_\Psi = P^{aa}_{2\Psi} a\bar{a} + P^{bb}_{2\Psi} b\bar{b} + P^{cc}_{2\Psi} c\bar{c} + P^{dd}_{2\Psi} d\bar{d} + P^{cc}_{2\Psi} c\bar{d} + P^{dc}_{2\Psi} d\bar{c}.$$

So the natural spin geminals are not necessarily eigenfunctions of S^2 since spin functions c and d in D^2_Ψ are mixed. However, a has $M_s = +1$, b—$M_s = -1$, and c, d—$M_s = 0$. Therefore natural spin geminals are eigenfunctions of S_z. Moreover, the last statement proves to be valid even if Ψ is only the eigenfunction of S_z. If $M = 0$ then $P^{cd}_{2\Psi} = P^{dc}_{2\Psi} = 0$ and natural spin geminals are "free" spin functions, i.e., they are equal to the space component by any spin functions a, b, c, and d. Moreover, in this case (due to $P^{aa}_2 = P^{bb}_2$) the spin functions a and b have the same space multiplier and, hence, the corresponding natural spin geminals have the same eigenvalue. However, the space components of natural spin geminals do not coincide in a general case with nags. In the case $S = M = 0$ the natural spin geminals equal the nags multiplied by the spin functions a, b, c, and d. Three triplet functions a, b, c, and d have the same space multiplier [Section II, Eq. (21)] and, hence, the corresponding eigenvalue is three times degenerated. Besides, the nags should be symmetric or antisymmetric depending upon whether they are triplet or singlet spin functions. Namely, since

$$\mathrm{S}^2_\Psi = S(S + 1)\Psi,$$

then

$$S(S + 1) = \mathrm{Tr}\mathrm{S}^2 D^2_\Psi,$$

where

$$\mathrm{S}^2 = \frac{N}{2}[\mathrm{S}_1^2 + \mathrm{S}_2^2 + 2(N - 1)\mathrm{S}_1\mathrm{S}_2]$$

or

$$\mathrm{S}^2 = \frac{N}{2}[(N - 1)\boldsymbol{\sigma}^2 - (N - 2)(\mathrm{S}_1^2 + \mathrm{S}_2^2)]$$

($\boldsymbol{\sigma}^2 = \mathrm{S}_1^2 + \mathrm{S}_2^2 + 2\mathrm{S}_1 \cdot \mathrm{S}_2$ is the operator of the spin square of two particles). Then eigenvalues of S^2 are $\frac{1}{2}N$ either $\frac{1}{2}N(-\frac{1}{2}N + 3)$ for singlets or $\frac{1}{2}N(\frac{1}{2}N + 1)$ for triplets. If we denote the eigenvalues for the singlet spin geminals by $\lambda_i^{(s)}$ and for triplet ones, $\lambda_i^{(t)}$, respectively, from the set of equations

$$\begin{cases} S(S+1) = \frac{1}{4}\left\{ N(N+2)\sum\limits_i \lambda_i^{(t)} + 3N(2-N)\sum\limits_j \lambda_j^{(s)} \right\} \\ \qquad\quad 1 = \sum\limits_i \lambda_i^{(t)} + \sum\limits_j \lambda_j^{(S)} \end{cases}$$

we have

$$\sum_i \lambda_i^{(S)} = \frac{N(N+2) - 4S(S+1)}{4N(N-1)},$$

$$\sum_i \lambda_i^{(t)} = \frac{3N(N+2) + 4S(S+1)}{4N(N-1)}.$$

In order to find a spin-adapted basis of natural spin geminals we should, as before, find $\tilde{D}_\Psi^2$, which is the "best" in the Frobenius metric and is invariant relative to spin rotations. It is not difficult to show that for an arbitrary Ψ, $\tilde{D}_\Psi^2$ has the following form (Kutzelnigg, 1963):

$$\tilde{D}_\Psi^2 = P_t(a\bar{a} + b\bar{b} + c\bar{c}) + P_S d\bar{d}.$$

3. In the case of the orbital symmetry of norbs and nags we may say the following. From Section III [Eq. (16)] it follows that natural spin orbitals when Ψ is the eigenfunction of $\mathbf{L}^2$ and L_z, are also the eigenfunctions of $\mathbf{l}^2$ and l_z. It is true also for the natural spin geminals at $L = M = 0$.

4. Now we consider the symmetry properties of the RDM-eigenfunctions in the general case corresponding to the wave functions that are the eigenfunctions of the so-called multiplicative operators of the form

$$\Lambda^{(N)} = \Lambda_1\Lambda_2 \cdots \Lambda_N, \tag{1}$$

where Λ_i acts only on the coordinates of the ith particle, $\{\Lambda_k\}$ being unitary operators. Then

$$\begin{aligned} D_\Psi^1 &= \mathrm{Tr}_{(N-1)}(|\Psi\rangle\langle\Psi|) = \mathrm{Tr}_{(N-1)}(\Lambda^{(N)}|\Psi\rangle\langle\Psi|\Lambda^{(N)}) \\ &= \mathrm{Tr}_{(N-1)}(\Lambda_1\Lambda_2 \cdots \Lambda_N|\Psi\rangle\langle\Psi|\Lambda_N^\dagger\Lambda_{N-1}^\dagger \cdots \Lambda_1^\dagger) \\ &= \Lambda_1\mathrm{Tr}_{(N-1)}(\Lambda_2 \cdots \Lambda_N|\Psi\rangle\langle\Psi|\Lambda_N^\dagger \cdots \Lambda_2^\dagger)\Lambda_1^\dagger \\ &= \Lambda_1\mathrm{Tr}_{(N-1)}(|\Psi\rangle\langle\Psi|)\Lambda_1^\dagger = \Lambda_1 D_\Psi^1 \Lambda_1^\dagger, \end{aligned}$$

i.e., we have proved the following theorem.

THEOREM I (Micha, 1963, 1964). If Ψ is the eigenfunction of the multiplicative operator $\Lambda^{(N)}$ of the form (1), then

$$[D_\Psi^1, \Lambda_1] = 0.$$

Then, naturally, $D_\Psi^1, D_\Psi^2, \ldots$ have the quasidiagonal form and their eigenfunctions are symmetry Λ adapted. In the general case, i.e., in the case of an arbitrary integral of motion for Ψ, we cannot say if its one-particle analog is the motion integral for D_Ψ^1. In particular, for atom systems when Ψ is the eigenfunction of the rotation operator around the z axis (Smith, 1964)

$$R_z^{(N)}(\delta\varphi) = e^{-i\delta\varphi l_z} = e^{-i\delta\varphi} \sum_{k=1}^{N} j_z^{(k)} = R_z^1(\delta\varphi) \cdots R_z^N(\delta\varphi)$$

of the inversion operator of the spatial coordinates

$$I^{(N)} = I_1 \cdots I_N$$

and the time reversal operator

$$k^{(N)} = k_1 \cdots k_N$$

($k_i = -i\sigma_y k_{0i}$, k_{0i} is the operator of complex conjugation, σ_y is the Pauli matrix), then

$$[D_\Psi^1, j_z] = [D_\Psi^1, I] = [D_\Psi^1, k] = 0. \tag{2}$$

In (Smith, 1964) the configuration p^2 is considered to illustrate the formula (2).

5. In the case of G-symmetry of the wave functions Ψ the natural spin orbitals and spin geminals are transformed, in general, over the irr of this group G. There holds the following:

THEOREM II (Kutzelnigg and Smith, 1964, 1968; Bingel and Kutzelnigg, 1968, 1970). If Ψ belongs completely to a symmetric, one-dimensional irr of G then the natural spin orbitals of Ψ are adapted on G.

Proof. We assume that

$$\Psi(x_1, \ldots, x_N) = \sum_i c_i \varphi_i(x_1) \varphi_i^{(N-1)}(x_2, \ldots, x_N)$$

and

$$\varphi_i = \sum_\alpha \sum_{k=1}^{f^\alpha} T_{ik}^\alpha \varphi_k^\alpha,$$

$$\varphi_i^{(N-1)} = \sum_\beta \sum_{m=1}^{f^\beta} S_{im}^\beta \varphi_m^{\beta(N-1)}$$

where $\{\varphi_k^\alpha\}$ and $\{\varphi_m^{\beta(N-1)}\}$ are transformed over irr α and β of G, respectively. Then

$$\begin{aligned}\Psi &= \frac{1}{[G:1]} \sum_{g\in G} g\Psi \\ &= \sum_{i\alpha k} \sum_{\beta m} c_i T^{\alpha}_{ik} S^{\beta}_{im} \sum_{rs} \varphi^{\alpha}_{r}(x_1) \varphi^{\beta(N-1)}_{s}(x_2, \ldots, x_N) \\ &= \frac{1}{[G:1]} \sum_{g\in G} [g]^{\alpha}_{kr} [g]^{\nu}_{ms} \\ &= \sum_{i\alpha k} \frac{1}{f^{\alpha}} T^{\alpha}_{ik} S^{\alpha}_{ik} \sum_{r} \varphi^{\alpha}_{r}(x_1) \varphi^{\alpha(N-1)}_{r}(x_2, \ldots, x_{N-1}) \\ &= \sum_{\alpha} \frac{1}{f^{\alpha}} \sum_{r=1}^{f\alpha} \left(\sum_{ik} c_i T^{\alpha}_{ik} S^{\alpha}_{ik} \right) \varphi^{\alpha}_{r}(x_1) \varphi^{\alpha(N-1)}_{r}(x_2, \ldots, x_{N-1}).\end{aligned}$$

Corollary. The multiplicity of eigenfunctions of D^1_Ψ is f^α for all the irr α entering in Eq. (3).

In the general case if Ψ is transformed over the kth line of the irr α of G there are two solutions of the dilemma of the construction of the G-adapted one-particle basis. The first way is connected with the notion of the "effective symmetry group" (Kutzelnigg and Smith, 1964, 1968; Smith and Kutzelnigg, 1968; Bingel and Kutzelnigg, 1968, 1970; Kryachko and Kruglyak, 1975).[7] The effective symmetry group relative to the irr α of the group G is called the maximal subgroup H_α of the group G such that α is induced by the one-dimensional representation of the group H_α. It is clear that the group H_α is not determined unambiguously. We find effective groups of the point symmetry group. It is sufficient to consider non-Abelian point groups (Kryachko and Kruglyak, 1975):

(*i*) The dihedral group D_m ($m = 1, 2, \ldots$): $a^m = 1$, $b^{-1}ab = a^{-1}$, $b^2 = 1$. As is known (Curtis and Reiner, 1962) all non-one-dimensional irr's of D_m are monomial and generated by a cyclic group $\{a\}$ of the order m, which in this case is an effective symmetry group of D_m.

(*ii*) T is the tetrahedral group. It is isomorphic to the alternation group A_4 of the permutational group S_4, which has only one degenerate irr that is the monomial representation induced by the maximal subgroup

$$H = \{(1), (12)(34), (13)(24), (14)(23)\}.$$

(*iii*) O is the octahedral group. It is isomorphic to the symmetric group S_4, which has one two-dimensional and two three-dimensional irr's. The two-dimensional irr, as in the case (*ii*), is induced by the one-dimensional representation of the subgroup H of the index 6. It is easy to

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[7] See also McWeeny and Kutzelnigg (1968) and Morrison *et al.* (1973).

show that S_4 does not contain subgroups of the index 3. There are the following classes of conjugate elements of this group:

$$\mathscr{C}_1 = \{(1)\}, \qquad \mathscr{C}_2 = \{2\text{-cycles}\}, \qquad \mathscr{C}_3 = \{3\text{-cycles}\},$$
$$\mathscr{C}_4 = \{4\text{-cycles}\}, \qquad \mathscr{C}_5 = \{(12)(34),\ (13)(24),\ (14)(23)\}.$$

It is evident that

$$\mathscr{C}_2\mathscr{C}_4 \cap \mathscr{C}_3 \neq \emptyset, \qquad \mathscr{C}_5\mathscr{C}_4 \cap \mathscr{C}_3 \neq \emptyset.$$

This would lead to the existence of elements of the third order in the group of the order 8 and would contradict the Lagrange theorem (Curtis and Reiner, 1962). So the effective symmetry groups with respect to three-dimensional irr's of S_4 are the subgroups isomorphic to A_4.

Another way of solving this dilemma is to construct a totally symmetric component of D^1_Ψ and to find its eigenfunctions, so-called symmetry-adapted norbs (SANO). In the general case the relation between nobs and SANO has not been studied (Kutzelnigg and Smith, 1964, 1968; Smith and Kutzelnigg, 1968; Bingel, 1970; Bingel and Kutzelnigg, 1968, 1970; McWeeny and Kutzelnigg, 1968).

6. Thus in this section we have considered the problems concerning the symmetry of 1- and 2-matrix eigenfunctions. The symmetry properties of norbs in the general case were studied by Kutzelnigg (1963) and Löwdin (1963) independently in the case of systems with the Abelian symmetry groups.

Norbs and nags, in general, possess a sufficiently complex symmetry and are not symmetry-adapted if even the corresponding wave functions have a high symmetry.[8] Therefore norbs and nags are a very nonconvenient basis for quantum chemical calculations. Hence it is desirable to fine somewhat modified orbitals and geminals that should be symmetry-adapted (SANO and SANG). Consequently SANO is used for the model description of systems with open and closed shells. Unfortunately, in the general case SANG are delocalized, which complicates the description of electron pairs in the theory of chemical valency in terms of SANG.

VII. Calculations of 1- and 2-Matrices of Projected Wave Functions

1.1. One of the possibilities of including correlation in the frame of the so-called "independent particle model" is realized in the "different

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[8] See also Davidson (1972, 1976) and Kutzelnigg (1964, 1969).

orbitals for different spins'' (DODS) method. The inner pair correlation of particles with opposite spins is taken into account just in this approximation since there they are allowed to be in different spatial regions. The DODS method was firstly introduced by Löwdin (1957) and is based on the approximated description of the system by the Slater-type determinant

$$\Phi = [\varphi_1\alpha\varphi_2\alpha \cdots \varphi_k\alpha|\psi_1\beta\psi_2\beta \cdots \psi_l\beta] \qquad (k + l = N), \tag{1}$$

where $\varphi_1, \varphi_2, \ldots, \varphi_k$ are the orbitals with the α spin and $\psi_1, \ldots, \psi_l$ are the orbitals with β spin.

In general, the determinant Φ does not satisfy the symmetry conditions of the system considered, and, first of all, is not the eigenfunction of S^2. The latter may be considered to be a lack of the DODS method since this method is usually used to describe different spin effects. One of the ways to adequately describe the system is the spin projection of Φ, i.e., the isolation of the component with an expectation symmetry.

It is necessary to notice that without the generalization boundedness, $\{\varphi_i\}$ and $\{\psi_i\}$ may be considered to satisfy the following orthogonality conditions (Amos and Hall, 1961):

$$\begin{aligned} \langle\varphi_i|\varphi_j\rangle &= \delta_{ij}, & \langle\psi_i|\psi_j\rangle &= \delta_{ij}, \\ \langle\varphi_i|\psi_j\rangle &= a_i\delta_{ij}, & 0 \le |a_{ij}| &\le 1 \end{aligned} \tag{2}$$

The matrix approach to the DODS method, in principle, consists in the spin projection of Φ and obtaining closed expressions for the spin-projected functions of 1- and 2-matrices (Hardisson and Harriman, 1967; Harriman, 1963, 1964, 1966, 1968, 1971, 1973; Mestechkin, 1966, 1967, 1968, 1973, 1975, 1977; Mestechkin and Whyman, 1974, 1975). In this case one uses either the Sasaki–Ohno technique (Sasaki and Ohno, 1963) based on the application of Sanibel coefficients (Smith and Harris, 1969) or the Fock–Dirac formula for the operator S^2 (Mestechkin, 1977). In this section to find 1- and 2-matrices for the spin-projected determinant we use the symmetric group technique, namely, the generalization of the Fock–Dirac formula (Löwdin and Goscinski, 1969, 1970):

$$\frac{f^{[\lambda]}}{N!} \sum_{P \in S_N} \chi^{[\lambda]}(P^{-1})P = \prod_{l \neq k} \frac{S^2 - l(l+1)}{k(k+1) - l(l+1)} = O_k, \tag{3}$$

where

$$[\lambda] = [\mu, \bar{v}], \qquad \mu = N/2 + k,\ v = N/2 - k.$$

1.2. We define, as previously, the 1-matrix in a form slightly different from the traditional one:

$$D^{1}_{\Psi_k}(x;x') = a_k^{-1} \int \bar{\Psi}_k(x_1, \ldots, x_{N-1}, x') \times \Psi_k(x_1, \ldots, x_{N-1}, x)\, dx_1 \ldots dx_{N-1}, \tag{4}$$

where

$$\Psi_k(x_1, \ldots, x_N) = O_k\Phi, \qquad a_k = \langle \Psi_k | \Psi_k \rangle.$$

It is known (Löwdin and Goscinski, 1969, 1970) that the antisymmetrizator $A_N(\equiv e^{[1^N]})$ is the sum of products of the conjugate primitive orthogonal idempotents for **r**- and S-spaces, respectively:

$$A_N = \sum_{[\lambda]} \frac{1}{f^{[\lambda]}} \sum_{k,l=1}^{f^{[\lambda]}} e^{[\tilde{\lambda}]}_{kl}(\mathbf{r}) e^{[\lambda]}_{kl}(S).$$

Then

$$O_k A_N = e^{[\lambda]}_{s} e^{[1^N]} = \frac{1}{f^{[\lambda]}} \sum_{k,l=1}^{f^{[\lambda]}} e^{[\tilde{\lambda}]}_{kl}(\mathbf{r}) e^{[\lambda]}_{kl}(S).$$

Thus $D^{1}_{\Psi_k}$ can be rewritten in the following form:

$$\begin{aligned} D^{1}_{\Psi_k}(x;x') = a_k^{-1} \left(\frac{1}{f^{[\lambda]}}\right)^2 \sum_{k,l,m,n=1}^{f^{[\lambda]}} \int\limits_{\substack{\mathbf{r}_1=\mathbf{r}'_1 \\ \vdots \\ \mathbf{r}_{N-1}=\mathbf{r}'_{N-1} \\ \mathbf{r}'_N=\mathbf{r}' \\ \mathbf{r}_N=\mathbf{r}}} & \varphi_1(\mathbf{r}'_1) \cdots \psi_N(\mathbf{r}'_N) e^{[\tilde{\lambda}]}_{kl}(\mathbf{r}') \\ & \times e^{[\lambda]}_{mn}(\mathbf{r}) \varphi_1(\mathbf{r}_1) \cdots \psi_N(\mathbf{r}_N)\, d\mathbf{r}_1 \cdots d\mathbf{r}_{N-1} \\ & \times \int\limits_{\substack{S'_1=S_1 \\ \vdots \\ S'_{N-1}=S_{N-1} \\ S_N=S \\ S'_N=S'}} \alpha(S'_1) \cdots \beta(S'_N) e^{[\lambda]}_{kl}(S') e^{[\lambda]}_{mn}(S) \alpha(S_1) \\ & \qquad \cdots \beta(S'_N)\, dS_1 \cdots dS_{N-1}, \end{aligned} \tag{4}$$

and the problem is reduced to the calculation of space and spin integrals. It is obvious that to simplify the calculations, it is necessary to consider the following reduction of the symmetric group:

$$S_N \supset S_{N-1} \times S_1 \supset (S_k \times S_{l-1}) \times S_1 \tag{5}$$

and the expansion (see, e.g., Kruglyak and Kryachko, 1974)

$$S_N = \bigcup_c P_c \bigcup_f P_f(S_k \times S_{l-1}),$$

$$P_c = (cN), \qquad c = 1, 2, \ldots, N;$$

$$P_f = (u_1, v_1)(u_2, v_2) \cdots (u_f, v_f)$$

takes place.

So, the finding of $D^{1}_{\Psi_k}$ by the formula (4) is reduced to the calculation of matrix elements of the elements of the symmetric group of the form $P_c'P_f'PTP_f''P_c''$ ($P \in S_k$, $T \in S_{l-1}$) in **r**- and S-spaces, taking into account the orthogonality relations (2). There are the following:

(*i*) spin part:

(a)

$$\langle S|(r_1N')(r_2N)|S\rangle = \begin{cases} \alpha(S_N)\bar{\alpha}(S_N'), & 1 \le r_1 = r_2 \le k; \\ \beta(S_N)\bar{\beta}(S_N'), & k+1 \le r_1, \quad r_2 \le N; \end{cases}$$

(b)

$$\langle S|(r_1N')P(r_2N)|S\rangle = \begin{cases} \alpha(S_N)\bar{\alpha}(S_N'), & 1 \le r_1 = P(r_2) \le k; \\ \beta(S_N)\bar{\beta}(S_N'), & k+1 \le r_1, \quad r_2 \le N; \end{cases}$$

(c)

$$\langle S|P_{f'}P_{f''}|S\rangle = \beta(S_N)\bar{\beta}(S_N'), \qquad P_{f'} = (P_{f''})^{-1};$$

(*ii*) spatial part:

(a)

$$\langle \mathbf{r}|(r_1N')(r_2N)|\mathbf{r}\rangle = \begin{cases} \bar{\varphi}_{r_2}(\mathbf{r}_N')\varphi_{r_1}(\mathbf{r}_N), & 1 \le r_1 = r_2 \le k; \\ \bar{\psi}_{r_1-k}(\mathbf{r}_N')\psi_{r_1-k}(\mathbf{r}_N), & k+1 \le r_1 = r_2 \le N; \\ \bar{\varphi}_{r_1}(\mathbf{r}_N')\Psi_{r_1}(\mathbf{r}_N), & r_2 = k + r_1, \quad 1 \le r_1 \le l; \\ \bar{\psi}_{r_1-k}(\mathbf{r}_N')\varphi_{r_1-k}(\mathbf{r}_N), & k+1 \le r_1 \le N, \quad r_2 = r_1 - k; \end{cases}$$

(b)

$$\langle \mathbf{r}|P_f|\mathbf{r}\rangle = \begin{cases} \bar{\psi}_N(\mathbf{r}_N')\psi_N(\mathbf{r}_N)a_{u_1}a_{u_2}\ \ldots\ a_{u_n}; \\ P_f = (u_1, v_1)(u_2, v_2)\ \ldots\ (u_n, v_n) \ne 1; \\ v_i \equiv u_i (\operatorname{mod} k), \qquad i = 1, 2, \ldots, n; \\ \bar{\psi}_N(\mathbf{r}_N')\psi_N(\mathbf{r}_N), \qquad P_f = 1; \end{cases}$$

(c)

$$\langle \mathbf{r}|P_f'P_f''|\mathbf{r}\rangle = \bar{\psi}_N(\mathbf{r}_N')\psi_N(\mathbf{r}_N)\begin{cases} a_{u_1}a_{u_2}\ \ldots\ a_{u_n}\bar{a}_{x_1}\bar{a}_{x_2}\ \ldots\ \bar{a}_{x_m}, \\ P_f'' = \prod_{i=1}^{u} (u_i, v_i), \qquad v_i \equiv u_i\ (\operatorname{mod} k), \\ P_f' = \prod_{i=1}^{m} (x_i, y_i), \qquad y_i \equiv x_i\ (\operatorname{mod} k); \\ 1, P_f' = (P_f'')^{-1}; \\ a_{u_1}\ \ldots\ a_{u_n}\bar{a}_{x_1}\ \ldots\ \bar{a}_{x_m}, \\ P_f' = \bar{P}_f'Q, \qquad P_f'' = Q\bar{P}_f'', \\ P_f'P_f'' = \bar{P}_f'\bar{P}_f'', \\ \bar{P}_f' = \prod_{i=1}^{m} (x_i, y_i), \qquad y_i \equiv x_i\ (\operatorname{mod} k), \\ \bar{P}_f'' = \prod_{i=1}^{u} (u_i, v_i), \qquad v_i \equiv u_i\ (\operatorname{mod} k). \end{cases}$$

(d)

$$\langle \mathbf{r}|(rN')P_f|\mathbf{r}\rangle = \begin{array}{l} \delta_{rl}a_l\bar{\varphi}_l(\mathbf{r}'_N)\psi_l(\mathbf{r}_N)a_{u_1}a_{u_2}\ \dots\ a_{u_n}, \\ P_f = \prod_{i=1}^{n}(u_i, v_i), \qquad u_i \equiv V_i(\mathrm{mod}\ k), \\ r \neq u_i, v_i; \qquad i = 1, 2, \dots, n. \end{array}$$

Using the theory of nonstandard representations of the symmetric groups we may represent the spin part of 1-matrix in the compact form:

$$\begin{aligned} \langle S|e^{[\lambda]}_{mn}e^{[\lambda]}_{kl}|S\rangle = {} & \frac{f^{[\lambda]}}{N!}\sum_{\substack{m_1m_2\\n_1n_2}}\sum_{\substack{k_1k_2\\l_1l_2}}\langle m|m_1m_2\rangle^{[\lambda]}\langle n_1n_2|n\rangle^{[\lambda]} \\ & \times \langle k|k_1k_2\rangle^{[\lambda]}\langle l_1l_2|l\rangle^{[\lambda]}\frac{f^{[\lambda]}k!l!}{f^{[\lambda_1]}f^{[\lambda_2]}N!}\sum_{u_1u_2}\sum_{P_f}\sum_{P\in S_k}\sum_{T\in S_l}[P^{-1}]^{[\lambda_1]}_{m_1u_1} \\ & \times [T^{-1}]^{[\lambda_2]}_{m_2u_2}\left\{\alpha(S_N)\bar{\alpha}(S'_N)\sum_{=1}^{k}\langle m_1m_2|(r_N)P_f|k_1k_2\rangle^{[\lambda]}\right. \\ & \times \langle u_1u_2|(rN)P_fPT|l_1l_2\rangle^{[\lambda]} + \beta(S_N)\bar{\beta}(S'_N)\sum_{r=k+1}^{N}\sum_{t=k+1}^{N} \\ & \left.\times \langle m_1m_2|(rN)P_f|k_1k_2\rangle^{[\lambda]}\langle u_1u_2|(tN)P_fPT|l_1l_2\rangle^{[\lambda]}\right\}, \end{aligned}$$

where $\langle m|m_1m_2\rangle^{[\lambda]}$ are the transformation matrices of the reduction (5).

We shall not study in detail the 1-matrix—the calculation technique is described at length in the articles of Harriman and Mestechkin. The closed expressions for the 1-matrix and its spinless and spin parts are given in the same works. It is worth noting that Harriman's theorem stating that norbs of a spinless matrix do not change under projection (Bingel and Kutzelnigg, 1968, 1970) is the well-known result.

1.3. The 2-matrix of the determinant Φ projected on the spin is considered analogously. It is necessary to consider the following reduction:

$$S_N \supset (S_k \times S_{l-2}) \times S_2$$

and using the orthogonality conditions (2) to calculate the space and spin parts separately.

2. In this subpart we consider the G-projection of the determinant Ψ of the form

$$\Psi(x_1, \dots, x_N) = A_N[\psi_1(x_1)\cdots\psi_N(x_N)] \tag{6}$$

where $\psi_1, \dots, \psi_N$ are arbitrary orthonormalized spin orbitals.

Then the wave function $\Psi_N^{(\alpha)}$ $(k = 1, 2, \ldots, f^\alpha)$ normalized to unit transforming with respect to the kth line of the irr α of the group G is isolated from Ψ by means of the projector e^α_{kk} (Simons, 1970; Simons and Harriman, 1969; Kruglyak and Kryachko, 1974).

$$\begin{aligned} \Psi_k^{(\alpha)} &= a_{\alpha k}^{-1/2} e^\alpha_{kk} \Psi, \\ a_\alpha &= \int \overline{(e^\alpha_{kk}\Psi)}(e^\alpha_{kk}\Psi)\, dx_1 \cdots dx_N. \end{aligned} \tag{7}$$

We assume the existence of M $(M \geq N)$ spin orbitals $\psi_1, \ldots, \psi_N, \psi_{N+1}, \ldots, \psi_M$, and the following relation takes place:

$$g\psi_k = \sum_{i=k}^{M} g_{ki}\psi_i. \tag{8}$$

Then the 1- and 2-matrices corresponding to the function $\Psi_k^{(\alpha)}$ have the following form:

$$D^1_{\Psi_k^{(\alpha)}}(x_1; x_1') = \sum_{n,l=1}^{M} D^1_{\Psi_k^{(\alpha)}}(l_n)\, \psi_l(x_1)\, \bar{\psi}_n(x_1'), \tag{9}$$

$$\begin{aligned} D^1_{\Psi_k^{(\alpha)}}(l_N) &= a_{\alpha k}^{-1} N^{-1} \left(\frac{f^\alpha}{[G:1]}\right)^2 \sum_{g\in G} \sum_{h\in G} [g^{-1}]^\alpha_{kk} \overline{[h^{-1}]}^\alpha_{kk} \\ &\times \sum_{ij=1}^{N} \bar{h}_{in} g_{jl} \sum_{k_i,\ldots,k_{N-1}=1}^{M} \left(\sum_{P\in S_{N-1}^{(i)}} (-1)^P \prod_{m-1}^{N-1} {}^{(i)}\bar{h}_{P_m k_m} \right) \\ &\times \left(\sum_{Q\in S_{N-1}^{(j)}} (-1)^Q \prod_{m=1}^{N-1} {}^{(j)}g_{Q_m, k_m} \right); \end{aligned} \tag{10}$$

$$D^2_{\Psi_k^{(\alpha)}}(x_1, x_2; x_1', x_2') = \sum_{\substack{p>q=1 \\ r>s=1}}^{M} D^2_{\Psi_k^{(\alpha)}}(pg, rs)\, \psi_s(x_1)\, \psi_r(x_2)\, \bar{\psi}_g(x_1')\, \bar{\psi}_p(x_2'), \tag{11}$$

$$\begin{aligned} D^2_{\Psi_k^{(\alpha)}}(pg, rs) &= a_\alpha^{-1} \binom{N}{2}^{-1} \left(\frac{f^\alpha}{[G:1]}\right)^2 \sum_{g\in G} \sum_{h\in G} \overline{[g^{-1}]}^\alpha_{kk} [h^{-1}]^\alpha_{kk} \\ &\times \sum_{ijnl=1}^{N} \bar{g}_{ip} \bar{g}_{jg} h_{nr} h_{ls} \sum_{k_1,\ldots,k_{N-2}=1}^{M} \\ &\times \left(\sum_{P\in S_{N-2}^{(lj)}} (-1)^P \prod_{m=1}^{N-2} {}^{(ij)}g_{P_m, k_m} \right) \\ &\times \left(\sum_{Q\in S_{N-2}^{(nl)}} (-1)^Q \prod_{m=1}^{N-2} {}^{(nl)}h_{Qm, km} \right) A_2^{(1,2)} A_2^{(1',2')}. \end{aligned} \tag{12}$$

The formulas (9)–(12) are the closed expressions for the 1- and 2-matrices. In particular, for calculations using these equations one should know only the matrices $\|g_{ik}\|$ for all the elements of the group G.

3. It is clear that in the two paragraphs above we touch upon the projection on the spin and point symmetry.[9] The L- and j-projection also would be considered (Hunter, 1971; Garrod, 1968). The essence of these methods is the same. We first approximate the true wave function Ψ by the determinant Φ and next we isolate the component of the considered symmetry from the solution of Φ corresponding to the absolute minimum using the projection operators. So the Hartree–Fock scheme has the symmetry properties of the above system according to Löwdin (1963) and the assumption concerning the symmetry adaptation of Φ leads to the energy that exceeds the absolute minimum. This is the so-called symmetry dilemma (Löwdin, 1963).

VIII. Discussion

We have thus considered all the usual types of RDM symmetry, namely, spin, orbital, permutational, and point symmetries. Our point of view is slightly different from an official one concerning the permutational symmetry problem. By the permutational symmetry is usually meant the Bose- or Fermi-statistics, which, though being trivial, just involves the essence of the N-representability problem. We have considered the permutational symmetry of more general spin-free RDM. In the RDM approach to find averages it is necessary to vary an operator on the class of N-representable RDM and besides to consider the symmetry properties of the system considered, i.e., there appears the problem of the contraction of the RDM to the class of symmetry-adapted N-representable RDM. It is evident that this problem of symmetry-adapted N-representable RDM is more complex than the N-representability problem. This problem is associated with the problems concerning the influence of the system symmetry on possible eigenvalues of RDM, the study of the symmetry properties of RDM corresponding to special types of functions; first of all, it concerns the so-called AGP-functions (Coleman, 1963; 1965, 1972; Peat, 1975).

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[9] See also Harris (1966), Sando and Harriman (1967), Lunnell (1972), and Whyman *et al.* (1976).

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Note Added in Proof

Professor Everett G. Larson has written an article on the role of symmetry in representing reduced density matrices [*Int. J. Quantum Chem. Symp.* **13**, 121 (1979)].

Quantum Theory of Atoms in Molecules—Dalton Revisited

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I. Introduction

A. The Atomic Hypothesis

Chemistry is the study of the properties of substances and their transformation. Since substances are identified and distinguished one from another by the elements they contain, and since the properties of each element are determined by the atoms unique to that element, chemistry is the study of matter at the atomic level. The realization of this fact by Dalton in 1807 marked the birth of chemistry as a branch of science—as a set of observations (the relative combining weights of the elements) to-

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gether with a theory that made these observations understandable and that predicted new relationships among them (the law of multiple proportions). Dalton was chemistry's first theoretician and his contribution has never been surpassed. Before the close of Dalton's century, there had evolved from his atomic hypothesis the concept of *molecular structure*—the notion that a molecule consists of a collection of atoms linked by a network of bonds, the bonds imparting the structure. This concept brings us directly to what is a presently acceptable definition of chemistry: the determination of molecular structure and the study of the change of one structure into another. With the knowledge of the molecular structure of a system, a chemist is able to bring to bear all the knowledge of modern chemistry, for he understands the properties of a substance in terms of the properties of its constituent atoms and of the bonds that link them. Dalton's theory has survived and has evolved into the conceptual basis of modern chemistry.

One might imagine that with the advent of quantum mechanics and its application to chemistry, Dalton's atomic theory as applied to chemistry would have been reinforced. This has not happened. Quantum mechanics has been shown to account for the properties of isolated atoms and for the total properties of a molecular system. The increased understanding that would result from the discovery of a firm theoretical basis for Dalton's theory has not been obtained because of a lack of a quantum definition of an atom in a molecule. This is not to say that the concepts of atoms and bonds do not appear in the quantum mechanical treatments of chemical systems. They do, but in the reverse manner to that described above. Rather than finding its quantum basis, the atomic concept is built into an approximate theory to model a real system. Thus in valence bond theory a molecular wave function is approximated in terms of products of atomic wave functions in appropriate valence states. Moffitt's "atoms in molecules approach" to the calculation of molecular binding energies is a further example (Moffitt, 1951; Moffitt and Scanlan, 1953a,b), as is the success of using atomic functions as a basis for the expansion of molecular orbitals. The properties of an ionic crystal strongly suggest that it is best regarded as a collection of interacting ions. Hence, one may successfully approximate the wave functions for such systems using free ion wave functions with adjustments for the overlap of nonorthogonal functions. This approach is elegantly illustrated by the work of Löwdin (1948, 1956) in an early theoretical calculation of the properties of ionic crystals.

The success of these and other models serve to demonstrate the fundamental nature and physical soundness of the atomic concept, but by building in the idea of atoms, they do not further the theory of atoms in molecules. Indeed, the modern consensus is to regard atoms and bonds, and thus structure itself, as useful, but undefinable concepts. It is the purpose of the present article to demonstrate the existence of a physical basis for the definition of an atom in a molecule and for the development of a complete theory of molecular structure.

B. Necessary Criteria for an Acceptable Theory of Molecular Structure

The concept of molecular structure as it has evolved from the application of the atomic theory to the organization and understanding of the observations of experimental chemistry embodies a number of essential features that a proposed theory of molecular structure must both predict and account for.

(1) The primary purpose in postulating the existence of atoms in molecules is to assign characteristic sets of properties (static, reactive, or spectroscopic) to a bound atom or to some functional grouping of atoms. One then identifies the presence of a given atom or functional group by the observation of these properties. Dalton defined the first of these atomic properties by assigning to each elemental atom a relative combining weight. As the body of descriptive chemistry grew, it was realized that the chemistry of some total system could be rationalized by assigning separate chemical properties to each type of atom or functional group in the system. Therefore:

(a) The definition of a bound atom must be such that it enables one to define all of its average properties. These definitions of atomic properties must, for reasons of physical continuity, reduce to the quantum mechanical definitions of the corresponding properties for an isolated atom.

(b) The atomic values for a given property should, when summed over all the atoms in a molecule, yield the average value of that property for the molecule.

(c) Atomic properties must be additive in the above sense to account for the observation that in certain series of molecules the atoms and their properties are transferable between molecules, leading to what are known as additivity schemes. An additivity scheme requires both that the property be additive over the atoms in a molecule and that the atoms be essentially transferable between different molecules. The theory must predict that atoms may in general exhibit characteristic properties that vary between relatively narrow limits and that may, in certain series of molecules, approach the limit of perfect transferability between systems. The theory should define the physical requirements for transferability of an atom and its properties.

(2) Chemical observations are made on systems at finite temperatures and in general, the times required for making the observations are

such that one obtains values that are averages over the nuclear motions of the system. Thus the definition of atomic properties must proceed from the general formulation of time-dependent quantum mechanics. The same considerations show that a definition of molecular structure must be independent of and sharply distinguished from molecular geometry. A definition of structure must be such that in general (for stable structures) a given structure is associated with an open neighborhood of the most probable nuclear geometry; i.e., the network of chemical bonds is invariant to the nuclear motions of a stable system. The theory of atoms and, in particular, structure must be independent of all models, including, for example, the Born–Oppenheimer approximation. Thus the theory should be formulated in terms of observable physical properties of the system.

(3) Matter occupies space and is made up of atoms. Hence atoms occupy real space and should be defined in real space. If an atom is identical in two different systems or at different sites within a given system (e.g., a solid), then it must contribute identical amounts to the total properties, including the energy, of the systems in which it occurs. The justification of this apparently elementary supposition of atomic theory requires a definition of an atom and its properties.

C. Quantum Topology—A Theory of Molecular Structure

We have developed a theory of molecular structure based on the properties of the observable distribution of charge of a molecular system in real space (Bader and Beddall, 1972; Bader *et al.*, 1979a,b). This theory results from the unfolding of a single assumption: that of identifying an atom with a particular region of real space as determined by the topological properties of a molecular charge distribution. By appealing to quantum mechanics, one finds that the atom so defined possesses a unique set of mechanical properties as determined by the variational principle. The above topological properties of the charge density also yield a definition of a chemical bond. The network of such bonds defines a *molecular graph* of a chemical system, which leads one to the definition of *molecular structure as an equivalence class of molecular graphs*. This definition of molecular structure leads in turn to a partitioning of the total nuclear configuration space of a chemical system into a finite number of structural regions, each region denoting a possible stable structure of the system. The boundary of a structural region denotes the configurations of the transitional or unstable structures that separate the associated stable structure from neighboring ones. This structural information constitutes a system's *structure diagram*, which, determining as it does all possible structures and all mechanisms of change of any one structure into another, is the culmination of this theory of atoms in molecules. Thus quantum topology is but an extension of Dalton's atomic theory, derived as it is from a single definition—that of an atom in a molecule.

This article is primarily concerned with the quantum mechanical definition of the average properties of an atom. It is demonstrated that the topological property that defines the atom determines the definition of its average properties. We will briefly review only the basic topological properties of a charge distribution in this article. Their role in the definition of molecular structure and its change has been recently reviewed in detail (Bader *et al.*, 1980).

A bound atom is an example of an open quantum system. Thus one must develop a quantum description of subsystems, free to exchange charge and momentum with their environment across boundaries that are defined in real space and that in general change with time. Inasmuch as its boundary is determined by a physical property, the atom defined here belongs to a class of open systems with particular variational properties. The development applies equally to a collection of atoms within some total system, e.g., to a molecule in a molecular crystal or to a substrate molecule adsorbed on an active site.

II. The Topological Atom

A. Definition

The definition of an atom given here is based on a partitioning of real space, whereby one assigns an open region of R^3 to a subsystem. A subsystem is thus not defined by an *a priori* partitioning of the Hamiltonian in the vector space of linear Hermitian operators acting on the abstract Hilbert space of the total system. Such a partitioning of the Hamiltonian would violate the indistinguishability of the electrons at the outset, and moreover, is arbitrary. Any attempt to overcome this arbitrariness would amount to building in the physics that is to be discovered. Instead, a subsystem is defined in terms of a property of the charge distribution ρ, which represents the distribution of *any one of the electrons as determined by an average over the motions of the remaining electrons.*

The charge distribution for a system containing N electrons and for a fixed configuration of the nuclei is defined by

$$\rho(\mathbf{r}, \mathbf{X}, t) = N \sum_{\text{spins}} \int \left\{ \prod_{j \neq 1} d\mathbf{r}_j \right\} \Psi^*(\mathbf{x}, \mathbf{X}, t)\Psi(\mathbf{x}, \mathbf{X}, t), \qquad (1)$$

where Ψ is a properly antisymmetrized solution to the general time-dependent Schrödinger equation, $\mathbf{X}$ denotes the collection of the nuclear coordinates, $\mathbf{x}$ the collection of electronic space and spin coordinates, and $\mathbf{r}$ the space coordinates of one electron. This form of integration will be employed throughout this article and will be designated in an abbreviated manner as

$$\rho(\mathbf{r}, \mathbf{X}, t) = N \int d\tau' \Psi^*(\mathbf{x}, \mathbf{X}, t)\Psi(\mathbf{x}, \mathbf{X}, t), \tag{2}$$

where τ' denotes the spin coordinates of all the electrons and the Cartesian coordinates of all the electrons but one. The topological analysis leading to the definition of atoms and structure can also be applied to the distribution that results from averaging ρ over the nuclear motion,

$$\bar{\rho}(\mathbf{r}, t) = \int d\mathbf{X}\, \rho(\mathbf{r}, \mathbf{X}, t)$$

The central observation in the topological study of a molecular charge distribution is that the only *local* maxima of the distribution occur at the positions of the nuclei. Elsewhere (Bader *et al.*, 1980) we have shown that for a given nuclear configuration $\mathbf{X}$ the topological properties of ρ are faithfully mapped out in the associated gradient vector field $\nabla\rho$, where $\nabla = \nabla_{\mathbf{r}}$. This vector field is exhibited via its trajectories in real space, which are called gradient paths. They are the parametrized integral curves of the differential equation

$$d\mathbf{r}(s)/ds = \nabla\rho(\mathbf{r}(s), \mathbf{X}, t) \tag{3}$$

for all possible initial conditions $\mathbf{r}(0) = \mathbf{r}_{\mathrm{m}} \in R^3$. A gradient path g_{m} through a given point $\mathbf{r}_{\mathrm{m}}$ is thus defined by

$$g_{\mathrm{m}} = \{\mathbf{r}(s) | (d\mathbf{r}(s)/ds) = \nabla\rho(\mathbf{r}(s), \mathbf{X}, t), \quad s \in R, \quad \mathbf{r}(0) = \mathbf{r}_{\mathrm{m}}\} \tag{4}$$

and is orthogonal to a contour of $\rho(\mathbf{r}, \mathbf{X}, t)$ at any of its points. The α-limit set of g_{m} is the origin of the path, mathematically defined as (Thom, 1975)

$$\alpha(g_{\mathrm{m}}) = \lim_{s \to -\infty} \mathbf{r}(s), \qquad \mathbf{r}(s) \in g_{\mathrm{m}}, \tag{5a}$$

while the ω-limit set of g_{m} is its terminus, defined by

$$\omega(g_{\mathrm{m}}) = \lim_{s \to +\infty} \mathbf{r}(s), \qquad \mathbf{r}(s) \in g_{\mathrm{m}}. \tag{5b}$$

The notions of α- and ω-limit sets are introduced in the description of general vector fields. In our application, where the vector field is the field of $\nabla\rho$, these limit sets are generally found to be coincident with the singletons of the critical points in ρ, points in real space where $\nabla\rho = 0$. By virtue of Eq. (3), no path of nonzero length can contain such a critical point, $\mathbf{r}_{\mathrm{c}}$. On the other hand, the points of a gradient path can come infinitesimally close to some critical point $\mathbf{r}_{\mathrm{c}}$, as $s \to -\infty$, in which case, $\mathbf{r}_{\mathrm{c}}$ constitutes the α-limit set of the path. Likewise, as $s \to +\infty$, the points of the path approach another critical point $\mathbf{r}'_{\mathrm{c}}$, which is the ω-limit set of the path.

Of particular interest in the present approach are those critical points that are identified as attractors of the gradient vector field of the charge distribution. An attractor of a vector field v over R^3 is, by definition (Thom, 1975), a closed subset (which can be a singleton) $G \subset R^3$, which

(1) is invariant with respect to the flow of v; i.e., any trajectory of v that contains a point of G is wholly contained in G;

(2) contains all trajectories originating (more precisely, having *α-limit set*) in G;

(3) is contained in some *open* subset $B \subset R^3$, such that any trajectory originating in B has its terminus (ω-limit set) in G. The maximal neighborhood B_{max} of G satisfying requirement (3) is called the basin of the attractor.

(4) G is indecomposable, in the sense that any trajectory in G is dense in G (i.e., the closure of the trajectory equals G itself).

The only closed subsets of R^3 exhibiting the properties (1)–(4) with respect to $\nabla\rho$ are the singletons determined by the local maxima in the charge distribution. Thus the nuclei act as the attractors of the gradient vector field derived from the charge distribution. The result of this identification is that the space of the molecular charge distribution, real space, is partitioned into disjoint regions, the basins, each of which contains one and only one point attractor or nucleus. This fundamental topological property of a charge distribution is illustrated in Fig. 1a, which depicts only those gradient paths of the charge density that terminate at each of the nuclear attractors in the molecule. *An atom, free or bound, is defined as the union of an attractor and its associated basin.* This definition results in a partitioning of a molecular system into a collection of nonoverlapping atomic regions.

Alternatively, the atom can be defined in terms of its boundary. Generally, this boundary comprises the union of a number of interatomic surfaces, separating two neighboring basins, and some portions that may be infinitely distant from the attractor. The interatomic surfaces as well as the surfaces found at infinity are the only closed surfaces S of R^3 that satisfy the equation

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0, \qquad \forall \quad \mathbf{r} \in S, \tag{6}$$

where $\mathbf{n}$ is the unit vector normal to the surface at $\mathbf{r}$.

A surface that satisfies Eq. (6) is called a *zero-flux surface*. Thus, an atom is a region of real space that contains a single nuclear attractor and is bounded by a zero-flux surface. Figure 1b illustrates the gradient paths for the same molecule as shown in Fig. 1a but now including those paths that terminate at the bond critical points (which are saddle points) and define the atomic surfaces, and those that originate at such critical points and define the bond paths. Clearly the space occupied by an atom is defined by

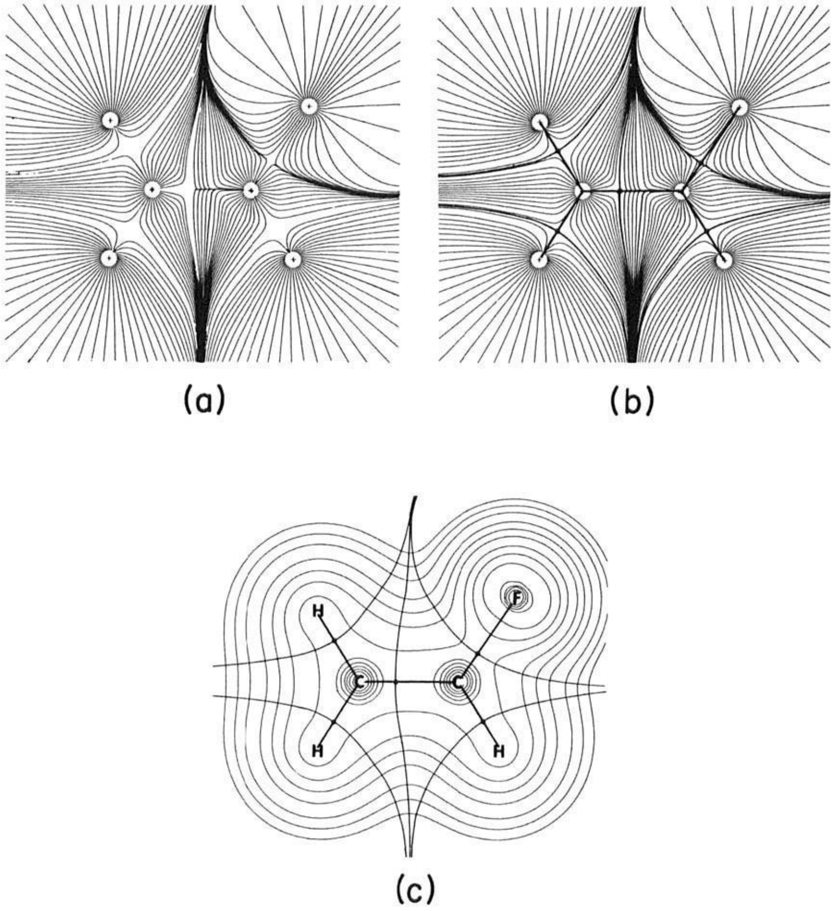


Fig. 1. A representation of the gradient vector field $\nabla\rho(\mathbf{r}, X)$ in terms of its gradient paths for the plane containing the nuclei of the molecule $FHC{=}CH_2$. (a) This diagram shows only those gradient paths that terminate at the various nuclei, thereby illustrating the definition of an atom as the union of an attractor and its basin. (b) Same as a, but now including those trajectories that both terminate and originate at the (3, −1) or bond critical points (as denoted by the solid circles) in the charge distribution. These trajectories define the interatomic surfaces of zero flux in $\nabla\rho(\mathbf{r}, X)$ and the bond paths. The union of the closure of the bond paths defines the molecular graph. (c) Contour map of the molecular charge distribution illustrating the partitioning (in this plane) of R^3 by the interatomic surfaces and the assignment of a structure by the bond paths. The gradient paths in a and b have been arbitrarily terminated at the surface of a small circle encompassing each nucleus whose position is denoted by a cross. The values of the contours in this figure and in Figs. 2 and 4–6 increase from the outermost contour inwards in steps of 2×10^n, 4×10^n, and 8×10^n with n increasing by unity and beginning with $n = -3$.

the union of a given attractor and its associated basin (Fig. 1a) or by its atomic surface (Fig. 1b).

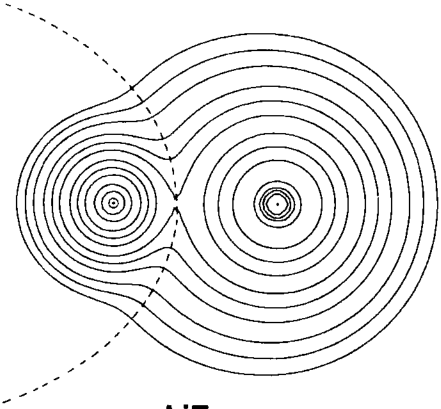
The union of two or more adjacent atoms is again a connected region bounded by a zero-flux surface. Such a union may represent a functional group and therefore is also of interest to a chemist. We thus consider generally a *connected* region $\Omega \subset R^3$ that is *bounded by a zero-flux surface* as representing a *subsystem* of the molecular system.

B. Observational Basis for the Definition of an Atom

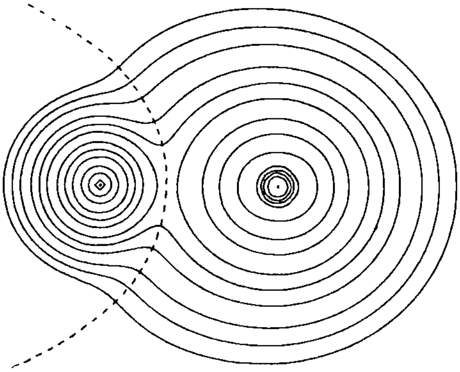
It is the nuclear charge that determines an atom's identity. The nuclear-electron force is the dominant force in a molecular system. Indeed, the nuclear potential field plays the dominant role in the determination of the topological properties of the charge density (Tal *et al.*, 1980). The definition of an atom as the union of an attractor and its basin is to be understood as the topological expression of the idea that the atomic surface should define a volume of space whose properties are determined primarily by the force exerted by the contained nucleus, thereby imparting to the atom a set of properties characteristic of a given element. The observation of this behavior for the topologically defined atoms forms the basis for their identification with the chemical atoms of a molecular system (Bader and Beddall, 1972). Since we wish to stress the observational basis of this theory, we briefly summarize this original set of observations.

Figure 2 shows contour plots of the ground-state charge distributions of LiF, LiO, and LiH, each at its equilibrium nuclear separation in a plane containing the nuclei. Superimposed on each of these plots is the intersection of the zero-flux interatomic surface with this plane. The distribution of charge within the Li atom so defined is seen to be remarkably similar in all three of these molecules in spite of the very different natures of the neighboring atom to which it is bonded. The net charge of the Li atom (as determined by an integration of $\rho(\mathbf{r})$ over the atomic volume and the subtraction of this number from the nuclear charge) is nearly identical in all three molecules (see Table I), the observed variation following the trend anticipated on the basis of a decreasing electronegativity $F > O > H$. This near constancy in the charge distribution of the Li correctly reflects the properties assigned to Li on the basis of the chemistry observed for compounds in which Li is bonded to a more electronegative element—those corresponding to a relatively small, tightly bound, singly charged positive ion. If anything, the properties of the Li atoms so defined exhibit less variation than a chemist might have hoped for.

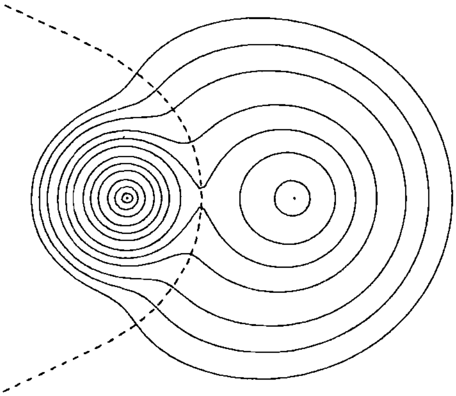
Figure 2 illustrates an elementary but important observation: the choice of the zero-flux surface for defining an atom maximizes the possibility of assigning an atomic identity to a given mononuclear region of a



LiF



LiO



LiH

Fig. 2. Contour plots of the ground-state molecular charge distributions of LiF, LiO, and LiH. A dashed line indicates the intersection of the interatomic surface with the plane shown in the diagram.

TABLE I

SOME PROPERTIES OF BOUND Li ATOMS[a]

Molecule	Net charge of Li atom	Average kinetic energy of Li atom in a.u.
$LiF(X^1\Sigma^+)$	+0.937	7.354
$LiO(X^2\Pi)$	+0.932	7.356
$LiH(X^1\Sigma^+)$	+0.913	7.368

[a] From Bader and Beddall, 1972; calculated from state functions close to the Hartree–Fock limit.

charge distribution. It is clear that any other choice of partitioning surface would either include a portion of the neighboring atom that is very different in all three cases, or omit a portion of the Li charge density that changes by only small amounts through the series of molecules.

Coupled with the observation of near constancy in the charge distributions of the Li atoms in this series of molecules was the further observation that the kinetic energy density distributions exhibited a corresponding degree of constancy. Thus it is an observation of this and, subsequently, in other systems that a constancy in the distribution of charge for such a topologically defined atom leads to a corresponding degree of constancy in the average kinetic energy of the atom (see Table I). If one now postulates the existence of an atomic virial theorem (Bader and Beddall, 1972) that would equate minus the average kinetic energy to the total average energy of the atom, then the above observation predicts that when the charge distribution of an atom is identical in two different systems, the atom will contribute identical amounts to the total energies of both systems. Equally important is the more general conclusion that the properties of such a topologically defined atom are directly determined by its charge distribution, the properties changing in direct response to changes in the density. Further studies (Bader and Beddall, 1973; Bader *et al.*, 1973a; Bader and Messer, 1974; Runtz and Bader, 1975; Bader and Runtz, 1975; Bader, 1975a; Curtiss *et al.*, 1975) have shown that the properties of such atoms, particularly their populations and energies and the changes in these properties, faithfully reflect those anticipated on chemical grounds. Thus the concept of an atom with a characteristic set of properties appears to be a consequence of the manner in which the total charge of a molecular system is distributed in real space.[1]

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[1] By characteristic properties we do not mean to imply that each atom's properties are as constant as those found above for the Li atom. The lithium atom possesses a relatively low ionization potential and hence much of its chemistry *is* understandable by assigning to it

The postulation of an atomic virial theorem for the topologically defined atoms leads to a number of important conclusions (Bader and Beddall, 1972):

(1) The total energy of a molecule is expressible as a sum of atomic energies.

(2) The average potential energy of an atom is defined as the average of the virial of the forces exerted on it.

(3) A relationship must exist between the distribution of charge and the virial of all the forces exerted on each element of the charge density, the virial field.

(4) The virial field–charge density relationship is the basis of the essential observation that if the distribution of charge for an atom is identical in two systems, then the atom will contribute identical amounts to the total energy in both systems.

(5) It is found that the atomic energies defined by the atomic virial theorem are physically meaningful. Thus, for example, the energies of the Li atoms in the molecules reported in Table I are greater than those of a Li atom because of the almost complete transfer of its valence charge density to its bonded neighbor, but less than (more stable than) the energy of a free Li^+ ion because the bound Li is in the presence of the stabilizing negative field exerted by its bonded neighbor.

It is upon the strength of these observations that the theory of quantum topology rests, for they form the basis for the identification of the topological atom with the chemical atom of a molecular system. In this article we show that these observations and the hypothesis of an atomic virial theorem are confirmed by quantum mechanics.

III. Variational Properties of Open Systems

A. Quantum Open Systems

In general, an open system, i.e., some subsystem of a total system that exchanges momentum and matter with the remainder of the system, can be formally described only by a density matrix, and not by a state function

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the properties of a "hard" ionic distribution of charge. The chemistry of hydrogen, on the other hand, depends very much on the immediate atomic environment. When bonded to a lithium atom it is hydridic in its behavior, when bonded to a saturated carbon atom it is assumed to be essentially electrically neutral, while when bonded to a fluorine atom it appears to bear a substantial net positive charge. These are the properties exhibited by the topologically defined hydrogen atom (Bader and Beddall, 1973; Bader and Messer, 1974).

(Davies, 1976). The quantum theory of open systems is still in its early stages of development. An alternative to this formal approach and the one followed here is provided by the specification of the average values of the subsystem properties.

The properties of an open system are derived from a single variational principle—the principle of stationary action for an atom. In particular, this principle yields an equation of motion, i.e., a force law, for an atom in a molecule and an atomic virial theorem. The open nature of the atom is reflected in the appearance, in each of the above relations, of the integrated flux of a corresponding vector current density across the atomic surface. A single stress tensor determines both the flux of the force per unit area of the atomic surface and the virial of this force, which is the surface energy of the atom (Bader, 1980). The atomic equation of motion and its differential expression are identical in form and physical content with the corresponding relationships of classical continuum mechanics (Malvern, 1969; Landau and Lifshitz, 1959).

B. Some Mechanical Consequences of the Zero-Flux Surface Condition

The principle of stationary action upon which our development of the quantum mechanics of open systems is based concerns the variation of the action integral. The quantum action integral for a total system is defined as follows (Srebrenik *et al.*, 1978; Srebrenik and Bader, 1975; Bader *et al.*, 1978):

$$W_{12}[\Psi] = \int_{t_1}^{t_2} dt \int L(\Psi, \nabla\Psi, \dot{\Psi}, t)\, d\tau = \int_{t_1}^{t_2} dt\, \mathscr{L}(\Psi, t), \tag{7}$$

where the Lagrangian integral $\mathscr{L}(\Psi, t)$ is defined in terms of the many-particle Lagrangian density

$$L(\Psi, \nabla\Psi, \dot{\Psi}, t) = \frac{i\hbar}{2}(\Psi^*\dot{\Psi} - \dot{\Psi}^*\Psi) - \frac{\hbar^2}{2m}\sum_i \nabla_i\Psi^* \cdot \nabla_i\Psi - \hat{V}\Psi^*\Psi \tag{8}$$

and where $\hat{V}$ is the potential energy operator for the total system.

By requiring that $W_{12}[\Psi]$ be stationary with respect to variations in Ψ and Ψ^* under the constraint that these variations vanish at the time endpoints, one obtains the Euler equations

$$i\hbar\dot{\Psi} = \hat{\mathscr{H}}\Psi \qquad \text{and} \qquad -i\hbar\dot{\Psi}^* = \hat{\mathscr{H}}\Psi^*, \tag{9}$$

which are Schrödinger's equations for a time-dependent system. When Eqs. (9) are satisfied, the Lagrangian density reduces to

$$L = -\frac{\hbar^2}{4m}\sum_i \nabla_i^2(\Psi^*\Psi). \tag{10}$$

Equation (10) is a consequence of the identity

$$-\tfrac{1}{4}\sum_i \left(\Psi^* \nabla_i^2\Psi + (\nabla_i^2\Psi^*)\Psi\right) = \tfrac{1}{2}\sum_i \boldsymbol{\nabla}_i\Psi^* \cdot \boldsymbol{\nabla}_i\Psi - \tfrac{1}{4}\sum_i \nabla_i^2(\Psi^*\Psi). \quad (11)$$

Because the many-particle Lagrangian density may be expressed in terms of a sum of single-particle operators, one may define an effective single-particle Lagrangian density $\mathscr{L}(\mathbf{r})$ [by the same mode of integration as used to define $\rho(\mathbf{r}, t)$, Eq. (2)],

$$\mathscr{L}(\mathbf{r}, t) = 4mN \int d\tau'\, L = (-\hbar^2/4mN)\, \nabla^2\rho(\mathbf{r}, t). \quad (12)$$

Correspondingly the Lagrangian integral of a many-particle system is given by

$$\mathscr{L}(\Psi, t) = 4mN \int d\mathbf{r}\, \mathscr{L}(\mathbf{r}, t) = (-\hbar^2/4mN) \int dr\, \nabla^2\rho(\mathbf{r}, t). \quad (13)$$

Since

$$\int d\mathbf{r}\, \nabla^2\rho(\mathbf{r}, t) = \oint dS(\mathbf{r}, t)\, \boldsymbol{\nabla}\rho(\mathbf{r}, t) \cdot \mathbf{n}(\mathbf{r}, t) \quad (14)$$

and since the flux in $\boldsymbol{\nabla}\rho$ vanishes at the boundary of a total system (where ρ and $\boldsymbol{\nabla}\rho$ are zero), the Lagrangian integral is zero for a total system. Thus, the Lagrangian integral $\mathscr{L}(\Psi, t)$ for a closed quantum mechanical system is zero at each time t and correspondingly the action integral vanishes for any time interval Δt.

The atomic Lagrangian integral is defined to be

$$\mathscr{L}[\Psi, \Omega, t] = \int_\Omega d\mathbf{r} \int d\tau' L(\Psi, \boldsymbol{\nabla}\Psi, \Psi, t). \quad (15)$$

where Ω denotes the atomic region. Correspondingly, the atomic action integral is

$$W_{12}[\Psi, \Omega] = \int_{t_1}^{t_2} dt\, \mathscr{L}[\Psi, \Omega, t]. \quad (16)$$

When Ψ and Ψ^* satisfy Eqs. (9), the atomic Lagrangian reduces to

$$\begin{aligned} \mathscr{L}[\Psi, \Omega, t] &= (-\hbar^2/4mN) \int_\Omega d\mathbf{r}\, \nabla^2\rho(\mathbf{r}, t) \\ &= (-\hbar^2/4mN) \oint dS(\mathbf{r}, t)\, \boldsymbol{\nabla}\rho(\mathbf{r}, t) \cdot \mathbf{n}(\mathbf{r}, t). \end{aligned} \quad (17)$$

Because of the zero-flux surface condition [Eq. (6)], the atomic action and Lagrangian integrals also vanish, and one may view the vanishing of the action over some total system as being the result of the action vanishing separately over the space of each atom in the system.

As a system in a given quantum state changes and evolves with time, the atomic surfaces evolve in a continuous manner and the property of exhibiting a zero flux in $\nabla\rho(\mathbf{r})$ is continuously maintained. Thus the atomic action integral will always vanish,

$$W_{12}[\Psi, \Omega] = (-\hbar^2/4mN) \int_{t_1}^{t_2} dt \int_{\Omega} d\mathbf{r}\, \nabla^2\rho(\mathbf{r}, t) = 0 \tag{18}$$

for any time interval, finite or infinitesimal. One may imagine an open system with an arbitrarily defined surface whose Lagrangian integral might vanish at some time t because of the vanishing in the *net* flux of $\nabla\rho(\mathbf{r}, t)$ across its surface in Eq. (17). However, in general, as the system changes with time, a net flux in $\nabla\rho(\mathbf{r}, t)$ through the surface would arise and the action integral for some time interval would not vanish. Thus the satisfaction of Eq. (18) for all time intervals demands that the open system be defined by a surface that itself evolves with time in a manner determined by a property of the open system, this property being one of a zero flux in $\nabla\rho$ at every point on its surface [Eq. (6)].

