Scattering of Electrons by Atomic Systems*

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The theory of the scattering of electrons by atoms or ions with any number of incomplete subshells is developed within the Hartree-Fock, or close-coupling, approximation. Allowance is made for the target system to be excited to any electronic configuration constructed from discrete orbitals. The one-electron orbitals of the discrete subshells are assumed known; the scattering (continuum) functions are given as the solutions of coupled integrodifferential equations with prescribed boundary conditions. The form of these equations is such that the continuum functions are orthogonal to all the discrete orbitals. The potential terms appearing in the equations are written in terms of the generalized angular momentum recoupling coefficients. A technique for calculating these coefficients on a computer, which is a complicated algebraic problem, is presented in an Appendix. A computer code for calculating the various elastic, inelastic, and photoionization cross sections has been written and is currently being tested.

1. INTRODUCTION

THE scattering of electrons by many electron systems has been studied by Seaton[1] and by Vainstein and Sobel'man.[2] Seaton showed that the only consistent means of obtaining antisymmetric wave functions in approximate solutions is to make the expansion explicitly antisymmetric. He then analyzed in detail the configuration $nl^q kl$. In this case, the antisymmetrized wave function for a system of $(N+1)$ electrons initially in the state Γ' is

$$\psi(\Gamma',\mathbf{x}_1\cdots\mathbf{x}_{N+1})=(N+1)^{-1/2}\sum_{p=1}^{N+1}(-1)^{N+1-p}\times\sum_{\Gamma}\Phi(\gamma l_p LS\mathbf{X}\hat{r}_p\sigma_p)\frac{F_{\Gamma\Gamma'}(r_p)}{r_p},\quad(1)$$

where $\mathbf{X}=\mathbf{x}_1\cdots\mathbf{x}_N$, with $\mathbf{x}_i$ denoting the space ($\mathbf{r}$) and spin (σ) coordinates of electron i. The quantity γ denotes all the quantum numbers of the N-electron target, while l_p represents the orbital and spin angular momentum of the projectile; L and S are the total quantum numbers.

Vainstein and Sobel'man considered the case of two groups of equivalent electrons.

Calculations of the cross sections for the collision of electrons with many electron atoms have been performed by numerous authors in a variety of different approximations, e.g., Bauer and Browne.[3] Extensive calculations are currently under study by Peterkop and Karule,[4] Krueger and Czyzak,[5] and Smith, Henry, and Burke.[6,7] All these calculations involve only a single incomplete subshell in the target atom, and only a single-electron configuration in the expansion over Γ in Eq. (1).

Recent developments in the calculation of matrix elements of one and two electron operators between wave functions describing configurations with several incomplete subshells (see Shore[8] and Fano[9]) have indicated the method for formulating the general electron-atom problem. In the present paper, the notation of Fano is used to take into account the actual or virtual excitation of any number of atomic terms.

The need for developing the formalism presented in this paper is due to the failure of single-configuration theories to predict the low-energy cross sections for electron-atom scattering (see Smith *et al.*[7]) to provide a close-coupling framework for discussing auto-ionization[10] and photo-ionization[11] since the close-coupling approximation has proved so successful for simple systems,[12] and to provide a theory which will allow the calculation of inelastic cross sections involving a change in the electron configuration.

In Sec. (2), the form of the trial wave function to be substututed into the variational principle is discussed. In Sec. (3), the techniques for evaluating the various matrix elements are presented. Finally, in Sec. (4), the radial equations for the continuum functions are derived.

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2. TRIAL WAVE FUNCTION

An unsymmetrized wave function of an N electron atomic system is (see Fano[9])

$$\psi_u(q\gamma_T\mathbf{X})=[\prod_\lambda (q_\lambda|nl_\lambda^{N_\lambda}\alpha_\lambda S_\lambda L_\lambda\})]^{\gamma_T}, \quad (2)$$

where γ_T denotes the complete set of quantum numbers which specify the target T. The wave function for each subshell λ, of principal quantum number n and orbital l, with resultant quantum numbers α_λ S_λ L_λ, is antisymmetrized and their angular momenta are compounded to give α S L for the target. The unsymmetrized wave function for an $(N+1)$ electron system can be expanded using the functions of Eq. (2) as a basis:

$$\psi_u(q\mathbf{X}\mathbf{x}_{N+1})=\sum_{\gamma_T}\psi_u(q\gamma_T\mathbf{X})\bar{F}_{\gamma_T}(\mathbf{x}_{N+1}), \quad (3)$$

where we shall assume the sum to include several distinct configurations, and the coefficients $\bar{F}$ can be expanded also in two steps:

$$\bar{F}_{\gamma_T}(\mathbf{x}_{N+1})=\sum_{m_s}\chi_{m_s}^{1/2}(\sigma_{N+1})\mathfrak{F}_{\gamma_T m_s}(\mathbf{r}_{N+1})$$

and

$$\mathfrak{F}_{\gamma_T m_s}(\mathbf{r}_{N+1})=\sum_{l_T m_T} f_{\gamma_T m_s l_T m_T}(r_{N+1})Y_{l_T m_T}(\hat{r}_{N+1})r_{N+1}^{-1},$$

where l_T is the orbital angular momentum of the projectile relative to the target.

Combining the above results we obtain

$$\psi_u(q\mathbf{X}\mathbf{x}_{N+1})=\sum_{\gamma_T l_T L M_L S M_S}[\psi_u(q\gamma_T\mathbf{X})\times(N+1|k_T l_T \tfrac{1}{2}\})]^\Gamma \times\frac{\tilde{F}_\Gamma(r_{N+1})}{r_{N+1}}, \quad (4)$$

where Γ denotes the complete set of quantum numbers $(\gamma_T \tfrac{1}{2} l_T L M_L S M_S)$ and where the $\times$ denotes the vector coupling of the N-electron function and the single-electron spin-angle function $(N+1|k_T l_T \tfrac{1}{2}\})$, and

$$\tilde{F}_\Gamma(r_{N+1})=\sum_{m_s m_T}(L_T l_T M_{L_T} m_T|LM_L) \times(S_T \tfrac{1}{2} M_{S_T} m_s|SM_S)f_{\gamma_T m_s l_T m_T}(r_{N+1}), \quad (5)$$

where $L_T M_{L_T} S_T M_{S_T}$ are the total orbital and spin quantum numbers of the target T and their z components.

The unsymmetrized wave function of Eq. (4) will be written

$$\psi_u(q\mathbf{X}\mathbf{x}_{N+1})=\sum_\Gamma\psi_u(q\Gamma,\mathbf{X}\hat{r}_{N+1}\sigma_{N+1})\tilde{F}_\Gamma(r_{N+1})r_{N+1}^{-1}. \quad (6)$$

Asymptotically, the radial functions are superpositions of ingoing and outgoing waves

$$\tilde{F}_\Gamma\sim A_\Gamma e^{-i\theta_\Gamma}-B_\Gamma e^{i\theta_\Gamma};$$

$$\theta_\Gamma=k_\Gamma r-\tfrac{1}{2}l_\Gamma\pi+\left(\frac{Z-N}{k}\right)\ln 2k_\Gamma r+\sigma_{l_\Gamma},$$

where the $\mathbf{S}$ matrix is defined by

$$B_\Gamma\equiv\sum_{\Gamma'}S_{\Gamma\Gamma'}A_{\Gamma'},$$

where the sum Γ' is taken over the incident channels.

Therefore a new radial function F can be defined by

$$\tilde{F}_\Gamma\equiv\sum_{\Gamma'}F_{\Gamma\Gamma'}(r)\sim\sum_{\Gamma'}A_{\Gamma'}[\delta_{\Gamma\Gamma'}e^{-i\theta_\Gamma}-S_{\Gamma\Gamma'}e^{i\theta_\Gamma}]. \quad (7)$$

In terms of these new radial functions F, Eq. (6) is therefore

$$\psi_u(q\mathbf{X}\mathbf{x}_{N+1})=\sum_{\Gamma\Gamma'}\psi_u(q\Gamma,\mathbf{X}\hat{r}_{N+1}\sigma_{N+1})\times F_{\Gamma\Gamma'}(r_{N+1})r_{N+1}^{-1}, \quad (8)$$

which is the total, unsymmetrized, wave function for the entire system (projectile+target).

For the system $(p+T)$ initially in the quantum state Γ', the wave function is

$$\psi_u(q\Gamma'\mathbf{X}\mathbf{x}_{N+1})\equiv\sum_\Gamma\psi_u(q\Gamma\mathbf{X}\hat{r}_{N+1}\sigma_{N+1})\times F_{\Gamma\Gamma'}(r_{N+1})r_{N+1}^{-1}. \quad (9)$$

The wave function for the target system will be constructed from Hartree-Fock orbitals, $P_{nl}(r)$, which, strictly speaking will depend upon Γ. In this paper we shall ignore this dependence. We can expect this assumption to be valid for inner closed-shell orbitals. Its validity for incomplete outer subshells will be tested by running the computer code with the different sets of P_{nl} and observing the variation of the cross sections. If this variation is substantial, then the problem will have to be reformulated including the Γ dependence in P_{nl}; this will result in considerable complication of the algebra and many more radial equations to be solved.

In order to have a properly antisymmetrized wave function, we antisymmetrize the target function, Eq. (2), as proposed by Fano[9]:

$$\psi(\gamma_T\mathbf{X})=\mathfrak{A}(N_\lambda)^{-1/2}\sum_q(-1)^{P_q}\psi_u(q,\gamma_T\mathbf{X}), \quad (10)$$

and then antisymmetrize with respect to the projectile as in (1) to give a total antisymmetric function

$$\psi(\Gamma',\mathbf{x}_1\cdots\mathbf{x}_{N+1})=(N+1)^{-1/2}\times\sum_{p=1}^{N+1}(-1)^{N+1-p}\sum_\Gamma\psi(\Gamma\mathbf{X}\hat{r}_p\sigma_p)F_{\Gamma\Gamma'}(r_p)r_p^{-1}, \quad (11)$$

instead of the unsymmetrized form given in Eq. (9),

where

$$\psi(\Gamma\mathbf{X}\hat{r}_p\sigma_p)=\mathfrak{N}(N_\lambda)^{-1/2}\sum_q(-1)^{P_q}\psi_u(q\Gamma\mathbf{X}\hat{r}_p\sigma_p)$$

$$=\mathfrak{N}(N_\lambda)^{-1/2}\sum_q(-1)^{P_q}[\prod_\lambda(q_\lambda|nl_\lambda^{N_\lambda}\alpha_\lambda L_\lambda S_\lambda\}]^{\gamma_T}\times(p|k_T l_T\tfrac{1}{2}\}]^\Gamma. \quad (12)$$

Here we assign even parity to the normal order of labels 1, 2, 3, $\cdots$, $p-1$, $p+1$, $\cdots$, N, $N+1$ and a parity P_q to any q according to the number of permutations by which it differs from normal.

The continuum functions $F_{\Gamma\Gamma'}(r_p)$ will be determined from a variational principle, subject to the constraint

$$\int_0^\infty dr\, F_{\Gamma\Gamma'}(r)P_{nl_\lambda}(r)=0. \quad (13)$$

This orthogonalization of F with respect to the discrete orbitals can be interpreted as preventing the projectile from being captured into any incomplete subshell included in the eigenfunction expansion, Eq. (3). Because of the assumed form of the Hamiltonian, each set of $LS\pi$ of the $(N+1)$ electron system is decoupled from the other sets. Consequently to allow for electron capture we must include in our trial function, $(N+1)$ electron wave functions in which there is an extra electron in one of the incomplete subshells included in the eigenfunction expansion, i.e., functions of the form

$$\Phi_\mu(LS\pi,\mathbf{x}_1\cdots\mathbf{x}_{N+1})=\mathfrak{N}(N_\lambda{}^\mu)^{-1/2}\times\sum_{q_\mu}(-1)^{P_q}\phi_u(q_\mu LS\pi\mathbf{x}_1\cdots\mathbf{x}_{N+1}), \quad (14)$$

where μ runs over all the incomplete subshells included in the eigenfunction expansion which can contribute to the $LS\pi$, $\sum_\lambda N_\lambda{}^\mu=N+1$, and ϕ_u is an unsymmetrized wave function of the form given in Eq. (2).

