Interaction between Configurations with Several Open Shells

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Antisymmetrized product wave functions are written for atomic configurations with an arbitrary number of partially or entirely filled shells. Interaction matrix elements between such wave functions are calculated and a numerical evaluation is given for the autoionization of an inner excitation level of neon. A suitable notation keeps the analytical complexities within reasonable bounds.

1. INTRODUCTION

THE calculation of energy matrix elements between states of atoms with many electrons is complicated by the requirements of antisymmetry of wave functions and of the addition of electron angular momenta. Calculation techniques introduced by Racah[1] and widely utilized thereafter include the following four transformations of N-electron wave functions listed by Rosenzweig[2]:

(A) Explicit antisymmetrization with respect to a particular inequivalent electron (Ref. 1, III 26);

$$\Psi(l^{N-1}\bar{\alpha}\bar{S}\bar{L}l'SL) = N^{-1/2}\sum_q(-1)^{N-q}\psi(l^{N-1}\bar{\alpha}\bar{S}\bar{L}l'_qSL), \quad (1)$$

where the subscript q on the right specifies that the electron q occupies the orbital l' whereas the remaining ones, $1, 2\cdots q-1, q+1, \cdots N$ belong to l^{N-1}.

(B) Addition of two or more angular momenta.

(C) Expansion of an antisymmetric wave function of N equivalent electrons in terms of fractional parentage (Ref. 1, III 10);

$$\Psi(l^N\alpha SL)=\sum_{\alpha' S' L'}\psi(l^{N-1}\alpha' S' L' l_N SL) \times(l^{N-1}\alpha' S' L' lLS\,]\,l^N\alpha SL), \quad (2)$$

where again the subscript N specifies that the electron N has been removed from the antisymmetrized part of the wave function.

(D) Recoupling of angular momenta.

Most of the applications of Racah's techniques have been concerned with states having one group of equivalent electrons plus singly occupied outer orbitals, in addition to filled shells that require no attention. More complex situations have been handled as the need arose by suitable extensions of existing techniques. A procedure of complete generality has been outlined by Innes and Ufford but developed only in an unpublished report.[3] This procedure handles the antisymmetrization between electrons of different shells by a formal extension of the fractional parentage expansion (C).[4] It also involves a sequence of recoupling transformations (D) designed to separate out completely the electrons that do and do not interact explicitly. Summations over products of recoupling coefficients can generally be carried out analytically in this procedure. This possibility implies that the procedure is redundant and could be replaced by a more direct one.

Recently, attention has been drawn to a particular type of application by the discovery of numerous autoionizing levels in the far ultraviolet, which decay by processes akin to the Auger effect. For example, Ne levels of the internally excited configurations $1s^22s2p^6np$ decay into the continuum configurations $1s^22s^22p^5Ed$ (or Es).[5] The theoretical analysis of decay[6] depends on energy matrix elements between these configurations, which involve transitions in or out of four different subshells. It also depends on the *sign* of these matrix elements as related to the signs of the dipole elements between either of these configurations and the ground state $1s^22s^22p^6$.

Under these circumstances it seemed worthwhile to develop and to present here a somewhat different procedure for the calculation of energy matrix elements. The first step of this procedure consists of generalizing the antisymmetrization rule A so as to construct explicitly antisymmetrized wave functions for states of configurations of arbitrary complexity, with a *standardized sign convention* (Sec. 2). Energy matrix elements between such states are reduced to simpler form in the following section utilizing the parentage expansion (C) for equivalent electrons *without any recoupling* of angular momenta (D). Recouplings are avoided even in the last stage of the calculation by means of a recently suggested procedure.[7] This procedure reduces the interaction matrix element to a transformation matrix element which is the inner product of two unsymmetrized angular-momentum wave functions, that is, a recoupling coefficient. The calculation is carried out for LS coupling wave functions—a restriction that appears in-

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[1] G. Racah, Phys. Rev. **62**, 438 (1942); and **63**, 367 (1943); referred to in the following as II and III.

[2] N. Rosenzweig, Phys. Rev. **88**, 580 (1952).

[3] F. R. Innes and C. W. Ufford, Phys. Rev. **111**, 194 (1958); P. S. Kelly, Physics Department, University of California at Los Angeles, Technical Report No. 3, OOR Contract No. Da-04-495-ORD-913, 1959 (unpublished).

[4] This extension originates from a particular application by S. Meshkov, Phys. Rev. **91**, 871 (1953). Since the antisymmetrization with respect to inequivalent electrons is independent of the addition of angular momenta, it does not actually require the concept of fractional parentage.

[5] R. P. Madden and K. Codling, Phys. Rev. Letters **10**, 516 (1963).

[6] U. Fano and J. W. Cooper, Phys. Rev. **137**, A1364 (1965).

[7] U. Fano, F. Prats, and Z. Goldschmidt, Phys. Rev. **129**, 2643 (1963)—referred to as FPG.

essential; in this case the recoupling coefficient resolves further into two factors pertaining to spin and orbital momenta, respectively.

The results obtained in this paper on the calculation of matrix elements are assembled in Sec. 6, and a numerical application to the interaction of an inner excited and an ionized configuration of Ne is given in Sec. 7. These results are intended to apply to all calculations with antisymmetrized product wave functions, but earlier methods may remain preferable for familiar special cases. A glossary of symbols is collected in Sec. 8.

Note added in proof. Other recent formulations of matrix elements, which overlap the present one extensively, have come to my attention. A concise development, in the Appendix of a paper by D. Layzer, Z. Horak, M. N. Lewis, and D. P. Thompson, Ann. Phys. (N. Y.) **29**, 101 (1964), is equivalent to the bookkeeping procedure of Secs. 2 and 3 below. The same results are obtained by B. W. Shore, Phys. Rev. **139**, A1042 (1965). I thank Dr. Shore for a copy of his paper and for helpful correspondence.

2. ANTISYMMETRIZED WAVE FUNCTIONS

We shall indicate the successive atomic subshells $1s$, $2s$, $2p$, $3s,\cdots$ by successive values of an index $\lambda=1, 2, 3, 4,\cdots$ and their pairs of quantum numbers by $n_\lambda l_\lambda$; e.g., $n_2=2$ and $l_2=0$. The configuration of an atom with N electrons, of which N_λ lie in the λth shell ($\sum_\lambda N_\lambda=N$), can be represented by

$$1s^{N_1}2s^{N_2}2p^{N_3}\cdots=\prod_\lambda n_\lambda l_\lambda^{N_\lambda}. \tag{3}$$

To construct wave functions of the spins and positions of the N electrons $(s_1\mathbf{r}_1,\cdots,s_i\mathbf{r}_i,\cdots,s_N\mathbf{r}_N)$ we start from antisymmetrized wave functions of the various subshells. The variables of a subshell wave function constitute a set $q_\lambda=\{s_i\mathbf{r}_i\}$ (or $q_\lambda=\{i\}$ for brevity) of N_λ elements, which we prescribe to be *ordered* in the sequence of *increasing* i. We indicate one such wave function, constructed by LS coupling in accordance with III[1] [i.e., of the type indicated on the left of (2)], by $(q_\lambda|n_\lambda l_\lambda^{N_\lambda}\alpha_\lambda S_\lambda L_\lambda M_{S\lambda}M_{L\lambda})$ and the set of wave functions with alternative M quantum numbers by

$$(q_\lambda|n_\lambda l_\lambda^{N_\lambda}\alpha_\lambda S_\lambda L_\lambda\}. \tag{4}$$

