SOVIET PHYSICS JETP VOLUME 12, NUMBER 3 MARCH, 1961

DEDUCTION OF THE RADIAL EQUATIONS OF THE THEORY OF COLLISIONS BETWEEN ELECTRONS AND ATOMS

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Submitted to JETP editor April 13, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) **39**, 767-775 (September, 1960)

Radial equations are derived for the excitation of an arbitrary level of a many-electron atom, with allowance for the nonorthogonality of the wave functions of the external and optical electrons. The well-known ambiguity which appears when approximate atomic wave functions are used is discussed. An approximate form of the equations is proposed, in which terms that contain simultaneously nonorthogonality integrals and higher multiple interactions are neglected. In this approximation the ambiguity disappears if semi-empirical wave functions are employed for the optical electron.

1 The various methods based on perturbation theory are as a rule insufficient in the calculation of the effective cross sections of the excitation of atoms by slow electrons. In the more general formulation, the problem reduces to the solution of a system of integro-differential equations for the radial wave functions of the external electron, analogous to the Hartree-Fock equations in the multiconfiguration approximation of electron theory. The present paper is devoted to a derivation of equations that describe the excitation of an arbitrary level of a multi-electron atom. The equations up to now are only for some particular cases (see, for example, reference 1).

Let us consider the following system: an atom with N electrons in state γLS and an outer electron with momentum l (γ is the totality of the remaining quantum numbers characterizing the LS term of the atom). The state of the system with specified values of total momenta $L_T S_T$ is defined by the set of quantum numbers $\Gamma = \gamma LS\tilde{l}L_T S_T$ (the quantum numbers M_{L_T} and M_{S_T}, which are of no importance in our problem, are omitted; the magnetic interactions are disregarded in this paper). The wave function of an arbitrary state of the system can be represented in the form

$$\Psi = \sum_{\Gamma} \Psi(\Gamma). \tag{1}$$

To separate the coordinate of the external electron it is necessary to change over to the incompletely antisymmetric functions

$$\Psi(\Gamma) \equiv \Psi(\gamma LS\tilde{l}L_T S_T) = \sum_i \frac{(-1)^{N+1-i}}{\sqrt{N+1}} \Psi(\gamma LS\tilde{l}_{(i)}L_T S_T). \tag{2}$$

The function $\Psi(\gamma LS\tilde{l}_{(i)}L_T S_T)$ is constructed in accordance with the general principle of addition of momenta, but unlike $\Psi(\gamma LS\tilde{l}L_T S_T)$ it is antisymmetric only in the electrons 1, 2, . . . , i − 1, i + 1, . . . , N + 1, while the i-th electron is assigned the state $\tilde{l}$. Using (2), we can separate the radial function of the external electron

$$\Psi(\Gamma) = \sum_i \frac{(-1)^{N+1-i}}{\sqrt{N+1}} \frac{F_\Gamma(r_i)}{r_i} \Phi(\gamma LS\tilde{l}_{(i)}L_T S_T). \tag{3}$$

The function $F_\Gamma(r)$ has an asymptotic value (Γ_0 is the initial state)

$$F_\Gamma(r) \sim \delta_{\Gamma\Gamma_0} \sin(kr - \tilde{l}\pi/2 + \eta \ln 2kr + \sigma_{\tilde{l}})$$
$$+ T_{\Gamma\Gamma_0} \exp\{i(kr - \tilde{l}\pi/2 + \eta \ln 2kr + \sigma_{\tilde{l}})\},$$
$$\eta = (Z-N)/k, \qquad \sigma_{\tilde{l}} = \arg\Gamma(\tilde{l}+1-i\eta). \tag{4}$$

The total cross section of the atomic transitions $\gamma_0 L_0 S_0 \rightarrow \gamma LS$ is expressed in terms of $T_{\Gamma\Gamma_0}$:

$$Q_{\gamma LS}^{\gamma_0 L_0 S_0} = \frac{4\pi a_0^2 k}{k_0^3} \sum_{\tilde{l}\tilde{l}_0 L_T S_T} \frac{(2S_T+1)(2L_T+1)}{2(2S_0+1)(2L_0+1)} |T_{\Gamma\Gamma_0}|^2. \tag{5}$$

Thus, the cross section is determined by the asymptotic values of the functions $F_\Gamma(r)$. A system of equations for these functions can be obtained from the variational principle

$$\delta(F_\Gamma)\langle\Psi|H-E|\Psi\rangle$$
$$= \sum_{\Gamma'} \delta(F_\Gamma)\langle\Psi(\Gamma)|H-E|\Psi(\Gamma')\rangle = 0. \tag{6}$$

The symbol $\delta(F_\Gamma)$ denotes variation over the function F_Γ in the left part of the matrix element. To carry out the variation in (6) in explicit form, it is necessary to express the matrix elements of $(H-E)$ in terms of the radial integrals.

