

## On the Algebraic Approximation of Scattering Wave Functions for Molecular Systems

Klaus D. Hänsel and Notker Rösch

Lehrstuhl für Theoretische Chemie, Technische Universität München, Postfach 20 24 20, D-8000 München, Federal Republic of Germany

The least-squares method for calculating scattering wavefunctions is discussed with respect to its applicability to molecular scattering events. Choosing an LCAO-like expansion, augmented by the appropriate asymptotic free components, for the radial wavefunction, one obtains a practical algorithm. The method reduces to the solution of an inhomogeneous system of linear equations. A basis set suitable for the description of molecular scattering events is suggested and its dependence on non-linear parameters is discussed. Applications are given for elastic *s*-wave scattering. The computational aspects of the method are discussed in detail, as well as generalizations to inelastic and reactive collisions.

**Key words:** Variational principle – Scattering wavefunctions, algebraic approximation of  $\sim$

### 1. Introduction

Within the last few years increasing interest in molecular collision processes has resulted in numerous experimental and theoretical investigations of elastic, inelastic and reactive processes [1–5]. From the theoretician's point of view all information pertinent to these processes is contained in the scattering matrix the elements of which are given by

$$S_{Enz \leftarrow E'm\beta} = \langle En\alpha^- | E'm\beta^+ \rangle \quad (1)$$

$E$  denotes the total energy,  $m, n$  the initial and final quantum numbers, and  $\alpha, \beta$  the initial and final asymptotic configurations.  $|S_{Enz \leftarrow E'm\beta}|^2$  is the probability of a transition from the initial state  $E'm\beta$  to the final state  $En\alpha^-$ .

From a practical point of view the scattering matrix  $S$  is obtained from the

corresponding wave function

$$\Psi_{En\alpha}^{(+)} = \langle \mathbf{r} | En\alpha^+ \rangle \quad (2)$$

The wave function (2), in turn, is usually obtained by expanding  $\Psi^{(+)}$  in terms of the eigenfunctions of the internal degrees of freedom  $|n\alpha\rangle$ ; this is the well-known close-coupling expansion. The radial part of the wave function describing the free motion in the different channels  $n\alpha$  is obtained by numerical integration of the system of coupled equations (cf. [6–8]). Integration of these coupled equations presents severe difficulties due to the closed channels which have to be included to insure convergence of the expansion. This is particularly true in the case of chemical reactions (cf. [9]). Special stabilization techniques have to be employed to suppress the (unwanted) exponentially growing solutions in the classically forbidden regions. Such techniques have been described among others by Gordon [6], Secrest and Johnson [7] and by Manz [8]. Basically, these techniques consist of obtaining piecewise solutions, and connecting these solutions. They do not, however, afford the wave function directly. For some applications (e.g. evaluating matrix elements) knowledge of the wave function may be desirable.

Furthermore, very efficient techniques have been developed for the calculation of bound-state wave functions [10], and it might be well worth while considering how these techniques might be adapted to the calculation of scattering wave functions. This way one could draw on the considerable computational experience of traditional quantum chemistry. This idea is followed in the following sections with emphasis on the computational point of view. In Section 2 we discuss different algebraic expansion techniques and variational principles as applied to scattering processes. In Sect. 3 computational aspects are considered in some detail; some results on  $s$ -wave scattering are given. In Sect. 4 we present variational corrections to the phase shift. Finally we discuss the feasibility of extending our calculations to inelastic and reactive scattering processes.

## 2. Algebraic Expansion Techniques

In the following we shall address ourselves to the question: Is it possible to build scattering wave functions in such a way that as much information as possible is included from the start? It should be clear from the discussion in the introduction that this can be done only when we expand the radial part of the wave function in terms of a suitable complete set of functions  $\{\phi_i\}$ , and not when we resort to numerical integration. All the problems that come up in connection with algebraic expansion techniques arise already with elastic collisions; hence we restrict ourselves to this simplest case.