The condition stated in Eq. (18), that the atomic action integral vanish for all time intervals, may be taken as the quantum definition of an atom. It is a direct consequence of the topological definition of an atom as the union of an attractor and its basin, and it is the basis for the particular variational properties possessed by an atom considered as an open system.

The kinetic energy operator, as it appears in the Hamiltonian operator or in the expression for the Lagrangian density, is a sum of single-particle operators. Thus Eq. (11) may be partially integrated to yield the following relationship between the single-particle kinetic energy densities:

$$\begin{aligned}(-\hbar^2/4m)&\{\nabla^2 + \nabla'^2)\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')\}_{\mathbf{r}=\mathbf{r}'} \\ &= (\hbar^2/2m)\{\nabla\cdot\nabla'\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')\}_{\mathbf{r}=\mathbf{r}'} - (\hbar^2/4m)\,\nabla^2\rho(\mathbf{r})\end{aligned} \tag{19}$$

or in abbreviated notation as

$$K(\mathbf{r}) = G(\mathbf{r}) + \mathscr{L}(\mathbf{r}). \tag{20}$$

Anticipating to some degree the definition of the average value of the kinetic energy of an atom in a molecule, $T(\Omega)$, one finds upon integration of Eq. (20) over an atomic volume

$$T(\Omega) = \int_{\Omega} d\mathbf{r}\, K(\mathbf{r}) = \int_{\Omega} d\mathbf{r}\, G(\mathbf{r}). \tag{21}$$

Thus one finds, again as a consequence of the zero-flux condition of the atomic surface, that the average kinetic energy of an atom is uniquely defined. Other physical properties of atoms, as exemplified later, also exhibit particular values because of the vanishing of a surface contribution.

C. Variation of Atomic Action Integral[2]

We shall be considering the change in the atomic action integral $W_{12}[\Psi, \Omega]$ of Eq. (16) ensuing from variations $\delta\Psi$ of Ψ such that the following conditions are fulfilled:

(1) $\Phi = \Psi + \delta\Psi$ and its first and second derivatives vanish whenever an electronic position vector is of infinite length.

(2) In terms of Φ, a region $\Omega(\Phi, t)$ can be defined that is bounded by a zero-flux surface in $\nabla\rho_{\Phi}$, where

$$\rho_{\Phi}(\mathbf{r}, t) = N \int d\tau' \, \Phi^*(\mathbf{r}, \tau', t) \, \Phi(\mathbf{r}, \tau', t). \tag{22}$$

Moreover, it is required that, as Φ tends to Ψ at any time t, $\Omega(\Phi, t)$ is continuously deformable into the region $\Omega(t) = \Omega(\Psi, t)$ associated with the atom. The region $\Omega(\Phi, t)$ thus represents the atom in the varied total system, which is described by the trial function $\Phi(\mathbf{r}, \tau', t)$, just as Ω represents the atom when the total system is in the state described by $\Psi(\mathbf{r}, \tau', t)$.

Requiring the fulfillment of condition (2) amounts to imposing the variational constraint that the divergence of $\nabla\rho_{\Phi}$ integrates to zero at all stages of the variation, i.e., that

$$I_{\Phi} = \int_{\Omega(\Phi, t)} \nabla^2\rho_{\Phi} \, d\mathbf{r} = 0 \tag{23a}$$

for all admissible Φ and for all t, which implies

$$\delta I_{\Psi} = \delta \left\{ \int_{\Omega(t)} d\mathbf{r} \, \nabla^2\rho(\mathbf{r}, t) \right\} = 0. \tag{23b}$$

The expression for the first-order change in $W_{12}[\Psi, \Omega]$ in the limit $\delta\Psi \rightarrow 0$ and when Ψ satisfies the time-dependent Schrödinger equation, Eq. (9), is the atomic variational principle. As will be discussed later, this principle requires that the atomic action integral $W_{12}[\Phi, \Omega]$ be stationary, in a broad sense, at $\Phi = \Psi$. We shall also derive statements of this principle in terms

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[2] Some of the mathematical detail has been suppressed in this section. A full account can be found in the thesis of Nguyen-Dang (1980).

of the Lagrangian $\mathscr{L}[\Psi, \Omega, t]$ and, for a conservative total system in a stationary state, in terms of the energy functional $E[\psi, \Omega]$ where

$$E[\psi, \Omega] = \left(\int_\Omega d\mathbf{r} \int d\boldsymbol{\tau}' \left\{\frac{\hbar^2}{2m}\sum_i \boldsymbol{\nabla}_i\psi^* \cdot \boldsymbol{\nabla}_i\psi + \hat{V}\psi^*\psi\right\}\right) \Big/ \langle\psi^*\psi\rangle_\Omega,$$
$$\langle\psi, \psi\rangle_\Omega = \int_\Omega d\mathbf{r} \int d\boldsymbol{\tau}'\psi^*\psi = \frac{1}{N}\int_\Omega d\mathbf{r}\rho(\mathbf{r}). \tag{24}$$

Rather than the functionals $W_{12}[\Psi, \Omega]$ and $E[\psi, \Omega]$ based on the Lagrangian $\mathscr{L}[\Psi, \Omega, t]$ of Eq. (15), one could consider the variations of the corresponding functionals W'_{12} and E' constructed from the Hamiltonian-based Lagrangian $\mathscr{L}'[\Psi, \Omega, t]$, where

$$\begin{aligned}\mathscr{L}'[\Psi, \Omega, t] &= \int_\Omega d\mathbf{r} \int d\boldsymbol{\tau}'\{(i\hbar/2)(\Psi^*\dot{\Psi} - \dot{\Psi}^*\Psi) - \tfrac{1}{2}(\Psi^*\hat{\mathscr{H}}\Psi + (\hat{\mathscr{H}}\Psi^*)\Psi)\} \\ &= \tfrac{1}{2}\int_\Omega d\mathbf{r} \int d\boldsymbol{\tau}'\{\Psi^*(i\hbar\, \partial\Psi/\partial t - \hat{\mathscr{H}}\Psi) + \text{c.c}\}.\end{aligned} \tag{25}$$

Thus,

$$W'_{12}[\Psi, \Omega] = \int_{t_1}^{t_2} dt\, \mathscr{L}'[\Psi, \Omega, t], \tag{26a}$$

$$\begin{aligned}E'[\Psi, \Omega] &= \langle\Psi, \Psi\rangle_\Omega^{-1}\Big\{-\mathscr{L}'[\Psi, \Omega, t] \\ &\quad + \int_\Omega d\mathbf{r} \int d\boldsymbol{\tau}'[(i\hbar/2)(\Psi^*\dot{\Psi} - \dot{\Psi}^*\Psi)]\Big\} \\ &= \tfrac{1}{2}\{H[\Psi, \Omega] + H^*[\Psi, \Omega]\},\end{aligned} \tag{26b}$$

where

$$H[\Psi, \Omega] = \int_\Omega dr \int d\tau' \left\{\Psi^* \frac{-\hbar^2}{2m}\sum_i \Psi^*\nabla_i^2\Psi + \hat{V}\Psi^*\Psi\right\} \Big/ \langle\Psi, \Psi\rangle_\Omega. \tag{26c}$$

Henceforth, we shall call the primed functionals of Eqs. (26) the Hamiltonian-based action integral and energy functionals, respectively. Likewise, the unprimed functionals of Eqs. (16) and (24) will be called the Lagrangian-based action integral and energy functionals, respectively. When no confusion is possible, these will also be referred to as *the* atomic action integral and energy functionals, respectively.

The relationship between the Hamiltonian- and Lagrangian-based functionals is as follows:

$$\mathscr{L}[\Psi, \Omega, t] = \mathscr{L}'[\Psi, \Omega, t] - \frac{\hbar^2}{4mN}\int_\Omega d\mathbf{r}\, \nabla^2\rho(\mathbf{r}, t), \tag{27a}$$

$$W_{12}[\Psi, \Omega] = W'_{12}[\Psi, \Omega] - \frac{\hbar^2}{4mN}\int_{t_1}^{t_2} dt \int_\Omega d\mathbf{r}\, \nabla^2\rho(\mathbf{r}, t), \tag{27b}$$

$$E[\psi, \Omega] = E'[\psi, \Omega] + \frac{\hbar^2}{4mN}\int_\Omega d\mathbf{r}\, \nabla^2\rho(\mathbf{r}). \tag{27c}$$

The restriction of Eqs. (23), which demands that the atomic volume be bounded by a zero-flux surface at any stage of the variation, ensures the following:

(1) At any stage of the variation, the Hamiltonian-based functionals are equal to the corresponding Lagrangian-based functionals. In particular, at the point of variation [$\Phi = \Psi$, Ψ satisfies Eq. (9)] one has

$$\mathscr{L}[\Psi, \Omega, t] = \mathscr{L}'[\Psi, \Omega, t] = 0, \qquad \forall t, \tag{28a}$$

which implies

$$W_{12}[\Psi, \Omega] = W'_{12}[\Psi, \Omega] = 0. \tag{28b}$$

When Ψ represents a stationary state with energy $\bar{E}$, we further have

$$E[\psi, \Omega] = E'[\psi, \Omega] = \bar{E}. \tag{28c}$$

(2) The variations of the Hamiltonian-based functionals are identical in form and in value to those of the Lagrangian-based functionals. The equivalence of the Hamiltonian- and Lagrangian-based functionals at all stages of the variation characterizes a total molecular system. It is only because the atomic surface is one of zero flux in the charge distribution, that this equivalence is maintained between the corresponding atomic functionals. Indeed, it is apparent from Eqs. (27) that if the volume Ω was arbitrary, not only would the primed and unprimed functionals differ in value, they would also lead to different variational results.

Without advancing any argument as to why the aforementioned equivalence should be maintained, there remains the philosophy underlying the present approach—that one's criterion for defining an open system with maximum physical significance be dictated by the requirement that it possess the same variational properties as does a total system and that its physics be governed by the same dynamical laws as for a total system.

We now derive the variational equations that characterize on an equal footing a subsystem and a total system. To impose the variational constraint given in Eqs. (23) and thereby define a particular class of open system, one must vary the surface of the subsystem. This requirement necessarily leads to a relaxation of the usual variational constraint that $\delta\Psi$ vanish at all boundaries of the system, or at the time end points in the variation of the action integral. The generalization of the variation of the action integral obtained by the removal of the constraints that $\delta\Psi$ and $\delta\Psi^*$

vanish at the time end points, and by the additional variation of the time end points leads to the principle of stationary action (Schwinger, 1951). The additional terms obtained at the time end points, *terms that necessarily appear in the variation of the atomic action integral,* are identified by this principle as the generators of infinitesimal unitary transformations. The quantum description of atomic properties as developed here is based upon this identification.

Applying the techniques of the calculus of variations (Courant and Hilbert, 1953) to the expression for $W_{12}[\Psi, \Omega]$, Eq. (16), one obtains

$$\begin{aligned}\delta W_{12}[\Psi, \Omega] = &\int_{t_1}^{t_2} dt \int_{\Omega} d\mathbf{r} \int d\tau'\{(-i\hbar\dot{\Psi}^* - \hat{H}\Psi^*)\delta\Psi + \text{c.c.}\}\\ &+ \int_{t_1}^{t_2} dt \oint dS(\mathbf{r}) \int d\tau'(-\hbar^2/2m)\{\nabla\Psi^*\delta\Psi \cdot \mathbf{n}(\mathbf{r}) + \text{c.c.}\}\\ &+ \int_{t_1}^{t_2} dt \oint dS(\mathbf{r})\, \mathscr{L}(\mathbf{r})\, \delta S(\mathbf{r})\\ &+ \int_{t_1}^{t_2} dt \oint dS(\mathbf{r}) \int d\tau'\{(-i\hbar/2)(\partial S(\mathbf{r})/\partial t)\Psi^*\delta\Psi + \text{c.c.}\}\\ &+ \left\{\frac{i\hbar}{2}\int_{\Omega} d\mathbf{r} \int d\tau'\Psi^*\delta\Psi + \text{c.c.} + \mathscr{L}[\Psi, \Omega, t]\delta t\right\}\Bigg|_{t_1}^{t_2}.\end{aligned} \tag{29}$$

In Eq. (29), $\delta S(\mathbf{r})$ denotes the infinitesimal normal shift of a surface element centered on $\mathbf{r}$, as conditioned by the continuous variation in the admissible trial function $\Phi = \Psi + \delta\Psi$, in a small neighborhood of the state function Ψ. The expression $\partial S(\mathbf{r})/\partial t$ appearing on the right-hand side of Eq. (29) denotes the time rate of change in the surface bounding the *unvaried* region $\Omega(t) = \Omega(\Psi, t)$. Since Ψ and Ψ^* satisfy Schrödinger's equation, Eq. (9), the first term on the right-hand side of Eq. (29) vanishes, as do the terms containing $\mathscr{L}[\Psi, \Omega, t]$ at the time end points [see Eq. (28a)]. Also at the point of variation, the Lagrangian density appearing in the third term is proportional to $\nabla^2\rho(\mathbf{r})$, Eq. (12). It is through this behavior of $\mathscr{L}(\mathbf{r})$ in the surface variation that the constraint given in Eq. (23) is introduced. One first notes that

$$\begin{aligned}\delta\left\{\frac{\hbar^2}{4m}\int_{\Omega} d\mathbf{r}\, \nabla^2\rho(\mathbf{r})\right\} = &\frac{\hbar^2}{4m}\oint dS(\mathbf{r})\, \nabla^2\rho(\mathbf{r})\, \delta S(\mathbf{r})\\ &+ \frac{\hbar^2}{4m}\oint dS(\mathbf{r}) \int d\tau'\{(\nabla\Psi^*)\,\delta\Psi\\ &+ \Psi^*\nabla(\delta\Psi) + \nabla(\delta\Psi^*)\Psi + \delta\Psi^*\nabla\Psi\}\cdot\mathbf{n}(\mathbf{r}).\end{aligned} \tag{30}$$

The quantity $\nabla^2\rho$ is a divergence expression, i.e., its variation yields only surface terms. Thus its addition to the integral to be varied will not alter the Euler equations so obtained. The substitution of the identity given in

Eq. (30) into Eq. (29) via the third term on the right-hand side of this latter equation *together* with the imposition of the variational constraint given in Eq. (23b) yields

$$\begin{aligned}
&\delta W_{12}[\Psi,\Omega]\\
&= \frac{-\hbar^2}{4m}\left\{\int_{t_1}^{t_2} dt \oint dS(\mathbf{r}) \int d\tau'[(\nabla\Psi^*)\delta\Psi - \Psi^*\nabla(\delta\Psi)]\cdot\mathbf{n}(\mathbf{r}) + \text{c.c.}\right\}\\
&\quad + \left\{\frac{-i\hbar}{2}\int_{t_1}^{t_2} dt \oint dS(\mathbf{r}) \int d\tau' \frac{\partial S}{\partial t}\Psi^*\delta\Psi + \text{c.c.}\right\}\\
&\quad + \left\{\frac{i\hbar}{2}\int_{\Omega} dr \int d\tau'\ \Psi^*\delta\Psi + \text{c.c.}\right\}\Bigg|_{t_1}^{t_2}. \qquad (31)
\end{aligned}$$

The result given in Eq. (31) for the variation of the atomic action integral is identical to that obtained from the unconstrained variation of the Hamiltonian-based integral $W'_{12}[\Psi, \Omega]$. Without the imposition of the variational constraint given in Eq. (23b), the expression for $\delta W_{12}[\Psi, \Omega]$, which would then apply to *any* subsystem, contains the additional term

$$\int_{t_1}^{t_2} dt\delta\left\{\frac{\hbar^2}{4m}\int_{\Omega} d\mathbf{r}\,\nabla^2\rho(\mathbf{r})\right\}$$

and the equivalence between the Lagrangian- and Hamiltonian-based functionals is no longer obtained.

The variational result of Eq. (31) can equivalently be written in terms of the Lagrangian $\mathscr{L}[\Psi, \Omega, t]$. For this purpose, we let $t_1 = t$, $t_2 = t + dt$, where t is an arbitrary instant of time and dt an infinitesimal time interval. Then

$$\begin{aligned}
\delta W_{t,t+dt}[\Psi, \Omega] &= (\delta\mathscr{L}[\Psi, \Omega, t])dt + \mathscr{L}[\Psi, \Omega, t]\delta(dt)\\
&= (\delta\mathscr{L}[\Psi, \Omega, t])dt, \qquad (32)
\end{aligned}$$

Thus,

$$\begin{aligned}
\delta\mathscr{L}[\Psi, \Omega, t] = &\left\{\frac{-\hbar^2}{4m}\oint dS(\mathbf{r}) \int d\tau'[(\nabla\Psi^*)\delta\Psi - \Psi^*\nabla(\delta\Psi)]\cdot\mathbf{n}(\mathbf{r})\right.\\
&- \frac{i\hbar}{2}\oint dS(\mathbf{r}) \int d\tau' \frac{\partial S}{\partial t}\Psi^*\delta\Psi\\
&\left.+ \frac{i\hbar}{2}\frac{d}{dt}\int_{\Omega} d\mathbf{r} \int d\tau'\ \Psi^*\delta\Psi\right\} + \text{c.c.} \qquad (33)
\end{aligned}$$

When the total system is a conservative system, the state function Ψ describes a stationary state, and satisfies

$$i\hbar\,\partial\Psi/\partial t = \hat{\mathscr{H}}\Psi = \bar{E}\Psi. \qquad (34)$$

When the variations $\delta\Psi$ to be used in Eqs. (31)–(33) are of the type

$$\delta\Psi(\boldsymbol{\tau}, t) = e^{(i/\hbar)\bar{E}t}\,\delta\psi(\boldsymbol{\tau}), \tag{35}$$

thereby preserving the separation between temporal and spatial (and spin) variables observed at the point of variation, the atomic Lagrangian reduces to the form

$$\mathscr{L}[\Psi, \Omega, t] = -\langle\Psi, \Psi\rangle_{\Omega}(E[\Psi, \Omega] - \bar{E}) \tag{36}$$

at all stages of the variation. The variation in $\mathscr{L}[\Psi, \Omega, t]$ is thus simply related to the variation in $E[\Psi, \Omega]$, which is given by

$$\delta E[\Psi, \Omega] = -\langle\Psi, \Psi\rangle_{\Omega}^{-1}\,\delta\mathscr{L}[\Psi, \Omega, t]. \tag{37}$$

Using Eqs. (33), (35), and (37), we have

$$\delta E[\Psi, \Omega] = \frac{\hbar^2}{4m}\,\langle\Psi, \Psi\rangle_{\Omega}^{-1}\oint dS\int d\boldsymbol{\tau}'[(\nabla\Psi^*)\delta\Psi - \Psi^*\nabla(\delta\Psi)]\cdot\mathbf{n} + \text{c.c.} \tag{38}$$

In deriving Eq. (38), use has been made of the definition of the bounding surface of Ω as a zero-flux surface in $\nabla\rho$.

The results expressed in Eqs. (31), (33), and (38) are various statements of a single variational principle that, as demonstrated in the following section, is the principle of stationary action (Schwinger, 1951). We have derived Eq. (31) and its consequences, Eqs. (33) and (38), from the assumption that Ψ obeys Schrödinger's equation. We can also consider the principle of stationary atomic action as a generating principle. Indeed, if Eq. (31) is to be obtained for any variation $\delta\Psi$, and any region Ω bounded by a zero-flux surface, it applies to the case $\Omega = R^3$, and $\delta\Psi$ satisfying the additional boundary condition $\delta\Psi(t_1) = \delta\Psi(t_2) = 0$. In this case, $W_{12}[\Psi, \Omega]$ becomes the functional $W_{12}[\Psi]$, of Eq. (7), and

$$\delta W_{12}[\Psi] = 0 \tag{39}$$

leads to a pair of Euler equations that are precisely Schrödinger's equation and its complex conjugate expression of Eqs. (9). Thus, the requirement that the action integral of the total system be stationary, in the sense of Eq. (39), is a particular case of the principle of stationary atomic action, Eq. (31).

D. Principle of Stationary Action

We summarize only briefly the manner in which the principle of stationary action provides a formal axiomatic development of quantum mechanics (Schwinger, 1951). Our primary purpose is the use of this principle in delineating the variational and mechanical properties of an atom.

The principle of stationary action as stated by Schwinger concerns the variation of the action integral *operator* $\hat{\mathscr{W}}_{12}$ associated with a total quantum mechanical system. For a quantized system described by the coordinate operators $\hat{q}(t)$ and their time derivatives $\dot{\hat{q}}(t)$, the action integral *operator* is constructed in the same manner as the corresponding classical action integral

$$\hat{\mathscr{W}}_{12} = \int_{t_1}^{t_2} dt\ \mathscr{L}(\hat{q}, \dot{\hat{q}}, t). \tag{40}$$

In performing an arbitrary general operator variation, the ensuing change in the action *operator* is the difference between the values at t_2 and t_1 of the generator, $\hat{\mathscr{F}}$, of a corresponding *infinitesimal unitary transformation*. This statement of the principle is embodied in the following mathematical expression:

$$\delta\hat{\mathscr{W}}_{12} = \hat{\mathscr{F}}(t_2) - \hat{\mathscr{F}}(t_1). \tag{41}$$

Formally, the change in the action integral as given by Eq. (41) is the same in the classical and quantized cases. Thus, Schwinger's principle of stationary action establishes the correspondence between the generator of a classical canonical transformation and the generator of a unitary transformation of the corresponding quantized system. The classical counterpart of Eq. (41) is a generalization of Hamilton's principle, obtained through the removal of a variational constraint. This variational constraint demands the vanishing of the variations in the dynamical variables of the classical system at the time end points of the action integral; its removal thus permits the inclusion of physically realizable alterations in the description of the system, i.e., canonical transformations. Similarly, in a quantized system, the same generalization of the variational procedure allows for the introduction of unitary transformations as causing the variations. From Schwinger's principle of stationary action, Eq. (41), one derives the commutation rules and the equations of motion in the Heisenberg picture.

While we have used the Schrödinger language in our variation of the atomic action integral, the result obtained in Eq. (29) is formally identical to that stated in Eq. (41) when the volume Ω refers to the total system.[3] In this case the variations over the volume and the surface terms of Eq. (29) vanish, the former yielding Schrödinger's equation of motion. The expression for the variation of $W_{12}[\Psi]$ reduces to

$$\delta W_{12}[\Psi] = \left\{\frac{i\hbar}{2}\int d\tau\,\Psi^*\delta\Psi + \text{c.c.} + \mathscr{L}[\Psi, t]\delta t\right\}\Bigg|_{t_1}^{t_2}. \tag{42}$$

---

[3] The variation of $\mathscr{W}_{12}[\Psi, \Omega]$ using the language of field theory has been given by Bader *et al.* (1978).

In analogy with the classical result

$$H = \sum_i p_i \dot{q}_i - L,$$

we express the Schrödinger-based average Hamiltonian $H[\Psi]$ as the Legendre transform of $\mathscr{L}[\Psi, t]$,

$$H[\Psi] = \frac{i\hbar}{2} \int d\tau (\Psi^* \dot{\Psi} - \dot{\Psi}^* \Psi) - \mathscr{L}[\Psi, t] - \frac{\hbar^2}{4m} \int d\mathbf{r}\, \nabla^2 \rho(\mathbf{r})$$

in order to rewrite Eq. (42) as

$$\delta W_{12}[\Psi] = \left\{ \frac{i\hbar}{2} \int d\tau \Psi^* \, \Delta\Psi + \text{c.c.} - H[\Psi]\delta t \right\} \Bigg|_{t_1}^{t_2}, \tag{43}$$

where the symbol $\Delta\Psi$ denotes the general variation

$$\Delta\Psi = \delta\Psi + \dot{\Psi}\delta t.$$

The principle of stationary action permits the identification of the generators of temporal and spatial unitary transformations in terms of their average values. For a temporal change, δt is arbitrary, $\Delta\Psi = 0$, and the change in $W_{12}[\Psi]$ reduces to the difference in the average values of $-\hat{\mathscr{H}}$ at the two time end points, thereby identifying the generator of temporal development as $-\hat{\mathscr{H}}\delta t$. Similarly, for a pure spatial change, $\delta t = 0$ and

$$\delta W_{12}[\Psi] = \tfrac{1}{2} \left\{ \varepsilon \int d\tau [\Psi^* \hat{\mathscr{F}} \Psi + (\hat{\mathscr{F}} \Psi^*) \Psi] \right\} \Bigg|_{t_1}^{t_2}, \tag{44}$$

where $\Delta\Psi = \delta\Psi = (-i/\hbar)\varepsilon\hat{\mathscr{F}}\Psi$. In this situation, $\hat{\mathscr{F}}$ is referred to as the generator. It is a Hermitian operator that may be a function of the coordinates (inducing a gauge transformation) and/or of the momenta (inducing a translation of coordinates).

If both sides of Eq. (43) are divided by $t_2 - t_1$ and the result is subjected to the limit $\Delta t \rightarrow 0$, one obtains, to first order, an expression for $\delta\mathscr{L}[\Psi, t]$,

$$\delta\mathscr{L}[\Psi, t] = \tfrac{1}{2}\{\varepsilon d\langle \hat{\mathscr{F}} \rangle / dt + \text{c.c.}\}, \tag{45}$$

which, through Heisenberg's relation for the time rate of change of the average value of a property F, may be re-expressed as

$$\delta\mathscr{L}[\Psi, t] = (\varepsilon/2)\{(i/\hbar)\langle[\hat{\mathscr{H}}, \hat{\mathscr{F}}]\rangle + \text{c.c.}\}. \tag{46}$$

For a stationary state, the corresponding expression is found to be

$$\delta E[\psi] = -(\varepsilon/2)\{(i/\hbar)\langle[\hat{\mathscr{H}}, \hat{\mathscr{F}}]\rangle + \text{c.c.}\} = 0. \tag{47}$$

The commutator average in Eq. (47) vanishes as a result of the hypervirial theorem (Hirschfelder, 1960). In the following section we apply the principle of stationary action to an atom in a molecule to obtain corresponding expressions for the variation of the atomic functions $\mathscr{L}[\Psi, \Omega]$ and $E[\psi, \Omega]$ that are the working expressions for the theory of atoms in molecules.

E. Atomic Statement of the Principle of Stationary Action

To provide a physical interpretation of the change in the atomic action, Eq. (31), we first introduce a number of definitions. The density of a property F is defined by

$$\rho_F(\mathbf{r}, t) = (N/2)\left\{\int d\boldsymbol{\tau}'\ \Psi^* \hat{\mathscr{F}}(\mathbf{r})\Psi + \text{c.c.}\right\} \tag{48}$$

and its corresponding average value over the volume Ω is

$$F(\Omega, t) = \int_\Omega d\mathbf{r}\ \rho_F(\mathbf{r}, t) \equiv \tfrac{1}{2}\{\langle \hat{\mathscr{F}} \rangle_\Omega + \text{c.c.}\}. \tag{49}$$

The vector current density associated with the property F is

$$\mathbf{J}_F(\mathbf{r}, t) = (N\hbar/4mi) \int d\boldsymbol{\tau}'\ \{\Psi^* \nabla(\hat{\mathscr{F}}\Psi) - (\nabla\Psi^*)(\hat{\mathscr{F}}\Psi)\}. \tag{50}$$

From Schrödinger's equation, the *total* time rate of change of a subsystem average value $F(\Omega, t)$ is (Srebrenik *et al.*, 1978)

$$\frac{dF(\Omega, t)}{dt} = \frac{N}{2}\left\{\frac{i}{\hbar}\langle[\hat{\mathscr{H}}, \hat{\mathscr{F}}]\rangle_\Omega + \text{c.c.}\right\} + \oint dS(\mathbf{r})\left\{\frac{\partial S(\mathbf{r})}{\partial t}\rho_F - (\mathbf{J}_F \cdot \mathbf{n}(\mathbf{r}) + \text{c.c.})\right\}. \tag{51}$$

(We have assumed, for simplicity of expression, that $\hat{\mathscr{F}}$ has no implicit time dependence, i.e., that $\partial\hat{\mathscr{F}}/\partial t = 0$.) Using a subsystem operator projection formalism (Bader *et al.*, 1978), one can show that the first term in Eq. (51) is the subsystem projection of the time rate of change of $F(t)$ for the total system. Thus corresponding to the Heisenberg equation

$$d\hat{\mathscr{F}}/dt = (i/\hbar)[\hat{\mathscr{H}}, \hat{\mathscr{F}}], \tag{52}$$

one has

$$\langle d\hat{\mathscr{F}}/dt \rangle_\Omega + \text{c.c.} = (i/\hbar)\{\langle[\hat{\mathscr{H}}, \hat{\mathscr{F}}]\rangle_\Omega + \text{c.c.}\}. \tag{53}$$

Equation (53) makes clear that the commutator averages in Eq. (51) do indeed describe the time change of $F(\Omega, t)$ over the volume Ω without any surface contributions. The two surface terms, unique to an open system, represent the change in $F(\Omega, t)$ with respect to time resulting from a change in the surface with time and from the net flux in the current density $\mathbf{J}_F$ across the surface. The two terms are of different sign, since when

$\partial S/\partial t > 0$, corresponding to an expansion of the volume Ω, it contributes to an increase in $F(\Omega, t)$, while when $\mathbf{J}_F\cdot\mathbf{n} > 0$, corresponding to a net outflow of the density ρ_F from the volume Ω, the result is a decrease in $F(\Omega, t)$.

We now use these definitions to re-express the change in the atomic action integral, Eq. (31), resulting from the application of an infinitesimal unitary transformation with generator $\hat{\mathscr{F}}$. We thus write

$$\delta W_{12}[\Psi, \Omega] = F(\Omega, t_2) - F(\Omega, t_1) - \int_{t_1}^{t_2} dt \oint dS(\mathbf{r})\{(\partial S/\partial t)\rho_F - (\mathbf{J}_F\cdot\mathbf{n} + \text{c.c.})\}. \quad (54)$$

One notes that the surface terms appearing in Eq. (54) are precisely those appearing in Eq. (51) for the time rate of change of $F(\Omega, t)$ but with their signs reversed. Thus the change in the atomic action integral may be written as

$$\delta W_{12}[\Psi, \Omega] = \varepsilon \int_{t_1}^{t_2} dt\{\langle d\hat{\mathscr{F}}/dt\rangle_\Omega + \text{c.c.}\}/2, \quad (55)$$

i.e., as the time integral of the temporal rate of change in the generator evaluated over just the volume of the atom, or equivalently,

$$\delta W_{12}[\Psi, \Omega] = \varepsilon \int_{t_1}^{t_2} dt\{(i/\hbar)\langle[\hat{\mathscr{H}}, \hat{\mathscr{F}}]\rangle_\Omega + \text{c.c.}\}/2. \quad (56)$$

The principle of stationary action as written in operator form in Eq. (41), may be re-expressed to yield a statement identical with the expression for the change in the atomic action [Eq. (56)]; namely

$$\delta\hat{\mathscr{W}}_{12} = \int_{t_1}^{t_2} dt\{d\hat{\mathscr{F}}/dt\} = \int_{t_1}^{t_2} dt\{(i/\hbar)[\hat{\mathscr{H}}, \hat{\mathscr{F}}]\}. \quad (57)$$

Thus as a statement of the principle of stationary action for an atom, Eq. (56) is seen to be identical in form and physical content to the operator statement of Schwinger's principle of stationary action, Eq. (57).

We now show the equivalence of the original statement of the principle, Eq. (41), and the corresponding atomic statement, Eq. (54).

Consider for visual simplicity (see Fig. 3) a two-dimensional system. As the system changes with time, it sweeps out a space–time volume bounded at t_1 and t_2 by the two *space-like* surfaces [the volumes $\Omega(t_1)$ and $\Omega(t_2)$ of the system at t_1 and t_2] joined by a *time-like* surface that is generated by the time evolution of the instantaneous boundary of the system, $S(\mathbf{r}, t)$. The principle of stationary action states that the total change in action is equal to the difference of the values of the generator $\hat{\mathscr{F}}(t)$ evaluated in the two *space-like* surfaces at t_2 and t_1. There is no contribution to

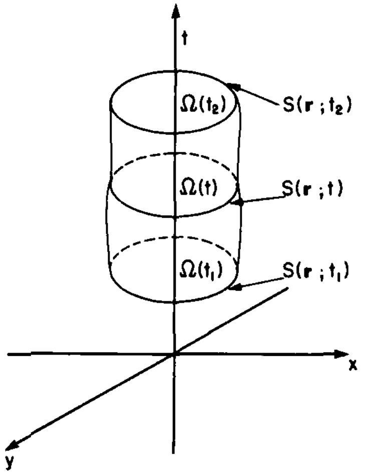

Fig. 3. Pictorial representation of the space–time development of a two-dimensional subsystem $\Omega(t)$ of a total system. The space-like surfaces are denoted by $\Omega(t)$, each being bounded by a surface $S(\mathbf{r}, t)$. The collection of the latter constitute a timelike surface, which together with $\Omega(t_1)$ and $\Omega(t_2)$ defines the space–time integration volume in the subspace action integral $W_{12}[\Psi, \Omega]$. (From Bader *et al.*, 1978.)

$\delta\hat{\mathscr{W}}_{12}$ from the interior of the space–time volume swept out as a consequence of the system evolving in time or, trivially for a total system, from the time-like surface.

It is a peculiarity of open systems that the difference in the average values of a property between two time end points implicitly includes, in addition to the difference in values determined in the interiors of the two space-like surfaces, an integrated contribution, over the time-like surface, arising from the flux in the property across the surface at each time t and from the change in the surface with time; i.e.,

$$\begin{aligned} F(\Omega, t_2) - F(\Omega, t_1) &= \int_{t_1}^{t_2} dt(dF(\Omega, t)/dt) \\ &= \int_{t_1}^{t_2} dt \left\{ \tfrac{1}{2}\langle d\hat{F}/dt \rangle_\Omega + \text{c.c.} + \oint dS[(\partial S/\partial t)\rho_F - (\mathbf{J}_F\cdot\mathbf{n} + \text{c.c.})] \right\}. \end{aligned} \tag{58}$$

Thus to obtain a statement of the principle of stationary action for an open system equivalent to that for the total system, one must subtract from the difference in the open system average values the integral over the time-like surface of the boundary contributions to this difference. This is precisely the expression given for the change in the atomic action integral in Eq. (54).[4]

Thus Eq. (54) or Eq. (56) demonstrates that the principle of stationary action may be generalized to describe an atom within some total system as well as the total system itself. One notes that the variation of $W_{12}[\Psi, \Omega]$ for an open system Ω with an arbitrary boundary includes the additional term

$$\int_{t_1}^{t_2} dt\delta \left\{ \frac{\hbar^2}{4m} \int_\Omega dr\, \nabla^2\rho(\mathbf{r}) \right\} = \int_{t_1}^{t_2} dt\delta \left\{ \frac{\hbar^2}{4m} \oint dS(\mathbf{r})\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \right\}.$$

The presence of this term violates the principle of stationary action since it represents a contribution to $\delta W_{12}[\Psi, \Omega]$ from the space–time volume. Because of its arbitrary value, it renders physically inadmissible the related operational expressions for $\delta \mathscr{L}[\Psi, \Omega]$ and $\delta E[\psi, \Omega]$.

It is clear from Eq. (56) that the change in atomic action for an infinitesimal time interval yields

$$\delta\mathscr{L}[\Psi, \Omega] = (\varepsilon/2)\{(i/\hbar)\langle[\mathscr{H}, \hat{\mathscr{F}}]\rangle_\Omega + \text{c.c.}\} \tag{59}$$

for the variation of the atomic Lagrangian integral as generated by an infinitesimal unitary transformation of the state function. For a stationary state, the corresponding variation of the atomic energy functional is (Srebrenik and Bader, 1975; Srebrenik *et al.*, 1978)[5]

$$\delta E[\psi, \Omega] = (-\varepsilon/2)\{(i/\hbar)\langle[\hat{\mathscr{H}}, \hat{\mathscr{F}}]\rangle_\Omega + \text{c.c.}\}/\langle\psi, \psi\rangle_\Omega \tag{60}$$

One notes that since both these expressions are derived from the variation of the atomic action integral, they do not contain any contributions from the atomic surface (Bader *et al.*, 1978), the unique variational property of the atomic class of subsystem. *Thus the variational expressions for the atomic functionals.* $\mathscr{L}[\Psi, \Omega]$ *and* $E[\psi, \Omega]$ *are identical in form and content to the corresponding expressions for the total system,* Eq. (46) and Eq. (47), respectively.

In the following section these statements of the atomic variational principle are used to derive the integrated atomic force law and the atomic virial theorem for both time-dependent and stationary state systems.

[4] The complete equivalence of the atomic and total system statements of the principle of stationary action was not fully realized in the original investigation (Bader *et al.*, 1978).

[5] The signs appearing in Eqs. (59) and (60) before the commutator averages are the opposite to those previously given (Srebrenik *et al.*, 1978; Bader *et al.*, 1978) because of the definition here of $\delta\Psi = -(i\varepsilon/\hbar)\hat{\mathscr{F}}\Psi$.

IV. Variational Basis for Atomic Properties

A. Variational Derivation of Atomic Force Law

1. *Integrated Force Law*

We use the atomic variational principle to derive an expression governing the average time-dependent force acting on an atom in a molecule. Ehrenfest's second relationship states that the average of the force acting on a quantum system is given by the time rate of change of its average momentum. Thus we consider a variation of $\mathscr{L}[\Psi, \Omega]$ with generator $\hat{\mathscr{F}} = \boldsymbol{\varepsilon} \cdot \hat{\mathbf{p}}$, where $\hat{\mathbf{p}}$ denotes the conjugate momentum associated with the electron whose coordinate $\mathbf{r}$ is integrated over the atomic volume Ω. Each of the components of the vector $\boldsymbol{\varepsilon}$ is an arbitrary, infinitesimal real number, fixed for all $\mathbf{r}$. For each given $\boldsymbol{\varepsilon}$, the generator $\hat{\mathscr{F}}$ then induces an infinitesimal unitary transformation corresponding to a uniform translation of the electronic coordinates $\mathbf{r}$ by $-\boldsymbol{\varepsilon}$,

$$\mathbf{r}' = \mathbf{r} - \boldsymbol{\varepsilon}.$$

Denoting by ∇_ε the gradient operator with respect to $\boldsymbol{\varepsilon}$, the atomic variational principle Eq. (59) states that

$$\boldsymbol{\varepsilon} \cdot \nabla_\varepsilon \mathscr{L}[\Psi_\varepsilon(t), \Omega] \Big|_{\varepsilon=0} = \tfrac{1}{2}\boldsymbol{\varepsilon} \cdot \{\langle (i/\hbar)[\hat{\mathscr{H}}, \hat{\mathbf{p}}]\rangle_\Omega + \text{c.c.}\}. \tag{61}$$

On the left-hand side of Eq. (61) we have introduced the notation Ψ_ε to denote the image of the state function Ψ, in the infinitesimal unitary transformation described by $\hat{\mathscr{F}}$:

$$\Psi_\varepsilon(\mathbf{r}, \boldsymbol{\tau}', t) = (\hat{1} - (i/\hbar)\boldsymbol{\varepsilon} \cdot \hat{\mathbf{p}})\Psi(\mathbf{r}, \boldsymbol{\tau}', t) = \Psi(\mathbf{r} - \boldsymbol{\varepsilon}, \boldsymbol{\tau}', t). \tag{62}$$

Substituting Ψ_ε for Ψ in the expression for $\mathscr{L}[\Psi, \Omega]$, Eq. (15), differentiating with respect to $\boldsymbol{\varepsilon}$, noting that

$$\nabla_\varepsilon \Psi_\varepsilon \Big|_{\varepsilon=0} = -\nabla\Psi.$$

one obtains (including the variation of the surface $\delta S = \boldsymbol{\varepsilon} \cdot \mathbf{n}$),

$$\begin{aligned}
&\nabla_\varepsilon \mathscr{L}[\Psi_\varepsilon, \Omega]\big|_{\varepsilon=0} \\
&\quad = -\int_\Omega d\mathbf{r} \int d\boldsymbol{\tau}' \Big\{ \tfrac{1}{2}i\hbar((\nabla\Psi^*)\dot{\Psi} + \Psi^*\nabla\dot{\Psi} - (\nabla\dot{\Psi}^*)\Psi - \dot{\Psi}^*\nabla\Psi) \\
&\qquad - \frac{\hbar^2}{2m}\sum_i ((\nabla\nabla_i\Psi^*)\cdot\nabla_i\Psi) + (\nabla\nabla_i\Psi)\cdot\nabla_i\Psi^*) \\
&\qquad - \hat{V}(\nabla\Psi^*\Psi + \Psi^*\nabla\Psi)\Big\} - \frac{\hbar^2}{4mN}\oint dS\, \nabla^2\rho\mathbf{n}.
\end{aligned} \tag{63}$$

In Eq. (63) we have used the dyadic notation to express the contributions to $\boldsymbol{\nabla}_\varepsilon \mathscr{L}[\Omega, \Psi_\varepsilon]$ arising from the kinetic energy part of the Lagrangian, $\mathscr{L}[\Omega, \Psi_\varepsilon]$. Explicitly, e.g., the term $(\boldsymbol{\nabla}\boldsymbol{\nabla}_i\Psi^*) \cdot \boldsymbol{\nabla}_i\Psi$ reads

$$(\boldsymbol{\nabla}\boldsymbol{\nabla}_i\Psi^*)\cdot\boldsymbol{\nabla}_i\Psi = \sum_i \mathbf{e}_k \left(\sum_l \frac{\partial^2\Psi^*}{\partial r_k\,\partial r_l^{(i)}}\cdot\frac{\partial\Psi}{\partial r_l^{(i)}}\right), \tag{64}$$

where r_k $(r_k^{(i)})$ is the component of $\mathbf{r}$ $(\mathbf{r}_i)$ along the direction of the unit vector $\mathbf{e}_k$, $k = 1, 2, 3$. It follows from Eq. (64) that

$$(\boldsymbol{\nabla}\boldsymbol{\nabla}_i\Psi^*)\cdot\boldsymbol{\nabla}_i\Psi = \boldsymbol{\nabla}_i\cdot(\boldsymbol{\nabla}_i\Psi\boldsymbol{\nabla}\Psi^*) - \boldsymbol{\nabla}\Psi^*\nabla_i^2\Psi, \tag{65}$$

where

$$\boldsymbol{\nabla}_i\Psi\boldsymbol{\nabla}\Psi^* = \sum_{l,k} \mathbf{e}_l\left(\frac{\partial\Psi}{\partial r_l^{(i)}}\frac{\partial\Psi^*}{\partial r_k}\right)\mathbf{e}_k.$$

Likewise, we can write the term $(\boldsymbol{\nabla}\boldsymbol{\nabla}_i\Psi)\cdot\boldsymbol{\nabla}_i\Psi^*$ as

$$(\boldsymbol{\nabla}\boldsymbol{\nabla}_i\Psi)\cdot\boldsymbol{\nabla}_i\Psi^* = \boldsymbol{\nabla}_i\cdot(\boldsymbol{\nabla}_i\Psi^*\boldsymbol{\nabla}\Psi) - \nabla_i^2\Psi^*\boldsymbol{\nabla}\Psi. \tag{66}$$

Using Eqs. (65), (66), and Schrödinger's equations, Eq. (9), we infer, from Eq. (63)

$$\begin{aligned}
&\boldsymbol{\nabla}_\varepsilon\mathscr{L}[\Psi_\varepsilon, \Omega]\big|_{\varepsilon=0}\\
&\quad = -\int_\Omega d\mathbf{r}\int d\boldsymbol{\tau}'\,\{\tfrac{1}{2}i\hbar(\dot\Psi^*\boldsymbol{\nabla}\Psi + \Psi^*\boldsymbol{\nabla}\dot\Psi - (\boldsymbol{\nabla}\dot\Psi^*)\Psi - (\boldsymbol{\nabla}\Psi^*)\dot\Psi)\}\\
&\qquad + (\hbar^2/2m)\oint dS\int' d\boldsymbol{\tau}'\{\boldsymbol{\nabla}\Psi^*\boldsymbol{\nabla}\Psi + \boldsymbol{\nabla}\Psi\boldsymbol{\nabla}\Psi^*\}\cdot\mathbf{n}\\
&\qquad - (\hbar^2/4mN)\oint dS\,\boldsymbol{\nabla}^2\rho\mathbf{n}
\end{aligned}$$

or, equivalently, using Eq. (50) for the definition of the current density $\mathbf{J}(\mathbf{r})$ for the case $\hat{\mathscr{F}} = \hat{1}$

$$\begin{aligned}
\boldsymbol{\varepsilon}\cdot\boldsymbol{\nabla}_\varepsilon\mathscr{L}[\Psi_\varepsilon, \Omega]\big|_{\varepsilon=0} &= \boldsymbol{\varepsilon}\cdot\frac{m}{N}\int_\Omega d\mathbf{r}\,\frac{\partial\mathbf{J}}{\partial t} - \boldsymbol{\varepsilon}\cdot\frac{\hbar^2}{4mN}\oint dS\,\boldsymbol{\nabla}^2\rho\mathbf{n}\\
&\quad + \boldsymbol{\varepsilon}\cdot\frac{\hbar^2}{2m}\oint dS\int d\boldsymbol{\tau}'\{\boldsymbol{\nabla}\Psi^*\boldsymbol{\nabla}\Psi + \boldsymbol{\nabla}\Psi\boldsymbol{\nabla}\Psi^*\}\cdot\mathbf{n}.
\end{aligned} \tag{67}$$

Since the subsystem is bounded by a zero-flux surface at all stages of the variations generated by $\hat{\mathscr{F}}$, the zero-flux variational constraint, Eq. (23b), applies. In the present case it assumes the form

$$\boldsymbol{\varepsilon}\cdot\frac{\hbar^2}{4m}\boldsymbol{\nabla}_\varepsilon\left(\int_\Omega \nabla^2\rho_{\Psi_\varepsilon}\,d\mathbf{r}\right)\bigg|_{\varepsilon=0} = 0. \tag{68}$$

Using the same procedure as above, we readily find the left-hand side of Eq. (68) to be given by

$$\begin{aligned}\boldsymbol{\varepsilon}\cdot\frac{\hbar^2}{4m}\boldsymbol{\nabla}_{\varepsilon}\left(\int_{\Omega}\nabla^2\rho_{\Psi_\varepsilon}\,d\mathbf{r}\right)\bigg|_{\varepsilon=0}
&= -\boldsymbol{\varepsilon}\cdot\frac{\hbar^2}{4m}\oint dS\int d\boldsymbol{\tau}'[(\boldsymbol{\nabla\nabla}\Psi^*)\Psi\\
&\quad+\boldsymbol{\nabla}\Psi^*\boldsymbol{\nabla}\Psi+\boldsymbol{\nabla}\Psi\boldsymbol{\nabla}\Psi^*+\Psi^*(\boldsymbol{\nabla\nabla}\Psi)]\cdot\mathbf{n}+\boldsymbol{\varepsilon}\cdot\frac{\hbar^2}{4m}\oint dS\,\boldsymbol{\nabla}^2\rho\mathbf{n}=0.\end{aligned}\tag{69}$$

The addition of this expression for the constraint to the right-hand side of Eq. (67) yields

$$\boldsymbol{\varepsilon}\cdot\boldsymbol{\nabla}_{\varepsilon}\mathscr{L}[\Psi_\varepsilon,\Omega]\Big|_{\varepsilon=0}=\boldsymbol{\varepsilon}\cdot\frac{1}{N}\left\{m\int_{\Omega}d\mathbf{r}\,\frac{\partial\mathbf{J}}{\partial t}-\oint dS\,\overleftrightarrow{\sigma}\cdot\mathbf{n}\right\},\tag{70}$$

where

$$\overleftrightarrow{\sigma}(\mathbf{r})=\frac{N\hbar^2}{4m}\int d\boldsymbol{\tau}'\{\boldsymbol{\nabla}(\boldsymbol{\nabla}\Psi^*)\Psi+\Psi^*\boldsymbol{\nabla}(\boldsymbol{\nabla}\Psi)-\boldsymbol{\nabla}\Psi^*\boldsymbol{\nabla}\Psi-\boldsymbol{\nabla}\Psi\boldsymbol{\nabla}\Psi^*\}\tag{71}$$

is a symmetric dyadic, referred to as the stress tensor. Its dot product with **n**(**r**) gives the density of the force exerted on the element of the atomic surface, which is specified by its outwardly directed normal, **n**(**r**). The stress tensor $\overleftrightarrow{\sigma}(\mathbf{r})$, which has the dimensions of an energy density, plays a dominant role in the description of the mechanical properties of an atom. It may be alternatively expressed as a functional of the one-density matrix (Löwdin, 1955) as

$$\overleftrightarrow{\sigma}(\mathbf{r})=(\hbar^2/4m)\{(\boldsymbol{\nabla\nabla}+\boldsymbol{\nabla}'\boldsymbol{\nabla}')-(\boldsymbol{\nabla\nabla}'+\boldsymbol{\nabla}'\boldsymbol{\nabla})\}\Gamma^{(1)}(\mathbf{r},\mathbf{r}')\Big|_{\mathbf{r}=\mathbf{r}'}.\tag{72}$$

Evaluation of the commutator appearing in Eq. (61) demonstrates that this variation of $\mathscr{L}[\Psi,\Omega]$ yields the atomic average of the total force acting on the electron described by **r**:

$$\boldsymbol{\varepsilon}\cdot\tfrac{1}{2}\{\langle(i/\hbar)[\hat{\mathscr{H}},\hat{\mathbf{p}}]\rangle_{\Omega}+\text{c.c.}\}=\boldsymbol{\varepsilon}\cdot\langle-\boldsymbol{\nabla}\hat{V}\rangle_{\Omega}=\boldsymbol{\varepsilon}\cdot(1/N)\mathbf{F}(\Omega,t).\tag{73}$$

Thus, specialized to the present case of an infinitesimal uniform displacement in the electronic coordinates **r**, the variational principle yields the integrated force law

$$\mathbf{F}(\Omega,t)=m\int_{\Omega}d\mathbf{r}(\partial\mathbf{J}(\mathbf{r})/\partial t)-\oint dS(\mathbf{r})\,\overleftrightarrow{\sigma}(\mathbf{r})\cdot n(\mathbf{r}).\tag{74}$$

Equation (74) is the generalization of Ehrenfest's theorem (Ehrenfest, 1927; Löwdin, 1967). It relates the forces acting on the subsystem to the time derivative of the momentum density $m\mathbf{J}$. It constitutes the quantum analog of Newton's equation of motion in classical mechanics expressed in terms of a vector current density and a stress tensor, both defined in real space.

2. *Differential Force Law*

Within a Lagrangian formulation of the mechanics of a field as used here, one may define an energy–momentum tensor whose components summarize the principal properties of the field (Morse and Feshbach, 1953; Landau and Lifshitz, 1975). We show that the divergence equations satisfied by the spatial components of this tensor for the Schrödinger field yield the differential form of the atomic force law, Eq. (74) (Bader, 1980).

Define a component of the energy–momentum tensor as

$$W_{\mu\nu} = \Psi_{\mu}(\partial L/\partial \Psi_{\nu}) + \text{c.c.} - \delta_{\mu\nu} L, \tag{75}$$

where μ and ν run over the $3N$ spatial degrees of freedom and the time, and $\Psi_{\nu} \equiv \partial\Psi/\partial x_{\nu}$. The spatial components $W_{j\nu}$ (j referring only to the $3N$ spatial coordinates) satisfy the following set of divergence equations:

$$\sum_{\nu} \frac{\partial W_{j\nu}}{\partial x_{\nu}} = \frac{\partial L}{\partial x_j}, \tag{76}$$

where $\partial L/\partial x_j$ vanishes unless L possesses an explicit dependence on x_j. In the case of the Lagrangian density defined here, Eq. (8)

$$\partial L/\partial x_j = -\Psi^*(\partial \hat{V}/\partial x_j)\Psi$$

and Eq. (76) yield

$$\begin{aligned} -\Psi^* \nabla_j \hat{V}\Psi = {} & \frac{i\hbar}{2}\frac{\partial}{\partial t}\left[(\nabla_j\Psi^*)\Psi - \Psi^*\nabla_j\Psi\right] - \frac{\hbar^2}{4m}\sum_k \nabla_k \cdot [(\nabla_k\nabla_j\Psi^*)\Psi \\ & + \Psi^*(\nabla_k\nabla_j\Psi) - \nabla_k\Psi^*\nabla_j\Psi - \nabla_k\Psi\nabla_j\Psi^*]. \end{aligned} \tag{77}$$

Equation (77) has been previously obtained by Pauli (1958) and by Epstein (1975), who termed it the differential force law. The integration of this expression over the coordinates of all electrons but one by the usual recipe [see Eq. (2)] yields an equation governing a force density $\mathbf{F}(\mathbf{r}, t)$ (Bader, 1980),

$$\mathbf{F}(\mathbf{r}, t) = m\,\partial \mathbf{J}(\mathbf{r})/\partial t - \nabla \cdot \overleftrightarrow{\sigma}(\mathbf{r}), \tag{78a}$$

where

$$\mathbf{F}(\mathbf{r}, t) = \int d\tau'\, \Psi^*(-\nabla\hat{V})\Psi. \tag{78b}$$

Equation (78a) is the differential form of the integrated atomic force law given in Eq. (74),

$$\mathbf{F}(\Omega, t) = \int_\Omega d\mathbf{r}\ \mathbf{F}(\mathbf{r}, t). \tag{79}$$

The force density $\mathbf{F}(\mathbf{r}, t)$ is seen to be the total instantaneous force exerted on the electron at $\mathbf{r}_i$

$$-\nabla_i \hat{V} = \sum_\alpha Z_\alpha \nabla_i(|\mathbf{r}_i - \mathbf{X}_\alpha|)^{-1} - \sum_{j\neq i} \nabla_i(|\mathbf{r}_i - \mathbf{r}_j|)^{-1}, \tag{80}$$

averaged over the motions of the remaining electrons in the system to yield

$$\mathbf{F}(\mathbf{r}, t) = \left[\sum_\alpha Z_\alpha \nabla(|\mathbf{r} - \mathbf{X}_\alpha|)^{-1}\right]\rho(\mathbf{r}) - 2\int d\mathbf{r}'\ \nabla(|\mathbf{r} - \mathbf{r}'|)^{-1}\ \Gamma^{(2)}(\mathbf{r}, \mathbf{r}') \tag{81}$$

[where $\Gamma^{(2)}(\mathbf{r}, \mathbf{r}')$ is the diagonal element of the two-density matrix (Löwdin, 1955)]. While $\mathbf{F}(\mathbf{r}, t)$ clearly involves two-body forces, it is totally determined by $\mathbf{J}(\mathbf{r})$ and $\overleftrightarrow{\sigma}(\mathbf{r})$, which are functionals of the one-density matrix, $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$ evaluated at the point $\mathbf{r} = \mathbf{r}'$ in real space. The force density $\mathbf{F}(\mathbf{r}, t)$ may be interpreted as the total force exerted on the element of charge density located at $\mathbf{r}$ and obeying an equation of motion in real space, Eq. (78a). This equation is identical in form and physical content to Cauchy's first equation of motion of classical continuum mechanics (Malvern, 1969).

The variational derivation of the integral atomic force law, Eq. (74), is applicable only to a region of space bounded by a zero-flux surface in $\nabla\rho(\mathbf{r})$, i.e., to an open system whose Lagrangian integral vanishes at the point of variation. Thus the variational derivation of the atomic force

$$\boldsymbol{\varepsilon} \cdot \nabla_\varepsilon \mathscr{L}[\Psi, \Omega]\Big|_{\varepsilon=0} = \boldsymbol{\varepsilon} \cdot \mathbf{F}(\Omega, t)/N \tag{82}$$

and its law of motion given in Eq. (74) may be regarded as a quantum mechanical definition of an atom in a molecule.

For a stationary state the corresponding expressions are

$$\boldsymbol{\varepsilon} \cdot \nabla_\varepsilon E[\psi, \Omega]\Big|_{\varepsilon=0} = (\boldsymbol{\varepsilon} \cdot \mathbf{F}(\Omega)/N)\langle\psi, \psi\rangle_\Omega, \tag{83}$$

where

$$\mathbf{F}(\Omega) = -\oint dS(\mathbf{r})\ \overleftrightarrow{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}). \tag{84}$$

In general physical terms, the average force exerted on some enclosed volume is equal to the negative of the integral of the pressure acting on each element of its surface—a statement of the physical content of Eq. (84). This same equation demonstrates that the effect of the environment on an open quantum system Ω is determined by just the flux in the forces across the boundary of Ω (Bader, 1980).

B. Variational Derivation of the Atomic Virial Theorem

1. *Atomic Virial Theorem*

The general time-dependent virial theorem for an atom in a molecule is derived from the atomic variational principle. We shall find a close connection between the expressions so obtained for the virial and those derived in the previous section for the force. In particular, the differential force law leads directly to a corresponding local expression for the virial theorem.

The generator of the infinitesimal unitary transformation, whose atomic projection determines the variation in $\mathscr{L}[\Psi, \Omega]$, is in this case $\hat{\mathscr{F}} = -\varepsilon \mathbf{r} \cdot \hat{\mathbf{p}}$, where ε is an infinitesimal real number. The virial theorem may be obtained by a scaling of the electronic coordinates (Löwdin, 1959), and the action of this generator is equivalent to a scaling of the electronic coordinate $\mathbf{r}$ by the factor $\zeta = 1 + \varepsilon$; i.e.,

$$\Psi_\varepsilon(\mathbf{r}, \boldsymbol{\tau}', t) = (1 + (i/\hbar)\varepsilon \mathbf{r} \cdot \hat{\mathbf{p}})\, \Psi(\mathbf{r}, \boldsymbol{\tau}', t) = \Psi(\zeta \mathbf{r}, \boldsymbol{\tau}', t).$$

The variational principle now states that

$$\frac{\partial}{\partial \varepsilon} \mathscr{L}[\Psi_\varepsilon, \Omega]\bigg|_{\varepsilon=0} = -\frac{1}{2}\left\{\left\langle \left(\frac{i}{\hbar}\right) [\hat{\mathscr{H}}, \hat{\mathbf{r}} \cdot \hat{\mathbf{p}}]\right\rangle_\Omega + \text{c.c.}\right\}. \tag{85}$$

Writing the expression for $\mathscr{L}[\Psi, \Omega]$, Eq. (15), explicitly in terms of ε, differentiating with respect to ε, and noting that

$$(\partial/\partial\varepsilon)\Big|_{\varepsilon \to 0} = \mathbf{r} \cdot \boldsymbol{\nabla},$$

one obtains (with $\delta S = -\varepsilon \mathbf{r} \cdot \mathbf{n}$),

$$\begin{aligned}
\frac{\partial}{\partial \varepsilon} \mathscr{L}[\Psi_\varepsilon, \Omega]\bigg|_{\varepsilon=0} = \int_\Omega d\mathbf{r} \int d\boldsymbol{\tau}' \mathbf{r} \cdot \Bigg[&\frac{i\hbar}{2} (\boldsymbol{\nabla}\Psi^* \dot{\Psi} + \Psi^* \boldsymbol{\nabla}\dot{\Psi} \\
&- (\boldsymbol{\nabla}\dot{\Psi}^*)\Psi - \dot{\Psi}^* \boldsymbol{\nabla}\Psi) \\
&- \frac{\hbar^2}{2m} \sum_i ((\boldsymbol{\nabla}\boldsymbol{\nabla}_i \Psi^*) \cdot \boldsymbol{\nabla}_i \Psi + (\boldsymbol{\nabla}\boldsymbol{\nabla}_i \Psi) \cdot \boldsymbol{\nabla}_i \Psi^*) \\
&- \hat{V}(\boldsymbol{\nabla}\Psi^* \Psi + \Psi^* \boldsymbol{\nabla}\Psi) \Bigg] + \frac{\hbar^2}{4mN} \oint dS\, \boldsymbol{\nabla}^2 \rho \mathbf{r} \cdot \mathbf{n} \\
&+ \int_\Omega d\mathbf{r} \int d\boldsymbol{\tau}' \left(-\frac{\hbar^2}{2m}\right) \boldsymbol{\nabla}\Psi^* \cdot \boldsymbol{\nabla}\Psi.
\end{aligned} \tag{86}$$

Equation (86) can be rearranged using Eqs. (65), (66), Schrödinger's equation, and the identities

$$\begin{aligned}
&\nabla_i \cdot (\nabla_i\Psi^*\nabla\Psi)\cdot\mathbf{r}\\
&\quad = \nabla_i \cdot [(\nabla_i\Psi^*\nabla\Psi)\cdot\mathbf{r}]\\
&\qquad - (\nabla_i\Psi^*\nabla\Psi)\cdot\nabla_i\mathbf{r},\\
&\nabla_i \cdot (\nabla_i\Psi\nabla\Psi^*)\cdot\mathbf{r}\\
&\quad = \nabla_i \cdot [(\nabla_i\Psi\nabla\Psi^*)\cdot\mathbf{r}]\\
&\qquad - (\nabla_i\Psi\nabla\Psi^*)\cdot\nabla_i\mathbf{r},
\end{aligned}$$

to yield

$$\begin{aligned}
&\frac{\partial}{\partial\varepsilon}\mathscr{L}[\Psi_\varepsilon, \Omega]\Big|_{\varepsilon=0}\\
&\quad = -\frac{m}{N}\int_\Omega d\mathbf{r}\left(\mathbf{r}\cdot\frac{\partial\mathbf{J}}{\partial t}\right)\\
&\quad + \frac{\hbar^2}{4mN}\oint dS\,\nabla^2\rho\mathbf{r}\cdot\mathbf{n}\\
&\quad - \frac{\hbar^2}{2m}\oint dS\int d\tau'\,\mathbf{r}\cdot[\nabla\Psi^*\nabla\Psi + \nabla\Psi\nabla\Psi^*]\cdot\mathbf{n}.
\end{aligned}\tag{87}$$

As the atom is to be bounded by a zero-flux surface at all stages of the variation, the variational constraint of Eq. (23b) must be imposed. This constraint in the present case demands that the variation

$$\begin{aligned}
&\frac{\hbar^2}{4m}\frac{\partial}{\partial\varepsilon}\left(\int_\Omega \nabla^2\rho_{\Psi_\varepsilon}d\mathbf{r}\right)\Big|_{\varepsilon=0}\\
&\quad = \frac{\hbar^2}{4m}\left\{\oint dS\int d\tau'\,\mathbf{r}\cdot[\nabla(\nabla\Psi^*)\Psi\right.\\
&\qquad + \Psi^*\nabla(\nabla\Psi) + \nabla\Psi^*\nabla\Psi\\
&\qquad + \nabla\Psi\nabla\Psi^*]\cdot\mathbf{n} + \int_\Omega d\mathbf{r}\,\nabla^2\rho(\mathbf{r})\\
&\qquad \left. - \oint dS\,\nabla^2\rho\mathbf{n}\right\}
\end{aligned}\tag{88}$$

vanishes in the limit of $\varepsilon \to 0$.