The trial function ψ_t is taken to be a linear superposition of functions (11) and (14), viz.,

$$\psi_t(\Gamma_i\mathbf{x}_1\cdots\mathbf{x}_{N+1})=\psi(\Gamma_i,\mathbf{x}_1\cdots\mathbf{x}_{N+1})+\sum_\mu C_\mu{}^{\Gamma_i}\mathfrak{N}(N_\lambda{}^\mu)^{-1/2}\times\sum_{q_\mu}(-1)^{P_q}\phi_u(q_\mu LS\pi,\mathbf{x}_1\cdots\mathbf{x}_{N+1}), \quad (15)$$

where the coefficients $C_\mu{}^\Gamma$ are completely arbitrary.

In Secs. (3.2) and (3.3), it will be necessary to separate out the interacting electron in the subshell ρ from its equivalent electrons. This is accomplished using coefficients of fractional parentage [see Fano's Eqs. (24) and (25)].

3. VARIATIONAL PRINCIPLE

We consider

$$\delta[L_{kl}-\tfrac{1}{2}K_{kl}]=0, \quad (16)$$

where the elements of the real and symmetric reactance matrix K_{kl} are defined in terms of the asymptotic form of F in the open channels

$$F_{\Gamma_k\Gamma_l}\sim k_k^{-1/2}[\delta_{kl}\sin\theta_k+K_{kl}\cos\theta_k], \quad (17)$$

and

$$L_{kl}=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi_t(\Gamma_k,\mathbf{x}_1\cdots\mathbf{x}_{N+1})\times[H_N+H_1(\mathbf{x}_{N+1})+\sum_{\alpha=1}^{N}r_{N+1,\alpha}{}^{-1}-E]\times\psi_t(\Gamma_l,\mathbf{x}_1\cdots\mathbf{x}_{N+1}), \quad (18)$$

where the variations in the continuum functions are such that

$$\delta F_{kl}\sim k_k^{-1/2}\delta K_{kl}\cos\theta_k, \quad (19)$$

subject to the constraint of Eq. (13), and the variations $\delta C_\mu{}^\Gamma$ are arbitrary. Substituting Eq. (15) into (18) gives three types of terms; first, terms independent of C but quadratic in F; second, terms linear in both C and F; third, terms quadratic in C, but independent of F. The first two types of terms will lead to the Hartree-Fock equations for F when we consider $F\rightarrow F+\delta F$. These equations will contain factors linear in C. When variations $C\rightarrow C+\delta C$ are taken in (16), the last two terms give an expression for the C's which will be substituted into the Hartree-Fock equations.

Making the substitution for the first ψ_t in Eq. (18)

$$L_{kl}=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\times[(N+1)^{-1/2}\sum_{p=1}^{N+1}(-1)^{N+1-p}\sum_{\Gamma_i}\psi(\Gamma_i\mathbf{X}\hat{r}_p\sigma_p)\times F_{ik}(r_p)r_p{}^{-1}+\sum_\mu C_\mu{}^{\Gamma_k}\Phi_\mu(L_kS_k\pi_k,\mathbf{x}_1\cdots\mathbf{x}_{N+1})]\times[H-E]\psi_t(\Gamma_i\mathbf{x}_1\cdots\mathbf{x}_{N+1}).$$

Since H is symmetric under interchange of any pair of electrons and $\psi_t(\Gamma_l)$ is antisymmetric, then

$$L_{kl}=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\{(N+1)^{1/2}\times\sum_{\Gamma_i}\psi(\Gamma_i\mathbf{X}\hat{r}_{N+1}\sigma_{N+1})F_{ik}(r_{N+1})r_{N+1}{}^{-1}+\sum_\mu C_\mu{}^{\Gamma_k}\Phi_\mu(L_kS_k\pi_k\mathbf{x}_1\cdots\mathbf{x}_{N+1})\}\times[H-E]\psi_t(\Gamma_i\mathbf{x}_1\cdots\mathbf{x}_{N+1}). \quad (20)$$

A. C-Independent Terms

The C-independent terms are

$$L_{ik,jl}=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}(N+1)^{1/2}\psi(\Gamma_i\mathbf{X}\hat{r}_{N+1}\sigma_{N+1})\times F_{ik}(r_{N+1})r_{N+1}{}^{-1}[H-E](N+1)^{-1/2}\times\sum_{p=1}^{N+1}(-1)^{N+1-p}\psi(\Gamma_j\mathbf{X}\hat{r}_p\sigma_p)F_{lj}(r_p)r_p{}^{-1}, \quad (21)$$

which can be separated into so-called direct and exchange terms by writing $\sum_p$ in the form

$$\psi(\Gamma_j \mathbf{X}\hat{r}_{N+1}\sigma_{N+1})F_{jl}(r_{N+1}) + \sum_{p=1}^{N}(-1)^{N+1-p}\psi(\Gamma_j \mathbf{X}\hat{r}_p\sigma_p)F_{lj}(r_p).$$

The fact that ψ is antisymmetric under interchange of any pair of labels in the target function can be used to give Eq. (21) in the form

$$L_{ik,jl}=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi(\Gamma_i \mathbf{X}\hat{r}_{N+1}\sigma_{N+1})\frac{F_{ik}(r_{N+1})}{r_{N+1}} \times[H-E]\psi(\Gamma_j \mathbf{X}\hat{r}_{N+1}\sigma_{N+1})\frac{F_{jl}(r_{N+1})}{r_{N+1}} -N\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi(\Gamma_i \mathbf{X}\hat{r}_{N+1}\sigma_{N+1}) \times\frac{F_{ik}(r_{N+1})}{r_{N+1}}[H-E]\psi(\Gamma_j \mathbf{X}\hat{r}_N\sigma_N)\frac{F_{jl}(r_N)}{r_N}, \quad (22)$$

where the first term is the direct term and the second is the exchange term.

1. Exchange Terms

The matrix element of the N electron Hamiltonian, H_N, will include an overlap integral

$$\int d\mathbf{x}_{N+1}F_{ik}(\mathbf{x}_{N+1})R_{nl}(\mathbf{x}_{N+1})=0, \quad (23)$$

and so will the E term. Furthermore, the term $H_1(x_{N+1})$ will contain

$$\int d\mathbf{x}_N R_{nl}(\mathbf{x}_N)F_{jl}(\mathbf{x}_N)=0. \quad (24)$$

Consequently, the second term in Eq. (22) reduces to

$$L_{ik,jl}{}^E=-N\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi(\Gamma_i \mathbf{X}\hat{x}_{N+1}) \times\frac{F_{ik}(r_{N+1})}{r_{N+1}}\frac{1}{r_{N+1,N}}\psi(\Gamma_j \mathbf{X}\hat{x}_N)\frac{F_{jl}(r_N)}{r_N}, \quad (25)$$

where $r_{N+1,N}=|\mathbf{r}_{N+1}-\mathbf{r}_N|$, since the other terms in $\sum_\alpha$ will contain (24). Substituting Eq. (12) into (25) gives

$$L_{ik,jl}{}^E=-N[\mathfrak{N}(N_\lambda{}^i)\mathfrak{N}(N_\lambda{}^j)]^{-1/2}\sum_{q_iq_j}(-1)^{P_{q^i}+P_{q^j}} \times\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}(r_Nr_{N+1})^{-1}\psi_u(q_i\Gamma_i \mathbf{X}\hat{x}_{N+1}) \times F_{ik}(r_{N+1})\frac{1}{r_{N,N+1}}\psi_u(q_j\Gamma_j \mathbf{X}\hat{x}_N)F_{jl}(r_N), \quad (26)$$

where the distributions q_i, q_j are such that electrons labeled $N+1$, N, respectively, are in the continuum; in other words, neither F_{ik} nor F_{jl} will contain "spectator" electrons. "Spectator" electrons are those with labels other than N and $N+1$, the labels of the two-electron operator. Consequently, in Eq. (26) only one interacting electron can appear in the discrete subshells. If the configuration of the electrons in γ_i differ by two electron jumps from the configuration in γ_j, then the matrix element vanishes, because there will be a factor

$$\int d\mathbf{x}R_{nl_i}(\mathbf{x})R_{nl_j}(\mathbf{x})=0 \quad \text{for} \quad (nl)_i\neq(nl)_j, \quad (27)$$

provided discrete one-electron orbitals are used which are orthogonal to one another whether the subshell is complete or incomplete. If the configuration of electrons differ by one electron jump, e.g., $1s^22s^22p^6$ compared with $1s^22s2p^6nl$, then the interacting electron will be assigned to a $2s$ orbital in the former configuration and to nl in the latter, and the configuration of the spectator electrons among the subshells is determined uniquely. If $\{N_\lambda{}^i\}$ and $\{N_\lambda{}^j\}$ are identical, then the second of the interacting electrons will be found in the same subshell in Γ_i and Γ_j and can be assigned to each of the subshells in turn; that is to say, there are as many configurations of spectator electrons as there are subshells with $N_\lambda{}^i=N_\lambda{}^j\neq0$. We note that the matrix element will vanish unless it is diagonal in the quantum numbers of the spectator electrons.

Symbolically, the exchange terms of Eq. (20) can be written as

$$L_{kl}{}^E=\sum_{\Gamma_i\Gamma_j}L_{ik,jl}{}^E=\sum_{\Gamma_i\Gamma_j}\prod_{\lambda=1s}^{\max(b_i,b_j)}\delta(N_\lambda{}^i,N_\lambda{}^j+\delta_{\lambda\rho_i}-\delta_{\lambda\rho_j}) \times\sum_{\bar{C}}\bar{L}_{ik,jl}{}^E, \quad (28)$$

where $\sum_C$ denotes the sum over possible configurations of spectator electrons. The interacting electron with label N is assigned to $R_{nl(\rho_i)}$ in $\psi(\Gamma_i)$, while the interacting electron with label $N+1$ is assigned to $R_{nl(\rho_j)}$ in $\psi(\Gamma_j)$. If more than one configuration is included in $\sum_\Gamma$ of Eq. (11) then the double sum over Γ_i and Γ_j in Eq. (28) will include terms with $N_\lambda{}^i\neq N_\lambda{}^j$ so that the δ will specify nonzero elements in this sum and designate the subshells which contain the interacting electrons. If $\rho_i\neq\rho_j$, then only a single configuration of spectator electrons is possible. If $\rho_i=\rho_j$, as in the formulations of Seaton and coworkers[5] and Smith, Henry, and Burke, then there will be as many terms in the sum over $\bar{C}$ as there are subshells with $N_\lambda{}^i=N_\lambda{}^j\neq0$.