To be specific, consider the scattering of a particle with angular momentum  $l$  at a potential  $V(r)$ , which is assumed to be reasonably well behaved at the origin, i.e.

$$V(r) \stackrel{r \rightarrow 0}{\sim} O(r^{-\delta}) \quad \delta < 1$$

Under this proviso we shall discuss the following model problem

$$(\mathcal{H} - E)(\Psi/r) = 0$$

$$\mathcal{H} = -\frac{1}{2m} \frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{2mr^2} \quad (3)$$

The following ansatz is made for the wave function

$$\Psi = S_l(r) + tC_l(r) + \sum_i C_i \phi_i(r) \quad (4)$$

The functions  $S_l(r)$ ,  $C_l(r)$  describe the long-range (asymptotic) behaviour of the wave function, i.e.

$$S_l(r) \xrightarrow{r \rightarrow \infty} (kr)j_l(kr)$$

$$C_l(r) \xrightarrow{r \rightarrow \infty} (kr)n_l(kr) \quad (5)$$

$$k = (2mE)^{1/2}$$

The  $\phi_i$  are a set of square integrable functions; they are used to describe the short range behaviour of the wave function under the influence of the potential  $V(r)$  and fulfil the boundary conditions at the origin:

$$C_i(0) = S_l(0) = \phi_i(0) = 0.$$

For the sake of clarity the expansion of bound state wave functions is contrasted with the expansion of scattering wave functions in Table 1. In the case of bound state wave functions a homogeneous system of linear equations results from the variational principle; upper bounds to the eigenenergies are obtained from this secular problem. In the case of scattering wave functions the total energy  $E$  of the system is fixed, and one can no longer hope to satisfy

$$(\mathcal{H} - E)\Psi_{\text{trial}} = 0$$

**Table 1.** Comparison of algebraic expansions for bound states and scattering states

	bound-state problem	scattering problem
trial function	$\Psi = \sum_{i=0}^N C_i \phi_i$	$\Psi = S + tC + \sum_{i=1}^N C_i \phi_i$
variational problem		$(\mathcal{H} - E)\Psi = 0$ $\delta \langle \Psi   \mathcal{H} - E   \Psi \rangle \neq 0$
system of equations	$(\mathbb{H} - E\mathbb{S})\mathbb{C} = 0$	$\begin{pmatrix} \mathbb{L}_{cc} & \mathbb{L}_{cb} \\ \mathbb{L}_{bc} & \mathbb{L}_{bb} \end{pmatrix} \begin{pmatrix} t \\ \mathbb{C} \end{pmatrix} = -\begin{pmatrix} \mathbb{L}_{sc} \\ \mathbb{L}_{sb} \end{pmatrix}$
matrix elements	$(\mathbb{H})_{ij} = \langle \phi_i   \mathcal{H}   \phi_j \rangle$ $(\mathbb{S})_{ij} = \langle \phi_i   \phi_j \rangle$	$(\mathbb{L})_{cc} = \langle C   \mathcal{H} - E   C \rangle$ $(\mathbb{L})_{sc} = \langle S   \mathcal{H} - E   C \rangle$ $(\mathbb{L})_{cb} = \langle \langle C   \mathcal{H} - E   \phi_i \rangle \rangle$ $(\mathbb{L})_{bb} = \langle \langle \phi_i   \mathcal{H} - E   \phi_j \rangle \rangle$

The best one can do is to obtain a wave function  $\Psi$  for which

$$J[\Psi] = \langle \Psi | \mathcal{H} - E | \Psi \rangle \quad (6)$$

is stationary. The variational principle,  $\delta J=0$  with the ansatz (4), known as Kohn's variational principle, leads to an inhomogeneous system of linear equations

$$\begin{pmatrix} \mathbb{1}_{cc} & \mathbb{1}_{cb} \\ \mathbb{1}_{bc} & \mathbb{1}_{bb} \end{pmatrix} \begin{pmatrix} t \\ C \end{pmatrix} = - \begin{pmatrix} \mathbb{1}_{sc} \\ \mathbb{1}_{sb} \end{pmatrix} \quad (7)$$

The fact that the variational principle is no longer a minimum principle, gives rise to the well known difficulties associated with the Kohn principle which have been discussed by numerous authors, notably by Nesbet [12], Harris [11] and more recently by Truhlar and coworkers [13]. The difficulties (non-uniform convergence, spurious (Schwartz) resonances) are due to the fact that

$$J[\Psi] = \langle \Psi | \mathcal{H} - E | \Psi \rangle$$

may become zero without  $\Psi$  being a solution of the Schrödinger equation (for a detailed discussion cf. [11, 12]).

There are several ways of avoiding these difficulties. Nesbet [12] suggests using two complementary variational principles, the Kohn principle and the Rubinow principle (Eq. (6) with the ansatz  $\Psi_{\text{trial}} = C_1 + t^{-1}S_t + \sum_i c_i \phi_i$ ); it may be shown that when one of them fails the other one will work. An alternative approach to the Kohn principle, the minimum norm method, has been devised by Harris and Michels [11].