Take one wave function (4) for each subshell of the configuration (3), with mutually exclusive sets of variables q_λ. The aggregate $q=\{q_\lambda\}$ of these sets represents one distribution of the N electrons in groups of N_λ elements. An *unsymmetrized* wave function of the whole atom is constructed by multiplying these wave functions and adding their angular momenta $S_\lambda L_\lambda$ (Rosenzweig's transformation B) according to some prescription indicated by α with resultants S and L. We indicate this wave function by

$$\begin{aligned}&\psi_u(q,\alpha SLM_SM_L)\\&=[(q_1|n_1l_1^{N_1}\alpha_1S_1L_1\}\\&\qquad\times(q_2|n_2l_2^{N_2}\alpha_2S_2L_2\}\cdots]^{(\alpha SL)}{}_{M_S\,M_L}\\&=[\textstyle\prod_\lambda(q_\lambda|n_\lambda l_\lambda^{N_\lambda}\alpha_\lambda S_\lambda L_\lambda\}]^{(\alpha SL)}{}_{M_SM_L}.\end{aligned} \tag{5}$$

A permutation of electrons between two subshells changes the distribution q into another one. Therefore we can antisymmetrize the wave function (5) by taking a linear combination of ψ_u for all possible q. In the example of $N=4$, $N_1=N_2=2$, there are 6 distributions $q=\{q_1,q_2\}$, namely

$$\begin{aligned}&\{q_1=\{1,2\},\ q_2=\{3,4\}\},\quad \{q_1=\{1,3\},\ q_2=\{2,4\}\},\\&\{q_1=\{1,4\},\ q_2=\{2,3\}\},\quad \{q_1=\{2,3\},\ q_2=\{1,4\}\},\\&\{q_1=\{2,4\},\ q_2=\{1,3\}\},\quad \{q_1=\{3,4\},\ q_2=\{1,2\}\}.\end{aligned} \tag{6}$$

We assign even parity to the first q, with its N indices i in natural order, and a parity P_q to any q according to the number of permutations by which it differs from the first one. Thus, the second and fifth distribution (6) are odd, the others even. In general, the number of distributions is

$$\mathfrak{N}(N_\lambda)=N!/\textstyle\prod_\lambda N_\lambda!. \tag{7}$$

The desired N-electron antisymmetric function with the coupling αSL is then

$$\begin{aligned}\Psi(\alpha SLM_LM_S)=\mathfrak{N}(N_\lambda)^{-1/2}\textstyle\sum_q(-1)^{P_q}\\\times\psi_u(q,\alpha SLM_SM_L).\end{aligned} \tag{8}$$

This equation is presented here as the generalization (A′) of Rosenzweig's transformation A; indeed it reduces to (1) when $N_\mu=N-1$, $N_\nu=1$ and $N_\lambda=0$ for $\lambda\neq(\mu,\nu)$.

Rosenzweig's transformation C, represented by (2) in the usual notation of spectroscopy, becomes in the notation of this paper

$$\begin{aligned}(q_\lambda|n_\lambda l_\lambda^{N_\lambda}\alpha_\lambda S_\lambda L_\lambda\}=\textstyle\sum[(\bar q_\lambda|n_\lambda l_\lambda^{N_\lambda-1}\bar\alpha_\lambda\bar S_\lambda\bar L_\lambda\}\\\times(i_{\max}(q_\lambda)|n_\lambda l_\lambda\}]^{(S_\lambda L_\lambda)}\\\times(l_\lambda^{N_\lambda-1}\bar\alpha_\lambda\bar S_\lambda\bar L_\lambda l_\lambda S_\lambda L_\lambda]|l_\lambda^{N_\lambda}\alpha_\lambda S_\lambda L_\lambda),\end{aligned} \tag{9}$$

where the summation is over the barred quantum numbers. Here $i_{\max}(q_\lambda)$ is the largest of the indices in the set q_λ, while $\bar q_\lambda$ indicates the set that results by removing $i_{\max}$ from q_λ.

3. UNSYMMETRIZED FORM OF THE MATRIX ELEMENTS

The nonrelativistic expression of the energy of N atomic electrons includes, besides one-particle terms that do not concern us, the two-particle interaction

$$V=\sum_{i>j}^{N}V_{ij}, \tag{10}$$

where, disregarding a factor e^2,

$$V_{ij}=1/|\mathbf{r}_i-\mathbf{r}_j|=\sum_k P_k(\hat{r}_i\cdot\hat{r}_j)r_<^k/r_>^{k+1}. \quad (10')$$

Here, P_k is a Legendre polynomial and $r_<$ and $r_>$ represent the smaller and the larger of r_i and r_j, respectively. Owing to the symmetry of V and of the wave functions Ψ with respect to electron permutations, it is well known that all terms of (10) contribute equally to the matrix elements of V, so that, e.g.,

$$(\Psi|V|\Psi')=\tfrac{1}{2}N(N-1)(\Psi|V_{N,N-1}|\Psi'). \quad (11)$$

Two of the electrons, namely, $N-1$ and N, are designated on the right of (11) as interacting electrons; the remaining ones, $1\cdots N-2$, may be called "spectator electrons." The drastic reduction in the number of terms of $(\Psi|V|\Psi')$, achieved in (11) through a loss of manifest symmetry, will be carried much further in this section with respect to the multiple summations that are introduced by substituting the explicit form (8) of the wave functions on the right of (11),[8]

$$(\Psi|V|\Psi')=\tfrac{1}{2}N(N-1)[\mathfrak{N}(N_\lambda)\mathfrak{N}(N_\lambda')]^{-1/2}$$
$$\times\sum_{q,q'}(-1)^{P_q+P_{q'}}(\psi_u(q,\alpha SL)|V_{N,N-1}|\psi_u'(q',\alpha'S'L')). \quad (12)$$

Additional summations will be introduced by the use of the expansion (9).

To achieve the desired reduction in the number of terms, we consider explicitly the configuration, the distribution among shells and the quantum numbers of the spectator electrons. Only those terms of (12) which are diagonal in these characteristics yield a nonzero contribution and many such contributions are identical.

(a) Configuration of Spectator Electrons

The configuration of the spectator electrons, which we indicate by

$$\prod_\lambda n_\lambda l_\lambda^{\bar{N}_\lambda}, \quad (13)$$

must be included in the configurations of Ψ and Ψ' which are represented by the sets of numbers $\{N_\lambda\}$, $\{N_\lambda'\}$. This condition is represented by

$$\bar{N}_\lambda\leqslant\min(N_\lambda,N_\lambda'). \quad (13a)$$

Equation (13a), together with

$$\sum_\lambda\bar{N}_\lambda=\bar{N}=N-2, \quad (13b)$$

determines the $\bar{N}_\lambda$ uniquely in the case of maximum off-diagonality of $(\Psi|V|\Psi')$, i.e., when Ψ and Ψ' differ by the shift of two electrons. Otherwise, alternative solutions $\{\bar{N}_\lambda\}$ to (13a) and (13b) must be listed at the outset, their contributions calculated separately and added at the end. Henceforth a single set $\{\bar{N}_\lambda\}$ will be considered explicitly. The relationships among $\{\bar{N}_\lambda\}$, $\{N_\lambda\}$, and $\{N_\lambda'\}$ consistent with (13a) and (13b) are represented by

$$\bar{N}_\lambda=N_\lambda-\delta_{\lambda\rho}-\delta_{\lambda\sigma} \qquad \rho\leqslant\sigma, \quad (14)$$
$$\bar{N}_\lambda=N_\lambda'-\delta_{\lambda\rho'}-\delta_{\lambda\sigma'} \quad \rho'\leqslant\sigma'. \quad (14')$$

(b) Electron Distributions among Subshells

Each of the electron distributions q and q' on the right of (12) includes a distribution, $\bar{q}$ or $\bar{q}'$, of the spectator electrons. The orthogonality of one-electron wave functions of different subshells causes each spectator electron to remain in its subshell, that is, only terms of (12) with $\bar{q}=\bar{q}'$ yield a nonzero contribution.