For the remainder of this subsection we shall consider a particular configuration of spectator electrons; quantities with a bar over them refer to spectator electrons. Both the distributions q_i and q_j include a distribution $\bar{q}_i=\bar{q}_j=\bar{q}$ in order to give nonvanishing

contributions to Eq. (26). The number of different distributions of spectator electrons will be

$$\mathfrak{N}(\bar{N}_\lambda)=(N-1)!/\prod_\lambda(\bar{N}_\lambda!),\quad \sum_\lambda \bar{N}_\lambda=N-1, \quad (29)$$

and their contributions to $\sum_{q_i q_j}$ will be identical. The distributions in the interacting subshells are uniquely specified

$$q_{\rho_i}=\{\bar{q}_{\rho_i},N\} \quad \text{and} \quad q_{\rho_j}=\{\bar{q}_{\rho_j},N+1\}.$$

Now $P_{\bar{q}}$ takes all the spectators to normal order and in $\psi(\Gamma_i)$ label N will be in subshell $\lambda=\rho_i$; consequently, further

$$\sum_{\lambda=\rho_i+1}^{b_i}\bar{N}_\lambda$$

permutations will be required to put the labels of the atomic electrons in normal order, where b_i is the outermost subshell containing an electron in Γ_i. Hence

$$P_{q_i}=P_{\bar{q}}+\sum_{\lambda=\rho_i+1}^{b_i}\bar{N}_\lambda,$$

and similarly for P_{q_j} (since in the exchange term, "normal" order for the atomic electrons is $1\cdots N-1$, $N+1$, the label N being in the continuum). Therefore

$$P_{q_i}+P_{q_j}=\sum_{\lambda=\rho_i+1}^{b_i}\bar{N}_\lambda+\sum_{\lambda=\rho_j+1}^{b_j}\bar{N}_\lambda\equiv\Delta P_{ij}. \quad (30)$$

We can now write, from (26) and (28)–(30), that

$$\bar{L}_{ik,jl}{}^E=-N\mathfrak{N}(\bar{N}_\lambda)[\mathfrak{N}(N_\lambda{}^i)\mathfrak{N}(N_\lambda{}^j)]^{-1/2}\times(-1)^{\Delta P_{ij}}\langle r_{N,N+1}{}^{-1}\rangle, \quad (31)$$

where the outside factor becomes

$$[N_{\rho_i}N_{\rho_j}]^{1/2}. \quad (32)$$

The matrix element in Eq. (31) vanishes unless the representations are diagonal in the quantum numbers of the spectator electrons. For those subshells which just contain spectators

$$\{nl_\lambda{}^{N_\lambda{}^i}\alpha_\lambda{}^i S_\lambda{}^i L_\lambda{}^i|q_\lambda{}^i\}=\{nl_\lambda{}^{\bar{N}_\lambda}\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda|\bar{q}_\lambda\}, \quad (33a)$$

and for those same subshells

$$(q_\lambda{}^j|nl_\lambda{}^{N_\lambda{}^j}\alpha_\lambda{}^j S_\lambda{}^j L_\lambda{}^j\}=(\bar{q}_\lambda|nl_\lambda{}^{\bar{N}_\lambda}\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda\}, \quad (33b)$$

while for the subshells ρ_i and ρ_j, containing the interacting electrons N and $N+1$ respectively, we separate out the interacting electron from the N equivalent particles in the subshell using coefficients of fractional parentage

$$\{nl_\rho{}^{N_\rho}\alpha_\rho S_\rho L_\rho|q_\rho)=\sum_{\bar{\alpha}_\rho\bar{S}_\rho\bar{L}_\rho}(l_\rho{}^{N_\rho}\alpha_\rho S_\rho L_\rho\{|l_\rho{}^{\bar{N}_\rho}\bar{\alpha}_\rho\bar{S}_\rho\bar{L}_\rho l_\rho)\times[\{nl_\rho{}^{\bar{N}_\rho}\bar{\alpha}_\rho\bar{S}_\rho\bar{L}_\rho|\bar{q}_\rho)\times\{nl_\rho|N)]^{S_\rho L_\rho}, \quad (34)$$

where the first factor in the sum is a coefficient of fractional parentage (see Racah[13]). A similar separation is carried out for the ρ_j subshell.

Substituting the above results into Eq. (31) we obtain

$$\bar{L}_{ik,jl}{}^E=[N_{\rho_i}N_{\rho_j}]^{1/2}(-1)^{\Delta P_{ij}+1}\sum_{\bar{\alpha}_i\cdots\bar{L}_j}(l_{\rho_i}{}^{N_{\rho_i}}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i}\{|l_{\rho_i}{}^{\bar{N}_{\rho_i}}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i}l_{\rho_i})\times(l_{\rho_j}{}^{\bar{N}_{\rho_j}}\bar{\alpha}_{\rho_j}\bar{S}_{\rho_j}\bar{L}_{\rho_j}l_{\rho_j}|\}l_{\rho_j}{}^{N_{\rho_j}}\alpha_{\rho_j}S_{\rho_j}L_{\rho_j})\langle\psi_{u\rho_i}(\Gamma_i)F_{ik}|\frac{1}{r_{N+1,N}}|\psi_{u\rho_j}(\Gamma_j)F_{jl}\rangle, \quad (35)$$

where $\psi_{u\rho_i}$ is defined by Fano to be

$$\psi_{u\rho_i}(\Gamma_i)=(\prod_{\lambda\neq\rho_i}\{nl_\lambda{}^{\bar{N}_\lambda}\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda|\bar{q}_\lambda)\times[\{nl_{\rho_i}{}^{\bar{N}_{\rho_i}}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i}|\bar{q}_{\rho_i})\times\{nl_{\rho_i}|N)]^{S_{\rho_i}L_{\rho_i}}]^{\gamma_i}\times\{l_ik_i|N+1)\}^{\Gamma_i}, \quad (36)$$

where we recall $\{l_ik_i|N+1)$ is the spin-angle function associated with the projectile orbital F_{ik}.

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. Writing

$$\mathcal{S}_i=\{\bar{S}_1\cdots\bar{S}_{\rho_i-1}(\bar{S}_{\rho_i}\tfrac{1}{2}(N))S_{\rho_i}\cdots\bar{S}_{b_i}\tfrac{1}{2}(N+1),\alpha_iS_i|, \quad (37a)$$

and

$$\Theta_i=\{\bar{L}_1\cdots\bar{L}_{\rho_i-1}(\bar{L}_{\rho_i}l_{\rho_i}(N))L_{\rho_i}\cdots\bar{L}_{b_i}l_i(N+1),\alpha_iL_i|, \quad (37b)$$

we obtain

$$\bar{L}_{ik,jl}{}^E=[N_{\rho_i}N_{\rho_j}]^{1/2}(-1)^{\Delta P_{ij}+1}\sum_{\bar{\alpha}_i\cdots\bar{L}_j}(l_{\rho_i}{}^{N_{\rho_i}}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i}\{|l_{\rho_i}{}^{\bar{N}_{\rho_i}}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i}l_{\rho_i})\times(l_{\rho_j}{}^{\bar{N}_{\rho_j}}\bar{\alpha}_{\rho_j}\bar{S}_{\rho_j}\bar{L}_{\rho_j}l_{\rho_j}|\}l_{\rho_j}{}^{N_{\rho_j}}\alpha_{\rho_j}S_{\rho_j}L_{\rho_j})\langle\mathcal{S}_i|\mathcal{S}_j)\rangle\langle\Theta_iF_{ik}|\frac{1}{r_{N,N+1}}|\Theta_jF_{jl}\rangle. \quad (38)$$

[13] G. Racah, Phys. Rev. 63, 367 (1943).

The spin recoupling coefficient $\langle \mathcal{S}_i | \mathcal{S}_j \rangle$ will depend upon the problem under consideration. For example, for a target atom with configuration $1s^2 2s^2 2p^q$ when no electron jumps are permitted, the sum over $\bar{C}$ in Eq. (28) will contain three terms, one of them having the factor

$$\langle (\bar{S}_{2p^{\frac{1}{2}}}(N))S_{2p^i},\tfrac{1}{2}(N+1);S_i|(\bar{S}_{2p^{\frac{1}{2}}}(N+1))S_{2p^j},\tfrac{1}{2}(N);S_j\rangle=\delta_{S_iS_j}[(2S_{2p^i}+1)(2S_{2p^j}+1)]^{1/2}W(S_{2p^i}\tfrac{1}{2}\tfrac{1}{2}S_{2p^j};\bar{S}_{2p}S_i). \quad (39)$$

Upon expanding $r_{N,N+1}^{-1}$ in terms of Legendre polynomials $P_t(\hat{r}_N\cdot\hat{r}_{N+1})$ the radial integrals reduce to Slater integrals and the matrix element is

$$\begin{aligned}\langle \Theta_i F_{ik}|\frac{1}{r_{N,N+1}}|\Theta_j F_{jl}\rangle&=\sum R_t(nl_{\rho_i}F_{ik},F_{jl}nl_{\rho_j})\langle \bar{L}_1\cdots(\bar{L}_{\rho_i}l_{\rho_i}(N))L_{\rho_i}\cdots\bar{L}_{b_i}l_i(N+1),L_i|\\ &\qquad\times P_t(\hat{r}_N\cdot\hat{r}_{N+1})|\bar{L}_1\cdots(\bar{L}_{\rho_j}l_{\rho_j}(N+1))L_{\rho_j}\cdots\bar{L}_{b_j}l_j(N),L_j\rangle\\ &=\sum_t R_t(nl_{\rho_i}F_{ik},F_{jl}nl_{\rho_j})(l_{\rho_i}\|C^t\|l_j)(l_{\rho_j}\|C^t\|l_i)[(2l_{\rho_i}+1)(2l_{\rho_j}+1)]^{-1/2}\\ &\qquad\times\langle \bar{L}_1\cdots[\bar{L}_{\rho_i}(l_j t)l_{\rho_i}]L_{\rho_i}\cdots\bar{L}_{b_i}l_i,L_i|\bar{L}_1\cdots[\bar{L}_{\rho_j}(tl_i)l_{\rho_j}]L_{\rho_j}\cdots\bar{L}_{b_j}l_j,L_j\rangle, \quad (40)\end{aligned}$$

using the method of Fano, Prats, and Goldschmidt[14] and where the orbital recoupling coefficient can be calculated in the same way as in the spin coefficient (see Appendix). Combining Eqs. (28), (38), and (40), we obtain

$$\begin{aligned}L_{kl}{}^E=\sum_{\Gamma_i\Gamma_j}\Big[\prod_\lambda \delta(N_\lambda{}^i,N_\lambda{}^j+\delta_{\lambda\rho i}-\delta_{\lambda\rho j})\Big]\sum_{\bar{C}}[N_{\rho_i}N_{\rho_j}]^{1/2}(-1)^{\Delta P_{ij}+1}[(2l_{\rho_i}+1)(2l_{\rho_j}+1)]^{-1/2}\\ \times\sum_{\bar{\alpha}_i\cdots\bar{L}_j}(l_{\rho_i}{}^{N_{\rho}{}^i}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i}\{|l_{\rho_i}{}^{\bar{N}_{\rho}{}^i}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i}l_{\rho_i})(l_{\rho_j}{}^{\bar{N}_{\rho}{}^j}\bar{\alpha}_{\rho_j}\bar{S}_{\rho_j}\bar{L}_{\rho_j}l_{\rho_j}|\}l_{\rho_j}{}^{N_{\rho}{}^j}\alpha_{\rho_j}S_{\rho_j}L_{\rho_j})\\ \times\langle \mathcal{S}_i|\mathcal{S}_j\rangle^E\sum_t R_t(nl_{\rho_i}F_{ik},F_{jl}nl_{\rho_j})(l_{\rho_i}\|C^t\|l_j)(l_{\rho_j}\|C^t\|l_i)\langle 0_i|0_j\rangle^E, \quad (41)\end{aligned}$$

where the final factor in Eq. (41) denotes the exchange orbital recoupling coefficient as written out in Eq. (40).