From a mathematical point of view the difficulties with Kohn's variational principle arise from the fact that the functional  $J$  is not positive definite. This observation suggests that one might consider alternative functionals. Several authors [13–16] studied variational methods based on minimizing

$$I[\Psi] = \langle (\mathcal{H} - E)\Psi | (\mathcal{H} - E)\Psi \rangle$$

or the slightly more generally

$$I_w[\Psi] = \int dr w(r) (\mathcal{H} - E)\Psi^*(r) (\mathcal{H} - E)\Psi(r)$$

with a strictly positive weight function  $w(r)$ . The functionals  $I, I_w$  satisfy all the axioms of a norm or, if one considers

$$\tilde{I}[\Psi, \Phi] = \langle (\mathcal{H} - E)\Psi | (\mathcal{H} - E)\Phi \rangle$$

of an inner product. This property guarantees that  $I=0$  is equivalent to  $\Psi$  being a solution of the Schrödinger equation. Therefore, better convergence and an intrinsic criterion for convergence is to be expected from expansions determined from the variational principle:

$$\delta I[\Psi] = 0 \quad (8)$$

Inserting the “LCAO-type” expansion (4) into (8) one obtains, in a straightforward manner, the inhomogeneous system of linear equations:

$$\begin{pmatrix} \mathbb{V}_{cc} & \mathbb{V}_{cb} \\ \mathbb{V}_{bc} & \mathbb{V}_{bb} \end{pmatrix} \begin{pmatrix} t \\ \mathbb{C} \end{pmatrix} = - \begin{pmatrix} \mathbb{V}_{cs} \\ \mathbb{V}_{bs} \end{pmatrix}$$

$$\mathbb{V}_{cc} = \langle (\mathcal{H} - E)C | (\mathcal{H} - E)C \rangle, \text{ etc.} \quad (9)$$

Note that the structure of Eq. (9) is identical to that of Eq. (7), the only difference being the matrix elements.

The variational principle (8) has been discussed by several authors [14–16] with electron-atom scattering in mind. To our knowledge, the principle (8) was first applied to scattering problems by K. J. Miller [14a] who also used it to derive bounds of the phase shift. His work includes extensive numerical studies, but computational problems are not given any special consideration. Furthermore, the limits of the applicability – from a practical point of view – cannot be assessed from Miller’s work. The scope of Ref. [14b] is similar. Its main concern is the approximation of  $I[\Psi]$  by a quadrature sum, and, again, upper and lower bounds to the phase shift. The work of Kanellopoulos [16] deals with the choice of basis sets enlarging and optimizing the basis set step by step; the case of multichannel scattering is also discussed. Phase shifts and upper and lower bounds are calculated with a basis set comprising only *two* square integrable functions. The possibility of approximating  $I[\Psi]$  by a quadrature sum is also investigated by Read [15a]; in a second paper [15b] he also discusses the optimal choice of the free functions for a potential that supports bound states, and hence allows for the possibility of resonances of the phase shift.

The work of Wladawsky [17] is closely related to the minimum variance methods being essentially an inner projection version of them. The ideas of Wladawsky have been put into practice by Truhlar and Abdallah, Jr. [18]. They studied inelastic ( $1s$ – $2s$ )-electron-hydrogen scattering, and obtained very encouraging results. Variational improvements of the reactance matrix were also given.

We wish to elaborate on references [14–16]. In particular, we look into the following questions as hinted in the introduction: 1) Computational efficiency, 2) applicability to heavy particle scattering and closely related, 3) limits of algebraic expansion methods.

### 3. Numerical Considerations

The system of linear equations (9) is the starting point of the following discussion. Three steps are necessary to implement this method:

- 1) Calculation of the integrals over the basis functions
- 2) Calculation of the matrix  $\mathbb{V}$  from the integrals over the basis functions
- 3) Solution of the linear equations.

This reminds one of the usual quantum chemical procedures. There is, however, no self-consistency problem.