To make clear the particular nature of the variational result obtained for the scaling generator when the zero-flux surface constraint is imposed on the variation, we first consider the variation of the functional $\mathscr{L}'[\Psi, \Omega]$, Eq. (25), which will yield a result applicable to any subsystem of some total system. This is achieved by simply adding to Eq. (87) the right-hand side of Eq. (88) to yield

$$\frac{\partial}{\partial \varepsilon} \mathscr{L}'[\Psi_\varepsilon, \Omega]\bigg|_{\varepsilon=0} = \frac{\partial}{\partial \varepsilon}\left\{\mathscr{L}[\Psi_\varepsilon, \Omega] + \frac{\hbar^2}{4m}\int_\Omega d\mathbf{r}\, \nabla^2\rho(\mathbf{r})\right\}$$
$$= -\frac{m}{N}\int_\Omega d\mathbf{r}\, \mathbf{r}\cdot\frac{\partial \mathbf{J}}{\partial t} + \oint dS(\mathbf{r})\mathbf{r}\cdot\overleftrightarrow{\sigma}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})$$
$$+ \frac{\hbar^2}{4m}\int_\Omega d\mathbf{r}\, \nabla^2\rho(\mathbf{r}), \tag{89}$$

where $\overleftrightarrow{\sigma}(\mathbf{r})$ is the stress tensor previously defined in Eq. (71). Evaluating the commutator of the right-hand side of Eq. (85)—a relationship which holds for $\delta\mathscr{L}'[\Psi, \Omega]$ as well—we find

$$\langle (i/\hbar)[\mathscr{H}, \hat{\mathbf{r}}\cdot\hat{\mathbf{p}}]\rangle_\Omega = 2\langle \Psi^*, -(\hbar^2/2m)\nabla^2\Psi\rangle_\Omega + \langle \Psi^*, -\mathbf{r}\cdot\nabla\hat{V}\Psi\rangle_\Omega.$$

Thus the commutator average in Eq. (85) yields

$$N\frac{\partial}{\partial \varepsilon}\mathscr{L}'[\Psi_\varepsilon, \Omega]\bigg|_{\varepsilon=0} = -2T_k(\Omega) - \mathscr{V}_b(\Omega), \tag{90}$$

where $T_k(\Omega)$ is the average kinetic energy of the subsystem defined specifically in terms of the density $K(\mathbf{r})$, Eqs. (20) and (21), and $\mathscr{V}_b(\Omega)$ is the virial of the forces exerted on an electron in the subsystem resulting from its instantaneous interactions with the nuclei and other electrons in the system,

$$\mathscr{V}_b(\Omega) = \int_\Omega d\mathbf{r}\int d\tau'\,\{-\mathbf{r}\cdot\nabla\hat{V}\}\Psi^*\Psi. \tag{91}$$

Equating the results given in Eqs. (89) and (90), one obtains an expression for the virial theorem of an open system with *an arbitrary boundary,*

$$-2T_K(\Omega) = \mathscr{V}_b(\Omega) + \mathscr{V}_s(\Omega) + \mathscr{V}_p(\Omega) + \frac{\hbar^2}{4m}\int_\Omega d\mathbf{r}\, \nabla^2\rho(\mathbf{r}). \tag{92}$$

The term $\mathscr{V}_s(\Omega)$ is the virial of the forces exerted on the surface of the subsystem, a term which is expressible in terms of the stress tensor previously defined in Eq. (71),

$$\mathscr{V}_s(\Omega) = \oint dS(\mathbf{r})\, \mathbf{r}\cdot\overleftrightarrow{\sigma}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) \tag{93}$$

($\overleftrightarrow{\sigma}\cdot\mathbf{n}$ is the outwardly directed force exerted per unit area of surface and $\mathbf{r}\cdot\overleftrightarrow{\sigma}\cdot\mathbf{n}$ is the virial of this force). The term $\mathscr{V}_p(\Omega)$, specific to a time-dependent system, is the virial of the forces arising from the time rate of change of the momentum density $m\mathbf{J}$ throughout the subsystem,

$$\mathscr{V}_p(\Omega) = -m\int_\Omega d\mathbf{r}\, \mathbf{r}\cdot\partial\mathbf{J}/\partial t. \tag{94}$$

While the values of the individual contributions to the virial of the subsystem are dependent upon the choice of origin for the vector $\mathbf{r}$, their sum, which determines the total subsystem virial

$$\mathcal{V}(\Omega) = \mathcal{V}_b(\Omega) + \mathcal{V}_s(\Omega) + \mathcal{V}_{\dot{\mathrm{p}}}(\Omega), \tag{95}$$

is, from Eq. (92), seen to be independent of this choice of origin.

The general result given in Eq. (92) for a subsystem with arbitrary boundaries contains a number of physical incongruities that are removed when the region Ω is constrained to be one bounded by a surface of zero flux in $\nabla\rho(\mathbf{r})$. While the final term on the right-hand side of Eq. (92) has the dimensions of an energy (because of the factor $\hbar^2/m$), it cannot be interpreted as the virial of a force acting on the subsystem, as can the other contributions that are equated to $-2T_k(\Omega)$. This term vanishes for an atom in a molecule because of the zero-flux surface condition. The kinetic energy appearing in Eq. (92) does not uniquely define the average kinetic energy of a subsystem, as it will in general differ from that defined in terms of the density $G(\mathbf{r})$, Eq. (20). Restricting the subsystem to one bounded by a zero-flux surface removes this disparity as the average kinetic energy of an atom is uniquely defined in terms of either density, Eq. (21). The subsystem virial theorem obtained from a variation of the atomic Lagrangian $\mathscr{L}[\Psi, \Omega]$ leads directly to the *atomic* statement of the virial theorem, which is

$$-2T(\Omega) = \mathcal{V}_b(\Omega) + \mathcal{V}_s(\Omega) + \mathcal{V}_{\dot{\mathrm{p}}}(\Omega). \tag{96}$$

The term $\mathcal{V}_b(\Omega)$ in this case becomes a measure of the virial of the forces exerted over the basin of the atom.

For a stationary state the corresponding constrained variation of $E[\Psi, \Omega]$ yields

$$-2T(\Omega) = \mathcal{V}_b(\Omega) + \mathcal{V}_s(\Omega) = \mathcal{V}(\Omega), \tag{97}$$

where again the total virial, $\mathcal{V}(\Omega)$, of the forces acting on the atom—over its basin and across its surface—is independent of the choice of scaling origin.

2. *Local Virial Relationship*

The average of the atomic virial $\mathcal{V}_b(\Omega)$, Eq. (91), as defined by the atomic variational principle, is the virial of the quantum mechanical force density as defined in the differential force law, averaged over the atomic volume (Bader, 1980). By taking the virial of $\mathbf{F}(\mathbf{r}, t)$ in Eq. (78), one obtains

$$\mathbf{r} \cdot \mathbf{F}(\mathbf{r}, t) = m\mathbf{r} \cdot \partial\mathbf{J}/\partial t - \mathbf{r} \cdot \nabla \cdot \overleftrightarrow{\sigma}. \tag{98}$$

Using the identity

$$\nabla \cdot (\mathbf{r} \cdot \overleftrightarrow{\sigma}) = \mathrm{Tr}|\overleftrightarrow{\sigma}| + \mathbf{r} \cdot \nabla \cdot \overleftrightarrow{\sigma},$$

where $\mathrm{Tr}|\overleftrightarrow{\sigma}|$ denotes the trace or spur of the stress tensor, Eq. (98) gives

$$\mathbf{r} \cdot \mathbf{F}(\mathbf{r}, t) = m\mathbf{r} \cdot \partial \mathbf{J}/\partial t + \mathrm{Tr}|\overleftrightarrow{\sigma}| - \nabla \cdot (\mathbf{r} \cdot \overleftrightarrow{\sigma}). \tag{99}$$

From Eq. (71) for the definition of $\overleftrightarrow{\sigma}(\mathbf{r})$ and Eqs. (19) and (20) for the definitions of the kinetic energy densities $K(\mathbf{r})$ and $G(\mathbf{r})$, $\mathrm{Tr}|\overleftrightarrow{\sigma}|$ may be variously expressed as

$$\begin{aligned} \mathrm{Tr}|\overleftrightarrow{\sigma}(\mathbf{r})| &= -K(\mathbf{r}) - G(\mathbf{r}) = -2K(\mathbf{r}) - (\hbar^2/4m)\nabla^2\rho(\mathbf{r}) \\ &= -2G(\mathbf{r}) + (\hbar^2/4m)\nabla^2\rho(\mathbf{r}). \end{aligned} \tag{100}$$

Its integral over an atomic volume yields the unique value

$$\int_\Omega d\mathbf{r}\, \mathrm{Tr}|\overleftrightarrow{\sigma}(\mathbf{r})| = -2T(\Omega). \tag{101}$$

Using the final identity given in Eq. (100), Eq. (99) may be expressed as

$$-2G(\mathbf{r}) = \mathbf{r} \cdot \mathbf{F}(\mathbf{r}, t) + \nabla \cdot (\mathbf{r} \cdot \overleftrightarrow{\sigma}(\mathbf{r})) - m\mathbf{r} \cdot \partial \mathbf{J}(\mathbf{r})/\partial t - (\hbar^2/4m)\nabla^2\rho(\mathbf{r}). \tag{102}$$

Integration of Eq. (102) over an atomic volume yields, term for term, the atomic virial theorem for a time-dependent system, Eq. (96), or for a stationary state, Eq. (97). Thus Eq. (102) is, in terms of its derivation and in terms of its integrated form, a local expression of the virial theorem. The atomic virial theorem provides the basis for the definition of the average energy of an atom as discussed in the following section.

The atomic force law and virial theorem were derived by determining directly the change in $\mathscr{L}[\Psi, \Omega]$ caused by an infinitesimal unitary transformation in the state function. These results may also be obtained by making use of the alternative expression for $\delta\mathscr{L}[\Psi, \Omega]$ [see Eqs. (59) and (51)], which is

$$\delta\mathscr{L}[\Psi, \Omega] = (\varepsilon/N)\left\{dF(\Omega)/dt - \oint dS(\mathbf{r})[(\partial S/\partial t)\rho_F - (\mathbf{J}_F \cdot \mathbf{n} + \mathrm{c.c.})]\right\} \tag{103}$$

and equating this result to the commutator expression for $\delta\mathscr{L}[\Psi, \Omega]$. This amounts to using Heisenberg's expression for the time rate of change of the average value of a subspace property, Eq. (51). One may, in fact, use this expression to determine the force law and virial theorem for an open system with arbitrary or fixed boundaries. This procedure has been adopted by Schweitz (1977), who has obtained an expression of the virial theorem generalized to an an open system with fixed, arbitrary boundaries. While not expressed in terms of the stress tensor $\overleftrightarrow{\sigma}(\mathbf{r})$, his result is the same as that obtained here in Eq. (89) through the variation of the Hamiltonian-based Lagrangian $\mathscr{L}'[\Psi, \Omega]$. The physical incongruities contained in the expression for the virial theorem for an open system with arbitrary boundaries has been commented on earlier, where it was also shown that these incongruities disappear when the open system is constrained to be one bounded by a zero-flux surface. Thus a variational derivation of the force law and virial theorem for an open system that preserves the variational property found for a total system,

$$\delta\mathscr{L}[\Psi, \Omega] = \delta\mathscr{L}'[\Psi, \Omega],$$

requires that the open region be bounded by a surface of zero flux in $\nabla\rho$. This is the property of the single atomic variational principle obtained from the principle of stationary action.

The expression corresponding to Eq. (103) for a stationary state with generator $\hat{\mathscr{F}}$ is (Srebrenik and Bader, 1975)

$$\delta E[\Psi, \Omega] = (\varepsilon/N) \oint dS\, \{\mathbf{J}_F + \text{c.c.}\} \cdot \mathbf{n}/\langle\Psi, \Psi\rangle_\Omega \qquad (104)$$

For a stationary state, the Heisenberg relation for $F(\Omega)$ reduces to

$$\{\langle[\mathscr{H}, \hat{\mathscr{F}}]\rangle_\Omega + \text{c.c.}\} = \hbar \oint dS\, \{i\mathbf{J}_F + \text{c.c.}\}\cdot\mathbf{n} \qquad (105)$$

which has been termed the subsystem hypervirial theorem (Epstein, 1974; Srebrenik and Bader, 1974). From this theorem, one may obtain useful theoretical relationships governing the behavior of atomic properties (Bader, 1980).

C. Summary of Atomic Variational Properties

The principle of stationary action provides a complete quantum mechanical description of a system in terms of the changes induced in the system by infinitesimal unitary transformations. The generators of such transformations describe all possible system changes, caused both by displacements or by a temporal development (Roman, 1965). It has been shown that this principle, which is a variational principle, applies uniquely to a connected region of real space bounded by a surface of zero flux in $\nabla\rho(\mathbf{r})$. Thus the principle of stationary action defines an atom as being a bounded region of space, the variational properties of which, as determined by the action of infinitesimal unitary transformations, are identical to those obtained for the total system. The generators of such transformations describe real physical changes in the system. *Thus a single variational principle serves to describe the properties of a total system and of an atom within the system.*

The operational statement of this principle is the atomic variational principle

$$\delta_{\hat{\mathscr{F}}}\mathscr{L}[\Psi, \Omega] = (\varepsilon/2)\{(i/\hbar)\langle[\hat{\mathscr{H}}, \hat{\mathscr{F}}]\rangle_{\Omega} + \text{c.c.}\}$$

or, for a stationary state,

$$\delta_{\hat{\mathscr{F}}}E[\Psi, \Omega] = -(\varepsilon/2)\{(i/\hbar)\langle[\hat{\mathscr{H}}, \hat{\mathscr{F}}]\rangle_{\Omega} + \text{c.c.}\}/\langle\psi, \psi\rangle_{\Omega}.$$

The generator $\hat{\mathscr{F}}$ causes an infinitesimal transformation in the state function describing the total system. The physical nature of this transformation is identified through the commutator of $\hat{\mathscr{H}}$ with $\hat{\mathscr{F}}$. The atomic value of the change caused by the transformation is given by the projection of the total system value over the atomic volume. Since a generator can be found to describe any change in a system, all atomic properties and the laws governing these properties can be derived from this principle. These derivations of atomic properties parallel the derivations of the corresponding properties for the total system, since both are described by the same variational principle.

For example, $\hat{\mathscr{F}} = \varepsilon\hat{\mathscr{N}} \equiv \varepsilon\hat{1}N$, where N is the total number of electrons in the system, generates a simple infinitesimal phase transformation, which leaves the Lagrangian $\mathscr{L}[\Psi, \Omega]$ invariant. In addition, since N is a constant of the motion for the total system, $[\hat{\mathscr{H}}, \hat{\mathscr{N}}] = 0$. However, the time rate of change of the average electronic population of an atom, $N(\Omega)$, is not zero in general and the equation of continuity governing the time evolution of $N(\Omega)$ is obtained directly from the equivalent statement of the atomic variational principle, Eq. (103), as

$$\frac{d}{dt}\int_{\Omega} d\mathbf{r}\;\rho(\mathbf{r}) = \dot{N}(\Omega) = -\oint dS\left\{(\mathbf{J}\cdot\mathbf{n} + \text{c.c.}) - \frac{\partial S}{\partial t}\rho\right\}. \quad (106)$$

As illustrated in Section III,A,1, setting the generator equal to $\boldsymbol{\varepsilon}\cdot\hat{\mathbf{p}}$ defines the atomic force and the variational principle leads to the integral atomic force law, or the equation of motion for an atom in a molecule. Finally it was shown that when $\hat{\mathscr{F}} = -\varepsilon\mathbf{r}\cdot\hat{\mathbf{p}}$, the commutator identifies the kinetic energy and virial for an atom, and the variational principle yields the relationship between these quantities, the atomic virial theorem. These three relationships—the equation of continuity, the equation of motion, and the virial theorem—form the basis for the understanding of the mechanics of an atom in a molecule.

Within this same formalism one obtains a definition of the energy–momentum tensor for the Schrödinger field. The many-particle divergence equation satisfied by the spatial components of this tensor, when integrated in the standard manner, Eq. (2), yields a differential expression of the atomic force law. The virial of the force density defined in this manner gives a local expression for the atomic virial theorem. Thus from a single formalism one obtains a description of the local mechanical properties of an atom as well as of their average values.

V. Atomic Properties

A. Single-Particle Basis for Atomic Properties

Throughout this article we have assumed a single recipe for the mode of integration over the electronic coordinates in the definition of atomic properties. We wish to show that this choice is not arbitrary, but is determined by the requirement that the definition of an open system as obtained from the principle of stationary action must be stated in terms of a physical property of the system. This requirement imposes a basic single-particle nature on the definition of an atom as expressed in Eq. (6) through a property of the charge density and on the definition of its average properties.

It has been shown that the principle of stationary action applies to a system bounded at infinity and to a system bounded by a surface of zero flux in $\nabla\rho(\mathbf{r})$. One may generalize the problem by asking for the set of all possible subsystems to which this principle is applicable. Thus one must consider the variation of an action integral $W_{12}[\Psi, \{\Omega_i\}]$ defined by a Lagrangian integral of the form

$$\mathscr{L}[\Psi, \{\Omega_i\}] = \int_{\Omega_1} d\mathbf{r}_1 \int_{\Omega_2} d\mathbf{r}_2 \cdots \int_{\Omega_N} d\mathbf{r}_N\, L(\Psi, \nabla\Psi, \dot{\Psi}, t),$$

where $\{\Omega_i\}$ denotes a set of subspaces, the integration of the coordinates of electron i being restricted to a region Ω_i. Carrying through the same variational procedure as that followed in the variation of $W_{12}[\Psi, \Omega]$, one finds (Srebrenik and Bader, 1975) that the condition for the satisfaction of the principle of stationary action is that each subsystem Ω_i must be bounded by a surface S_i satisfying a zero-flux condition of the form

$$\nabla_i\rho_i(\mathbf{r}_i) \cdot \mathbf{n}(\mathbf{r}_i) = 0, \qquad \mathbf{r}_i \in S_i \tag{107}$$

where

$$\rho_i(\mathbf{r}_i) = \int_{\Omega_1} \cdots \int_{\Omega_j} \cdots \int_{\Omega_N} \Big(\prod_{j\neq i} d\mathbf{r}_j\Big)\, \Psi^*\Psi.$$

The quantity $\rho_i(\mathbf{r}_i)$ is the probability density that one electron is at $\mathbf{r}_i$ when each of the remaining electrons is in one of the subsystem volumes Ω_j. Thus $\rho_i(\mathbf{r}_i)$ does not, in general, describe a physically realizable distribution of charge and it requires the diagonal element of the N-particle density matrix for its evaluation. In only one instance does $\rho_i(\mathbf{r}_i)$ assume a physical meaning. This occurs when all the surfaces S_j but one are taken at infinity, in which case ρ_i reduces to $(1/N)\rho$, where ρ is the measurable charge density distribution. The defining condition of the subspaces Ω_i, Eq. (107), then reduces to the zero-flux surface condition on $\nabla\rho$, Eq. (6). Thus out of the complete set of solutions to the problem of determining subsystems that preserve the equivalence of their variational properties with those of the total system, only one solution is physically realizable.

This same mode of integration, which defines the atomic Lagrangian as

$$\mathscr{L}[\Psi, \Omega] = \int_{\Omega} d\mathbf{r}_1 \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N \, L = \int_{\Omega} d\mathbf{r} \int d\boldsymbol{\tau}' L$$

(the integration over spins is always assumed), carries through to the definition of the commutator average in the derived atomic variation principle, which in turn defines the atomic properties. The atomic average of the property F associated with the operator $\hat{\mathscr{F}}$ must satisfy the atomic statement of the Heisenberg relation, Eq. (51). Hence $F(\Omega, t)$ must be given by

$$F(\Omega, t) = \int_{\Omega} d\mathbf{r} \int d\boldsymbol{\tau}' \, \tfrac{1}{2}\{\Psi^* \hat{\mathscr{F}} \Psi + (\hat{\mathscr{F}} \Psi^*)\Psi\} \tag{108}$$

The form of the operator is not yet specified in Eq. (108). When F is a one-electron property then, using the notation of Eq. (108), $\hat{\mathscr{F}}$ must equal $N\hat{\mathscr{F}}(\mathbf{r})$. The atomic average of the property F then becomes

$$F(\Omega, t) = N \int_{\Omega} d\mathbf{r} \int d\boldsymbol{\tau}' \, \tfrac{1}{2}\{\Psi^* \hat{\mathscr{F}}(\mathbf{r}) \Psi + \text{c.c.}\}, \tag{109}$$

i.e., the atomic average of F is simply N times the value obtained for any electron in the system (the electrons are treated in an equivalent manner). Because of this equivalence, the atomic average can be expressed in terms of $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$

$$F(\Omega) = \int_{\Omega} d\mathbf{r} \, \hat{\mathscr{F}}(\mathbf{r}) \Gamma^{(1)}(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'},$$

as can any one-electron property for the total system (Löwdin, 1955). If $\hat{\mathscr{F}}$ is a function of coordinates other than $\mathbf{r}$, then the electrons are not treated in an equivalent manner in taking a subspace average. For example, if $\hat{\mathscr{F}} = \Sigma_i \hat{\mathscr{F}}(\mathbf{r}_i)$, the atomic average is given by the sum of two different terms

$$\frac{1}{N} \int_{\Omega} d\mathbf{r} \, \hat{\mathscr{F}}(\mathbf{r}) \, \Gamma^{(1)}(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'} + \frac{2}{N} \int_{\Omega} d\mathbf{r} \int d\mathbf{r}' \, \hat{\mathscr{F}}(\mathbf{r}') \, \Gamma^{(2)}(\mathbf{r}, \mathbf{r}'),$$

where the first term yields $1/N$ of the average defined in Eq. (109), while the second term, from the $N - 1$ electrons whose coordinates are integrated over all space, yields a contribution expressible only in terms of the second-order density matrix. This term attributes to the subsystem value of a one-electron property, contributions from the operators for the remaining $N - 1$ electrons averaged over the total system.

With the mode of integration fixed and with the generator $\hat{\mathscr{F}}$ set equal to $N\hat{\mathscr{F}}(\mathbf{r})$ to preserve the indistinguishability of the electrons, the average value of any atomic property as determined through the use of the atomic variation principle is defined. Properties, such as the average force, determined directly by the commutator average follow from the same definition. Such a property $F(\Omega)$ is given by

$$F(\Omega) = N \int_\Omega d\mathbf{r} \int d\tau' \, \tfrac{1}{2}\{\Psi^*[\hat{\mathscr{H}}, \hat{\mathscr{F}}'(\mathbf{r})]\Psi + \text{c.c.}\}, \tag{110}$$

where F is the property associated with the operator $\hat{\mathscr{F}}$ as determined by

$$\hat{\mathscr{F}} = (i/\hbar)[\hat{\mathscr{H}}, \hat{\mathscr{F}}'(\mathbf{r})]. \tag{111}$$

The operator $\hat{\mathscr{F}}$ may itself be a or contain two-particle operator(s). However, in such a case because of the presence of $\hat{\mathscr{F}}'(\mathbf{r})$ in the commutator expression for $\hat{\mathscr{F}}$, each such two-particle operator $\hat{g}_{12}$ appearing in $\hat{\mathscr{F}}$ will be a function of the coordinate vectors $\mathbf{r}$ integrated over Ω, and of $\mathbf{r}'$ integrated over all space; i.e., $\hat{g}_{12} = \hat{g}_{12}(\mathbf{r}, \mathbf{r}')$ and a knowledge of $\Gamma^{(2)}(\mathbf{r}, \mathbf{r}')$ is sufficient to determine $F(\Omega)$.

Thus any atomic property F defined through the use of the atomic variation principle is the atomic average of an effective single-particle density $\rho_F(\mathbf{r})$

$$F(\Omega) = \int_\Omega d\mathbf{r} \, \rho_F(\mathbf{r}), \tag{112}$$

where

$$\rho_F(\mathbf{r}) = N \int d\tau' \, \tfrac{1}{2}\{\Psi^* \hat{\mathscr{F}}(\mathbf{r})\Psi + \text{c.c.}\} \tag{113}$$

or

$$\rho_F(\mathbf{r}) = N \int d\tau' \, \tfrac{i}{2}\{\Psi^*[\hat{\mathscr{H}}, \hat{\mathscr{F}}'(\mathbf{r})]\Psi + \text{c.c.}\}. \tag{114}$$

If $[\hat{\mathscr{H}}, \hat{\mathscr{F}}'(\mathbf{r})]$ generates two-electron interactions, then $\rho_F(\mathbf{r})$ is the density of the corresponding property at $\mathbf{r}$ as determined by the average interaction of the electron at $\mathbf{r}$ with the other electrons in the system.

Atomic properties have the necessary property of yielding the value of F for the total system when summed over all the atoms in the system,

$$\bar{F} = \langle \hat{\mathscr{F}} \rangle = \sum_\Omega F(\Omega). \tag{115}$$

This property derives from the spatial definition of an atom and from the definition of an atomic property as a corresponding spatial average of an effective single-particle density distribution.

B. Average Energy of an Atom

1. *Introduction*

The energy is a fundamental property of a system. Hence the definition of the average energy of an atom in a molecule through the application of the atomic variation principle merits a detailed discussion. The principal difficulty in partitioning the total average energy of a system consisting of indistinguishable, interacting particles is associated with the partitioning of the average energy of interaction between its subsystems. Consider the partitioning of some total system into two subsystems A and B. There is some internal energy of A and of B and an energy of interaction between them. How does one partition the energy of interaction into separate contributions for each of the subsystems? Physics provides a unique answer to this question if the forces acting within the system are of the inverse square type.

We first show how the concept of the virial (which is the virtual work for a set of finite displacements) allows for the definition of the *electronic energy* of a total molecular system via an extremum principle. The electronic energy so defined obeys the virial theorem and is expressible as N times the average energy of a single electron in the system. The atomic virial theorem yields a definition of the average electronic energy of an atom with properties identical to those found for the electronic energy of the total system.

2. *Electronic Energy of a Molecule*

We shall confine the discussion to a stationary state with the state function expressed for a rigid nuclear framework within the Born–Oppenheimer approximation. The Hamiltonian for the system is

$$\mathcal{H} = \hat{T} + \hat{V} = \frac{-\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_i \sum_\alpha Z(|\mathbf{r}_i - \mathbf{X}_\alpha|)^{-1} + \sum_{i>j} (|\mathbf{r}_i - \mathbf{r}_j|)^{-1} + \sum_{\alpha>\beta} Z_\alpha Z_\beta (|\mathbf{X}_\alpha - \mathbf{X}_\beta|)^{-1}, \tag{116}$$

yielding an average energy

$$\bar{E} = \langle \psi, \mathcal{H}\psi \rangle.$$

The potential energy may be alternatively expressed in terms of the virials of corresponding forces exerted on the electrons and nuclei as

$$\sum_i (-\mathbf{r}_i \cdot \nabla_i \hat{V}) + \sum_\alpha (-\mathbf{X}_\alpha \cdot \nabla_\alpha \hat{V}) = \hat{V} \tag{117}$$

or as

$$\sum_i (\mathbf{r}_i \cdot \hat{\mathbf{F}}_i) + \sum_\alpha (\mathbf{X}_\alpha \cdot \hat{\mathbf{F}}_\alpha) = \hat{V}. \tag{118}$$

A force operator $\hat{\mathbf{F}}_\kappa$ for particle κ is the classical force exerted on this particle by all the particles in the system. Correspondingly, one may consider the virial of this force, $\mathbf{r}_\kappa \cdot \hat{\mathbf{F}}_\kappa$, to be the potential energy operator for particle κ since, according to Eq. (118), the sum of such operators for all the particles in the system yields the total potential energy operator $\hat{V}$. We shall first demonstrate that such an identification leads to the correct physics for the total system and then show that it forms the basis for the definition of the energy of an atom in a molecule.

The first summation in Eq. (118)—the sum of the potential energy operators for the electrons—should, together with $\hat{T}$, define the electronic Hamiltonian of the system and this in turn, its electronic energy E_e. Thus

$$E_e = \langle \hat{\mathscr{H}}_e \rangle = \langle (\hat{T} + \sum_i \mathbf{r}_i \cdot \hat{\mathbf{F}}_i) \rangle. \tag{119}$$

The average electronic potential energy V_e is thus defined as the average of the virials of the forces exerted on the electrons, the electronic virial,

$$V_e = \mathscr{V} = \left\langle \left(\sum_i \mathbf{r}_i \cdot \hat{\mathbf{F}}_i \right) \right\rangle \tag{120}$$

Correspondingly, the nuclear energy of the system is purely potential in origin and is given by

$$E_n = \left\langle \sum_\alpha \mathbf{X}_\alpha \cdot \hat{\mathbf{F}}_\alpha \right\rangle = -\sum_\alpha \mathbf{X}_\alpha \cdot \nabla_\alpha \bar{E}. \tag{121}$$

This contribution to $\bar{E}$ is trivially determined from a knowledge of just $\rho(\mathbf{r})$. One then has

$$\bar{E} = E_e + E_n, \tag{122}$$

where $\bar{E}$ is the total energy of the molecule for the nuclei clamped in a given configuration $\mathbf{X} = \{\mathbf{X}_\alpha\}$. When a molecule is in an equilibrium configuration, the external forces on the nuclei vanish as does E_n and in this case $E_e = \bar{E}$. The molecule can be in mechanical equilibrium in a given arbitrary configuration $\mathbf{X}$ only if each of the nuclear forces $\langle \hat{\mathbf{F}}_\alpha \rangle$ is balanced by an applied external force. This force, by the Hellmann–Feynman theorem (Feynman, 1939), is given by

$$\langle \hat{\mathbf{F}}_\alpha \rangle = -\nabla_\alpha \bar{E} \tag{123}$$

Now we wish to show that the electronic energy E_e of Eq. (119) may be obtained from an extremum principle subject to the constraints imposed on the system via the external forces that must be applied to the nuclei to maintain the configuration $\mathbf{X}$ (Srebrenik *et al.*, 1978).

The variational problem thus defined is analogous to the extension of Hamilton's principle in classical mechanics to describe a nonconservative system subject to forces of constraint. In this situation the classical action integral is replaced by the variational integral (Goldstein, 1965),

$$I = \int_{t_1}^{t_2} dt \left(T + \sum_i \mathbf{r}_i \cdot \mathbf{F}_i\right), \tag{124}$$

which is to be compared with the expression for E_e in Eq. (119).

The quantity $\sum_i F_i \cdot \delta\mathbf{r}_i$ is the virtual work, the work done by the forces acting on the system during the virtual displacement from the actual to the varied path. A virtual displacement denotes a change in the configuration of the system resulting from arbitrary infinitesimal changes of the coordinates *consistent with the forces and constraints imposed on the system* at each time t. Because of the constraints, the $\delta\mathbf{r}_i$ are not independent variations. The variation of I is possible only when the virtual work is expressed in terms of a generalized set of coordinates $\mathbf{q}_i$ that implicitly contain the constraints imposed on the system, thereby insuring that the $\delta\mathbf{q}_i$ are independent. The modified form of Hamilton's principle obtained by the variation of I then states that the integral of the variation of the kinetic energy plus the virtual work involved in the variation must be zero. The same interpretation may be given to the variation of the corresponding quantum integral, Eq. (119), with the quantum analog of the virtual work defined as

$$\delta\left\langle\psi\middle|\sum_k \mathbf{r}_k \cdot \hat{\mathbf{F}}_k\middle|\psi\right\rangle = \left\langle\delta\psi\middle|\sum_k \mathbf{r}_k \cdot \hat{\mathbf{F}}_k\middle|\psi\right\rangle + \left\langle\psi\middle|\sum_k \mathbf{r}_k \cdot \hat{\mathbf{F}}_k\middle|\delta\psi\right\rangle.$$

The condition of constraint as given for each nucleus in Eq. (123) may be imposed on the variation of the quantum integral in the form

$$\langle(\mathbf{X}_\alpha \cdot \hat{\mathbf{F}}_\alpha + \mathbf{X}_\alpha \cdot \nabla_\alpha \bar{E})\rangle = 0, \qquad \alpha = 1, 2, \ldots, n. \tag{125}$$

These constraints amount to imposing the condition that the virtual work of the forces of constraint $\delta\langle\mathbf{X}_\alpha \cdot \hat{\mathbf{F}}_\alpha\rangle$ must vanish as is true for the classical system.

The variation of the integral in Eq. (119) subject to the set of constraints in Eq. (125) demonstrates (Srebrenik *et al.*, 1978) that the electronic energy E_e is the average energy obtained by extremizing the variation of the *electronic* kinetic energy plus the *virtual work of the electrons*. Having separated out the energy of the (motionless) nuclei from $\bar{E}$, as the virial of the forces of constraint acting on the molecule, the remaining energy E_e should satisfy the virial theorem, since the virial theorem relates the average kinetic energy of a system of moving particles to their virial or, if the forces are conservative, to *their* average potential energy. Thus one finds that E_e of Eq. (119) satisfies

$$E_e = -T \quad \text{and} \quad E_e = \tfrac{1}{2}V_e, \tag{127}$$

where the average electronic potential energy V_e is equal to the virial $\mathcal{V}$ of the electronic forces, Eq. (120). These expressions, along with

$$-2T = \mathcal{V},$$

are satisfied for any nuclear configuration $\mathbf{X}$. This follows since

$$\mathcal{V} = \langle \hat{V} \rangle + \sum_{\alpha} \mathbf{X}_\alpha \cdot \nabla_\alpha \overline{E},$$

and hence

$$-2T = \langle \hat{V} \rangle + \sum_{\alpha} \mathbf{X}_\alpha \cdot \nabla_\alpha E, \tag{128}$$

which is Slater's original statement of the virial theorem for a molecular system (Slater, 1933).

3. *Electronic Energy of an Atom*

The importance of expressing the electronic energy in the form of Eq. (119) is that it enables one to express $\hat{\mathcal{H}}_e$ and hence E_e as sums over single-particle contributions:

$$\hat{\mathcal{H}}_e = \sum_i \hat{\mathcal{H}}_i = \sum_i (-\tfrac{1}{2}\nabla_i^2 - \mathbf{r}_i \cdot \nabla_i \hat{V}) \tag{129}$$

and

$$E_e = N\langle \hat{\mathcal{H}}_i \rangle = N \int d\mathbf{r} \int d\tau' \, \{\psi^*(-\tfrac{1}{2}\nabla_i^2 - \mathbf{r}_i \cdot \nabla_i \hat{V})\psi\}. \tag{130}$$

Thus *the electronic energy is N times the average energy of a single electron, and* E_e may be expressed as an integral over an effective single-particle energy density

$$E_e = \int d\mathbf{r} \, (K(\mathbf{r}) + \mathcal{V}(\mathbf{r})). \tag{131}$$

In Eq. (131), $K(\mathbf{r})$ is the kinetic energy density, Eq. (20), and $\mathcal{V}(\mathbf{r})$ is the virial field:

$$\mathcal{V}(\mathbf{r}) = N \int d\tau' \, \{\psi^*(-\mathbf{r} \cdot \nabla \hat{V})\psi\}, \tag{132}$$

the field which determines the atomic virial $\mathcal{V}_b(\Omega)$, Eq. (91). The virial field $\mathcal{V}(\mathbf{r})$ is N times the potential energy density of one electron at $\mathbf{r}$ as determined by its average energy of interaction with all other particles in the system. $\mathcal{V}(\mathbf{r})$ is an exact prescription of the "average field" experienced by a single electron in a many-particle system.

Thus the electronic energy, since it may be expressed as an integral over effective single-particle kinetic and potential energy densities, may be defined for an atom by restricting the integration in Eq. (131) to the atomic volume Ω,

$$E_e(\Omega) = T(\Omega) + \mathcal{V}_b(\Omega), \tag{133}$$

where $\mathcal{V}_b(\Omega)$ has been previously defined in Eq. (91). If the subsystem energy $E_e(\Omega)$ is to have the same properties as E_e for a total system, i.e.,

$$E_e(\Omega) = -\int_\Omega d\mathbf{r}\, K(\mathbf{r}) = -\int_\Omega d\mathbf{r}\, G(\mathbf{r}) = -T(\Omega) \tag{134}$$

and

$$E_e(\Omega) = \tfrac{1}{2}\mathcal{V}_b(\Omega), \tag{135}$$

then the region Ω must be an atomic volume. Only the atomic virial theorem as derived from the variation of $E[\psi, \Omega]$, Eq. (97), defines an $E_e(\Omega)$ through Eq. (133), which satisfies the virial relationships in Eqs. (134) and (135). Equations (133) and (135) are written for the choice of scaling origin that causes $\mathcal{V}_s(\Omega)$ to vanish. In general for any origin one has

$$E_e(\Omega) = \tfrac{1}{2}\mathcal{V}(\Omega) = T(\Omega) + \mathcal{V}(\Omega) = -T(\Omega). \tag{136}$$

One finds from the virial theorem for a subsystem with the arbitrary boundary of Eq. (92) [in a stationary state ($\mathcal{V}_{\dot{\mathbf{p}}} = 0$)] that

$$E_e(\Omega) = -T_k(\Omega) - \frac{\hbar^2}{4m}\int_\Omega d\mathbf{r}\ \nabla^2\rho(\mathbf{r}) \tag{137}$$

and

$$E_e(\Omega) = \tfrac{1}{2}\mathcal{V}_b(\Omega) + \tfrac{1}{2}\mathcal{V}_s(\Omega) + \frac{\hbar^2}{8m}\int_\Omega d\mathbf{r}\ \nabla^2\rho(\mathbf{r}). \tag{138}$$

For such a subsystem, the average kinetic energy is not uniquely defined and the Lagrangian integral does not vanish as it does for an atom and for the total system. Hence only for an atom does $E_e(\Omega)$ obey the same virial relationships for *any* nuclear configuration X as does E_e for the total system.

In summary, through the concept of the average force exerted on an electron at r—the force density F(r) of the differential form of the equation of motion, Eq. (78a)—one may define a corresponding single-particle potential energy density as the virial of this force—the virial field. The atomic average of the virial field is related to an average kinetic energy through the atomic virial theorem. The kinetic and potential energies so obtained define the electronic energy of the atom, $E_e(\Omega)$. The energy $E_e(\Omega)$ satisfies the same theorems as E_e for the total system since both are defined in terms of the same variational principle with the same generator.

The partitioning of an energy of interaction between two subsystems is thus accomplished through the definition of a single-particle potential energy density as determined by the virial of all the forces exerted on the particle—the virial field $\mathcal{V}(\mathbf{r})$. This field describes the average energy of interaction of the density at r with the *total system*. Its integration over an atomic volume includes the interaction between all elements of charge within the atom and the interaction of each of these elements with the remainder of the system.

The explicit contributions to the potential energy of an atom have been given and discussed elsewhere (Bader, 1975a; Srebrenik and Bader, 1975). We note that the definition of the atom's electronic potential energy in terms of the virial of the forces exerted on it includes a partitioning of the nuclear-nuclear repulsive energies into separate atomic contributions.

C. Transferability of Atomic Properties

The atomic energies $E_e(\Omega)$, $T(\Omega)$, and $\mathcal{V}(\Omega)$ possess a most important property: The extent of constancy of the atom as it is manifested in the real space of various systems is reflected in a corresponding constancy in its contribution to the total energy of a system, the limit of this property being a constant contribution to the total energy when the atom is perfectly transferrable between systems. The observation that regions of space bounded by a surface of zero flux, Eq. (6), satisfied this requirement with respect to an energy defined as in Eq. (133), formed the original basis for the identification of such spatial regions with the chemical atoms of a system (Bader and Beddall, 1972). This observation may now be predicted from theory as a consequence of the properties of the stress tensor $\overleftrightarrow{\sigma}(\mathbf{r})$.

In a stationary state the stress tensor determines the force density $\mathbf{F}(\mathbf{r})$ [see Eq. (78)]:

$$\mathbf{F}(\mathbf{r}) = -\boldsymbol{\nabla}\cdot\overleftrightarrow{\sigma}(\mathbf{r}) \tag{139}$$

and, since the virial field is the virial of this force, it determines $\mathcal{V}(\mathbf{r})$ as well:

$$\mathcal{V}(\mathbf{r}) = \mathbf{r}\cdot\mathbf{F}(\mathbf{r}) = -\mathbf{r}\cdot\boldsymbol{\nabla}\cdot\overleftrightarrow{\sigma}(\mathbf{r}). \tag{140}$$

The integral of $\mathcal{V}(\mathbf{r})$ yields the virial of the forces over the basin of the atom $\mathcal{V}_b(\Omega)$. The local expression for the virial theorem Eq. (99) may be used to obtain a virial density $\mathcal{V}'(\mathbf{r})$ that integrates to the total virial of an atom $\mathcal{V}_b(\Omega) + \mathcal{V}_s(\Omega)$. This is given by

$$\mathcal{V}'(\mathbf{r}) = \mathbf{r}\cdot\mathbf{F}(\mathbf{r}) + \boldsymbol{\nabla}\cdot(\mathbf{r}\cdot\overleftrightarrow{\sigma}(\mathbf{r})) = \mathrm{Tr}|\overleftrightarrow{\sigma}(\mathbf{r})| \tag{141}$$

From the virial theorem for an atom, Eq. (135), or for the total system, Eq. (127), Eq. (141) is seen to yield an expression for the energy density $E_e(\mathbf{r})$ in terms of the trace of the stress tensor:

$$E_e(\mathbf{r}) = \tfrac{1}{2}\,\mathrm{Tr}|\overset{\leftrightarrow}{\sigma}(\mathbf{r})|, \tag{142}$$

and

$$E_e(\Omega) = \tfrac{1}{2}\int_{\Omega} d\mathbf{r}\ \mathrm{Tr}|\overset{\leftrightarrow}{\sigma}(\mathbf{r})| = \int_{\Omega} d\mathbf{r}\ (G(\mathbf{r}) + \mathscr{V}'(\mathbf{r})) \tag{143}$$

where Ω may refer to an atomic volume or to the volume of the total system.[6]

The energy density $E_e(\mathbf{r})$, the virial fields $\mathscr{V}(\mathbf{r})$ or $\mathscr{V}'(\mathbf{r})$, and the force density $\mathbf{F}(\mathbf{r})$ all involve two-electron interactions and require $\Gamma^{(2)}(\mathbf{r}, \mathbf{r}')$ for their direct evaluation. Yet from the above relationships, they may all be expressed in terms of the stress tensor that is a functional of the first-order density matrix, $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$, Eq. (71) (Bader, 1980). The kinetic energy density is determined by the trace of the stress tensor, Eq. (100).

The trace of $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$ determines the charge density at the point $\mathbf{r} = \mathbf{r}'$. If the properties of $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$ in the neighborhood of its diagonal elements $\mathbf{r} = \mathbf{r}'$ are identical over the basin of a given atom in two different molecular systems, then the atom's distribution of charge will be identical in the two systems, as will its spatial distribution of energy, Eq. (142), and its potential and kinetic components, Eqs. (141) and (100). In such a case, the atom will appear identical in the two different systems and will contribute identical amounts to the total energies of both systems.

Much effort is being expended to obtain a theory that equates the energy of a molecular system to a functional of the charge density (Hohenberg and Kohn, 1964; March, 1980) or the one-electron density matrix (Berrondo and Goscinski, 1975; Donnelly and Parr, 1978). A density functional theory *must* possess the properties exhibited by the expression for $E_e(\mathbf{r})$ in Eq. (142): When the distribution $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$ in the neighborhood of $\mathbf{r} = \mathbf{r}'$ and hence $\rho(\mathbf{r})$ are identical over well-defined regions of space in two different systems, these regions must contribute identical amounts to the energies of both systems. This observation, which has been shown to be a quantum mechanical property of a molecular system, is the physical basis and raison d'être for the belief that a density functional theory for the energy can be found.

Thus there is a relation between the virial field and the distribution of charge in a molecular system as was originally proposed on the basis of the observed properties of the topological atoms (Bader and Beddall, 1972). They are related through $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$ by the quantum mechanical stress tensor.

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[6] The remaining contribution to the total energy $\bar{E}$, the nuclear energy E_n (which vanishes when no *net* external forces act on the nuclei), is readily determined *from a knowledge* of $\rho(\mathbf{r})$ alone via the Hellman–Feynman theorem.

Absolute transferability of an atom and its properties between systems is probably never obtained. This is unimportant. The limit of perfect transferability or the approach to this limit serves to establish the principle that an atom and its properties are defined by the distribution of charge in real space, and the extent to which its properties change is directly determined by the extent to which its distribution of charge changes. The present theory *predicts* that an atom as defined here may exhibit a characteristic set of properties that will vary between relatively narrow limits. The average atomic energy $E_e(\Omega)$ is proportional to the sum of the virials of the forces originating within the atom and those exerted on it by the remainder of the molecule, the inner $\mathcal{V}^{i}(\Omega)$ and outer $\mathcal{V}^{o}(\Omega)$ virials,

$$E_e(\Omega) = \tfrac{1}{2}(\mathcal{V}^{i}(\Omega) + \mathcal{V}^{o}(\Omega)). \tag{144}$$

For the atom to be identical in two different systems and possess the same energy and hence the same $\mathcal{V}^{i}(\Omega)$, the outer virial must remain unchanged on transfer of the atom between molecular systems. The individual contributions to $\mathcal{V}^{o}(\Omega)$ do, of course, change on this transfer, but the atom, as a consequence of the atomic virial theorem, behaves in a semiautonomous manner and changes only in response to the virial of the *net* force exerted on it and *not* to changes in the individual contributions. This requirement of a near constancy in the outer virial to yield a near constancy in an atom's properties on transfer is physically realizable and observed (Bader and Beddall, 1972; Bader and Messer, 1974; Bader, 1975b), and hence one observes characteristic properties for atoms.

We illustrate this prediction of the theory for a relatively simple system for which all the contributions to the atomic energies have been determined (Bader *et al.*, 1973b; Bader, 1975b). Figure 4 illustrates the charge distributions of the ground states of BeH and BeH_2. The distributions of charge in the hydrogen atoms in these two molecules are very similar. The average electronic population of H, $N(H)$, is 1.868 in BeH and 1.861 in BeH_2. Correspondingly, the average kinetic energies [and hence their electronic energies $E_e(H)$] differ by only 6 kcal/mole. This degree of constancy in $N(H)$ and $T(H)$ between these two molecules is found in spite of the very large differences in the individual forces acting on the hydrogen atom in the two molecules. For example, the electron-nuclear attractive energy for H changes by ~ -220 kcal/mole and the repulsion of the electrons in H with those in the remainder of the system increases by ~ 120 kcal/mole between BeH and BeH_2. However, the *sum* of all the virials of the external forces exerted on the hydrogen atom in BeH and BeH_2 changes by only 3 kcal/mole. Thus when the total external virial field acting on an atom changes by only a small amount, the changes in the atom are correspondingly small.

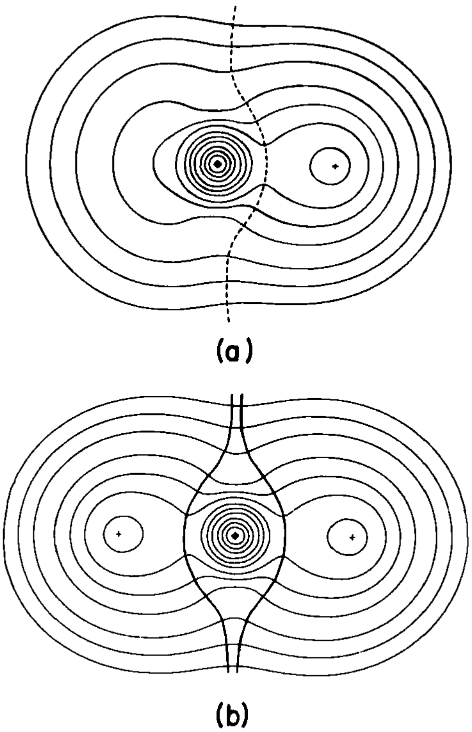


Fig. 4. Contour maps of the electronic charge distributions for the ground states of BeH (a) and BeH_2 (b) showing the positions of the interatomic surfaces. Note the great similarity in the distribution of charge in the hydrogen atoms in the two systems. (a) $N(\mathrm{H}) = 1.868e$, $E(\mathrm{H}) = -0.7717$ a.u.; (b) $N(\mathrm{H}) = 1.861e$, $E(\mathrm{H}) = -0.7623$ a.u. $\mathcal{V}^{\circ}(\mathrm{H}) \sim 3$ kcal/mole. (For computational details see Bader *et al.*, 1973b.)

D. Quantum Topology

1. *Topological Analysis*

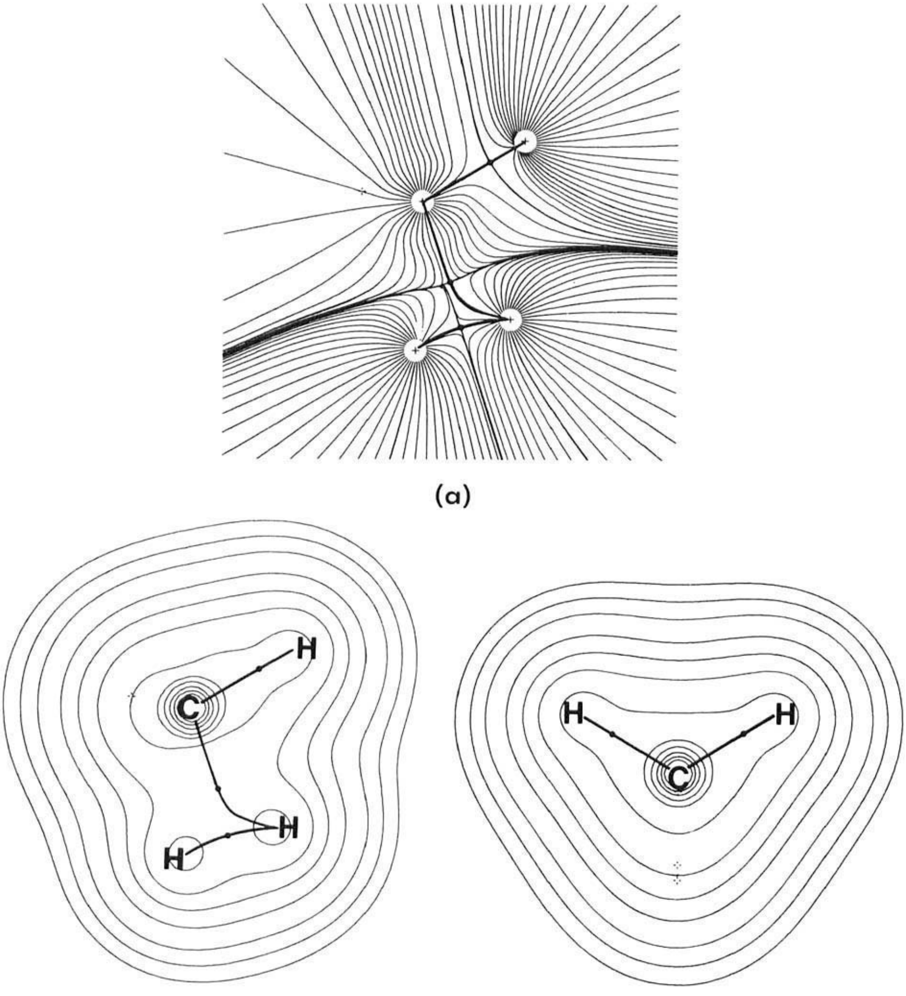
Starting with a knowledge of a system's charge distribution, quantum topology enables one to assign to the system a unique molecular structure as determined by the topological properties of this charge density. This is exemplified in Fig. 5 for the CH_5^+ molecular-ion to which classical models of bonding do not apply. From the further knowledge of the dependence of the charge density on the nuclear coordinates, the persistence of this structure and the mechanism of its change into neighboring structures may be determined.

A bond between two neighboring atoms and their interatomic surface are defined and characterized by the properties of a $(3, -1)$ critical point in the charge density. With a chemical bond defined, its properties may be studied and parametrized in terms of the properties of the charge density. The value of the charge density at the (3, − 1) or bond critical point, $\rho(\mathbf{r}_c)$, allows one to relate the concept of bond order, defined originally in terms of the products of coefficients of the molecular orbitals for just the "π electrons" of a system (Coulson, 1939), to a property of the total charge density. Thus for example, a plot of the values of $\rho(\mathbf{r}_c)$ for the carbon–carbon bonds in ethane, benzene, ethylene, and acetylene versus their equilibrium bond lengths shows these quantities to be linearly related. The eigenvalues of the Hessian matrix of $\rho(\mathbf{r}_c)$ and the eigenvalues of $\overleftrightarrow{\sigma}(\mathbf{r}_c)$ mirror other bond properties, such as the extent of charge transfer ("ionic-covalent" character), the behavior of the kinetic energy changes involved in the formation of the bond, and the degree of "double bond" character as related to the height of a corresponding rotational barrier. It has been shown (Bader, 1980) that the properties of a critical point in the gradient vector field of $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$ in the neighborhood of $\mathbf{r} = \mathbf{r}'$ [as opposed to a critical point in just its diagonal elements, $\rho(\mathbf{r})$] are determined by its block diagonal Hessian matrix formed from the elements of $\nabla\nabla\rho$ and $\overleftrightarrow{\sigma}$. Thus the field of the quantum mechanical stress tensor that determines both the force exerted on and the energy of an element of charge density, also plays a role in the theory that relates structure and structural stability in a chemical system to the topological properties of $\rho(\mathbf{r})$.

A change in structure necessitates the passage of the system point in nuclear configuration space through a catastrophe point (Bader *et al.*, 1979b, 1980). If the change in structure involves the making or breaking of a chemical bond, then the corresponding bond critical point is transformed into a singularity in the charge density, i.e., a critical point whose Hessian has one or more zero roots. Having defined the bond and the breaking of a bond, one may now inquire into the nature of the forces that are responsible for one or more of the second derivatives of the charge density vanishing at a critical point, and thereby obtain an understanding of the mechanics of bond breaking and bond formation.

While the relationships between $\rho(\mathbf{r}_c)$ and the properties of bonds discussed above are of a correlative or empirical nature, they do relate an observable property of a system to the mechanics that govern it. Therefore, such relationships are ultimately capable of theoretical expression and prediction as predicated by an increase of our understanding of the mechanics governing the distribution of charge in a molecular system.

Deb and co-workers (Deb and Bamzai, 1978, 1979; Deb and Ghosh, 1979) have also recently introduced the concept of a stress tensor into chemistry to obtain a further understanding of the forces acting within a molecular system.


(a)

(b)

(c)

Fig. 5. (a) Representation of the gradient vector field $\nabla\rho(\mathbf{r}, \mathbf{X})$ for a plane of the CH_5^+ molecular-ion (T.-H. Tang, unpublished work, 1980). (b) Contour map of the charge density for the same plane as (a) showing the molecular structure as determined by the field $\nabla\rho$. (c) Contour map and structure for the plane containing the two remaining H atoms. The projected positions of these two protons onto the plane of a and b are indicated by crosses. The molecular graph for this particular nuclear configuration X, in the close neighborhood of the minimum energy geometry X_m, denotes a structure in which three hydrogens are bonded to carbon in a normal manner, while the remaining two are bonded to one another (to yield a stretched H_2 fragment) and bonded to carbon through one of them. This particular configuration lies close to a conflict catastrophe point (Bader *et al.*, 1979b, 1980), and since the energy hypersurface is relatively flat in the neighborhood of X_m with respect to internal motions of the H_2 fragment (Lathan *et al.*, 1970; Dyczmons *et al.*, 1970), the bond from carbon switches from one proton of H_2 to the other during the course of its internal motions.

2. *Quantum Analysis*

The topological analysis of the charge density defines the atoms as well as the structure of a molecular system (see, for example, Figs. 1 and 5), and quantum mechanics defines the average atomic properties. The theory makes possible the interpretation of chemical observations in terms of a set of atomic properties that are governed by the same quantum mechanical laws as those that govern the properties of the total system.

While the hypervirial theorem is of somewhat limited use for a total system ($\langle[\hat{\mathscr{H}}, \hat{\mathscr{F}}]\rangle = 0$ for every $\hat{\mathscr{F}}$), the atomic statement of this theorem, Eq. (105), can be used to obtain useful relationships between atomic properties (Bader, 1980). Any empirically discovered relationship between atomic properties, obtained, for example, through a study of a series of molecules, is ultimately capable of theoretical expression, since all properties are defined by quantum mechanics.

The simplest atomic property and the one with the longest history of attempts to define it, is the average electronic population. Table II lists the atomic populations [in the form of a net atomic charge $\mathscr{C}(\Omega) = Z_\Omega - N(\Omega)$] for a series of substituted acetylenes ACCH, A = H, Li, F, Cl, CN (Messer, 1977). These populations exemplify the proposal based on chemical observations: The effect of a substituent may be transmitted to an atom removed from the site of substitution if there is an intervening region of easily polarizable charge density. Replacement of H by Li results in a charge transfer to CCH of nearly one electronic charge. However, the C_β atom has a larger net negative charge than does C_α, to which the Li is bonded. Substitution of F for H results in a transfer of charge from CCH to F of ~0.8 e, but the largest net positive charge is found for C_β, rather than C_α. The substitution of Cl results in a much smaller charge transfer than does substitution of F, but the charge distribution in the C—C internuclear region still undergoes considerable rearrangement, with C_β again

TABLE II

ATOMIC NET CHARGES[a] IN ACCH

A	$\mathscr{C}(A)$	$\mathscr{C}(C_\alpha)$	$\mathscr{C}(C_\beta)$	$\mathscr{C}(H)$
H	+0.142	−0.142	−0.142	+0.142
Li	+0.927	−0.122	−0.898	+0.093
F	−0.765	+0.167	+0.441	+0.156
Cl	−0.091	−0.247	+0.200	+0.140
CN	−0.100	−0.018	−0.037	+0.156

[a] Calculated from wave functions obtained by McLean and Yoshimine (1968).

exhibiting the largest net positive charge. As anticipated on chemical grounds, and as distinct from a hydrogen bonded to a saturated carbon (Bader *et al.*, 1980), the acetylenic hydrogen possesses a net positive charge, a reflection of its acidic nature. Figure 6 shows contour plots of the charge distributions for these molecules and the positions of the interatomic surfaces. The redistribution of charge with substitution as indicated by the data in Table II is reflected in the behavior of the atomic surfaces. Note in particular the shift in the C_α—C_β interatomic surface toward C_α when a more electropositive element such as Li is substituted

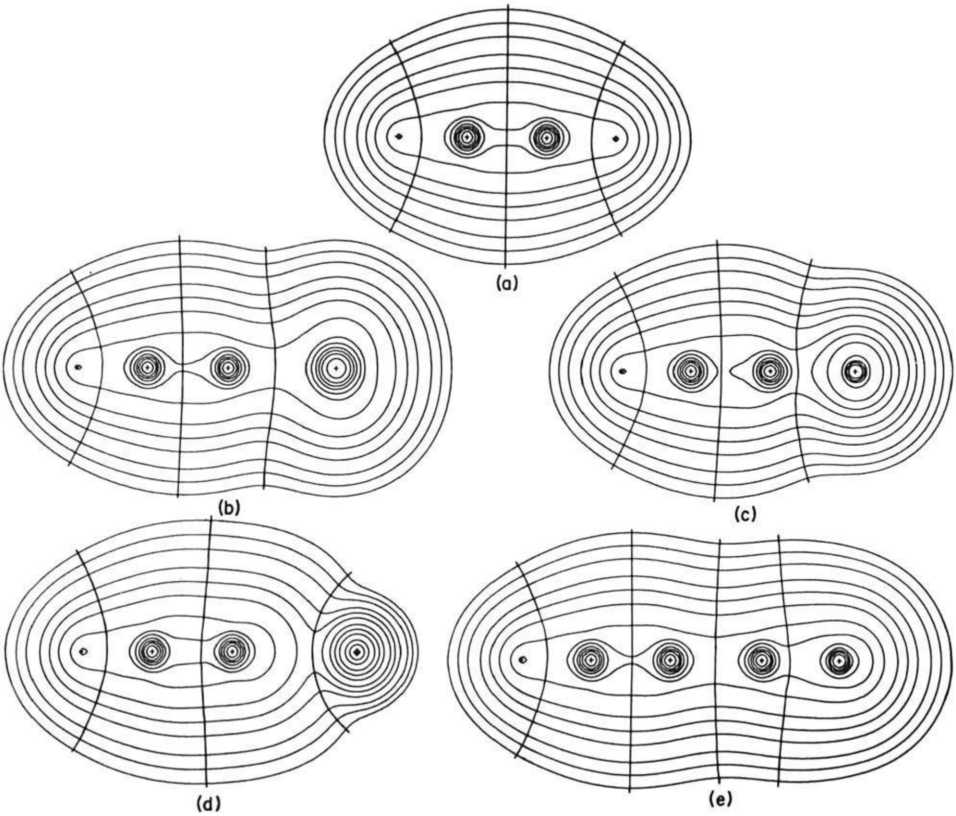


Fig. 6. Contour plots of the ground-state molecular charge distributions of acetylene and its monosubstituted derivatives $AC_\alpha C_\beta H$. (a) A = H, (b) A = Cl, (c) A = F, (d) A = Li, (e) A = CN. Note the displacement of the C_α–C_β interatomic surface in response to the effect of substitution on the charge distribution of the CCH group. Note that the identical effect is observed for the C–C interatomic surface in $FHC{=}CH_2$ (Fig. 1). Substitution of F for H in $CH_2{=}CH_2$ causes the C=C interatomic surface (which is coincident with a symmetry plane in $CH_2{=}CH_2$) to be displaced towards the unsubstituted carbon nucleus.

for H, and towards C_β when a more electronegative element such as F is substituted for H.

A knowledge of the net charges and multipole moments for atoms in common bonded situations can be used to rationalize the chemical reactivities of molecules in terms of their charge distributions. The dipolar and quadrupolar polarizations as well as the net charge are characteristic for a given atom in a given bonded situation. These polarizations impart to an atomic charge distribution its directional properties, properties that are frequently invoked and rationalized in terms of models such as the directed "lone pair" model.

Through the definition of an atom's average energy, one may isolate those *spatial* regions of a reacting system in which potential energy is at first accumulated and then later released, either to drive the same reaction to completion or to initiate a subsequent one (Bader, 1975a). This ability to spatially identify the "energy-rich" atoms of a molecular system can be used to understand in a detailed way the mechanics of an enzyme–substrate interaction and to quantify the concept of "high-energy bonds" and the role they are assigned in biochemical reactions. Related concepts such as steric acceleration could also be tested in a quantitative manner.

Quantitative expression can often be found for qualitative concepts that have proved useful in the past. An example is the extent of localization of electrons to given regions of space. The spatial localization of some average number of indistinguishable particles to a region of space is a property of the pair density (Bader and Stephens, 1975). For a system of electrons, the extent of localization is determined by the extent to which the Fermi correlation is similarly localized, and this in turn is calculable from the fluctuation in the average electronic population $N(\Omega)$ of the region.[7] As anticipated on chemical grounds, ionic distributions are found to be strongly localized in both pair space and real space. The charge distributions of the lithium atom as exemplified in Fig. 2 are ~95% localized, and its average population of approximately two in these molecules is very nearly the result of a perfect pairing of an α and a β electron. The bound fluorine atom is generally characterized not only by a net negative charge in excess of $0.7\,e$, but also by a high degree of spatial localization of its charge density. The charge transferred to fluorine is not only tightly bound, it is also strongly paired within the atom. Thus in the absence of charge transfer, bonds to fluorine are relatively weak (as, for example, in F_2) because of the absence of interatomic pairing of the electrons. In

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[7] An electron has a doppelgänger, its Fermi hole, which goes wherever the electron goes. Conversely, the electron may go only to regions of space in which its Fermi hole is nonvanishing. If the Fermi hole is localized to a given region of space, so is the electron.

contrast, the charge distributions of nitrogen and carbon atoms, particularly in multiply bonded systems, are considerably delocalized, an observation again in accord with chemical expectations.

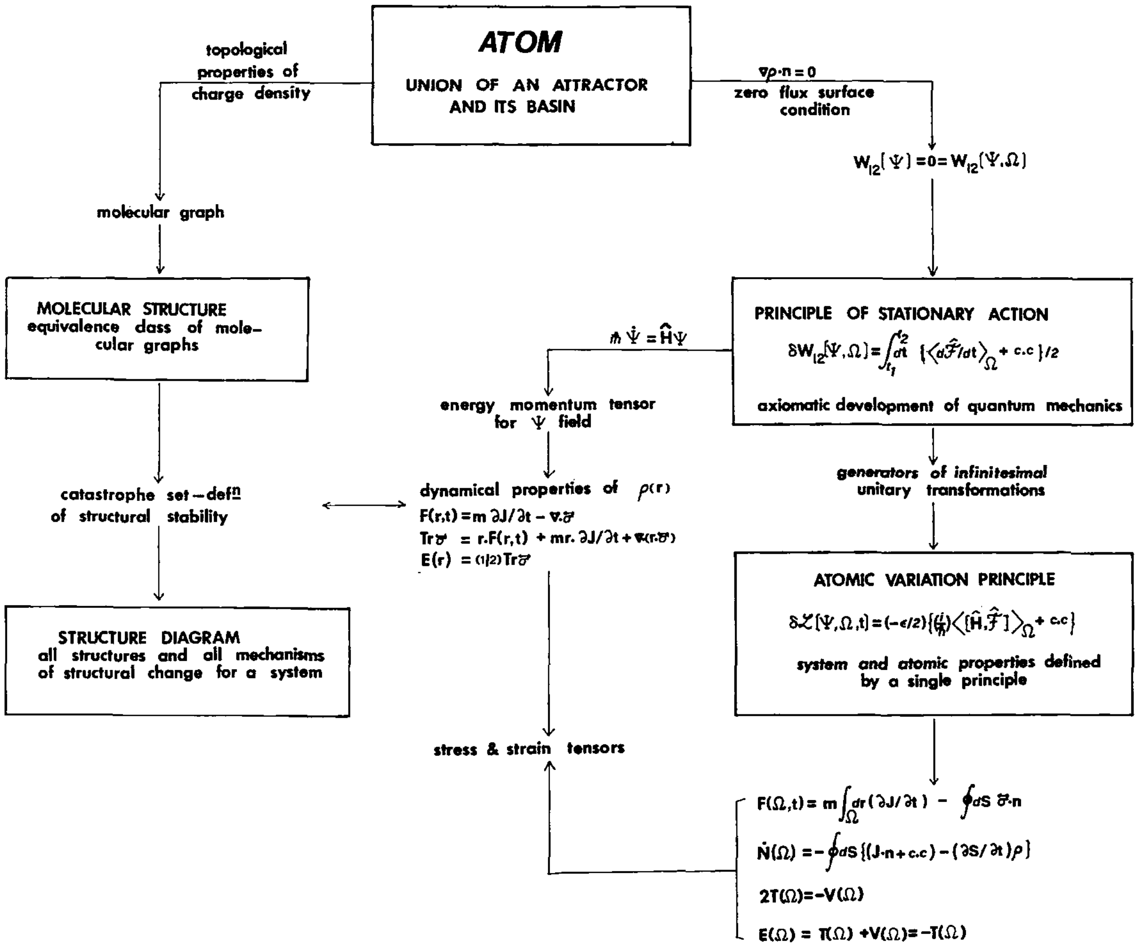
The underlying assumption of quantum topology is that chemical properties of a system are faithfully mirrored in the properties of its charge distribution. If true, the above examples serve to show the possibility of obtaining a theory of chemistry based upon the mechanical properties of the charge distribution.