2. Direct Terms

These terms are given by the first term in Eq. (22)

$$L_{ik,jl}{}^D=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi(\Gamma_i\mathbf{X}\hat{x}_{N+1})\frac{F_{ik}(r_{N+1})}{r_{N+1}}[H-E]\psi(\Gamma_j\mathbf{X}\hat{x}_{N+1})\frac{F_{jl}(r_{N+1})}{r_{N+1}}, \quad (42)$$

where ψ is defined in Eq. (12). It will be assumed (as in Smith *et al.*[6]) that

$$\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_N\psi(\gamma_i\mathbf{X})[H_N-\mathcal{E}]\psi(\gamma_j\mathbf{X})=0. \quad (43)$$

Any calculation on $N>1$ target systems must use approximate wave functions, i.e., functions which are the eigenfunctions of an N-electron Hamiltonian $H_N(\text{approx})\neq H_N(\text{exact})$. Consequently, (43) introduces an inconsistency which should lead to a small error if accurate atomic orbitals are used. Because of this assumption, the H_N term in Eq. (42) is

$$\int dr_{N+1}F_{ik}(r_{N+1})\mathcal{E}_i\delta_{ij}F_{jl}(r_{N+1}). \quad (44)$$

Due to the orthonormality of $\psi(\gamma_i\mathbf{X})$ the H_1 term is

$$\delta_{ij}\int dr_{N+1}F_{ik}(r_{N+1})\left[-\frac{1}{2}\left(\frac{d^2}{dr_{N+1}{}^2}-\frac{l_i(l_i+1)}{r_{N+1}{}^2}+\frac{2Z}{r_{N+1}}\right)\right]F_{jl}(r_{N+1}), \quad (45)$$

which leaves us with the evaluation of

$$\int d\hat{x}_{N+1}\int d\mathbf{x}_1\cdots d\mathbf{x}_N\psi(\Gamma_i\mathbf{X}\hat{x}_{N+1})\sum_{\alpha=1}^{N}\frac{1}{r_{N+1,\alpha}}\psi(\Gamma_j\mathbf{X}\hat{x}_{N+1})\equiv V_{ij}(r_{N+1}). \quad (46)$$

[14] U. Fano, F. Prats, and Z. Goldschmidt, Phys. Rev. **129**, 2634 (1963).

As for exchange terms, the matrix element will be nonzero only for zero or one-electron jumps, i.e.,

$$V_{ij}(r)=\prod_{\lambda=1a}^{\max(b_i,b_j)}\delta(N_\lambda{}^i,N_\lambda{}^j+\delta_{\lambda\rho i}-\delta_{\lambda\rho j})\sum_{\bar{C}}V_{ij}{}^D(r)\,, \tag{47}$$

with

$$V_{ij}{}^D(r)=[N_{\rho i}N_{\rho j}]^{1/2}(-1)^{\Delta Pij}\sum_{\bar{\alpha}_i\cdots\bar{L}_j}(l_{\rho i}{}^{N_\rho i}\alpha_{\rho i}S_{\rho i}L_{\rho i}\{|l_{\rho i}{}^{\bar{N}_\rho i}\bar{\alpha}_{\rho i}\bar{S}_{\rho i}\bar{L}_{\rho i}l_{\rho i})$$
$$\times(l_{\rho j}{}^{\bar{N}_\rho i}\bar{\alpha}_{\rho j}\bar{S}_{\rho j}\bar{L}_{\rho j}l_{\rho j}|\}l_{\rho j}{}^{N_\rho i}\alpha_{\rho j}S_{\rho j}L_{\rho j})\langle\mathcal{S}_i|\,\mathcal{S}_j\rangle^D[(2l_{\rho i}+1)(2l_j+1)]^{-1/2}$$
$$\times\sum_t y_t(nl_{\rho i}nl_{\rho j}r)(l_{\rho i}\|C^t\|l_{\rho j})(l_j\|C^t\|l_i)\langle 0_i|\,0_j\rangle^D\,, \tag{48}$$

where the direct orbital recoupling coefficient is defined by

$$\langle 0_i|\,0_j\rangle^D=\langle\bar{L}_1\cdots[\bar{L}_{\rho i}(l_{\rho j}t)l_{\rho i}]L_{\rho i}\cdots\bar{L}_{b_i}l_i,\alpha_iL_i|\,\bar{L}_1\cdots(\bar{L}_{\rho j}l_{\rho j})L_{\rho j}\cdots\bar{L}_{b_j}(tl_i)l_j,\alpha_jL_j\rangle\,, \tag{49a}$$

and the direct spin recoupling coefficient is defined to be

$$\langle\mathcal{S}_i|\,\mathcal{S}_j\rangle^D=\langle\bar{S}_1\cdots(\bar{S}_{\rho i\frac{1}{2}}(N)S_{\rho i}\cdots\bar{S}_{b_i\frac{1}{2}}(N+1),\alpha_iS_i|\,\bar{S}_1\cdots(\bar{S}_{\rho j\frac{1}{2}}(N))S_{\rho j}\cdots\bar{S}_{b_j\frac{1}{2}}(N+1),\alpha_jS_j\rangle. \tag{49b}$$

Collecting the various factors of the direct terms together gives

$$L_{ik,jl}{}^D=\int dr_{N+1}F_{ik}(r_{N+1})\left[\delta_{ij}\left(-\frac{1}{2}\left\{\frac{d^2}{dr_{N+1}{}^2}-\frac{l_i(l_i+1)}{r_{N+1}{}^2}+\frac{2Z}{r_{N+1}}\right\}+\mathcal{E}_i-E\right)+V_{ij}(r_{N+1})\right]F_{ij}(r_{N+1})\,. \tag{50}$$

B. Terms Linear in C

From Eqs. (15) and (20) we see that the two terms linear in C are

$$L_{ik,jl}{}^C=\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}(N+1)^{1/2}\Big\{\psi(\Gamma_i\mathbf{X}\hat{x}_{N+1})\frac{F_{ik}(r_{N+1})}{r_{N+1}}[H-E]\sum_\nu C_\nu{}^l\Phi_\nu(L_lS_l\pi_l)$$
$$+\sum_\mu C_\mu{}^k\Phi_\mu(L_kS_k\pi_k)[H-E]\psi(\Gamma_j\mathbf{X}\hat{x}_{N+1})\frac{F_{jl}(r_{N+1})}{r_{N+1}}\Big\}. \tag{51}$$

The full term can be written

$$L_{kl}{}^C=\sum_i(L_{ik,l}{}^C+L_{k,il}{}^C)\,, \tag{52}$$

where the two terms on the right are defined in Eq. (51). The matrix elements of (H_N-E) vanish because they contain a factor like the l.h.s. of Eq. (23). From Green's theorem and the boundary conditions of the discrete one-electron orbitals Eq. (52) can be written in the form

$$L_{kl}{}^C=\sum_i(L_{ik,l}{}^C+L_{il,k}{}^C)\,, \tag{53}$$

where the two terms have the same structure, viz.,

$$L_{il,k}{}^C=(N+1)^{1/2}\sum_\mu C_\mu{}^k\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}\psi(\Gamma_i\mathbf{X}\hat{x}_{N+1})\frac{F_{il}(r_{N+1})}{r_{N+1}}\left[H_1(N+1)+\frac{N}{r_{N+1,N}}\right]\Phi_\mu(L_kS_k\pi_k\mathbf{x}_1\cdots\mathbf{x}_{N+1}). \tag{54}$$

We note that the configurations of $\psi(\Gamma_i)$ and $\Phi_\mu(L_kS_k\pi_k)$ necessarily differ by one electron jump, hence for a non-zero matrix element we must have an interacting electron in the "extra" orbital of Φ_μ. For the one-electron operator this implies that we must have the label $N+1$ in the extra orbital. To calculate the matrix element we must separate off $R_\rho(r_{N+1})$, the radial function of the only interacting electron, from Φ_μ using coefficients of fractional parentage; for the two-electron operator a further two fractional parentage coefficients are introduced, one each from ψ and Φ_μ. We have the matrix element

$$\langle H_1\rangle=(N+1)^{1/2}\prod_\lambda\delta(N_\lambda{}^i,N_\lambda{}^\mu-\delta_{\lambda\rho})[\mathfrak{N}(N_\lambda{}^i)\mathfrak{N}(N_\lambda{}^\mu)]^{-1/2}\sum_{q^iq^\mu}(-1)^{P_{q^i}+P_{q^\mu}}\int\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_{N+1}$$
$$\times(l_\rho{}^{N_\rho}\alpha_\rho{}^\mu L_\rho{}^\mu S_\rho{}^\mu|\}l_\rho{}^{N_\rho i}\alpha_\rho{}^iL_\rho{}^iS_\rho{}^il_\rho)\psi_u(q_i\Gamma_i)\frac{F_{il}(r_{N+1})}{r_{N+1}}H_1(N+1)\phi_{u\rho}(q_\mu L_kS_k\pi_k)\frac{R_\rho(r_{N+1})}{r_{N+1}}, \tag{54a}$$

where

$$\mathfrak{N}(N_\lambda{}^\mu)=\frac{(N+1)!}{\prod_\lambda (N_\lambda{}^\mu!)}, \tag{55}$$

and ψ_u and $\phi_{u\rho}$ do not include the radial functions of the electron with label $(N+1)$. Here, $N_\lambda{}^\mu$ denotes the number of electrons in the discrete subshell λ, with an extra electron in subshell $\lambda=\mu$ (compared with the configuration of the parent state γ.) For a properly antisymmetrized $(N+1)$ electron wave function we must allow for the label $(N+1)$ to be in any of the subshells for which $N_\lambda{}^\mu\neq 0$. The number of alternative configurations of electrons which are spectators for the interaction $H_1(N+1)$ is

$$\mathfrak{N}(\bar{N}_\lambda)=\frac{N!}{\prod_\lambda (\bar{N}_\lambda!)}.$$

Equation (54a) becomes

$$\langle H_1\rangle=\prod_\lambda \delta(N_\lambda{}^i,N_\lambda{}^\mu-\delta_{\lambda\rho})N_\rho{}^{1/2}(-1)^{\Sigma_{\lambda=\rho+1}{}^{b^\mu}N_\lambda}\ (l_\rho{}^{N_\rho{}^\mu}\alpha_\rho{}^\mu S_\rho{}^\mu L_\rho{}^\mu|\}l_\rho{}^{N_\rho{}^i}\alpha_\rho{}^i S_\rho{}^i L_\rho{}^i l_\rho)$$
$$\times\int dr F_{il}\left\{-\frac{1}{2}\left(\frac{d^2}{dr^2}-\frac{l_\rho(l_\rho+1)}{r^2}+\frac{2Z}{r}\right)\right\}P_{nl_\rho}(r)$$
$$\times\langle S_\rho{}^i\cdots S_b{}^i\tfrac{1}{2},S_i|(S_\rho{}^i\tfrac{1}{2})S_\rho{}^\mu\cdots S_b{}^\mu,S_k\rangle\langle L_\rho{}^i\cdots L_b{}^i l_i,L_i|(L_\rho{}^i l_\rho)L_\rho{}^\mu\cdots L_b{}^\mu,L_k\rangle. \tag{56}$$

We note that $\langle L_\rho{}^i\cdots L_b{}^i l_i,L_i|(L_\rho{}^i l_\rho)L_\rho{}^\mu\cdots L_b{}^\mu,L_k\rangle$ will be nonzero only for $l_i=l_\rho$ since it contains

$$\int d\hat{x}_{N+1}Y_{l_i m}{}^*(\hat{x}_{N+1})\ Y_{l_\rho m}(\hat{x}_{N+1}).$$

This is equivalent to saying that the incident electron can only be captured into the incomplete subshell ρ if its orbital angular momentum equals that of the subshell. In general $\rho\neq\mu$ since the 'extra' orbital μ of Φ_μ may be matched by one in Γ_i. For example, if the target atom in state γ_i has configuration $1s^22s^22p^4$ and Φ_μ has configuration $1s^22s^22p^5(=1s^22s2p^5+2s)$ then $\mu=2\mu$ but $\rho=2p$.