2. We assume henceforth that the atomic functions are Hartree-Fock functions of single-configuration approximation. In the case of complicated atoms, the Hartree-Fock functions are the most exact functions that can be used in real calculations.

Generally speaking, the single-electron functions that enter into $\Psi(\Gamma)$ and $\Psi(\Gamma')$ may not be completely orthonormal. We shall consider only the nonorthogonality of the functions of the external and valence electrons, which plays the greatest role in the present problem. A full account of the nonorthogonality would lead to an excessive complication of the derivations and of the final expressions.

The energy of the system is made up of the energy of the atom E_a and the energy of the external electron $k^2/2$. For the energy of the atom it is necessary to use the same approximation as used for the wave functions in the calculation of the matrix elements, or else the contribution to E_a from the internal shells will not be compensated for by the corresponding terms in $\langle \Gamma | H | \Gamma \rangle$. It is physically obvious that the energy of the internal shells, which exceeds by many times the energy of the interaction of the external electron with the atom, should not enter into the equation for $F(r)$.

When using the approximate expression for the energy of the atom, the two representations

$$E = E_a + k^2/2, \qquad E = E_a' + k'^2/2 \tag{7}$$

are not equivalent. In the case of diagonal elements, the choice of the representation for E is dictated by the requirement of regular asymptotic behavior of the wave functions, viz., it is necessary to use the first representation in (7) for $\langle \Gamma | H - E' | \Gamma \rangle$ and the second for $\langle \Gamma' | H - E | \Gamma' \rangle$. As regards the nondiagonal matrix elements, either representation can be used with equal justification. This ambiguity, which arises in the use of approximate atomic functions, is known in literature as the prior—post divergence.[2]

3. If we disregard the excitation of the electrons of the internal shells, we can confine ourselves to matrix elements of three types

$$\langle T_c l_1^{n-1}\tau_1 \tilde{l}\tau l T \,|\, H - E \,|\, T_c l_1^{n-1}\tau_1' \tilde{l}'\tau' l' T\rangle, \tag{8}$$

$$\langle T_c l^n \tau \tilde{l} T \,|\, H - E \,|\, T_c l^{n-1}\tau_1' l'\tau' \tilde{l}' T\rangle, \tag{9}$$

$$\langle T_c l^n \tau \tilde{l} T \,|\, H - E \,|\, T_c l^n \tau' \tilde{l}' T\rangle. \tag{10}$$

Here and henceforth T will mean a pair of quantum numbers of the orbital and spin momenta of the system $T = (L_T S_T)$. Analogously, $\tau = (LS)$, $\tau_1 = (L_1 S_1)$, etc., while T_c includes all the closed shell of the atomic residue.* To shorten the notation, we shall denote the totality of the single-electron quantum numbers nl as simply l.

The Hamiltonian of the system H contains terms of two types:

$$H = F + Q = \sum_i f_i + \tfrac{1}{2}\sum_{ij}{}' q_{ij}. \tag{11}$$

The calculation of the matrix elements begins with a separation of the coordinates of the external electrons with the aid of formula (2). Some of the terms in the sum (2) will contain, in implicit form, nonorthogonality integrals of the type

$$\Delta(\tilde{l}l) = \delta_{\tilde{l}l}\int_0^\infty F_\Gamma(r)\,P_l(r)\,dr, \tag{12}$$

where $P_l(r)$ and $F_\Gamma(r)$ are the radial wave functions of the atomic (l) and external $(\tilde{l})$ electrons. To separate the nonorthogonality integrals it is necessary to separate the coordinates of one of the atomic electrons. Formula (2) cannot be applied to the equivalent electrons. For two groups of equivalent electrons, the relation needed has the form

$$\begin{aligned}\Psi(l'^n T', l''^m T'', T) &= \sqrt{\frac{n}{n+m}}(-1)^{n-i}\sum_{T_1'} G^{T'}_{T_1'}\Psi(l'^{n-1}T_1' l'_{(i)}T', l''^m T'', T)\\ &+ \sqrt{\frac{m}{n+m}}(-1)^{n+m-i}\sum_{T_1''} G^{T''}_{T_1''}\Psi(l'^n T', l''^{m-1}T_1'' l''_{(i)}T'', T),\end{aligned} \tag{13}$$

where $G^T_{T_1}$ are the partial parentage coefficients introduced by Racah.[4] In Racah's notation

$$G^T_{T_1} \equiv G^{\alpha LS}_{\alpha_1 L_1 S_1}(l^n) \equiv (l^{n-1}[\alpha_1 L_1 S_1]\,lLS\,|\}\,l^n\alpha LS) \tag{14}$$

(see the preceding footnote concerning the quantum numbers α and α_1).