VI. Discussion

This account of the theory of quantum topology has been mostly concerned with definitions. The theory as it stands makes conceptual predictions: Atoms, atomic properties, bonds, structure, and structural stability are all consequences of the properties of the distribution of charge in real space. Through the statements of the differential force law and virial theorem and the equation of continuity, we have reached the threshold of understanding the mechanics that governs the distribution of charge (see Fig. 7 for a summary of the theory). However, the answers to specific chemical questions must await the accumulation of data on the properties of atoms in a variety of systems and the further development of the theory. These two avenues of approach are not unrelated.

A new program for the determination of atomic properties, by the integration of the corresponding property densities over the atomic volume, has been developed in this laboratory. This program avoids the direct (and often difficult) determination of an atomic surface by implementing the definition of an atom as the union of an attractor and its basin. By integrating along the trajectories of $\nabla\rho(\mathbf{r})$ that terminate at a given nucleus, one must necessarily cover the basin of an atom. In addition, because of the zero-flux surface condition, it is impossible to cross an interatomic surface into the basin of a neighboring atom.

This description of the new integration program is by way of introducing a coordinate transformation with important theoretical consequences. This coordinate transformation maps the Cartesian coordinates (x, y, z) of a point $\mathbf{r}$ in an atomic basin into a triple (s, θ, ϕ). The parameter s, Eq. (3), determines the position of the point $\mathbf{r}$ along the gradient path that is defined by some initial set of angular coordinates, θ and ϕ. This local coordinate system resembles the spherical coordinate system with the radial coordinate r replaced by the path parameter s, and the rays replaced by the generally curved gradient paths that traverse the basin of a given atom. Since the limits of s are $\pm\infty$, the mapping sends the bounded space


ATOM
UNION OF AN ATTRACTOR AND ITS BASIN
topological properties of charge density
molecular graph
MOLECULAR STRUCTURE
equivalence class of molecular graphs
catastrophe set – defn of structural stability
STRUCTURE DIAGRAM
all structures and all mechanisms of structural change for a system
$\nabla\rho\cdot n = 0$
zero flux surface condition
$W_{12}[\Psi] = 0 = W_{12}[\Psi, \Omega]$
PRINCIPLE OF STATIONARY ACTION
$\delta W_{12}[\Psi,\Omega] = \int_{t_1}^{t_2} dt \; \{\langle d\hat{\mathcal{F}}/dt\rangle_\Omega + c.c\}/2$
axiomatic development of quantum mechanics
$i\hbar\dot{\Psi} = \hat{H}\Psi$
energy momentum tensor for Ψ field
dynamical properties of $\rho(r)$
$F(r,t) = m\,\partial J/\partial t - \nabla.\overleftrightarrow{\sigma}$
$Tr\overleftrightarrow{\sigma} = r.F(r,t) + mr.\partial J/\partial t + \nabla(r.\overleftrightarrow{\sigma})$
$E(r) = (1/2)Tr\overleftrightarrow{\sigma}$
stress & strain tensors
generators of infinitesimal unitary transformations
ATOMIC VARIATION PRINCIPLE
$\delta\mathcal{L}[\Psi,\Omega,t] = (-\epsilon/2)\{(\frac{i}{\hbar})\langle[\hat{H},\hat{\mathcal{F}}]\rangle_\Omega + c.c\}$
system and atomic properties defined by a single principle
$F(\Omega,t) = m\int_\Omega dr(\partial J/\partial t) - \oint dS\;\overleftrightarrow{\sigma}\cdot n$
$\dot{N}(\Omega) = -\oint dS\{(J\cdot n + c.c) - (\partial S/\partial t)\rho\}$
$2T(\Omega) = -V(\Omega)$
$E(\Omega) = T(\Omega) + V(\Omega) = -T(\Omega)$

of each atom into a complete space homeomorphic to R^3. The transformation assigns a complete space to each atom in the system. The collection of atomic basins and the associated coordinate transformations yield an atlas for the molecule.

One is led, by this coordinate transformation, to the definition of a strain tensor. The strains described by this tensor are those produced by the continuous deformation of the original radially directed gradient paths of a free atom's basin into the curved paths characteristic of a bound atom (see Figs. 1 and 5). The bending of the gradient paths upon chemical combination is a result of the persistence of the zero-flux atomic surface at all stages of the reaction.

Attention has been drawn to the fact that the differential statement of the equation of motion for the charge density as determined by quantum mechanics

$$\mathbf{F}(\mathbf{r}, t) = m\, \partial \mathbf{J}(\mathbf{r})/\partial t - \nabla \cdot \overleftrightarrow{\sigma}(\mathbf{r}) \tag{78a}$$

is identical in form and physical content with the corresponding Newtonian law, which is the equation of motion for the material density of a continuous medium, e.g., fluids or solids. The further element that the quantum and classical theories of densities have in common is the concept of a strain tensor. A given stress generates a given strain in a material. Hence classical continuum mechanics has models and theorems relating the stress to a given strain. Hooke's model of a stress–strain relationship is a simple example.

One sees the possibility of developing similar models and eventually perhaps, a quantum theory to relate the strain induced in an atom as a result of chemical change to the corresponding change in the quantum stress $\Delta\overleftrightarrow{\sigma}$. Since the strain operative in an atom is determined entirely by the charge distribution, one would obtain an expression for the corresponding *change* in the atom's energy $\Delta E_e(\Omega)$ solely from a knowledge of the change in the charge distribution; i.e., having determined $\Delta\overleftrightarrow{\sigma}$ as a function of the strain, one could determine the change in the electronic energy of the system through Eq. (143) as

$$\Delta E_e = \sum_{\Omega} \Delta E_e(\Omega) = \tfrac{1}{2} \sum_{\Omega} \int_{\Omega} d\mathbf{r}\ \mathrm{Tr}|\Delta\overleftrightarrow{\sigma}(\mathbf{r})|.$$

Fig. 7. A diagrammatic summary of the theory of quantum topology. The diagram illustrates that the definitions of molecular structure and of the quantum mechanical properties of an atom are both consequences of a single assumption: that of identifying the chemical atom with the union of an attractor and its basin as determined by the topological properties of the charge density.

The goal of quantum topology is to provide a predictive theory of chemistry based on the mechanics of the charge density. This goal is no more unattainable than is the goal of classical continuum mechanics, which is to predict the properties of materials through a classical description of the motion of material density. Indeed, based on the universality of the force law, Eq. (78a), both the classical and quantum theories are attempting identical descriptions. The force density $\mathbf{F}(\mathbf{r}, t)$ in either the quantum or classical theory is an exceedingly complex quantity, because it is the resultant of all the forces exerted on an element of density at a given point in space. If $\mathbf{F}(\mathbf{r}, t)$ were to be evaluated from first principles for a quantum system, it would demand knowledge of the state function. However, after the integration over the coordinates of all the particles but one to obtain $\mathbf{F}(\mathbf{r}, t)$, Eq. (78b), one has in a very real sense discarded all the unnecessary information contained in $\Psi^*\Psi$, and the resulting *physical* force is determined by the greatly reduced amount of information contained in $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$ as required to determine $\mathbf{J}(\mathbf{r})$ and $\overset{\leftrightarrow}{\sigma}(\mathbf{r})$ in Eq. (78a).[8]

The underlying philosophy of quantum topology is to obtain a theory of chemistry that employs only the information essential for the understanding of the properties of a chemical system—the information contained in the charge density.

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One of us (R. F. W. Bader) wishes to express his gratitude to the Swedish Research Council for the award of a grant allowing him to visit the Institute for Quantum Chemistry, University of Uppsala, for a six-month period ending December, 1979. He wishes to express his thanks for the warm hospitality and encouragement shown to him by Professor Löwdin and other members of the Institute. Work on the quantum mechanical stress tensor was initiated during the course of this visit.

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[8] Not even all of the information contained in $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$ is required. A Taylor series expansion of $\Gamma^{(1)}$ expressed in terms of $\mathbf{R} = \frac{1}{2}(\mathbf{r} + \mathbf{r}')$ and $\mathbf{P} = \frac{1}{2}(\mathbf{r} - \mathbf{r}')$ about the point $(\mathbf{R}, \mathbf{P} = 0)$ shows that $\mathbf{J}(\mathbf{R})$ and $\overset{\leftrightarrow}{\sigma}(\mathbf{R})$ are determined, respectively, by just the first- and second-order terms in this expansion (Bader, 1980).

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Group Theoretical Techniques and the Many-Electron Problem

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I. Introduction

The application of group theoretical methods to problems in many-electron systems has been known for the past few decades. In view of the availability of large computer systems, interest in such applications has increased substantially in recent years. In this article we would like to discuss some of the recent developments in this field which have led to efficient programs for implementing large-scale studies of atomic and molecular structure. Though group theory forms the basis for the entire discussion, the emphasis here is on techniques rather than abstract formalism.

The procedures outlined in the following sections deal with the problem of diagonalizing the spin-free, nonrelativistic N-electron Hamiltonian operator,

$$H = \sum_{i=1} f(i) + \sum_{i<j} g(i, j), \tag{1}$$

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where

$$f(i) = -\tfrac{1}{2}\nabla_i^2 + V(i) \tag{2}$$

$$g(i, j) = 1/r_{ij}, \tag{3}$$

where the right-hand side of Eq. (2) represents the sum of the kinetic and potential energies of the ith electron, and that of Eq. (3) the Coulomb interaction between the ith and the jth electrons. The fact that the right-hand side of Eq. (1) does not contain any spin-dependent operators implies that the solutions of the corresponding Schrödinger equation are also eigenfunctions of the spin operators S^2 and S_z. In addition, the wave functions so obtained have also to satisfy the Pauli antisymmetry requirement since we are dealing with an N fermion system. Using an effective independent particle approximation, we can realize the N-electron wave functions satisfying the above requirements as linear combinations of Slater determinants of N-spin–orbitals $\{\chi_i | i = 1, 2, \ldots, 2n\}$, which form an orthonormal set spanning a linear vector space V_{2n}. The N-electron determinantal wave functions are the basis spanning the alternating representation occuring in the reduction of the primitive tensor space $V_{2n}\otimes^N$ of these spin orbitals. A further reduction of this alternating representation to yield basis states of S^2 and S_z follows readily if we note that each spin orbital can be expressed as a product of orbital (ϕ_i) and spin (θ_i) parts. This leads to the result that each element of $V_{2n}\otimes^N$ can be expressed as a product of Nth rank tensors of orbital and spin parts. Thus we need only consider the subspace $(V_n\otimes^N) \otimes (V_2\otimes^N)$ of the primitive configuration space $V_{2n}\otimes^N$. The procedure for generating spin-adapted determinantal wave functions is now evident. We first reduce the spin space $V_2\otimes^N$ to obtain the eigenfunctions of the operators S^2 and S_z and multiply these by elements of $V_n\otimes^N$ and antisymmetrize the whole product (cf. Pauncz, 1967; McWeeny and Sutcliffe, 1969).

One of the most direct methods for generating spin eigenfunctions is due to Löwdin (1964). In this procedure a projection operator is applied to a spin monomial of Nth rank corresponding to the eigenvalue M of S_z. This operator annihilates all spin contributions other than the desired one and leads to a proper spin eigenfunction. This procedure applied to suitably chosen linearly independent set of spin monomials yields, in turn, a set of linearly independent spin eigenfunctions. Orthonormalization of the resulting set leads to a basis $\{\Theta^N_{S,M;k} | k = 1, \ldots, f^N_S\}$ (Löwdin, 1958; Pauncz, 1967, 1979) spanning the given spin state. Another frequently used method for generating this set of spin eigenfunctions is the geneological one suggested by Kotani *et al.* (1955). In this method we presuppose a knowledge of the complete orthonormal set of spin functions for an $N - 1$

electron system in the spin states $S \pm \frac{1}{2}$ and use vector-coupling methods to generate the required functions for the N-electron system. Whatever the method used, the spin functions $\Theta^{N}_{S,M;k}$ are linear combinations of elements of $V_2 \otimes^{N}$ having $\frac{1}{2}N + M$ spins $\alpha(m_s = +\frac{1}{2})$ and $\frac{1}{2}N - M$ spins $\beta(m_s = -\frac{1}{2})$. As an illustration of the form of these functions, we list the states $S_1 = \frac{1}{2}$, $M = \frac{1}{2}$ of a three-electron system:

$$\Theta^{3}_{1/2,1/2:1} = (1/\sqrt{6})(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha),$$

$$\Theta^{3}_{1/2,1/2:2} = (1/\sqrt{2})(\alpha\beta\alpha - \beta\alpha\alpha).$$

We now consider the elements spanning $V_n \otimes^{N}$, which are realized using an ordered orthonormal set of single-particle orbitals $\{\phi_i | i = 1, 2, \ldots, n\}$ as

$$V_n \otimes^{N}: \quad \{(N_1 N_2 \cdots N_n) \equiv \phi_1^{N_1} \phi_2^{N_2} \cdots \phi_n^{N_n}\}, \tag{4}$$

where $N_1, N_2, \ldots, N_n$ are nonnegative orbital-occupancy indices satisfying

$$\sum_i N_i = N. \tag{5}$$

Equations (4) and (5) define a primitive tensor basis applicable to any N-particle system. If, however, we consider the antisymmetric product of the elements of Eq. (4) and the elements of $V_2 \otimes^{N}$, we find that the result is zero unless the occupancy indices of Eq. (5) satisfy

$$2 \geq N_i \geq 0 \qquad \text{for all} \quad i = 1, 2, \ldots, n. \tag{6}$$

Thus, we can define the possible N-electron wave functions for the Hamiltonian of Eq. (1) as

$$\psi^{N}_{S,M;k}(N_1 N_2 \cdots N_n) = \mathscr{A}(N_1 N_2 \cdots N_n)\Theta^{N}_{S,M;k}, \tag{7}$$

where

$$\mathscr{A} = (1/\sqrt{N!}) \sum_{P \in S_N} \delta_p P \tag{8}$$

is the Hermitian N-electron antisymmetizer (Pauncz, 1967). The multiconfiguration wave function for the system is a linear combination of wave functions of the type given on the right-hand side of Eq. (7). The coefficients defining the linear combination are obtained by setting up the Hamiltonian over the basis defined by Eq. (7) and diagonalizing it.

The expansion of $\Theta^{N}_{S,M;k}$ as a linear combination of spin monomials permits the right-hand side of Eq. (7) to be expressed as a linear combination of Slater determinants so that the interconfigurational matrix elements can be determined using simple rules (Slater, 1929, 1931). A computer program is available for generating the configuration interaction (CI) matrix using this approach (cf. ALCHEMY developed at IBM Research Center, San Jose, California, by P. S. Bagus *et al.*). The main drawback of this determinantal approach is that it slows down as the number of monomials defining each $\Theta^N_{S,M;k}$ increases (cf. Rettrup, 1977, 1978). It is in this context that the spin-free approach due to Matsen (1964) becomes an extremely powerful tool for CI studies. This method, which is essentially group theoretic in nature, will be the subject of discussion in the following sections. Among some of the other workers who have investigated this field are Gallup and Norbeck (1976), Gerratt (1971), Paldus (1974, 1975), Wormer and Van der Avoird (1972), and Sarma and Rettrup (1977).

II. Spin-Free CI Studies and the Permutation Group

Spin-free studies of many electron systems are based on the result that the spin functions $\Theta^N_{S,M;k}$ ($k = 1, \ldots, f^N_S$) transform as real orthogonal basis spanning the irreducible representation (irrep) $[\frac{1}{2}N + S, \frac{1}{2}N - S]$ under the action of elements P^σ of the permutation group S_N on the spin coordinates of the electrons (Pauncz, 1967). It can in fact be shown (McIntosh, 1960; Murty and Sarma, 1975) that the Young orthogonal basis is, apart from a phase factor, the same as the set of orthonormalized Löwdin (1956) spin projections.

If P^σ is any permutation of the spin coordinates, we have thus

$$P^\sigma \Theta^N_{S,M;k} = \sum_{m=1}^{f^N_S} [P]^{\tilde{\lambda}}_{mk} \Theta^N_{S,M;m}, \tag{9}$$

where $[\tilde{\lambda}] = [\frac{1}{2}N + S, \frac{1}{2}N - S]$, and $[P]^{\tilde{\lambda}}_{mk}$ are elements of the real orthogonal Young's representation matrix. We also observe that the separability of orbital and spin spaces permits every permutation of electrons to be expressed as a product of orbital and spin-coordinate permutations as,

$$P = P^r P^\sigma. \tag{10}$$

Using the right-hand sides of Eqs. (9) and (10) on the right-hand side of Eq. (7), with the definition of the antisymmetrizer as on the right-hand side of Eq. (8), we obtain

$$\begin{aligned}\psi^N_{S,M;k}&(N_1N_2\cdots N_n)\\ &= (N!)^{-1/2}\sum_{P\in S_N}\sum_{m=1}^{f^N_S}\delta_p[P]^{\tilde{\lambda}}_{mk}[P^r(N_1\cdots N_n)]\Theta^N_{S,M;m}\\ &= (f^N_S)^{-1/2}\sum_{m=1}^{f^N_S}[e^{[\lambda]}_{mk}(N_1\cdots N_n)]\Theta^N_{S,M;m},\end{aligned} \tag{11}$$

where (Kaplan, 1974),

$$e^{[\lambda]}_{mk} = (f^N_S/N!)^{1/2}\sum_{p\in S_N}[P]^{\lambda}_{mk}P^r \tag{12}$$

is the Wigner operator for the irrep,

$$[\lambda] \equiv [2^{N/2-S},\ 1^{2S}], \tag{13}$$

conjugate to $[\tilde{\lambda}]$ and

$$[P]^{\lambda}_{mk} = \delta_p[P]^{\tilde{\lambda}}_{mk}. \tag{14}$$

Expressing both sides of Eq. (11) as

$$\begin{aligned}|(N_1N_2&\cdots N_n);\ S,\ M;k\rangle^N\\ &= (f^N_S)^{-1/2}\sum_{m=1}^{f^N_S}|(N_1N_2\cdots N_n);\ mk\rangle^N\Theta^N_{S,M;m},\end{aligned} \tag{15}$$

we obtain a compact expression for the required spin-projected N-electron wave function.

For the Hamiltonian of Eq. (1), these wave functions yield the matrix elements

$$\begin{aligned}\langle(N_1'N_2'&\cdots N_n');S',M',k'|H|(N_1N_2\cdots N_n);\ S,\ M,\ k\rangle\\ &= (f^N_S)^{-1}\sum_m\langle(N_1'N_2'\cdots N_n');mk'|H|(N_1N_2\cdots N_n);mk\rangle^{\lambda}\\ &\quad\times\ \delta_{S'S}\,\delta_{M'M}\\ &= \langle(N_1'N_2'\cdots N_n');mk'|H|(N_1N_2\cdots N_n);mk\rangle\\ &\quad\times\ \delta_{S'S}\,\delta_{M'M}.\end{aligned} \tag{16}$$

Using the fact that the operators $e^{[\lambda]}_{mk}$ defined by Eq. (12) satisfy (Kaplan, 1974),

$$e^{[\lambda]}_{rs}e^{[\lambda']}_{tu} = (N!/f^N_S)^{1/2}e^{[\lambda]}_{ru}\,\delta_{\lambda\lambda'}\,\delta_{st}, \tag{17}$$

$$(e^{[\lambda]}_{rs})^+ = e^{[\lambda]}_{sr}, \tag{18}$$

and commute with the Hamiltonian, we obtain the result

$$\begin{aligned}
&\langle (N_1'N_2' \cdots N_n');\, S,\, M,\, k'|H|(N_1N_2 \cdots N_n);\, S,\, M,\, k\rangle \\
&\quad = (f_S^N/N!)^{1/2} \\
&\quad\quad \times \langle (N_1'N_2' \cdots N_n')|H|e_{k'k}^{[\lambda]}(N_1N_2 \cdots N_n)\rangle \\
&\quad = \sum_{p\in S_N} \langle (N_1'N_2' \cdots N_n')|H|P^r(N_1N_2 \cdots N_n)\rangle [P]_{k'k}^{\lambda}.
\end{aligned} \tag{19}$$

The above result shows that the Hamiltonian matrix elements are independent of the index m of $e_{mk}^{[\lambda]}$. This in turn, implies that the set of functions forming a basis for a given row of the irrep $[\lambda] \equiv [2^{N/2-S}, 1^{2S}]$ of S_N, which form an orthonormal and complete set, may be used for generating the CI matrix.

The form given in Eq. (19) was successfully used by Gallup and Norbeck (1976) and Karwowski (1973a,b, 1981) to define the class of nonzero matrix elements of a spin-free Hamiltonian if the defining orbitals formed an orthonormal set. A major drawback in this method is the difficulty in defining explicitly the matching permutations needed for the nonzero elements.

A possible alternative to the permutation group approach outlined in this section is to realize that a complete orthonormal set of the orbital tensor basis, $\{|(N_1N_2 \cdots N_n);\, mk\rangle^{\lambda}\}$, with a fixed index m defines also a basis for the irrep, $\langle\lambda\rangle \equiv \langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle$ of the unitary group $U(n)$. Such a duality between unitary and permutation groups (cf. Robinson, 1961, and Wybourne, 1970, for details) has been successfully exploited in studies of atomic and molecular structure by Wormer and Van der Avoird (1972), Sarma and Rettrup (1977), Paldus and Wormer (1979), and Harter and Patterson (1976a,b) among others. In a recent note Sarma and Sahasrabudhe (1980) were able to realize a tensor basis of this form for the general irreps,

$$\begin{gathered}
\langle\lambda\rangle = \langle\lambda_1, \lambda_2, \cdots, \lambda_n\rangle, \qquad \lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n \geq 0, \\
\lambda_1 + \lambda_2 + \cdots + \lambda_n = N,
\end{gathered} \tag{20}$$

of $U(n)$. It was shown by these authors that the matrix elements of the generators of $U(n)$ obtained using such a basis were identical with the corresponding ones due to Gel'fand and Zetlin (1950). Some of these unitary group approaches and their application to many-electron systems will be discussed next.

III. Unitary Group Approaches and Many-Electron Systems

A. General Introduction

Use of unitary group methods in CI studies of many-electron systems is based on the fact that for spin-free Hamiltonians, the orbital and spin-tensor spaces are separable. Since the spin–orbitals defined for the system span the fundamental representation space V_{2n} of the unitary group $U(2n)$, the separability of the spin and orbital components leads us to consider the representation space $V_n \otimes V_2$ of the subgroup $U(n) \otimes U(2) \subseteq U(2n)$. This fact and the duality between the unitary and permutation group enables us to use the arguments of the previous section to conclude that we need to generate only the product representations $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle \otimes \langle N/2 + S, N/2 - S\rangle$ of $U(n) \otimes U(2)$ subduced from the totally antisymmetric irrep $\langle 1^N\rangle$ of $U(2n)$. Weyl (1946) was the first to attempt a detailed study of the problem of such subgroup-adapted (subduced) basis for the alternating representation of $U(2n)$. Using a generalized version of the standard Young tableaux of S_N, he was able to obtain the basis spanning the irreps $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle$, $\langle N/2 + S, N/2 - S\rangle$ of $U(n)$, $U(2)$, respectively. Computational schemes based on the Weyl tableaux approach have been recently developed by Harter and Patterson (1976a,b) and used in the studies of atomic structure.

Systematic methods for generating basis states spanning finite dimensional irreducible representations of $U(n)$ were first developed by Gel'fand and Zetlin (1950). These authors were able to generate a canonical basis subgroup adapted to the chain $U(n) \supseteq U(n-1) \supseteq \cdots \supseteq U(2) \supseteq U(1)$, using the eigenvalues of the Casimir operators of the group to label the states. Extensive studies of the many-body problem were undertaken using the Gel'fand–Zetlin (GZ) basis by Moshinsky and co-workers (1968), Baird and Biedenharn (1963), Ciftan and Biedenharn (1969), and Ciftan (1969). As a first step in our review, we consider the procedures useful in generating the Gel'fand–Zetlin tableaux (GZT) for $U(n)$.

The GZT is characterized by a triangular array,

$$|m\rangle \equiv \left| \begin{array}{ccccccc} m_{1n} & & m_{2n} & & \cdots & & m_{nn} \\ & m_{1n-1} & & m_{2n-1} & \cdots & m_{n-1n-1} & \\ & & & & \vdots & & \\ & & & m_{12} & & m_{22} & \\ & & & & m_{11} & & \end{array} \right\rangle, \tag{21}$$

where nonnegative integers m_{ij} $(i = 1, 2, \ldots, j)$ in the jth row specify the partitions defining an irrep of $U(j) \subseteq U(n)$. The branching rules for the canonical basis defining the irreps of $U(n)$ imply that the m_{ij} satisfy the triangular conditions,

$$m_{ij} \geq m_{ij-1} \geq m_{i+1j}. \tag{22}$$

All possible choices of the $n(n+1)/2$ nonnegative integers subject to the triangular inequality (22) yield the possible GZT spanning the irrep

$$\langle m \rangle = \langle m_{1n}, m_{2n}, \ldots, m_{nn} \rangle \tag{23}$$

of $U(n)$. (The maximal GZT is defined as the one with $m_{ij} = m_{in}$ for all $i = 1, 2, \ldots$, for each j.) A complete lexically ordered set of GZT can be readily generated starting with the maximal one and decreasing the m_{ij} by unity starting with the lowest row subject to Eq. (22) being satisfied. As an illustration consider the eight GZT spanning the irrep $\langle 2,1,0 \rangle$ of $U(3)$, which may be obtained using the above procedure as,

$$\begin{matrix} 2\;1\;0 \\ 2\;1 \\ 2 \end{matrix} \qquad \begin{matrix} 2\;1\;0 \\ 2\;1 \\ 1 \end{matrix} \qquad \begin{matrix} 2\;1\;0 \\ 2\;0 \\ 2 \end{matrix} \qquad \begin{matrix} 2\;1\;0 \\ 2\;0 \\ 1 \end{matrix}$$

$$\begin{matrix} 2\;1\;0 \\ 2\;0 \\ 0 \end{matrix} \qquad \begin{matrix} 2\;1\;0 \\ 1\;1 \\ 1 \end{matrix} \qquad \begin{matrix} 2\;1\;0 \\ 1\;0 \\ 1 \end{matrix} \qquad \begin{matrix} 2\;1\;0 \\ 1\;0 \\ 0 \end{matrix}$$

The correspondence of the GZT with an orbital description of the tensor basis follows if we identify the orbital occupancy index as,

$$N_j = \sum_{i=1}^{j} m_{ij} - \sum_{i=1}^{j-1} m_{ij-1}. \tag{24}$$

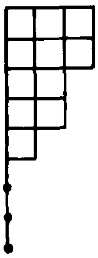
These GZT provide a simple labeling scheme for the basis spanning the irreps $\langle \lambda \rangle$ of $U(n)$. The entries in each of the n rows of the tableaux characterize a subgroup $U(j)$ of $U(n)$ embedded entirely in the given irrep of the group. This ensures the canonical nature of the basis, which is generated using GZT if the branching rules of $U(n)$ are used in the process. There are, however, some drawbacks in using this tableaux basis. First, $n(n+1)/2$ entries are needed in the proper sequence to identify each GZT. This problem becomes acute for the electronic GZT, which span the irrep $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S} \rangle$ of $U(n)$. This irrep can only admit the m_{ij} satisfying $2 \geq m_{ij} \geq 0$ ($i = 1, 2, \ldots, j$; $j = 1, 2, \ldots, n$) so that just the integers 2, 1, 0 repeatedly occurring in the rows have to be stored in an ordered manner. Second, the dimensionalities of the irreps of $U(n)$ can be quite large so that the utilization of the whole irreducible space may not be feasible in many applications. The subspace to be used is generally decided by the possible orbital occupancy set $(N_1 N_2 \cdots N_n) \in V_n \otimes^N$ most applicable to the physics of the situation. To generate the GZT spanning a small subspace of this type to the exclusion of the rest of the irreducible space is generally not an easy task.

In view of the above limitations it would be useful to examine the alternatives to the GZT scheme for labeling the states of the irrep $\langle\lambda\rangle$ of $U(n)$. One of these is to use the standard Weyl tableaux (Hamermesh, 1962) spanning the irreps of $U(n)$. These tableaux follow on using the nontrivial partitions $\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_p > 0$ $(p \leq n)$ to define the corresponding Young shape for $[\lambda] = [\lambda_1, \lambda_2, \ldots, \lambda_p]$, $\sum_{i=1}^{p} \lambda_i = N$ of S_N, and assigning the orbital indices $1, 2, \ldots, n$ to the boxes in all possible ways so that they define a nondecreasing sequence along each row and an increasing sequence along each column. The standard Weyl tableaux (SWT) so generated have a unique correspondence with the corresponding GZT. In order to facilitate easy visualization of this correspondence it is convenient to add a set of nodes to the extreme left column of the Young shape to indicate the trivial partitions $\lambda_{p+1} = \lambda_{p+2} = \cdots = \lambda_n = 0$ of $\langle\lambda\rangle$. As an illustration, consider the correspondence,

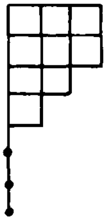
$$\begin{array}{ccccccccccc}
3 & & 2 & & 1 & & 1 & & 0 & & 0 \\
& 3 & & 2 & & 1 & & 1 & & 0 & \\
& & 3 & & 1 & & 1 & & 0 & & \\
& & & 2 & & 1 & & 1 & & & \\
& & & & 1 & & 1 & & & & \\
& & & & & 1 & & & & &
\end{array}
\quad \Leftrightarrow \quad
\begin{array}{lll}
1 & 3 & 4 \\
2 & 5 & \\
3 & & \\
5 & & \\
\cdot & & \\
\cdot & &
\end{array}$$

between the GZT and the SWT for the irrep $\langle 3,2,1,1,0,0\rangle$ of $U(6)$. One of the interesting features of the SWT is that each one displays explicitly the orbital occupancies $(N_1 N_2 \cdots N_n)$ of the orbitals. This should permit one to generate the subset of tableaux corresponding to a given $(N_1 N_2 \cdots N_n) \in V_n \otimes^N$ readily. Such a set is useful when one is interested in carrying out a limited CI calculation with, say, all singly excited configurations, or with all singly and doubly excited ones, and so on. We now outline briefly the procedure for generating the above subset of SWT.

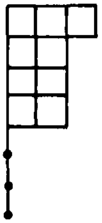
Since identical indices cannot share a column in the SWT, we find that the regular removal of N_n boxes from the Young shape defining an irrep $\langle\lambda\rangle \equiv \langle\lambda_1, \lambda_2, \ldots, \lambda_n\rangle$ of $U(n)$ so that no two of the boxes share a column, results in the Young shapes for $\langle\lambda'\rangle \equiv \langle\lambda'_1, \lambda'_2, \ldots, \lambda'_{n-1}\rangle$ of $U(n-1)$ embedded in the irrep $\langle\lambda\rangle$. If the resulting Young shapes of $U(n-1)$ contain less than $n-1$ rows, we add a corresponding number of nodes in the extreme left column to make up the total number of rows to $n-1$. As an illustration, consider the irrep $\langle 3,3,2,2,1,0,0,0\rangle$ of $U(8)$, which has the Young shape:



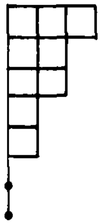
Let us assume that $N_8 = 2$ so that we have to determine the possible Young shapes resulting from the deletion of two boxes which do not share a column from the above shape. We readily find that the following are the only possible irreps of $U(7)$ embedded in $\langle 3,3,2,2,1,0,0,0\rangle$ of $U(8)$:



(a)



(b)



(c)

The corresponding top two rows of the GZT follow as:

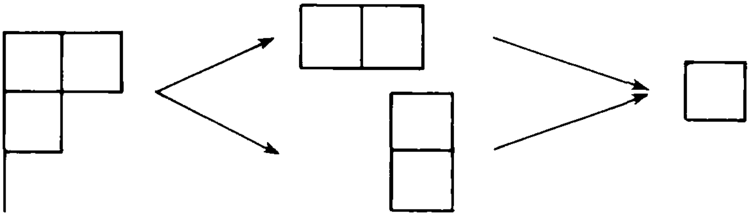
3 3 2 2 1 0 0 0
3 3 2 1 0 0 0
(a)

3 3 2 2 1 0 0 0
3 2 2 2 0 0 0
(b)

3 3 2 2 1 0 0 0
3 2 2 1 1 0 0
(c)

The location of the orbital index 8 in the SWT is fixed by the deleted boxes and we can proceed in the same manner starting with the irreps of $U(7)$ and deduce all the SWT having specified orbital occupancies. The procedure for obtaining the SWT is thus evident. We remove successively N_n, $N_{n-1}, \ldots, N_1$ boxes and obtain a branching diagram. If at any stage an $N_i = 0$, we just delete a node. Keeping track of the locations of the deleted boxes, we obtain the possible SWT having a specified orbital occupancy set. This procedure is repeated for the other occupancies.

As an illustration of the procedure consider the irrep $\langle 2,1,0\rangle$ of $U(3)$ and the SWT corresponding to $N_1 = N_2 = N_3 = 1$. Using the procedure outlined above, we obtain the branching diagram,



leading to the two SWT and hence the corresponding GZT,

$$\begin{array}{l} 1\;2 \\ 3 \end{array} \;\Leftrightarrow\; \begin{array}{c} 2\;1\;0 \\ 2\;0 \\ 1 \end{array} \qquad \begin{array}{l} 1\;3 \\ 2 \end{array} \;\Leftrightarrow\; \begin{array}{c} 2\;1\;0 \\ 1\;1 \\ 1 \end{array}$$

Although the above procedure for generating the SWT is relatively simple, it involves the use of Young shapes and is difficult to implement as a computer program. To get over this difficulty Rettrup and Sarma (1980) proposed an algebraic equivalent of the above SWT procedure. We now consider this procedure briefly.

Consider the irrep $\langle\lambda\rangle \equiv \langle\lambda_1, \lambda_2, \dots, \lambda_n\rangle$ in which $\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n \geq 0$, in which λ_1 occurs $p^n_{\lambda_1}$ times, where the superscript on p is used to indicate explicitly that we are dealing with the group $U(n)$. Let $p^n_{\lambda_1-1}$, $p^n_{\lambda_1-2}, \dots, p^n_0$ be the frequencies of occurrence of the integers $\lambda_1 - 1$, $\lambda_1 - 2, \dots, 0$, respectively in $\langle\lambda\rangle$. The collection $p^n_{\lambda_1}, p^n_{\lambda_1-1}, \dots, p^n_0$ can be used to characterize any irrep $\langle\lambda\rangle$ of $U(n)$. Thus, the irrep $\langle 3,3,2,2,1,0,0,0\rangle$ of $U(8)$ may be characterized as $[p^8_3 = 2, p^8_2 = 2, p^8_1 = 1, p^8_0 = 3]$. For $N_8 = 2$, the deletion of two boxes not sharing a column in the Young shape for this irrep, led to the irreps (a), (b), (c) of $U(7)$ listed earlier for this example. In the present notation these irreps are characterized as

$$\text{(a)} = [2, 1, 1, 3]; \qquad \text{(b)} = [1, 3, 0, 3]; \qquad \text{(c)} = [1, 2, 2, 2],$$

where the frequencies correspond to $[p^7_3, p^7_2, p^7_1, p^7_0]$. Thus, given an irrep of $U(n)$ characterized as $p^n_f, p^n_{f-1}, \dots, p^n_0]$, where $f \equiv \lambda_1$ is the maximal entry in the defining partition for $\langle\lambda\rangle$ and a value of N_n, we can characterize the irreps of $U(n-1)$ embedded in it using the set $[p^{n-1}_f, p^{n-1}_{f-1}, \dots, p^{n-1}_0]$. Such a characterization is applicable to any orbital index $1 \leq i \leq n$. This leads to a unique correspondence between every SWT and the corresponding $(f + 1) \times n$ matrix tableau $[p^n]$, which can be expressed as:

$$\mathrm{SWT} \Leftrightarrow \begin{bmatrix} p^n_f & p^n_{f-1} & \cdots & p^n_1 & p^n_0 \\ p^{n-1}_f & p^{n-1}_{f-1} & \cdots & p^{n-1}_1 & p^{n-1}_0 \\ & & \vdots & & \\ p^1_f & p^1_{f-1} & \cdots & p^1_1 & p^1_0 \end{bmatrix} \tag{25}$$

Though the formulation is now in an algebraic form, the procedure for determining the rows of the p^n tableau is not quite straight forward. Given a $[p^j_f p^j_{f-1} \cdots p^j_0]$ and an N_j, the determination of possible $(j - 1)$th rows $[p^{j-1}_f p^{j-1}_{f-1} \cdots p^{j-1}_0]$ involve successive determinations of this latter set for the occupancies $0, 1, \ldots, N_j - 1$ before generating the required set for the given occupancy (Sarma and Rettrup, 1980; cf. also Paldus, 1972, for electronic SWT with $\lambda_1 \leq 2$). In view of this, an alternative tableaux scheme was considered by Rettrup and Sarma (1980) which led to a relatively simple algorithm. In order to generate these tableaux, consider the partial sums of the entries in the p^n tableaux defined as,

$$M^j_i = \sum_{k=f}^{i} p^j_k; \qquad i = f, f-1, \ldots, 0; \quad j = 1, 2, \ldots, n, \tag{26}$$

since the total number of rows of any irrep of $U(j)$ is j, we obtain the result,

$$M^j_0 = \sum_{k=0}^{f} p^j_k = j, \tag{27}$$

using Eq. (26). Since the right-hand side of Eq. (27) is just the row index in a possible M^n array, we observe that we need only the set $[M^j_f M^j_{f-1} \cdots M^j_1]$ $(j = 1, 2, \ldots, n)$ of ordered (increasing as read from left to right) nonnegative integers which have a unique correspondence with the p^n array, and hence with the corresponding SWT and GZT. It can be shown that given such a set for the jth row and an N_j, the possible $(j - 1)$th rows follow on selecting N_j entries at a time and subtracting unity from each so that the result again defines a nondecreasing sequence of nonnegative integers as read from left to right. Each of the possible choices defines a set $[M^{j-1}_f M^{j-1}_{f-1} \cdots M^{j-1}_1]$.

As an illustration of the above procedure, consider again the irrep $\langle 3,3,2,2,1,0,0,0 \rangle$ of $U(8)$ having $N_8 = 2$ considered earlier. We observe readily that the top row of the M^8 array is characterized by the entries $[M^8_3 = 2,\ M^8_2 = 4,\ M^8_1 = 5]$. There are three possibilities of subtracting unity from two of them taken at a time so that the result is a nondecreasing sequence of nonnegative integers. The possible seventh-row entries $[M_3^7$ $M_2^7 M_1^7]$ are

$$[2\quad 3\quad 4]; \qquad [1\quad 4\quad 4]; \qquad [1\quad 3\quad 5],$$

which correspond to entries in the second row from top of the GZTs,

$$\langle 3,3,2,1,0,0,0\rangle; \qquad \langle 3,2,2,2,0,0,0\rangle; \qquad \langle 3,2,2,1,1,0,0\rangle,$$

respectively. This result is in agreement with the corresponding one obtained earlier using the SWT scheme. Henceforth we will designate the present scheme as the M tableau (MT) scheme.

In this section we have summarized the various tableau schemes for labeling the basis states spanning the irreps of $U(n)$. It is worth noting that the MT scheme is quite general and applicable to any N-particle system whose basis states span the irreps of $U(n)$. Unlinking of the procedures from lexical ordering and associating them with orbital occupancies has the advantage that we can choose the configurations relevant to the physical problem under consideration.

In the next section we consider the explicit realization of the basis for the finite dimensional irreps and determine the matrix elements of the generators of the group.

B. Tensor Basis for $U(n)$

The problem of generating a basis set spanning an irrep $\langle\lambda\rangle$ of $U(n)$ is one of reducing the space $V_n X^N$ defined by Eq. (4) into irreducible subspaces $V_n^{\langle\lambda\rangle}$. A direct procedure for effecting such a reduction leading to a canonical basis for $U(n)$ is the one due to Gel'fand and Zetlin (1950). Their method has been the subject of extensive studies during the past two decades (Moshinsky, 1968; Baird and Biedenharn, 1963; Ciftan and Biedenharn, 1969; Louck, 1970). The Gel'fand–Zetlin (1950) procedure assumes the existence of an invariant subspace $V_n^{\langle\lambda\rangle}$, on which acts a set of linear operators, E_{ij} $(i, j = 1, \ldots, n)$ called the generators of $U(n)$, and the mapping $V_n^{\langle\lambda\rangle} \rightarrow V_n^{\langle\lambda\rangle}$. These operators satisfy

$$[E_{ij}, E_{km}] = E_{im}\,\delta_{jk} - E_{kj}\,\delta_{im} \tag{28}$$

$$E_{ij}^{+} = E_{ji} \tag{29}$$

A basis for this space is generated using the real nonnegative integers m_{ij} $(i \leq j = 1, 2, \ldots, n)$, in terms of which the eigenvalues of a complete set of the mutually commuting invariants I_{kr} $(k \leq r = 1, 2, \ldots, n)$ can be expressed. The invariants I_{kr} are expressed in terms of E_{ij} as follows:

$$I_{kr} = \sum_{i_1, i_2, \ldots, i_k = 1}^{r} E_{i_1 i_2} E_{i_2 i_3} \cdots E_{i_k i_1} \tag{30}$$

The m_{ij} define a set of $n(n+1)/2$ nonnegative integers which are arranged in a triangular array as on the right-hand side of Eq. (21). The basis spanning $V_n^{\langle\lambda\rangle}$ is characterized in terms of these arrays which are called the GZT [cf. Eq. (21)].

Let us now consider an alternative to the above approach for generating a canonical basis for $U(n)$. This approach is based on the duality between the permutation and unitary groups (Robinson, 1961). Weyl (1946) was the first to employ this duality successfully for generating a $U(n)$ basis using essentially idempotent Young operators of the permutation group. These operators, which define an invariant subalgebra for an irrep $[\lambda] \equiv [\lambda_1, \lambda_2, \ldots, \lambda_p]$ $(\lambda_1 \geq \lambda_2 \geq \lambda_p > 0;\ \lambda_1 + \lambda_2 + \lambda_p = N)$ of S_N, are usually not Hermitian so that they do not define an orthonormal basis for $V_n^{\langle\lambda\rangle}$ (cf. Matsen, 1964; Hamermesh, 1962; Boerner, 1968). Recent studies by Kaplan (1974) and Harter and Patterson (1976a,b) and Sarma and Rettrup (1977) lead to the possibility of generating a tensor basis which is closely related to the Weyl basis of $U(n)$. In addition to these studies which were restricted to the irreps $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle$ applicable to many-electron systems, Sarma and Sahasrabudhe (1980) studied the more general irreps of $U(n)$. This approach will now be outlined briefly to reveal its application to many-electron systems.

Consider an element $(N_1 N_2 \cdots N_n)$ of the tensor space $V_n \otimes^N$ defined as on the right-hand side of Eq. (4). Let $V_n^{\langle\lambda\rangle}$ be a subspace of $V(n)$ which is irreducible under the generators E_{ij} defined by Eqs. (28) and (29). The nontrivial elements λ_i $(i = 1, 2, \ldots, p;\ p \leq n)$ of the irrep $\langle\lambda\rangle \equiv \langle\lambda_1, \lambda_2, \ldots, \lambda_n\rangle$ of $U(n)$, such that $\sum_{i=1}^{p} \lambda_i = N$, define a partition of N, and therefore, an irrep $[\lambda] = [\lambda_1, \lambda_2, \ldots, \lambda_p]$ of S_N for the N-particle system. As a first step in the reduction of $V_n \otimes^N$, we define the standard Wigner operators for the irrep $[\lambda]$ of S_N as [cf. Eq. (12)],

$$e_{rs}^{[\lambda]} = (f_N^\lambda / N!)^{1/2} \sum_{P \in S_N} [P]_{rs}^\lambda P \tag{31}$$

where $[P]_{rs}^\lambda$ are elements of the real orthogonal Young representation matrix for $P \in S_N$. These operators satisfy [cf. Eqs. (17) and (18)],

$$e_{rs}^{[\lambda]} e_{tu}^{[\lambda']} = (N!/f_N^\lambda)^{1/2} e_{ru}^{[\lambda]}\, \delta_{st} \quad \delta_{\lambda\lambda'}, \tag{32}$$

$$e_{rs}^{[\lambda]} = (e_{sr}^{[\lambda]})^+. \tag{33}$$

Applying these operators to $(N_1, N_2, \ldots, N_n)$, we obtain a set of functions,

$$e_{rs}^{[\lambda]}\ (N_1, N_2, \ldots, N_n) = |(N_1, N_2, \ldots, N_n); rs\rangle^\lambda. \tag{34}$$

Applying permutation Q on the right- and left-hand sides of $e_{rs}^{[\lambda]}$, we obtain

$$Q e_{rs}^{[\lambda]} = \sum_t [Q]_{tr}^\lambda e_{ts}^{[\lambda]}, \tag{35a}$$

$$e_{rs}^{[\lambda]} Q = \sum_{t} [Q]_{st}^{\lambda} e_{rt}^{[\lambda]}. \tag{35b}$$

These properties will now be used to obtain a complete orthonormal basis from the set defined in Eq. (34). If $N_i = 0$ or 1 for $i = 1, 2, \ldots, n$, we observe that a set of f_N^λ nonvanishing and linearly independent functions is possible, where f_N^λ is the dimensionality of irrep $[\lambda]$ of S_N. If the single-particle orbitals are orthonormal, this set, in turn, defines an orthonormal Young basis for the irrep $[\lambda]$. On the other hand, if some of the $N_i > 1$, then the functions of Eq. (34) do not form a linearly independent set (Kaplan, 1974). This can be illustrated using the primitive tensor basis $|(1, 2, 0)\rangle \equiv |\phi_1\phi_2^2\rangle$ of $V_3 \otimes^3$ symmetry adapted to the irrep $\langle 2, 1, 0\rangle$ of $U(3)$. Using the Wigner operator (Kaplan, 1974)

$$e_{11}^{[2,1]} = \sqrt{2/3} \sum_{P \in S_3} [P]_{11}^{[2,1]} P$$

for S_3 and the transformation properties of the Young representations under the elementary transpositions (Kaplan, 1974), we obtain the result

$$e_{11}^{[2,1]} |(1, 2, 0)\rangle = (1/\sqrt{3}) e_{12}^{[2,1]} |(1, 2, 0)\rangle$$

where $e_{12}^{[2,1]}$ is the second Wigner operator for the two-dimensional subspace of $[2, 1]$ of S_3. Since there is only one SWT corresponding to this occupancy for $\langle 2, 1, 0\rangle$ of $U(3)$, this linear dependence leads to problems of unique identification (Patterson and Harter, 1976).

For orbital configurations of electrons which span the irrep $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle$ Kaplan (1974), Karwowski (1973a,b), and Sarma and Rettrup (1977) solved this problem by assigning all doubly occupied orbitals to the first subset of electrons followed by the assignment of singly occupied orbitals to the rest. This led to the primitive tensor space being defined as,

$$|(i, p)\rangle^N = \phi_{i_1}^2 \phi_{i_2}^2 \cdots \phi_{i_p}^2 \phi_{i_{p+1}} \phi_{i_{p+2}} \cdots \phi_{i_{p+q}} \tag{36}$$

where

$$1 \leq i_1, i_2, \ldots, i_{p+q} \leq n, \tag{37}$$

subject to

$$i_1 < i_2 \cdots < i_p; \qquad i_{p+1} < i_{p+2} < \cdots < i_{p+q} \tag{38}$$

Using such a primitive basis and the Wigner operator defined as before, we can readily show that only $e_{11}^{[2,1]}$ yields a nonzero basis for the given example. Sarma and Dinesha (1978) and Dinesha (1979) have shown that the basis spanning the irrep $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle$ obtained using the primitive tensors of Eq. (36) differ only by a phase factor from the corresponding canonical Weyl or Gel'fand basis. In the case of the above example it can be easily shown that

$$e^{[2,1]}_{11}|\phi_2^2\phi_1\rangle = (-)\left|\begin{matrix}1 & 2\\ 2 & \end{matrix}\right\rangle \equiv (-)\left|\begin{matrix}2 & 1 & 0\\ & 2 & 1\\ & 1 & \end{matrix}\right\rangle .$$

The reordering of orbital tensor products, which is easy to define when no N_i is greater than 2, becomes rather difficult if some of the N_i have values greater than this. Second, a consistent phase factor relationship is also not easy to establish, as in the case of the many electron configurations. In view of these difficulties we now consider a brief outline of the procedure due to Sarma and Sahasrabudhe (1980).

The main reason for the ambiguity discussed above is that the primitive monomial $(N_1N_2 \cdots N_n)$ is invariant under all permutations P belonging to the subgroup $S_{N_1} \otimes S_{N_2} \otimes \cdots \otimes S_{N_n}$ of S_N, whereas the Wigner operators of Eq. (31) undergo the transformations as in Eq. (35). One obvious way out of this difficulty is to choose linear combinations of these operators so that they exhibit the same invariance. Such linear combinations can be chosen using the elementary transpositions $P = (k, k+1)$ (where $k = 1, \ldots, N_1 - 1, N_1 + 1, \ldots, N_1 + N_2 - 1, \ldots, (N_1 + N_2 + \cdots + N_{n-1} + 1), \ldots, (N_1 + N_2 + \cdots N_n - 1)$, and demanding that

$$e^{[\lambda]}_{r(\bar{s})} = \sum_{s=1}^{f_N^\lambda} a^{[\lambda]}_{s(\bar{s})}\, e^{[\lambda]}_{rs}, \tag{39}$$

satisfies $e^{[\lambda]}_{r(\bar{s})} P = e^{[\lambda]}_{r(\bar{s})}$ for any

$$P = (k, k+1) \in S_{N_1} \otimes S_{N_2} \otimes \cdots \otimes S_{N_n}. \tag{40}$$

The meaning of the symmetrization index $(\bar{s})$ will become clear below. Since the Young representation matrices have a very simple form for elementary transpositions (Hamermesh, 1962), the above combinations can be readily generated. As an illustration consider the primitive tensor (1211200) belonging to $V_8\otimes^7$ which is required to be symmetry adapted, say, to the irrep $\langle 2^2,1^3,0^3\rangle$ of $U(8)$. Using the elementary transpositions (2,3), (6,7) which leave the primitive tensor product invariant and noting that,

$$\begin{aligned} e^{[2^2,1^3]}_{r\begin{pmatrix}\overline{12}\\36\\4\\5\\7\end{pmatrix}}|(12112000)\rangle &= e^{[2^2,1^3]}_{r\begin{pmatrix}\overline{12}\\36\\4\\5\\7\end{pmatrix}}(2,3)|(12112000)\rangle \\ &= e^{[2^2,1^3]}_{r\begin{pmatrix}\overline{12}\\36\\4\\5\\7\end{pmatrix}}(6,7)|(12112000)\rangle, \end{aligned}$$

we obtain the symmetrized and normalized linear combination,

$$e_{r\begin{pmatrix}\overline{12}\\36\\4\\5\\7\end{pmatrix}}^{[2^2,1^3]} = (4\sqrt{2})^{-1}\left\{\sqrt{3}e_{r\begin{pmatrix}\overline{12}\\36\\4\\5\\7\end{pmatrix}}^{[2^2,1^3]} + \sqrt{5}e_{r\begin{pmatrix}\overline{12}\\37\\4\\5\\6\end{pmatrix}}^{[2^2,1^3]}\right.$$

$$\left. + 3e_{r\begin{pmatrix}\overline{13}\\26\\4\\5\\7\end{pmatrix}}^{[2^2,1^3]} + \sqrt{15}e_{r\begin{pmatrix}\overline{13}\\27\\4\\5\\6\end{pmatrix}}^{[2^2,1^3]}\right\}.$$

It is rather difficult to obtain closed expressions as those above for the basis states spanning the general irreps $\langle\lambda\rangle$ of $U(n)$. However, in these cases it is possible to obtain a recursive form for the symmetrized operator combination. In the general case, let $[\lambda]$ be the irrep of S_N corresponding $\langle\lambda\rangle$ of $U(n)$ and $e_{rs}^{[\lambda]}$ the Wigner operator as defined by Eq. (31). Keeping the index r fixed let us apply this operator to the tensor product $(N_1N_2 \cdots N_n)$. The result will be zero if any pair of the groups of the first N_1, next N_2, . . . , last N_n share a column in the standard Young tableau t_s^λ. This follows since the tensor is completely symmetric in each of the groups of these entries, whereas the entries sharing a column imply an antisymmetry within the group for which this happens. This, in turn, implies that in all such tableaux the first N_1 entries can occur only in the first row, the next N_2 entries can be at most in the first and/or second rows, etc., so that ultimately the last N_n entries can be in any or all of the n rows. Let N_{ij} represent the subset of the ith group of N_i entries occuring in the jth row of the standard tableau t_s^λ. Since the total number of entries in the ith group is N_i, we have the result

$$\sum_{j=1}^{i} N_{ij} = N_i, \qquad i = 1, 2, \ldots, n. \tag{41}$$

Since we require symmetrization over each of the groups of entries, we define the combination of Eq. (39) as,

$$e^{[\lambda]}_{r[(N_{11})(N_{21}N_{22})\cdots N_{n1}N_{n2}\cdots N_{nn}]} = \sum_{S=1}^{f_N^{[\lambda]}} e_{rs}^{[\lambda]}\, a^{\lambda}_{s[(N_{11})(N_{21}N_{22})\cdots]}. \tag{42}$$

Using this notation and omitting the fixed index r, we can represent the required tensor basis spanning the irrep $\langle\lambda\rangle$ of $U(n)$ as

$$e^{[\lambda]}_{r[(N_{11})(N_{21}N_{22})\cdots(N_{n1}N_{n2}\cdots N_{nn})]}\,|(N_{n1}\cdots N_{nn})]\rangle^{<\lambda>},$$

$$= |[(N_{11})(N_{21}N_{22})\cdots(N_{n1}\cdots N_{nn})]\rangle^{<\lambda>}, \tag{43}$$

where the index set $(N_1 N_2 \cdots N_n)$ has been omitted since it is already contained in the specification of the row entry index i in N_{ij}, and symmetrization over the groups of Wigner operators has been indicated by using the parentheses.

Consider now the transformations induced in this basis by the generators E_{ij} of $U(n)$. In view of the commutation and Hermiticity properties [cf. Eqs. (28) and (29)] of these generators, we observe that we need study explicitly only the transformations induced by E_{i-1i}. These generators are symmetrical in particle coordinates so that they commute with $e_{rs}^{[\lambda]}$ of Eq. (31) and operate on the primitive tensor $(N_1 N_2 \cdots N_n)$ (Sarma and Dinesha, 1978; Lezuo, 1972; Harter and Patterson, 1976b). The transformation of the primitive tensor is given by

$$\begin{aligned}&(N_1, \ldots, N_{i-1}, N_i, \ldots, N_n)\\ &\quad\xrightarrow{E_{i-1i}} (N_1, \ldots, N_{i-1}+1, N_i-1, \ldots, N_n).\end{aligned}$$

Thus, the only nonzero matrix elements which result are

$$\begin{aligned}&\langle[(N_{11}) \cdots (N_{i-11} \cdots N_{i-1k}+1 \cdots N_{i-1i-1})(N_{i1} \cdots N_{ik}-1 \cdots N_{ii})\\ &\qquad \cdots (N_{n1} \cdots N_{nn})]\|E_{i-1i}\|[(N_{11}) \cdots (N_{i-11} \cdots N_{i-1k} \cdots N_{i-1i-1})\\ &\qquad \times (N_{i1} \cdots N_{ik} \cdots N_{ii}) \cdots (N_{n1} \cdots N_{nn})]\rangle\\ &\quad = [(N_{i-1}+1)N_i]^{1/2}\langle[(N_{11}) \cdots (N_{i-11} \cdots N_{i-1k}+1 \cdots N_{i-1i-1})\\ &\qquad \times (N_{i1} \cdots N_{ik}-1 \cdots N_{ii}) \cdots (N_{n1} \cdots N_{nn})]\rangle\\ &\qquad \times |e^{[\lambda]}_{1[(N_{11}) \cdots (N_{i-11} \cdots N_{i-1k} \cdots N_{i-1i-1})(N_{i1} \cdots N_{ik} \cdots N_{ii}) \cdots (N_{n1} \cdots N_{nn})]}\\ &\qquad \times (N_1, \ldots, N_{i-1}+1, N_i-1, \ldots, N_n), \qquad (44)\end{aligned}$$

for $k = 1, \ldots, i-1$.

The evaluation of the above matrix element is difficult in view of the fact that the operator combination defined for the ket vector is the one corresponding to a primitive tensor $(N_1 \cdots N_{i-1} N_i \cdots N_n)$, whereas after the operation of E_{i-1i}, we have a tensor $(N_1, \ldots, N_{i-1}+1, N_i-1, \ldots, N_n)$. This problem was solved by Sarma and Sahasrabudhe (1980) by expressing both the bra and ket Wigner operators required for Eq. (44) in terms of those for the primitive tensor $(N_1, \ldots, N_{i-1}-1, N_i-1, \ldots, N_n)$. The procedure leading to the matrix elements of E_{i-1i} is lengthy but straightforward and was found to yield the Baird–Biedenharn expression (Baird and Biedenharn, 1963) which was obtained by the latter authors using the Gel'fand–Zetlin (1950) basis. This expression, which is expressed in terms of the m_{ij} of the GZT can be readily restated using the N_{ik} ($k = 1, \ldots, i$; $i = 1, \ldots, n$) of Eq. (44) and the identification,

$$m_{ij} = \sum_{k=i}^{j} N_{ki} \qquad (45a)$$

as,

$$(-1)^{1/2}\left[\frac{\displaystyle\prod_{\alpha=1}^{i}\left(\sum_{\beta=\alpha}^{i} N_{\beta\alpha}-\sum_{\beta=k}^{i-1} N_{\beta k}-\alpha+\quad\right)\times\prod_{\alpha=1}^{i-2}\left(\sum_{\beta=\alpha}^{i-2} N_{\beta\alpha}-\sum_{\beta=k}^{i-1} N_{\beta k}-\alpha+k-1\right)}{\displaystyle\prod_{\substack{\alpha=1\\(\alpha\neq k)}}^{i-1}\left(\sum_{\beta=\alpha}^{i-1} N_{\beta\alpha}-\sum_{\beta=k}^{i-1} N_{\beta k}-\alpha+k\right)\times\prod_{\substack{\alpha=1\\(\alpha\neq k)}}^{i-1}\left(\sum_{\beta=\alpha}^{i-1} N_{\beta\alpha}-\sum_{\beta=k}^{i-1} N_{\beta k}-\alpha+k\right)}\right]^{1/2} \tag{45b}$$

Though the above result is just a restatement of the standard (Baird and Biedenharn, 1963) one, the interesting feature of the present study is the relation of Eq. (45a) between m_{ij} and the partial sum over N_{ik}. Using the correspondence between the tensor and Weyl basis, we observe that m_{ij} can be interpreted as the partial sum of the entries i occuring in the SWT in the rows $k = 1, 2, \ldots, j$. This, in turn, leads to a simple relationship between m_{ij} and the N_j defined by Eq. (24). This relationship was exploited by Sarma and Rettrup (1980) and Rettrup and Sarma (1980) in developing a computer programme for obtaining the matrix elements of the generators for the basis spanning an irrep $\langle\lambda\rangle$ of $U(n)$.

The method outlined in this section is extremely general and applicable to any many-particle system. Since the present article is concerned mainly with many-electron systems, we will outline in the next section some of the simplifications that result on using the irreps $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle$.

C. Spin-Free CI Studies

In Section II we briefly formulated the CI problem for a spin-free Hamiltonian. The difficulties of the permutation group approaches were pointed out in the discussion following Eq. (19). From the results of the previous section we can easily see that the matrix elements of the Hamiltonian obtained in Eq. (16) are between two basis functions which transform according to the irrep $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle$ of $U(n)$. For these irreps many simplifications in the general formalism described in the earlier section are possible.