This contribution is independent of $\bar{q}$. Therefore we shall consider only one fixed $\bar{q}$, which may remain unspecified, and replace the summation over $\bar{q}$—implicit in $\sum_{qq'}$—by multiplication by the number $\mathfrak{N}(\bar{N}_\lambda)$ of alternative $\bar{q}$.

Once $\bar{q}$ is fixed, the distributions q and q' are almost completely determined, in view of (14) and (14'). We indicate each of the two possible distributions q by $q^{(\epsilon)}=\{q_\lambda^{(\epsilon)}\}$, with $\epsilon=0$, 1 and define them as follows:

$$q_\lambda^{(\epsilon)}=\bar{q}_\lambda, \qquad \text{for} \quad \lambda\neq(\rho,\sigma); \quad (15)$$
$$q_\rho^{(\epsilon)}=\{\bar{q}_\rho, N-1+\epsilon\}, \quad q_\sigma^{(\epsilon)}=\{\bar{q}_\sigma, N-\epsilon\}, \qquad \text{for} \quad \rho\neq\sigma; \quad (16)$$
$$q_\rho^{(\epsilon)}=\{\bar{q}_\rho, N-1, N\}\delta_{\epsilon 0}, \quad \text{for} \quad \rho=\sigma. \quad (17)$$

The two corresponding distributions $q'^{(\epsilon')}$ are defined by equations identical to (15), (16), (17) among primed quantities.

These circumstances enable us to perform in (12) the substitution

$$\sum_{q,q'}\rightarrow\mathfrak{N}(\bar{N}_\lambda)\sum_{\epsilon,\epsilon'=0,1}(1-\epsilon\delta_{\rho\sigma})(1-\epsilon'\delta_{\rho'\sigma'}). \quad (18)$$

Notice that

$$N(N-1)[\mathfrak{N}(N_\lambda)\mathfrak{N}(N_\lambda')]^{-1/2}\mathfrak{N}(\bar{N}_\lambda)$$
$$=\prod_\lambda[N_\lambda!^{1/2}N_\lambda'!^{1/2}/\bar{N}_\lambda!]$$
$$=[N_\rho(N_\sigma-\delta_{\rho\sigma})N'_{\rho'}(N'_{\sigma'}-\delta_{\rho'\sigma'})]^{1/2}. \quad (19)$$

(c) Calculation of $P_q+P_{q'}$

The distributions $q^{(\epsilon)}$ and $q'^{(\epsilon')}$ have the parities

$$P_q{}^{(\epsilon)}=P_{\bar{q}}+\sum_{\lambda=\rho+1}^{\infty}\bar{N}_\lambda+\sum_{\lambda=\sigma+1}^{\infty}\bar{N}_\lambda+\epsilon,$$
$$=P_{\bar{q}}+\sum_{\lambda=\rho+1}^{\sigma}\bar{N}_\lambda+\epsilon, \quad (20)$$
$$P_{q'}{}^{(\epsilon')}=P_{\bar{q}}+\sum_{\lambda=\rho'+1}^{\sigma'}\bar{N}_\lambda+\epsilon', \quad (20')$$

where the equalities are modulo 2. Hence we can substitute in (12)

$$P_q+P_{q'}=\Delta P+\epsilon-\epsilon', \quad \Delta P=\sum_{\lambda=\rho+1}^{\sigma}\bar{N}_\lambda-\sum_{\lambda=\rho'+1}^{\sigma'}\bar{N}_\lambda. \quad (21)$$

[8] Magnetic quantum numbers M_S and M_L are omitted henceforth for brevity.

Owing to (18), (19), and (21), (12) reduces to

$$(\Psi|V|\Psi')=\tfrac{1}{2}(-1)^{\Delta P}[N_\rho(N_\sigma-\delta_{\rho\sigma})N_{\rho'}(N_{\sigma'}-\delta_{\rho'\sigma'})]^{1/2}\times\sum_{\epsilon,\epsilon'=0,1}(1-\epsilon\delta_{\rho\sigma})(1-\epsilon'\delta_{\rho'\sigma'})(-1)^{\epsilon-\epsilon'}\times(\psi_u(q^{(\epsilon)},\alpha SL)|V_{N-1,N}|\psi_u'(q'^{(\epsilon')},\alpha'S'L'))\,. \quad (22)$$

The factor $(-1)^{\Delta P}$ establishes a standard normalization of the sign of matrix elements. The factor $[\cdots]^{1/2}$ makes the squared matrix element proportional to the number of electrons available for transfer out of each relevant subshell.

(d) Quantum Numbers of Spectator Electrons

The matrix element in (22) vanishes unless it is diagonal in the set of quantum numbers $\bar\alpha_\lambda\bar S_\lambda\bar L_\lambda$ which identifies the state of the $\bar N_\lambda$ spectator electrons in each subshell. The states of spectator electrons do not appear explicitly in the representation (5) of ψ_u or ψ_u'; therefore a modified representation of these wave functions will be sought. For subshells that contain only spectator electrons the modification is provided trivially by the identities

$$\{n_\lambda l_\lambda^{N_\lambda}\alpha_\lambda S_\lambda L_\lambda|q^{(\epsilon)}{}_\lambda)=\{n_\lambda l_\lambda^{\bar N_\lambda}\bar\alpha_\lambda\bar S_\lambda\bar L_\lambda|\bar q_\lambda)\,,\qquad \lambda\neq(\rho,\sigma)\,, \quad (23)$$

$$(q'^{(\epsilon')}{}_\lambda|n_\lambda l_\lambda^{N\lambda'}\alpha_\lambda'S_\lambda'L_\lambda'\}=(\bar q_\lambda|n_\lambda l_\lambda^{\bar N_\lambda}\bar\alpha_\lambda\bar S_\lambda\bar L_\lambda\}\,,\qquad \lambda\neq(\rho',\sigma')\,. \quad (23')$$

For subshells with interacting electrons, the wave function is resolved into factors pertaining to spectator and interacting electrons by means of the fractional parentage expansion (9). In general ($\rho\neq\sigma$), ψ_u contains the two subshell factors $\lambda=\rho$ and $\lambda=\sigma$ which include interacting electrons and are to be expanded separately. The expansion represents ψ_u in terms of wave functions $\bar\psi_{u\rho\sigma}$ which are analogs of ψ_u for the spectator electrons augmented by interacting electrons coupled onto (but no longer antisymmetrized with) the subshell factors ρ and σ. Thus we have

$$\psi_u(q^{(\epsilon)},\alpha SL)=\sum(l_\rho^{N\rho}\alpha_\rho S_\rho L_\rho[l_\rho^{\bar N\rho}\bar\alpha_\rho\bar S_\rho\bar L_\rho l_\rho S_\rho L_\rho)\times(l_\sigma^{N\sigma}\alpha_\sigma S_\sigma L_\sigma[l_\sigma^{\bar N\sigma}\bar\alpha_\sigma\bar S_\sigma\bar L_\sigma l_\sigma S_\sigma L_\sigma)\bar\psi_{u\rho\sigma}(q^{(\epsilon)},\alpha SL)\,, \quad (24)$$

where the summation is over the barred quantum numbers, and

$$\bar\psi_{u\rho\sigma}(q^{(\epsilon)},\alpha SL)=[\prod_{\lambda\neq(\rho,\sigma)}\{n_\lambda l_\lambda^{\bar N_\lambda}\bar\alpha_\lambda\bar S_\lambda\bar L_\lambda|\bar q_\lambda)\times[\{n_\rho l_\rho^{\bar N_\lambda}\bar\alpha_\rho\bar S_\rho\bar L_\rho|\bar q_\rho)\times\{n_\rho l_\rho|N-1+\epsilon)]^{(S_\rho L_\rho)}\times[\{n_\sigma l_\sigma^{\bar N_\sigma}\bar\alpha_\sigma\bar S_\sigma\bar L_\sigma|\bar q_\sigma)\times\{n_\sigma l_\sigma|N-\epsilon)]^{(S_\sigma L_\sigma)}]^{(\alpha SL)}. \quad (25)$$