We shall also use the quantities

$$\overline{G}^T_{T_1} = \sqrt{n}\,G^T_{T_1}. \tag{15}$$

As above, the subscript (i) (in parentheses) following l will denote that the i-th electron is in the state l. The generalization of (13) to the case of three and more groups is obvious.

Let us consider a matrix element of the type (8). After all the transformations are made, it is represented in the form

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*In order to specify the term of configuration $l^n (l \geq 2)$ it is necessary to introduce additional quantum numbers, for example, the seniority quantum number v for $l = 2$.[3] We shall omit these quantum numbers throughout. We note that the dependence on these quantum numbers is expressed in the following formulas only through the parentage coefficients.

$$\langle \Gamma | H - E | \Gamma' \rangle = \sum_{r=0}^{6} M_r (\Gamma\Gamma'), \tag{16}$$

$$M_0 = \delta_{\Gamma\Gamma'} \langle T_c \tilde{l}_{(N)} | H_N - k^2/2 | T_c \tilde{l}'_{(N)} \rangle, \tag{17}$$

$$M_1 = \delta_{nl,\,n'l'} \sum_{T_2} A_1 A_1' \langle l_1^{n-1} \tau_1 \tilde{l}_{(N)} T_2 | q_N | l_1^{n-1} \tau_1' \tilde{l}'_{(N)} T_2 \rangle, \tag{18}$$

$$M_2 = \delta_{\tau_1\tau_1'} \sum_{T_2} A_2 A_2' \langle l_{(1)} \tilde{l}_{(2)} T_2 | q_{12} (1 - P_{12}) | l'_{(1)} \tilde{l}'_{(2)} T_2 \rangle, \tag{19}$$

$$\begin{aligned} M_3 = &- \Delta (l\tilde{l}') A_3 [\langle T_c l_1^{n-1} \tau_1 \tilde{l}_{(N)} \tau' | H_N | T_c l_1^{n-1} \tau_1' l'_{(N)} \tau' \rangle \\ &- \tfrac{1}{2} \delta_{\tau_1\tau_1'} \Delta (\tilde{l} l') E_3] - \Delta (\tilde{l} l') \\ &\times A_3' [\langle T_c l_1^{n-1} \tau_1 l_{(N)} \tau | H_N | T_c l_1^{n-1} \tau_1' \tilde{l}'_{(N)} \tau \rangle \\ &- \tfrac{1}{2} \delta_{\tau_1\tau_1'} \Delta (l\tilde{l}') E_3], \end{aligned} \tag{20}$$

$$\begin{aligned} M_4 = &- \Delta (l_1 \tilde{l}') \\ &\times \sum_{\tau_2\tau_2' T_2} A_4 [\langle T_c l_1^{n-2} \tau_2 \tilde{l}_{(N)} T_2 l \tau' | H_N | T_c l_1^{n-2} \tau_2' l_{1(N)} \tau_1' l' \tau' \rangle \\ &- \tfrac{1}{2} \delta_{\Gamma\Gamma'} \Delta (\tilde{l} l_1) E_4] - \Delta (\tilde{l} l_1) \\ &\times \sum_{\tau_2\tau_2' T_2} A_4' [\langle T_c l_1^{n-2} \tau_2 l_{1(N)} \tau_1 l \tau | H_N | T_c l_1^{n-2} \tau_2' \tilde{l}'_{(N)} T_2 l' \tau \rangle \\ &- \tfrac{1}{2} \delta_{\Gamma\Gamma'} \Delta (l_1 \tilde{l}') E_4], \end{aligned} \tag{21}$$

$$\begin{aligned} M_5 = &- \delta_{\tau\tau'} (1 - \delta_{\Gamma\Gamma'}) \Delta (l_1 \tilde{l}') \Delta (\tilde{l} l_1) \\ &\times \sum_{\tau_2\tau_2' T_2} A_5 A_5' \langle T_c l_1^{n-2} \tau_2 l_{(N)} T_2 | H_N | T_c l_1^{n-2} \tau_2' l'_{(N)} T_2 \rangle, \end{aligned} \tag{22}$$

$$\begin{aligned} M_6 = &\Delta (l_1 \tilde{l}') \Delta (\tilde{l} l') \sum_{\tau_2\tau_2'} A_6 \langle T_c l_1^{n-2} \tau_2 l_{(N)} \tau_1' | H_N | T_c l_1^{n-2} \tau_2' l_{1(N)} \tau_1' \rangle \\ &+ \Delta (l\tilde{l}') \Delta (\tilde{l} l_1) \sum_{\tau_2\tau_2'} A_6' \langle T_c l_1^{n-2} \tau_2 l_{1(N)} \tau_1 | H_N | T_c l_1^{n-2} \tau_2' l'_{(N)} \tau \rangle. \end{aligned} \tag{23}$$