Consider an N-electron molecular system in the spin state S. The ordered set of n orthonormal molecular orbitals $\{\phi_i | i = 1, 2, \ldots, n\}$, spanning a vector space V_n can be used to define the primitive configuration space of the system as

$$V_n \otimes^N: \left\{ \Phi^{(N)} \right.$$

$$\left. \equiv \phi_1^{N_1} \phi_2^{N_2} \cdots \phi_n^{N_n} \middle| N_1, N_2, \ldots, N_n \geq 0; \sum_{i=1}^{n} N_i = N \right\} \cdot$$

The spin-free configurations of the system span the irrep $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S} \rangle$ {for the remainder of this section we will write this as $\langle \lambda \rangle$ and the associated irrep of $S_N[2^{N/2-S}, 1^{2S}]$ as $[\lambda]$ of $U(n)$} and can be obtained by a reduction of $V_n \otimes^N$ using the operators $e_{r\bar{s}}^{[\lambda]}$ of S_N defined by Eq. (39). The fact that the Young diagram corresponding to the irrep $[\lambda]$ of S_N has at most two columns implies that a nonzero basis $|e_{r\bar{s}}^{[\lambda]} \Phi^{(N)} \rangle$ of $U(n)$ results only if $\Phi^{(N)}$ of Eq. (4) has no orbital with occupancy greater than 2. If a particular primitive configuration $\Phi^{(N)}$ of such a set has p doubly occupied orbitals, the operator $e_{r\bar{s}}^{[\lambda]}$ has to be defined as a symmetric linear combination of standard Wigner operators $e_{rs}^{[\lambda]}$ as explained in the previous section. This expansion in terms of $e_{rs}^{[\lambda]}$ is quite tedious to obtain and is avoidable in the case of the irrep $\langle \lambda \rangle$ of $U(n)$ being considered in the present section. For this purpose we choose a primitive tensor set

$$\begin{aligned} \Gamma: \quad \{ \varphi^{(N)} \equiv \phi_{i_1}^2 \phi_{i_2}^2 \cdots \phi_{i_p}^2 \phi_{i_{p+1}} \cdots \phi_{i_{N-p}} | \\ i_1, i_2, \ldots, = 1, 2, \ldots, n; \\ i_1 < i_2 < \cdots < i_p;\ i_{p+1} < \cdots < i_{N-p} \} \end{aligned} \tag{46}$$

in place of the set defined by Eq. (4). We note that the sets of functions defined by Eq. (46) are related to those of Eq. (4), subject to $N_i \leq 2$, through a permutation which shifts all doubly occupied orbitals to the extreme left. As observed by Kaplan (1974), the use of $\varphi^{(N)}$ of Eq. (46) to define a tensor basis $|e_{rs}^{[\lambda]} \varphi^{(N)} \rangle$ eliminates the need to define linear combinations $e_{r\bar{s}}^{[\lambda]}$ as in $e_{r\bar{s}}^{[\lambda]} \Phi^{(N)} \rangle$. This follows since each of the p pairs of electrons for the doubly occupied orbitals have entries (1,2), (3,4), . . . , $(2p-1, 2p)$ in the top p rows of the defining tableau t_s^λ. It has been shown by Sarma and Dinesha (1978, 1979b) that the two basis sets introduced above are identical to within a phase factor such as,

$$|e_{r\bar{s}}^{[\lambda]} \Phi^{(N)} \rangle = \left(\prod_{i=1}^{p} \varepsilon_i \right) |e_{rs'}^{[\lambda]} \varphi^{(N)} \rangle \tag{47}$$

where $\varepsilon_i = +1(-1)$ if the smaller of the pair of entries for ϕ_i^2 is even(odd) and the tableau $t_{s'}^\lambda$ will be specified shortly. As a prelude to demonstrating this result, we introduce a compact notation for a two-column standard Young tableau (SYT) spanning the irrep $[\lambda]$ of S_N. For every standard tableau of this type we list in an increasing order from left to right entries occuring in the $N/2 - S$ boxes of the second column. Thus, for example, we have a typical correspondence such as

$$\begin{array}{|cc|}\hline 1 & 3 \\ 2 & 6 \\ \cline{2-2} 4 & \multicolumn{1}{|c}{} \\ 5 & \multicolumn{1}{|c}{} \\ \cline{1-1} \end{array} \Leftrightarrow (3,6)$$

for the irrep $[2^2, 1^2]$ of S_6. The standard Wigner operator corresponding to a tableau with the entries $(q_1, q_2, \ldots, q_{N/2-S})$ in the second column is represented in our notation

$$e^{[\lambda]}_{r(q_1,\ldots,q_{N/2-S})}.$$

Let a doubly occupied orbital ϕ_i^2 occuring in $\Phi^{(N)}$ correspond to the kth and $(k+1)$th electrons. The k, $k+1$ entries for these electrons share either row or axial positions in the tableaux defining $e^{[\lambda]}_{r\bar{s}}$. This necessarily means that in this pair of tableaux, if $(k+1)$ occurs in the second column of one of them then k occurs in the second column of the other. Without loss of generality we can display every such pair in our notation by mentioning the larger of the two entries in the set $(q_1, q_2, \ldots, q_{N/2-S})$ of second column entries and indicate symmetrization with respect to its immediate predecessor by a bar over the entry. Thus, if p doubly occupied orbitals occur in a given $\Phi^{(N)}$ and correspond to the electron pairs (k_1, k_1+1), $(k_2+k_2+1), \ldots,$ (k_p, k_p+1), we represent the symmetrized Wigner operator as

$$e^{[\lambda]}_{r\bar{s}} = e^{[\lambda]}_{r(q_1,q_2,\ldots,\overline{k_1+1},\ldots,\overline{k_2+1},\ldots,q_{N/2-S})}. \tag{48}$$

In order to illustrate the validity of Eq. (48), consider a primitive tensor

$$\Phi^{(N)} = \phi_1(1) \cdots \phi_i(k)\phi_j(k+1)\phi_j(k+2) \cdots, \tag{49}$$

which has only one doubly occupied orbital ϕ_j^2 occuring for the $(k+1)$, $(k+2)$ electron pair. The required basis function for the irrep $\langle\lambda\rangle$ of $U(n)$ is

$$\begin{aligned} e^{[\lambda]}_{r(\ldots,\overline{k+2},\ldots)}\Phi^{(N)} = (2d)^{-1/2}\{&(d-1)^{1/2}e^{[\lambda]}_{r(\ldots,k+1,\ldots)} \\ &+ (d+1)^{1/2}e^{[\lambda]}_{r(\ldots,k+2,\ldots)}\}\Phi^{(N)}, \end{aligned} \tag{50}$$

where d is the axial distance between $(k+1)$, $(k+2)$ in the given tableau. Noting that the two-column Young diagrams corresponding to this $[\lambda]$ do not admit total symmetry over more than two entries, we immediately obtain the result (cf. Sarma and Rettrup, 1977),

$$\begin{aligned} & e^{[\lambda]}_{r(\dots,\overline{k+2},\dots)}(\cdots \phi_i(k)\phi_j(k+1)\phi_j(k+2)\cdots) \\ &= -e^{[\lambda]}_{r(\dots,k+2,\dots)}\{(\cdots \phi_j(k)\phi_i(k+1)\phi_j(k+2)\cdots) \\ &\quad +(\cdots \phi_j(k)\phi_j(k+1)\phi_i(k+2)\cdots)\} \\ &= -2e^{[\lambda]}_{r(\dots,\overline{k+2},\dots)}(\cdots \phi_j(k)\phi_j(k+1)\phi_i(k+2)\cdots). \end{aligned} \tag{51}$$

where the factor 2 in the last equality arises due to symmetry of $e^{[\lambda]}_{r(\dots,\overline{k+2},\dots)}$ over $(k+1)$ and $(k+2)$. Further manipulation of Eq. (51) leads to

$$\begin{aligned} & e^{[\lambda]}_{r(\dots,\overline{k+2},\dots)}(\cdots \phi_i(k)\phi_j(k+1)\phi_j(k+2)\cdots) \\ &= -e^{[\lambda]}_{r(\dots,\overline{k+1},\dots)}(\cdots \phi_j(k)\phi_j(k+1)\phi_i(k+2)\cdots). \end{aligned} \tag{52}$$

This procedure can be continued until the doubly occupied orbital is shifted to the extreme left as in $\varphi^{(N)}$ defined by Eq. (46). If more than one doubly occupied orbital occurs, repetition of the above procedure leads to the identity of Eq. (47). As an illustration of the above correspondence consider the basis

$$|e^{[2^4,1]}_{r(\bar{4},5,\bar{8},9)}(\phi_1\phi_2\phi_3^2\phi_4\phi_5\phi_6^2\phi_7)\rangle$$

of $U(7)$. As outlined in the procedure we have,

$$\begin{aligned} |e^{[2^4,1]}_{r(\bar{4},5,\bar{8},9)}(\phi_1\phi_2\phi_3^2\phi_4\phi_5\phi_6^2\phi_7) &= |e^{[2^4,1]}_{r(2,5,\bar{7},9)}(\phi_3^2\phi_1\phi_2\phi_4\phi_5\phi_6^2\phi_7)\rangle \\ &= |e^{[2^4,1]}_{r(2,4,7,9)}(\phi_3^2\phi_6^2\phi_1\phi_2\phi_4\phi_5\phi_7)\rangle. \end{aligned}$$

The general rule for obtaining the tableau $t^{\lambda}_{s'}$ in Eq. (47) is the following: Let the symmetrized tableau be $\bar{s} = (q_1, \dots, q_{m_1-1}, \bar{q}_{m_1}, q_{m_1+1}, \dots, \dots, q_{m_p-1}, \bar{q}_{m_p}, q_{m_p+1}, \dots, q_{N/2-S})$, where $m_1, m_2, \dots, m_p$ specify the symmetrization over the pairs (q_{m_1-1}, q_{m_1}), (q_{m_2-1}, q_{m_2}), $\dots$, (q_{m_p-1}, q_{m_p}), respectively. The tableau s' is obtained by writing 2, 4, $\dots$, $2p$ as the first p second-column entries, increasing each entry corresponding to a singly occupied orbital in $\bar{s}$ by twice the number of doubly occupied orbitals to its right and writing it successively after $2p$ in s'. Thus we have,

$$\begin{aligned} s' = (&2, 4, \dots, 2p, q_1 + 2p, \dots, q_{m_1-1} + 2p, q_{m_1+1} + 2p - 2, \dots, \\ &q_{m_2-1} + 2p, q_{m_2+1} + 2p - 4, \dots, q_{m_p-1} + 2, \\ &q_{m_p+1}, \dots, q_{N/2-S}). \end{aligned} \tag{53}$$

We now discuss the effect of the generators E_{ij} of $U(n)$ on the basis set developed above using $\varphi^{(N)}$ of Eq. (46). These operators are symmetric in the electron coordinates and commute with $e^{[\lambda]}_{rp}$, where t^{λ}_{p}

is an SYT with the top p second-column entries being 2, 4, . . . , $2p$. Thus E_{ij} acting on $\varphi^{(N)}$ changes the occupancies of i and j as $(N_i, N_j) \to (N_i + 1, N_j - 1)$. Since the occupancy of any orbital is restricted to $2 \geq N_i \geq 0$, we need consider only the following cases for $\varphi^{(N)}$:

(i) $N_i = 0, \quad N_j = 1$; (ii) $N_i = 1, \quad N_j = 1$;
(iii) $N_i = 0, \quad N_j = 2$; (iv) $N_i = 1, \quad N_j = 2$.

The transformations induced by E_{ij} on the basis states of the irrep $\langle\lambda\rangle$ of $U(n)$ will now be studied for each of these cases. For purposes of clarity we illustrate each case with a specific example from the basis set spanning $\langle 2^4, 1^3, 0^3\rangle$ of $U(10)$. The general results in each case are summarized from Sarma and Rettrup (1977) and Sahasrabudhe *et al.* (1980a).

Case (i) $N_i = 0, \ N_j = 1$. Consider a basis state $|e^{[2^4,1^3]}_{1\rho}(\phi_1^2\phi_3^2\phi_4^2\text{-}\phi_2\phi_5\phi_6\phi_7\phi_9)\rangle$ of $U(10)$. The generator E_{85} acting on this leads to $|e^{[2^4,1^3]}_{1\rho}(\phi_1^2\phi_3^2\phi_4^2\phi_2\phi_8\phi_6\phi_7\phi_9)\rangle$. The transformed monomial is now not in the ordered form as in Eq. (46). The permutation $P = (8910)^{-1}$ brings it to this form. Using Eq. (35) we obtain, in general,

$$E_{ij}e^{[\lambda]}_{1\rho}\varphi^{(N)} = \sum_{\rho'} [P]^{\lambda}_{\rho'\rho}e^{[\lambda]}_{1\rho'}\varphi'^{(N)} \tag{54}$$

where P is the matching open-shell cyclic permutation and $\varphi'^{(N)}$ is given by $\varphi'^{(N)} = \varphi^{(N)}(\phi_j(r_j) \to \phi_i(r_i))$.

Case (ii) $N_i = N_j = 1$. Let us consider $\varphi^{(N)} = \phi_1^2\phi_3^2\phi_2\phi_4\phi_5\phi_6\phi_8\phi_9\phi_{10}$ and effect of E_{49} on it.

$$E_{49}\varphi^{(N)} = \phi_1^2\phi_3^2\phi_2\phi_4\phi_5\phi_6\phi_8\phi_4\phi_{10} = P\phi_1^2\phi_3^2\phi_2\phi_4^2\phi_6\phi_8\phi_{10} = P\varphi'^{(N)},$$

where $P = (78910)$, which is an open-shell cyclic permutation. Hence, in general,

$$E_{ij}e^{[\lambda]}_{1\rho}\varphi'^{(N)} = e^{[\lambda]}_{1\rho}P\varphi'^{(N)} = \sum_{s=1} [P]^{\lambda}_{s\rho}e^{[\lambda]}_{1s}\varphi'^{(N)}. \tag{55}$$

The monomial $\varphi'^{(N)}$ is not in the ordering defined in Eq. (46). A doubly occupied orbital (here, ϕ_4^2) occurs in the middle of singly occupied orbitals. However, using Eq. (52) we can shift the doubly occupied orbital to the electron coordinates $(2p + 1)$ and $(2p + 2)$ and get another projection with a properly ordered monomial; in general,

$$E_{ij}e^{[\lambda]}_{1\rho}\varphi^{(N)} = \sum_{s=1}^{f^{\lambda}_{N}} \varepsilon_s g_s[P]^{\lambda}_{s\rho}e^{[\lambda]}_{1s'}\varphi''^{(N)}, \tag{56}$$

where $g_s = [(d \pm 1)/2d]^{1/2}$ is the conversion factor from $e^{[\lambda]}_{1s}$ to the symmetrized operator $e^{[\lambda]}_{1s}$, d being the axial distance in t^{λ}_{s} between entries of electrons occupying ϕ_i in $\varphi'^{(N)}$. The plus (minus) sign is used when the larger entry is in the second (first) column, s', is the tableau obtained from the symmetrized tableau $\bar{s}$ according to Eq. (53). $\varphi''^{(N)}$ corresponds to the ordering defined in Eq. (46).

Case (iii) $N_i = 0,\ N_j = 2$. Let $\varphi^{(N)} = \phi_1^2\phi_2^2\phi_4^2\phi_3\phi_5\phi_6\phi_7\phi_8$, then

$$e_{1\rho}^{[\lambda]} E_{92}\varphi^{(N)} = 2e_{1\rho}^{[\lambda]}(\phi_1^2\phi_2\phi_9\phi_4^2\phi_3\phi_5\phi_6\phi_7\phi_8) = 2e_{1\rho}^{[\lambda]}\varphi'^{(N)}.$$

In the monomial $\varphi'^{(N)}$, ϕ_2 and ϕ_9 are singly occupied and hence for nonvanishing matrix elements

$$\langle e_{1\rho'}^{[\lambda]}\varphi'^{(N)}|E_{ij}|e_{1\rho}^{[\lambda]}\varphi^{(N)}\rangle, \tag{57}$$

the monomial $\varphi'^{(N)}$ should belong to case (ii). Now, noting that $E_{ij}^{+} = E_{ji}$, we find that the nonvanishing matrix elements can be written as

$$\langle E_{ji}e_{1\rho'}^{[\lambda]}\varphi'^{(N)}|e_{1\rho}^{[\lambda]}\varphi^{(N)}\rangle. \tag{58}$$

The effect of E_{ji} on $e_{1\rho'}^{[\lambda]}\varphi'^{(N)}$ has already been discussed in case (ii).

Case (iv) $N_i = 1,\ N_j = 2$. Let $\phi^{(N)} = \phi_1^2\phi_3^2\phi_4^2\phi_2\phi_5\phi_6\phi_7\phi_9$. Now,

$$\begin{aligned} E_{63}e_{1\rho}^{[\lambda]}\varphi^{(N)} &= e_{1\rho}^{[\lambda]}((39) + (49))\phi_1^2\phi_6^2\phi_4^2\phi_2\phi_5\phi_3\phi_7\phi_9 \\ &= e_{1\rho}^{[\lambda]}((39) + (49))\varphi'^{(N)} = -e_{1\rho}^{[\lambda]}\varphi'^{(N)}, \end{aligned}$$

where the last step follows from arguments similar to those used in writing Eq. (51). Now, to bring the monomial $\varphi'^{(N)}$ to proper ordering we need an open-shell cyclic permutation P [in this example it is (789)]. Hence, in general,

$$E_{ij}e_{1\rho}^{[\lambda]}\varphi^{(N)} = -e_{1\rho}^{[\lambda]}P\varphi''^{(N)} = -\sum_{s=1}^{f_N^{\lambda}}[P]_{s\rho}^{\lambda}\,e_{1\rho}^{[\lambda]}\varphi''^{(N)} \tag{59}$$

In all four cases we see that the effect of E_{ij} is expressed in terms of representation matrices of *open-shell cyclic permutation P of the type* $(k, k \pm 1, k \pm 2, \ldots, k \pm l)$. However, ρ is an SYT in which the first ρ-row entries are (1,2), (3,4), . . . , $(2p - 1, 2p)$, respectively. This means that we need the representation matrices of $P \in S_M$ (M being the number of open shells) and not $P \in S_N$ (Kaplan, 1974). This results in a great reduction of labor in obtaining the matrix elements of E_{ij}. The task is further simplified by the fact that we need representation matrices of only cyclic permutations of the type $(s, s + 1, \ldots, s + t)$.

A simple procedure to evaluate the representation matrices of cyclic permutation was given recently by Sahasrabudhe *et al.* (1980a). The fact that only cyclic open-shell permutations are necessary for determining the matrix representations has also been recognized by others (Ruttink, 1978; Paldus and Wormer, 1979).

Until now we have discussed procedures for obtaining the matrix elements of generators of $U(n)$ between the basis functions spanning two-column irreps of $U(n)$. The spin-free Hamiltonian expressed in terms of the generators of $U(n)$ (Harter and Patterson, 1976a; Paldus, 1974; Matsen, 1975) is

$$H = \sum_{ij} f_{ij}E_{ij} + \tfrac{1}{2} \sum_{ijkm} g_{ij;km}(E_{ik}E_{jm} - \delta_{jk}E_{im}),$$

where $f_{ij} = \langle \phi_i|f|\phi_j\rangle$ and $g_{ij;km} = \langle \phi_i\phi_j|1/r_{12}|\phi_k\phi_m\rangle$ are the one- and two-electron integrals over the molecular orbitals. The procedure outlined above permits us to readily generate the CI matrix of the Hamiltonian. Rettrup and Sarma (1977, 1980) recently developed a program for generating this matrix. The program developed on IBM 370/165 at the University of Sheffield, United Kingdom has proved to be quite efficient. It is worth pointing out that the procedures discussed in this section and the programs based on them are well suited for application in areas such as limited CI studies and perturbative approach to many-particle correlations, etc., where specific configurations need to be used. The graphical approach due to Shavitt (1976, 1977) can also be used for these purposes but with considerable modification.

The basis set used in this section is canonical in nature and only the permutation symmetry is incorporated in it. In general, physical systems do have other symmetries such as the point group symmetries for molecules and the $R(3)$ (rotation group in three dimensions) symmetry for atoms, etc. If the point group of the molecule considered is abelian, the spatial symmetry adaptation is straightforward and has been trivially incorporated by the programs developed by Rettrup and Sarma (1977, 1980). In the case of atoms, the subgroup adaptation $U(n) \supset R(3)$ requires angular momentum projected basis. Another important area of application is to consider an N-electron system in spin state S to be composed of subsystems of N_1 and N_2 electrons having spins S_1 and S_2, respectively (Kaplan, 1974). These two problems will be dealt with in the next two sections.

D. Angular Momentum Basis for Atomic Electrons

In the previous section we assumed that the only symmetry admissible to the system considered was one of permutation. If, however, we consider an N-electron atom, we observe that in addition to the permutation symmetry, we also have to consider the symmetry $R(3)$ of the Hamiltonian. The restriction of $U(n)$ to the subgroup $R(3)$ leads to the decomposition of the irreps of $U(n)$ to those of $R(3)$. This requires that we be able to obtain the basis spanning $R(3)$ as a linear combination of the basis spanning a given irrep of $U(n)$. In order to develop a simple procedure for this purpose, we discuss in the present section an N-electron atom for which the L–S coupling scheme is valid. Since the total spin S is a good quantum number we have to consider the spin-free configurations spanning the irrep $\langle\lambda\rangle \equiv \langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle$ of $U(n)$.

In the L–S coupling scheme, the tensor basis set for the above irrep is generated using single-particle orbitals $|l, m\rangle$, which are eigenstates of the angular momentum operators l^2 and l_z. Let $l_1^{N_1} l_2^{N_2} \cdots l_p^{N_p}$ represent a subshell distribution of the individual electrons where

$$\sum_{i=1}^{p} N_i = N. \tag{60}$$

For such a distribution of electrons, the linear vector space V_n spanned by $\{|l_i, m_{l_i}\rangle | i = 1, 2, \ldots, p;\ m_{l_i} = l_i, l_i - 1, \ldots, -l_i\}$, is the direct sum

$$V_n = \sum_{i=1}^{p} \oplus V_{l_i}, \tag{61}$$

of $(2l_i + 1)$-dimensional subspaces for each fixed l_i. The primitive orbital tensor space is then

$$V_n \otimes^{N} = \prod_{i=1}^{p} \otimes (V_{l_i} \otimes^{N_i}). \tag{62}$$

This is a reducible space for $U(n)$, and the reduction into irreducible subspaces is affected using the Wigner operators $e_{rs}^{[\lambda]}$ defined in Eq. (39) (hereafter $[\lambda]$, $\langle\lambda\rangle$ stand for $[2^{N/2-S}, 1^{2S}]$, $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle$ throughout the present section). Such a reduction leading to the orthonormal basis $|e_{rs}^{[\lambda]}\Phi^{(N)}\rangle$ where $\Phi^{(N)}$ defined in terms of $|l, m\rangle$ is in the ordering given by Eq. (4) with $|l, m\rangle$ preceding $|l, m'\rangle$ if $m > m'$ and $|l, m\rangle$ preceding $|l', m'\rangle$ for all m, m' if $l > l'$.

The space $V^{\langle\lambda\rangle}$ obtained as above is stable under the generators $E_{i,j}$ of $U(n)$ but not under the generators $L_\pm = L_x \pm iL_y$ and $L_0 \equiv L_z$ of $R(3)$. A restriction $U(n) \downarrow R(3)$ leads to a decomposition of the irrep $\langle\lambda\rangle$ of $U(n)$ into irreps $D^{(L)}$ of $R(3)$ characterized by the angular momentum L. The irreps $D^{(L)}$ which occur in this reduction can be determined using the procedure due to Hamermesh (1962). Extensive tabulation of this decomposition for the subgroup chain $U(n) \supset R(n) \supset R(3)$, where $R(n)$ is the rotation group in n dimensions, have been given by Wybourne (1970).

Consider the N-particle angular momentum operators $L_\pm$, L_0, which are infinitesimal generators of $R(3)$ and which can be represented in terms of the corresponding single-particle operators $l_\pm$, l_0 as

$$L_\pm = \sum_{k=1}^{N} l_{k_\pm}, \qquad L_0 = \sum_{k=1}^{N} l_{k0}. \tag{63}$$

Since these operators are symmetric in the electron coordinates, they commute with $e_{r\bar{s}}^{[\lambda]}$ and operate on the monomial part $\Phi^{(N)}$ of the tensor basis spanning $\langle\lambda\rangle$. Since the defining orbital $|l, m; (k)\rangle$ of the kth electron in this product is an eigenstate of l_{k0} with eigenvalue m, we obtain the result

$$\begin{aligned} L_0|e_{r\bar{s}}^{[\lambda]}\Phi^{(N)}\rangle &= |e_{r\bar{s}}^{[\lambda]} \sum_{k=1}^{N} l_{k0}\Phi^{(N)}\rangle \\ &= M|e_{r\bar{s}}^{[\lambda]}\Phi^{(N)}\rangle, \end{aligned} \tag{64}$$

where

$$M = \sum_{i=1}^{p} \sum_{m_{l_i}=-l_i}^{l_i} m_{l_i} N_{l_i,m_{l_i}}, \tag{65}$$

$N_{l_i,m_{l_i}}$ being the occupancy of $|l_i, m_{l_i}\rangle (0 \le N_{l_i,m_{l_i}} \le 2)$. The result of Eq. (64) permits us to classify the basis spanning $\langle\lambda\rangle$ of $U(n)$ into sets according to specific M values as $|e_{r\bar{s}}^{[\lambda]}\Phi_M^{(N)}\rangle$. If we consider a set corresponding to $M \ge 0$, we can generate linear combinations which are eigenstates $|(l_1^{N_1} l_2^{N_2} \cdots l_p^{N_p}); LM\rangle^{<\lambda>}$ of L^2, L_z with angular momentum values $L \ge M$, M, respectively. Applying L_+ to any such combination and equating the result to zero, we can eliminate all contributions to it from states with $L > M$. Obtaining the coefficients defining the combinations using the linear equations resulting from

$$L_+|(l_1^{N_1} l_2^{N_2} \cdots l_p^{N_p}); LM\rangle^{<\lambda>} = 0, \tag{66}$$

we can generate eigenstates $|(l_1^{N_1} l_2^{N_2} \cdots l_3^{N_p}); MM\rangle^{<\lambda>}$ with angular momentum eigenvalues M, M. The transformation induced by L_+ on the tensor basis can be determined as for L_0 since

$$L_+|e_{r\bar{s}}^{[\lambda]}\Phi_M^{(N)}\rangle = |e_{r\bar{s}}^{[\lambda]} \sum_{k=1}^{N} l_{k_+}\Phi_M^{(N)}\rangle. \tag{67}$$

Now, l_{k_+} operates only on $|l_i, m_{l_i}; (k)\rangle \in \Phi_M^{(N)}$ and transforms it into $|l_i, m_{l_i} + 1; (k)\rangle$ according to

$$l_{k_+}|l_i, m_{l_i}; (k)\rangle = \tau_i(k)|l_i, m_{l_i} + 1; (k)\rangle, \tag{68}$$

where

$$\tau_i(k) = \{(l_i - m_{l_i})(l_i + m_{l_i} + 1)\}^{1/2}(k), \tag{69}$$

and the index k is explicitly introduced to indicate that we are dealing with $|l_i, m_{l_i}\rangle$ values associated with the kth electron orbital.

Using the result of Eq. (68) on the right-hand side of Eq. (67), we obtain,

$$L_+|e^{[\lambda]}_{r\bar{s}}\Phi^{(N)}_M\rangle = \sum_{k=1}^{N} \tau_i(k)|e^{[\lambda]}_{r\bar{s}}\Phi^{(N)}_{M+1}(l_i, m_{l_i} \to l_i, m_{l_i} + 1; (k)) \tag{70}$$

where $(l_i, m_{l_i} \to l_i, m_{l_i} + 1; (k))$ implies a monomial obtained from $\Phi^{(N)}_M$ by replacing $|l_i, m_{l_i}; (k)\rangle$ by $|l_i, m_{l_i} + 1; (k)\rangle$ and $\tau_i(k)$ is as defined in Eq. (69). The state on the right-hand side of Eq. (70) may not, in general, be a proper basis for $\langle\lambda\rangle$ of $U(n)$ since there is a change in occupancies of $|l_i, m_{l_i}\rangle$ and $|l_i, m_{l_i} + 1\rangle$, whereas $e^{[\lambda]}_{r\bar{s}}$ has been symmetrized for the original occupancies. This fact, combined with the result that the orbital occupancies $N_{l_i}, m_{l_i} \leq 2$ for the many-electron system leads to the four trivial cases,

(i) $N_{l_i,m_{l_i}} = 1, \quad N_{l_i,m_{l_i}+1} = 0;$
(ii) $N_{l_i,m_{l_i}} = 1, \quad N_{l_i,m_{l_i}+1} = 1;$
(iii) $N_{l_i,m_{l_i}} = 2, \quad N_{l_i,m_{l_i}+1} = 0;$
(iv) $N_{l_i,m_{l_i}} = 2, \quad N_{l_i,m_{l_i}+1} = 1;$

as in Section III,C. Using an analysis similar to the one given in that section we can easily establish the validity of the following results:

(i)
$$|e^{[\lambda]}_{r\bar{s}}l_{k_+}\Phi^{(N)}_M\rangle = \tau_i(k)|e^{[\lambda]}_{r\bar{s}}\Phi^{(N)}_{M+1}(l_i, m_{l_i} \to l_i, m_{l_i} + 1(k)\rangle \tag{71}$$

(ii)
$$\begin{aligned} &|e^{[\lambda]}_{r\bar{s}}l_{k_+}\Phi^{(N)}_M(l_i m_{l_1}(k), l_i m_{l_i} + 1(k+1))\rangle \\ &\quad = \tau_i(k)\{(d_k \pm 1)/d_k\}^{1/2} \\ &\qquad \times |e^{[\lambda]}_{r\bar{s}'}\Phi^{(N)}_{M+1}(l_i m_{l_i+1}(k), l_i m_{l_i+1}(k+1))\rangle \end{aligned} \tag{72}$$

where d_k is the axial distance between the entries k, $k + 1$ in the tableau defining $e^{[\lambda]}_{r\bar{s}}$; the $+(-)$ sign is to be used if k is in the first(second) column and $k + 1$ is in the second(first) column in the defining tableaux; $e^{[\lambda]}_{r\bar{s}'}$ has symmetrization as in $e^{[\lambda]}_{r\bar{s}}$ and is additionally symmetric in the entries k, $k + 1$; and the concerned orbitals have been explicitly displayed in $\Phi^{(N)}_M$ and $\Phi^{(N)}_{M+1}$.

(iii) As far as the matrix element evaluation is concerned, this case is the Hermitian adjoint of case (ii).

(iv)
$$\begin{aligned} &|e^{[\lambda]}_{r\bar{s}}(l_{k_+} + l_{(k+1)_+})\Phi^{(N)}_M(l_i m_{l_i}(k), l_i m_{l_i}(k+1), l_i m_{l_i} + 1(k+2))\rangle \\ &\quad = \tau_i(k)|e^{[\lambda]}_{r\bar{s}}\Phi^{(N)}_{M+1}(l_i m_{l_i} + 1(k+1), l_i m_{l_i} + 1(k+2))\rangle \end{aligned} \tag{73}$$

where $e^{[\lambda]}_{r\bar{s}}$ is symmetrized as in $e^{[\lambda]}_{r\bar{s}}$, except for the k, $k + 1$, which are replaced by symmetrization over $k + 1$, $k + 2$.

In Eqs. (71)–(73), $\tau_i(k)$ is as defined by Eq. (69). As these results indicate, the right-hand side of Eq. (70) is determined in terms of the tensor basis spanning the irrep $\langle\lambda\rangle$ of $U(n)$ for the eigenvalue $M + 1$ of L_0. Since these basis states, in turn, define an orthonormal set, we obtain a set of equations for the coefficients of the linear combinations defining $|(l_1^{N_1} l_2^{N_2} \cdots l_p^{N_p});\ L = M,M\rangle^{<\lambda>}$ using Eq. (66). The number of such equations is equal to the number of distinct states $e^{[\lambda]}_{r\bar{s}}\Phi^{(N)}_{M+1}\rangle$ which occur for $M + 1$. If the number of unknowns is equal to this set, a unique determination of the coefficients is possible. If not, the state has a multiple occurrence in $\langle\lambda\rangle$ and the ambiguity can be resolved using consistent schemes (Harter and Patterson, 1976a) which, however, do not lead to unique solutions. The states $|(l_1^{N_1}, \ldots, l_p^{N_p}); LM\rangle$ with $M < L$ can be obtained from the states with $M = L$ by successive applications of L_- (Sahasrabudhe and Sarma, 1980) and use of Eqs. (71)–(73) in which $\tau_i(k) = \{(l_i + m_{l_i})(l_i - m_{l_i} + 1)\}^{1/2}$.

As an illustration of the scheme we consider atomic configuration d^2p^2 in the spin state $S = 1$. The $|l, m\rangle$ basis is represented as:

$$\begin{array}{lcccccccccc} |l, m\rangle & = & |2,2\rangle & |2,1\rangle & |2,0\rangle & |2,-1\rangle & |2,-2\rangle & |1,1\rangle & |1,0\rangle & |1,-1\rangle, \\ i & = & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8. \end{array}$$

Consider the tensor basis set spanning $\langle 2, 1^2, 0^5\rangle$ and corresponding to $M = 4$. We have $M = 4$:

$$\Psi_1 = |e_{r(2)}1^2 68\rangle, \qquad \Psi_2 = |e_{r(2)}1267\rangle,$$

$$\Psi_3 = |e_{r(3)}1267\rangle, \qquad \Psi_4 = |e_{r(4)}1267\rangle,$$

$$\Psi_5 = |e_{r(\bar{4})}136^2\rangle,$$

where $[\lambda] = [2,1^2]$ has been omitted from $e^{[\lambda]}_{r\bar{s}}$ and the second-column notation defined in the previous section has been used for $\bar{s}$. The ϕ's have been omitted, e.g., $1^2 68 \equiv \phi_1^2\phi_6\phi_8$. Let $\Psi = \sum_{i=1}^{5} a_i\Psi_i$ be a linear combination of these basis states. If Ψ were to represent $|(d^2)(p^2)4,4\rangle$, we require that $L_+\Psi = L_+\sum_{i=1}^{5} a_i\Psi_i = 0$. Using the procedures of this section we obtain the result

$$(\sqrt{2}a_1 + 4a_2)|e_{r(2)}1^2 67\rangle$$
$$+ [(2/\sqrt{3})a_3 + (2\sqrt{2}/\sqrt{3})a_4 + \sqrt{6}a_5]|e_{r(\bar{4})}126^2\rangle = 0,$$

where $|e_{r(2)}1^2 67\rangle$, $|e_{r(\bar{4})}126^2\rangle$ are states with $M = 5$. Since these states are orthonormal, the above equation leads to

$$a_2 = -(2\sqrt{2})^{-1}a_1 \qquad \text{and} \qquad a_5 = -\tfrac{1}{3}\sqrt{2}a_3 - \tfrac{2}{3}a_4,$$

so that

$$\begin{aligned}|(d^2)(p^2); 4{,}4\rangle = a_1[\Psi_1 - (2\sqrt{2})^{-1}\Psi_2]\\ + a_3(\Psi_3 - \tfrac{1}{3}\sqrt{2}\Psi_5) + a_4(\Psi_4 - \tfrac{2}{3}\Psi_5).\end{aligned}$$

Thus the linearly independent states are

$$\begin{aligned}|(p^2); 4{,}4\rangle_1 &= \tfrac{1}{3}(2\sqrt{2}\Psi_1 - \Psi_2),\\ |(d^2)(p^2);\rangle_2' &= (1/\sqrt{11})(3\Psi_3 - \sqrt{2}\Psi_5),\\ |(d^2)(p^2); 4{,}4\rangle_3' &= (1/\sqrt{13})(3\Psi_4 - 2\Psi_5).\end{aligned}$$

The first of these states in orthogonal to the remaining two. Schmidt orthogonalization of the last two leads to

$$\begin{aligned}|(d^2)(p^2); 4{,}4\rangle_2 &= (1/\sqrt{11})(3\Psi_3 - \sqrt{2}\Psi_5),\\ |(d^2)(p^2); 4{,}4\rangle_3 &= (1/\sqrt{165})(2\sqrt{2}\Psi_3 - 11\Psi_4 + 6\Psi_5).\end{aligned}$$

The procedure outlined in this section is relatively simple and can be implemented as a computer program. The only problem occurs with multiply occurring $D^{(k)}$ in $\langle\lambda\rangle$. This, however, is a problem faced by the other approaches also (Patera and Sharp, 1972; Harter and Patterson, 1976a).

E. Subduction Coefficients

In this section, so far, we have treated an N-electron system in a spin state S as a composite one. Sometimes it will be advantageous to consider an N-electron system as being composed of subsystems of N_1, N_2 particles ($N_1 + N_2 = N$) in well-defined spin states S_1 and S_2 ($|S_1 - S_2| \leq S \leq S_1 + S_2$). A number of applications of this factorization of a system have been considered by Kaplan (1974), Gerratt (1971), and Patterson *et al.* (1979). The group theoretical techniques involve essentially a subgroup adaptation of the basis spanning an irrep $\langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-S}\rangle$ of $U(n)$ to the product irreps of $U(n_1) \otimes U(n_2)$ where $n_1 + n_2 = n$. Using spin-coupling algebras, Patterson and Harter (1979) were able to obtain the transformation coefficients for the restriction $U(n) \downarrow U(n_1) \otimes U(n_2)$ using recursive formulas. The procedure could become quite tedious for general cases. We now discuss an alternative approach to the problem (Sarma and Dinesha, 1979b), which essentially involves the Wigner operators of the subgroups S_{N_1} and S_{N_2} of S_N.

Let the one-electron basis for the first N_1 electrons be

$$V_{n_1}\colon \quad \{\phi_1, \phi_2, \ldots, \phi_{n_1}\}, \tag{74}$$

and for the last N_2 electrons be

$$V_{n_2}: \quad \{\psi_1, \psi_2, \ldots, \psi_{n_2}\}, \tag{75}$$

so that the one-electron space for the composite system is $V_{n_1} \oplus V_{n_2}$. As discussed earlier, we obtain the reducible tensor space subsystems as [c.f. Eq. (47)]:

$$\begin{aligned} V_{n_1}\otimes^{N_1}: \quad \{\Psi_{(p)}^{(N_1)} = {} & \psi_{i_1}(1)\psi_{i_1}\psi_{i_2}(3)\psi_{i_2}(4) \\ & \cdots \psi_{i_p}(2p-1)\psi_{i_p}(2p) \\ & \times \psi_{i_{p+1}}(2p+1)\cdots \psi_{i_{N_1-p}}(N) \\ & \times |i_1 < i_2 \cdots < i_p\,;\, i_{p+1} < i_{p+2} \cdots < i_{N_1-p}\}, \end{aligned} \tag{76}$$

$$\begin{aligned} V_{n_2}\otimes^{N_2}: \quad \{\varphi_{(q)}^{(N_2)} = {} & \phi_{j_1}(N_1+1)\phi_{j_1}(N_1+2) \\ & \cdots \phi_{j_q}(N_1+2q-1) \\ & \times \phi_{j_q}(N_1+2q)\phi_{j_{q+1}}(N_1+2q+1) \\ & \cdots \phi_{j_{N_2-q}}|j_1 > j_2 < \cdots \\ & < j_q\,;\, j_{q+1} < j_{q+2} < \cdots < j_{N_2-q}\}, \end{aligned} \tag{77}$$

where p and q are the number of doubly occupied orbitals in the monomials $\Psi_{(p)}^{(N_1)}$ and $\varphi_{(q)}^{(N_2)}$, respectively. For the sake of convenience, henceforth we will write $\Psi^{(N_1)}$ for $\Psi_{(p)}^{(N_1)}$ and $\varphi^{(N_2)}$ for $\varphi_{(q)}^{(N_2)}$. The antisymmetrized functions for the first and second systems can be respectively written as:

$$\Psi_{\rho_1}{}^{N_1,S_1} = \mathscr{A}_1\{\Psi^{(N_1)}\Theta_{\bar{\rho}_1}{}^{\bar{\lambda}_1,N_1}\}, \tag{78}$$

$$\Psi_{\rho_2}{}^{N_2,S_2} = \mathscr{A}_2\{\varphi^{(N_2)}\Theta_{\bar{\rho}_2}{}^{\bar{\lambda}_2,N_2}\}, \tag{79}$$

where $\mathscr{A}_1$ and $\mathscr{A}_2$ are the antisymmetrizers for the first N_1 and the last N_2 electrons and $\Theta_{\bar{\rho}_1}{}^{\lambda_1,N_1}$ and $\Theta_{\bar{\rho}_2}{}^{\lambda_2,N_2}$ are spin eigenfunctions with $[\bar{\lambda}_1] = [(N_1/2) + S_1,\ (N_1/2) - S_1]$ and $[\bar{\lambda}_2] = [(N_2/2) + S_2,\ (N_2/2) - S_2]$, respectively. Using arguments similar to those leading to Eq. (15) from Eq. (7) we have,

$$\Psi_{\rho_1}{}^{N_1,S_1} = \sum_{m_1=1}^{f_{s_1}{}^{N_2}} (e_{m_1\rho_1}{}^{[\lambda_1]}\Psi^{(N_1)})(\Theta_{m_1}{}^{[\bar{\lambda}_1],N_1}), \tag{80}$$

$$\Phi_{\rho_2}{}^{N_2,S_2} = \sum_{m_2=1}^{f_{s_2}{}^{N_2}} (e_{m_2\rho_2}{}^{[\lambda_2]}\varphi^{(N_2)})(\Theta_{m_2}{}^{[\bar{\lambda}_2],N_2}), \tag{81}$$

where $[\lambda_1] = [2^{N_1/2-S_1}, 1^{2S_1}]$ and $[\lambda_2] = [2^{N_2/2-S_2}, 1^{2S_2}]$. The antisymmetrized N-electron wave function can be written as

$$\Psi_{\rho_1,\rho_2}{}^{(N)} = \mathscr{A}(\Psi_{\rho_1}{}^{N_1,S_1}\Phi_{\rho_2}{}^{N_2,S_2}), \tag{82}$$

where $\mathscr{A}$ is the N-electron antisymmetrizer. Using Eqs. (80) and (81), this can be written as

$$\begin{aligned}\Psi_{\rho_1\rho_2}{}^{(N)} = \sum_{m_1,m_2} &\mathscr{A}\{(e^{[\lambda_1]}{}_{m_1\rho_1}\Psi^{(N_1)}e^{[\lambda_2]}{}_{m_2\rho_2}\varphi^{(N_2)}) \\ &\times (\Theta_{m_1}{}^{[\bar\lambda_1],N_1}\Theta_{m_2}{}^{[\bar\lambda_2],N_2})\}.\end{aligned} \tag{83}$$

Now the product $\Theta_{m_1}{}^{[\bar\lambda_1],N_1}\Theta_{m_2}{}^{[\bar\lambda_2],N_2}$ can be expressed as linear combinations of spin eigenfunctions corresponding to the N-electron system (Gerratt, 1971) using vector coupling coefficients as

$$\begin{aligned}&\Theta_{m_1}{}^{[\bar\lambda_1],N_1}\Theta_{m_2}{}^{\bar\lambda_2,N_2} \\ &\quad = \sum_{[\lambda]'}^{f_N^{\lambda}} \sum_{\rho=1}^{f_N^{\lambda}} \langle\bar\lambda'\rho|\bar\lambda_1 m_1;\, \bar\lambda_2 m_2\rangle\Theta_\rho{}^{[\lambda]',N}\end{aligned} \tag{84}$$

where the irrep $[\bar\lambda]' \equiv [N/2 + S', N/2 - S']$ of S_N corresponding to the spin state S' (the allowed S' values are given by $S_1 - S_2 \leq S' \leq S_1 + S_2$) of the composite N-electron system. Substituting Eq. (84) in Eq. (83) we obtain,

$$\begin{aligned}\Psi^{(N)}{}_{\rho_1\rho_2} = \sum_{[\lambda]'} \sum_{\rho=1}^{f_N^{\lambda'}} \sum_{m_1,m_2} &\langle\bar\lambda'\rho|\bar\lambda_1 m_1;\, \bar\lambda_2 m_2\rangle \\ \times\, &\mathscr{A}\{e^{[\lambda_1]}{}_{m_1\rho_1}\Psi^{(N_1)}e^{[\lambda_2]}{}_{m_2\rho_2}\varphi^{(N_2)})\Theta_\rho{}^{[\bar\lambda]',N}\}.\end{aligned} \tag{85}$$

From Eq. (85) it is clear that the wave function $\Psi^{(N)}{}_{\rho_1\rho_2}$ is a function which is an admixture of various spin states. Since the composite N-electron system is in a definite spin state S, we choose only the part belonging to this spin state from Eq. (85) and write it symbolically as $[\lambda] \downarrow \Psi_{\rho_1\rho_2}{}^{(N)}$. Using arguments given to obtain Eq. (15) from Eq. (7) we have,

$$\begin{aligned}[\lambda] \downarrow \Psi_{\rho_1\rho_2}{}^{(N)} = \sum_{\rho=1}^{f_N^{\lambda}} \sum_{m_1,m_2} &\langle\bar\lambda\rho|\bar\lambda_1 m_1;\, \bar\lambda_2 m_2\rangle \\ &\times \sum_{m=1}^{f_N^{\lambda}} \{e^{[\lambda]}{}_{m\rho}e_{m_1\rho_1}{}^{[\lambda_1]}e_{m_2\rho_2}{}^{[\lambda_2],(N_1)}\varphi^{(N_2)}\} \\ &\times \Theta_m{}^{[\bar\lambda],N}.\end{aligned} \tag{86}$$

The matrix elements of the Hamiltonian between two such functions are given by

$$
\begin{aligned}
&\langle[\lambda]\downarrow\Psi_{\rho'_1\rho'_2}{}'^{(N)}|H|[\lambda]\downarrow\Psi_{\rho_1\rho_2}{}^{(N)}\rangle \\
&\quad=\sum_{\rho',\rho}\ \sum_{\substack{m_1,m_2\\ m_{1'},m_{2'}}}\langle\lambda\rho|\lambda_1m_1;\ \lambda_2m_2\rangle \\
&\qquad\times\ \langle\lambda\rho'|\lambda_1m'_1;\ \lambda_2m'_2\rangle \\
&\qquad\times\ \langle e^{[\lambda]}{}_{1\rho}e^{[\lambda_1]}{}_{m'_1\rho'_1}e^{[\lambda_2]}{}_{m'_2\rho'_2}\Psi'^{(N_1)}\varphi'^{(N_2)}| \\
&\qquad\times\ |H|e^{[\lambda]}{}_{1\rho}e^{[\lambda_1]}{}_{m_1\rho_1}e^{[\lambda_2]}{}_{m'_2\rho'_2}\Psi^{(N_1)}\varphi^{(N_2)}\rangle.
\end{aligned}
\tag{87}
$$

Now the problem is reduced to that of finding the matrix elements of the Hamiltonian between functions of the type $e^{[\lambda]}{}_{1\rho}e^{[\lambda_1]}{}_{m_1\rho_1}e^{[\lambda_2]}{}_{m_2\rho_2}$-$\Psi^{(N_1)}\varphi^{(N_2)}$. If we can express these functions as linear combinations of functions of the type $e^{[\lambda]}{}_{1k}\Psi^{(N)}$, then using the procedures described in section III,C, we can evaluate the matrix element of the Hamiltonian. For this purpose we note that $e^{[\lambda_1]}{}_{m_1\rho_1}e^{[\lambda_2]}{}_{m_2\rho_2}$ is an element of the group algebra of the permutation group S_N and hence it can be expressed as a linear combination of the projection operators $e^{[\lambda]}{}_{k_1k_2}$ of S_N (Boerner, 1968). Hence,

$$
e^{[\lambda_1]}{}_{m_1\rho_1}e^{[\lambda_2]}{}_{m_2\rho_2}=\sum_{\lambda'}\sum_{u,v}K\begin{pmatrix}\lambda_1 & \lambda_2 & \lambda'\\ m_1\rho_1 & m_2\rho_2 & uv\end{pmatrix}e^{[\lambda']}{}_{uv},
\tag{88}
$$

where

$$
K\begin{pmatrix}\lambda_1 & \lambda_2 & \lambda'\\ m_1\rho_1 & m_2\rho_2 & uv\end{pmatrix}
$$

are known constants. Now using Eq. (17),

$$
\begin{aligned}
&e^{[\lambda]}{}_{m\rho}e^{[\lambda_1]}{}_{m_1\rho_1}e^{[\lambda_2]}{}_{m_2\rho_2}\\
&\quad=\sum_{v}K\begin{pmatrix}\lambda_1 & \lambda_2 & \lambda\\ m_1\rho_1 & m_2\rho_2 & \rho v\end{pmatrix}e^{[\lambda]}{}_{mv},
\end{aligned}
\tag{89}
$$

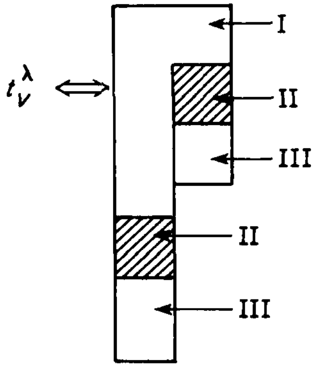
It has been shown (Sarma and Dinesha, 1979b) that the coefficients K in Eq. (89) can be expressed as a product of two factors as

$$
\begin{aligned}
&K\begin{pmatrix}\lambda_1 & \lambda_2 & \lambda\\ m_1\rho_1 & m_2\rho_2 & \rho v\end{pmatrix}\\
&\quad=[\lambda\rho\colon\ \lambda_1m_1,\ \lambda_2m_2]\\
&\qquad\times[\lambda_1\rho_1,\ \lambda_2\rho_2\colon\ \lambda v].
\end{aligned}
\tag{90}
$$

Hence,

$$\begin{aligned}
e^{[\lambda]}{}_{m\rho}e^{[\lambda_1]}{}_{m_1\rho_1}e^{[\lambda_2]}{}_{m_2\rho_2}\Psi^{(N_1)}\varphi^{(N_2)} &\equiv [\lambda\rho;\ \lambda_1 m_1,\ \lambda_2 m_2]\\
&\quad\times \sum_v [\lambda_1\rho_1,\ \lambda_2\rho_2;\ \lambda v]\\
&\quad\times e^{[\lambda]}{}_{mv}\Psi^{(N_1)}\varphi^{(N_2)}.
\end{aligned}\tag{91}$$

The above transformation implies that the subgroup adapted wavefunction, except to within a multiplicative constant is independent of the indices m_1, m_2, and m. Hence we can absorb this in the as yet undetermined constant $[\lambda_1\rho_1,\ \lambda_2\rho_2\text{: } \lambda v]$. Let us first find the allowed tableaux v's in the right-hand side of Eq. (91). We note that the first N_1 entries in t_v form an SYT for S_{N_1}. For nonzero coefficients $[\lambda_1\rho_1,\ \lambda_2\rho_2\text{: } \lambda v]$, we find that the SYT formed by the first N_1 entries of t_v^λ should be identical to that of $t^\lambda_{\rho_1}$. Also, since there are q doubly occupied orbitals in $\varphi^{(N_2)}$, for nonzero S_1 the entries $(N_1 + 1,\ N_1 + 2)$, $(N_1 + 3,\ N_1 + 4)$, . . . , $(N_1 + 2q - 1,\ N_1 + 2q)$ of t_v^λ should necessarily be in axial positions. The general structure of the tableau t_v^λ should necessarily be in axial positions. The general structure of the tableau t_v^λ is shown below.



(92)

The entries (1,2, . . . , N_1) occur in region I. The entries $(N_1 + 1,\ N_1 + 2)$, $(N_1 + 3,\ N_1 + 4)$, . . . , $(N_1 + 2q - 1,\ N + 2q)$ occur in region II, and the entries from $N_1 + 2q + 1$ to $N_1 + N_2 (= N)$ occur in region III. In region II the entry $(N_1 + 2K)$ or $(N_1 + 2K - 1)$ can be in the second column. There are 2^q such SYTs. These 2^q projections $e^{[\lambda]}_{mv}\Psi^{(N_1)}\varphi^{(N_2)}$ are related to each other. For convenience let us define the SYT with second-column entries $(N_1 + 1,\ N_1 + 3,\ .\ .\ .\ ,\ N_1 + 2q - 1)$ as $t^\lambda_{v(0)}$ and an SYT which is obtained by applying j transpositions of the type $(N_1 + 2K - 1,\ N_1 + 2K)$ $(K \le q)$ as $t^\lambda_{v(j)}$. Then it can be easily shown that

$$e^{[\lambda]}_{mv(j)}\Psi^{(N_1)}\varphi^{(N_2)} = [(S_1 + 1)/S_1)]^{j/2}\, e^{[\lambda]}_{mv(0)}\Psi^{(N_1)}\varphi^{(N_2)}. \tag{93}$$

This relation is true for all the ${}^{q}C_j$ ($j = 0, \ldots, q$) tableaux of the above type so that we obtain the normalized state as

$$e^{[\lambda]}{}_{m\bar{v}}\Psi^{(N_1)}\varphi^{(N_2)} = [S_1/(2S_1 + 1)]^{q/2} \times \sum_{j=0}^{q}[(1 + S_1)/S_1]^{j/2} \times e^{[\lambda]}{}_{mv(j)}\Psi^{(N_1)}\varphi^{(N_2)}, \tag{94}$$

where $e^{[\lambda]}{}_{mv(j)}\Psi^{(N_1)}\varphi^{(N_2)}$ is a totally symmetric sum of the ${}^{q}C_j$ states of a given type. By construction, we find that the state defined by the left-hand side of Eq. (94) is invariant under all products of right transpositions $(N_1 + 2K,\ N_1 + 2K - 1)$, $(k = 1, \ldots, q)$ on $e^{[\lambda]}{}_{m\bar{v}}$. The set of such states with distinct indices $\bar{v}$ are linearly independent and form a basis for the irrep $\langle\lambda\rangle \equiv \langle 2^{N/2-S}, 1^{2S}, 0^{n-N/2-2S}\rangle$ of $U(n)$. It is also clear that each $e^{[\lambda]}{}_{mv}\Psi^{(N_1)}\varphi^{(N_2)}$ is proportional to the corresponding $e^{[\lambda]}{}_{m\bar{v}}\Psi^{(N_1)}\varphi^{(N_2)}$. Using this we can rewrite Eq. (91) as,

$$e^{[\lambda]}{}_{m\rho}e^{[\lambda_1]}{}_{m_1\rho_1}e^{[\lambda_2]}{}_{m_2\rho_2}\Psi^{(N_1)}\varphi^{(N_2)} = \sum_{v}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{v} & \rho_1 & \rho_2\end{bmatrix} e^{[\lambda]}{}_{m\bar{v}}\Psi^{(N_1)}\varphi^{(N_2)} \tag{95}$$

The overall multiplicative constant $[\lambda m;\ \lambda_1 m_1,\ \lambda_2 m_2]$ is absorbed in the coefficient

$$\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \rho & \rho_1 & \rho_2\end{bmatrix}.$$

The coefficients

$$\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \rho & \rho_1 & \rho_2\end{bmatrix}$$

are the "subduction coefficients" and the matrix of subduction coefficients is orthogonal (Patterson and Harter, 1979; Sarma and Dinesha, 1979b) i.e.,

$$\sum_{v}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{v} & v_1 & v_2\end{bmatrix}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{v} & v_1' & v_2'\end{bmatrix} = \delta_{v_1v_1}\,\delta_{v_2v_2}, \tag{96}$$

$$\sum_{v_1,v_2} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & v_1 & v_2 \end{bmatrix} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & v_1 & v_2 \end{bmatrix} = \delta_{v,v'} \tag{97}$$

As an illustration of the procedure to determine the subduction coefficients, let us consider a 13-electron system divided into subsystems of 4 and 9 electrons. Let $\lambda = [2^6,1]$, $[\lambda_1] = [2,1^2]$, and $[\lambda_2] = [2^3,1^3]$. Let

$$\begin{aligned} \Psi^{(N_1)} \equiv \Psi^{(4)} &= \psi_1(1)\psi_1(2)\psi_2(3)\psi_3(4) \\ \varphi^{(N_2)} \equiv \varphi^{(9)} &= \phi_1(5)\phi_1(6)\phi_2(7)\phi_2(8)\phi_3(9)\phi_4(10)\phi_5(11)\phi_6(12)\phi_7(13)\,. \end{aligned}$$

Then,

$$t_1^{\lambda_2} = \begin{array}{|cc|} \hline 5 & 6 \\ 7 & 8 \\ 9 & 10 \\ \cline{2-2} \multicolumn{1}{|c|}{11} & \\ \multicolumn{1}{|c|}{12} & \\ \multicolumn{1}{|c|}{13} & \\ \cline{1-1} \end{array} \tag{98}$$

The allowed $t_{\bar{v}}^{[2^6,1]}$ are,

$$\begin{aligned} t_{\bar{1}}^{\lambda} &= (2,\bar{5},\bar{7},9,11,13), \\ t_{\bar{3}}^{\lambda} &= (2,\bar{5},\bar{7},10,11,12), \\ t_{\bar{5}}^{\lambda} &= (2,\bar{5},\bar{7},10,12,13). \\ t_{\bar{2}}^{\lambda} &= (2,\bar{5},\bar{7},9,11,12), \\ t_{\bar{4}}^{\lambda} &= (2,\bar{5},\bar{7},9,12,13), \\ t_{\bar{6}}^{\lambda} &= (2,\bar{5},\bar{7},10,11,13). \end{aligned}$$

Let us try to relate all

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & v_1 & 1 \end{bmatrix}$$

to the coefficient

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{1} & v_1 & 1 \end{bmatrix}$$

We note that $t_{\bar{1}}^{\lambda}$ and $t_{\bar{2}}^{\lambda}$ are related by the transposition (12,13). From Eq. (98) we see that the tableau $t_1^{\lambda_2}$ is antisymmetric under (12,13).

Hence, from Eq. (95),

$$\begin{aligned}
&e^{[\lambda]}{}_{m\rho}e^{[\lambda_1]}{}_{m_1\rho_1}e^{[\lambda_2]}{}_{m_2 1}\Psi^{(4)}\varphi^{(9)}\\
&\quad = -e^{[\lambda]}{}_{m\rho}e^{[\lambda_1]}{}_{m_1\rho_1}e^{[\lambda_2]}{}_{m_2 1}(12,13)\Psi^{(4)}\varphi^{(9)}\\
&\quad = -\sum_{v}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{v} & \rho_1 & 1\end{bmatrix} e^{[\lambda]}{}_{m\bar{v}}(12,13)\Psi^{(4)}\varphi^{(9)},
\end{aligned}$$

i.e.,

$$\begin{aligned}
&\sum_{\bar{v}}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{v} & \rho_1 & 1\end{bmatrix} e^{[\lambda]}{}_{m\bar{v}}\Psi^{(4)}\varphi^{(9)}\\
&\quad = -\sum_{\bar{v}}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{v} & \rho_1 & 1\end{bmatrix} (12,13)\Psi^{(4)}\varphi^{(9)}. \qquad (99)
\end{aligned}$$

Now,

$$\begin{aligned}
e^{[\lambda]}{}_{m\bar{1}}(12,13) &= -\tfrac{1}{2}e^{[\lambda]}{}_{m\bar{1}} + \tfrac{1}{2}\sqrt{3}e^{[\lambda]}{}_{m\bar{2}},\\
e^{[\lambda]}{}_{m\bar{2}}(12,13) &= \tfrac{1}{2}\sqrt{3}e^{[\lambda]}{}_{m\bar{1}} + \tfrac{1}{2}e^{[\lambda]}{}_{m\bar{2}}, \text{ etc.}
\end{aligned}$$

Substituting these results in Eq. (99) and comparing the coefficients of $e^{[\lambda]}{}_{m\bar{v}}\Psi^{(4)}\varphi^{(9)}$ on both sides, we get

$$\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{1} & \rho_1 & 1\end{bmatrix} = +\frac{1}{2}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{1} & \rho_1 & 1\end{bmatrix} - \frac{\sqrt{3}}{2}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{2} & \rho_1 & 1\end{bmatrix},$$

$$\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{4} & \rho_1 & 1\end{bmatrix} = +\frac{1}{2}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{4} & \rho_1 & 1\end{bmatrix} - \frac{\sqrt{3}}{2}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{5} & \rho_1 & 1\end{bmatrix},$$

this implies

$$\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{2} & \rho_1 & 1\end{bmatrix} = -\frac{1}{\sqrt{3}}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{1} & \rho_1 & 1\end{bmatrix},$$

$$\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{5} & \rho_1 & 1\end{bmatrix} = -\frac{1}{\sqrt{3}}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{4} & \rho_1 & 1\end{bmatrix}.$$

Similarly, use of transposition (11,12) gives

$$\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{2} & \rho_1 & 1\end{bmatrix} = -\frac{1}{\sqrt{2}}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{3} & \rho_1 & 1\end{bmatrix},$$

$$\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{5} & \rho_1 & 1\end{bmatrix} = -\sqrt{2}\begin{bmatrix}\lambda & \lambda_1 & \lambda_2\\ \bar{6} & \rho_1 & 1\end{bmatrix},$$

and use of transposition (9,10) gives

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{4} & \rho_1 & 1 \end{bmatrix} = \sqrt{2} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{1} & \rho_1 & 1 \end{bmatrix},$$

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{5} & \rho_1 & 1 \end{bmatrix} = \sqrt{2} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{2} & \rho_1 & 1 \end{bmatrix},$$

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{6} & \rho_1 & 1 \end{bmatrix} = \sqrt{2} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{3} & \rho_1 & 1 \end{bmatrix}.$$

From the above relations we easily obtain

$$\begin{aligned} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{1} & \rho_1 & 1 \end{bmatrix} &= -\sqrt{3} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{2} & \rho_1 & 1 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{4} & \rho_1 & 1 \end{bmatrix} \\ &= -\frac{\sqrt{3}}{2} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{5} & \rho_1 & 1 \end{bmatrix} = \sqrt{3} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{6} & \rho_1 & 1 \end{bmatrix}. \end{aligned} \tag{100}$$

Using the normalization condition

$$\sum_{\bar{v}} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & 1 \end{bmatrix}^2 = 1,$$

we get

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{1} & \rho_1 & 1 \end{bmatrix} = \frac{\sqrt{2}}{3}.$$

The other coefficients are obtained using Eq. (100).

In the above example, we note that we have used only those elementary transpositions which leave the tableau $t_{\bar{1}}^{\lambda_2}$ invariant or at most change its sign. This is a general result. The elementary transpositions which leave $t_{\bar{1}}^{\lambda_2}$ invariant (or change its sign) and the normalization conditions are sufficient to determine the coefficients

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & 1 \end{bmatrix}.$$

A closed expression for these coefficients has been obtained. We will just state the final result. For this purpose we note that the entries in allowed $t_{\bar{v}}^{\lambda}$ tableaux differ only in the boxes of region III [cf. Eq. (92)] and, further, these entries are integers from $N_1 + 2q + 1$ to $N_1 + N_2$ $(=N)$.

Let us divide this set into two sets, viz., $\bar{K}_1 \equiv \{N_1 + 2q + 1, \ldots, N - 2S_2 - 1\}$ and $\bar{K}_2: \{N - 2S_2, N - 2S_2 + 1, \ldots, N\}$. Let us take the tableau with $(N_1 + 2q + 1, N + 2q + 3, \ldots, N - 2S_2 - 3, N - 2S_2 - 1, N - 2S_2 + 1, N - 2S_2 + 2, \ldots, N + S_1 - S_2 - 5)$ as the second-column entries in region III [cf. Eq. (92)] as reference tableau $t^{\lambda}{}_{\bar{v}^{(0)}}$. We note that for any general tableau $\bar{v}$, the second-column entries in region III are such that the first $(N_2/2 - S_2 - q)$ entries are from the set $\bar{K}_1$ and the rest of $(S_1 + S_2 - S)$ entries are from the set $\bar{K}_2$. Let these entries be $(K_1, K_2, \ldots, K_{N/2-S_2-q})$ and $(L_1, L_2, \ldots, L_{S_1+S_2-S})$, respectively, for the tableau $\bar{v}$ and corresponding entries for the reference tableau $\bar{v}^{(0)}$ be $(K_1^0, K_2^0, \ldots, K_{N/2-S_2-q}^0)$ and $(L_1^0, L_2^0, \ldots, L_{S_1+S_2-S}^0)$. Let $K = \Sigma_{i=1}{}^{N/2-S-q}(K_i - K_i^0)$ and $\{l_i = L_i - L_i^0 | i = 1, \ldots, S_1 + S_2 - S\}$. Then the coefficient

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & 1 \end{bmatrix}$$

is related to

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v}^{(0)} & \rho_1 & 1 \end{bmatrix}$$

by (Sarma and Dinesha, 1979b),

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & 1 \end{bmatrix} = (-1)^{\sum_{i=1}^{S_1+S_2-S} l_i} \prod_{i=1}^{S_1S_2-S} \left\{ \frac{(d' + i)(d' + i + 1)}{(d' + l_{i'} + i)(d' + l_{i'} + i + 1)} \right\}^{1/2} \times \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v}^{(0)} & \rho_1 & 1 \end{bmatrix}, \tag{101}$$

where $i' = S_1 + S_2 - S - i + 1$. After obtaining the coefficients

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & \rho_2 \end{bmatrix},$$

using Eq. (101) we can successively determine all other coefficients corresponding to

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & \rho_2 \end{bmatrix}$$

by noting that all other SYTs $t^{\lambda_2}_{\rho_2}$ can be generated from $t_2^{\lambda_2}$ using elementary transpositions. As an illustration let us try to obtain the coefficients

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & 1 \end{bmatrix},$$

where $t_2^{\lambda_2} = (6,8,11)$, and $t_2^{\lambda_2} = (10,11)t_1^{\lambda_2}$. For this case we note that in addition to the six tableaux three more tableaux will have nonzero coefficients. The three additional tableaux are $t_{\bar{7}}^{\lambda_2} = (2,\bar{5},\bar{7},9,10,12)$, $t_{\bar{8}}^{\lambda_2} = (2,\bar{5},\bar{7},9,10,13)$, and $t_{\bar{9}}^{\lambda_2} = (2,\bar{5},\bar{7},9,10,12)$. Now, noting that $e_{m_21}^{[\lambda_2]}(10,11) = -\frac{1}{2}e_{m_21}^{[\lambda_2]} + \frac{1}{2}\sqrt{3}e_{m_22}^{[\lambda_2]}$, we get

$$\begin{aligned} &e_{m\rho}^{[\lambda]} e_{m_1\rho_1}^{[\lambda_1]} e_{m_2}^{[\lambda_2]}(10,11)\Psi^{(4)}\varphi^{(9)} \\ &\quad = -\tfrac{1}{2}e_{m\rho}^{[\lambda]} e_{m_1\rho_1}^{[\lambda_1]} e_{m_21}^{[\lambda_2]}\Psi^{(4)}\varphi^{(9)} + \tfrac{1}{2}\sqrt{3}e_{m\rho}^{[\lambda]} e_{m_1\rho_1}^{[\lambda_1]} e_{m_22}^{[\lambda_2]}\Psi^{(4)}\varphi^{(9)}. \end{aligned} \tag{102}$$

From the procedure described for determining the coefficients

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & 1 \end{bmatrix},$$

it is clear that these coefficients are same whether the monomial is $\Psi^{(4)}\varphi^{(9)}$ or $(10,11)\Psi^{(4)}\varphi^{(9)}$. Hence,

$$\begin{aligned} &e_{m\rho}^{[\lambda]} e_{m_1\rho_1}^{[\lambda_1]} e_{m_21}^{[\lambda_2]}(10,11)\Psi^{(4)}\varphi^{(9)} \\ &\quad = \sum_{\bar{v}=1}^{6} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & 1 \end{bmatrix} e_{m\bar{v}}{}^{[\lambda]}(10,11)\Psi^{(4)}\varphi^{(9)} \\ &\quad = \sum_{\bar{v}} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & 1 \end{bmatrix} \{(\varepsilon_{\bar{v}}/d_{\bar{v}})e_{m\bar{v}}{}^{[\lambda]} \\ &\qquad + [1 - (d_{\bar{v}}^2)^{-1}]^{1/2}e^{[\lambda]}{}_{m\bar{v}'}\}\Psi^{(4)}\varphi^{(9)} \end{aligned} \tag{103}$$

where $d_{\bar{v}}$ is the axial distance between 10 and 11 in the tableau $t_{\bar{v}}^{\lambda}$, and $\varepsilon_{\bar{v}} = +1$ if 11 is in second column and $= -1$ if 10 is in second column of $\bar{v}$. $\bar{v}'$ is the standard tableau obtained from $\bar{v}$ by interchanging 10 and 11 (if $\bar{v}'$ does not exist then $d_{\bar{v}} = \pm 1$ and the term will not be present). By equating the right-hand side of Eqs. (102) and (103) and by equating the coefficients of $e_{m\bar{v}}{}^{[\lambda]}$ from the resulting equation we can easily express

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & 2 \end{bmatrix}$$

in terms of

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & 1 \end{bmatrix}.$$

In this manner we can obtain all the coefficients

$$\begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & \rho_2 \end{bmatrix}$$

that occur in Eq. (95) using just elementary transpositions and normalization conditions. But, in Eq. (95) the monomial $\Psi^{(N_1)}\varphi^{(N_2)}$ is not in the standard ordering. The doubly occupied orbitals of $\varphi^{(N_2)}$ occur between singly occupied orbitals of $\Psi^{(N_1)}$ and $\varphi^{(N_2)}$. However, using Eq. (47) we can shift all the doubly occupied orbitals to the extreme left by inserting just a phase factor. Using this result Eq. (95) can be written as,

$$e^{[\lambda]}_{m\rho} e^{[\lambda_1]}_{m_1\rho_1} e^{[\lambda_2]}_{m_2\rho_2} \Psi^{(N_1)}\varphi^{(N_2)} = (-1)^{\sum_i \varepsilon_i} \sum_{\bar{v}} \begin{bmatrix} \lambda & \lambda_1 & \lambda_2 \\ \bar{v} & \rho_1 & \rho_2 \end{bmatrix} e^{[\lambda]}_{mv'} (\Psi\varphi)^N \tag{104}$$

where the quantities ε_i and the SYT $t^{\lambda}_{v'}$ are defined in Eq. (47) and $(\Psi\varphi)^N$ is the monomial obtained from $\Psi^{(N_1)}\varphi^{(N_2)}$ by arranging all the doubly occupied orbitals to the extreme left and the singly occupied orbitals with increasing orbital indices. Substituting Eq. (104) in Eq. (87), we find that the matrix elements of the Hamiltonian between the subsystem adapted wave functions can be obtained in terms of the matrix elements of the Hamiltonian between wave functions of the type $e^{[\lambda]}_{mv'}$. The procedures described in the previous section can be used for this purpose.