For $\rho=\sigma$, the wave function ψ_u contains a single subshell factor with both interacting electrons. This factor is to be expanded twice in succession, separating first the interacting electron N and then $N-1$. Additional quantum numbers $\tilde\alpha_\rho\tilde S_\rho\tilde L_\rho$ are required to identify the state that results from the first expansion. We find

$$\psi_u(q^{(\epsilon)},\alpha SL)=\sum(l_\rho^{N\rho}\alpha_\rho S_\rho L_\rho[l_\rho^{N\rho-1}\tilde\alpha_\rho\tilde S_\rho\tilde L_\rho l_\rho,S_\rho L_\rho)\times(l_\rho^{N\rho-1}\tilde\alpha_\rho\tilde S_\rho\tilde L_\rho[l_\rho^{\bar N\rho}\bar\alpha_\rho\bar S_\rho\bar L_\rho l_\rho,\tilde S_\rho\tilde L_\rho)\bar\psi_{u\rho\rho}(q^{(\epsilon)},\alpha SL)\delta_{\epsilon0}\,, \quad (26)$$

where the summation is over the quantum numbers with bars and tildes, and

$$\bar\psi_{u\rho\rho}(q^{(0)},\alpha SL)=[\prod_{\lambda\neq\rho}\{n_\lambda l_\lambda^{\bar N_\lambda}\bar\alpha_\lambda\bar S_\lambda\bar L_\lambda|\bar q_\lambda)+[[\{n_\rho l_\rho^{\bar N\rho}\bar\alpha_\rho\bar S_\rho\bar L_\rho|\bar q_\rho)\times\{n_\rho l_\rho|N-1)]^{(\tilde S_\rho\tilde L_\rho)}\times\{n_\rho l_\rho|N)]^{(S_\rho L_\rho)}]^{(\alpha SL)}. \quad (27)$$

Each of the summations over $\bar\alpha\bar S\bar L$ in (24) and (26) reduces to a single term owing to (23′), except for coincidences between (ρ,σ) and (ρ',σ'). Formulas analogous to (24)–(27) apply to the expansion of ψ_u'.

Substitution of these expansions of ψ_u and ψ_u' into (22) reduces the calculation of $(\Psi|V|\Psi')$ to a sum of comparatively few terms containing matrix elements

$$(\bar\psi_{u\rho\sigma}(q^{(\epsilon)},\alpha SL)|V_{N,N-1}|\bar\psi'_{u\rho'\sigma'}(q'^{(\epsilon')},\alpha'S'L'))\,, \quad (28)$$

where the ρ and σ may coincide.

The process of taking advantage of symmetries under electron permutations is now completed. Henceforth, we shall deal primarily with the further calculation of matrix elements (28) with $\rho\neq\sigma$, $\rho'\neq\sigma'$. The extension to variants with indices $\rho\rho$ or $\rho'\rho'$ is straightforward because (27) differs from (25) only by certain quantum numbers and by the coupling of angular momenta; some indications on these variants will be given.

4. SEPARATION OF VARIABLES

This section contains straightforward or well-known operations designed to bring (28) to an explicit and tractable form.

In LS coupling, spin and orbital variables are tied together in the matrix element only by the connection between antisymmetrization and addition of angular momenta within each subshell. Having completed the parentage expansion in Sec. 3d, we can now separate these variables. We set in (28)

$$\bar\psi_{u\rho\sigma}(q^{(\epsilon)},\alpha SL)=\Phi(\rho\sigma\epsilon,\alpha S)X(\rho\sigma\epsilon,\alpha L) \quad (29)$$

and proceed to obtain expressions for Φ and X from (25).

Since the distributions of the spectator electron variables $\bar q_\lambda$ are identical for the wave functions $\bar\psi$ and $\bar\psi'$ of (28), these variables need no longer be carried along explicitly. Moreover, the group of spectator electrons of each subshell affects (28) merely as a carrier of spin and orbital angular momentum; therefore the indices $n_\lambda l_\lambda^{\bar N_\lambda}\bar\alpha_\lambda$ are also redundant. We shall then simplify and factor out the wave function of each group of equivalent spectator electrons by the change of symbols

$$\{n_\lambda l_\lambda^{\bar N_\lambda}\bar\alpha_\lambda\bar S_\lambda\bar L_\lambda|\bar q_\lambda)\rightarrow\{\bar S_\lambda|\{\bar L_\lambda|\,. \quad (30)$$

An analogous notation will be used for the wave functions of the interacting electrons, through substitutions of the type

$$\{n_\sigma l_\sigma | N) \rightarrow \{s_N | \{n_\sigma l_{\sigma N}|. \tag{31}$$

Here it has been necessary to preserve an indication of the identity of electron N by appropriate subscripts, to introduce the symbol s to denote the wave function of a single spin, and to preserve the indication of the shell quantum number n_σ.

Application of (30) and (31) to (25) reduces this equation to the form (29) with

$$\begin{aligned}\Phi(\rho\sigma\epsilon,\alpha S)&=[\textstyle\prod_{\lambda\neq(\rho,\sigma)}\{\bar{S}_\lambda|\ [\{\bar{S}_\rho|\times\{s_{N-1+\epsilon}|\,]^{(S_\rho)}[\{\bar{S}_\sigma|\times\{s_{N-\epsilon}|\,]^{(S_\sigma)}]^{(\alpha S)}\\&=\{\bar{S}_1\cdots\bar{S}_{\rho-1}(\bar{S}_\rho s_{N-1+\epsilon})S_\rho\cdots(\bar{S}_\sigma s_{N-\epsilon})S_\sigma\cdots,\alpha S|,\end{aligned} \tag{32}$$

$$\begin{aligned}X(\rho\sigma\epsilon,\alpha L)&=[\textstyle\prod_{\lambda\neq(\rho,\sigma)}\{\bar{L}_\lambda|\ [\{\bar{L}_\rho|\times\{n_\rho l_{\rho,N-1+\epsilon}|\,]^{(L_\rho)}[\{\bar{L}_\sigma|\times\{n_\sigma l_{\sigma,N-\epsilon}|\,]^{(L_\sigma)}]^{(\alpha L)}\\&=\{\bar{L}_1\cdots\bar{L}_{\rho-1}(\bar{L}_\rho l_{\rho,N-1+\epsilon})L_\rho\cdots(\bar{L}_\sigma l_{\sigma,N-\epsilon})L_\sigma\cdots,\alpha L|.\end{aligned} \tag{33}$$

The matrix element (28) now factors out, upon substitution of (29) and of an analogous expression for $\bar{\psi}'_{u\rho'\sigma'}$:

$$\begin{aligned}&(\psi_{u\rho\sigma}(q^{(\epsilon)},\alpha SL)\,|\,V_{N,N-1}\,|\,\bar{\psi}'_{u\rho'\sigma'}(q'^{(\epsilon')},\alpha'S'L'))\\&\qquad=(\Phi(\rho\sigma\epsilon,\alpha S)\,|\,\Phi'(\rho'\sigma'\epsilon',\alpha'S'))(X(\rho\sigma\epsilon,\alpha L)\,|\,V_{N,N-1}\,|\,X'(\rho'\sigma'\epsilon',\alpha'L')).\end{aligned} \tag{34}$$