In addition, another term arises, proportional to $\Delta(\tilde{l}\tilde{l}')$. We cannot account for this term and still use the asymptotic values of the radial functions. It is therefore omitted throughout. The following notation is used in (17) — (23)

$$H_N = f_N + q_N, \qquad q_N = \sum_i q_{Ni} (1 - P_{Ni}); \tag{24}$$

$$\begin{aligned} A_1 &= (\tau_1 l [\tau] \tilde{l} T | \tau_1 \tilde{l} [T_2] l T) (1 - \delta_{l_1 l}) (1 - \delta_{l_1 l'}), \\ A_2 &= (\tau_1 l [\tau] \tilde{l} T | \tau_1, l\tilde{l} [T_2] T), \\ A_3 &= (\tau_1 l [\tau] \tilde{l} T | \tau_1 \tilde{l} [\tau'] l T), \\ A_4 &= \overline{G}^{\tau_1}_{\tau_2} \overline{G}^{\tau_1'}_{\tau_2'} (\tau_2 l_1 [\tau_1] l [\tau] \tilde{l} T | \tau_2 \tilde{l} [T_2] l [\tau'] l_1 T), \\ A_5 &= \overline{G}^{\tau_1}_{\tau_2} (\tau_2 l_1 [\tau_1] l \tau | \tau_2 l [T_2] l_1 \tau), \\ A_6 &= \overline{G}^{\tau_1}_{\tau_2} \overline{G}^{\tau_1'}_{\tau_2'} (\tau_2 l_1 [\tau_1] l \tau \tilde{l} T | \tau_2 l [\tau_1'] \tilde{l} [\tau'] l_1 T). \end{aligned} \tag{25}$$

The coefficients A_r' are obtained by means of the substitution $\tau_1 l \tau \tilde{l} \rightleftarrows \tau_1 l' \tau' \tilde{l}'$.

These formulas are valid for both diagonal and nondiagonal matrix elements. If we disregard the uninteresting transitions between terms of excited configurations, then the terms M_0 and M_1 contribute only to the diagonal matrix elements. We shall therefore write from now on $\delta_{\Gamma\Gamma'}$ in M_1 instead of $\delta_{nl,n'l'}$.

In the case of nondiagonal matrix elements, we can have two representations for E_2 and E_3:

$$\begin{aligned} E_2 &= \varepsilon_l + k^2/2, &\qquad E_3 &= \varepsilon_{l_1} + k^2/2; \\ E_2 &= \varepsilon_{l'}' + k'^2/2, &\qquad E_3 &= \varepsilon_{l_1}' + k'^2/2. \end{aligned} \tag{26}$$

ϵ_l and ϵ_{l_1} are the energy parameters of the Hartree-Fock equations for the l and l_1 electrons, corresponding to the atomic state τ; $\epsilon_{l'}'$ and ϵ_{l_1}' are the parameters of the l' and l_1 electrons, corresponding to the atomic state τ_1 (see Appendix).

The expression such as (9) for the matrix element can be obtained by replacing in the sum $\sum_r M_r$ [Eq. (16)] all the M_r except M_0 by $\sum_{\tau_1} \overline{G}^{\tau}_{\tau_1} M_r$, and by putting $l_1 = l$ and $M_1 = M_5 = 0$. In addition, E_2 is written in (26) in the form

$$E_2 = \varepsilon_l + \frac{k^2}{2} - \sum_{\tau_1} [\delta_{\tau_1\tau_1'} - (G^{\tau}_{\tau_1})^2] \langle l_1^{n-1} \tau_1 | Q | l_1^{n-1} \tau_1 \rangle. \tag{27}$$

The expression for the matrix element (10) can be obtained by replacing in the sum $\sum_r M_r$ all the M_r except M_0 by $\sum_{\tau_1\tau_1'} \overline{G}^{\tau}_{\tau_1} \overline{G}^{\tau'}_{\tau_1'} M_r$, and by putting $l_1 = l = l'$ and $M_1 = M_4 = M_5 = M_6 = 0$. In formula (24) it is necessary to leave out the exchange terms if the electrons $l_{(i)}$ and $l_{(N)}$ are equivalent.