IV. Conclusion

The present article has been devoted entirely to the study of the many-electron systems using tensor bases for the irreps of the unitary group. Various ways of enumerating the basis states of the unitary group have been discussed. Procedures for calculation of CI matrix elements have been described. The discussion of the basis states of irreps of $U(n)$ is general enough so as to be easily extendable to any many-fermion system, although applications have been restricted to the study of many-electron systems. Much of the procedure outlined has been computerized. The construction of angular momentum states for multishell configurations of electron in atoms, described in this article, could equally well be used for isospin-free nuclear shell model studies in the *j–j* coupling scheme.

Generalization of these ideas to wave functions constructed from nonorthogonal single-particle states is straightforward and leads to the study of irreps of $GL(n)$. This study has been carried out using one-parameter alternant molecular orbital basis in a CI-calculation on some molecules by Sarma and Dinesha (1979a; also Dinesha, 1979). We have not discussed the details of this extension in the present article, since our primary aim was to consider the use of irreps of $U(n)$ in CI studies.

We have carried out preliminary studies in the direction of some of the generalizations mentioned above by obtaining viable algorithms for handling inner and outer products of the general irreps of the permutation group (Sahasrabudhe *et al.*, 1981; Sarma, 1981). The dualism (Robinson, 1961) between permutation and unitary groups should lead to simplifications for the subgroup reductions $U(n+m) \supset U(n) \otimes U(m)$ and $U(nm) \supset U(n) \otimes U(m)$ as pointed out by Bohr and Mottelson (1969). It should, however, be pointed out that the procedures outlined here could equally well have been carried through using the algebras of generators of $U(n)$ alone without any reference to the permutation group. Such procedures lead to algorithms developed by Paldus (1975) and Shavitt (1977, 1978). These latter deemphasize the orbital description of N-electron wave functions. It is for this reason that we have made extensive use of the permutation group.

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Feshbach Resonances in Chemical Reactions*

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I. Introduction

Resonances in molecular collisions have been theoretically investigated for over a decade. In several reviews, discussions are presented of both the physical interpretations and mathematical formalisms (Levine, 1970; Micha, 1972, 1974; Yamabe *et al.*, 1978). Computational results have appeared for compound-state rotational resonances in *nonreactive* atom–diatom collisions (Bernstein and Muckerman, 1970; Levine and Shapiro, 1970), for an atom–polyatomic collision, Ar + CH_4 (Smith *et al.*, 1979), and for compound-state vibrational resonances in a collinear atom–diatom collision, He + H_2^+ (Chapman and Hayes, 1975, 1976). Resonances in chemical *reactions* have also been reported in studies of the following reactions: H + H_2, 1D (collinear) (Levine and Wu, 1971); H + H_2, 2D and 3D (Schatz and Kuppermann, 1975; Walker *et al.*, 1978); F + H_2, 1D

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(Wu *et al.*, 1973; Schatz *et al.*, 1973; Connor *et al.*, 1975, 1978; Wyatt *et al.*, 1978); F + H_2, 3D (Redmon and Wyatt, 1979; Wyatt, 1980; McNutt and Wyatt, 1981); Cl + H_2, 1D (Baer, 1974); I + H_2, 1D (Chapman and Hayes, 1977); H + FH, 1D (Schatz and Kuppermann, 1980); I + HI, 1D (Kuppermann, 1981); and He + H_2^+, 1D (Kouri and Baer, 1974; Adams, 1975). In these examples, compound-state mechanisms have been suggested for the H + H_2 and I + H_2 reactions, while a shape resonance mechanism has been recently suggested to be important in the F + H_2 reaction (E. F. Hayes and R. B. Walker, private communication; Babamov and Kuppermann, 1981). The status of quantum reaction dynamics, including mention of resonances, has been discussed in several recent reviews (Connor, 1980; Walker and Light, 1981).

On the experimental side, resonances have been observed in atom–atom and atom–molecule nonreactive collisions (Grover *et al.*, 1977). In addition, a resonance effect has recently been observed in the F + H_2 reaction (Sparks *et al.*, 1979). The resonance appears as a sudden alteration in the angular distribution of the FH product as the collision energy is increased by only 1 kcal/mole. This effect is at least qualitatively in accord with results from recent quantum mechanical close-coupling calculations on the 3D reaction (Redmon and Wyatt, 1979).

There are many quantum mechanical approaches to the theory of resonances, including the following: Feshbach projection operator method (Feshbach, 1958); an integral equation formulation of Feshbach theory (Kouri and Sams, 1970, 1971); R-matrix theory (Lane and Thomas, 1958; Eu and Ross, 1966); the Siegert eigenvalue technique (Siegert, 1939; Isaacson *et al.*, 1978; Isaacson and Miller, 1979); the Fano "configuration interaction" method (Fano, 1961; Grabenstetter and Le Roy, 1979); the stabilization method (Taylor, 1970; Hazi and Taylor, 1970), the variational-wave operator method (Micha and Brändas, 1971), Stieltjes-moment techniques (Hazi, 1978); decoupling of the close-coupled equations (Levine, 1969; Muckerman, 1969; Bernstein *et al.*, 1969); and complex coordinate methods[1] (Lefèbvre, 1980). There has clearly been considerable theoretical and experimental interest in collisional resonance phenomena! In addition, the theory of collisional resonances is closely allied to theories of the decay of a prepared state, occurring, for example, in predissociation (Bandrauk and Laplante, 1976), autoionization (Bhatia, 1974), radiationless intramolecular decay (Jortner and Mukamel, 1974), unimolecular decomposition (Mies, 1969), and isomerization reactions (Matsen, 1978).

In this article, the Feshbach formalism (Feshbach, 1958, 1962, 1967)

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[1] See the whole issue of *Int. J. Quantum Chem.* 14, No. 4 (1978).

will be analyzed and developed in such a way as to facilitate its application to chemical reactions. The form and structure of the equations will be emphasized rather than the details of any particular reaction. This approach has pedagogic usefulness in introducing various methods for calculating resonance states and resonance parameters, Green functions, poles of the S-matrix, etc. Then, the Feshbach theory will be applied to a model reaction that has multiple open and multiple closed channels. Parameters in the model will be altered to illustrate the features of the formal theory and the qualitative nature of resonance phenomena. Numerical results for the model problem provide many useful insights into resonance phenomena that should carry over to more realistic and complicated examples.

In Section II the Feshbach formalism is utilized in a time-independent study of resonances in chemical reactions. In Section II,A, the basic theory is reviewed. The level operator, resonance states, and Siegert states are defined. Perturbative approximations to resonance states are developed, and a comparison is made between different definitions of resonance parameters. In Section II,B the equations are converted to a computationally oriented form for collinear reactions of the type $A + BA \rightarrow AB + A$. Methods are described for handling multiple open and multiple closed channels. Also, the Siegert resonance theory is presented in a way that unifies it with the Feshbach formalism. Then, in Section II,C a number of computational results are presented for a four-channel (two open plus two asymptotically closed) reactive scattering model. Resonance states and Siegert states are plotted and the dependence of resonance energies upon basis size, total energy, and coupling strength are described. Also, the energy dependence of transition probabilities and S-matrix elements (on Argand diagrams) are discussed. Then, in Section III a time-dependent study of the same model problem is presented. The relationship between the resonance parameters and the time delay (Smith, 1960) of the scattered wave packet is described first. Plots are then presented that show the time evolution of the translational wave functions during the reaction. In this way, excitation and decay of the resonant states in the collision complex are clearly depicted. Finally, a brief summary is presented in Section IV.

II. Time-Independent Resonance Theory

Resonances in chemical reactions can be understood through the analysis of solutions to the time-independent Schrödinger equation:

$$(E - H)\Psi = 0, \tag{1}$$

where H denotes the Hamiltonian of the complete collision system and Ψ represents the complete wave function. The term "resonances" is associated with highly energy-dependent solutions to Eq. (1). The Feshbach projection operator theory of resonances (Feshbach, 1958, 1962, 1967; Feshbach and Levin, 1973) is a method of analyzing solutions to Eq. (1) that provides an intuitive understanding of resonances and the associated strong energy dependence of the solutions. To establish notation and terminology, a formal development of the Feshbach theory will be presented. The formalism presented here represents a specialization of the original work.

A. Formal Feshbach Theory

Suppose we are interested in describing the reaction of a "structureless" atom with a target molecule, such as the collision of an atom with a diatomic molecule. In the absence of any interaction with the atom, the state of the isolated target molecule can be any of a number of different internal states, $\Phi_i(\mathbf{r})$, where $\mathbf{r}$ denotes the set of internal coordinates. For example, in the case of a diatomic molecule, Φ_i would represent the rotation–vibration state and $\mathbf{r}$ would denote the vibrational coordinate and two rotational coordinates. Suppose the atom is far removed from the target molecule so that it no longer interacts with the molecule. Then at any given total system energy, only a definite number of internal states of the reactant molecule are energetically accessible (assuming the set $\{\Phi_i\}$ has a discrete spectrum of eigenvalues). Those states are referred to as asymptotically open (reactant) channels. Likewise, all product states that are energetically accessible are referred to as asymptotically open (product) channels.

In applying the Feshbach projection operator theory, one selects an operator P, which projects out of the total wave function Ψ a part of it $P\Psi$ that corresponds to all reactant and product asymptotically open channels. (This definition of P does not determine a unique P. In Section II,B we shall specialize the discussion by choosing a particular projection operator appropriate for the discussion of a one-dimensional reactive collision.) It is not necessary that P contain all the open channels. For example, one may choose P such that it projects out only the elastic channel. However, we will limit the discussion to the case in which P contains all the open channels. The remaining part of Ψ that is not contained in $P\Psi$ is denoted $Q\Psi$; i.e., Q is the orthogonal complement of P and projects out of Ψ its component that corresponds to asymptotically closed channels. Mathematically speaking:

$$\Psi = P\Psi + Q\Psi = (P + Q)\Psi, \qquad P + Q = 1, \quad PQ = 0. \tag{2a}$$

Of course, P and Q also have the usual properties of projection operators:

$$P^2 = P, \qquad Q^2 = Q, \qquad P = P^{\dagger}, \qquad Q = Q^{\dagger}. \tag{2b}$$

Writing the wave function as a sum of its mutually orthogonal parts, Eq. (1) becomes

$$(E - H)(P\Psi + Q\Psi) = 0. \tag{3}$$

If one operates on this equation from the left first with P, then with Q, and makes the following definitions:

$$H_{PP} \equiv PHP, \qquad H_{QQ} \equiv QHQ, \qquad H_{PQ} \equiv PHQ, \qquad H_{QP} \equiv QHP, \tag{4}$$

then the wave equation can be written as a set of coupled equations:

$$(E - H_{PP})P\Psi = H_{PQ}Q\Psi, \tag{5a}$$

$$(E - H_{QQ})Q\Psi = H_{QP}P\Psi. \tag{5b}$$

The coupled equations (5) are entirely equivalent to the Schrödinger equation. However, they are more convenient for analyzing the role of resonances in collision processes because they explicitly separate the open (P part) and closed (Q part) channel components of the wave function. The separation of open and closed channel components of Ψ is quite natural since these components obey different asymptotic boundary conditions. Asymptotically $Q\Psi$ must vanish whereas $P\Psi$ does not. Prior to the collision, while the atom is far removed from the target molecule, the system is in a state contained in the P subspace by definition of P. As the collision occurs, the Q component of the wave function can be excited through the coupling H_{QP}. Excitation of $Q\Psi$ corresponds to the formation of a translationally bound intermediate. It is the excitation and deexcitation of the Q part of the wave function that gives rise to highly energy-dependent scattering, or "resonances." This type of resonance is referred to as an "internal excitation resonance" or a "Feshbach resonance."

In writing a formal solution to the coupled equations (5) there are two possible approaches. The first is to write a formal solution to Eq. (5b) and substitute into Eq. (5a) to obtain a single equation for $P\Psi$. The second and equivalent possibility is to write a formal solution to Eq. (5a) and substitute into Eq. (5b) to obtain a single equation for $Q\Psi$. We shall follow the second approach because it focuses on the Q part of the wave function, whose excitation corresponds to the formation of a long-lived intermediate. Following the second approach, the formal solution to Eq. (5a) is

$$P\Psi = \Psi^{0} + (E^{(+)} - H_{PP})^{-1}H_{PQ}Q\Psi. \tag{6}$$

Here Ψ^{o} is the solution to the corresponding homogeneous equation:

$$(E - H_{PP})\Psi^{o} = 0. \tag{7}$$

In other words, Ψ^{o} is the solution to the scattering problem in the absence of any coupling to the closed channels. Ψ^{o} contains both the incoming wave and outgoing waves in the open channels. The solution to Eq. (7) is usually only mildly energy-dependent and is not associated with resonant scattering.

In Eq. (6), E has been labeled with a (+) to indicate that $+ic$, $c \to 0^{+}$, has been added to E. This ensures the existence of the inverse operator $(E - H_{PP})^{-1}$, as well as guaranteeing that the second term of Eq. (6) gives rise to outgoing waves. The inverse operator of Eq. (6) is called the open-channel Green operator G_{PP}^{o+}:

$$G_{PP}^{o\pm} \equiv \lim_{c\to 0^{+}} (E \pm ic - H_{PP})^{-1}. \tag{8}$$

We shall henceforth omit the superscript + on G_{PP}^{o} except when explicitly needed. The superscript o is used to distinguish $(E - H_{PP})^{-1}$ from $P(E - H)^{-1}P$, which are not equivalent.

The formal solution (6) is substituted into Eq. (5b) and then rearranged to give an equation for $Q\Psi$ only:

$$(E - H_{QQ} - H_{QP}G_{PP}^{o}H_{PQ})Q\Psi = H_{QP}\Psi^{o}. \tag{9}$$

The form of Eq. (9) leads us to define an effective closed-channel Hamiltonian L_{QQ}:

$$L_{QQ}(E) \equiv H_{QQ} + H_{QP}G_{PP}^{o}(E)H_{PQ}. \tag{10}$$

The effective closed-channel Hamiltonian L_{QQ} is referred to as the *level operator* and the second term of Eq. (10) is the *level shift operator* R_{QQ}:

$$R_{QQ}(E) \equiv H_{QP}G_{PP}^{o}(E)H_{PQ}. \tag{11}$$

Note that L_{QQ} and R_{QQ} are energy-dependent and non-Hermitian due to the Green operator G_{PP}^{o}.

If Eq. (9) could be solved for $Q\Psi$, then Eq. (6) would give the corresponding solution for $P\Psi$, and thus the total wave function would be known. There are two possible approaches in solving Eq. (9) for $Q\Psi$. The first is to construct eigenfunctions of the level operator and then expand $Q\Psi$ using these eigenfunctions. The second is to expand $Q\Psi$ directly in terms of eigenstates of the closed-channel Hamiltonian H_{QQ}. The two approaches are equivalent and both require a knowledge of eigenstates of the closed-channel Hamiltonian:

$$H_{QQ}\phi_{l} = W_{l}\phi_{l}, \qquad l = 1, 2, 3, \ldots . \tag{12}$$

The functions ϕ_l are referred to as *translationally bound states*. Since $Q\Psi$ is the closed-channel component of the total wave function, it must vanish asymptotically in reactants and products. Thus it seems reasonable to expand $Q\Psi$ in translationally bound states that also vanish asymptotically (assuming the spectrum of eigenvalues W_l is discrete):

$$Q\Psi = \sum_l d_l \phi_l. \tag{13}$$

In general, the closed-channel Hamiltonian H_{QQ} will have both a discrete and a continuous spectrum of eigenvalues. To simplify notation, we shall ignore the closed-channel continuum and express a state expanded in the set $\{\phi_l\}$ as a summation over the discrete spectrum rather than both a summation over the discrete spectrum and an integration over the continuous spectrum.

1. *Eigenfunctions of the Level Operator: Resonance States*

In solving Eq. (9) for $Q\Psi$, it is useful to define eigenfunctions and eigenvalues of L_{QQ}:

$$L_{QQ}(E)\chi_j(E) = \varepsilon_j(E)\chi_j(E), \qquad j = 1, 2, \ldots . \tag{14}$$

Since the operator L_{QQ} is both energy-dependent and non-Hermitian, the eigenvalues ε_j will depend on E and in general are complex. Likewise, the eigenfunctions χ_j will be energy-dependent. χ_j is termed a *resonance state* and the associated eigenvalue ε_j gives the *position* Ω_j and the *width* Γ_j of the jth resonance:

$$\varepsilon_j = \Omega_j - i\Gamma_j/2. \tag{15}$$

The meaning of the position and width will be taken up later. Note that both the position and the width of the resonance as defined by Eq. (15) are energy-dependent.

Using the definition of the level shift operator (11), the level operator can be written as the sum of the closed-channel Hamiltonian and the level shift operator:

$$L_{QQ}(E) = H_{QQ} + R_{QQ}(E). \tag{16}$$

Using the eigenvalue property (12), the matrix representation of the level operator in a basis of translationally bound states is

$$L_{kl}(E) \equiv \langle \phi_k | L_{QQ} | \phi_l \rangle = W_k \delta_{kl} + R_{kl}(E), \tag{17}$$

where

$$R_{kl}(E) \equiv \langle \phi_k | R_{QQ} | \phi_l \rangle. \tag{18}$$

The matrix representing the level operator, L, can be diagonalized to solve the matrix eigenvalue problem:

$$\mathbf{L}(E)\mathbf{C}_j(E) = \varepsilon_j(E)\mathbf{C}_j(E) \tag{19}$$

corresponding to the operator Eq. (14). The eigenvector $\mathbf{C}_j$ gives the expansion coefficients of the jth resonance state in a basis of translationally bound states:

$$\chi_j(E) = \sum_l C_{lj}(E)\phi_l. \tag{20}$$

The matrix **L** is non-Hermitian since **R** is symmetric:

$$R_{kl} = R_{lk}, \tag{21a}$$

$$L_{kl} = L_{lk} \tag{21b}$$

(for details see Appendix A). This results in a peculiar orthogonality of the resonance states:

$$\tilde{\mathbf{C}}_j\mathbf{C}_k = \delta_{jk} \tag{22a}$$

or, equivalently,

$$\langle\chi_j^\dagger|\chi_k\rangle = \int \chi_j\chi_k\,\mathbf{dx} = \delta_{jk}. \tag{22b}$$

Here x represents the complete set of coordinates for the problem at hand. In Eq. (22b) $\chi_j^\dagger$ has been used in the Dirac notation to indicate that χ_j is used in the integration to compute the scalar product rather than the usual $\chi_j^\dagger$. This peculiarity of the resonance states can be demonstrated as follows. Equation (19) can be rearranged as

$$(\varepsilon_j\mathbf{1} - \mathbf{L})\mathbf{C}_j = 0. \tag{23}$$

Taking the transpose of Eq. (23) gives

$$\tilde{\mathbf{C}}_j(\varepsilon_j\mathbf{1} - \tilde{\mathbf{L}}) = 0. \tag{24}$$

Since L is symmetric, we have

$$\tilde{\mathbf{C}}_j(\varepsilon_j\mathbf{1} - \mathbf{L}) = 0. \tag{25}$$

Multiplying Eq. (25) from the right by $\mathbf{C}_k$ and using the eigenvalue property (19) yields

$$(\varepsilon_j - \varepsilon_k)\tilde{\mathbf{C}}_j\mathbf{C}_k = 0, \tag{26}$$

from which Eq. (22) follows for $j \neq k$.

The orthogonality expressed in Eqs. (22) introduces two subtleties in the manipulation of the resonance states. First of all, the resolution of unity in the Q subspace using the $\{\chi_j\}$ basis must be written

$$\sum_j |\chi_j\rangle\langle\chi_j^\dagger| = 1 \quad \text{or} \quad \sum_j \mathrm{C}_j\tilde{\mathrm{C}}_j = 1. \tag{27}$$

Second, the normalization specified by Eq. (22) implies a particular choice of phase of the resonance states. For example, if we change the phase of the jth resonance state by an arbitrary, nonzero amount δ, then the normalization becomes

$$\langle\chi_j^\dagger|\chi_j\rangle = \int \chi_j\chi_j\,\mathbf{dx} = e^{2i\delta} \neq 1. \tag{28}$$

Thus the resonance states can have complex "length." For this reason, the resonance "states" cannot be considered to be good quantum mechanical *states*. However this does not preclude their use in calculating the total wave function of the system. Submitting to the momentum of common practice, we shall continue to refer to the χ_j as resonance "states."

The non-Hermitian level operator matrix also has the peculiar property that the imaginary part of its eigenvalues are negative definite. This can be understood as follows. Using the well-known operator identity (see Roman, 1965, p. 718)

$$(E^{(+)} - H_{PP})^{-1} = [\mathcal{P}/(E - H_{PP})] - i\pi\delta(E - H_{PP}) \tag{29}$$

($\mathcal{P}$ denotes Cauchy principal value), the diagonal matrix elements of R_{QQ} are

$$\begin{aligned} R_{kk} = {} & \langle\phi_k|H_{QP}[\mathcal{P}/(E - H_{PP})]H_{PQ}|\phi_k\rangle \\ & - i\pi\langle\phi_k|H_{QP}\delta(E - H_{PP})H_{PQ}|\phi_k\rangle. \end{aligned} \tag{30}$$

If the eigenfunctions of H_{PP} are normalized as

$$\langle\Psi^{q}(E', \alpha')|\Psi^{q}(E'', \alpha'')\rangle = \rho^{-1}(E', \alpha')\delta(E' - E'')\delta_{\alpha'\alpha''}, \tag{31}$$

then the resolution of unity in the P subspace can be expressed as

$$\sum_\alpha \int dE'|\Psi^{q}(E', \alpha)\rangle\rho(E', \alpha)\langle\Psi^{q}(E', \alpha)| = 1. \tag{32}$$

Here α denotes all quantum mechanical observables necessary to form a complete set of commuting observables for the problem at hand. Using Eq. (32) in Eq. (30) yields

$$\operatorname{Im}(R_{kk}) = -\pi \sum_\alpha |\langle\Psi^{q}(E, \alpha)|H_{PQ}|\phi_k\rangle|^2. \tag{33}$$

Since $\operatorname{Im}(L_{kk}) = \operatorname{Im}(R_{kk})$, the trace of L is negative and thus:

$$\sum_j \operatorname{Im}(L_{jj}) = \sum_j \operatorname{Im}(\varepsilon_j) < 0. \tag{34}$$

In fact, $\mathrm{Im}(\varepsilon_j) < 0$ for all j. Recalling the definition of the width in Eq. (15), we conclude that $\Gamma_j > 0$.

Having discussed eigenvalues and eigenfunctions of L_{QQ}, Eq. (9) can now be solved for $Q\Psi$. Let us expand $Q\Psi$ as a superposition of resonance states:

$$Q\Psi = \sum_j \beta_j \chi_j. \tag{35}$$

Substituting Eq. (35) into Eq. (9) and using the eigenvalue property (14) yields

$$Q\Psi = \sum_j \frac{|\chi_j\rangle\langle\chi_j^*|H_{QP}|\Psi^{\mathrm{o}}\rangle}{E - \varepsilon_j}. \tag{36}$$

Equation (36) can be used in Eq. (6) to give

$$P\Psi = \Psi^{\mathrm{o}} + \sum_j \frac{G_{PP}^{\mathrm{o}} H_{PQ}|\chi_j\rangle\langle\chi_j^*|H_{QP}|\Psi^{\mathrm{o}}\rangle}{E - \varepsilon_j}. \tag{37}$$

Equations (36) and (37) together determine the total wave function for the collision system, $(P + Q)\Psi$.

Comparing Eq. (36) and the second term of Eq. (37), it appears useful to define a second type of "resonance state," κ_j (Feshbach and Levine, 1973):

$$\kappa_j \equiv G_{PP}^{\mathrm{o}} H_{PQ}|\chi_j\rangle. \tag{38}$$

The definition (38) is an integral equation for the solution to the following inhomogeneous equation:

$$(E - H_{PP})\kappa_j = H_{PQ}\chi_j. \tag{39}$$

In other words, κ_j is the open-channel response corresponding to the "driving term" $H_{PQ}\chi_j$. The *response function* κ_j contains the outgoing waves due to the de-excitation of the jth resonance state χ_j. Using the definition (38), Eq. (37) can be written as

$$P\Psi = \Psi^{\mathrm{o}} + \sum_j \frac{\langle\chi_j^*|H_{QP}|\Psi^{\mathrm{o}}\rangle}{E - \varepsilon_j}\kappa_j. \tag{40}$$

Equations (36) and (40) are particularly useful in understanding the energy dependence of solutions to the Schrödinger equation. The energy dependence of Ψ, as written in Eqs. (36) and (40), is of two sources. The first is the inherent energy dependence of Ψ^{o}, ε_j, χ_j, and κ_j. The solution to the Schrödinger equation containing only open channels, Ψ^{o}, is usually only mildly energy-dependent. The resonance states χ_j and κ_j, and the complex eigenvalue ε_j are also mildly energy-dependent provided the open/closed channel coupling, H_{PQ} and H_{QP}, is small (the energy dependence of ε_j, χ_j, and κ_j will be discussed in Sections II,A,4 and 6). The second and most obvious energy dependence is the "resonant denominator" $E - \varepsilon_j$ in Eq. (36) and the second term of Eq. (40). This explicit energy dependence is also the most important (assuming H_{PQ} and H_{QP} are small). If we are solving the Schrödinger equation at an energy E' such that

$$E' \simeq \mathrm{Re}(\varepsilon_k) = \Omega_k, \tag{41}$$

then the kth resonant denominator $(E - \varepsilon_k)$ will be small. At this energy, the kth closed-channel resonance state χ_k makes a significant contribution to $Q\Psi$, and the corresponding open-channel resonance state κ_k becomes an important outgoing wave. It is clear why Ω_k is referred to as the "position" of the kth resonance. As the energy of the system is varied in the neighborhood of Ω_k, both the Q and P components of the state of the system change drastically. The strong energy dependence of $P\Psi$ for energies near Ω_k gives rise to a strong energy dependence in the probability amplitudes, or S-matrix elements, for the target molecule to undergo a change in internal state or to react as a result of the collision (explicit expressions for one-dimensional reactive and nonreactive S-matrix elements will be given in Section II,B,1).

The range of energies near Ω_k for which the kth resonance states χ_k and κ_k are important is determined by the "width" Γ_k. The resonant denominator of Eqs. (36) and (40) is

$$E - \varepsilon_k = (E - \Omega_k) + i\Gamma_k/2. \tag{42}$$

The size of the resonant denominator at the position of the resonance $E = \Omega_k$ is determined by the width. If Γ_k is small, the resonance is said to be "narrow," and if Γ_k is large, the resonance is termed "broad." Thus for a narrow resonance, the state of the system changes sharply as the energy is varied near the position of the resonance. However, as the energy is changed by only a small amount away from the position of the resonance,

$$|E - \Omega_k| \gtrsim \Gamma_k/2, \tag{43}$$

the resonant denominator increases substantially compared to its minimum value $\Gamma_k/2$. Thus a narrow resonance is important over a narrow range of energies. Likewise, a broad resonance is characterized by a somewhat more gradual change in the state of the system (e.g., changes in transition probabilities) occurring over a larger range of energies near the position of the resonance. In this qualitative discussion, we are assuming that Ω_k and Γ_k are relatively constant over a range of energies $\Delta E \approx \Gamma_k$ centered at $E' \approx \Omega_k$.

In discussing time-dependent theory, we shall see that an incoming wave packet constructed from a superposition of highly energy-dependent stationary states will emerge from the interaction region only after a lengthy time delay. Thus a long time delay is associated with a highly energy-dependent narrow resonance (small width). The time delay is due to the time elapsed between the excitation of $Q\Psi(t)$, or the formation of the intermediate, and its subsequent decay. A long time delay is therefore associated with a long lifetime of the collision complex. Likewise, a broad resonance is associated with a somewhat shorter time delay and lifetime.

In general, there will be both resonances whose positions Ω_j are near the system energy E and so-called *far resonances* whose positions are not at all close to E. Far resonances do not exhibit a strong energy dependence even if narrow. Thus in the time-dependent theory, far resonances (far with respect to the energy spread of the wave packet) do not contribute to time-delayed scattering of wave packets, but contribute to a promptly scattered wave packet.

2. *Expansion of $Q\Psi$ in Translationally Bound States*

In solving Eq. (9) for $Q\Psi$ we used an expansion in resonance states (35). The resonance states in turn are calculated by an expansion in translationally bound states (20). It would seem simpler to expand $Q\Psi$ directly in translationally bound states:

$$Q\Psi = \sum_{l=1}^{N} d_l\phi_l. \tag{44}$$

Substituting the expansion (44) into Eq. (9) and taking projections $\langle\phi_k|$ yields

$$\sum_{l=1}^{N} [L_{kl} - E\delta_{kl}]d_l = -\langle\phi_k|H_{QP}|\Psi^{\circ}\rangle. \tag{45}$$

Here we have used the eigenvalue property (12) and definition (17). Equations (45) are a set of complex simultaneous linear algebraic equations for the amplitudes d_l. Equation (45) can be written in matrix form:

$$(\mathbf{L} - E\mathbf{1})\mathbf{d} = \mathbf{I}, \tag{46}$$

where $\mathbf{I}$ is an $N \times 1$ vector containing the inhomogeneity of Eq. (45). To solve Eq. (46) for $\mathbf{d}$, consider the spectral resolution of $(L_{QQ} - E)^{-1}$ in the $\{\chi_j\}$ basis:

$$(\mathbf{L} - E\mathbf{1})^{-1} = \sum_j [\mathbf{C}_j\tilde{\mathbf{C}}_j/(\varepsilon_j - E)]. \tag{47}$$

Here we have used the resolution of unity (27). Using Eq. (47) to solve Eq. (46) we have

$$\mathbf{d} = \sum_j [\mathbf{C}_j(\tilde{\mathbf{C}}_j\mathbf{I})/(\varepsilon_j - E)]. \tag{48}$$

Simplifying the scalar product in Eq. (48):

$$\tilde{\mathbf{C}}_j\mathbf{I} = -\langle \chi_j^* | H_{QP} | \Psi^{\mathrm{o}} \rangle \tag{49}$$

and looking at the lth element of Eq. (48) gives

$$d_l = \sum_j \frac{C_{lj}\langle \chi_j^* | H_{QP} | \Psi^{\mathrm{o}} \rangle}{E - \varepsilon_j}. \tag{50}$$

Equation (50) provides the link between the expansion of $Q\Psi$ in translationally bound states and the expansion of $Q\Psi$ in resonance states. From Eq. (50), one can see that if E is close to Ω_j, then all the amplitudes d_l become large according to the eigenvector factor C_{lj}, which determines the extent to which the lth translationally bound state contributes to the jth resonance state. In other words, it is the linear combination of translationally bound states called the jth resonance state that "blows up" as E nears Ω_j.

If the expression (50) for d_l is substituted into the expansion (44) and summed over l, we recover Eq. (36).

3. *An Isolated Resonance*

The formal development presented in Section II,A,1 is particularly convenient if there are a number of resonances whose positions lie within the range of energies of interest, ΔE, for the problem at hand. The procedure of diagonalizing the level operator is also the desired approach if there are *overlapping resonances*. Two resonances are said to be overlapping if the distance between their positions is less than the half-width of either resonance:

$$|\Omega_k - \Omega_j| \lesssim \Gamma_k/2 \quad \text{or} \quad \Gamma_j/2. \tag{51}$$

If a resonance is not overlapping, it is said to be an *isolated resonance*.

If there is only a single isolated resonance in the range of interest ΔE (i.e., all other resonances are far resonances with respect to all energies in the range ΔE), then there is an alternate description that is convenient (Feshbach, 1962; see also Kouri and Sams, 1971). This alternate description places the slow energy dependence of $P\Psi$ associated with the far resonances into the solution $\Psi^{\mathrm{o}'}$ of a modified open-channel problem. In addition, this formalism will lead to a different definition of the position and width of the resonance. An analytic comparison between the definitions given in Section II,A,1 and those presented here will be given in Section II,A,5.

In developing a description appropriate for an isolated resonance, we return to the coupled Eqs. (5). Inserting the formal solution to (5b) into (5a) yields an equation containing only $P\Psi$:

$$(E - H_{PP})P\Psi = H_{PQ}(E - H_{QQ})^{-1}H_{QP}P\Psi. \tag{52}$$

Introducing the spectral resolution of the inverse operator,

$$(E - H_{QQ})^{-1} = \sum_{l} \frac{|\phi_l\rangle\langle\phi_l|}{E - W_l}, \tag{53}$$

Eq. (52) becomes

$$(E - H_{PP})P\Psi = \sum_{l} \frac{H_{PQ}|\phi_l\rangle\langle\phi_l|H_{QP}|P\Psi\rangle}{E - W_l}. \tag{54}$$

Suppose that only W_k lies in or close to the range of energies of interest. Then the strong energy dependence of $P\Psi$ arises only from the term $l = k$ in Eq. (54). It is desirable to separate out the term $l = k$:

$$(E - H'_{PP})P\Psi = \frac{H_{PQ}|\phi_k\rangle\langle\phi_k|H_{QP}|P\Psi\rangle}{E - W_k}. \tag{55}$$

Here we have introduced a modified open-channel Hamiltonian:

$$H'_{PP} \equiv H_{PP} + \sum_{\substack{l \\ l\neq k}} \frac{H_{PQ}|\phi_l\rangle\langle\phi_l|H_{QP}}{E - W_l}. \tag{56}$$

Suppose we know the solution to the corresponding modified open-channel problem:

$$(E - H'_{PP})\Psi^{0'} = 0, \tag{57}$$

then the formal solution to Eq. (55) is

$$P\Psi = \Psi^{0'} + \frac{(E - H'_{PP})^{-1}H_{PQ}|\phi_k\rangle\langle\phi_k|H_{QP}|P\Psi\rangle}{E - W_k}. \tag{58}$$

Equation (58) is not the final solution for $P\Psi$ since the right-hand side contains the matrix element $\langle\phi_k|H_{QP}|P\Psi\rangle$. Using Eq. (58), this matrix element satisfies the algebraic equation

$$\begin{aligned}\langle\phi_k|H_{QP}|P\Psi\rangle &= \langle\phi_k|H_{QP}|\Psi^{0'}\rangle \\ &\quad + \frac{\langle\phi_k|H_{QP}(E - H'_{PP})^{-1}H_{PQ}|\phi_k\rangle\langle\phi_k|H_{QP}|P\Psi\rangle}{E - W_k}.\end{aligned} \tag{59}$$

Solving Eq. (59) for the matrix element $\langle \phi_k | H_{QP} | P\Psi \rangle$ and substituting into Eq. (58) gives the sought solution:

$$P\Psi = \Psi^{0'} + \frac{(E - H'_{PP})^{-1} H_{PQ} |\phi_k\rangle \langle \phi_k | H_{QP} | \Psi^{0'} \rangle}{E - \langle \phi_k | L'_{QQ} | \phi_k \rangle}. \tag{60}$$

Here we have introduced a modified level operator based on the modified open-channel Hamiltonian:

$$L'_{QQ} \equiv H_{QQ} + H_{QP}(E - H'_{PP})^{-1} H_{PQ}. \tag{61}$$

The second term of Eq. (60) has a resonant denominator that suggests the following definition of the position and width of the kth resonance:

$$\langle \phi_k | L'_{QQ} | \phi_k \rangle \equiv \Omega'_k - i\Gamma'_k/2 = (W_k + \Delta'_k) - i\Gamma'_k/2. \tag{62}$$

Here we have labeled the position and width with a (′) to indicate that their values differ slightly from those obtained by diagonalizing the matrix representation of the (unmodified) level operator. If the open/closed channel coupling is sufficiently small, then the position and width are essentially the same as those defined by Eqs. (14) and (15). In Eq. (62) we have introduced the "shift," Δ'_k, of the kth resonance, which gives the amount by which the position of the kth resonance is shifted from the translationally bound state eigenvalue W_k.

4. *Closed-Channel Resonance State as a Perturbed Translationally Bound State*

In Section II,A,1 we introduced the resonance states χ_j as eigenfunctions of the level operator with associated eigenvalues ε_j. If the open/closed channel coupling, H_{PQ} and H_{QP}, is sufficiently small, then the level shift operator R_{QQ} can be considered a small energy-dependent perturbation to the closed-channel Hamiltonian H_{QQ}. In that case, it would seem reasonable to treat the resonance state as a perturbed translationally bound state. The non-Hermitian perturbation R_{QQ} causes the zero-order eigenvalue W_k to shift by Δ_k as well as broaden (become complex) by an amount $\Gamma_k/2$; i.e., the zero-order translationally bound state has a zero width that implies an infinite lifetime. The presumably small perturbation R_{QQ} gives the resonance state a small but nonzero width and, thus, a long but finite lifetime because the small perturbation R_{QQ} allows the probability amplitude associated with $Q\Psi$ to "leak" back into the open-channel continuum (for other discussions based on perturbation theory see Micha, 1974; Yambe *et al.*, 1978).

Perturbation theory is appropriate only when the open/closed coupling is small, or equivalently, when the resonance is narrow and the shift small. Perturbation theory is entirely equivalent, of course, to diagonalizing the matrix representation of the level operator. However, if the open/closed coupling is not small, then matrix diagonalization is preferred as a numerical technique.

We approach the discussion of resonance states as perturbed bound states using the usual Rayleigh–Schrödinger (RS) perturbation theory. We shall investigate the dependence of the shift and width on the size of the open/closed channel coupling by scaling the true coupling by the adjustable parameter $\lambda^{1/2}$ (real and positive) in the following manner:

$$\text{replace } H_{QP} \text{ with } \lambda^{1/2} H_{QP}, \tag{63a}$$

$$\text{replace } H_{PQ} \text{ with } \lambda^{1/2} H_{PQ}. \tag{63b}$$

Using the scheme (63), the level operator becomes

$$L_{QQ}(E, \lambda) = H_{QQ} + \lambda R_{QQ}(E). \tag{64}$$

As $\lambda \rightarrow 0$, $L_{QQ} \rightarrow H_{QQ}$ and as $\lambda \rightarrow 1$, L_{QQ} becomes the "true" level operator. If we consider L_{QQ} to be a function of λ, then its eigenfunctions and eigenvalues must also be functions of λ. Thus we can expand χ_j and ε_j in Taylor series about $\lambda = 0$:

$$\chi_j = \phi_j + \sum_{n=1}^{\infty} \lambda^n \chi_j^{(n)}, \tag{65}$$

$$\varepsilon_j = W_j + \sum_{n=1}^{\infty} \lambda^n \varepsilon_j^{(n)}, \tag{66}$$

where

$$\chi_j^{(K)} \equiv \frac{1}{K!} \frac{\partial^K \chi_j}{\partial \lambda^K}\bigg|_{\lambda=0}, \tag{67}$$

$$\varepsilon_j^{(K)} \equiv \frac{1}{K!} \frac{\partial^K \varepsilon_j}{\partial \lambda^K}\bigg|_{\lambda=0}. \tag{68}$$

Note that the summation in Eq. (66) contains the shift and half-width of the jth resonance:

$$\sum_{n=1}^{\infty} \lambda^n \varepsilon_j^{(n)} = \Delta_j - i\Gamma_j/2. \tag{69}$$

The expansions (65) and (66) are substituted into the eigenvalue problem in Eq. (14) in the usual way:

$$(H_{QQ} + \lambda R_{QQ}) \left(\phi_j + \sum_{n=1}^{\infty} \lambda^n \chi_j^{(n)} \right) = \left(W_j + \sum_{n=1}^{\infty} \lambda^n \varepsilon_j^{(n)} \right) \left(\phi_j + \sum_{n=1}^{\infty} \lambda^n \chi_j^{(n)} \right), \tag{70}$$

and then terms of like powers of λ are collected and equated. Equating terms associated with λ^0 yields the bound-state problem of Eq. (12). Equating terms associated with λ^1 yields

$$(H_{QQ} - W_j)\chi_j^{(1)} = (\varepsilon_j^{(1)} - R_{QQ})\phi_j. \tag{71}$$

Expanding the first-order correction to the resonance state in translationally bound states:

$$\chi_j^{(1)} = \sum_k a_{kj}\phi_k \tag{72}$$

and taking projections $\langle\phi_l|$ yields

$$a_{lj}(W_l - W_j) = \varepsilon_j^{(1)}\delta_{lj} - R_{lj}, \tag{73}$$

where R_{lj} is defined in Eq. (18). For $l = j$, we find

$$\varepsilon_j^{(1)} = R_{jj} \tag{74}$$

or

$$\varepsilon_j(E, \lambda) \simeq W_j + \lambda R_{jj}(E); \tag{75}$$

i.e., to first order, the complex eigenvalue is simply the diagonal matrix element of the level operator. To first order, the shift and width vary linearly with λ, which implies a quadratic dependence with respect to the size of the open/closed coupling. Thus, for small coupling we expect narrow resonances with positions only slightly shifted from the bound-state eigenvalues. The approximate quadratic dependence of the shift and width will be illustrated numerically for a model problem in Section II,C,4.

For $l \neq j$, Eq. (73) provides the expansion coefficient a_{lj}:

$$a_{lj} = R_{lj}/(W_j - W_l). \tag{76}$$

Equation (76) does not determine a_{jj}, which we will show to be zero by the normalization requirement of Eq. (22b):

$$\langle\chi_j^*|\chi_m\rangle = \int \left(\phi_j + \sum_k a_{kj}\phi_k\right)\left(\phi_m + \sum_l a_{lm}\phi_l\right)\mathbf{dx} = \delta_{jm} \tag{77}$$

or

$$\langle\chi_j^*|\chi_m\rangle = \delta_{jm} + a_{mj} + a_{jm} + \mathcal{O}(a_{lj}^2) = \delta_{jm}. \tag{78}$$

Since $R_{mj} = R_{jm}$, then $a_{mj} = -a_{jm}$ for $m \neq j$. For $m = j$, we must require $a_{jj} = 0$ in order for Eq. (78) to hold. Thus through first order, the jth resonance state is

$$\chi_j = \phi_j + \lambda \sum_{\substack{l \\ l\neq j}} [R_{lj}/(W_j - W_l)]\phi_l + \cdots . \tag{79}$$

The contribution from adjacent bound states varies linearly with λ or quadratically with the open/closed coupling. Note that it is the contribution of translationally bound states $l \neq j$ that contains the energy dependence of χ_j. If the coupling is small, χ_j will not vary appreciably with energy.

Higher-order corrections to the resonance state and its complex eigenvalue can be obtained by continuing the process of equating terms of like powers of λ in the usual fashion.

5. *A Comparison of Definitions of the Shift and Width*

In the general theory, applicable to either overlapping or isolated resonances, the complex energy ε_j was defined as an eigenvalue of the level operator by Eq. (14). In the treatment of an isolated resonance given in Section II,A,3, ε_j' was defined by Eq. (62) as a diagonal matrix element of a modified level operator. One may reasonably query whether the two definitions of the shift and width of a given resonance are equivalent. The purpose of this section is to compare definitions (14) and (62).

In making the comparison of definitions we need explicit equations for ε_j based on the two definitions. The RS perturbative expansion in Eq. (66) is one such explicit expression for ε_j based on definition (14). However, the form of this equation is not convenient for the comparison of definitions. To develop a convenient expansion of ε_j based on Eq. (14), we use Lennard-Jones–Brillouin–Wigner (LBW) perturbation theory (see Bates, 1961). The LBW expansion for ε_j is entirely equivalent to that of RS perturbation theory, since both are based on the eigenvalue definition in Eq. (14). Definition (14) can be rearranged as follows:

$$(H_{QQ} - \varepsilon_j)\chi_j = -R_{QQ}\chi_j. \tag{80}$$

Next we expand the resonance state in translationally bound states:

$$\chi_j = \sum_k \beta_{kj}\phi_k, \tag{81}$$

and substitute into the left-hand side of Eq. (80). Taking projections $\langle\phi_l|$ gives an expression for the expansion coefficient:

$$\beta_{lj} = \frac{\langle\phi_l|R_{QQ}|\chi_j\rangle}{\varepsilon_j - W_l}. \tag{82}$$

Using Eq. (82) the resonance state can be written (exactly) as

$$\chi_j = \beta_{jj}\phi_j + \sum_{\substack{l \\ l\neq j}} \frac{\langle\phi_l|R_{QQ}|\chi_j\rangle}{\varepsilon_j - W_l}. \tag{83}$$

Note that we have explicitly removed the term $l = j$ from the summation. Expression (83) is not an explicit expression for χ_j as the expansion coefficients in Eq. (82) also contain χ_j. A perturbative expansion for χ_j can be developed in the following fashion. For χ_j in the matrix element $\langle \phi_l | R_{QQ} | \chi_j \rangle$ in the second term of Eq. (83), we repetitively insert Eq. (83) to obtain

$$\chi_j = \beta_{jj}\left[\phi_j + \sum_{\substack{l \\ l \neq j}} \frac{R_{lj}\phi_l}{\varepsilon_j - W_l} + \sum_{l \neq j} \sum_{k \neq j} \frac{R_{kl}R_{lj}\phi_k}{(\varepsilon_j - W_k)(\varepsilon_j - W_l)} + \cdots \right]. \tag{84}$$

Here we have used the definition of R_{kl} in Eq. (18). The expansion in Eq. (84) continues in an obvious repetitive pattern. Using Eq. (84), we calculate the matrix element $\langle \phi_j | R_{QQ} | \chi_j \rangle$:

$$\begin{aligned} &\langle \phi_j | R_{QQ} | \chi_j \rangle \\ &\quad = \beta_{jj}\left[R_{jj} + \sum_{\substack{l \\ l \neq j}} \frac{R_{jl}R_{lj}}{\varepsilon_j - W_l} + \sum_{l \neq j} \sum_{k \neq j} \frac{R_{jk}R_{kl}R_{lj}}{(\varepsilon_j - W_l)(\varepsilon_j - W_k)} + \cdots \right]. \end{aligned} \tag{85}$$

Comparing Eq. (85) to the definition of β_{jj}:

$$\langle \phi_j | R_{QQ} | \chi_j \rangle = \beta_{jj}[\varepsilon_j - W_l], \tag{86}$$

we see that ε_j can be expressed as

$$\varepsilon_j = W_j + R_{jj} + \sum_{\substack{l \\ l \neq j}} \frac{R_{jl}R_{lj}}{\varepsilon_j - W_l} + \sum_{\substack{l \\ l \neq j}} \sum_{\substack{k \\ k \neq j}} \frac{R_{jk}R_{kl}R_{lj}}{(\varepsilon_j - W_k)(\varepsilon_j - W_l)}. \tag{87}$$

Equation (87) does not give ε_j explicitly due to the presence of ε_j in the denominators of the second- and higher-order corrections. However, the self-consistent solution to Eq. (87) is the eigenvalue defined by Eq. (14). Equation (87) expresses ε_j in a form that is useful in comparing the definitions in Eqs. (14) and (62). In addition, the LBW perturbative expansion in Eq. (87) has the advantage that any given higher-order correction can immediately be written due to the obvious repetitive pattern.

A perturbative expansion similar in form to Eq. (87) can be written for ε_j' as defined in Eq. (62). In order to do this, we relate $(E^{(+)} - H_{PP})^{-1}$ to $(E^{(+)} - H'_{PP})^{-1}$ through the following well-known operator identity. If $H' = H + V$, then

$$(E - H')^{-1} = (E - H)^{-1}[1 + V(E - H')^{-1}]. \tag{88}$$

Equation (88) can be written as an infinite (or Born) series:

$$\begin{aligned} &(E - H')^{-1} \\ &\quad = (E - H)^{-1}[1 + V(E - H)^{-1} + V(E - H)^{-1}V(E - H)^{-1} + \cdots]. \end{aligned} \tag{89}$$

Using Eq. (56), we can now relate $(E^{(+)} - H_{PP})^{-1}$ and $(E^{(+)} - H'_{PP})^{-1}$:

$$(E - H'_{PP})^{-1} = (E - H_{PP})^{-1} \times \left[1 + \sum_{\substack{l \\ l \neq j}} \frac{H_{PQ}|\phi_l\rangle\langle\phi_l|H_{QP}(E - H_{PP})^{-1}}{E - W_l} + \cdots \right]. \tag{90}$$

Forming the matrix element $\langle\phi_k|H_{QP}(E - H'_{PP})^{-1}H_{PQ}|\phi_k\rangle$ required by Eq. (62) gives the desired explicit expression for ε'_j:

$$\varepsilon'_j = W_j + R_{jj} + \sum_{\substack{l \\ l \neq j}} \frac{R_{jl}R_{lj}}{(E - W_l)} + \sum_{\substack{l \\ l \neq j}} \sum_{\substack{k \\ k \neq j}} \frac{R_{jl}R_{lk}R_{kj}}{(E - W_l)(E - W_k)} + \cdots . \tag{91}$$

We can compare ε_j and ε'_j defined in Eqs. (14) and (62) by comparing Eqs. (87) and (91), respectively. Both equations are identical in form through any given order. However, in Eq. (91), E plays the role of ε_j in Eq. (87). Hence the two definitions of the resonance parameters are genuinely different. However, through first order the shift and width defined by Eqs. (14) and (62) are identical:

$$\Delta_j \cong \mathrm{Re}(R_{jj}), \tag{92a}$$

$$\Gamma_j \cong -2\,\mathrm{Im}(R_{jj}) = 2\pi \sum_{\alpha} |\langle\Psi^0(E, \alpha)|H_{PQ}|\phi_j\rangle|^2. \tag{92b}$$

In Eq. (92b) we have made use of Eq. (33). For small open/closed channel coupling we expect the shifts and widths calculated according to the two definitions to be essentially the same. However, for somewhat larger coupling ε'_j is more strongly energy-dependent due to the explicit appearance of E in Eq. (91).

Equation (91) becomes singular for any $E = W_l$, $l \neq j$. This is simply a reminder that the treatment of an isolated resonance given in Section II,A,3 has a limited range of applicability, within the band ΔE. For energies outside this range, it is necessary to redefine the modified open channel Hamiltonian H'_{PP}. For this reason, we prefer to use the general treatment based on the definition in Eq. (14) even though this treatment retains the slowly energy-dependent far resonances in the resonant expansion.

The moral of this section is that both the position (or shift) and width of a resonance are not unique quantities for any given physical system. They depend on both the definition and the energy (see Section II,A,7, however, for a definition of energy-independent resonance parameters). The resonance parameters Ω_j and Γ_j simply give *crude* but useful information about the energy dependence of stationary solutions to the Schrödinger equation. That is, Ω_j tells one to expect the solutions of the Schrödinger equation (and the corresponding transition probabilities, cross sections, etc.) to vary appreciably with energy for energies near Ω_j. Γ_j tells one roughly the range of energies associated with the resonance structure roughly centered at Ω_j.

6. *The Energy Dependence of the Shift and Width*

Suppose we are interested in applying the Feshbach formalism to a system characterized by rather small open/closed channel coupling. In that case, the complex eigenvalue ε_j is given approximately by the first-order perturbation theory result [$\lambda = 1$ in Eq. (75)]:

$$\varepsilon_j(E) \cong W_j + R_{jj}(E). \tag{93}$$

Having calculated positions and widths at a particular energy E_1, we may question how these resonance parameters would vary if the calculation were repeated at a slightly different energy (for a discussion based on the Hellmann–Feynman theorem see Yambe *et al.*, 1978). In other words, we are interested in the energy derivative of ε_j:

$$d\varepsilon_j/dE \cong dR_{jj}/dE = \langle\phi_j|dR_{QQ}/dE|\phi_j\rangle. \tag{94}$$

Computing the derivative of the level operator we have

$$d\varepsilon_j/dE \Big|_{E=E_1} \cong -\langle\phi_j|H_{QP}[G^0_{pp}(E_1)]^2H_{PQ}|\phi_j\rangle. \tag{95}$$

If we scale the open/closed channel coupling according to the scheme (63), then the magnitude of the energy derivative varies linearly with λ or quadratically with the coupling strength parameter $\lambda^{1/2}$. Thus for small coupling, not only are the shift and width small, but also they are relatively independent of energy (as anticipated in Section II,A,4).

Equation (95) may be useful for computationally determining the extent to which Δ_j and Γ_j vary with energy near energy E_1. The inverse operator G^0_{pp} needed to calculate $R_{jj}(E_1)$ is realized in practice by generating an open-channel Green function (see Section II,B,2) at $E = E_1$. Rather than regenerating a new Green function at $E = E_2$ to recalculate $R_{jj}(E_2)$, one can compute the convolution of the Green function corresponding to $[G^0_{pp}(E_1)]^2$ and then approximate $\varepsilon_j(E_2)$ using a Taylor series:

$$\varepsilon_j(E_2) \cong W_j + R_{jj}(E_1) - \langle\phi_j|H_{QP}[G^0_{PP}(E_1)]^2H_{PQ}|\phi_j\rangle(E_2 - E_1). \tag{96}$$

Of course, Eq. (96) is useful only when both $(E_2 - E_1)$ and the open/closed channel coupling are sufficiently small.

The energy dependence of $d\varepsilon_j/dE$ can be explored by using the resolution of unity (32) in Eq. (95):

$$\left.\frac{d\varepsilon_j}{dE}\right|_{E=E_1} \cong -\sum_{\alpha}\int \frac{dE'\rho(E',\alpha)|\langle\Psi^{0}(E',\alpha)|H_{PQ}|\phi_j\rangle|^2}{(E_1^{(+)}-E')^2}. \tag{97}$$

Since E_1 appears in the denominator of Eq. (97), the magnitude of the rate of variation of the shift and width with energy is generally expected to decrease as the energy increases. (However, if one continues to increase the energy, eventually a new channel will open and it becomes necessary to choose new projection operators, P and Q, if we insist that P always projects onto all the open channels.) The general decrease of $|d\varepsilon_j/dE|$ as the energy increases can also be appreciated from a somewhat different viewpoint. The Green function corresponding to G^0_{PP} becomes more oscillatory as the energy increases, just as any continuum wave function would. Consequently, in convoluting the Green function (corresponding to the operator $[G^0_{PP}]^2$) destructive interference is more likely to occur at higher energies due to the higher frequency of oscillation. (However, if the energy is increased up to the point where a new channel opens, the Green function acquires a new component of slow oscillation and destructive interference is now less likely to occur.)

7. *The Siegert Eigenvalue Problem in the Context of the Feshbach Formalism*

Throughout much of Section II,A we have been concerned with the complex, *energy-dependent* eigenvalues ε_j of the level operator. However, it is possible to define in the context of the Feshbach formalism an *energy-independent* complex eigenvalue $\varepsilon_j^{\mathrm{S}}$. These complex eigenvalues correspond to poles of the S-matrix elements in the complex energy plane. The procedure that follows is the equivalent of the treatments of Siegert and Humblet and Rosenfeld in the sense that it specifies the poles of the S-matrix elements (Siegert, 1939; Humblet and Rosenfeld, 1961).

A set of coupled equations, analogous to Eqs. (5a) and (5b), can be written connecting the open-channel response function κ_j with the closed-channel resonance state χ_j (Feshbach and Levin, 1973). After multiplying Eq. (38) by H_{QP}, we note that

$$R_{QQ}\chi_j = H_{QP}\kappa_j. \tag{98}$$

Using Eq. (98) in definition (14) yields the first coupled equation (99a). Equation (99b) is simply Eq. (39) rewritten here for the sake of convenience:

$$(\varepsilon_j - H_{QQ})\chi_j = H_{QP}\kappa_j, \tag{99a}$$

$$(E - H_{PP})\kappa_j = H_{PQ}\chi_j. \tag{99b}$$

Note the analogy between coupled Eqs. (99) and coupled Eqs. (5). The two sets of equations differ only in two respects. First of all, Eqs. (99) represent an eigenvalue problem since Eq. (99a) contains ε_j. Secondly, κ_j satisfies an outgoing only boundary condition in contrast to the asymptotic boundary condition satisfied by $P\Psi$. Solving Eq. (99a) for χ_j and substituting into Eq. (99b) yields an equation containing only κ_j:

$$(E - H_{PP} - H_{PQ}(\varepsilon_j - H_{QQ})^{-1}H_{QP})\kappa_j = 0. \tag{99c}$$

This Schrödinger-like equation contains a "complex potential energy" term, $H_{PQ}(\varepsilon_j - H_{QQ})^{-1}H_{QP}$, which makes possible solutions κ_j satisfying outgoing only boundary conditions.

The energy dependence of the solutions to Eqs. (99) enters through the explicit appearance of E in Eq. (99b). If we replace E in Eq. (99b) by the eigenvalue ε_j^s, we obtain a similar set of coupled equations (Feshbach and Levin, 1973):

$$(\varepsilon_j^s - H_{QQ})\chi_j^s = H_{QP}\kappa_j^s, \tag{100a}$$

$$(\varepsilon_j^s - H_{PP})\kappa_j^s = H_{PQ}\chi_j^s. \tag{100b}$$

The solutions to Eqs. (100) have been labeled with a superscript "s" (Siegert) to indicate they differ from the solutions of Eqs. (99) in several ways. The solutions $\varepsilon_j{}^s$, $\chi_j{}^s$, and $\kappa_j{}^s$ are now independent of energy, of course. The eigenvalue $\varepsilon_j{}^s$ corresponds to a pole of the S-matrix elements in the complex energy plane (to be explained in Section II,B,5). The new open-channel response function κ_j^s is not only outgoing but also has an exponentially *increasing* envelope (see Section II,B,5), in contrast to κ_j whose asymptotic envelope is *constant*. In addition, the closed-channel resonance states χ_j^s are not orthogonal:

$$\langle(\chi_j^s)^*|\chi_k^s\rangle \neq \delta_{jk}. \tag{101}$$

Therefore, it is not appropriate to resolve the identity operator directly in the $\{\chi_j^s\}$ basis:

$$\sum_j |(\chi_j^s)^*\rangle\langle\chi_j^s| \neq 1. \tag{102}$$

The Siegert eigenvalue problem in Eq. (100) can be written in a form similar to the definition in Eq. (14) of the energy-dependent resonance states χ_j and eigenvalues ε_j. We simply replace $R_{QQ}(E)$ by $R_{QQ}(\varepsilon_j^s)$:

$$[H_{QQ} + R_{QQ}(\varepsilon_j^s)]\chi_j^s = \varepsilon_j^s\chi_j^s. \tag{103}$$

Equation (103) is equivalent to Eqs. (100). A numerical technique for solving Eq. (103) for the poles of the S-matrix elements ε_j^s will be presented in Section II,B,5.

B. The Application of the Feshbach Resonance Theory to Collinear Reactive Scattering

In Section II,B we will specialize the general theory of the preceding section by choosing a particular form for the Hamiltonian of the collision system as well as particular projection operators P and Q. We shall restrict the discussion to collinear collisions to avoid additional complications associated with a particular angular momentum coupling scheme. In addition, we shall simplify the discussion by considering reactions in which the products and reactants are identical, for example:

$$\mathrm{A} + \mathrm{BA} \rightarrow \mathrm{AB} + \mathrm{A}. \tag{104}$$

This restriction is not necessary but it simplifies the discussion in that all asymptotically open reactant channels correspond to asymptotically open product channels. One could easily extend this treatment to both higher angular momentum and more general reactions if one is willing to pay the price of a more complicated notation. However, we are more interested in the features of the Feshbach theory arising from the *form* of the equations than the details of any particular reaction. The principal goal of this section is to produce a computationally oriented matrix notation as well as present computational techniques necessary for the application of the Feshbach theory within the restrictions noted above.

In discussing coordinates for collinear reactions, we choose *natural coordinates* (R, r), which are defined in Fig. 1. (These coordinates are similar to those defined by Marcus, 1966.) Here R is the translational coordinate and r is the vibrational coordinate, both of which are defined relative to the reference curve (RC) shown in this figure. These coordinates have the advantage of blending smoothly from the reactant region $(R > L)$, through the interaction region $(0 < R < L)$, and into the product region $(R < 0)$. As $R \rightarrow +\infty$ or $R \rightarrow -\infty$, the system separates into reactants or products, respectively. In terms of these coordinates, the Hamiltonian in the polar (or interaction) region, $0 < R < L$, is

$$H = -\frac{\hbar^2}{2\mathscr{M}}\left(\frac{1}{\eta^2}\frac{\partial^2}{\partial R^2} + \frac{1}{\eta}\frac{\partial}{\partial r}\eta\frac{\partial}{\partial r}\right) + V_{\mathrm{vib}}(r) + V_{\mathrm{tr}}(R; r), \tag{105a}$$

and in the Cartesian regions, $R > L$ or $R < 0$, it is

$$H = -\frac{\hbar^2}{2\mathscr{M}}\left(\frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2}\right) + V_{\mathrm{vib}}(r) + V_{\mathrm{tr}}(R, r). \tag{105b}$$

Here $\mathscr{M}$ is the effective reduced mass,

$$\mathscr{M} = (\mu_{\mathrm{AB}}\mu_{\mathrm{A,AB}})^{1/2}, \tag{106}$$

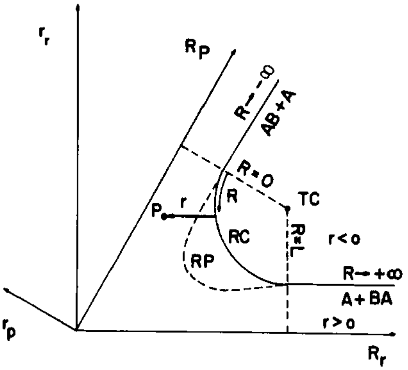


Fig. 1. Coordinate systems for a collinear reactive collision. R_r and r_r denote mass-scaled translational and vibrational coordinates for reactants, while R_p and r_p denote the set of product mass-scaled coordinates. R and r are natural collision coordinates for point P, where R is the distance measured along the reference curve (RC), and r is the vibrational displacement from the RC. The origin $R = 0$ is at the polar–Cartesian boundary in products and $R \to -\infty$ or $+\infty$ denote asymptotic product or reactant regions, respectively. In the interaction region, R is the arc length along the circular reference curve, which does not need to coincide with the reaction path (RP) on the potential energy surface. The turning center (TC) for the circular reference curve is indicated.

where the vibrational and atom–diatom reduced masses are

$$\mu_{AB} = m_A m_B/(m_A + m_B), \tag{107a}$$

$$\mu_{A,AB} = m_A(m_A + m_B)/(2m_A + m_B), \tag{107b}$$

in which m_A and m_B are atomic masses. η is related to the curvature κ of the reference curve by

$$\eta = 1 + \kappa r. \tag{108}$$

In the reactant and product valleys we have $\kappa = 0$ and $\eta = 1$. In Eq. (105) we employ a "split potential" in which $V_{vib}(r)$ is the vibrational potential in the reactant and product valleys; $V_{tr}(R; r)$ is the remaining portion of the interaction, which takes care of changes in the potential energy surface in going from reactants to products. Asymptotically V_{tr} becomes independent of r and approaches a constant.

In treating such collinear problems, it is computationally convenient to scale the wave function as (Light and Walker, 1976; Wyatt *et al.*, 1978)

$$\Psi_s(R, r) = \eta^{1/2}\Psi(R, r), \tag{109}$$

where Ψ_s is the scaled wave function. Substituting the scaled wave function into the time-independent Schrödinger equation using the Hamiltonian of Eq. (105), we find that the unscaled wave function satisfies

$$\left[-\frac{\hbar^2}{2\mathcal{M}}\left(\frac{\partial^2}{\partial R^2}+\frac{\kappa^2}{4}\right)+\eta H^{\circ}_{\text{vib}}\eta+\eta^2(V_{\text{tr}}-E)\right]\Psi(R;r)=0, \qquad (110)$$

where H°_{vib} is the asymptotic vibrational Hamiltonian of the diatomic:

$$H^{\circ}_{\text{vib}}=-\frac{\hbar^2}{2\mathcal{M}}\frac{\partial^2}{\partial r^2}+V_{\text{vib}}(r). \qquad (111)$$

The eigenstates of H°_{vib} are defined as

$$H^{\circ}_{\text{vib}}(r)\Phi_j(r)=\xi_j\Phi_j(r). \qquad (112)$$

It is assumed that the vibrational eigenstates are orthonormal, $\langle\phi_k|\phi_j\rangle=\delta_{kj}$.