For the two-electron operator in Eq. (54) let ρ_μ and σ_μ be the subshells containing the interacting electrons. For a nonzero matrix element we must have identical distributions $\bar{q}$ of spectator electrons and for each $\bar{q}$ there are in general two possible distributions of interacting electrons labeled by $\epsilon=0,1$. Viz., for $\lambda\neq\rho_\mu$ or σ_μ, $q_\lambda{}^\epsilon=\bar{q}_\lambda$, $\epsilon=0$ or 1, and for $\lambda=\rho_\mu$ or σ_μ either $\rho_\mu\neq\sigma_\mu$, $q_{\rho_\mu}{}^\epsilon=\{\bar{q}_{\rho_\mu},N+\epsilon\}$ and $q_{\sigma_\mu}{}^\epsilon=\{\bar{q}_{\sigma_\mu}N+1-\epsilon\}$ or

$$\rho_\mu=\sigma_\mu,\ q_{\rho_\mu}{}^\epsilon=\{\bar{q}_{\rho_\mu}N,N+1\},\ \epsilon=0\quad\text{or}\quad 1. \tag{57}$$

Substituting Eqs. (12) and (14) into Eq. (54) and using Eq. (57) we get for a function f of q_i and q_μ, that

$$\sum_{q_i q_\mu} f(q_i q_\mu)\rightarrow\mathfrak{N}(\bar{N}_\lambda)\sum_{\epsilon=0,1}(1-\epsilon\delta_{\rho_\mu\sigma_\mu})g(\epsilon\rho_i\rho_\mu\sigma_\mu).$$

Defining ΔP to be the number of permutations to take the N electron of ρ_i, and the interacting electrons of ρ_μ and σ_μ, out to normal order, the matrix element of the two-electron operator is

$$\left\langle\frac{1}{r_{N,N+1}}\right\rangle=\prod_{\lambda=1s}^{\max(b_i b_\mu)}\delta(N_\lambda{}^i,N_\lambda{}^\mu+\delta_{\lambda\rho_i}-\delta_{\lambda\rho_\mu}-\delta_{\lambda\sigma_\mu})\sum_{\bar{C}}[N_{\rho_i}N_{\rho_\mu}(N_{\sigma_\mu}-\delta_{\rho_\mu\sigma_\mu})]^{1/2}(-1)^{\Delta P}\sum_\epsilon(-1)^\epsilon(1-\epsilon\delta_{\rho_\mu\sigma_\mu})$$
$$\times\left\langle\psi_u(q_i\Gamma_i)F_{il}\left|\frac{1}{r_{N,N+1}}\right|\phi_u(q_\mu{}^\epsilon L_k S_k\pi_k)\right\rangle, \tag{58}$$

where

$$\Delta P=\sum_{\lambda=\rho_i+1}^{b_i}\bar{N}_\lambda-\sum_{\lambda=\rho_\mu+1}^{\sigma_\mu}\bar{N}_\lambda.$$

We recall there is only one term in $\sum\bar{C}$ if $\psi(\Gamma_i)$ and ϕ_u differ by two electron jumps, but "b" terms when they differ by only one electron jump, and the matrix element vanishes unless it is diagonal in the quantum numbers of the

spectator electrons. The matrix element on the r.h.s. of Eq. (58) can be expanded out into the form

$$\sum_{\bar{\alpha}_{\rho_i}\cdots\bar{L}_{\sigma_\mu}} (l_{\rho_i}{}^{N_{\rho^i}}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i}\{|l_{\rho_i}{}^{\bar{N}_{\rho^i}}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_{\rho_i}l_{\rho_i})(l_{\rho_\mu}{}^{\bar{N}_{\rho^\mu}}\bar{\alpha}_{\rho_\mu}\bar{S}_{\rho_\mu}\bar{L}_{\rho_\mu}l_{\rho_\mu}|\}l_{\rho_\mu}{}^{N_{\rho^\mu}}\alpha_{\rho_\mu}S_{\rho_\mu}L_{\rho_\mu})(l_{\sigma_\mu}{}^{\bar{N}_{\sigma^\mu}}\bar{\alpha}_{\sigma_\mu}\bar{S}_{\sigma_\mu}\bar{L}_{\sigma_\mu}l_{\sigma_\mu}|\}l_{\sigma_\mu}{}^{N_{\sigma^\mu}}\alpha_{\sigma_\mu}S_{\sigma_\mu}L_{\sigma_\mu})$$

$$\times\langle\bar{S}_1\cdots(\bar{S}_{\rho_i\frac{1}{2}}(N))S_{\rho_i}\cdots\bar{S}_{b_i\frac{1}{2}}(N+1),S_i|\bar{S}_1\cdots(\bar{S}_{\rho_\mu\frac{1}{2}}(N+\epsilon))S_{\rho_\mu}\cdots(\bar{S}_{\sigma_\mu\frac{1}{2}}(N+1-\epsilon))S_{\sigma_\mu}\cdots,S_k\rangle$$

$$\times\langle\bar{L}_1\cdots(\bar{L}_{\rho_i}l_{\rho_i})L_{\rho_i}\cdots\bar{L}_{b_i}l_i,L_i|P_\nu(\hat{r}_N\cdot\hat{r}_{N+1})|\bar{L}_1\cdots(\bar{L}_{\rho_\mu}l_{\rho_\mu}(N+\epsilon))L_{\rho_\mu}\cdots(\bar{L}_{\sigma_\mu}l_{\sigma_\mu}(N+1-\epsilon))L_{\sigma_\mu}\cdots,L_k\rangle, \quad (59)$$

where $\langle P_\nu\rangle$ can be evaluated using the method of Fano, Prats, and Goldschmidt as in Eq. (40).

Writing Eq. (53) as

$$L_{il,k}{}^C=\sum_\mu C_\mu{}^k\left\{\langle il|H_1|\mu\rangle+\left\langle il\left|\frac{1}{r}\right|\mu\right\rangle\right\}$$

$$\equiv\sum_\mu C_\mu{}^k\int d\mathbf{x}_{N+1}V_{\mu,i}(r_{N+1})F_{il}(r_{N+1}), \quad (53a)$$

where the first term on the r.h.s. is written out explicitly in Eq. (56) and

$$\left\langle il\left|\frac{1}{r}\right|\mu\right\rangle=\prod_{\lambda=1s}\delta(N_\lambda{}^i,N_\lambda{}^\mu+\delta_{\lambda\rho_i}-\delta_{\lambda\rho_\mu}-\delta_{\lambda\sigma_\mu})\sum[N_{\rho_i}N_{\rho_\mu}(N_{\sigma_\mu}-\delta_{\rho_\mu\sigma_\mu})]^{1/2}(-1)^{\Delta P}\sum_{\epsilon=0,1}(-1)^\epsilon(1-\epsilon\delta_{\rho_\mu\sigma_\mu})$$

$$\times\sum_{\bar{\alpha}_{\rho_i}\cdots\bar{L}_{\sigma_\mu}}(l_{\rho_i}{}^{N_{\rho^i}}\alpha_{\rho_i}S_{\rho_i}L_{\rho_i}\{|l_{\rho_i}{}^{\bar{N}_{\rho^i}}\bar{\alpha}_{\rho_i}\bar{S}_{\rho_i}\bar{L}_il_i)(l_{\rho_\mu}{}^{\bar{N}_{\rho^\mu}}\bar{\alpha}_{\rho_\mu}\bar{S}_{\rho_\mu}\bar{L}_{\rho_\mu}l_{\rho_\mu}|\}l_{\rho_\mu}{}^{N_{\rho^\mu}}\alpha_{\rho_\mu}S_{\rho_\mu}L_{\rho_\mu})$$

$$\times(l_{\sigma_\mu}{}^{\bar{N}_{\sigma^\mu}}\bar{\alpha}_{\sigma_\mu}\bar{S}_{\sigma_\mu}\bar{L}_{\sigma_\mu}l_{\sigma_\mu}|\}l_{\sigma_\mu}{}^{N_{\sigma^\mu}}\alpha_{\sigma_\mu}S_{\sigma_\mu}L_{\sigma_\mu})\langle\mathcal{S}_i|\mathcal{S}_\mu\rangle^\epsilon\sum_\nu R_\nu(\rho_iF_{il}\eta\zeta)(l_{\rho_i}\|C^\nu\|l_\eta)(l_\zeta\|C^\nu\|l_i)$$

$$\times[(2l_{\rho_i}+1)(2l_\zeta+1)]^{-1/2}\langle 0_i|0_\mu\rangle^\epsilon, \quad (60)$$

where the last factor is the orbital recoupling coefficient

$$\langle\bar{L}_1\cdots(\bar{L}_{\rho_i}l_{\rho_i})L_{\rho_i}\cdots\bar{L}_{b_i}(l_\zeta\nu)l_i,L_i|\bar{L}_1\cdots[\bar{L}_\zeta(\nu l_{\rho_i})l_\eta]L_\eta\cdots(\bar{L}_\zeta l_\zeta)L_\zeta\cdots L_k\rangle, \quad (60a)$$

where η is the subshell containing N in distribution ϵ and ζ is subshell containing $N+1$.

C. Terms Quadratic in C

The matrix elements of the two-electron operators which are quadratic in C, i.e., do not involve the continuum functions F, are precisely the quantities studied by Fano. From Eqs. (15) and (20) the terms quadratic in C are seen to be

$$L_{kl}{}^{C^2}=\sum_{\mu,\nu}\int\cdots\int d\mathbf{x}\cdots d\mathbf{x}_{N+1}C_\mu{}^kC_\nu{}^l\Phi_\mu(L_kS_k\pi_k)[H-E]\Phi_\nu(L_lS_l\pi_l). \quad (61)$$

The $(N+1)$ electron Hamiltonian will be expanded out as in Eq. (18). The matrix elements of $\sum_\alpha r_{N+1,\alpha}{}^{-1}$ will all contribute equally and the contribution to Eq. (61) will be

$$\sum_{\mu\nu}C_\mu{}^kC_\nu{}^lN\left\langle\Phi_\mu(L_kS_k\pi_k)\left|\frac{1}{r_{N,N+1}}\right|\Phi_\nu(L_lS_l\pi_l)\right\rangle=\sum_{\mu,\nu}C_\mu{}^kC_\nu{}^l(N+1)^{-1}\sum_{\bar{C}}[N_{\rho_\mu}(N_{\sigma_\mu}-\delta_{\rho_\mu\sigma_\mu})N_{\rho_\nu}(N_{\sigma_\nu}-\delta_{\rho_\nu\sigma_\nu})]^{1/2}$$

$$\times\prod_\lambda\delta(N_\lambda{}^\mu,N_\lambda{}^\nu+\delta_{\lambda\rho_\mu}+\delta_{\lambda\sigma_\mu}-\delta_{\lambda\rho_\nu}-\delta_{\lambda\sigma_\nu})\sum_{\epsilon_\mu-\epsilon_\nu}(-1)^{\Delta P}(1-\epsilon_\mu\delta_{\rho_\mu\sigma_\mu})(1-\epsilon_\nu\delta_{\rho_\nu\sigma_\nu})(-1)^{\epsilon_\mu-\epsilon_\nu}$$

$$\times\left\langle\phi_u(q_{\epsilon_\mu}L_kS_k\pi_k)\left|\frac{1}{r_{N,N+1}}\right|\phi_u(q_{\epsilon_\nu}L_\nu S_\nu\pi_\nu)\right\rangle, \quad (62)$$

where the quantities ϵ_μ, ϵ_ν, and ΔP are defined in Fano.