The first problem to be solved is the choice of a basis set. Requirements to be fulfilled are: a) easy and rapid evaluation of the pertinent integrals, b) stable linear equations and c) rapid convergence. The fulfilment of requirement c) cannot be assessed a priori, requirements a) and b) suggest the choice of orthogonal polynomials for the square integrable functions. In the case of  $l$ -wave scattering the following boundary conditions are to be met

$$\begin{aligned} \lim_{r \rightarrow \infty} \Psi(r) &\sim (t_l n_l(kr) + j_l(kr))kr \\ \lim_{r \rightarrow \infty} \Psi(r) &\sim (kr)^{2l+1}, \quad t_l = \tan \delta_l \end{aligned}$$

$k = (2mE)^{1/2}$  being the radial momentum and  $\delta_l$  being the  $l$ -wave phase shift. This fixes the choices of the square-integrable functions

$$\phi_i^{(l)}(r) = N_i^{(l)} \exp(-r/2d)(r/d)^{2l+1} L_i^{(2l+1)}(r/d) \quad (10)$$

$L_i^{(2l+1)}(r/d)$  are associated Laguerre polynomials [19].  $N_i^{(l)}$  is a normalization factor the  $\phi_i^{(l)}$  fulfilling the normalization condition

$$\langle \phi_i^{(l)} | \phi_j^{(l)} \rangle = \delta_{ij} \quad (10a)$$

The properties of the basis set (10) and its application to scattering calculations were reviewed by Rotenberg [20]. We were also interested in the question whether there is a trade-off between b) and c). To this end we also investigated the two-parameter basis set

$$\phi_i^{(l)}(r) = N_i \exp(-r/2d_1)(r/d_2)^{l+1} L_i^{(2l+1)}(r/d_2) \quad (10b)$$

One might hope for faster convergence through the additional flexibility offered by this nonorthogonal basis set.

The choice of the “free” functions is straightforward

$$\begin{aligned} S_l(r) &= kr j_l(kr) \\ C_l(r) &= (1 - \exp(-\gamma r))^{2l+1} kr n_l(kr) \end{aligned} \quad (10c)$$

The factor  $F_{2l+1}(r) = (1 - \exp(-\gamma r))^{2l+1}$  in front of the irregular spherical Bessel function  $n_l$  removes its singularity at the origin which goes as  $(kr)^{-l-1}$  and ensures the correct asymptotic behaviour at the origin.

(To effect more rational evaluation of our matrix elements, we used in some of our calculations the alternative function

$$\hat{S}_l(r) \equiv F_{2l+1}(r) S_l(r)$$

The results were virtually unaffected by this alternative choice.)

For the purpose of making test calculations, we chose an exponential repulsive potential

$$V(r) = V_0 \exp(-r/a)$$

which, for the case of  $s$ -wave scattering, admits an exact solution of the Schrödinger

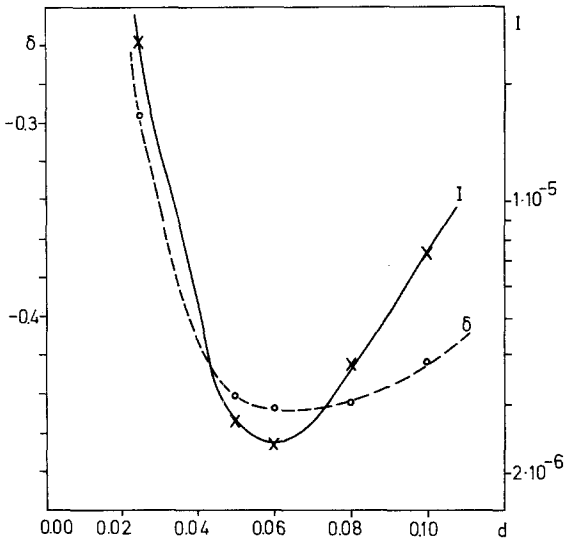


Fig. 1. Optimization of the range parameter  $d$ . Fixed parameters:  $N=15$ ,  $E=0.05$ ,  $\gamma=30.0$

equation [21]. The following parameters were fixed to mimic atom-molecule scattering:  $m=2000$  a.u.,  $a=0.5$  a.u.,  $w(r)=1$ . (Note that atomic units are used throughout the paper.) Changing  $V_0$  amounts to changing the size of the potential at the origin or to shifting the classical turning point.  $V_0$  has to be chosen such that it is essentially infinite at the origin in order that the exact solution which is computed for the interval  $-\infty \leq r \leq \infty$ , and the converged computed solution (with the boundary condition at  $r=0$ ) coincided. In the calculations discussed below  $V_0$  was chosen accordingly. The choice of  $\gamma$  had no significant influence on the accuracy of the solution over a wide range ( $1 \leq \gamma \leq 50$ ), and hence the dependence of the phase shift on  $\gamma$  is discussed no further.