If we start out directly with the expressions (16) — (23), we obtain exceedingly complicated equations for the functions F(r). The use of such equations serves no purpose. We therefore confine ourselves to an approximate but much simpler representation. Assuming the nonorthogonality integrals to be small, we omit from (17) — (23) part of those terms that contain simultaneously nonorthogonality integrals and multipole interactions of second or higher order. It can be shown that this is equivalent to neglecting in the terms that contain the nonorthogonality integrals the difference in the terms of the considered configuration, compared with the average energy of the term. In this approximation, the matrix element of type (8) becomes

$$\begin{aligned}\langle\Gamma|H-E|\Gamma'\rangle &= \delta_{\Gamma\Gamma'}\langle T_c\tilde{l}_{(N)}|H_N-\tfrac{1}{2}k^2|T_c\tilde{l}_{(N)}\rangle\\ &+\delta_{\Gamma\Gamma'}\sum_{T_2}A_1A_1'\langle l_1^{n-1}\tau_1\tilde{l}_{(N)}T_2|q_N|l_1^{n-1}\tau_1'\tilde{l}'_{(N)}T_2\rangle\\ &+\delta_{\tau_1\tau_1'}\sum_{T_2}A_2A_2'\langle l_{(1)}\tilde{l}_{(2)}T_2|q_{12}(1-P_{12})\\ &+\lambda_{\Gamma\Gamma'}P_{12}|l'_{(1)}\tilde{l}'_{(2)}T_2\rangle, \end{aligned} \tag{28}$$

$$\lambda_{\Gamma\Gamma'}=-\varepsilon_{l'}'+k^2/2 \quad\text{or}\quad \lambda_{\Gamma\Gamma'}=-\varepsilon+k'^2/2. \tag{29}$$

If Γ is the initial state and Γ' the final state, then the first expression corresponds to the "prior" approximation, while the second to the "post" approximation. Thus, the difference between these two approximation reduces to the difference between the multipliers of the nonorthogonality integrals in the nondiagonal matrix elements* (the two expressions coincide for the diagonal elements). Even this difference disappears, however, if we take for $\epsilon_{\tilde{l}}$ and $\epsilon_{\tilde{l}'}$ the experimental values of the energies of the corresponding states. This way appears to us to be the most advantageous. Lack of space prevents us from giving many arguments in favor of this. We note only that the calculation of the energy parameters of the Hartree-Fock equations with complete self-consistency is a very laborious task.

Matrix elements of type (9) and (10) are obtained by averaging the ion terms, as was done above. In addition, the second term and the right half of (28) is equal to zero.

4. We proceed to separate the radial integrals from the matrix elements. The result can be represented in the following form

$$\begin{aligned}\langle\Gamma|H-E|\Gamma'\rangle &= \delta_{\Gamma\Gamma'}\Big[I_\Gamma+\sum_{\varkappa}a_\Gamma^\varkappa R_\varkappa(l_1\tilde{l},\ l_1\tilde{l})\\ &-\sum_{\varkappa}b_\Gamma^\varkappa R_\varkappa(l_1\tilde{l},\ \tilde{l}l_1)\Big]+\sum_{\varkappa}\alpha_{\Gamma\Gamma'}^\varkappa R_\varkappa(l\tilde{l},\ l'\tilde{l}')\\ &-\sum_{\varkappa}\beta_{\Gamma\Gamma'}^\varkappa\Big[R_\varkappa(l\tilde{l},\tilde{l}'l')-\delta_{\varkappa 0}\frac{(-1)^{l+l'}\lambda_{\Gamma\Gamma'}}{(2l_0+1)^{1/2}(2l'+1)^{1/2}}\\ &\times\Delta(l\tilde{l}')\,\Delta(\tilde{l}\,l')\Big], \end{aligned}\tag{30}$$

$$\begin{aligned}&R_\varkappa(l\tilde{l},\ l'\tilde{l}')\\ &=\iint dr_1dr_2r_<^\varkappa r_>^{-\varkappa-1}P_l(r_1)P_{l'}(r_1)F_\Gamma(r_2)F_{\Gamma'}(r_2),\end{aligned}\tag{31}$$

where $r_<$ ($r_>$) is the smaller (larger) of the r_1 or r_2.

We denote by I_Γ the first term in (28), which contains additive operators and the operator of interaction with the filled shell. The separation of the radial integral from this term entails no difficulty (see, for example, reference 5).