Since the interaction V is spin independent, the first factor on the right of (34) is simply the inner product of two different functions of the same spin variables, that is, a spin recoupling coefficient. This coefficient is represented explicitly by

$$\begin{aligned}(\Phi(\rho\sigma\epsilon,\alpha S)\,|\,\Phi'(\rho'\sigma'\epsilon',\alpha'S'))&=(\bar{S}_1\cdots\bar{S}_{\rho-1}(\bar{S}_\rho s_{N-1+\epsilon})S_\rho\cdots(\bar{S}_\sigma,s_{N-\epsilon})S_\sigma\cdots,\\&\quad\times\alpha\,|\,\bar{S}_1\cdots\bar{S}_{\rho'-1}(\bar{S}_{\rho'}s_{N-1+\epsilon'})S'_{\rho'}\cdots(\bar{S}_{\sigma'}s_{N-\epsilon'})S'_{\sigma'}\cdots,\alpha')^{(S)}\delta_{SS'},\end{aligned} \tag{35}$$

and can be evaluated numerically by established procedures and tables[9] once the quantum numbers $\bar{S}_\lambda$, S_ρ, S_σ, $S'_{\rho'}$, $S'_{\sigma'}$, and S are given, together with the coupling-scheme data indicated by α and α'. There are four possible pairs (ϵ,ϵ'), but (35) has only two distinct values, for $|\epsilon-\epsilon'|=0, 1$. Any of the $\bar{S}_\lambda$ that vanishes, as e.g., the spin of spectator closed shells, can of course be ignored in (35). When $\rho=\sigma$, set $\epsilon=0$ and perform the substitution

$$(\bar{S}_\rho s_{N-1})S_\rho(\bar{S}_\sigma s_N)S_\sigma \rightarrow [(\bar{S}_\rho s_{N-1})\bar{S}_\rho s_N]S_\rho \tag{35a}$$

on the right of (35).

The last factor on the right of (34) can be further resolved into contributions arising from the radial and azimuthal factors of one-particle wave functions. The radial factors of the groups of spectator electrons are irrelevant here and those of electrons $N-1$ and N contribute standard Slater integrals.[10] Introduction of the form (10′) of $V_{N,N-1}$ into the last factor of (34) yields

$$\begin{aligned}(X(\rho\sigma\epsilon,\alpha L)\,|\,V_{N,N-1}\,|\,X'(\rho'\sigma'\epsilon',\alpha'L'))&=\textstyle\sum_k[\delta_{\epsilon\epsilon'}R^k(n_\rho l_\rho n_\sigma l_\sigma,n_{\rho'}l_{\rho'}n_{\sigma'}l_{\sigma'})\\&\quad+(1-\delta_{\epsilon\epsilon'})R^k(n_\rho l_\rho n_\sigma l_\sigma,n_{\sigma'}l_{\sigma'}n_{\rho'}l_{\rho'})](\bar{L}_1\cdots\bar{L}_{\rho-1}(\bar{L}_\rho l_{\rho,N-1+\epsilon})L_\rho\cdots(\bar{L}_\rho l_{\sigma,N-\epsilon})L_\sigma\cdots,\alpha L|\\&\quad\times|\,P_k(\hat{r}_N\cdot\hat{r}_{N-1})\,|\,\bar{L}_1\cdots\bar{L}_{\rho'-1}(\bar{L}_{\rho'}l_{\rho',N-1+\epsilon'})L_{\rho'}\cdots(\bar{L}_{\sigma'}l_{\sigma',N-\epsilon'})L_{\sigma'}\cdots,\alpha'L)\delta_{LL'},\end{aligned} \tag{36}$$

where an explicit notation similar to that of (35) has been used in the last matrix element. The two Slater integrals in the brackets correspond, respectively, to the alternative double jumps $(\rho'\rightarrow\rho,\ \sigma'\rightarrow\sigma)$ and $(\rho'\rightarrow\sigma,\ \sigma'\rightarrow\rho)$. When $\rho=\sigma$, set $\epsilon=0$ and perform the substitution

$$(\bar{L}_\rho l_{\rho,N-1})L_\rho(\bar{L}_\sigma l_{\sigma N})L_\sigma \rightarrow [(\bar{L}_\rho l_{\rho,N-1})\bar{L}_\rho l_{\rho N}]L_\rho \tag{36a}$$

on the right of (36); the two Slater integrals R^k coincide in this case. The matrix element on the right of (36) is independent of the dynamics of the atom under consideration and is only a function of the various orbital angular momenta, of their coupling, and of k. This function can be calculated by alternative paths, as discussed in the next section.

5. ORBITAL COUPLING

Calculations of matrix elements of the Legendre polynomial P_k utilize the well known expansion in terms of one-particle spherical wave functions[11]

$$P_k(\hat{r}_N\cdot\hat{r}_{N-1})=\textstyle\sum_q C^{(k)}{}_q(\hat{r}_N)C^{(k)}{}_q{}^*(\hat{r}_{N-1}). \tag{37}$$

When (37) is substituted in (36), one may regard the $C^{(k)}{}_q{}^*(\hat{r}_{N-1})$ as 2^k-pole operators that absorb k units of angular momentum from the orbital motion of the elec-

[9] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959)—referred to as FR; M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3j and 6j Symbols* (Technology Press, Cambridge, Massachusetts, 1959).

[10] See, e.g., E. U. Condon and G. H. Shortley, *The Theory of Atomic Collisions* (Cambridge University Press, Cambridge, England, 1963), p. 175.

[11] The normalization introduced by Racah, Ref. 1 II, is used here.

tron $N-1$ in the many-electron wave function X', whereas the $C^{(k)}{}_q(\hat{r}_N)$ return the same angular momentum to the electron N in the state X. Racah (Ref. 1 II) has given a basic formula for matrix elements of (36) between two-particle states. He factors out single-particle reduced matrix elements $(l\|C^{(k)}\|l')$ which are characteristic of the $C_q{}^{(k)}$ as distinguished from other 2^k-pole operators. The residual operation of angular-momentum transfer he identifies, in effect, as a single standard recoupling transformation (see Ref. 9, FR, Chaps. 15 and 16c) whose result depends on the resultant angular momentum $\hat{L}$ of the two electrons. To utilize this result for many-electron wave functions, the orbital momenta within the two wave functions have first to be recoupled (Rosenzweig's transformation D) so that the electrons $N-1$ and N have a definite resultant angular momentum $\hat{L}$. Then the matrix element of P_k is evaluated for this value of $\hat{L}$ and finally a summation is carried out over all possible values of $\hat{L}$. This procedure is further complicated, in Kelly's general treatment,[3] by the simultaneous role of recoupling in the process of antisymmetrization.