In the following we present some typical results in detail:

- 1) Optimization of the range parameter  $d$  or  $(d_1, d_2)$ ,
- 2) Dependence on the size of the basis set,
- 3) Energy dependence of the phase shift.

Figure 1 shows the dependence of the phase shift and the variance integral on the range parameter  $d$ . Note that the scale for  $\delta$  is linear whereas the scale for the variance integral is logarithmic.  $\delta$  is seen to depend significantly but not critically on  $d$  as is, in fact, to be expected. The quality of the wave function deteriorates when the expansion functions are concentrated in too narrow a range or distributed over too wide a range with respect to the interaction region. The phase shift and the variance integral correlate nicely so that  $I[\Psi]$  can be used as a measure of the quality of the wave function with some confidence.

Similar results are obtained for the more general basis set (10b). It turns out, however, that the best results are obtained for  $d_1 \approx d_2$ . Therefore, we conclude that

$N$	$\delta$	$I$
10	-0.0924	1.0(-3)
15	-0.8521	1.8(-4)
20	-1.0877	4.6(-5)
25	-1.2042	3.6(-6)
30	-1.2170	3.9(-7)
exact	-1.2223	0.0

**Table 2.** Convergence of the expansion Eq. (4). Parameters:  $d_1=0.065$ ,  $d_2=0.050$ ,  $\gamma=10.0$ ,  $V_0=0.155$ ,  $E=0.015$

basis set (10a) is preferable because of its orthogonality. A few representative results with basis set (b) are included in the results in Tables 2 and 3.

Table 2 illustrates the convergence of the expansion Eq. (4). It is uniform. The variance integral  $I$  drops by about an order of magnitude for every 5 functions one adds to the basis set. The accuracy of the phase shift is rather poor for small basis sets, it rises sharply as  $N$  (the number of square integrable functions) is increased from 10 to 15.

Table 3 summarizes various aspects of the energy dependence of the phase shift. The number  $N$  of the basis functions in the expansion has not been kept constant. The reason is that more and more basis functions are necessary to achieve a given accuracy as the energy is increased. At the highest energy given in the table ( $E=0.095$ ) even 48 functions do not lead to satisfactory convergence. The accuracy deteriorates at higher energies because the number of nodes/length increases, and thus more basis functions are needed to build the wave function. It is not uninteresting to describe the behaviour of the expansion at higher energies: As the energy is increased the functions  $\phi_i$  with small  $i$  (say  $0 \leq i \leq 10$ ) become less and less important; at the same time the functions with large  $i$  (say  $25 \leq i \leq 48$ ) contribute significantly. This seems to indicate that at higher energies functions with many nodes are important, and that an alternative basis set might be advantageous.

**Table 3.** Energy dependence of the phase shift. Parameters:  $d_1=0.05$ ,  $d_2=0.065$ ,  $\gamma=10.0$ ,  $V_0=0.155$

$E$	$N$	$\delta_0$	$I$	$\delta_K$
$\delta_{\text{exact}}$				
0.015	20	-1.0877	4.6(-5)	-1.2013
-1.2223	25	-1.2042	3.6(-6)	-1.2218
0.035	20	0.6761	1.5(-3)	0.8113
0.9104	25	0.9282	3.3(-4)	0.9302
0.055	30	0.6248	1.7(-3)	0.9000
1.1109	40	1.1233	2.5(-4)	1.1167
0.075	45	-1.0489	7.3(-4)	-1.2713
-1.3963	48	-1.1530	5.5(-4)	-1.3153
0.095	45	-0.2439	5.0(-4)	-0.5423
-0.5473	48	-0.2666	3.9(-4)	-0.5434



Use of contracted basis sets as discussed by Abdallah and Truhlar [22] may be a first step to improving the convergence of the minimum variance method. Another means of improving the convergence is the application of variational corrections to be discussed in the next section.

#### 4. Variational Corrections

Up to now only that part of the Hilbert space which is explicitly included in our expansion has been considered. It is, however, possible to estimate the contribution of the functions not included in the expansion. This is the purpose of *variational corrections*. To arrive at a correction to the phase shift assume that a zero order wave function  $\Psi$  has been obtained somehow (e.g. by the minimum variance method discussed in this paper). Following Ref. [13], the *exact* wave function can then be partitioned into

$$\Psi = \Psi_{\text{exact}} + \delta\Psi$$

and, similarly the exact phase shift may be rewritten as

$$\delta t = t - t_{\text{exact}}$$

From the asymptotic behaviour of the wave function one concludes that  $\delta\Psi \sim C_t(r) \delta t$  as  $r \rightarrow \infty$ .