The coefficients a and b are expressed in terms of α and β of the preceding ion

$$a_\Gamma^\varkappa=\sum_{T_2}(A_1)^2\alpha_{\Gamma^*\Gamma^*}^\varkappa,\qquad b_\Gamma^\varkappa=\sum_{T_2}(A_1)^2\beta_{\Gamma^*\Gamma^*}^\varkappa,\qquad \Gamma^*=l_1^{n-1}\tau_1\tilde{l}T_2. \tag{32}$$

The coefficients α and β are of greatest interest, and we shall discuss them in greater detail. Using (25) and the general methods for calculating the matrix elements from the product of tensor operators,[3] we obtain

$$\alpha_{\Gamma\Gamma'}^\varkappa=\delta_{SS'}(-1)^{L_T+l+\tilde{l}'}(l\|C^\varkappa\|l')(\tilde{l}\|C^\varkappa\|\tilde{l}')\begin{Bmatrix}\varkappa & L & L'\\ L_T & \tilde{l}' & \tilde{l}\end{Bmatrix}\mu_{\Gamma\Gamma'}^\varkappa, \tag{33}$$

$$\beta_{\Gamma\Gamma'}^\varkappa=(-1)^{S_T+3/2-S+l+l'}(l\|C^\varkappa\|\tilde{l}')(\tilde{l}\|C^\varkappa\|l')\begin{Bmatrix}\varkappa & L & \tilde{l}'\\ L_T & L' & \tilde{l}\end{Bmatrix}\nu_{\Gamma\Gamma'}^\varkappa. \tag{34}$$

The reduced matrix elements $(l\|C^\kappa\|l')$ are expressed in terms of the 3-j symbols

$$(l\|C^\varkappa\|l')=(-1)^l(2l+1)^{1/2}(2l'+1)^{1/2}\begin{pmatrix}l & \varkappa & l'\\ 0 & 0 & 0\end{pmatrix}. \tag{35}$$

In the case when $L_1=S_1=0$ (for example, one electron outside the filled shell) $\mu^\kappa=\nu^\kappa=1$. In the more general case, we have for the matrix element of type (8)

$$\mu_{\Gamma\Gamma'}^\varkappa=\delta_{\tau_1\tau_1'}(-1)^{\varkappa+L+L'}(2L+1)^{1/2}(2L'+1)^{1/2}\begin{Bmatrix}\varkappa & L & L'\\ L_1 & l' & l\end{Bmatrix}, \tag{36}$$

$$\begin{aligned}\nu_{\Gamma\Gamma'}^\varkappa &=\delta_{\tau_1\tau_1'}(-1)^{-S_T-1/2-S'}(2S+1)^{1/2}(2S'+1)^{1/2}\begin{Bmatrix}S_T & 1/2 & S'\\ S_1 & 1/2 & S\end{Bmatrix}\\ &\times(2L+1)^{1/2}(2L'+1)^{1/2}\begin{Bmatrix}\varkappa & L & \tilde{l}'\\ L_T & L' & \tilde{l}\end{Bmatrix}^{-1}\sum_{L_2}(2L_2+1)\\ &\times\begin{Bmatrix}\tilde{l} & l & L_2\\ L_1 & L_T & L\end{Bmatrix}\begin{Bmatrix}\tilde{l}' & l' & L_2\\ L_1 & L_T & L'\end{Bmatrix}\begin{Bmatrix}\tilde{l} & l & L_2\\ \tilde{l}' & l' & \varkappa\end{Bmatrix}. \end{aligned}\tag{37}$$

For the matrix elements of type (9) and (10) it is necessary to average μ^κ and ν^κ over τ_1 or, respectively, over τ_1 and τ_1', i.e., we must take

$$\sum_{\tau_1}\overline{G}_{\tau_1}^{\tau}\begin{pmatrix}\mu_{\Gamma\Gamma'}^\varkappa\\ \nu_{\Gamma\Gamma'}^\varkappa\end{pmatrix}\ \text{or}\ \sum_{\tau_1\tau_1'}\overline{G}_{\tau_1}^{\tau}\overline{G}_{\tau_1}^{\tau'}\begin{pmatrix}\mu_{\Gamma\Gamma'}^\varkappa\\ \nu_{\Gamma\Gamma'}^\varkappa\end{pmatrix}. \tag{38}$$

Although the parentage coefficients for most configurations of interest were tabulated by Racah, the calculations become most complicated, particularly of matrix element of type (10). However, Racah[3,4] has developed special methods which greatly simplify the calculation in many cases.