An alternative procedure[7] carries the factorization of the coupling further. It bypasses the recoupling and summation by representing the orbit-orbit coupling with transfer of k units of momentum as proceeding by the emission and reabsorption of a mock-particle O, which might be called an "orbiton," with angular momentum k. To this end one rewrites (37) in the form

$$P_k(\hat{r}_N\cdot\hat{r}_{N-1})=[\textstyle\sum_q C^{(k)}{}_q(\hat{r}_N)(k_Oq|\,]\times[\sum_{q'}|k_Oq')C^{(k)}{}_{q'}{}^*(\hat{r}_{N-1})], \quad (38)$$

whose equivalence to (37) follows from the orthonormality of the orbiton wave functions, $(k_Oq|\,|k_Oq')=(k_Oq|k_Oq')=\delta_{qq'}$. On the right of (38) we have two independent *scalar* operators, each of which acts on a *single electron*. One of them takes k units of momentum from electron $N-1$ and transfers them to the emitted orbiton, the other absorbs the orbiton and transfers its momentum to electron N. These two operators can be applied separately to the states X' and X *without interfering with their respective couplings of angular momenta.*

The operator represented in each bracket of (38) transforms the orbital wave function with angular momentum l of one electron into the product of another wave function of that electron and of the orbiton wave function, the electron and orbiton momenta adding up to the initial value l. As shown in FPG[7] or directly by use of the general formulas (14.4, FR[9]) or (29, II[1]), one has

$$\begin{aligned}&(lm|N)\textstyle\sum_q C^{(k)}{}_q(\hat{r}_N)(kq|O)\\&=\sum_q\sum_{l''}(lm|C^{(k)}{}_q|l''m-q)(l''m-q|N)(kq|O)\\&=\sum_{l''}(l\|C^{(k)}\|l'')(2l+1)^{-1/2}\\&\quad\times\sum_q(l''klm|l''m-q,kq)(l''m-q|N)(kq|O)\\&=(2l+1)^{-1/2}\sum_{l''}(l\|C^{(k)}\|l'')\\&\qquad\times[\{l''|N)\times\{k|O)]^{(l)}{}_m. \quad (39)\end{aligned}$$

Here $(l\|C^{(k)}\|l'')$ is a standard reduced matrix element, well known in theoretical spectroscopy and given as a function of k, l, and l'' by (FR, 14.12).[9] The sum over l'' reduces to a single term $l''=l'$ when (39) is applied to the calculation of a matrix element, owing to orthonormality of $\{l''|N)$ and $(N|l'\}$. In the notation of (36), Eq. (39) becomes

$$\begin{aligned}&\{l_N|\,[\textstyle\sum_q C^{(k)}{}_q(\hat{r}_N)(k_Oq|\,]\\&\quad=(2l+1)^{-1/2}\textstyle\sum_{l''}(l\|C^{(k)}\|l'')[\{l_N''|\times\{k_O|\,]^{(l)}, \quad (40)\end{aligned}$$

and similarly we have

$$\begin{aligned}&[\textstyle\sum_{q'}|k_Oq')C^{(k)}{}_{q'}{}^*(\hat{r}_{N-1})]\;|l'_{N-1}\}=\sum_{l''}[|k_O\}\\&\qquad\times|l''_{N-1}\}]^{(l'')}(l''\|C^{(k)}\|l')(2l'+1)^{-1/2}. \quad (40')\end{aligned}$$

Notice the permutation of factors in the addition of momenta in (40′) with respect to (40) [(40′) and (40) are Hermitian conjugates].

Substitution of (38), (40), and (40′) into the orbital coupling matrix element of (36) reduces it to a transformation matrix element, the inner product of two different many-particle states constructed from the same set of one-particle orbital wave functions, that is, to a recoupling coefficient. The *orbiton is included* here among the particles and, as noted in Sec. 4, each group of equivalent spectator electrons is also regarded as a single particle. Two different matrix elements occur for $\epsilon'=\epsilon$ and $\epsilon'=1-\epsilon$, respectively, but the result is seen to be otherwise independent of ϵ, owing to the permutability of N and $N-1$ in (38). Indeed, particle-identifying labels such as $N-\epsilon$ can be dropped after the appropriate values of l'' in (40) and (40′) have been substituted as required by orthogonality (see above). Thereby (36) becomes

$$\begin{aligned}&(X(\rho\sigma\epsilon,\alpha L)\,|\,V_{N,N-1}|\,X'(\rho'\sigma'\epsilon',\alpha'L'))\\&=\textstyle\sum_k[\delta_{\epsilon\epsilon'}R^k(n_\rho l_\rho n_\sigma l_\sigma,n_{\rho'}l_{\rho'}n_{\sigma'}l_{\sigma'})[(2l_\sigma+1)(2l_{\rho'}+1)]^{-1/2}(l_\rho\|C^{(k)}\|l_{\rho'})(l_\sigma\|C^{(k)}\|l_{\sigma'})\\&\quad\times(\bar{L}_1\cdots\bar{L}_{\rho-1}(\bar{L}_\rho l_\rho)L_\rho\cdots[\bar{L}_\sigma(l_{\sigma'}k)l_\sigma]L_\sigma\cdots,\alpha|\,\bar{L}_1\cdots\bar{L}_{\rho'-1}[\bar{L}_{\rho'}(kl_\rho)l_{\rho'}]L_{\rho'}\cdots(\bar{L}_{\sigma'}l_{\sigma'})L_{\sigma'}\cdots,\alpha')^{(L)}\\&\quad+(1-\delta_{\epsilon\epsilon'})R^k(n_\rho l_\rho n_\sigma l_\sigma,n_{\sigma'}l_{\sigma'}n_{\rho'}l_{\rho'})[(2l_\sigma+1)(2l_{\sigma'}+1)]^{1/2}(l_\rho\|C^{(k)}\|l_{\sigma'})(l_\sigma\|C^{(k)}\|l_{\rho'})\\&\quad\times(\bar{L}_1\cdots\bar{L}_{\rho-1}(\bar{L}_\rho l_\rho)L_\rho\cdots[\bar{L}_\sigma(l_{\rho'}k)l_\sigma]L_\sigma\cdots,\alpha|\,\bar{L}_1\cdots\bar{L}_{\rho'-1}(\bar{L}_{\rho'}l_{\rho'})L_{\rho'}\cdots[\bar{L}_{\sigma'}(kl_\rho)l_{\sigma'}]L_{\sigma'}\cdots,\alpha')^{(L)}]\delta_{LL'}. \quad (41)\end{aligned}$$

The recoupling coefficients in this orbital formula can be calculated like the one in the spin formula.[9] In fact, (41) results by direct application of (FPG, 10) to (36); the treatment in this section was intended as further illustration of the procedure. When $\rho=\sigma$, perform the substitutions

$$(\bar{L}_\rho l_\rho)L_\rho[\bar{L}_\sigma(l_{\sigma'}k)l_\sigma]L_\sigma \rightarrow [(\bar{L}_\rho l_\rho)\tilde{L}_\rho(l_{\sigma'}k)l_\rho]L_\rho\,,$$
$$(\bar{L}_\rho l_\rho)L_\rho[\bar{L}_\sigma(l_{\rho'}k)l_\sigma]L_\sigma \rightarrow [(\bar{L}_\rho l_\rho)\tilde{L}_\rho(l_{\rho'}k)l_\rho]L_\rho\,, \quad (41a)$$

respectively, in the first and second recoupling coefficient of (41).

6. PRESCRIPTION FOR THE CALCULATION OF A MATRIX ELEMENT

A single but lengthy expression for $(\Psi|V|\Psi')$, suitable for numerical evaluation, can be obtained by combining (41), (35), (34), (24), and (22). Instead, we give here a procedure for a step-by-step calculation of the final result.

(1) List, for each subshell λ, the number $\bar{N}_\lambda$ of spectator electrons and their quantum numbers $(\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda)$, as, e.g., in the table of Sec. 7. If alternative values of these numbers are consistent with (13a), (13b), (23), and (23′), alternative lists should be made and separate calculations carried out for each of them. Comparison of the sets $\{\bar{N}_\lambda\}$, $\{N_\lambda\}$, and $\{N_\lambda'\}$ identifies the subshells λ that are to be labelled ρ, σ, ρ' and σ' in accordance with (14) and (14′). If $\rho=\sigma$ and/or $\rho'=\sigma'$, the possible sets $(\bar{\alpha}_\rho\bar{S}_\rho\bar{L}_\rho)$ and/or $(\bar{\alpha}_{\rho'}\bar{S}_{\rho'}\bar{L}_{\rho'})$ should also be listed and separate calculations carried out for each of them.