Using Fano's Eqs. (24), (34)–(36), and (41) we have

$$\left\langle \phi_u(q_{\epsilon_\mu} L_k S_k \pi_k) \left| \frac{1}{r_{N,N+1}} \right| \phi_u(q_{\epsilon_\nu} L_\nu S_\nu \pi_\nu) \right\rangle = \sum_{\bar{\alpha}_\rho \cdots \bar{L}_{\sigma_\nu}} (l_{\rho_\mu}{}^{N_{\rho\mu}} \alpha_{\rho_\mu} S_{\rho_\mu} L_{\rho_\mu} \{ | l_{\rho_\mu}{}^{\bar{N}_{\rho\mu}} \bar{\alpha}_{\rho_\mu} \bar{S}_{\rho_\mu} \bar{L}_{\rho_\mu} l_{\rho_\mu})$$

$$\times (l_{\sigma_\mu}{}^{N_{\sigma\mu}} \alpha_{\sigma_\mu} S_{\sigma_\mu} L_{\sigma_\mu} \{ | l_{\sigma_\mu}{}^{\bar{N}_{\sigma\mu}} \bar{\alpha}_{\sigma_\mu} \bar{S}_{\sigma_\mu} \bar{L}_{\sigma_\mu} l_{\sigma_\mu}) (l_{\rho_\nu}{}^{\bar{N}_{\rho\nu}} \bar{\alpha}_{\rho_\nu} \bar{S}_{\rho_\nu} \bar{L}_{\rho_\nu} l_{\rho_\nu} | \} l_{\rho_\nu}{}^{N_{\rho\nu}} \alpha_{\rho_\nu} S_{\rho_\nu} L_{\rho_\nu}) (l_{\sigma_\nu}{}^{\bar{N}_{\sigma\nu}} \bar{\alpha}_{\sigma_\nu} \bar{S}_{\sigma_\nu} \bar{L}_{\sigma_\nu} l_{\sigma_\nu} | \} l_{\sigma_\nu}{}^{N_{\sigma\nu}} \alpha_{\sigma_\nu} S_{\sigma_\nu} L_{\sigma_\nu})$$

$$\langle \bar{S}_1 \cdots (\bar{S}_{\rho_\mu \frac{1}{2}}(N+\epsilon_\mu)) S_{\rho_\mu} \cdots (\bar{S}_{\sigma_\mu \frac{1}{2}}(N+1-\epsilon_\mu)) S_{\sigma_\mu} \cdots \alpha_k S_k | \bar{S}_1 \cdots (\bar{S}_{\rho_\nu \frac{1}{2}}(N+\epsilon_\nu)) S_{\rho_\nu} \cdots (\bar{S}_{\sigma_\nu \frac{1}{2}}(N+1-\epsilon_\nu)) S_{\sigma_\nu} \cdots, \alpha_l S_l \rangle$$

$$\times \sum_t [\delta_{\epsilon_\mu \epsilon_\nu} R_t(\rho_\mu \sigma_\mu \rho_\nu \sigma_\nu) [(2l_{\sigma_\mu}+1)(2l_{\rho_\nu}+1)]^{-1/2} (l_{\rho_\mu} \| C^t \| l_{\rho_\nu}) (l_{\sigma_\nu} \| C^t \| l_{\sigma_\mu}) \langle \bar{L}_1 \cdots (\bar{L}_{\rho_\mu} l_{\rho_\mu}) L_{\rho_\mu} \cdots [\bar{L}_{\sigma_\mu} (l_{\sigma_\nu} t) l_{\sigma_\mu}] L_{\sigma_\mu} \cdots$$

$$\bar{L}_{b_\mu}, \alpha_k L_k | \bar{L}_1 \cdots [\bar{L}_{\rho_\nu} (t l_{\rho_\mu}) l_{\rho_\nu}] L_{\rho_\nu} \cdots, \alpha_l L_l \rangle + (1-\delta_{\epsilon_\mu \epsilon_\nu}) R_t(\rho_\mu \sigma_\mu \sigma_\nu \rho_\nu) [(2l_{\sigma_\mu}+1)(2l_{\sigma_\nu}+1)]^{-1/2} (l_{\rho_\mu} \| C^t \| l_{\sigma_\mu}) (l_{\rho_\nu} \| C^t \| l_{\sigma_\mu})$$

$$\times \langle \bar{L}_1 \cdots (\bar{L}_{\rho_\mu} l_{\rho_\mu}) L_{\rho_\mu} \cdots [\bar{L}_{\sigma_\mu} (l_{\rho_\nu} t) l_{\sigma_\mu}] L_{\sigma_\mu} \cdot \alpha_k L_k | \bar{L}_1 \cdots (\bar{L}_{\rho_\nu} l_{\rho_\nu}) L_{\rho_\nu} \cdots [\bar{L}_{\sigma_\nu} (t l_{\rho_\mu}) l_{\sigma_\nu}] L_{\sigma_\nu} \cdots, \alpha_l L_l \rangle]. \quad (62a)$$

Within the distributions $q_{\lambda\mu}$ and $q_{\lambda\nu}$, $(N+1)$ and (N) are the interacting electrons. When Φ_μ and Φ_ν have identical configurations then there will be several ways of determining $\{\bar{N}_\lambda\}$, hence $\sum \bar{c}$ appearing in Eq. (62). When these functions differ by one jump, e.g.,

$$\left\langle 1s^2 2s^2 2p^q \left| \frac{1}{r_{N,N+1}} \right| 1s^2 2s 2p^q 3s \right\rangle,$$

then label $(N+1)$ could be assigned to $2s$ on the left and $3s$ on the right; the interacting label (N) could then be in any of the three common subshells and once again a $\sum \bar{c}$. For Φ_μ and Φ_ν differing by two electron jumps, there is a unique configuration of the spectators.

The matrix element of $H_1(x_{N+1})$ is

$$\langle \Phi_\mu | H_1 | \Phi_\nu \rangle = [\mathfrak{N}(N_\lambda{}^\mu) \mathfrak{N}(N_\lambda{}^\nu)]^{-1/2} \sum_{q_\mu q_\nu} (-1)^{P_{q^\mu} + P_{q^\nu}} \langle \phi_{\mu u}(q_\mu L_k S_k \pi_k) | H_1 | \phi_{\mu\nu}(q_\nu L_l S_l \pi_l) \rangle. \quad (63)$$

If Φ_μ and Φ_ν differ by a single electron jump, then this must be the interacting electron and there is a unique configuration of spectator electrons. For two or more electron jumps, the matrix element vanishes. For $\Phi_\mu = \Phi_\nu$, then $(N+1)$ will be found in the same subshell in Φ_μ and Φ_ν and there will be as many terms in $\sum \bar{c}$ as there are occupied subshells.

$$\langle \Phi_\mu | H_1 | \Phi_\nu \rangle = \sum_{\bar{c}} \mathfrak{N}(\bar{N}_\lambda) [\mathfrak{N}(N_\lambda{}^\mu) \mathfrak{N}(N_\lambda{}^\nu)]^{-1/2} \prod_\lambda \delta(N_\lambda{}^\mu, N_\lambda{}^\nu + \delta_{\rho_\mu \lambda} - \delta_{\rho_\nu \lambda})$$

$$\times (-1)^{\Delta P} \sum_{\bar{\alpha}_{\rho_\mu} \cdots \bar{L}_{\rho_\nu}} (l_{\rho_\mu}{}^{N_{\rho\mu}} \alpha_{\rho_\mu} S_{\rho_\mu} L_{\rho_\mu} \{ | l_{\rho_\mu}{}^{\bar{N}_{\rho\mu}} \bar{\alpha}_{\rho_\mu} \bar{S}_{\rho_\mu} \bar{L}_{\rho_\mu} l_{\rho_\mu}) (l_{\rho_\nu}{}^{\bar{N}_{\rho\nu}} \bar{\alpha}_{\rho_\nu} \bar{S}_{\rho_\nu} \bar{L}_{\rho_\nu} l_{\rho_\nu} | \} l_{\rho_\nu}{}^{N_{\rho\nu}} \alpha_{\rho_\nu} S_{\rho_\nu} L_{\rho_\nu})$$

$$\times \langle [\prod_{\lambda \neq \rho_\mu} \{ n l_\lambda{}^{\bar{N}_\lambda} \bar{\alpha}_\lambda \bar{S}_\lambda \bar{L}_\lambda | \bar{q}_\lambda) \times [\{ n l_{\rho_\mu}{}^{\bar{N}_{\rho\mu}} \bar{\alpha}_{\rho_\mu} \bar{S}_{\rho_\mu} \bar{L}_{\rho_\mu} | \bar{q}_\mu) \times \{ n l_{\rho_\mu} | N+1)]^{L_{\rho\mu} S_{\rho\mu}}] ^{L_k S_k} H_1(N+1)$$

$$\times [\prod_{\lambda \neq \rho_\nu} (\bar{q}_\lambda | n l_\lambda{}^{\bar{N}_\lambda} \bar{\alpha}_\lambda \bar{S}_\lambda \bar{L}_\lambda \} \times [(\bar{q}_{\rho_\nu} | n l_{\rho_\nu}{}^{\bar{N}_{\rho\nu}} \bar{\alpha}_{\rho_\nu} \bar{S}_{\rho_\nu} \bar{L}_{\rho_\nu} \} \times (N+1 | n l_{\rho_\nu} \}]^{L_{\rho\nu} S_{\rho\nu}}]^{L_l S_l}, \quad (64)$$

which will include a spin recoupling coefficient

$$\langle \bar{S}_1 \cdots (\bar{S}_{\rho_\mu \frac{1}{2}}(N+1)) S_{\rho_\mu} \cdots \bar{S}_{b_\mu} \alpha_k S_k | \bar{S}_1 \cdots (\bar{S}_{\rho_\nu \frac{1}{2}}(N+1)) S_{\rho_\nu} \cdots \bar{S}_{b_\nu} \alpha_l S_l \rangle \quad (65)$$

and the factor

$$\langle P(n l_{\rho_\mu}) | H_1 | P(n l_{\rho_\nu}) \rangle \langle \bar{L}_1 \cdots (\bar{L}_{\rho_\mu} l_{\rho_\mu}) L_{\rho_\mu} \cdots \alpha_k L_k | \bar{L}_1 \cdots (\bar{L}_{\rho_\nu} l_{\rho_\nu}) L_{\rho_\nu} \cdots \alpha_l L_l \rangle. \quad (66)$$

Combining the above results together

$$\langle \Phi_\mu | H_1 | \Phi_\nu \rangle = \sum_{\bar{c}} (N+1)^{-1} [N_{\rho_\mu} N_{\rho_\nu}]^{1/2} \prod_\lambda \delta(N_\lambda{}^\mu, N_\lambda{}^\nu + \delta_{\lambda \rho_\mu} - \delta_{\lambda \rho_\nu}) (-1)^{\Delta P}$$

$$\times \sum_{\bar{\alpha}_{\rho_\mu} \cdots L_{\rho_\nu}} (l_{\rho_\mu}{}^{N_{\rho\mu}} \alpha_{\rho_\mu} S_{\rho_\mu} L_{\rho_\mu} \{ | l_{\rho_\mu}{}^{\bar{N}_{\rho\mu}} \bar{\alpha}_{\rho_\mu} \bar{S}_{\rho_\mu} \bar{L}_{\rho_\mu} l_{\rho_\mu}) (l_{\rho_\nu}{}^{\bar{N}_{\rho\nu}} \bar{\alpha}_{\rho_\nu} \bar{S}_{\rho_\nu} \bar{L}_{\rho_\nu} l_{\rho_\nu} | \} l_{\rho_\nu}{}^{N_{\rho\nu}} \alpha_{\rho_\nu} S_{\rho_\nu} L_{\rho_\nu})$$

$$\times \langle \bar{S}_1 \cdots (\bar{S}_{\rho_\mu \frac{1}{2}}) S_{\rho_\mu} \cdots \alpha_k S_k | \bar{S}_1 \cdots (\bar{S}_{\rho_\nu \frac{1}{2}}) S_{\rho_\nu} \cdots \alpha_l S_l \rangle \langle \bar{L}_1 \cdots (\bar{L}_{\rho_\mu} l_{\rho_\mu}) L_{\rho_\mu} \cdots \alpha_k L_k | \bar{L}_1 \cdots (\bar{L}_{\rho_\nu} l_{\rho_\nu}) L_{\rho_\nu} \cdots \alpha_l L_l \rangle$$

$$\times (-\tfrac{1}{2}) \int dr P_{n l_{\rho_\mu}}(r) \left[\frac{d^2}{dr^2} - \frac{l_{\rho_\mu}(l_{\rho_\mu}+1)}{r^2} + \frac{2Z}{r} \right] P_{n l_{\rho_\nu}}(r), \quad (67)$$

where

$$\Delta P=\sum_{\lambda=\min(\rho_\mu,\rho_\nu)}^{\max(\rho_\mu,\rho_\nu)}\bar{N}_\lambda.$$