5. We can now derive in explicit form the radial integro-differential equations from the variational principle (6). Inasmuch as all the matrix elements are diagonal in L_TS_T, we obtain an independent system of equations for each such pair L_TS_T. This system can be represented in the form

$$\left\{\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-2U_\Gamma(r)+k^2\right\}F_\Gamma(r)=2\sum_{\Gamma'}{}'\,\delta_{TT'}U_{\Gamma\Gamma'}(r)F_{\Gamma'}(r), \tag{39}$$

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*Moreover, only in the exchange terms (see reference 2).

$$U_\Gamma F_\Gamma = \frac{1}{r}\Big[-Z + \sum_{l_1\varkappa} a_\Gamma^\varkappa y^\varkappa_{l_1 l_1}(r)\Big] F_\Gamma(r) - \frac{1}{r}\sum_{l_1\varkappa} b_\Gamma^\varkappa y^\varkappa_{l_1\tilde{l}}(r) P_{l_1}(r)$$
$$+ \frac{1}{r}\sum_\varkappa \alpha^\varkappa_{\Gamma\Gamma}\, y^\varkappa_{ll}(r)\, F_\Gamma(r)$$
$$- \sum_\varkappa \beta^\varkappa_{\Gamma\Gamma}\Big[\frac{1}{r} y^\varkappa_{l\tilde{l}}\,(r) - \delta_{\varkappa 0}\,\frac{\lambda_\Gamma}{2l+1}\,\Delta(l\tilde{l})\Big] P_l(r), \qquad (40)$$

$$U_{\Gamma\Gamma'}F_{\Gamma'} = \frac{1}{r}\sum_\varkappa \alpha^\varkappa_{\Gamma\Gamma'} y^\varkappa_{ll'}(r)\, F_{\Gamma'}(r) - \sum_\varkappa \beta^\varkappa_{\Gamma\Gamma'}\Big[\frac{1}{r} y^\varkappa_{l\tilde{l}'}(r)$$
$$- \delta_{\varkappa 0}\,\frac{(-1)^{l+l'}\lambda_{\Gamma\Gamma'}}{(2l+1)^{1/2}(2l'+1)^{1/2}}\Big] P_{l'}(r). \qquad (41)$$

Here Z is the charge of the nucleus and $\sum_{l_1}$ denotes the summation over all the shells except the outer shell. For filled shells we have

$$a^\varkappa_\Gamma = n_1\delta_{\varkappa 0}, \qquad b^\varkappa_\Gamma = \frac{n_1}{2}\begin{pmatrix} l_1 & \varkappa & \tilde{l} \\ 0 & 0 & 0\end{pmatrix}, \qquad (42)$$

where n_1 is the number of electrons in the shell. For unfilled shells, a_Γ^K and b_Γ^K are determined in accordance with (32). The radial integrals $y^K(r)$ have the form

$$y^\varkappa_{l\tilde{l}}(r) = \int_0^r \Big(\frac{r_1}{r}\Big)^\varkappa P_l(r_1) F_\Gamma(r_1)\, dr_1 + \int_{r_1}^\infty \Big(\frac{r}{r_1}\Big)^{\varkappa+1} P_l(r_1) F_\Gamma(r_1)\, dr_1. \qquad (43)$$

Equations (39) represent an infinite system of coupled integro-differential equations. In practical calculations one frequently uses the approximation of distorted waves, in which only one term with $\Gamma = \Gamma_0$ is left in the right half of (39). In this case, the transition amplitude $T_{\Gamma\Gamma_0}$ can be represented in the form

$$T_{\Gamma\Gamma_0} = -e^{i(\delta_\Gamma+\delta_{\Gamma_0})}\,\frac{2}{k}\int \bar{F}_\Gamma U_{\Gamma\Gamma_0}\bar{F}_{\Gamma_0} dr$$
$$= -e^{i(\delta_\Gamma+\delta_{\Gamma_0})}\,\frac{2}{k}\Big\{\sum_\varkappa \alpha^\varkappa_{\Gamma\Gamma_0}\bar{R}_\varkappa(l_0\tilde{l}_0, l\tilde{l}) - \sum_\varkappa\Big[\beta^\varkappa_{\Gamma\Gamma_0}\bar{R}_\varkappa(l_0\tilde{l}_0, \tilde{l}l)$$
$$+ \frac{(-1)^{l_0+l}\,\delta_{\varkappa 0}\,\lambda_{\Gamma\Gamma_0}}{(2l_0+1)^{1/2}(2l+1)^{1/2}}\,\bar{\Delta}(l_0\tilde{l})\,\Delta(\tilde{l}_0 l)\Big]\Big\}, \qquad (44)$$

where the functions $\bar{F}(r)$ are solutions of Eqs. (39) without the right halves, with use of the asymptotic expression

$$\bar{F}_\Gamma \sim \sin(kr - l\pi/2 + \eta\ln 2kr + \sigma_l + \delta_\Gamma). \qquad (45)$$

The bar over R and Δ denotes the use of $\bar{F}$ instead of F.