(2) Evaluate the right hand side of (41) for the relevant values of the various quantum numbers and for the coupling schemes specified by α and α'. The evaluation of the Slater integrals R^k is often conveniently delayed. The remaining coefficients often reduce to simple algebraic combinations of small integers.

(3) Evaluate similarly the right hand side of (35), for the two alternative values of $|\epsilon-\epsilon'|$.

(4) Multiply the results of (2) and (3) to obtain the matrix element (34).

(5) Obtain the coefficients of fractional parentage relevant to the expansion (24), or (26), of $\psi_u(q^{(\epsilon)},\alpha SL)$ *and* to the corresponding expansion of $\psi_u'(q^{(\epsilon')},\alpha'SL)$. The procedure for obtaining these coefficients is defined by III[1] and also in Sec. 13 of FR[9]; many of them are found in the literature and in trivial cases are unity. Multiply these coefficients by the matrix element (34).

(6) Carry out steps (2) through (5) for all the sets of numbers $(\bar{\alpha}\bar{S}\bar{L})$ and, where relevant, $(\tilde{\alpha}\tilde{S}\tilde{L})$ which are included in the list (1) and add up the partial results. Thereby are obtained the matrix elements to be entered on the right of (22) for the alternative values of (ϵ,ϵ').

(7) Evaluate (22) using the matrix elements so obtained and the value of ΔP from (21).

(8) Repeat the whole procedure for all alternative sets $\{\bar{N}_\lambda\}$, if any, and add up the partial results.

7. EXAMPLE: $(1s^22s2p^63p\ ^1P|V|1s^22s^22p^5El\ ^1P)$

Step (1). In this example, where $l=0$ or 2, the relevant subshell parameters are

Subshell:	$1s$	$2s$	$2p$	$3p$	El
Symbol:		ρ'	ρ	σ	σ'
$\bar{N}$	2	1	5	0	0
$\bar{L}$	0	0	1	0	0
$\bar{S}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	0
L or L'		0	0	1	l
S or S'		0	0	$\frac{1}{2}$	$\frac{1}{2}$

The situation is made rather simple by maximum off-diagonality and by the large number of zero entries in the table. No quantum number $\bar{\alpha}$ is required, the $\bar{N}$, $\bar{S}$, and $\bar{L}$ are fixed and no quantum numbers (α,α') are required to specify the addition of angular momenta for the given character ^1P (i.e., $S=0$, $L=1$) of the states Ψ and Ψ'.

Step (2). Substitution of the zero values of $\bar{L}_{1s}$, $\bar{L}_{2s}$, L_{2p}, $\bar{L}_{3p}$, $\bar{L}_l$, and l_{2s}, taking into account that only $k=l_{2p}=1$ yields a nonzero contribution owing to triangular conditions, reduces (41) to

$$(X(2p3p\epsilon,L)|V_{N,N-1}|X'(2sEl\epsilon',L))=\delta_{\epsilon\epsilon'}R^1(2p3p,2sEl)3^{-1/2}(l_{2p}\|C^{(1)}\|0)(l_{3p}\|C^{(1)}\|l)$$
$$\times(00(\bar{L}_{2p}l_{2p})0[0(lk)l_{3p}]L_{3p}0\,|\,0[0(kl_{2p})0]0\bar{L}_{2p}0(0l)L_l)^{(L)}+(1-\delta_{\epsilon\epsilon'})R^1(2p3p,El2s)[3(2l+1)]^{-1/2}$$
$$\times(l_{2p}\|C^{(1)}\|l)(l_{3p}\|C^{(1)}\|0)(00(\bar{L}_{2p}l_{2p})0[0(l_{2s}k)l_{3p}]L_{3p}0\,|\,0(0l_{2s})0\bar{L}_{2p}0[0(kl_{2p})l]L_l)^{(L)}. \quad (42)$$

From Chap. 14 of FR we find, for $l_{2p}=l_{3p}=1$,

$$(l_{2p}\|C^{(1)}\|0)=(l_{3p}\|C^{(1)}\|0)=1\,, \quad (43)$$
$$(l_{2p}\|C^{(1)}\|l)=(l_{3p}\|C^{(1)}\|l)=(1+\tfrac{1}{2}l)^{1/2}. \quad (44)$$

Deletion of irrelevant zeros in the recoupling coefficients of (42) (the spectator closed shell $1s^2$ drops out at this point) and use of data from FR Chaps. 11 and 12 and of values of remaining quantum numbers reduce these coefficients to

$$((\bar{L}_{2p}l_{2p})0(lk)1\,|\,(kl_{2p})0\bar{L}_{2p}l)^{(1)}=((\bar{L}_{2p}l_{2p})0(lk)1\,|\,(\bar{L}_{2p}l)1(l_{2p}k)0)^{(1)}$$
$$=3\begin{vmatrix}1&1&0\\l&1&1\\1&0&1\end{vmatrix}=3\begin{vmatrix}0&1&1\\1&l&1\\1&1&0\end{vmatrix}=\begin{pmatrix}0&1&1\\l&1&1\end{pmatrix}=\begin{pmatrix}1&1&l\\1&1&0\end{pmatrix}=\tfrac{1}{3}, \quad (45)$$

$$((\bar{L}_{2p}l_{2p})0(l_{2s}k)1\,|\,l_{2s}\bar{L}_{2p}(kl_{2p})l)^{(1)}=((\bar{L}_{2p}l_{2p})0k\,|\,\bar{L}_{2p}(l_{2p}k)l)^{(1)}$$
$$=(2l+1)^{1/2}\begin{pmatrix}1 & 1 & l\\ 1 & 1 & 0\end{pmatrix}=(2l+1)^{1/2}\tfrac{1}{3}. \tag{46}$$

Substitution of (43)–(46) into (42) yields finally

$$(X(2p3p\epsilon,L)\,|\,V_{N,N-1}\,|\,X'(2s2l\epsilon',L))=3^{-3/2}(1+\tfrac{1}{2}l)^{1/2}[\delta_{\epsilon\epsilon'}R^1(2p3p,2sEl)+(1-\delta_{\epsilon\epsilon'})R^1(2p3p,El2s)]. \tag{47}$$

Step (3). Stepwise substitution of the numerical values of the spin quantum numbers into (35) yields

$$(\Phi(2p3p\epsilon,S)\,|\,\Phi'(2sEl\epsilon',S))=\delta_{\epsilon\epsilon'}(0\bar{S}_{2s}(\bar{S}_{2p}s_{N-1})0(0s_N)S_{3p}0\,|\,0(\bar{S}_{2s}s_{N-1})0\bar{S}_{2p}0(0s_N)S_l)^{(S)}$$
$$+(1-\delta_{\epsilon\epsilon'})(0\bar{S}_{2s}(\bar{S}_{2p}s_{N-1})0(0s_N)S_{3p}0\,|\,0(\bar{S}_{2s}s_N)0\bar{S}_{2p}0(0s_{N-1})S_l)^{(S)}$$
$$=\delta_{\epsilon\epsilon'}((\bar{S}_{2s}s_N)0(\bar{S}_{2p}s_{N-1})0\,|\,(\bar{S}_{2s}s_{N-1})0(\bar{S}_{2p}s_N)0)^{(0)}$$
$$+(1-\delta_{\epsilon\epsilon'})((\bar{S}_{2s}s_N)0(\bar{S}_{2p}s_{N-1})0\,|\,(\bar{S}_{2s}s_N)0(\bar{S}_{2p}s_{N-1})0)^{(0)}$$
$$=\delta_{\epsilon\epsilon'}(-1)\begin{pmatrix}\frac{1}{2} & \frac{1}{2} & 0\\ \frac{1}{2} & \frac{1}{2} & 0\end{pmatrix}+(1-\delta_{\epsilon\epsilon'})1$$
$$=\delta_{\epsilon\epsilon'}\tfrac{1}{2}+(1-\delta_{\epsilon\epsilon'}). \tag{48}$$