The unscaled wave function is most conveniently expanded in a basis of vibrational eigenstates:

$$\Psi(R,r)=\sum_{j=1}^{n+m}f_j(R)\Phi_j(r), \qquad (113)$$

where the expansion coefficients $f_j(R)$ are known as the *translational wave functions*. Substituting the expansion (113) into Eq. (110) and taking projections $\langle\Phi_k|$ yields the close-coupled equations:

$$\begin{aligned}&[T_R+H_{kk}(R)+\xi_k-E]f_k(R)\\&\quad=-\sum_{\substack{j\\j\neq k}}H_{kj}(R)f_j(R),\qquad k=1,\ldots,n+m,\end{aligned} \qquad (114)$$

where $T_R=(-\hbar^2/2\mathcal{M})(\partial^2/\partial R^2)$ and H_{kj} is given by

$$\begin{aligned}H_{kj}\equiv{}&\langle\Phi_k|\eta^2V_{\text{tr}}|\Phi_j\rangle+\left\{\frac{\xi_k+\xi_j}{2}-E\right\}[2\kappa\langle\Phi_k|r|\Phi_j\rangle\\&+\kappa^2\langle\Phi_k|r^2|\Phi_j\rangle]+\frac{3\kappa^2\hbar^2}{8\mathcal{M}}\delta_{kj}.\end{aligned} \qquad (115)$$

Note that $H_{kj}\to V_{\text{tr}}(\pm\infty)$ as $R\to\pm\infty$. In Section II,B,1 we shall rewrite Eqs. (114) using a computationally oriented matrix notation as well as sketch the Feshbach formalism using the new notation.

The total system energy appears in both the channel potential $H_{kk}(R)$ and the coupling between channels $H_{kj}(R)$ in Eq. (115). This is due to the curvature κ used in the natural coordinate system in describing the rearrangement in going from products to reactants. In addition, when using the natural coordinate system, one must perform orthogonal transformations on the asymptotic wave functions at the polar–Cartesian boundaries to insure continuity. To avoid these complications, we shall formally consider a simplified "one-dimensional" model for which $\kappa = 0$ and $\eta = 1$. For this model, the scaled and unscaled wave functions are identical, and H_{kj} simplifies to the first term of Eq. (115) with $\eta = 1$.

At energy E, those vibrational states Φ_k satisfying

$$E > \xi_k + V_{\mathrm{tr}}(\pm\infty) \tag{116}$$

are energetically accessible asymptotically and correspond to the open (product and reactant) channels. Suppose the first n vibrational channels are open. Then a convenient choice of projection operators is

$$P = \sum_{j=1}^{n} |\Phi_j\rangle\langle\Phi_j|, \tag{117a}$$

$$Q = \sum_{j=n+1}^{n+m} |\Phi_j\rangle\langle\Phi_j|. \tag{117b}$$

Using Eqs. (117a) and (113) we see that the first n translational wave functions are associated with open channels. Likewise, the remaining m translational wave functions correspond to closed channels for our one-dimensional model.

1. *Matrix Notation*

Employing the collinear Hamiltonian in natural collision coordinates (105), we have developed a set of close-coupled equations appropriate for the one-dimensional model. These coupled equations are equivalent to the formal coupled equations (5). [Equations (114) could have been derived by forming the operators PHP, PHQ, QHP, and QHP explicitly and substituting into Eqs. (5).] We now convert Eqs. (114) into a pair of coupled matrix equations by making the following definitions. First we divide the interaction matrix defined by Eq. (115) into four submatrices:

$$\mathbf{H}(R) = \left[\begin{array}{c|c} \mathbf{H}_{oo} & \mathbf{H}_{oc} \\ \hline \mathbf{H}_{co} & \mathbf{H}_{cc} \end{array}\right]. \tag{118}$$

Here $\mathbf{H}_{oo}$ is an $n \times n$ matrix containing the coupling between open channels (hence the subscript "oo"). Likewise $\mathbf{H}_{cc}$ is an $m \times m$ matrix containing the coupling between closed channels. $\mathbf{H}_{oc}$ is an $n \times m$ matrix representing the coupling between open and closed channels. $\mathbf{H}_{oc}$ and $\mathbf{H}_{co}$ are related in the following manner: $\mathbf{H}_{oc} = \tilde{\mathbf{H}}_{co}$. Next we introduce an $n \times 1$ column vector containing the translational wave functions in the open channels, $\mathbf{F}_o$, and an $m \times 1$ column vector of functions representing the translational wave functions in the closed channels, $\mathbf{F}_c$:

$$\mathbf{F}_o = \begin{bmatrix} f_1(R) \\ \vdots \\ f_n(R) \end{bmatrix}, \qquad \mathbf{F}_c = \begin{bmatrix} f_{n+1}(R) \\ \vdots \\ f_{n+m}(R) \end{bmatrix}. \tag{119}$$

Using the notation introduced here, Eqs. (116) can be written more compactly as

$$[(T_R - E)\mathbf{1}_o + \boldsymbol{\xi}_o + \mathbf{H}_{oo}]\mathbf{F}_o = -\mathbf{H}_{oc}\mathbf{F}_c, \tag{120a}$$

$$[(T_R - E)\mathbf{1}_c + \boldsymbol{\xi}_c + \mathbf{H}_{cc}]\mathbf{F}_c = -\mathbf{H}_{co}\mathbf{F}_o, \tag{120b}$$

where $\boldsymbol{\xi}_o$ and $\boldsymbol{\xi}_c$ are diagonal matrices containing the vibrational eigenvalues, and $\mathbf{1}_o$ and $\mathbf{1}_c$ are $n \times n$ and $m \times m$ unit matrices, respectively. The coupled matrix equations are now in a form resembling the formal equations (5).

In order to deal with Eqs. (120) according to the procedure outlined in the formal theory, we need to invert the operator in brackets in Eq. (120a). Toward this end, we define an $n \times n$ Green function matrix by

$$[(T_R - E)\mathbf{1}_o + \boldsymbol{\xi}_o + \mathbf{H}_{oo}]\mathbf{G}_o(R, R') = \delta(R - R')\mathbf{1}_o, \tag{121}$$

i.e., $\mathbf{G}_o(R, R')$ contains the responses in the open channels at R due to a unit source at R'. If the unit source $\delta(R - R')$ is in the lth channel, then the lth column of $\mathbf{G}_o$ contains the response in all n open channels due to that unit source. $\mathbf{G}_o$ obeys the reciprocity condition:

$$\mathbf{G}_o(R, R') = \tilde{\mathbf{G}}_o(R', R), \tag{122}$$

which says the response in the kth channel at R due to a source in the lth channel at R' is equivalent to the response in the lth channel at R' due to a source in the kth channel at R. As $R \to \pm\infty$, the channels uncouple, and therefore the elements of the Green function matrix asymptotically are outgoing free waves:

$$[\mathbf{G}_o(R, R')]_{jl} \xrightarrow{R\to+\infty} -[e^{+i\mathcal{K}_jR}/(\mathcal{K}_j)^{1/2}][\mathcal{A}^+(R')]_{jl}, \tag{123a}$$

$$[\mathbf{G}_o(R, R')]_{jl} \xrightarrow{R\to-\infty} -[e^{-i\mathcal{K}_jR}/(\mathcal{K}_j)^{1/2}][\mathcal{A}^-(R')]_{jl}, \tag{123b}$$

where

$$\mathcal{K}_j = \frac{1}{\hbar}[2\mathcal{M}(E - \xi_j - V_{tr}(\pm\infty))]^{1/2}. \tag{124}$$

Equations (123) define the asymptotic amplitudes $\mathcal{A}^{\pm}(R')$ of the Green function matrix. The factor of $-\mathcal{K}_j^{-1/2}$ has simply been added for convenience [see the standard asymptotic form of the translational wave functions given by Eq. (142)]. Equations (123) can be written more compactly in matrix notation:

$$\mathbf{G}_0(R, R') \xrightarrow{R\rightarrow\pm\infty} \mathbf{\Lambda}^{\pm}(R)\mathscr{A}^{\pm}(R'), \tag{125}$$

where

$$(\mathbf{\Lambda}^{\pm})_{jl} = -[e^{\pm i\mathscr{K}_j R}/(\mathscr{K}_j)^{1/2}]\delta_{jl}. \tag{126}$$

The inversion of the operator in brackets in Eq. (120a) is accomplished by performing an integration over R' using the Green function matrix. For example, to apply the inverse operator to some functions of R, $\mathbf{Z}(R)$, we have

$$\hat{\mathscr{G}}_0\mathbf{Z}(R) = \int \mathbf{G}_0(R, R')\mathbf{Z}(R')\, dR' \tag{127}$$

Here we are using $\hat{\mathscr{G}}_0$ to distinguish the integral operator and the kernel $\mathbf{G}_0$. $\hat{\mathscr{G}}_0$ corresponds to $-\mathbf{G}_{PP}^{o+}$ in the formal theory; the factor of -1 arises from the factor of -1 connecting Eqs. (5) and (120). A numerical technique for generating $\mathbf{G}_0$ will be presented in Section II,B,2.

Using the Green function matrix to solve Eq. (120a) we have

$$\mathbf{F}_0 = \mathbf{F}_0^0 - \hat{\mathscr{G}}_0\mathbf{H}_{oc}\mathbf{F}_c, \tag{128}$$

where $\mathbf{F}_0^0$ is the solution to the open-channel-only problem:

$$[(T_R - E)\mathbf{1}_o + \boldsymbol{\xi}_o + \mathbf{H}_{oo}]\mathbf{F}_0^0 = \mathbf{0}. \tag{129}$$

Equations (128) and (129) correspond to the formal Eqs. (6) and (7), respectively. Using Eq. (128) in Eq. (120b), we obtain:

$$[(T_R - E)\mathbf{1}_c + \boldsymbol{\xi}_c + \mathbf{H}_{cc} - \mathbf{H}_{co}\hat{\mathscr{G}}_0\mathbf{H}_{oc}]\mathbf{F}_c = -\mathbf{H}_{co}\mathbf{F}_0^0, \tag{130}$$

which corresponds to Eq. (9).

From Eq. (130) we identify the level operator $\mathbf{L}_{cc}$ and the level shift operator $\mathbf{R}_{cc}$ as:

$$\mathbf{L}_{cc} = T_R\mathbf{1}_c + \boldsymbol{\xi}_c + \mathbf{H}_{cc} + \mathbf{R}_{cc}, \tag{131}$$

$$\mathbf{R}_{cc} = -\mathbf{H}_{co}\hat{\mathscr{G}}_0\mathbf{H}_{oc}. \tag{132}$$

The apparent difference in sign between Eqs. (132) and (11) is due to the factor of -1 relating the Green operators. As before, we define eigenvectors and eigenvalues of the level operator:

$$\mathbf{L}_{cc}\boldsymbol{\chi}_j = \varepsilon_j\boldsymbol{\chi}_j. \tag{133}$$

The resonance states are now $m \times 1$ column vectors containing m functions of R. The resonance states are orthogonal in a fashion similar to Eq. (22):

$$\langle\boldsymbol{\chi}_j^{\dagger}|\boldsymbol{\chi}_k\rangle = \delta_{jk}. \tag{134}$$

Here we use the adjoint symbol † to mean transpose complex conjugate. The orthogonality in Eq. (134) is a consequence of the reciprocity condition (122) since this orthogonality follows from the symmetry of L (see Appendix A).

The resonance states are found by diagonalizing the matrix representation of the level operator in translationally bound states. The translationally bound states ($m \times 1$ column vectors) are defined as

$$[T_R \mathbf{1}_c + \boldsymbol{\xi}_c + \mathbf{H}_{cc}]\boldsymbol{\phi}_l = W_l \boldsymbol{\phi}_l. \tag{135}$$

A numerical technique for solving the coupled closed channels problem (135) is presented in Section II,B,3. Using the eigenvalue property (135), the matrix elements of the level operator are

$$L_{kj} = W_k \delta_{kj} - \langle \tilde{\boldsymbol{\phi}}_k | \mathbf{H}_{co} \hat{\mathscr{G}}_o \mathbf{H}_{oc} | \boldsymbol{\phi}_j \rangle. \tag{136}$$

In Appendix A, the symmetry of L is related to the reciprocity condition (122). Diagonalizing the matrix representation of the level operator provides eigenvalues ε_j and eigenvectors for computing resonance states:

$$\boldsymbol{\chi}_j = \sum_{l=1}^{N} c_{lj} \boldsymbol{\phi}_l. \tag{137}$$

By expanding $\mathbf{F}_c$ in resonance states, we can solve Eq. (130):

$$\mathbf{F}_c = \sum_{j=1}^{N} \frac{\langle \boldsymbol{\chi}_j^\dagger | \mathbf{H}_{co} | \mathbf{F}_o^\circ \rangle}{E - \varepsilon_j} \boldsymbol{\chi}_j. \tag{138}$$

Substituting Eq. (138) in Eq. (128) we obtain the equation corresponding to Eq. (37):

$$\mathbf{F}_o = \mathbf{F}_o^\circ + \sum_{j=1}^{N} \frac{\langle \boldsymbol{\chi}_j^\dagger | \mathbf{H}_{co} | \mathbf{F}_o^\circ \rangle}{E - \varepsilon_j} \boldsymbol{\kappa}_j, \tag{139}$$

where the open-channel response function is

$$\boldsymbol{\kappa}_j = -\hat{\mathscr{G}}_o \mathbf{H}_{oc} | \boldsymbol{\chi}_j \rangle. \tag{140}$$

In writing expressions for S-matrix elements (probability amplitudes for undergoing transitions), we need to consider the asymptotic form of Eq. (139). The asymptotic form of $\boldsymbol{\kappa}_j$ can be determined by substituting the asymptotic form of $\mathbf{G}_o$ given by Eq. (125) into Eq. (140):

$$\boldsymbol{\kappa}_j \xrightarrow{R \to \pm\infty} -\boldsymbol{\Lambda}^\pm(R) \int \mathscr{A}^\pm(R') \mathbf{H}_{oc}(R') \boldsymbol{\chi}_j(R')\, dR' = -\boldsymbol{\Lambda}^\pm \mathbf{V}_j^\pm. \tag{141}$$

Equation (141) defines $\mathbf{V}_j^\pm$. Suppose the incident plane wave enters from $+\infty$ through the lth channel. Then the operational definition of the nonreactive S-matrix elements is

$$f_j(R) \xrightarrow{R \to +\infty} [c(\mathscr{K}_j)/(\mathscr{K}_j)^{1/2}][e^{-i\mathscr{K}_l R}\delta_{lj} - S_{jl}^{\mathrm{nr}} e^{+i\mathscr{K}_j R}], \tag{142a}$$

where $c(\mathscr{K}_j)$ is an arbitrary complex function of $\mathscr{K}_j$. Likewise, the operational definition for the reactive S-matrix elements is

$$f_j(R) \xrightarrow{R \to -\infty} -[c(\mathscr{K}_j)/(\mathscr{K}_j)^{1/2}]S_{jl}^{\mathrm{r}} e^{-i\mathscr{K}_j R}. \tag{142b}$$

Equations (142) give the asymptotic forms of both $\mathbf{F}_0$ and $\mathbf{F}_0^{\mathrm{o}}$. Using Eqs. (142) and (141) with (139), the S-matrix elements are given by

$$\mathbf{S}_{\mathrm{nr}} = S_{\mathrm{nr}}^{\mathrm{o}} - \sum_{j=1}^{N} \frac{\langle \chi_j^{\dagger} | \mathbf{H}_{\mathrm{co}} | \mathbf{F}_0^{\mathrm{o}} \rangle}{E - \varepsilon_j} \mathbf{V}_j^{+}, \tag{143a}$$

$$\mathbf{S}_{\mathrm{r}} = \mathbf{S}_{\mathrm{r}}^{\mathrm{o}} - \sum_{j=1}^{N} \frac{\langle \chi_j^{\dagger} | \mathbf{H}_{\mathrm{co}} | \mathbf{F}_0^{\mathrm{o}} \rangle}{E - \varepsilon_j} \mathbf{V}_j^{-}. \tag{143b}$$

In Eqs. (143) the subscripts "r" and "nr" denote "reactive" and "nonreactive," respectively. The superscript "o" indicates S-matrix elements for the corresponding open channel only problem given by Eq. (129). The $n \times 1$ vectors $\mathbf{S}_{\mathrm{nr}}$ and $\mathbf{S}_{\mathrm{r}}$ give those elements of the S-matrix associated with input flux in channel "l"; for example,

$$\mathbf{S}_{\mathrm{nr}} = \begin{bmatrix} S_{1l}^{\mathrm{nr}} \\ \vdots \\ S_{nl}^{\mathrm{nr}} \end{bmatrix}. \tag{144}$$

Here S_{jl}^{nr} is the probability amplitude for entering in channel l and exiting in channel j by the nonreactive process. The corresponding transition probability is given by $|S_{jl}^{\mathrm{nr}}|^2$. Conservation of probability requires

$$\sum_{j=1}^{n} (|S_{jl}^{\mathrm{nr}}|^2 + |S_{jl}^{\mathrm{r}}|^2) = 1 \tag{145a}$$

or

$$\mathbf{S}_{\mathrm{nr}}^{\dagger}\mathbf{S}_{\mathrm{nr}} + \mathbf{S}_{\mathrm{r}}^{\dagger}\mathbf{S}_{\mathrm{r}} = 1. \tag{145b}$$

The number of terms included in the summation in Eqs. (143) is equal to the basis size (N) used in constructing the matrix representation of the level operator. Hence the numerical values of the S-matrix elements depend on the number of translationally bound states used and lead to convergence provided a sufficiently large number are included (the sensitivity of the solution to basis size is discussed in Section II,B,4. However, Eq. (145) is satisfied for any basis size, as the Feshbach theory is inherently unitary (see Feshbach, 1967). Thus in applying the Feshbach theory, the calculation should conserve probability regardless of basis size, but conservation of probability does not guarantee converged S-matrix elements.

In computing a transition probability $|S_{jl}|^2$, one can see from Eq. (143) that there are three types of contributions. The first is the contribution from the open-channel-only S-matrix element, which is direct scattering. The second contribution is due to the formation and decay of the resonance states given by the summation in Eq. (143). The third contribution is due to "cross terms" between the summation and the open-channel-only S-matrix element. This third contribution represents interference between direct scattering and the formation and decay of the collision complex. An additional interference effect is due to interfering resonances in computing the magnitude square of the summation in Eq. (143).

2. *The Generation of the Open-Channel Green Function by the Technique of Redistributed Sources*

In applying the Feshbach theory, one needs to calculate $\mathbf{G}_o(R, R')$ in order to construct the matrix representation of the level operator. In addition, one needs to calculate the open-channel Green function matrix to apply the perturbation theory presented in Section II,A, or to calculate Siegert eigenvalues (the generation of $\mathbf{G}_o$ is slightly different for complex energies and will be discussed in Section II,B,5). The purpose of this section is to present the technique of redistributed sources for generating the open-channel Green function matrix (this numerical technique can be extended to the generation of the Green function matrix corresponding to the operator $(E - H)^{-1}$, where H is the total Hamiltonian of the system, by applying the proper boundary conditions to the closed-channel components). The technique of redistributed sources is based on a variation of well-known propagation techniques (Light, 1971; Light and Walker, 1976) used to numerically solve the coupled Schrödinger equations for nonreactive or reactive scattering problems.

We begin by separating the Green function matrix into n separate column vectors:

$$\mathbf{G}_o = [\mathbf{G}_1 \mathbf{G}_2 \cdots \mathbf{G}_n]. \tag{146}$$

On the column vectors $\mathbf{G}_j$ we omit the subscript "o" with the understanding that we are generating the *open-channel-only* Green function. Using the definition of the Green function matrix (121), the jth column vector $\mathbf{G}_j$ satisfies

$$[(T_R - E)\mathbf{1}_o + \boldsymbol{\xi}_o + \mathbf{H}_{oo}]\mathbf{G}_j(R, R') = \delta(R - R')\mathbf{1}_j, \tag{147}$$

where $\mathbf{1}_j$ is the jth column of the $n \times n$ identity matrix. For a given R', we shall solve (147) for the asymptotic amplitudes $\mathscr{A}_j^{\pm}(R')$ [jth column of $\mathbf{G}^{\pm}(R')$] and use a propagation technique to map the asymptotic ($R \to \pm\infty$) solution into the interaction region for all R. This process is repeated for all j and all R'.

Equation (147) can be rearranged as:

$$\frac{d^2}{dR^2}\mathbf{G}_j = \mathbf{U}(R)\mathbf{G}_j - \frac{2\mathcal{M}}{\hbar^2}\,\delta(R - R')\mathbf{1}_j, \tag{148}$$

where $\mathbf{U}$ is defined as

$$U_{kl}(R) \equiv (2\mathcal{M}/\hbar^2)[H_{kl}(R) + (\xi_k - E)\delta_{kl}]. \tag{149}$$

Note that $\mathbf{U}$ becomes diagonal in the asymptotic regions and the elements of $\mathbf{G}_j$ decouple. The source function $\delta(R - R')$ is contained in the jth channel. Hence $\mathbf{G}_j$ gives the response in all n open channels due to a unit point source in channel j. Integrating Eq. (148) from $R' - \delta$ to $R' + \delta$, where δ is a small positive number, we find

$$\frac{d}{dR}\mathbf{G}_j\bigg|_{R'+\delta} - \frac{d}{dR}\mathbf{G}_j\bigg|_{R'-\delta} = -\frac{2\mathcal{M}}{\hbar^2}\mathbf{1}_j. \tag{150a}$$

Hence the real parts of the *diagonal elements* of $\mathbf{G}_0$ have a first derivative that is discontinuous at the source point R' by the amount $-2\mathcal{M}/\hbar^2$.

We divide the interaction region into a large number of "sectors," each sufficiently small that $\mathbf{U}(R) \approx$ constant (see Fig. 2). Next we define a new column vector $\mathbf{G}_j^u$ within a given sector by the local transformation:

$$\mathbf{G}_j(R, R') = \mathbf{T}(R)\mathbf{G}_j^u(R, R'), \tag{151}$$

where $\mathbf{T}$ is the orthogonal matrix whose columns are the eigenvectors of $\mathbf{U}$. Substituting Eq. (151) into Eq. (148), and noting that $\mathbf{T}$ is approximately constant within a sector, we obtain

$$\frac{d^2}{dR^2}\mathbf{G}_j^u = \tilde{\mathbf{T}}\mathbf{U}\mathbf{T}\mathbf{G}_j^u - \frac{2\mathcal{M}}{\hbar^2}\,\delta(R - R')\tilde{\mathbf{T}}\mathbf{1}_j. \tag{152}$$

The matrix $\mathbf{D}$, defined by $\mathbf{D} \equiv \tilde{\mathbf{T}}\mathbf{U}\mathbf{T}$, is diagonal since we chose $\mathbf{T}$ to be the matrix of eigenvectors of $\mathbf{U}$: $D_{ij} = \lambda_i^2\delta_{ij}$. The eigenvalues λ_i^2 are real since $\mathbf{U}$ is Hermitian.

For $R \neq R'$, Eq. (152) simplifies to

$$\frac{d^2}{dR^2}\mathbf{G}_j^u(R, R') = \mathbf{D}\mathbf{G}_j^u(R, R'). \tag{153}$$

The elements of $\mathbf{G}_j^u$ are now uncoupled (hence the superscript "u") since $\mathbf{D}$ is diagonal. Solutions in the uncoupled picture can be propagated (both across sectors and across boundaries between sectors) from R_2

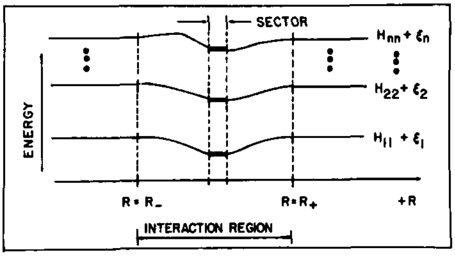


Fig. 2. Schematic illustration of a typical "sector" in which the potential energy curves are approximately constant.

to R_1 by the $2n \times 2n$ propagation matrix $\mathscr{P}(R_1, R_2)$ (see Appendix B):

$$\begin{bmatrix} \mathrm{G}_j^\mu(R_1, R') \\ \hdashline \mathrm{G}_j^\mu(R_1, R') \end{bmatrix} = \mathscr{P}(R_1, R_2) \begin{bmatrix} \mathrm{G}_j^\mu(R_2, R') \\ \hdashline \mathrm{G}_j^{\mu\prime}(R_2, R') \end{bmatrix}. \tag{154}$$

Here $\mathrm{G}_j^{\mu\prime}$ is the derivative of G_j^μ with respect to R. If we can determine G_j^μ at one particular R, we can use Eq. (154) to generate G_j^μ at all other R. As $R \to \pm\infty$, U becomes diagonal and T becomes the unit matrix. Thus G_j^μ and G_j become equivalent in the asymptotic region [see Eq. (125)]:

$$\mathrm{G}_j^\mu \xrightarrow{R\to\pm\infty} \Lambda^\pm(R)\mathscr{A}_j^\mp(R'). \tag{155}$$

Once the asymptotic amplitudes $\mathscr{A}_j^\mp$ are known, Eqs. (154) and (155) can be applied to calculate G_j^μ at any particular R. Then transformation (151) generates $\mathrm{G}_j(R, R')$ at that R. The problem now reduces to solving for the asymptotic amplitudes $\mathscr{A}_j^\mp(R')$.

In Eq. (152), the source function $\delta(R - R')$ is contained in all n open channels provided the elements of the jth row of T are nonzero. By introducing the decoupling transformation (151), we have redistributed the source function $\delta(R - R')$ among all n open channels. Thus we have placed in the uncoupled representation in channel "l" a source function $T_{jl}\delta(R - R')$ which is equivalent to a "unit source," $\delta(R - R')$, in channel j in the coupled representation. Integrating Eq. (152) from $R' - \delta$ to $R' + \delta$ we obtain

$$\frac{d}{dR}\mathrm{G}_j^\mu\bigg|_{R'+\delta} - \frac{d}{dR}\mathrm{G}_j^\mu\bigg|_{R'-\delta} = -\frac{2\mathscr{M}}{\hbar^2}\tilde{\mathrm{T}}\mathrm{1}_j. \tag{150b}$$

Thus in the uncoupled representation, *all elements* of G_j^μ in general will have a discontinuous first derivative in contrast to Eq. (150a). Applying the transformation (151) to Eq. (150b) we recover Eq. (150a).

Suppose we choose $R = R_+$ sufficiently large and $R = R_-$ sufficiently small that both $\mathrm{U}(R_+)$ and $\mathrm{U}(R_-)$ are diagonal. Then $\mathrm{G}_j^\mu(R_\pm, R')$ satisfies the asymptotic forms in Eq. (155). Suppose we propagate the asymptotic forms of $\mathrm{G}_j^\mu(R_\pm, R')$ and $\mathrm{G}_j^{\mu\prime}(R_\pm, R')$ in from the asymptotic region to the source point R' according to Eq. (154). Then inside the sector containing R', G_j^μ should be continuous at R' and $\mathrm{G}_j^{\mu\prime}$ should be discontinuous at R' according to Eq. (150b). (Matching must be done *within* a sector as the functions in the uncoupled picture, G_j^μ, are not continuous across the boundaries between sectors. See Appendix B.) In other words:

$$\mathcal{P}(R', R_-)\begin{bmatrix}\Lambda^-(R_-)\mathcal{A}_j^-(R')\\ \hdashline \Lambda^{-\prime}(R_-)\mathcal{A}_j^-(R')\end{bmatrix} = \mathcal{P}(R', R_+)\begin{bmatrix}\Lambda^+(R_+)\mathcal{A}_j^+(R')\\ \hdashline \Lambda^{+\prime}(R_+)\mathcal{A}_j^+(R')\end{bmatrix} + \frac{2\mathcal{M}}{\hbar^2}\begin{bmatrix}0\\ \hdashline \tilde{\mathrm{T}}(R')\mathrm{1}_j\end{bmatrix}. \qquad (156)$$

Here $\Lambda^{\pm\prime}$ are the derivatives with respect to R of $\Lambda^\pm$. Equations (156) are a set of $2n$ complex linear algebraic equations for the $2n$ asymptotic amplitudes $\mathcal{A}_j^\mp(R')$. Solving Eqs. (156) for $\mathcal{A}_j^\mp$ determines the asymptotic form of $\mathrm{G}_j(R, R')$. Then G_j^μ can be determined at all R:

$$\begin{bmatrix}\mathrm{G}_j^\mu(R, R')\\ \hdashline \mathrm{G}_j^{\mu\prime}(R, R')\end{bmatrix} = \mathcal{P}(R, R_+)\begin{bmatrix}\Lambda^+(R_+)\mathcal{A}_j^+(R')\\ \hdashline \Lambda^{+\prime}(R_+)\mathcal{A}_j^+(R')\end{bmatrix}. \qquad (157)$$

Applying Eq. (151) determines the desired column $\mathrm{G}_j(R, R')$ of the Green function matrix.

3. *Solving the Coupled Closed-Channel Problem*

In order to construct the matrix representation of the level operator, we must solve Eq. (135) for the eigenfunctions ϕ_l and eigenvalues W_l. The solution of Eq. (135) is complicated by the presence of $\mathrm{H}_{\mathrm{cc}}(R)$, which couples the m closed-channel components of ϕ_l. Suppose we can solve the one-dimensional Schrödinger equation associated with each *uncoupled* closed channel for its translational bound states and eigenvalues. For closed channel $n + k$ (recall there are n open channels):

$$(T_R + H_{n+k,n+k} + \xi_{n+k})\zeta_{n+k,j} = \omega_{n+k,j}\zeta_{n+k,j}, \\ j = 1, 2, \ldots, M(k), \quad k = 1, 2, \ldots, m. \qquad (158)$$

$\zeta_{n+k,j}$ represents the jth translational bound state in vibrational channel $n + k$ and $\omega_{n+k,j}$ is the associated eigenvalue. $M(k)$ is the number of translational bound states in the kth uncoupled closed channel that we wish to use in constructing a solution to Eq. (135). Since ϕ_{kl}, the kth element of $\boldsymbol{\phi}_l$, is associated with channel $n + k$, we expand ϕ_{kl} as follows:

$$\phi_{kl} = \sum_{j=1}^{M(k)} \alpha_{kjl} |\zeta_{n+k,j}\rangle . \tag{159}$$

Equation (135) is simply the matrix notation of Section II,B,1 for the eigenvalue problem:

$$(H - W_l)\Psi_l = 0, \tag{160}$$

where

$$\Psi_l = \sum_{k=1}^{m} \phi_{kl} |\Phi_{n+k}\rangle . \tag{161}$$

Equations (160) and (161) are equivalent to formal Eq. (12) as the summation in Eq. (161) extends only over closed channels. However, $\boldsymbol{\phi}_l$ [and not Ψ_l in Eq. (160)] in the matrix notation of Section II,B,1 plays the role of ϕ_l in the formal theory because we have eliminated the internal states $|\Phi_{n+k}\rangle$ in setting up the coupled Eqs. (116). Substituting Eq. (159) in Eq. (161) gives an expansion of Ψ_l in a basis consisting of products of "translational" and internal (vibrational) functions:

$$\Psi_l = \sum_{k=1}^{m} \sum_{j=1}^{M(k)} \alpha_{kjl} |\zeta_{n+k,j}\rangle |\Phi_{n+k}\rangle . \tag{162}$$

For simplicity we replace the channel index $n + k$ by a single letter with the understanding that we are interested in closed channels only. Let $\mathcal{O}_{tu}^{rs}$ denote the overlap between $|\zeta_{rs}\rangle|\Phi_r\rangle$ and $|\zeta_{tu}\rangle|\Phi_t\rangle$. Then

$$\mathcal{O}_{tu}^{rs} = \langle \Phi_r | \Phi_t \rangle \langle \zeta_{rs} | \zeta_{tu} \rangle = \delta_{rt}\delta_{su} . \tag{163}$$

The product basis is orthogonal since both H_{vib}^{0} and the operator in Eq. (158) are Hermitian operators with nondegenerate spectra of eigenvalues.

We can solve Eq. (160) by diagonalizing the matrix representation of H in the product basis of Eq. (162). Let us define the matrix representation of H, h_{tu}^{rs}, as follows:

$$h_{tu}^{rs} \equiv \langle \zeta_{rs} | \{ \langle \Phi_r | H | \Phi_t \rangle \} | \zeta_{tu} \rangle \tag{164}$$

or

$$h_{tu}^{rs} = \langle \zeta_{rs} | [(T_R + \xi_t)\delta_{rt} + H_{rt}(R)] | \zeta_{tu} \rangle . \tag{165}$$

Here we have used the definition of $H_{rt}(R)$ given by Eqs. (117). For $r = t$

(same channel) Eq. (165) becomes

$$h^{ts}_{tu} = \omega_{tu}\delta_{su} \tag{166}$$

with the aid of Eq. (158). For $r \neq t$, we have

$$h^{rs}_{tu} = \langle \zeta_{rs} | H_{rt}(R) | \zeta_{tu} \rangle . \tag{167}$$

Using Eqs. (166) and (167) we can set up the matrix equation corresponding to Eq. (160):

$$\mathbf{h}\boldsymbol{\alpha}_l = W_l \boldsymbol{\alpha}_l . \tag{168}$$

Diagonalizing **h** provides the eigenvalues W_l, and the eigenvector coefficients α_{kjl} needed in Eq. (159) to construct $\boldsymbol{\phi}_l$. [For the matrix Eq. (168), the double indices "rs" and "tu" in h^{rs}_{tu} must be regarded as single indices where "rs" denotes the row and "tu" denotes the column. Likewise, for α_{kjl}, "kj" denotes the particular element in the lth eigenvector $\boldsymbol{\alpha}_l$.]

4. *The Effect of a Finite Basis of Translationally Bound States on the Accuracy of the Solution*

The closed-channel (translational) wave function $\mathbf{F}_c$ is expressed either directly, or indirectly through resonances states, as an expansion in translationally bound states. What one calculates, therefore, is not the exact closed-channel wave function F^x_c, but an approximate closed channel wave function $\mathbf{F}^a_c$. The difference between the two is the error $\mathbf{F}^e_c$ associated with using a finite basis:

$$\mathbf{F}^x_c(R) = \mathbf{F}^a_c(R) + \mathbf{F}^e_c(R). \tag{169}$$

The error in the closed-channel wave function introduces a corresponding error in the open-channel wave function and S-matrix elements. Substituting $\mathbf{F}^a_c$, which one actually calculates, into Eq. (128) gives the approximate open-channel wave function $\mathbf{F}^a_o$:

$$\mathbf{F}^a_o = \mathbf{F}^o_o - \mathcal{G}_o\mathbf{H}_{oc}\mathbf{F}^x_c + \mathcal{G}_o\mathbf{H}_{oc}\mathbf{F}^e_c. \tag{170}$$

The first two terms of Eq. (170) are the exact open-channel wave function whose asymptotic form gives the correct S-matrix elements. The last term is the negative of the error in the open-channel wave function $-\mathbf{F}^e_o$:

$$\mathbf{F}^e_o = -\int \mathbf{G}(R, R')\mathbf{H}_{oc}(R')\mathbf{F}^e_c(R')\, dR'. \tag{171}$$

From Eq. (171), one can see that the error in the closed-channel wave function at all R' is superimposed by the nonlocal operator $\mathcal{G}$ to give the error in the open-channel wave function at each R. Thus one would expect the error in the open-channel wave function to be rather sensitive to the number of translationally bound states used in the calculation. Associated with the asymptotic form of Eq. (171) is the corresponding error introduced in the S-matrix elements:

$$-\int \mathcal{A}^{\pm}(R')\mathbf{H}_{oc}(R')\mathbf{F}_{c}^{e}(R')\,dR'.$$

Thus one would expect that the S-matrix elements may converge slowly with respect to the basis size of translationally bound states for large open/closed channel coupling. This is indeed the case and will be illustrated numerically for the model problem presented in Section II,C,5.

5. *A Technique for Calculating Siegert Eigenvalues and Siegert States*

As discussed in Section II,A,7, the Siegert states satisfy a set of coupled equations (100). Corresponding to these formal equations are the following matrix equations:

$$[(T_R - \varepsilon_j{}^s)\mathbf{1}_o + \boldsymbol{\xi}_o + \mathbf{H}_{oo}]\boldsymbol{\kappa}_j{}^s = \mathbf{H}_{oc}\boldsymbol{\chi}_j{}^s, \tag{172a}$$

$$[(T_R - \varepsilon_j{}^s)\mathbf{1}_c + \boldsymbol{\xi}_c + \mathbf{H}_{cc}]\boldsymbol{\chi}_j{}^s = \mathbf{H}_{co}\boldsymbol{\kappa}_j{}^s. \tag{172b}$$

The open-channel Siegert state $\boldsymbol{\kappa}_j{}^s$ and the closed-channel Siegert state $\boldsymbol{\chi}_j{}^s$ are $n \times 1$ and $m \times 1$ column vectors, respectively. The coupled equations (172) are equivalent to the following matrix equation:

$$[T_R\mathbf{1}_c + \boldsymbol{\xi}_c + \mathbf{H}_{cc} + \mathbf{R}_{cc}(\varepsilon_j{}^s)]\boldsymbol{\chi}_j{}^s = \varepsilon_j{}^s\boldsymbol{\chi}_j{}^s, \tag{173}$$

which corresponds to formal Eq. (103). In Eq. (173), the level shift operator is calculated for the complex energy $E = \varepsilon_j^s$:

$$\mathbf{R}_{cc}(\varepsilon_j^s) = -\mathbf{H}_{co}\hat{\mathcal{G}}_o(\varepsilon_j^s)\mathbf{H}_{oc}. \tag{174}$$

The Siegert eigenvalue $\varepsilon_j{}^s$ and the closed-channel Siegert state $\boldsymbol{\chi}_j{}^s$ can be found by iteratively solving Eq. (173) for the jth self-consistent eigenvalue and eigenvector. Suppose we diagonalize the matrix representation of the level operator at some energy near the position of the jth resonance, $E \approx \mathrm{Re}(\varepsilon_j)$. This provides the jth eigenvector, which we take to be an estimate of the expansion coefficients for $\boldsymbol{\chi}_j{}^s$ (all other eigenvectors are ignored), and an eigenvalue ε_j, which we take to be an estimate of the energy-independent eigenvalue ε_j^s. We now calculate the level operator at this new energy, $\mathbf{L}_{cc}(\varepsilon_j)$, and once more diagonalize the matrix representation of the level operator to obtain a better estimate of the energy-independent eigenvalue. Continuing in this fashion generates the self-consistent solutions $\varepsilon_j{}^s$ and $\boldsymbol{\chi}_j{}^s$ to Eq. (173). This procedure is demonstrated in Section II,C,4 for the model problem. It has been found to converge uniformly and rapidly provided the open/closed channel coupling is not large. Convergence is expected to be most rapid for narrow resonances (small coupling) as the initial guess for ε_j^s is real.

The open-channel Siegert state can be calculated once $\boldsymbol{\varepsilon}_j^s$ and $\boldsymbol{\chi}_j^s$ are known:

$$\boldsymbol{\kappa}_j^s = -\hat{\mathscr{G}}_0(\boldsymbol{\varepsilon}_j^s)\mathbf{H}_{oc}|\boldsymbol{\chi}_j^s\rangle. \tag{175}$$

The asymptotic form of $\boldsymbol{\kappa}_j^s$ is given by

$$\boldsymbol{\kappa}_j^s \xrightarrow{R\to\pm\infty} -\boldsymbol{\Lambda}^{\pm}(R) \int \mathscr{A}^{\pm}\mathbf{H}_{oc}\boldsymbol{\chi}_j^s \, dR', \tag{176}$$

which is similar to Eq. (125). An important difference is that each asymptotic wave number $\mathscr{K}_l$ in $\Lambda^{\pm}$ is calculated for a complex value of the energy. Substituting ε_j^s for E in Eq. (124) gives

$$\mathscr{K}_l = (1/\hbar)[2\mathscr{M}(\Omega_j^s - \xi_l - V_{\text{tr}}(\pm\infty)) - i\mathscr{M}\Gamma_j^s]^{1/2}, \tag{177}$$

where $\varepsilon_j^s = \Omega_j^s - i\Gamma_j^s/2$. Since $\Omega_j^s > \xi_l + V_{\text{tr}}(\pm\infty)$ and $\Gamma_j^s > 0$, we have $\text{Re}(\mathscr{K}_l) > 0$, $\text{Im}(\mathscr{K}_l) < 0$. Using these results in Eq. (126) shows that $\boldsymbol{\kappa}_j^s$ is an outgoing wave with an exponentially *increasing* envelope as $R \to \pm\infty$ in all n open channels. This will be illustrated numerically in Section II,C,3 for the model problem.

The Siegert eigenvalue problem is arrived at by replacing E in the Feshbach formalism by the self-consistent eigenvalue ε_j^s [see Eqs. (99) and (100)]. From the expressions for the S-matrix elements given by Eqs. (143), one can see that ε_j^s corresponds to a pole of all of the S-matrix elements in the complex energy plane.

To apply the iterative scheme outlined above, it is necessary to compute the Green function matrix for complex energy. Since the energy is complex, the asymptotic boundary conditions contain the complex wave numbers $\mathscr{K}_l(\varepsilon_j^s)$. This presents no problem. In addition, the matrix **U** defined by Eq. (149) now contains the complex eigenvalue ε_j^s on the diagonal. Thus the eigenvalues λ_l^2 of **U** are now complex. This changes the propagation matrix $\mathscr{P}$ described in Eq. (154) (for details, see Appendix B).

C. The Application of Resonance Theory to a Model Problem

In this section we shall illustrate the features of the Feshbach theory through application to a simple one-dimensional ($\kappa = 0$, $\eta = 1$) model problem. The particular model chosen is one of the simplest for demonstrating the general features of the theory. In order to illustrate the techniques presented in Section II,B for handling multiple open and closed channels, we have chosen two open and two closed channels. The two open channels have been chosen such that there is a single "sector" with nonzero coupling between open channels. This simplifies the application

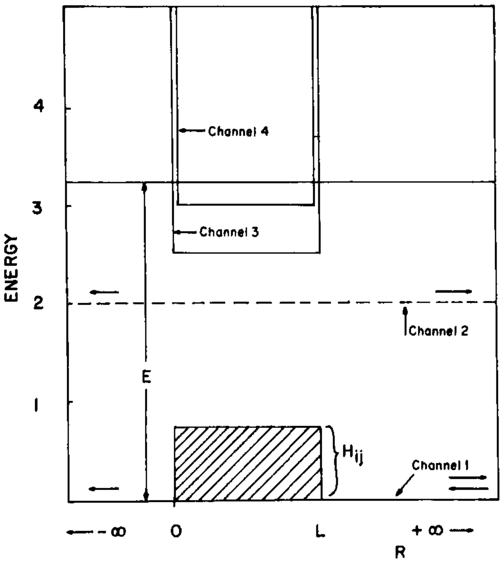


Fig. 3. Potential energy curves for the four-channel model.

of the technique of redistributed sources for generating the open-channel Green function matrix. In addition, the two closed channels have been chosen such that they remain asymptotically closed at all energies. Thus we can neglect the effects of a closed-channel continuum and the definitions of P and Q remain independent of energy for all energies above the threshold for the second channel. We shall see in Section II,C,2 that the particular closed channels chosen are ideally suited for studying both isolated and overlapping resonances.

The potential energy curves for the four-channel model are illustrated in Fig. 3. Channel 1 has a constant potential everywhere and defines the zero of energy:

$$H_{11}(R) + \xi_1 = 0.0 \tag{178}$$

($\hbar$ and $\mathcal{M}$ both are given the numerical value of unity). Likewise, channel 2 has a constant translational potential:

$$H_{22}(R) + \xi_2 = 2.0. \tag{179}$$

Channels 1 and 2 are open channels as we shall consider only $E > 2$. Channels 3 and 4 have constant potentials in the interaction region $0 \leq R \leq L$:

$$H_{33}(R) + \xi_3 = 2.5, \qquad 0 < R < L, \tag{180a}$$

$$H_{44}(R) + \xi_4 = 3.0, \qquad 0 < R < L, \tag{180b}$$

and become infinite at $R = 0$ and $R = L$. All four channels are coupled only in the interaction region by a constant matrix element indicated by H_{ij} in Fig. 3. H_{ij} is independent of R in the interaction region, but does depend upon the channel labels i and j. In illustrating the resonance theory, we shall find it convenient to vary both the coupling between closed channels and the coupling between open and closed channels. As indicated by the arrows in Fig. 3, we shall consider the incoming wave entering from $+\infty$ in channel 1. Except for the calculation illustrated later in Fig. 18, we shall take $L = 2$.

1. *Open-Channel Green Function Matrix*

The technique of redistributed sources presented in Section II,B,2 is exact for the open channels illustrated in Fig. 3 as the potentials are indeed constant in the "sector" $0 < R < L$. Figure 4 illustrates both $\mathbf{G}_\mathrm{I}^\mathrm{u}$ and $\mathbf{G}_\mathrm{I}$ for $R' = 0.5$, $E = 4.0$, and $H_{12} = 1.0$. Note in Fig. 4a and b that the source, represented by the discontinuous first derivative at $R' = 0.5$, has been "redistributed" among both channels 1 and 2. Note also that the functions G_{11}^u and G_{21}^u are *discontinuous* at the boundaries between sectors [see Eq. (B15) in Appendix B]. Upon transforming $\mathbf{G}_\mathrm{I}^\mathrm{u}$ according to Eq. (151), we obtain $\mathbf{G}_\mathrm{I}$ illustrated in Fig. 4c and d. This orthogonal transformation "magically" removes the discontinuities at $R = 0$ and $R = L$ while simultaneously removing the discontinuity in the first derivative of the off-diagonal element G_{21} as required by Eq. (150a). In the asymptotic

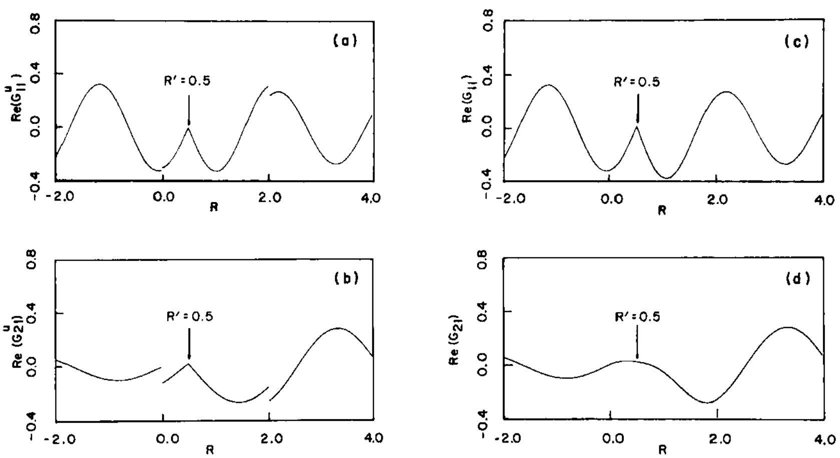


Fig. 4. $\mathbf{G}_\mathrm{I}^\mathrm{u}$ and $\mathbf{G}_\mathrm{I}$ as a function of R for $R' = 0.5$, $E = 4.0$, and $H_{12} = 1.0$.

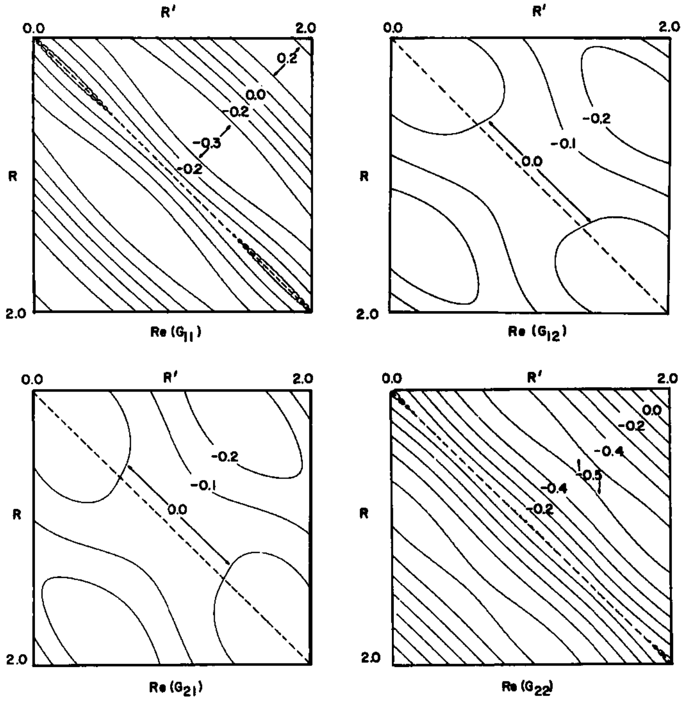


Fig. 5. Contours of the real part of G(R, R'), illustrating the reciprocity condition.

regions $R < 0$ and $R > L$, G_1^u and G_1 are identical since the channels are uncoupled and T = 1.

Figure 5 shows contours of the real parts of each element of the Green function matrix for $E = 4.0$ and $H_{12} = 1.0$. These contours demonstrate numerically the reciprocity condition (122), which gives rise to the symmetry of the matrix representation of the level operator and the orthogonality of the resonance states. The diagonal elements G_{11} and G_{22} are symmetric about the dashed line representing $R = R'$. The off-diagonal elements have the following symmetry: The region $R < R'$ of G_{12} is the same as the region $R > R'$ of G_{21}, and vice versa. The imaginary parts also have the same symmetry as required by Eq. (122). In addition, the real parts of G_{11} and G_{22} have a "crease" along $R = R'$ due to the discontinuity in slope at $R = R'$ (see Fig. 4c, which is a cut through this surface at $R' = 0.5$).

2. *The Coupled Closed Channels*

For the model problem illustrated in Fig. 3, the two closed channels are a pair of coupled "infinitely deep wells" extending from $R = 0$ to

$R = L$ [see Eqs. (180)]. In this region they are coupled by the constant matrix element H_{34}. The translational bound states and eigenvalues in each *uncoupled* closed channel satisfying Eq. (158) are the familiar infinitely deep well solutions. For channel 3 the solutions are

$$\zeta_{3j} = (2/L)^{1/2} \sin(j\pi R/L), \tag{181a}$$

$$\omega_{3j} = 2.5 + (\hbar^2/2\mathcal{M})(j\pi/L)^2, \qquad j = 1, 2, \ldots, M(1), \tag{181b}$$

and for channel 4 the solutions are

$$\zeta_{4k} = (2/L)^{1/2} \sin(k\pi R/L), \tag{181c}$$

$$\omega_{4k} = 3.0 + (\hbar^2/2\mathcal{M})(k\pi/L)^2, \qquad k = 1, 2, \ldots, M(2). \tag{181d}$$

Here $M(1)$ and $M(2)$ are the number of basis functions in the first and second closed channels, respectively, that we wish to use in constructing ϕ_l and W_l.

In order to construct the functions ϕ_l, we need to solve the eigenvalue problem given by Eq. (168). For the elements of the matrix $\mathbf{h}$, we have

$$h_{3k}^{3j} = \omega_{3k}\delta_{jk}, \tag{182a}$$

$$h_{4k}^{4j} = \omega_{4k}\delta_{jk}, \tag{182b}$$

$$h_{3k}^{4j} = h_{4k}^{3j} = H_{34}\delta_{jk}, \tag{182c}$$

corresponding to Eqs. (166) and (167). From Eq. (182c), we see that only the jth translational bound state in channel 3 will "mix" with the jth translational bound state in channel 4. Therefore, it is convenient for this problem to use the same number of bound states in each channel: $M(1) = M(2) = M$. Thus $\mathbf{h}$ is of dimension $2M \times 2M$ and we shall obtain $2M$ translationally bound states ϕ_l. As given by Eqs. (182), $\mathbf{h}$ is a tridiagonal matrix. This tridiagonal matrix can be rearranged as a block diagonal matrix with 2 × 2 matrices on the diagonal. Each 2 × 2 matrix is of the form:

$$\begin{bmatrix} \omega_{3j} & H_{34} \\ H_{34} & \omega_{4j} \end{bmatrix}, \qquad j = 1, 2, \ldots, M, \tag{183}$$

and can be diagonalized separately. The eigenvalues W_l of the translationally bound states ϕ_l are roots of

$$W_l^2 - (\omega_{3j} + \omega_{4j})W_l + \omega_{3j}\omega_{4j} - H_{34}^2 = 0, \tag{184}$$

where $l = 2j - 1$ and $l = 2j$. The translationally bound states are of the form:

$$\phi_l = (2/L)^{1/2} \begin{bmatrix} \alpha_{1jl} \sin(j\pi R/L) \\ \alpha_{2jl} \sin(j\pi R/L) \end{bmatrix}, \tag{185}$$

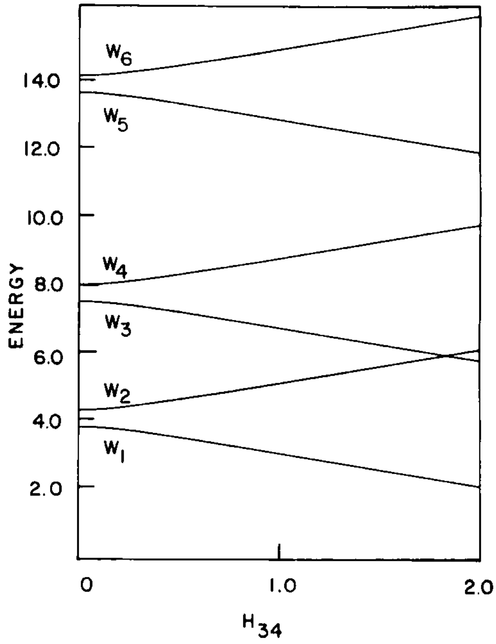


Fig. 6. A correlation diagram showing the translationally bound-state eigenvalues W_l, $l = 1, \ldots, 6$, as a function of the coupling between closed channels.

where the (normalized) eigenvector coefficients α_{1jl} and α_{2jl} are the nonzero solutions of

$$\begin{bmatrix} \omega_{3j} - W_l & H_{34} \\ H_{34} & \omega_{4j} - W_l \end{bmatrix} \begin{bmatrix} \alpha_{1jl} \\ \alpha_{2jl} \end{bmatrix} = 0. \tag{186}$$

Figure 6 shows a correlation diagram of the bound-state eigenvalues W_l as a function of H_{34} for $l = 1, 2, \ldots, 6$ (or $j = 1, 2, 3$). Since only the jth translationally bound state, ζ_{3j}, in the uncoupled channel 3 will "mix" with ζ_{4j} under the constant interaction H_{34}, it is possible for the eigenvalues W_l to cross at a particular coupling H_{34} provided they do not both arise from the roots of Eq. (184) with the same index j. This feature makes this particular model well suited for the study of overlapping resonances. Recall that for sufficiently small H_{oc}, the eigenvalues W_l roughly correspond to the positions of the resonances. Thus we could make H_{oc} small and set $H_{34} = 1.0$ to observe isolated resonances. Then we could increase H_{34} to a value near 1.8 and allow the resonances associated with W_2 and W_3 to interfere and overlap. As H_{34} is increased further, other crossings also occur. In Section II,C,5 we shall compare the qualitative features of both isolated and overlapping resonances.

3. *Resonance States and Siegert States*

Figure 7 shows both the real and imaginary parts of the channel-3 and channel-4 components of χ_3 for $E = 4.0$; $H_{12} = H_{34} = 1.0$; and $H_{ij} = 0.4$, $i = 1, 2$, and $j = 3, 4$. It was calculated by diagonalizing the level operator in a basis of $2M = 20$ translationally bound states. As one would expect from Eqs. (79) and (185), the shape of $\text{Re}(\chi_3)$ is the same as the zero-order contribution ϕ_3, which has the appearance $\sim \pm \sin(2\pi R/L)$ in both channels 3 and 4. Note that the amplitude of the real part of χ_3 is much larger than the amplitude of the imaginary part. This difference in amplitude arises since there is no zero-order contribution to the imaginary part of the resonance state [see Eq. (79)]. In addition, since $\text{Im}(\chi_3)$ also has the appearance of $\sin(2\pi R/L)$, the most significant first-order contribution is the term $\text{Im}(R_{43})\phi_4(W_3 - W_4)^{-1}$. Thus the imaginary part of the resonance state varies more rapidly than the real part with changes in energy or open/closed channel coupling.

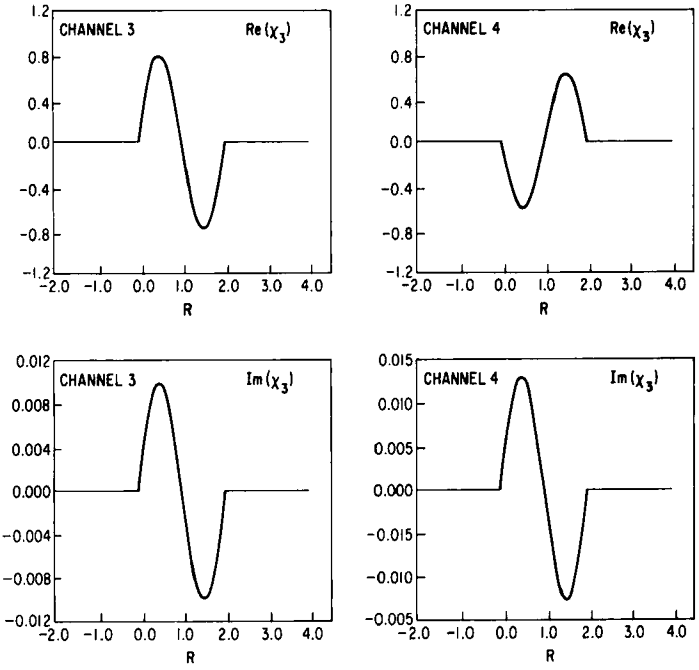


Fig. 7. Real and imaginary parts of the closed-channel resonance state χ_3.

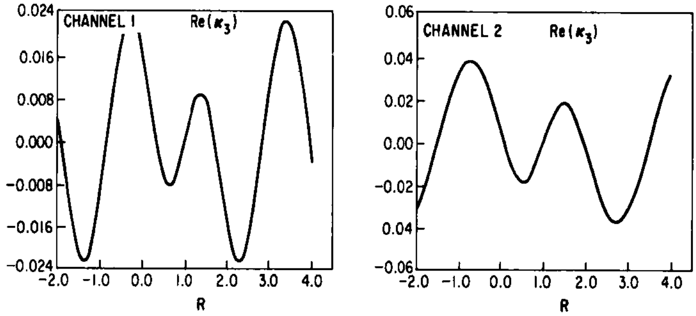


Fig. 8. Real part of the open-channel response function κ_3.

The open-channel response function corresponding to χ_3 is κ_3, whose real part is presented in Fig. 8. This function is antisymmetric about the center of the interaction region, $R = L/2 = 1.0$. All κ_j for this model are either symmetric or antisymmetric with respect to $R = L/2$. The type of symmetry or antisymmetry of κ_j is not a general feature of the open-channel response function but is only a reflection of the symmetric channel potentials and the symmetry of the outgoing-only boundary conditions of Eq. (141).

Figure 9 illustrates the real part of the energy-independent closed-channel Siegert state χ_3^s corresponding to the energy-dependent resonance state χ_3 in Fig. 7. χ_3^s was also calculated by diagonalizing the level operator (calculated at ε_j^s) in a basis of 20 translationally bound states using the same coupling parameters as in Fig. 7. The perturbative expansion of Eq. (79) is appropriate for χ_j^s as well as χ_j provided we evaluate the matrix elements R_{ij} at the complex eigenvalue energy ε_j^s. Thus we expect Re(χ_3^s) ≈ ϕ_3 for small coupling, which is verified by Fig. 9.

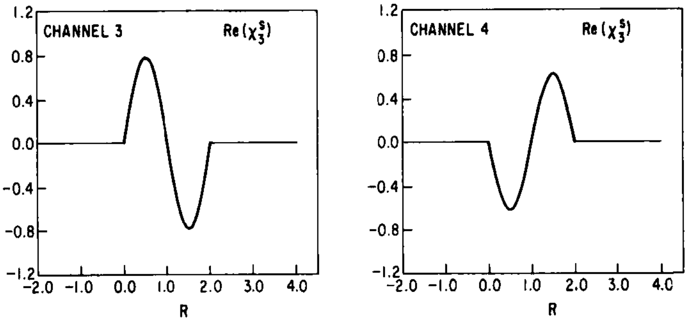


Fig. 9. Real part of the closed-channel Siegert state χ_3^s.

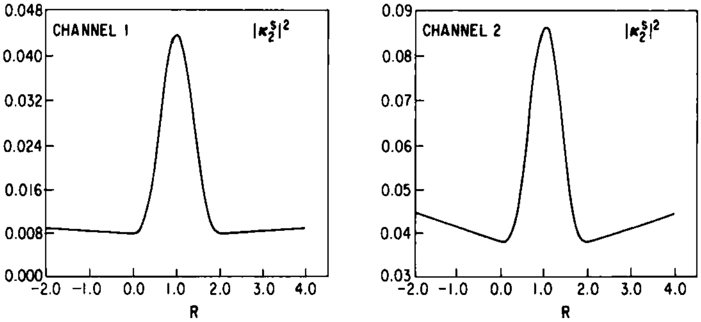


Fig. 10. The magnitude square of both channel components of κ_2^S, demonstrating the exponentially increasing envelope of the open-channel Siegert states.

The magnitude squares of the channel-1 and channel-2 components of κ_2^S are shown in Fig. 10. Here we are showing the magnitude square since it clearly demonstrates the *increasing* envelope of the open-channel Siegert state. Recall from the discussion of Section II,B,5 that the asymptotic form of the channel-l component of κ_j^s is $\sim\exp[\pm i\,\mathrm{Re}(\mathcal{K}_l)R]\ \exp[\pm\mathrm{Im}(\mathcal{K}_l)R]$. Then the asymptotic form of the magnitude square of each component is $\sim\exp[\pm 2\,\mathrm{Im}(\mathcal{K}_l)R]$. Since $\mathrm{Im}(\mathcal{K}_l) < 0$, this leads to the exponentially increasing density in the asymptotic regions, which is illustrated in Fig. 10. This exponentially increasing density is, of course, ''nonphysical'' and reflects the fact that the eigenvalues ε_j^s correspond to poles of the S-matrix in the complex energy plane.

4. *Resonance Parameters*

The convergence of the iterative technique of Section II,B,5 for calculating Siegert eigenvalues is demonstrated in Table I. The first five iterations in calculating ε_2^S are shown for the following set of parameters: $H_{12} = H_{34} = 1.0$; $H_{ij} = 0.4$, $i = 1, 2$, and $j = 3, 4$. The rather rapid convergence of ε_2^S is typical of the results that we have obtained in calculating other eigenvalues for small open/closed channel coupling. As one would expect, convergence is most rapid for small coupling and inherently narrow resonances.

In addition to the Siegert eigenvalue, one can define an energy-independent eigenvalue ε_k^F by calculating $\varepsilon_k(E)$ at the energy $\mathrm{Re}(\varepsilon_k)$:

$$\varepsilon_k^F \equiv \varepsilon_k(\mathrm{Re}(\xi_k^F)). \tag{187}$$

Thus ε_k^F is simply the Feshbach eigenvalue calculated at a particular real energy. Table II compares ε_k^S and ε_k^F for $k = 1, 2, 3$, and open/closed

TABLE I

CONVERGENCE OF A SIEGERT EIGENVALUE[a]

Iteration	Re(ε_2^S)	Im(ε_2^S)
0	5.0145	0.0000
1	5.2935	−0.1362
2	5.2839	−0.1015
3	5.2820	−0.1048
4	5.2824	−0.1047
5	5.2824	−0.1047

[a] The convergence of ε_2^S is shown for $H_{12} = H_{34} = 1.0$; $H_{ij} = 0.4$, $i = 1, 2$, and $j = 3, 4$.

TABLE II

COMPARISON OF ε_k^F AND ε_k^S[a]

		ε_k^F		ε_k^S	
k	H_{ij}	Real	Imaginary	Real	Imaginary
1	0.2	2.9539	−0.0030	2.9539	−0.0030
	0.4	2.9590	−0.0094	2.9591	−0.0094
	0.6	2.9675	−0.0124	2.9677	−0.0123
	0.8	2.9743	−0.0111	2.9744	−0.0110
2	0.2	5.0829	−0.0321	5.0836	−0.0315
	0.4	5.2748	−0.1129	5.2824	−0.1047
	0.6	5.5601	−0.2110	5.5818	−0.1811
	0.8	5.9086	−0.3013	5.9451	−0.2384
3	0.2	6.6543	−0.0009	6.6543	−0.0009
	0.4	6.6555	−0.0033	6.6555	−0.0033
	0.6	6.6579	−0.0064	6.6579	−0.0065
	0.8	6.6617	−0.0093	6.6617	−0.0093

[a] $H_{12} = H_{34} = 1.0$; H_{ij} represents all matrix elements coupling open and closed channels.