Finally we have to evaluate the matrix element of H_N, the N-electron Hamiltonian:

$$\langle\Phi_\mu(L_kS_k\pi_k)|H_N|\Phi_\nu(L_lS_l\pi_l)\rangle=[\mathfrak{N}(N_\lambda{}^\mu)\mathfrak{N}(N_\lambda{}^\nu)]^{-1/2}\sum_{q_\mu q_\nu}(-1)^{Pq^\mu+Pq^\nu}\langle\phi_{u\mu}(q_\mu L_kS_k\pi_k)|H_N|\phi_{u\nu}(q_\nu L_lS_l\pi_l)\rangle. \quad (68)$$

Separating off the noninteracting electron we have

$$\begin{aligned}\langle\phi_{u\mu}(L_kS_k\pi_k)|H_N|\phi_{u\nu}(L_lS_l\pi_l)\rangle=&\sum_{\bar{\alpha}_{\rho_i}\cdots m_{\rho_\nu}}(l_{\rho_\mu}{}^{N_{\rho^\mu}}\alpha_{\rho_\mu}S_{\rho_\mu}L_{\rho_\mu}\{|l_{\rho_\mu}{}^{\bar{N}_{\rho^\mu}}\bar{\alpha}_{\rho_\mu}\bar{S}_{\rho_\mu}\bar{L}_{\rho_\mu}l_{\rho_\mu})\\&\times(l_{\rho_\nu}{}^{\bar{N}_{\rho^\nu}}\bar{\alpha}_{\rho_\nu}\bar{S}_{\rho_\nu}\bar{L}_{\rho_\nu}l_{\rho_\nu}|\}l_{\rho_\nu}{}^{N_{\rho^\nu}}\alpha_{\rho_\nu}S_{\rho_\nu}L_{\rho_\nu})(\bar{L}_{\rho_\mu}l_{\rho_\mu}M_{\bar{L}_\mu}m_{l_\mu}|L_{\rho_\mu}M_{L_\mu})(\bar{S}_{\rho_\mu}\tfrac{1}{2}M_{\bar{s}_\mu}m_{s_\mu}|S_{\rho_\mu}M_{S_\mu})\\&\times(\bar{L}_{\rho_\nu}k_{\rho_\nu}M_{\bar{L}_\nu}m_{l_\nu}|L_{\rho_\nu}M_{L_\nu})(\bar{S}_{\rho_\nu}\tfrac{1}{2}M_{\bar{s}_\nu}m_{s_\nu}|S_{\rho_\nu}M_{S_\nu})\langle nl_{\rho_\mu}|nl_{\rho_\nu}\rangle\langle\Phi_\mu(L_kS_k\pi_k\bar{q}_k)|H_N|\Phi_\nu(L_lS_l\pi_l\bar{q}_l)\rangle, \quad (69)\end{aligned}$$

where Φ is an unsymmetrized wave function of N electrons. In order to evaluate the "direct" terms we have made the assumption that

$$\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_N\psi(\gamma_i\mathbf{X})[H_N-\mathcal{E}]\psi(\gamma_j\mathbf{X})=0,$$

where $\psi(\gamma_i\mathbf{X})$ is a properly antisymmetrized wave function of N electrons [see Eq. (43)]. H_N is symmetric under interchange of labels of any pair of electrons and so it can be readily shown, using the expansion of Eq. (10), that this implies that

$$\int\cdots\int d\mathbf{x}_1\cdots d\mathbf{x}_N\psi_u(\gamma_i\mathbf{X})[H_N-\mathcal{E}]\psi_u(\gamma_j\mathbf{X})=0.$$

Hence we have

$$\langle\bar{\phi}_\mu(\bar{\gamma}_k\bar{q}_k)|H_N|\bar{\phi}_\nu(\bar{\gamma}_l\bar{q}_l)\rangle=E^{\bar{\gamma}k}\delta_{\bar{\gamma}_l\bar{\gamma}_k}\delta_{\bar{q}_l\bar{q}_k}, \quad (70)$$

and

$$\begin{aligned}\langle\Phi_\mu(L_kS_k\pi_k)|H_N|\Phi_\nu(L_lS_l\pi_l)\rangle=&[\mathfrak{N}(N_\lambda)]^{-1}\sum_{q\bar{\alpha}_\rho\bar{S}_\rho\bar{L}_\rho}(l_\rho{}^{N_{\rho^\mu}}\alpha_\rho{}^\mu L_\rho{}^\mu S_\rho{}^\mu\{|l_\rho{}^{\bar{N}_\rho}\bar{\alpha}_\rho\bar{L}_\rho\bar{S}_\rho l_\rho)\\&\times(l_\rho{}^{\bar{N}_\rho}\bar{\alpha}_\rho\bar{L}_\rho\bar{S}_\rho l_\rho|\}l_\rho{}^{N_{\rho^\nu}}\alpha_\rho{}^\nu L_\rho{}^\nu S_\rho{}^\nu)E^{\bar{L}_\rho\bar{S}_\rho}\delta_{N\lambda\mu N\lambda^\nu}. \quad (71)\end{aligned}$$

The noninteracting electron $N+1$ may be found in any subshell for which $N_\lambda\neq0$, and from the symmetry of H_N (for a given configuration) each distribution of interacting electrons contributes equally, hence

$$\begin{aligned}\langle\Phi_\mu(L_kS_k\pi_k|H_N|\Phi_\nu(L_lS_l\pi_l)\rangle=&\frac{1}{N+1}\sum_{\lambda=1s}^{b}N_\lambda\sum_{\bar{\alpha}_\lambda\bar{L}_\lambda\bar{S}_\lambda}(l_\lambda{}^{N_{\lambda\mu}}\alpha_\lambda{}^\mu S_\lambda{}^\mu L_\lambda{}^\mu|\}l_\lambda{}^{\bar{N}_\lambda}\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda l_\lambda)\\&\times(l_\lambda{}^{\bar{N}_\lambda}\bar{\alpha}_\lambda\bar{S}_\lambda\bar{L}_\lambda l_\lambda|\}l_\lambda{}^{N_{\lambda^\nu}}\alpha_\lambda{}^\nu S_\lambda{}^\nu L_\lambda{}^\nu)E^{\bar{L}_\lambda\bar{S}_\lambda}\delta_{N\lambda\mu N\lambda^\nu}. \quad (72)\end{aligned}$$

4. RADIAL EQUATIONS

A. Derivation

As in Smith *et al.*,[6] Eq. (16) can be written out explicitly with the help of Eqs. (50), (41), (53), and (61),

$$\begin{aligned}\delta\Big[\sum_{i,j}\int F_{ik}\mathfrak{L}_{ij}F_{jl}dr+\sum_{j,\mu}C_\mu{}^k\int V_{\mu,j}F_{jl}dr+\sum_{i,\nu}C_\nu{}^l\\\times\int V_{\nu,i}F_{ik}dr+\sum_{i,\nu}C_\mu{}^kC_\nu{}^lA_{\mu\nu}-\tfrac{1}{2}K_{kl}\Big]=0, \quad (73)\end{aligned}$$

where

$$\begin{aligned}\mathfrak{L}_{ij}=-\frac{1}{2}\Big[\frac{d^2}{dr^2}-\frac{l_i(l_i+1)}{r^2}+\frac{2Z}{r}+2(E-\mathcal{E}_i)\Big]\delta_{ij}\\+V_{ij}+W_{ij}, \quad (74)\end{aligned}$$

and $A_{\mu\nu}$ is defined in terms of Eqs. (62a), (67), and (72). For variations of $F_{m,n}$ of the form Eq. (19), Eq. (73) yields the integrodifferential equations

$$\sum_j\mathfrak{L}_{ij}F_{jl}+\sum_\mu C_\mu{}^lV_{\mu,i}=0. \quad (75)$$

Variations of (73) with respect to $C_\lambda{}^m$ lead to

$$\sum_\nu A_{\mu\nu}C_\nu{}^l+\sum_j\int V_{\mu,j}F_{jl}dr=0. \quad (76)$$

The solutions of Eqs. (75) and (76) are to be subjected to the further requirement and that they are orthogonal to all subshells of the target system with the same orbital angular momentum, i.e., Eq. (13).

Introducing this requirement into (74) using

LaGrange multipliers, $\mathfrak{M}$ gives (75) to be

$$\sum_j \mathfrak{L}_{ij}F_{jl}+\sum_\mu C_\mu{}^l V_{\mu,i}+\sum_\lambda \mathfrak{M}_\lambda P_{nl\lambda}\delta_{l_i l_\lambda}=0. \quad (77)$$

B. Numerical Method

An algorithm for the solution of the system of second-order integro-differential equations $\mathfrak{L}_{ij}F_{jl}=0$ for $k_i{}^2>0$ has been given by Smith[15] and for $k_i{}^2<0$ by Smith and Burke.[16] Both these papers are based on iterative techniques. Noniterative techniques are implied in the work of Hartree[17,18] and have been developed for collision problems with $k_i{}^2>0$ by Marriott[19] and Omidvar[20] for the system $\mathfrak{L}_{ij}F_{jl}=0$. The noniterative alogrithm for the system of equations in (77) for all real nonzero $k_i{}^2$ has been developed by Smith *et al.*[6]

A FORTRAN program has been written to solve Eq. (77) and is currently being tested. Given a set of $(LS\pi)$, the configurations to be coupled together and their term values, the code calculates the number of channels and potentials and sets up the distinct exchange terms to be obtained as the solutions of differential equations. It then proceeds to solve the equations, using an extension to the algorithm presented in Smith *et al.*,[6] and prints out the partial-wave cross sections. Some of the early production runs with the code will be to calculate the total cross sections for the scattering of low-energy electrons by atomic oxygen in order to compare with the absolute measurements of Sunshine *et al.*[21] Calculations will also be carried out to determine the positions and widths of resonances in the photo-ionization continuum of *Ne I* (20–150 eV), as these have been observed by Codling *et al.*[22] Carroll *et al.*,[23] have observed a new Rydberg series in the absorption spectrum of atomic nitrogen which they attributed to transitions from the $^4S^0$ ground state of the nitrogen atom to the Rydberg terms $2s\,2p^3\,(^5S^0)np\,{}^4P$; it will be possible to calculate the parameters of these autoionized levels with the code.