Step (4). Multiplication of (47) and (48) gives

$$(\bar{\psi}_{u2p3p}(\epsilon,SL)\,|\,V_{N,N-1}\,|\,\bar{\psi}'_{u2s}El(\epsilon',SL))=3^{-3/2}(1+\tfrac{1}{2}l)^{1/2}[\delta_{\epsilon\epsilon'}\tfrac{1}{2}R^1(2p3p,2sEl)+(1-\delta_{\epsilon\epsilon'})R^1(2p3p,El2s)]. \tag{49}$$

Step (5). The relevant fractional parentage coefficients are trivially unity.
Step (6). No alternative parentage.
Step (7). Substitution of (48) and other data in (22) yields

$$(\Psi\,|\,V_{N,N-1}\,|\,\Psi')=\tfrac{1}{2}(-1)^{0-5}(2\times6)^{1/2}3^{-3/2}(1+\tfrac{1}{2}l)^{1/2}\textstyle\sum_{\epsilon\epsilon'}[\delta_{\epsilon\epsilon'}\tfrac{1}{2}R^1(2p3p,2sEl)+(1-\delta_{\epsilon\epsilon'})(-1)R^1(2p3p,El2s)] \tag{50}$$
$$=\tfrac{1}{3}(1+\tfrac{1}{2}l)^{1/2}[-R^1(2p3p,2sEl)+2R^1(2p3p,El2s)].$$

This is the result utilized in Eq. (7.9) of Ref. 6.
Step (8). Does not occur.

8. GLOSSARY OF SYMBOLS

N_λ	Number of electrons in subshell λ.
$N=\sum_\lambda N_\lambda$	Number of electrons in atom.
q_λ	A set of N_λ electrons drawn from $(1,2,\cdots i\cdots N)$, and ordered by increasing i, to be assigned to subshell λ.
$q=\{q_\lambda\}$	A distribution of N electrons in mutually exclusive sets q_λ.
$\mathfrak{N}(N_\lambda)$	Number of different q, Eq. (7).
P_q	Parity of distribution q, relative to ordered set $(1,2,\cdots i\cdots N)$, Eq. (20).
$(i\,\|\,nlmlm_s)=(s_i\,\|\,m_s)(\mathbf{r}_i\,\|\,nlm_l)\}$	Wave function of ith electron in nl subshell.
$(i\,\|\,nl\}=\|\,s_i\}\,\|\,nl_i\}$	Set of same wave functions with all different values of m_lm_s.
$[(i\,\|\,n_1l_1\}\times(h\,\|\,n_2l_2\}]^{(SL)}{}_{M_SM_L}$ $=[\,\|\,s_i\}\times\|\,s_h\}]^{(S)}{}_{M_S}$ $\times[\,\|\,n_1l_{1i}\}\times\|\,n_2l_{2h}\}]^{(L)}{}_{M_L}$ $=\|\,(s_is_h)SM_S)\,\|\,(n_1l_{1i}n_2l_{2h})LM_L)$	Wave function of two electrons i and h with spin and orbital momenta adding up to S and L, respectively.
$(q_\lambda\,\|\,n_\lambda l_\lambda^{N_\lambda}\alpha_\lambda S_\lambda L_\lambda M_{S\lambda}M_{L\lambda})$	Antisymmetrized λ-subshell wave function of electron set q_λ, as in Ref. 1 III.
α_λ	Quantum number that distinguishes different states of subshell λ with equal S_λ, L_λ.
$\psi_u(q,\alpha SLM_SM_L)$	Unsymmetrized LS-coupled product of antisymmetrized subshell wave functions.
α	Quantum number that distinguishes different ways of adding the S_λ and L_λ vectorially to yield S and L.
$\Psi(\alpha SLM_SM_L)$	Antisymmetrized and normalized superposition of all ψ_u with different q [Eq. (8)].

$(l^{N-1}\bar{\alpha}\bar{S}\bar{L}lSL\|\|l^N\alpha SL)$	Coefficient of fractional parentage as in Ref. 1 III.
$\bar{N}_\lambda, \bar{q}, \bar{q}_\lambda, \bar{\alpha}_\lambda, \bar{S}_\lambda, \bar{L}_\lambda$	Analogs of N_λ, q, q_λ, α_λ, S_λ, L_λ for spectator electrons.
$\tilde{\alpha}_\rho\tilde{S}_\rho\tilde{L}_\rho$	Intermediate quantum numbers in two-step parentage expansion (26).
$\epsilon=0, 1$	Index distinguishing alternative q that include a given $\bar{q}$.
$\bar{\psi}_{u\rho\sigma}$	Unsymmetrized product of spectator electron antisymmetric subshell wave functions coupled to wave functions of interacting electrons in subshells ρ and σ [Eqs. (25) and (27)].
Φ	Spin factor of $\bar{\psi}_{u\rho\sigma}$.
X	Orbital factor of $\bar{\psi}_{u\rho\sigma}$.
R^k	Slater integral as in Ref. 10.
$(l\|\|C^{(k)}\|\|l')$	Reduced matrix element as in Ref. 1 II or Ref. 9, FR, Chap. 14.
$(j_1j_2\cdots,\alpha\|\,j_1j_2\cdots,\alpha')^{(J)}$	Transformation matrix element, i.e., inner product of two different products of the same set of angular momentum eigenstates $(j_1j_2\cdots)$ whose momenta add up vectorially in different ways, distinguished by α and α', with the same resultant J. Replacement of α and α' by explicit description of vector couplings is a prerequisite of numerical evaluation.

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Equilibrium Charge-State Populations of Carbon Ions from 2 to 10 MeV/amu in H_2, N_2, Ar, and Ni*

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Measurements of the equilibrium fractions of C^{6+}, C^{5+}, and C^{4+} ions as a function of ion energy have been made using a gas cell with differentially pumped exit slits and a magnet which spatially separates ions emerging from the slits in different charge states. The separated ion beams are intercepted with different thicknesses of foil and stopped in a junction counter, and charge-state populations are determined from the relative number of counts in each peak of the resulting pulse-height spectrum. Estimated errors are as small as ± 0.002 in the population and ± 0.05 MeV/amu in the energy. The rms charge of the ions is found to be a function of the material through which they are passing. The rms charge in gaseous N_2 and Ar is higher than in solids of neighboring atomic number at ion energies of 3 MeV/amu, but is the same in these gases and in the solids at 8 MeV/amu. At all energies measured, the charge in H_2 is anomalously high. The increased charge in solids is ascribed to a large electron-loss cross section at low energies, which shortens the time between collisions to the extent that the loss cross section is affected by excitation of the electron of the carbon ion. Estimates based on a crude model indicate that electron capture by the carbon ions takes place predominantly from the K shell of N_2 and the L shell of Ar. The anomalous charge in H_2 is apparently due to the absence of a shell from which capture is highly probable.

I. INTRODUCTION

ALTHOUGH considerable information has been obtained in recent years regarding the stopping of particles more massive than protons in the energy range between 2 and 10 MeV/amu,[1] less information is available concerning the charge of these ions as they are slowing down.[1,2] The fraction in each state of ionization has been measured for various ions in alumi-

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[1] L. C. Northcliffe in *Annual Reviews of Nuclear Science* (Annual Reviews, Inc., Palo Alto, 1963), Vol. 13, p. 67.
[2] C. S. Zaidins, California Institute of Technology, 1962 (unpublished).