Now consider the functional

$$J[\Psi] = \langle \Psi | \mathcal{H} - E | \Psi \rangle$$

The difference is

$$\delta J = J[\Psi] - J[\Psi_{\text{exact}}] \simeq \frac{1}{2m} \delta t$$

to first order. This estimate is obtained from the nonvanishing surface terms obtained by partial integration. Bearing in mind that  $J[\Psi_{\text{exact}}] = 0$  ( $\Psi_{\text{exact}}$  is a solution of the Schrödinger equation!) the following estimate for the exact phase shift is obtained

$$t_{\text{exact}} \simeq t - \frac{2m}{k} \langle \Psi | \mathcal{H} - E | \Psi \rangle + \text{second and higher order terms.}$$

This correction is termed ‘‘Kohn correction’’ in references [13] and [18]. The effect of applying it to our model problem can be seen in the last column of Table 3. The accuracy of the phase shifts is improved by one to two figures or even more in some critical cases. Note that the effort necessary to apply the correction is almost negligible as all the integrals required for the evaluation of  $J[\Psi]$  have already been calculated (for details see the Appendix). The evaluation of  $J$  is a process that is proportional to  $N^2$ .

## 5. Summary and Outlook

This paper was intended as a preliminary study of the applicability of the minimum variance method to realistic molecular scattering problems. Important questions regarding the use of this method can be answered in this case on the basis of a simple potential scattering problem: The essentially new aspect is the use of a basis set for the *radial* part of the wave function. All problems arising in this context can, however, be studied with a one-dimensional problem.

More specifically one has the following advantages and disadvantages as compared to methods using numerical integration.

### A. Advantages:

- 1) The wave function fulfils the boundary conditions automatically; no problems with closed channels arise.
- 2) The wave function is available without additional effort.
- 3) All the bound-bound integrals may be stored for repeated use as they are not energy-dependent (cf. Appendix).
- 4) The minimum variance method furnishes a criterion for the accuracy achieved.
- 5) Variational corrections may be applied easily.
- 6) Computational experience from quantum chemical procedures may be used (e.g. contraction of basis sets).

### B. Disadvantages:

- 1) Matrix elements involving  $(\mathcal{H} - E)^2$  have to be evaluated.
- 2) A suitable basis set has to be chosen and its parameters have to be optimized.
- 3) Large basis sets preclude keeping all the matrix elements in core; hence great care must be exercised in the organization of I/O-operations and files on a background storage.
- 4) With increasing energy and/or reduced masses more and more basis functions are necessary to attain convergence.

We should like to point out the great potential economy of this method. Repeated use of integrals is already implemented in our programs. Attention should also be drawn to the fact that the wave function is available for further use; this may be important for the evaluation of certain matrix elements, e.g. transition dipole moments. This might be useful for the study of processes such as photodissociation.

The extension of the formalism to inelastic, and, more important, to reactive processes is trivial; expansion (4) needs to be supplemented by appropriate internal functions, and free functions for the inelastic channels. These matters will be discussed in more detail in a forthcoming study [23] of the Secrest-Johnson model [24]. The minimum-variance method in its present stage of development is particularly suited for process with low total energies ( $E < 1$  eV); rotationally

inelastic scattering of light molecules is such a process of chemical and astrophysical interest. Computational studies pertaining to these processes are in preparation.

### Appendix : Evaluation of the Matrix Elements

In this appendix we outline briefly how the matrix elements for the basis set (10) are evaluated. For sake of simplicity, we consider the orthogonal basis set, Eq. (10), only. First consider the action of  $(\mathcal{H} - E)$  on the expansion function. Let us define

$$(\mathcal{H} - E)f \equiv \hat{f} \quad (\text{A1})$$

Then we have

$$\hat{C}_l(r) = \left[ \left( -\frac{1}{2m} \frac{d^2 F_{2l+1}}{dr^2} + F_{2l+1}(r)V(r) \right) kr + \frac{kl}{m} \frac{dF_{2l+1}}{dr} \right] n_l(kr) - \frac{k}{m} \frac{dF_{2l+1}}{dr} kr n_{l-1}(kr) \quad (\text{A2})$$

$$\hat{\phi}_n^{(l)}(r) = \left\{ -\frac{1}{2ma^2} \left( \frac{1}{4} - \frac{d(l+1+n)}{r} \right) + V(r) - E \right\}$$

for the “bound” and the “free” functions, respectively. Forming matrix elements  $\langle \hat{f} | \hat{g} \rangle$  we have to consider three classes of integrals