APPENDIX

The energy of the atom in the state $T_c l_1^{n-1}\tau_1 l\tau$ can be represented in the form

$$E_a = \langle T_c l_1^{n-1}\tau_1 | H | T_c l_1^{n-1}\tau_1\rangle$$
$$+ \langle T_c l_1^{n-1}\tau_1 l_{(N)}\tau | H_N | T_c l_1^{n-1}\tau_1 l_{(N)}\tau\rangle. \qquad (A1)$$

The Hartree-Fock equations are obtained by varying E_a with respect to P_l. It is easy to show that the second term in (A1) is equal to the energy parameter ϵ_l, since it is the only one that contains the function P_l.

In the case of the state $T_c l^n\tau$ we have

$$E = \sum_{\tau_1}(\bar{G}^\tau_{\tau_1})^2\langle T_c l^{n-1}\tau_1 | H | T_c l^{n-1}\tau_1\rangle$$
$$+ \sum_{\tau_1\tau_1'}\bar{G}^\tau_{\tau_1}\bar{G}^\tau_{\tau_1'}\langle T_c l^{n-1}\tau_1 l^\tau_{(N)} | H_N | T_c l^{n-1}\tau_1 l_{(N)}\tau\rangle. \qquad (A2)$$

To obtain the Hartree-Fock equation it is necessary to vary both terms. It can be shown, however, that the second term is equal to ϵ_l as before. Separating the radial integrals from (A2), we write E_a in the form

$$E_a = \Big[E(T_c) + (n-1)I(l) + \sum_\varkappa \alpha_1^\varkappa R_\varkappa(ll)\Big]$$
$$+ \Big[I(l) + \sum_\varkappa \alpha_2^\varkappa R_\varkappa(ll)\Big] \qquad (A3)$$

On the other hand, the matrix element is

$$\langle T_c l^n\tau | H | T_c l^n\tau\rangle = E(T_c) + nI(l) + \sum_\varkappa \alpha^\varkappa R_\varkappa(ll). \qquad (A4)$$

Varying this expression, we obtain the Hartree-Fock equation for the *l* electron

$$\Big[\mathcal{H} + \frac{2}{n}\sum_\varkappa \alpha^\varkappa y^\varkappa(r)\Big] P_l(r) = \varepsilon_l P_l(r). \qquad (A5)$$

The operator $\mathcal{H}$ occurs when the matrix element $I(l)$ of the single-electron operator is varied. The diagonal matrix elements of the two-electron operator of the atom and the ion are connected by the simple relation

$$\alpha_1^\varkappa = (n-2)\alpha^\varkappa/n, \qquad \text{i.e.}\ \ \alpha_2^\varkappa = 2\alpha^\varkappa/n, \qquad (A6)$$

therefore the second term in (A3) is

$$I(l) + \sum_\varkappa \alpha_2^\varkappa R_\varkappa(ll) = \int_0^\infty dr P_l(r)\Big[\mathcal{H} + \sum_\varkappa \alpha_2^\varkappa y^\varkappa(r)\Big] P_l(r) = \varepsilon_l,$$

and, consequently,

$$\sum_{\tau_1\tau_1'} G^\tau_{\tau_1}\bar{G}^\tau_{\tau_1'}\langle T_c l^{n-1}\tau_1 l_{(N)}\tau\, | H_N | T_c l^{n-1}\tau_1 l_{(N)}\tau\rangle = \varepsilon_l. \qquad (A7)$$

Moreover, it is seen from the derivation that formula (A7) can be generalized by replacing the radial wave function of the *l* electron in the left half of the matrix element:

$$\sum_{\tau_1\tau_1'}\bar{G}^\tau_{\tau_1}\bar{G}^\tau_{\tau_1'}\langle T_c l^{n-1}\tau_1\tilde{l}_{(N)}\tau | H_N | T_c l^{n-1}\tau_1 l_{(N)}\tau\rangle = \varepsilon_l\Delta(\tilde{l}l), \qquad (A8)$$

provided the orbital quantum numbers $\tilde{l}$ and *l* are equal.

It is possible to obtain quite analogously an expression for the energy parameter of the internal electron ϵ_{l_1}.

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[1] J. Percival, M. Seaton, Proc. Cambr. Phil. Soc. **53**, 654 (1957).

[2] Bates, Fundaminsky, Lech, and Massey, Phil. Trans. Roy. Soc. London **243**, 93 and 117 (1950).

[3] G. Racah, Phys. Rev. **62**, 438 (1942).

[4] G. Racah, Phys. Rev. **53**, 367 (1943).

[5] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, Cambridge, 1951.

Translated by J. G. Adashko
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