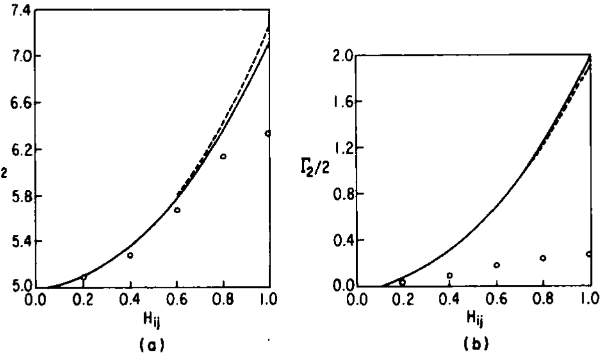


Fig. 11. Resonance parameters as a function of the coupling between open and closed channels: exact (solid line); first order (dashed line); Siegert (O).

channel couplings of $H_{ij} = 0.2, 0.4, 0.6, 0.8$. $\varepsilon_k^{\mathrm{F}}$ and $\varepsilon_k^{\mathrm{s}}$ are essentially identical for all H_{ij} for the inherently narrow resonances $k = 1$ and $k = 3$. This is to be expected since $\mathrm{Im}(\varepsilon_k^{\mathrm{s}})$ is small for narrow resonances. However, for the inherently broad resonance $k = 2$, $\varepsilon_k^{\mathrm{F}}$ and $\varepsilon_k^{\mathrm{s}}$ differ somewhat, even for small coupling. From Table II, it is apparent that $\mathrm{Re}(\varepsilon_k^{\mathrm{s}}) > \mathrm{Re}(\varepsilon_k^{\mathrm{F}})$ and $\mathrm{Im}(\varepsilon_k^{\mathrm{s}}) > \mathrm{Im}(\varepsilon_k^{\mathrm{F}})$. Note that the half-widths $\Gamma_k^{\mathrm{s}}/2$ and $\Gamma_k^{\mathrm{F}}/2$ corresponding to $\varepsilon_k^{\mathrm{s}}$ and $\varepsilon_k^{\mathrm{F}}$ do not vary as the square of the coupling (as the energy-dependent half-widths), but increase much more slowly. In fact, $\Gamma_1^{\mathrm{F}}/2$ and $\Gamma_1^{\mathrm{s}}/2$ both *decrease* in increasing H_{ij} from 0.6 to 0.8. If H_{ij} is increased to 1.0, this trend continues: $\Gamma_1^{\mathrm{F}}/2 = 0.0089$ and $\Gamma_1^{\mathrm{s}}/2 = 0.0088$.

Figure 11 compares the energy-dependent resonance parameters Ω_2 and $\Gamma_2/2$ calculated for $E = 4.0$, $H_{12} = H_{34} = 1.0$ as a function of open/closed channel coupling. The solid lines represent the "exact" resonance parameters, which were found by diagonalizing the representation of the level operator in a basis of 20 translationally bound states. The dashed line represents the first-order resonance parameters, which agree quite well with the exact resonance parameters, even for larger coupling. As predicted by the perturbation theory of Section II,A,4, the energy-dependent Feshbach resonance parameters vary quadratically with the strength of the open/closed channel coupling. For comparison, a few of the Siegert resonance parameters have also been plotted. The Siegert resonance parameters are quite different from the energy-dependent Feshbach resonance parameters since the latter are calculated at $E = 4.0$ (however, recall the close comparison of the self-consistent Feshbach eigenvalues and Siegert eigenvalues in Table II). As noted in the discussion of Table II, the Siegert resonance parameters do not show a quadratic dependence on the coupling strength.

The energy dependence of the Feshbach eigenvalue ε_2 is illustrated in Fig. 12. As before, $H_{12} = H_{34} = 1.0$, and $\varepsilon_2(E)$ is shown for $E = 4.0$–8.0 in increments of 0.4 and for open/closed channel couplings of both $H_{ij} = 0.4$ and 0.8. As the energy increases from 4.0 to 8.0, the real part of ε_2 monotonically decreases and the imaginary part increases as the eigenvalue moves closer to the real axis. As predicted in Section II,A,6, the energy dependence is strongest for the larger coupling, and the energy derivative is greatest at lower energies. Figure 12 also illustrates the perturbation theory of Section II,A,4. Increasing the coupling by a factor of 2 from 0.4 to 0.8 moves the eigenvalues approximately 4 times their original distance from the real axis. For comparison, ε_2^S and ε_2^F have been plotted for $H_{ij} = 0.8$. Notice that ε_2^F lies on a smooth curve passing through the points $\varepsilon_2(E)$, whereas ε_2^S does not. The Feshbach resonance parameters $\varepsilon_j(E)$ lie on a smooth curve not containing ε_j^S since $\varepsilon_j(E)$ is an analytic function evaluated at a real energy, while ε_j^S is the same function evaluated at a complex energy.

5. *Qualitative Features of Resonances*

In this section the qualitative features of both broad and narrow, and isolated and overlapping resonances are illustrated via the four-channel model.

Figure 13 shows transition probabilities as a function of energy for the following parameters: $H_{12} = H_{34} = 1.0$; $H_{ij} = 0.4$, $i = 1, 2$, and $j = 3, 4$; $4.0 \leq E \leq 8.0$. From Table II the resonance parameters for this case are $\varepsilon_2^S = (5.2824, -0.1047)$ and $\varepsilon_3^S = (6.6555, -0.0033)$. These resonance parameters suggest that we should observe a broad resonance around $E = 5.28$ and a narrow resonance centered at $E = 6.65$. In addition, ac-

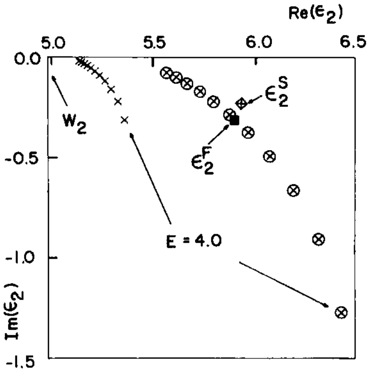


Fig. 12. The Feshbach eigenvalue ε_2 as a function of energy. (×)$H_{ij} = 0.4$; (⊗)$H_{ij} = 0.8$.

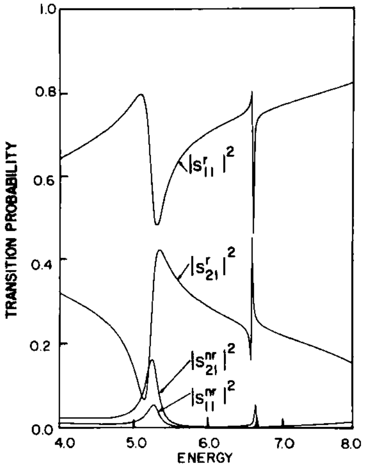


Fig. 13. Transition probabilities for a range of energies encompassing both a broad and a narrow resonance.

cording to the definition (51), the two resonances are isolated (not overlapping). These resonance parameters accurately predict the positions of the resonance structures of the transition probabilities in Fig. 13. However, the range of energies for which the resonances dominate the transition probabilities is actually somewhat larger than Γ_2^s and Γ_3^s. In any case $\Gamma_3^s < \Gamma_2^s$ predicts the third resonance to be more narrow than the second, which is qualitatively affirmed by Fig. 13. Of course, *all* transition probabilities change rapidly in the vicinity of each resonance, as is obvious from Eqs. (143).

Argand diagrams of S-matrix elements for energies near the broad resonance centered at $E = 5.28$ are shown in Fig. 14. The S-matrix elements are plotted for energies in the range $5.0 \leq E \leq 5.5$ in increments of 0.02. The direction of increasing energy is indicated by the arrow in the figure. The increasing separation of the plotted symbols as E nears 5.28 reflects the strong energy dependence of the S-matrix elements in the vicinity of the resonance. The nearly circular paths in the complex plane are characteristic of an isolated resonance.

As discussed in Section II,A,1, both $P\Psi$ and $Q\Psi$ change drastically for energies near a resonance. The rapid asymptotic variation of $P\Psi$, of course, is reflected in the S-matrix elements and transition probabilities. The rapid variation of $Q\Psi$ near a resonance is indicated in Fig. 15 by showing $|f_4|^2$ at $E = 5.18$, 5.28, and 5.38. As E nears the position of the resonance, $E \simeq 5.28$, the density associated with channel 4, $|f_4|^2$, increases substantially. Of course, a similar buildup of density occurs in channel 3 also.

By increasing H_{34}, we can drive the broad and narrow resonances of Fig. 13 closer together so that they overlap and interfere (recall the correlation diagram in Fig. 6). Table III presents the resonance parameters for $H_{34} = 1.6$, 1.7, and 1.8. For $H_{34} = 1.6$, the narrow resonance occurs at higher energies than for the broad resonance. As H_{34} is increased to 1.7, the resonances overlap according to the definition (51). Upon increasing H_{34} further to 1.8, the narrow resonance now occurs at lower energies than the broad resonance. Transition probabilities for these three cases are shown in Fig. 16. For $H_{34} = 1.6$ and 1.8, the narrow resonance intro-

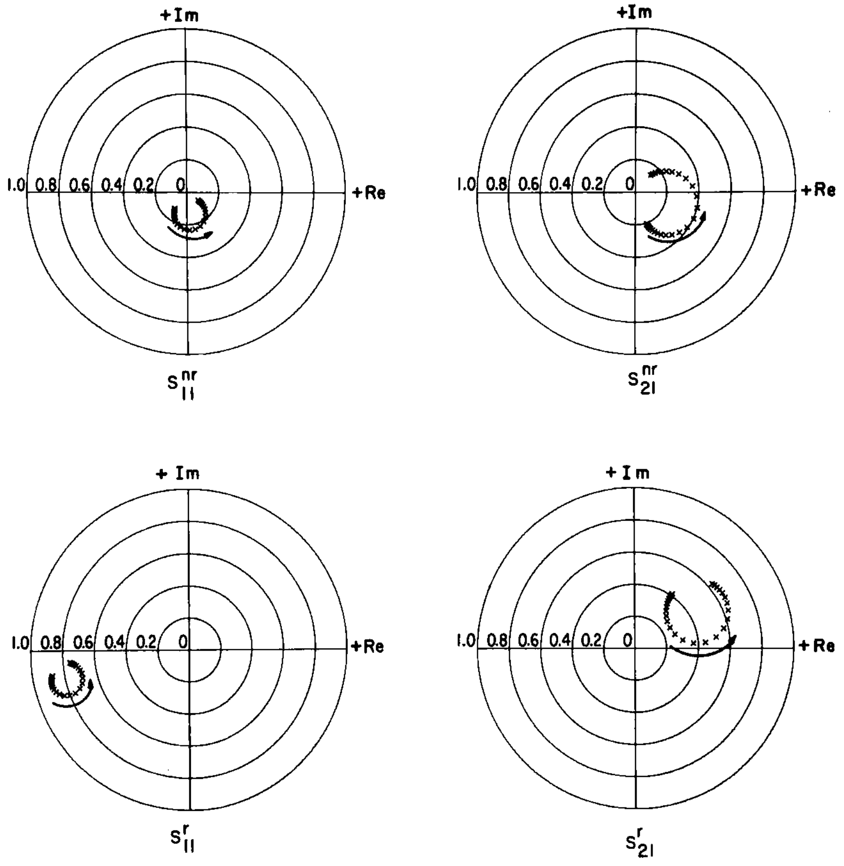


Fig. 14. Argand diagrams of S-matrix elements for a range of energies near an isolated resonance.

TABLE III

$\varepsilon_k^{\S}$ AS A FUNCTION OF H_{34}[a]

k	H_{34}	Re($\varepsilon_k^{\S}$)	Im($\varepsilon_k^{\S}$)
2	1.6	5.8341	−0.0734
(broad)	1.7	5.9275	−0.0692
	1.8	6.0212	−0.0652
3	1.6	6.0658	−0.0015
(narrow)	1.7	5.9998	−0.0014
	1.8	5.8677	−0.0012

[a] $H_{12} = 1.0$, $H_{ij} = 0.4$, $i = 1, 2$, and $j = 3, 4$.

duces an additional structure on curves that are otherwise qualitatively of the same shape as the isolated broad resonance of Fig. 13. For $H_{34} = 1.7$, the transition probabilities are qualitatively similar in shape to those of the isolated resonance of Fig. 13 except for the tiny irregularities indicated by the arrows and by the sharpness of the second extrema in $|S_{21}^{r}|^2$ and $|S_{11}^{r}|^2$. It is quite possible for one to mistake these strongly overlapping resonances for a single isolated resonance, based on the shape of these transition probabilities. However, if one looks at Argand diagrams of the S-matrix elements, it is clear that this resonance structure is due to overlapping resonances. Figure 17 shows the S-matrix elements as a function of energy for $5.0 \leq E \leq 5.5$ in increments of 0.02. The direction of increasing energy is indicated by the arrows. The interfering narrow reso-

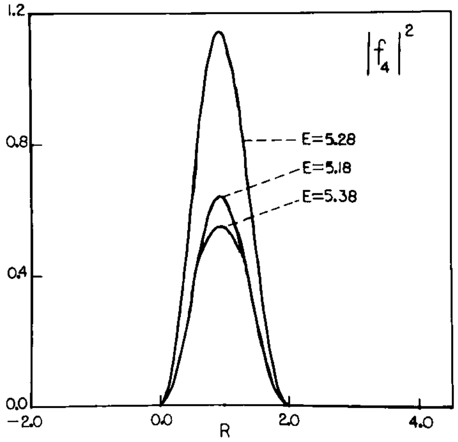


Fig. 15. The rapid variation of $Q\Psi$ for energies near a resonance is demonstrated by $|f_4|^2$ for energies below, on, and above resonance.

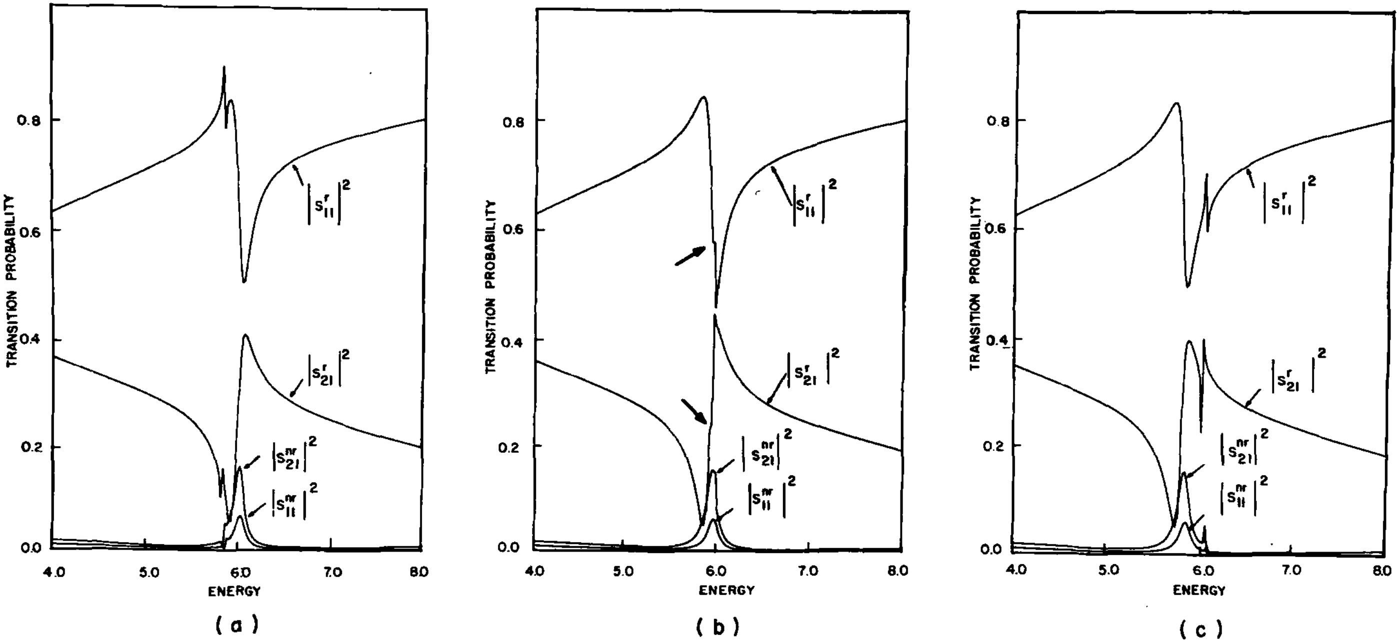


Fig. 16. Transition probabilities as a function of energy for H_{34} = 1.8 (a), 1.7 (b), and 1.6 (c).

nance introduces an additional structure (indicated by arrows in the figure), which distorts the large circular patterns that otherwise would be similar to those of Fig. 14.

Instead of varying H_{34}, we can also cause the resonances to overlap and interfere by increasing the length L of the interaction region. Increasing L causes the bound-state spectrum to become more dense. As the eigenvalues W_l crowd closer together, so do the positions Ω_j of the resonances since $\{W_l\}$ represent zero-order positions. Figure 18 compares S_{21}^{nr} for $L = 2.0$ and 8.0 (for $H_{12} = H_{34} = 1.0$; $H_{ij} = 0.4$, $i = 1, 2$, and $j = 3, 4$) for the same energies as Figs. 14 and 17. For $L = 2.0$ we get the usual circulation pattern characteristic of an isolated resonance. For $L = 8.0$,

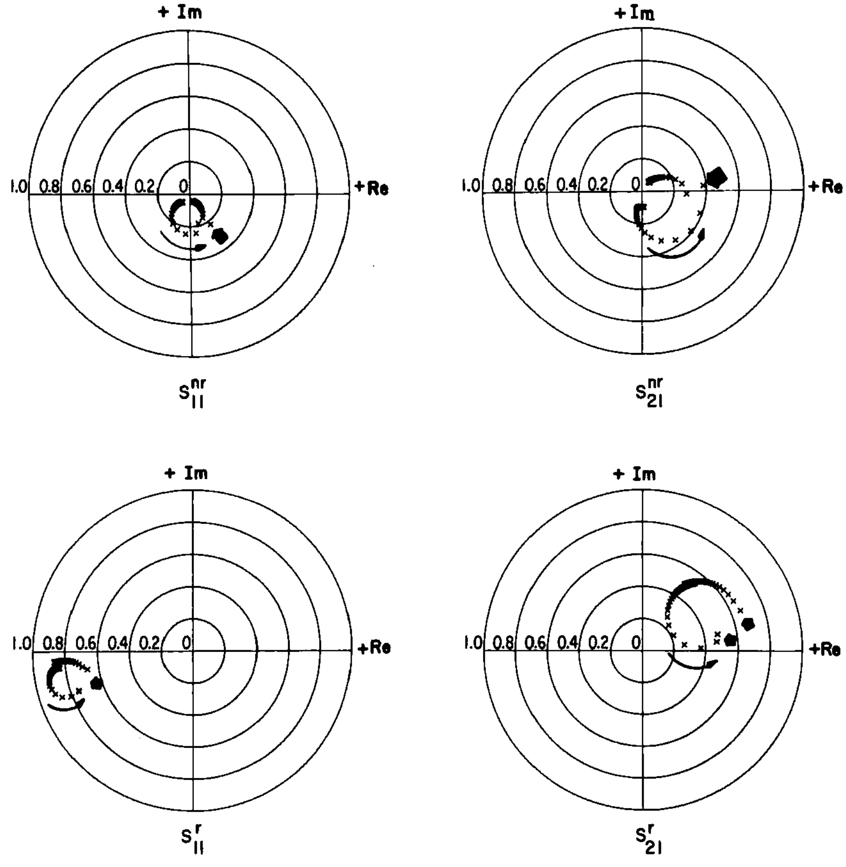
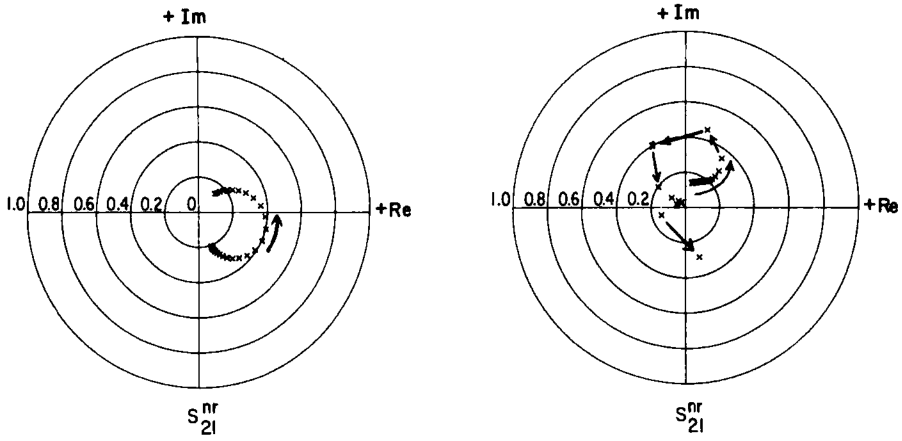


Fig. 17. Argand diagrams of S-matrix elements for a range of energies encompassing a pair of overlapping resonances.



(a) (b)

Fig. 18. Argand diagrams of S_{21}^{nr} comparing L = 2.0 (a) and 8.0 (b) for energies in the range $5.0 \leq E \leq 5.5$.

however, there appears to be a loss of correlation between neighboring points of an energy scan of increments of 0.02 for some energy ranges. The "loss of correlation" is only artificial in that by using a smaller increment one would find the S-matrix elements to be continuous functions of E, but very strongly energy-dependent due to the overlapping and interfering resonances.

Figure 18 was not generated using the Feshbach theory, but rather was solved by a propagation technique similar to that discussed in Section II,B,2 and Appendix B. As L is increased beyond 2.0, the Feshbach method rapidly requires a much larger basis of translationally bound states in order to generate converged S-matrix elements and quickly becomes unsuitable as a means of solving the stationary-state Schrödinger equation. As L increases, the eigenvalues W_l become more dense, and those resonances that were far resonances for small L now become strongly energy-dependent and make significant contributions to $Q\Psi$. Thus one needs to include additional "zero-order resonance states" ϕ_l in the calculation in order to properly calculate both $Q\Psi$ and S-matrix elements (see Section II,B,4). In addition, as the open/closed channel coupling is increased, a larger basis of translationally bound states is required. (See Table IV for a quantitative comparison.) However, the Feshbach technique is more sensitive to increasing L than to increasing the size of the open/closed channel coupling.

TABLE IV

S-MATRIX ELEMENTS AS A FUNCTION OF BASIS SIZE[a]

H_{ij}	Basis size, $2M$	S_{11}^{nr}		S_{21}^{nr}	
0.1	2	−0.058	−0.070	0.099	−0.036
	4	−0.058	−0.069	0.099	−0.034
	Exact	−0.058	−0.069	0.099	−0.034
0.4	2	−0.072	−0.103	0.155	−0.088
	4	−0.063	−0.086	0.143	−0.065
	6	−0.061	−0.088	0.144	−0.065
	Exact	−0.061	−0.088	0.143	−0.064

H_{ij}	Basis size, $2M$	S_{11}^{r}		S_{21}^{r}	
0.1	2	−0.739	−0.110	0.508	0.405
	4	−0.740	−0.111	0.507	0.405
	Exact	−0.740	−0.111	0.507	0.405
0.4	2	−0.769	−0.129	0.433	0.396
	4	−0.786	−0.137	0.407	0.402
	6	−0.786	−0.140	0.406	0.402
	Exact	−0.787	−0.140	0.405	0.402

[a] $H_{12} = H_{34} = 1.0$; $H_{ij} = 0.4$, $i = 1, 2$, and $j = 3, 4$; $E = 4.0$; $L = 2.0$.

III. Time-Dependent Theory

The time evolution of a quantum mechanical system can be described by the integrated form of the time-dependent Schrödinger equation:

$$\Psi(\mathrm{x}, t) = e^{-iH\Delta t/\hbar}\Psi(\mathrm{x}, t'), \tag{188}$$

where $\Delta t = t - t'$ and x denotes the complete set of coordinates for the problem at hand. In describing the time development of a collinear chemical reaction [of the form of Eq. (104)], let us form an initial wave packet at $t = t'$, or $\Delta t = 0$:

$$\Psi(\mathrm{x}, t') = (2\pi)^{-1/2} \int_0^\infty a(\mathcal{K}_1')\Psi(\mathrm{x}, \mathcal{K}_1')\, d\mathcal{K}_1'. \tag{189}$$

The factor $(2\pi)^{-1/2}$ is inserted for convenience in normalizing the initial wave packet. In Eq. (189) we are using the asymptotic wave vector in vibrational channel 1, $\mathscr{K}_1(E)$, as the variable of integration in superimposing the stationary solutions $\Psi(\mathrm{x}, \mathscr{K}_1)$ (E could also be used.) Inserting Eq. (189) into Eq. (188) and using the eigenvalue property of $\Psi(\mathrm{x}, \mathscr{K}_1')$ gives

$$\Psi(\mathrm{x}, t) = (2\pi)^{-1/2} \int_0^\infty a(\mathscr{K}_1')e^{-iE'\Delta t/\hbar}\Psi(\mathrm{x}, \mathscr{K}_1')\, d\mathscr{K}_1', \tag{190}$$

where $E' = E(\mathscr{K}_1')$. Performing the integration over $\mathscr{K}_1'$ for any given x and t (or Δt) gives the corresponding state of the collision system $\Psi(\mathrm{x}, t)$.

A. Translational Wave Packets

Since the experimentalist typically observes the product molecules or the unreacted molecules, we shall consider the form of Eq. (190) appropriate in the asymptotic reactant region $R > R_+$ and in the asymptotic product region $R < R_-$. Projecting on the internal states $\langle\Phi_j|$, the asymptotic form of Eq. (190) is

$$f_j(R, t) = (2\pi)^{-1/2} \int_0^\infty a(\mathscr{K}_1')e^{-iE'\Delta t/\hbar} f_j(R, \mathscr{K}_1')\, d\mathscr{K}_1',$$

$$j = 1, \ldots, n, \tag{191a}$$

$$f_j(R, t) = 0, \qquad j = n + 1, \ldots, n + m, \tag{191b}$$

where $f_j(R, t)$ are the *translational wave packets.* Equations (191) determine $P\Psi(t)$ in the asymptotic region (note that Eq. (191a) is valid for the truly collinear case $\kappa \neq 0$, as well as the one-dimensional case $\kappa = 0$, since the discussion is based on the asymptotic form of the wave function. Of course, Eq. (191b) implies $Q\Psi(t) = 0$ in the asymptotic region.

Suppose the initial wave packet is localized at $\Delta t = 0$ in channel l. Then in the asymptotic reactant region $R > R_+$, Eq. (191a) becomes

$$\begin{aligned} f_j(R, t) = {} & \delta_{lj}(2\pi)^{-1/2} \int_0^\infty [a(\mathscr{K}_1')/(\mathscr{K}_l')^{1/2}] \\ & \times \exp\{-i[\mathscr{K}_l'(R - R_0) + E'\,\Delta t/\hbar]\}\, d\mathscr{K}_1' \\ & -(2\pi)^{-1/2} \int_0^\infty [a(\mathscr{K}_1')/(\mathscr{K}_j')^{1/2}] S_{jl}^{\mathrm{nr}}(\mathscr{K}_1') \\ & \times \exp\{+i[\mathscr{K}_j'R + \mathscr{K}_l'R_0 - E'\,\Delta t/\hbar]\}\, d\mathscr{K}_1', \end{aligned} \tag{192}$$

where the asymptotic form of $f_j(R, \mathscr{K}_1')$ given by Eq. (142a) has been used and in which we have chosen $c(\mathscr{K}_l') = e^{+i\mathscr{K}_l'R_0}$ to set the initial conditions on the wave packet. In Eq. (192), $\mathscr{K}_j'(E)$ is considered to be a function of $\mathscr{K}_1'(E)$, and $\mathscr{K}_1(\xi_l)$ denotes the threshold of channel l in terms of $\mathscr{K}_1$. The first term of Eq. (192) represents the incoming wave packet and the second term is the reflected nonreactive wave packet. A corresponding equation can be written for $R < R_-$ describing the reactive wave packet.

Let us consider the kinematics of the incoming wave packet. The "position" of the incoming wave packet is taken to be the position at which the superposition of incoming waves constructively interferes. Constructive interference (superposition of waves of approximately the same wave number) occurs when the "phase" $\delta_l(\mathcal{K}_1)$ of the exponential:

$$\delta_l(\mathcal{K}_1) = \mathcal{K}_l(R - R_0) + E\,\Delta t/\hbar, \tag{193}$$

is stationary as a function of $\mathcal{K}_1$. Computing $d\delta_l/d\mathcal{K}_1$, we have

$$\frac{d\delta_l}{d\mathcal{K}_1} = (R - R_0)\frac{\mathcal{K}_1}{\mathcal{K}_l} + \frac{\Delta t}{\hbar}\left(\frac{\hbar^2\mathcal{K}_1}{\mathcal{M}}\right). \tag{194}$$

Here we have used $d\mathcal{K}_l/d\mathcal{K}_1 = \mathcal{K}_1/\mathcal{K}_l$ and the definition (124). Let $\bar{\mathcal{K}}_1$ represent the value of $\mathcal{K}_1$ for which the spectral distribution $a(\mathcal{K}_1)\mathcal{K}_l^{-1/2}$ is a maximum. Then equating $d\delta_l/d\mathcal{K}_1$ to zero and evaluating at $\mathcal{K}_1 = \bar{\mathcal{K}}_1$, we obtain

$$R = R_0 - \bar{V}_l\,\Delta t, \tag{195a}$$

where

$$\bar{V}_l \equiv \hbar\bar{\mathcal{K}}_l/\mathcal{M}. \tag{195b}$$

At $\Delta t = 0$ the wave packet is "located" near R_0. As Δt increases, the wave packet moves toward the interaction region with "speed" $\bar{V}_l$. Of course, Eq. (195a) is valid only for $R > R_+$, since we have based the discussion on the asymptotic form of the translational wave function. Equation (195a) is valid, therefore, for $\Delta t < \bar{V}_l^{-1}(R_0 - R_+)$.

Of course, the initial wave packet must be normalized:

$$\langle\Psi(\mathrm{x}, t')|\Psi(\mathrm{x}, t')\rangle = 1. \tag{196}$$

Since the time evolution operator $e^{-iH\Delta t/\hbar}$ is unitary, $\Psi(\mathrm{x}, t)$ remains normalized for all t. Since the wave packet is localized in the entrance channel l at $t = t'$, Eq. (196) becomes

$$1 = \int_{\mathcal{K}_1(\xi_l)}^{\infty}\int_{\mathcal{K}_1(\xi_l)}^{\infty}\frac{a^*(\mathcal{K}_1'')a(\mathcal{K}_1')}{(\mathcal{K}_l'\mathcal{K}_l'')^{1/2}}\,d\mathcal{K}_1'\,d\mathcal{K}_1''\,\frac{1}{2\pi} \times \int_{R_+}^{\infty}\exp[-i(\mathcal{K}_l' - \mathcal{K}_l'')(R - R_0)]\,d(R - R_0). \tag{197}$$

Since the initial wave packet is localized in the asymptotic region $R_+ < R < \infty$, the lower limit of the integral, R_+, may be formally extended to $-\infty$. Then this integral is just the Fourier representation of the

Dirac delta function, $\delta(\mathcal{K}_l' - \mathcal{K}_l'')$. Substituting $\delta(\mathcal{K}_l' - \mathcal{K}_l'') = (\mathcal{K}_l''/\mathcal{K}_1'')$ $\delta(\mathcal{K}_1' - \mathcal{K}_1'')$, the normalization condition is

$$\int_{\mathcal{K}_1(\xi_l)}^{\infty} |a(\mathcal{K}_1')|^2 \mathcal{K}_1'^{-1}\, d\mathcal{K}_1' = 1. \tag{198}$$

One possible choice of $a(\mathcal{K}_1)$ satisfying Eq. (198) is the Gaussian distribution:

$$a(\mathcal{K}_1)\mathcal{K}_1^{-1/2} = (2\pi)^{-1/4}(\Delta\mathcal{K}_1)^{-1/2} \exp[-(\mathcal{K}_1 - \mathcal{K}_1^0)^2/4\,\Delta\mathcal{K}_1^2], \qquad \mathcal{K}_1 > \mathcal{K}_1(\xi_l), \tag{199a}$$

$$a(\mathcal{K}_1)\mathcal{K}_1^{-1/2} = 0, \qquad \mathcal{K}_1 \le \mathcal{K}_1(\xi_l). \tag{199b}$$

For this spectral distribution $a(\mathcal{K}_1)\mathcal{K}_1^{-1/2}$ is peaked about $\overline{\mathcal{K}}_1 = \mathcal{K}_1^0$ with a width measured by $\Delta\mathcal{K}_1$. Since $a(\mathcal{K}_1) \equiv 0$ for $\mathcal{K}_1 < \mathcal{K}_1(\xi_l)$, we must choose $\mathcal{K}_1^0 \gg \mathcal{K}_1(\xi_l)$ for Eq. (199a) to satisfy Eq. (198).

The kinematics of the outgoing, nonreactive wave packet can be understood in a similar fashion. Substituting

$$S_{jl}^{\mathrm{nr}}(\mathcal{K}_1') = |S_{jl}^{\mathrm{nr}}(\mathcal{K}_1')| e^{i\delta_{jl}^{\mathrm{nr}}(\mathcal{K}_1')} \tag{200}$$

in the second term of Eq. (192), the outgoing, nonreactive wave packet in vibrational channel j is

$$-(2\pi)^{-1/2} \int_0^{\infty} \frac{a(\mathcal{K}_1')|S_{jl}^{\mathrm{nr}}|}{\sqrt{\mathcal{K}_j'}} e^{+i\delta_o(\mathcal{K}_1')}\, d\mathcal{K}_1', \tag{201a}$$

where the phase of the outgoing wave, $\delta_o(\mathcal{K}_1')$, is given by

$$\delta_0(\mathcal{K}_1') = \mathcal{K}_j' R + \mathcal{K}_l' R_0 + \delta_{jl}^{\mathrm{nr}}(\mathcal{K}_1') - E'\,\Delta t/\hbar. \tag{201b}$$

Computing the derivative of $\delta_0(\mathcal{K}_1')$, we have

$$\frac{d\delta_0}{d\mathcal{K}_1'} = R\,\frac{\mathcal{K}_1'}{\mathcal{K}_j'} + R_0\,\frac{\mathcal{K}_1'}{\mathcal{K}_l'} + \frac{d\delta_{jl}^{\mathrm{nr}}}{d\mathcal{K}_1'} - \frac{\hbar\mathcal{K}_1'}{\mathcal{M}}\,\Delta t. \tag{202}$$

Next we must equate $d\delta_0/d\mathcal{K}_1'$ to zero and evaluate it at the maximum of the spectral distribution $a(\mathcal{K}_1')|S_{jl}^{\mathrm{nr}}(\mathcal{K}_1')|\mathcal{K}_j'^{-1/2}$. The effect of the factor $|S_{jl}^{\mathrm{nr}}|$ is to shift the maximum away from the maximum of the original incoming spectral distribution $a(\mathcal{K}_1')\mathcal{K}_l'^{-1/2}$ at $\mathcal{K}_1' = \bar{\mathcal{K}}_1$ to a different value, $\mathcal{K}_1' = \tilde{\mathcal{K}}_1$. In fact, if there are several resonances in the range of energies for which $a(\mathcal{K}_1')$ is of appreciable amplitude, there may be several maxima of $a(\mathcal{K}_1')|S_{jl}^{\mathrm{nr}}|\mathcal{K}_j'^{-1/2}$. Thus each resonance can give rise to an outgoing wave packet, each moving with a different velocity. Let us suppose that a particular maximum of the spectral distribution occurs at $\mathcal{K}_1' = \tilde{\mathcal{K}}_1$. Then setting Eq. (202) equal to zero and evaluating at $\mathscr{K}'_1 = \tilde{\mathscr{K}}_1$ yields

$$R = \frac{\tilde{\mathscr{K}}_j}{\tilde{\mathscr{K}}_l} R_0 - \frac{\tilde{\mathscr{K}}_j}{\tilde{\mathscr{K}}_1} \frac{d\delta_{jl}^{\mathrm{nr}}}{d\mathscr{K}'_1} + \tilde{V}_j \, \Delta t, \tag{203a}$$

$$\tilde{V}_j \equiv \hbar \tilde{\mathscr{K}}_j / \mathscr{M}. \tag{203b}$$

In Eq. (203a), $\tilde{\mathscr{K}}_j = \mathscr{K}_j(\tilde{\mathscr{K}}_1)$. Likewise, $d\delta_{jl}^{\mathrm{nr}}/d\mathscr{K}'_1$ is evaluated at $\mathscr{K}'_1 = \tilde{\mathscr{K}}_1$. Thus an outgoing, nonreactive wave packet moves away from the interaction region with "velocity" $\tilde{V}_j$.

Since the discussion above is based on the asymptotic form of the translational wave functions, $R > R_+$, Eq. (203a) is valid only for $\Delta t > \Delta t_{\mathrm{min}}$, where

$$\Delta t_{\mathrm{min}} = \frac{\mathscr{M}}{\hbar \tilde{\mathscr{K}}_j} \left(R_+ + \frac{\tilde{\mathscr{K}}_j}{\tilde{\mathscr{K}}_l} R_0 \right) + \frac{\mathscr{M}}{\hbar \tilde{\mathscr{K}}_1} \frac{d\delta_{jl}^{\mathrm{nr}}}{d\mathscr{K}'_1}. \tag{204}$$

The term in Eq. (204) *not* associated with the initial position (i.e., R_0) or the definition of the asymptotic region (i.e., R_+) must be the *time delay* τ due to the excitation and subsequent decay of $Q\Psi(t)$. Therefore, we define the time delay as

$$\tau = \frac{\mathscr{M}}{\hbar \tilde{\mathscr{K}}_1} \left. \frac{d\delta_{jl}^{\mathrm{nr}}}{d\mathscr{K}'_1} \right|_{\mathscr{K}'_1 = \tilde{\mathscr{K}}_1} = \hbar \frac{d\delta_{jl}^{\mathrm{nr}}}{dE}. \tag{205}$$

(For other discussions of the time delay, see Bohm, 1951; Wigner, 1955; Smith, 1960.) Associated with each maximum of $a(\mathscr{K}'_1)|S_{jl}^{\mathrm{nr}}|\mathscr{K}_j'^{-1/2}$ there will be an outgoing wave packet whose kinematics is described by Eq. (203a) and suffering a time delay given by Eq. (205). Qualitatively, we know from the Feshbach formalism that the S-matrix is more strongly energy-dependent for energies in the vicinity of a narrow resonance than for energies near a broad resonance. Thus from Eq. (205) we see that a broad resonance is associated with a short time delay and a narrow resonance is associated with a long time delay.

If the spectral distribution of the outgoing wave packet is rather broad, then the wave packet will be somewhat localized and the kinematics of Eq. (203a) will be convenient. However, if the spectral distribution is narrow, then the wave packet will be spread out and the "position" given by Eq. (203a) will not be distinct. Thus for a peak in the spectral distribution due to a *broad* resonance we expect Eq. (203a) to be applicable. By the same token, Eq. (203a) is of little use for wave packets arising from narrow resonances. In addition, both the incoming wave packet and all outgoing wave packets continually spread at Δt increases.

B. Time-Dependent Theory and Resonance Parameters

From the discussion of Feshbach resonance theory of Section II, it would seem reasonable that an S-matrix element S_{jl} could be approximately parameterized as

$$\begin{aligned} S_{jl}(E') &\cong \alpha_{jl} + \frac{\beta_{jl}}{(E' - \Omega_k) + i\Gamma_k/2} \\ &= S_{jl}(\text{background}) + S_{jl}(\text{res}; E') \end{aligned} \tag{206}$$

for a range of energies near an isolated resonance centered at $E' = \Omega_k$. Equation (206) is the well-known *Breit–Wigner parameterization* (e.g., see Taylor, 1971; Roman, 1965). Here α_{jl} and β_{jl} are taken to be independent of E' for the range of energies in question: Ω_k and Γ_k are taken to be energy-independent resonance parameters, such as the Siegert or self-consistent Feshbach resonance parameters. Naturally, α_{jl} contains both the contribution of the open-channel-only S-matrix element and the contributions from far resonances. Upon substituting Eq. (206) into the outgoing wave packet of Eq. (192), we would obtain two integrals. The wave packet associated with α_{jl} corresponds to a promptly scattered wave packet since α_{jl} is approximately constant for the range of energies in question. The second term of Eq. (206) gives rise to the time-delayed wave packet. Defining $\beta_{jl} = \beta_{\mathrm{R}} + i\beta_{\mathrm{I}}$, we have for the phase and magnitude of $S_{jl}(\text{res}; E')$:

$$\delta_{jl}(E') \cong \tan^{-1}\left(\frac{\beta_{\mathrm{I}}(E' - \Omega_k) - \beta_{\mathrm{R}}\Gamma_k/2}{\beta_{\mathrm{R}}(E' + \Omega_k) + \beta_{\mathrm{I}}\Gamma_k/2}\right), \tag{207a}$$

$$|S_{jl}(\text{res}; E')| \cong |\beta_{jl}|[(E' - \Omega_k)^2 + \Gamma_k^2/4]^{-1/2}. \tag{207b}$$

From Eq. (207b) it is evident that the spectral distribution $a(\mathcal{K}_1')|S_{jl}^{\mathrm{r}}|\mathcal{K}_j^{-1/2}$ is peaked at approximately $E' = \Omega_k$, or $\tilde{\mathcal{K}}_1 = \mathcal{K}_1(\Omega_l)$, provided $a(\mathcal{K}_1')$ is not strongly peaked. Computing the derivative of Eq. (207a) with respect to $\mathcal{K}_1'$, we have

$$\frac{d\delta_{jl}}{d\mathcal{K}_1'} \approx \left(\frac{\hbar^2\mathcal{K}_1}{\mathcal{M}}\right) \frac{|\beta_{jl}|^2\Gamma_k/2}{[\beta_{\mathrm{R}}(E' - \Omega_k) + \beta_{\mathrm{I}}\Gamma_k/2]^2 + [\beta_{\mathrm{I}}(E' - \Omega_k) - \beta_{\mathrm{R}}\Gamma_k/2]^2}. \tag{208}$$

Evaluating Eq. (208) at $E' = \Omega_k$ and substituting into Eq. (205) yields the connection between the time delay τ and the resonance width parameter Γ_k:

$$\tau_k \approx 2\hbar/\Gamma_k. \tag{209}$$

Here we have added the subscript k to the time delay to emphasize that it arises from the kth resonance. Thus a broad resonance gives rise to a short time delay, and a narrow resonance gives rise to a lengthy time delay. It must be emphasized that Eq. (209) should be regarded only as a qualitative connection between Γ_k and τ_k because it is based on a number of severe assumptions that may seldom be realized. Note that the factor β_{jl} does not appear in Eq. (209). Thus τ_k is the same for *all* exit channels.

The resonance parameters Ω_k and Γ_k determine the qualitative nature of the time-delayed wave packets. The resonance parameter Ω_k determines the "velocity" of the outgoing wave packet in *each* exit channel j, $\bar{V}_j = h\bar{\mathscr{K}}_j/\mathscr{M} \cong h\mathscr{K}_j(\Omega_k)/\mathscr{M}$, since Eq. (207b) is peaked about $E' = \Omega_k$. The resonance parameter Γ_k determines both the time delay for *all* exit channels and the "width" of the peak approximately centered at $\mathscr{K}_1(\Omega_k)$ in the spectral distribution $a(\mathscr{K}_1)|S_{jl}(\text{res};\ E')|\mathscr{K}_j^{-1/2}$. Thus a narrow resonance is associated with a long time delay and a broad wave packet, whereas a broad resonance is associated with a short time delay and a somewhat more localized wave packet.

C. The Time Evolution of the Model Problem

In this section, we shall illustrate the discussion of the time-dependent theory using the model problem of Section II,C. For the results presented below, the following coupling parameters were used: $H_{12} = H_{34} = 1.0$; $H_{ij} = 0.8$, $i = 1, 2$, and $j = 3, 4$. In addition, $a(\mathscr{K}_1)$ is given the functional form in Eq. (199) with $\Delta\mathscr{K}_1 = 0.9$ and $\mathscr{K}_1^0 = 5.1$ (corresponding to an average energy of 13.0). The initial wave packet is localized in channel 1 at $R_0 = 6.0$.

The initial incoming translational wave packet (magnitude-square) is illustrated in Fig. 19. $|f_1|^2$ has a maximum of 0.69 centered at $R = R_0 = 6.0$. At $\Delta t = 0.6$, the incoming wave packet has moved toward the interaction region and broadened somewhat. Even though the leading edge of the wave packet has entered the interaction region, all probability (on this scale) remains localized in the entrance channel.

This distribution of probability at $\Delta t = 1.2$ is shown in Fig. 20. The bulk of the incoming wave packet has plowed through the interaction region and is being promptly transmitted. In addition, considerable excitation of the closed channels has occurred and a promptly scattered reactive wave packet is leaving the interaction region in channel 2. The "bumps" of the reactant site of the channel-1 wave packet result from interference between the promptly scattered, nonreactive, elastic wave packet and the trailing portions of the incoming wave packet.

Figure 21 illustrates the spectral distribution $a(\mathscr{K}_1)|S_{21}^{\text{nr}}|\mathscr{K}_2^{-1/2}$ as a function of $\mathscr{K}_1$ for the outgoing wave packets corresponding to the nonreactive, inelastic process of forming vibrationally excited reactants. The peaks corresponding to the inherently broad resonances 2, 4, 6, and 8 are

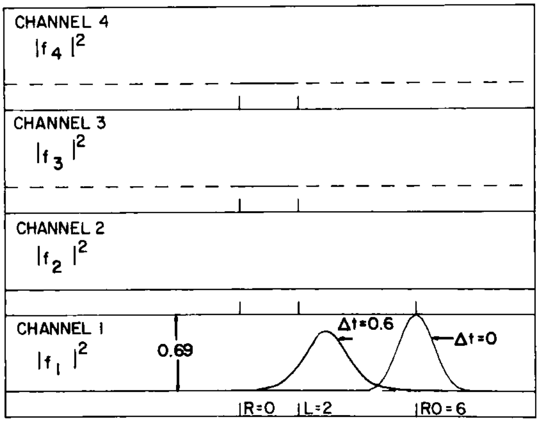


Fig. 19. Magnitude square of the incoming wave packet at $\Delta t = 0$ and 0.6.

labeled. The smaller structures are due to the inherently narrow resonances 1, 3, 5, and 7 (in order of increasing position). The positions of these structures are accurately predicted by the Siegert positions Ω_j^s. The amplitudes of peaks (4) and (6) are larger, in part, due to the maximum of $a(\mathcal{K}_1)$ near $\mathcal{K}_1 = 5.0$. The outgoing wave packets corresponding to peaks (4) and (6) are indicated in Fig. 22 by the cross-hatched areas under the arrows. The positions of the arrows were calculated using Eqs. (203a) and (209). For resonances 4 and 6, the time delays calculated from the Siegert widths are 2.07 and 2.21, respectively. Note that the scale (0.034) used in plotting Fig. 22 is approximately 20 times smaller than that of Figs. 19 and 20.

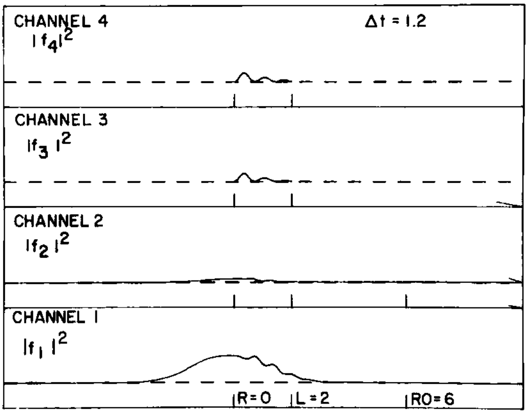


Fig. 20. Magnitude square of the translational wave packets at $\Delta t = 1.2$.

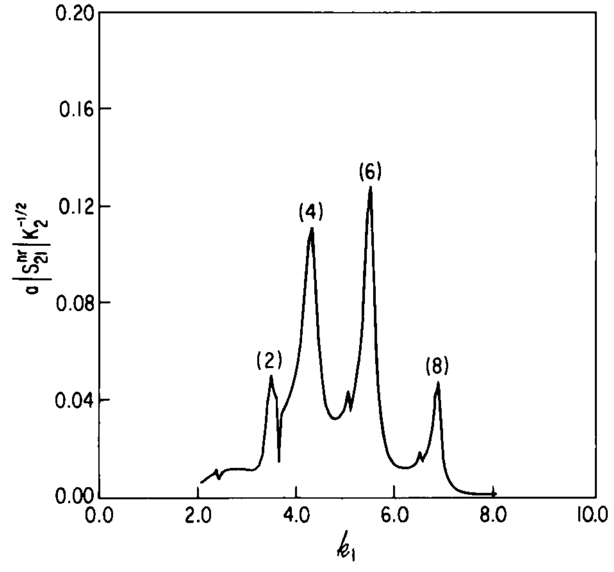


Fig. 21. The spectral distribution for the nonreactive, outgoing wave packets in channel 2. The peaks labeled (2), (4), (6), and (8) are positioned at $\mathcal{K}_1(\Omega_j^s)$, $j = 2, 4, 6$, and 8.

The total probability in the closed channels as a function of Δt is shown in Fig. 23. Note the rapid excitation followed by rapid decay as the incoming wave packet moves through the interaction region. For longer times, however, the decay is much slower and clearly nonexponential. If

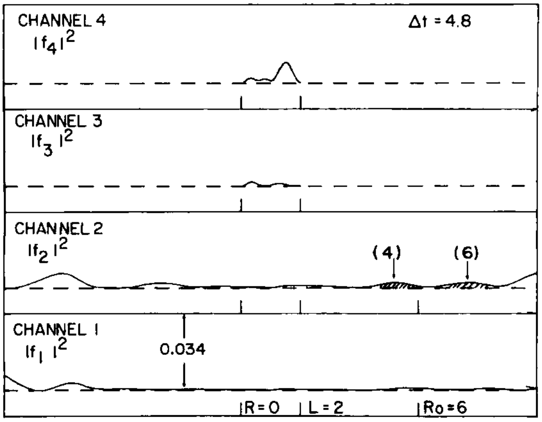


Fig. 22. Magnitude square of the outgoing wavelets corresponding to peaks (4) and (6) in Fig. 21.

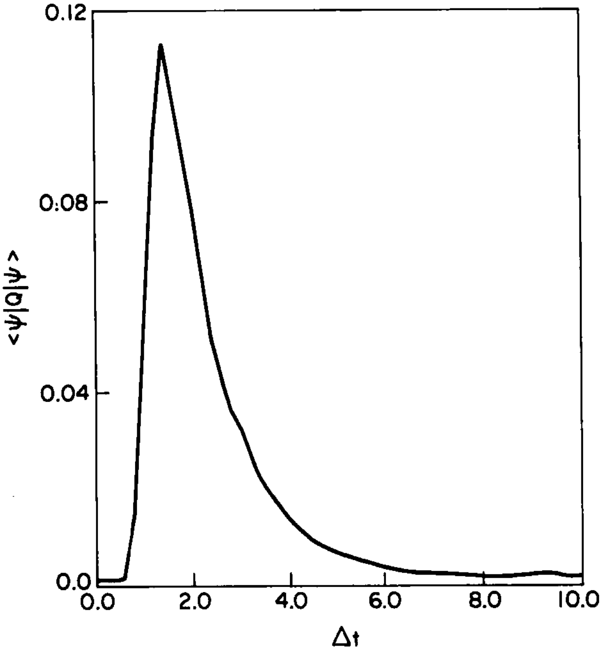


Fig. 23. Total probability in the closed channels as a function of Δt.

the open/closed channel coupling were increased, the maximum of this peak would increase and the peak would become more narrow, corresponding to broader resonances with shorter time delays.

IV. Summary

Feshbach theory has been reviewed and then developed for applications to chemical reactions. The time-independent formulation was then applied to a model four-channel reaction involving two open channels interacting with two asymptotically closed channels. The generation of the multichannel Green function for the open channels and the solution of the bound-state problem for the interacting closed channels was discussed in detail. A perturbative analysis of two definitions of resonance parameters was presented. The dependence of the complex eigenvalues of the level operator upon collision energy and upon the coupling strength between the open and closed channels was numerically investigated. In addition, comparisons were made with energy-independent Siegert eigenvalues. Plots were presented of typical resonance states and their open-channel response functions. Finally, transition probabilities for isolated and overlapping resonances were analyzed in terms of Argand diagrams, which show the energy dependence of individual S-matrix elements. Then, in Section III, a time-dependent study of the same four-channel reaction was presented. The time evolution of translational wave packets was discussed analytically and graphically. The growth and decay of probability in the closed channels was shown graphically. Also, the relation between the evolution of the open-channel scattered wave packets and the time delay was discussed. All of this analysis clearly shows that resonances in chemical reactions are a beautiful class of phenomena that serve as a very sensitive probe of the dynamics and structure of the "collision complex."

Appendix A. Symmetry of the Matrix Representation of the Level Shift Operator

Applying the identity $\langle a|A|b\rangle = \langle b|A^{\dagger}|a\rangle^{*}$ to the matrix representation of R_{QQ} yields $R_{kl} = \langle \phi_l|R_{QQ}^{\dagger}|\phi_k\rangle^{*}$, or

$$R_{kl} = \langle \phi_l|(H_{QP}G_{PP}^{0,+}H_{PQ})^{\dagger}|\phi_k\rangle^{*}. \tag{A1}$$

Using $(G_{PP}^{0,+})^{\dagger} = G_{PP}^{0,-}$, $(H_{PQ})^{\dagger} = H_{QP}$, and $(H_{QP})^{\dagger} = H_{PQ}$, Eq. (A1) becomes

$$R_{kl} = \langle \phi_l|H_{QP}G_{PP}^{0,-}H_{PQ}|\phi_k\rangle^{*} = \left[\int \phi_l^{*}\, H_{QP}G_{PP}^{0,-}H_{PQ}\phi_k\, \mathbf{dx}\right]^{*}, \tag{A2}$$

Since the bound-state functions are real and $(G_{PP}^{0,-})^{*} = G_{PP}^{0,+}$, Eq. (A2) becomes

$$R_{kl} = \int \phi_l H_{QP}G_{PP}^{0,+}H_{PQ}\phi_k\, \mathbf{dx},$$

or $R_{kl} = R_{lk}$. Thus the matrix representation of the level shift operator is symmetric. Since the Hermitian operator H_{QQ} is diagonal in the basis of translationally bound states, the matrix representation of the level operator L_{QQ} is also symmetric: $L_{kl} = L_{lk}$.

The symmetry of the matrix representation of the level shift operator can also be demonstrated using the matrix notation of Section II,B,1. Using this notation, we shall see that the symmetry of **R** is a direct consequence of the reciprocity condition (122) satisfied by the open-channel Green function matrix. In matrix notation:

$$R_{kl} = \iint \boldsymbol{\phi}_k(R)\mathbf{H}_{\mathrm{co}}(R)\mathbf{G}_{\mathrm{o}}(R,\, R')\mathbf{H}_{\mathrm{oc}}(R')\boldsymbol{\phi}_l(R')\, dR\, dR'. \tag{A3}$$

Since the integrand in Eq. (A3) is simply a number (in contrast to a vector etc.), it must equal its transpose:

$$R_{kl} = \iint \phi_l(R')\mathbf{H}_{co}(R')\tilde{\mathbf{G}}_o(R, R')\mathbf{H}_{oc}(R)\,\phi_k(R)\,dR\,dR'. \tag{A4}$$

Here we have made use of $\mathbf{H}_{co} = \tilde{\mathbf{H}}_{oc}$. Using the reciprocity condition (122), we obtain

$$R_{kl} = \iint \phi_l(R')\mathbf{H}_{co}(R')\mathbf{G}_o(R', R)\mathbf{H}_{oc}(R)\,\phi_k(R)\,dR'\,dR, \tag{A5}$$

so that $R_{kl} = R_{lk}$, with R_{lk} written explicitly in matrix notation. Since the orthogonality of the resonance states follows from the symmetry of L [see Eqs. (23)–(26)], the orthogonality of the resonance states is also a direct consequence of the reciprocity condition (122).

Appendix B. Generation of the Propagation Matrix

In order to generate the $n \times n$ open-channel Green function matrix, one must generate a number of $2n \times 2n$ propagation matrices $\mathscr{P}$, defined in Eq. (154). The purpose of Appendix B is to explain how these propagation matrices may be calculated.

Consider first the propagation of solutions in the uncoupled representation within a given sector. Within that sector the uncoupled solutions $\mathbf{G}_j^u(R, R')$ solve Eq. (153). Each element of $\mathbf{G}_j^u$ satisfies an equation of the form:

$$\frac{d^2}{dR^2}\, G_{ij}^u(R, R') = \lambda_i^2 G_{ij}^u(R, R'), \tag{B1}$$

where G_{ij} is the ith element of $\mathbf{G}_j$. From here on we shall drop superscripts and subscripts as well as the argument (R, R') with the understanding that we are interested in propagating a typical element of $\mathbf{G}_j^u(R, R')$ within a given sector. Thus Eq. (B1) becomes

$$G''(R) = \lambda^2 G. \tag{B2}$$

The eigenvalue of U, λ^2, is either negative or positive, corresponding to either a *locally open* or *locally closed* channel, respectively.

Suppose we know $G(R_0)$ and $G'(R_0)$ and would like to find $G(R)$ and $G'(R)$. Let us define the distance ΔR within the sector we wish to propagate the solutions:

$$\Delta R \equiv R - R_0. \tag{B3}$$

Using Eq. (B3), we can expand $G(R)$ in a Taylor series about R_0:

$$G(R) = \sum_{n=0}^{\infty} (1/n!)G^{(n)}(R_0)\,\Delta R^n, \tag{B4}$$

where $G^{(n)}$ denotes the nth derivative of G with respect to R. The summation in Eq. (B4) can be separated into terms containing even or odd powers of ΔR:

$$G(R) = \sum_{n=0}^{\infty} [1/(2n)!]G^{(2n)}(R_0)\, \Delta R^{2n} + \sum_{n=0}^{\infty} [1/(2n+1)!]G^{(2n+1)}(R_0)\, \Delta R^{2n+1}. \tag{B5}$$

The summations in Eq. (B5) can be simplified using the form of the differential equation (B2) satisfied by G. Differentiating Eq. (B2), we obtain

$$G^{(3)}(R) = \lambda^2 G'(R). \tag{B6}$$

Equation (B6) can be differentiated to obtain

$$G^{(4)}(R) = \lambda^2 G''(R) = \lambda^4 G(R). \tag{B7}$$

Continuing this process of differentiation, the following pattern develops:

$$G^{(2n)}(R) = \lambda^{2n} G(R), \tag{B8a}$$

$$G^{(2n+1)}(R) = \lambda^{2n} G'(R). \tag{B8b}$$

Using Eqs. (B8) in Eq. (B5), we obtain

$$G(R) = \left(\sum_{n=0}^{\infty} \frac{(\lambda\, \Delta R)^{2n}}{(2n)!}\right) G(R_0) + \left(\sum_{n=0}^{\infty} \frac{\lambda^{2n}\, \Delta R^{2n+1}}{(2n+1)!}\right) G'(R_0). \tag{B9}$$

If $\lambda^2 < 0$ (locally open), then the terms in the infinite series alternate in sign and we obtain

$$G(R) = G(R_0) \cos|\lambda|\, \Delta R + |\lambda|^{-1} G'(R_0) \sin|\lambda|\, \Delta R. \tag{B10a}$$

If $\lambda^2 > 0$ (locally closed), then the terms in the series do not alternate in sign:

$$G(R) = G(R_0) \cosh|\lambda|\, \Delta R + |\lambda|^{-1} G'(R_0) \sinh|\lambda|\, \Delta R. \tag{B10b}$$

As in Eq. (B4), $G'(R)$ can be expanded in a Taylor series and Eqs. (B8) can be used in a similar fashion. For $\lambda^2 < 0$, we obtain

$$G'(R) = -|\lambda| G(R_0) \sin|\lambda|\, \Delta R + G'(R_0) \cos|\lambda|\, \Delta R. \tag{B10c}$$

For $\lambda^2 > 0$:

$$G'(R) = |\lambda| G(R_0) \sinh|\lambda|\, \Delta R + G'(R_0) \cosh|\lambda|\, \Delta R. \tag{B10d}$$

If the eigenvalue λ^2 is complex, as in the technique for generating Siegert eigenvalues (Section II,B,5), then Eqs. (B10b) and (B10d) must be used with λ replacing $|\lambda|$ (in this case, either complex square root of

λ^2 may be used for λ). Equations (B10a)–(B10d) can be written more conveniently as a single matrix equation (see Light and Walker, 1976) using a $2n \times 2n$ *local* propagation matrix:

$$\begin{bmatrix} \mathbf{G}_j^{\mu}(R, R') \\ \hline \mathbf{G}_j^{\mu\prime}(R, R') \end{bmatrix} = \left[\begin{array}{c|c} \mathbf{P}_1 & \mathbf{P}_2 \\ \hline \mathbf{P}_3 & \mathbf{P}_4 \end{array}\right] \begin{bmatrix} \mathbf{G}_j^{\mu}(R_0, R') \\ \\ \mathbf{G}_j^{\mu}(R_0, R') \end{bmatrix}. \tag{B11}$$

The $n \times n$ matrices $\mathbf{P}_1$, $\mathbf{P}_2$, $\mathbf{P}_3$, and $\mathbf{P}_4$ of the local propagation matrix are defined as

$$(\mathbf{P}_1)_{ij} = (\mathbf{P}_4)_{ij} = \begin{cases} \delta_{ij} \cosh|\lambda|\, \Delta R & \text{for } \lambda^2 > 0, \\ \delta_{ij} \cos|\lambda|\, \Delta R & \text{for } \lambda^2 < 0, \end{cases} \tag{B12a}$$

$$(\mathbf{P}_2)_{ij} = \begin{cases} \delta_{ij}|\lambda|^{-1} \sinh|\lambda|\, \Delta R & \text{for } \lambda^2 > 0, \\ \delta_{ij}|\lambda|^{-1} \sin|\lambda|\, \Delta R & \text{for } \lambda^2 < 0, \end{cases} \tag{B12b}$$

$$(\mathbf{P}_3)_{ij} = \begin{cases} \delta_{ij}|\lambda| \sinh|\lambda|\, \Delta R & \text{for } \lambda^2 > 0, \\ -\delta_{ij}|\lambda| \sin|\lambda|\, \Delta R & \text{for } \lambda^2 < 0. \end{cases} \tag{B12c}$$

In Eqs. (B12), R is positive for propagation in the direction of increasing R or negative for propagation in the direction of decreasing R.

Equation (B11) provides a prescription for the propagation of solutions within a sector. However, to propagate solutions from any R_2 to any R_1 as required by Eq. (154), we must also be able to cross boundaries between sectors. At the boundary $R = R_b$ between sector i and sector $i - 1$ the solutions $\mathbf{G}_j(R, R')$ (in the coupled representation) and their derivatives must be continuous. Using the local transformation given by Eq. (157), the conditions for continuity are

$$\mathbf{T}^{i-1}\mathbf{G}_j^{\mu}(R_\mathrm{b} - \delta R, R') = \mathbf{T}^{i}\mathbf{G}_j^{\mu}(R_\mathrm{b} + \delta R, R'), \tag{B13a}$$

$$\mathbf{T}^{i-1}\mathbf{G}_j^{\mu\prime}(R_\mathrm{b} - \delta R, R') = \mathbf{T}^{i}\mathbf{G}_j^{\mu\prime}(R_\mathrm{b} + \delta R, R'). \tag{B13b}$$

Here the superscripts $i - 1$ and i remind us that the eigenvectors of $\mathbf{U}$ differ from sector to sector. Equations (B13) can be combined as a single equation:

$$\begin{bmatrix} \mathbf{G}_j^{\mu}(R_\mathrm{b} - \delta R, R') \\ \hline \mathbf{G}_j^{\mu\prime}(R_\mathrm{b} - \delta R, R') \end{bmatrix} = \left[\begin{array}{c|c} \tilde{\mathbf{T}}^{i-1} & 0 \\ \hline 0 & \tilde{\mathbf{T}}^{i-1} \end{array}\right] \left[\begin{array}{c|c} \mathbf{T}^{i} & 0 \\ \hline 0 & \mathbf{T}^{i} \end{array}\right] \begin{bmatrix} \mathbf{G}_j^{\mu}(R_\mathrm{b} + \delta R, R') \\ \hline \mathbf{G}_j^{\mu\prime}(R_\mathrm{b} + \delta R, R') \end{bmatrix}. \tag{B14}$$

Note that $\mathbf{G}_J^{u}(R)$ is *not continuous* across the boundaries between sectors in the interaction region since

$$\tilde{\mathbf{T}}^{i-1}\mathbf{T}^{i} \neq 1. \tag{B15}$$

Equations (B11) and (B14) provide the means for both crossing a sector and jumping the boundary between sectors, respectively, in the uncoupled representation. The $2n \times 2n$ propagation matrix $\mathcal{P}(R_1, R_2)$ in Eq. (154) is obtained by assembling the appropriate products of the matrices in Eqs. (B11) and (B14) for crossing the appropriate sectors and jumping the appropriate boundaries lying between R_2 and R_1.

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