- 1) bound-bound integrals
- 2) bound-free integrals
- 3) free-free integrals

which will be discussed separately in the following. In case 2) only the integrals pertinent to  $s$ -wave scattering will be given. The free-free integrals are integrals over trigonometric functions and exponentials in the case of  $s$ -wave scattering and are not given.

#### a) Bound-bound integrals:

After expanding  $\langle \hat{\phi}_n^{(l)} | \hat{\phi}_m^{(l)} \rangle$  two types of integrals arise

$$I_1 = \int_0^\infty y^{2l+2} \exp(-y) y^{-r} L_n^{(2l+1)}(y) L_m^{(2l+1)}(y) dy$$

$$I_2 = \int_0^\infty y^{2l+2} \exp(-y) V(y) y^{-r} L_n^{(2l+1)}(y) L_m^{(2l+1)}(y) dy \quad (\text{A3})$$

and a similar integral involving  $V^2(y)$ . Here an exponential is assumed for  $V(y)$ . Hence,  $I_2$  takes the form

$$I_2 = \int_0^\infty y^{2l+2} \exp(-y) \exp(-y/a) y^{-r} L_n^{(2l+1)}(y) L_m^{(2l+1)}(y) dy$$

All these integrals can then be reduced to the normalization integral

$$\begin{aligned} (N_n^{(l)})^{-2} &= \int_0^\infty y^{2l+1} \exp(-y) L_n^{(2l+1)}(y) L_m^{(2l+1)}(y) dy \\ &= \delta_{nm} \Gamma(2l+2) \binom{n+2l+1}{n} \end{aligned}$$

by means of the following sum rules [19]

$$\sum_{m=0}^n \frac{(\alpha-\beta)_m}{m!} L_{n-m}^{(\beta)}(y) = L_n^{(\alpha)}(y) \quad (\text{A4})$$

$$\sum_{m=0}^n \binom{n+\alpha}{m} z^{n-m} (1-z)^m L_{n-m}^{(\alpha)}(y) = L_n^{(\alpha)}(zy) \quad (\text{A5})$$

Applying sum rule (A4), i.e. expanding the polynomials  $L_n^{(2l+1)}$  in terms of the polynomials  $L_m^{(2l+2-r)}$  the integrals  $I_1$  can be evaluated in a straightforward manner:

$$\begin{aligned} \int_0^\infty y^{2l+2-r} \exp(-y) L_n^{(2l+1)}(y) L_m^{(2l+1)}(y) dy \\ = \sum_{i=0}^{\min(n,m)} \frac{(r)_{n-i} (r)_{m-i}}{(n-i)! (m-i)!} \Gamma(2l+3-r) \binom{i+2l+2-r}{i} \end{aligned}$$

The more general integral  $I_2$  is reduced to the case discussed above by rescaling it using sum rule (A5):

$$\begin{aligned} I_2 &= \int_0^\infty dy y^{2l+2-r} \exp[-(1+\rho)y] L_n^{(2l+1)}(y) L_m^{(2l+1)}(y) \\ &= (1+\rho)^{r-2l-3} \int_0^\infty dy' y'^{2l+2-r} \exp(-y') L_n^{(2l+1)}(y'/(1+\rho)) \\ &\quad \times L_m^{(2l+1)}(y'/(1+\rho)) \\ &= (1+\rho)^{r-2l-3} \int_0^\infty dy' y'^{2l+2-r} \left[ \sum_{i=0}^n \binom{n+2l+1}{i} (1+\rho)^{-n+i} \left( \frac{\rho}{1+\rho} \right)^i \right. \\ &\quad \left. \times L_{n-i}^{(2l+1)}(y') \right] \left[ \sum_{j=0}^m \binom{m+2l+1}{j} (1+\rho)^{-m+j} \left( \frac{\rho}{1+\rho} \right) L_{m-j}^{(2l+1)}(y') \right] \end{aligned}$$