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APPENDIX

Evaluation of the Recoupling Coefficients

The subshell angular momenta L_λ, S_λ together with the angular momenta l_T and $\frac{1}{2}$ of the projectile are coupled according to a prescribed coupling scheme to give total angular momenta L, S. If the intermediate couplings leading to a given L, S are not unique, then to each coupling there corresponds a distinct state Γ_i specified by the quantum numbers L, S, π together with an additional parameter α_i which specifies the coupling. We shall couple the vectors $L_1\cdots L_b$, l_i to give a total L_i according to the scheme

$$|(L_1L_2)(L_2{}^{\alpha_i}L_3)(L_3{}^{\alpha_i}\cdots L_\lambda)(L_\lambda{}^{\alpha_i}\cdots)(L_{b_i}{}^{\alpha_i}l_i)L_i\rangle, \quad (1a)$$

where $L_\lambda{}^{\alpha_i}$ denotes the result of coupling L_λ to the resultant of $L_1\cdots L_{\lambda-1}$. For the purposes of recoupling we may regard the continuum electron as being in a subshell $b+1$ where b is the outermost of the discrete orbitals and where $\bar{L}_{b+1}=0$, $L_{b+1}=l_i$. We shall define subshell ρ to contain electron N and σ to contain $N+1$. The general form of the orbital recoupling coefficient is

$$\langle \bar{L}_1\bar{L}_2\cdots L_{\rho_i-1}{}^{\alpha_i}[\bar{L}_{\rho_i}(l_{\rho_j}k)l_{\rho_i}]L_{\rho_i}L_{\rho_i}{}^{\alpha_i}\cdots\bar{L}_{\sigma_j}\cdots (\bar{L}_{\sigma_i}l_{\sigma_i})\cdots\bar{L}_{\sigma_j}\cdots,L_i|\bar{L}_1\bar{L}_2\cdots\bar{L}_{\rho_i}\cdots(\bar{L}_{\rho_j}l_{\rho_j})L_{\rho_j}\cdots \bar{L}_{\sigma_i}\cdots[\bar{L}_{\sigma_j}(kl_{\sigma_i})l_{\sigma_j}]L_{\sigma_j}L_{\sigma_j}{}^{\alpha_j}\cdots,L_j\rangle.$$

We note that there are three vectors to be recoupled, namely, l_N l_{N+1} and k. We must recouple l_N from ρ_i to ρ_j or vice versa when ρ_j lies inside ρ_i, as we do not know *a priori* which is the smaller, then recouple l_{N+1} from σ_i to σ_j and k from ρ_i to σ_j. To evaluate the above recoupling coefficient we generalize the method of Biedenharn[24] by first recoupling $l_{\rho_i}(=l_N)$ step by step from ρ_i to ρ_j, each intermediate recoupling contributing a Racah coefficient and then recouple the vectors $[\bar{L}_{\rho_j},(l_{\rho_j}k)l_{\rho_i}]L_{\rho_j}\rightarrow[(\bar{L}_{\rho_j}l_{\rho_j})L_{\rho_j},k]$. Next recouple k step by step from ρ_j to σ_i, couple it to $l_{\sigma_i}(=l_{N+1})$ to give l_{σ_j} and finally recouple l_{σ_j} from σ_i to σ_j. The recoupling coefficient will then have been expressed as a product or, in the case when the intermediate recoupling vector is not found on the r.h.s. of the coefficient, a sum of products of Racah coefficients. Three basic types of recoupling occur:

(*a*) *Direct:* in which $\max(\rho_i\rho_j)\leqslant\min(\sigma_i\sigma_j)$ as in Eqs. (49a), (56), (67), and, depending upon the particular configurations considered, in Eqs. (60a) and (62a), see Fig. 1(a). Alternatively we may have $\max(\sigma_i\sigma_j)\leqslant\min(\rho_i\rho_j)$ which can occur in Eqs. (60a) and (62a). In either case, we do not, at any stage in the recoupling, have to recouple both l_N and l_{N+1} through the same

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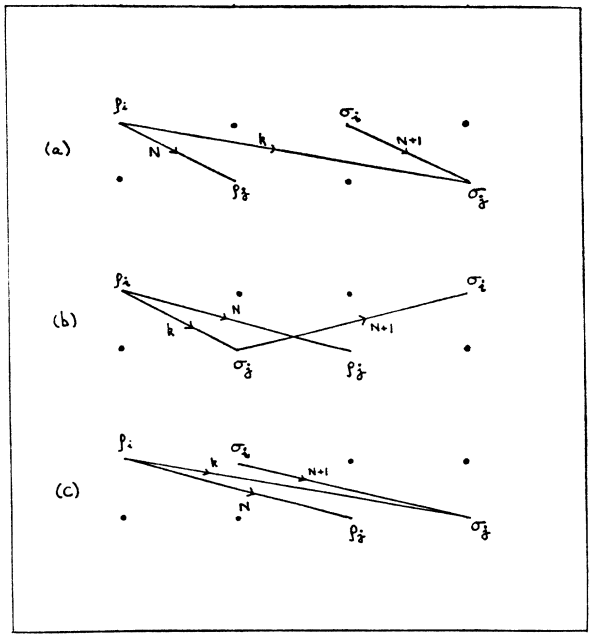

FIG. 1. Schematic representation of the three types of recoupling schemes encountered in the angular-momentum recoupling coefficients: (a) direct, (b) exchange, (c) translation.

range. This will give rise to a single product of Racah coefficients since we may use the property

$$\langle(L_{\lambda-1}{}^{\alpha i}L_\lambda)\tilde{L}_\lambda l_N;\ L_\lambda{}^{\alpha i}|\,(L_{\lambda-1}{}^{\alpha i}L_\lambda)L_\lambda{}^{\alpha j}l_N;\ L_\lambda{}^{\alpha i}\rangle=\delta_{\tilde{L}_\lambda L_\lambda}\alpha_j$$

to eliminate the summation over the intermediate couplings, $\tilde{L}$;

(*b*) *Exchange:* $\min(\rho_i\rho_j)\leqslant\min(\sigma_i\sigma_j)<\max(\rho_i\rho_j)$ as in Eq. (40) or alternatively $\min(\sigma_i\sigma_j)\leqslant\min(\rho_i,\rho_j)\leqslant\max(\sigma_i\sigma_j)$. Both cases may also occur in Eq. (60a) and (62a). In the former case we will have to recouple both l_{ρ_j} and l_{σ_i} through the range σ_j to ρ_j and will therefore have to sum over the intermediate couplings of this range. A schematic representations of these exchange recouplings are presented in Fig. 1(b);

(*c*) *Translation:* $\max(\rho_i\sigma_i)<\min(\rho_j\sigma_j)$ or alternatively $\max(\rho_j\sigma_j)<\min(\rho_i\sigma_i)$. This type of recoupling will only only occur in terms linear or quadratic in C, Eqs. (60a) and (62a), where both interacting electrons can appear in discrete orbitals. For example the recoupling coefficient of Eq. (60) arising from the configurations $1s^22s^22p^43skl-1s^22s^22p^6$ (where $\rho_i=3s$, $\sigma_i=kl$ continuum, and $\rho_j=\sigma_j=2p$), will be of this form. In the former case we will have to recouple both l_{ρ_i} and l_{σ_i} from σ_i to ρ_j. This is most easily achieved by coupling l_{ρ_i} $l_{\sigma_i}(\tilde{l}_i)$ and recoupling $\tilde{l}_i$ from σ_i to ρ_j then summing over all possible $\tilde{l}_i$. Schematically, these recouplings can be by Fig. 1(c).

The general form of the spin recoupling coefficient is

$$\langle\bar{S}_1\cdots S_{\rho_i-1}{}^{\alpha i}(\bar{S}_{\rho_i\frac{1}{2}}(N))S_{\rho_i}\cdots\bar{S}_{\rho_j}\cdots S_{\sigma_i-1}{}^{\alpha i}(\bar{S}_{\sigma_i\frac{1}{2}}(N+1))\cdots S_{\sigma_i}S_{\sigma_i}{}^{\alpha i}\cdots,\alpha_iS_i|\bar{S}_1\cdots\bar{S}_{\rho_i}\cdots S_{\rho_j-1}{}^{\alpha j}(\bar{S}_{\rho_j\frac{1}{2}}(N))S_{\rho_j}\cdots\bar{S}_{\sigma_i}\cdots S_{\sigma_j-1}{}^{\alpha j}(\bar{S}_{\sigma_j\frac{1}{2}}(N+1))S_{\sigma_j}\cdots,\alpha_jS_j\rangle.$$

The evaluation can be carried out in the same way as the orbital recoupling coefficient, giving rise to the same 3 types of recoupling but will be simplified by the fact that there are only two vectors $\frac{1}{2}(N)$, $\frac{1}{2}(N+1)$ to be recoupled.

For example, the direct spin recoupling coefficient is, for $\rho_i<\rho_j$,

$$\langle\bar{S}_1\cdots S_{\rho_i-1}{}^{\alpha i}(\bar{S}_{\rho_i\frac{1}{2}}(N))S_{\rho_i}\cdots\bar{S}_{\rho_j}\cdots S_{b_i}{}^{\alpha i}\tfrac{1}{2}(N+1),S_i|\bar{S}_1\cdots\bar{S}_{\rho_i}\cdots(\bar{S}_{\rho_j\frac{1}{2}}(N))\cdots S_{b_j}{}^{\alpha i}\tfrac{1}{2}(N+1),S_j\rangle$$

$$=\langle S_{\rho_i-1}{}^{\alpha i},\bar{S}_{\rho_i\frac{1}{2}}(S_{\rho_i});S_{\rho_i}{}^{\alpha i}|S_{\rho_i-1}{}^{\alpha i}\bar{S}_{\rho_i}(S_{\rho_i}{}^{\alpha j}),\tfrac{1}{2};S_{\rho_i}{}^{\alpha i}\rangle\prod_{\lambda=\rho_i+1}^{\rho_j-1}\langle S_{\lambda-1}{}^{\alpha i}\tfrac{1}{2}(S_{\lambda-1}{}^{\alpha i}),\bar{S}_\lambda;S_\lambda{}^{\alpha i}|S_{\lambda-1}{}^{\alpha i}\bar{S}_\lambda(S_\lambda{}^{\alpha j}),\tfrac{1}{2};S_\lambda{}^{\alpha i}\rangle$$

$$\times\langle S_{\rho_j-1}{}^{\alpha i}\tfrac{1}{2}(S_{\rho_j-1}{}^{\alpha i}),\bar{S}_{\rho_j};S_{\rho_j}{}^{\alpha i}|S_{\rho_j-1}{}^{\alpha i},\bar{S}_{\rho_j\frac{1}{2}}(S_{\rho_j});S_{\rho_j}{}^{\alpha i}\rangle\prod_{\lambda=1}^{\rho_i-1}\delta(S_\lambda{}^{\alpha i}S_\lambda{}^{\alpha j})\prod_{\lambda=\rho_j+1}^{b_i}\delta(S_\lambda{}^{\alpha i}S_\lambda{}^{\alpha j})\delta_{b_ib_j}\delta_{S_iS_j},$$

where the recoupling coefficients are given in terms of Racah coefficients by[24]

$$[(2S_{\rho_i}+1)(2S_{\rho_j}{}^{\alpha j}+1)]^{1/2}W(S_{\rho_i-1}{}^{\alpha i}\bar{S}_{\rho_i}S_{\rho_i}{}^{\alpha i}\tfrac{1}{2};\ S_{\rho_i}{}^{\alpha j}S_{\rho_i})\prod_{\lambda=\rho_i+1}^{\rho_j-1}[(2S_{\lambda-1}{}^{\alpha i}+1)(2S_\lambda{}^{\alpha j}+1)]^{1/2}$$

$$\times W(S_{\lambda-1}{}^{\alpha i}\tfrac{1}{2}\bar{S}_\lambda S_\lambda{}^{\alpha j};\ S_{\lambda-1}{}^{\alpha j}S_\lambda{}^{\alpha i})[(2S_{\rho_j-1}{}^{\alpha i}+1)(2S_{\rho_j}+1)]^{1/2}(-1)^{S_{\rho j}+1/2-S_{\rho j}}W(S_{\rho_j-1}{}^{\alpha j}\tfrac{1}{2}S_{\rho_i}{}^{\alpha i}\bar{S}_{\rho_j};\ S_{\rho_j-1}{}^{\alpha i}S_{\rho_j}).$$