b) *Bound-free integrals:*

The most general type of integral arising in the case of  $s$ -wave scattering is given by

$$I_3 = \int_0^\infty dy \exp(-y/2 - \rho y + ik y) y^{l+1-r} L_n^{(2l+1)}(y)$$

This can be evaluated by analytically continuing the integral  $I_2$  and applying the

techniques outlined above for the bound-bound integrals. The final result is

$$I_3 = \frac{\Gamma(l+n-r+1)}{n!} \frac{(\rho - ik - \frac{1}{2})^n}{(\rho - ik + \frac{1}{2})^{l+n+1-r}} \times {}_2F_1\left(-n, l+r+2; -l+r-n; \frac{\rho - ik + \frac{1}{2}}{\rho - ik - \frac{1}{2}}\right)$$

where  ${}_2F_1$  is Gauss' hypergeometric function which in the present case reduces to a polynomial.

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## References

1. Lawley, K. P., Ed.: *Molecular Scattering*. *Advan. Chem. Phys.* **30**, (1976)
2. *Modern theoretical chemistry*, Vol. 1 and 2, Miller, W. H., Ed. New York: Plenum Press, 1976
3. Fluendy, M. A. D., Lawley, K. P.: *Chemical applications of molecular beam scattering*. London: Chapman and Hall, 1973
4. *Potential energy surfaces*, *Faraday Discuss. Chem. Soc.* **62** (1976), to appear
5. *Energy transfer processes in chemical reactions*, Königstein/Taunus, 13.9.-16.9. 1976. Proceedings to be published in *Ber. Bunsenges. Phys. Chem.*
6. Gordon, R. G.: *J. Chem. Phys.* **50**, 14 (1969); *Methods Comp. Phys.* **10**, 81 (1971)
7. Johnson, B. R., Secrest, D.: *J. Math. Phys.* **7**, 2187 (1966); Secrest, D.: *Methods Comp. Phys.* **10**, 243 (1971)
8. Manz, J.: *Mol. Phys.* **28**, 399 (1974)
9. Wu, S.-F., Levine, R. D.: *Mol. Phys.* **22**, 881 (1971)
10. Reviews of recent developments in computational quantum chemistry can be found in: *Computational methods of quantum chemistry and solid state physics*, Sutcliffe, B. T., Diercksen, G. H. F., Veillard, A., Eds. Dordrecht: Reidel, 1975
11. Harris, F. E., Michels, H. H.: *Methods Comp. Phys.* **10**, 144 (1971)
12. Nesbet, R. K., Oberoi, R. S.: *Phys. Rev.* **A6**, 1855 (1972); Nesbet, R. K.: *Advan. Quantum Chem.* **9**, 215 (1975)
13. Truhlar, D. G., Abdallah Jr., J., Smith, R. L.: *Advan. Chem. Phys.* **25**, 295 (1974)
14. a) Miller, K. J.: *Phys. Rev.* **A3**, 607 (1971);  
b) Bardsley, J. N., Gerjuoy, E., Sukumar, C. V.: *Phys. Rev.* **A6**, 1813 (1972)
15. Read, F. H.: *Chem. Phys. Letters* **12**, 549 (1972); *J. Phys.* **B6**, L 15 (1973)
16. Kanellopoulos, E. J., Kanellopoulos, Th. V.: *J. Phys.* **A8**, 637 (1975)
17. Wladawsky, I.: *J. Chem. Phys.* **58**, 1826 (1973)
18. Abdallah Jr., J., Truhlar, D. G.: *J. Chem. Phys.* **60**, 4670 (1974)
19. Magnus, W., Oberhettinger, F., Soni, R. P.: *Formulas and theorems for the special functions of mathematical physics*, Chapt. V. New York: Springer-Verlag, 1966
20. Rotenberg, M.: *Advan. At. Mol. Phys.* **6**, 233 (1970)
21. Flügge, S.: *Practical quantum mechanics*, Vol. I, p. 196. Berlin: Springer-Verlag, 1971
22. Abdallah Jr., J., Truhlar, D. G.: *J. Chem. Phys.* **61**, 30 (1974)
23. Hänsel, K. D., Rösch, N., Taylor, H. S., Yaris, R.: A variational method for calculating inelastic scattering cross sections. I. *Vibrationally inelastic scattering*. To be submitted to *Chem. Phys. Letters* (1977)
24. Secrest, D., Johnson, B. R.: *J. Chem. Phys.* **45**, 4556 (1966)

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