Matrix elements of the Breit Hamiltonian

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A formulation has been developed for the evaluation of the matrix representation, in sets of $|SM_SLM_L\rangle$, $|SLJM_J\rangle$, or $|JIFM_F\rangle$ functions (as required), of the complete atomic Hamiltonian operator consisting of the electronic, the *SL*-nonsplitting (specific mass, mass variation, Darwin, spin-spin contact, and orbit-orbit) correction terms, and the fine- (spin-orbit and spin-spin dipole) and hyperfine-structure (magnetic dipole, electric quadrupole, and magnetic octupole) interactions. This formulation may be easily implemented in a computer program, appropriate for the accurate evaluation of the energy levels of any atomic system.

INTRODUCTION

Impressive advances have been made throughout the years in the study of atomic structure, at both the experimental and theoretical levels. And yet, the scarcity of information available on atomic energy levels is overwhelming, especially for highly ionized atoms.[1]

At the same time, the need for data is becoming more and more pressing because of the developments in such diverse field as astrophysics and nuclear fusion, plasma, and laser research, all of them of fundamental importance as well as practical impact.

Considerable efforts have been made, in order to face this demand for results, in the development of theoretical formulations and in their implementation in actual calculations. Thus, for example, the formulation of Eissner *et al.*[2] for the matrix elements of some of the terms of the Breit Hamiltonian has been used by Froese Fischer[3] (with multiconfigurational Hartree-Fock radial functions) and in the program SUPERSTRUCTURE (usually employed for configuration-interaction calculations with eigenfunctions of the scaled Thomas-Fermi-Dirac-Amaldi potential, as in the work of Kastner *et al.*[4]). A more complete formulation has been reported by Glass and Hibbert[5] for the matrix elements of the *SL*-nonsplitting corrections and the fine-structure interactions; this formulation has been applied to calculations (e.g., by Glass,[6] using analytical radial functions) and complemented by Glass[7] with the matrix elements of the magnetic dipole and the electric quadrupole hyperfine interactions in a basis of *IJF* functions.

In this work we present all the operators of the Breit Hamiltonian, as well as those corresponding to the electric quadrupole and magnetic octupole interactions, in tensor form, which is then used to derive the expressions of the corresponding matrix elements in a basis of *SL* functions. The present formulation may easily be implemented for practical calculations, as outlined below.

THEORETICAL FORMULATION

Hamiltonian operator

The Breit Hamiltonian operator, after elimination of the dependence on the center-of-mass coordinates and reduction to a nonrelativistic form (Schrödinger operator) plus relativistic and magnetic terms,[8] may be written (for a system centered at the origin of coordinates, with total momentum equal to zero, and retaining only the terms to first order in $1/m_a$, where m_a is the nuclear mass) as

$$H_B = H + H^{(m)} + H^{(H)} + H^{(mH)}$$

The first term in this equation

$$H = H_{\rm el} + H_{\rm SM} + \alpha^2 H_{\rm rel}$$

includes the electronic Hamiltonian $H_{\rm el}$ (electron kinetic energy, nuclear attraction, and electrostatic repulsion), the operator for the specific mass effect, $H_{\rm SM}$, and the relativistic corrections, consisting of the mass variation ($H_{\rm MV}$), the Darwin corrections ($H_{D,1}$ and $H_{D,2}$), the electron spin-spin contact interaction ($H_{\rm SSC}$), the orbit-orbit interaction ($H_{\rm OO}$), the spin-orbit coupling ($H_{\rm SO,1}$ and $H_{\rm SO,2}$), and the electron spin-spin dipole coupling ($H_{\rm SSD}$), α being the fine-structure constant. (The electron-nucleus magnetic dipole interaction, which also appears in H, is presented below together with the interactions with the nuclear electric quadrupole and the nuclear magnetic octupole.)

The terms in H are defined (in units of $\hbar = e = 1$, with $\hbar = h/2\pi$, and where h is the Planck constant and e represents the absolute value of the electron charge) as

$$H_{\rm el} = (1/2\mu)\sum_{\rho} p_\rho^2 - Z\sum_{\rho} r_\rho^{-1} + \sum_{\substack{\rho,\sigma \\ (\rho<\sigma)}} r_{\rho\sigma}^{-1} ,$$

$$H_{\rm SM} = (1/m_a) \sum_{\substack{\rho,\sigma \\ (\rho<\sigma)}} (\mathbf{p}_\rho \cdot \mathbf{p}_\sigma) ,$$

$$H_{\rm MV} = -(1/8m^3)\sum_{\rho} p_\rho^4 ,$$

$$H_{D,1} = (\pi Z/2m^2)\sum_{\rho} \delta(\mathbf{r}_\rho) ,$$

$$H_{D,2} = -(\pi/m^2) \sum_{\substack{\rho,\sigma \\ (\rho<\sigma)}} \delta(\mathbf{r}_{\rho\sigma}) ,$$

$$H_{\rm SSC} = -(8\pi/3m^2) \sum_{\substack{\rho,\sigma \\ (\rho<\sigma)}} (\mathbf{s}_\rho \cdot \mathbf{s}_\sigma)\delta(\mathbf{r}_{\rho\sigma}) ,$$

$$H_{OO}=-(1/2m^2)\sum_{\substack{\rho,\sigma\\(\rho<\sigma)}}\{r_{\rho\sigma}^{-1}(\mathbf{p}_\rho\cdot\mathbf{p}_\sigma)+\mathbf{r}_{\rho\sigma}\cdot[r_{\rho\sigma}^{-3}(\mathbf{r}_\rho\cdot\mathbf{p}_\rho)\mathbf{p}_\sigma]\},$$

$$H_{SO,1}=(Z/2m^2)\sum_\rho r_\rho^{-3}[\mathbf{s}_\rho\cdot(\mathbf{r}_\rho\times\mathbf{p}_\rho)],$$

$$H_{SO,2}=(1/2m^2)\sum_{\substack{\rho,\sigma\\(\rho\neq\sigma)}} r_{\rho\sigma}^{-3}[\mathbf{s}_\rho\cdot(2\mathbf{r}_{\rho\sigma}\times\mathbf{p}_\sigma-\mathbf{r}_{\rho\sigma}\times\mathbf{p}_\rho)],$$

$$H_{SSD}=-(1/m^2)\sum_{\substack{\rho,\sigma\\(\rho<\sigma)}} r_{\rho\sigma}^{-5}[3(\mathbf{s}_\rho\cdot\mathbf{r}_{\rho\sigma})(\mathbf{s}_\sigma\cdot\mathbf{r}_{\rho\sigma})-r_{\rho\sigma}^2(\mathbf{s}_\rho\cdot\mathbf{s}_\sigma)],$$

where the summations extend over the electrons, ρ and σ. Each electron is characterized by its position vector $\mathbf{r}_\rho$, (referred to the nucleus), linear momentum vector $\mathbf{p}_\rho$, and electron spin vector $\mathbf{s}_\rho$; $\mathbf{r}_{\rho\sigma}$ is the position vector $\mathbf{r}_{\rho\sigma}=\mathbf{r}_\rho-\mathbf{r}_\sigma$. The electron mass is denoted by m, μ stands for the reduced mass, Z is the nuclear charge, and $\delta(\mathbf{r}_\rho)$ represents the three-dimensional Dirac function.

The remaining terms ($H^{(m)}$, $H^{(H)}$, and $H^{(mH)}$) will not be considered here, as they are proportional to α^2/m_a, depend on the external magnetic field, or both, respectively.

Tensor operators

The matrix elements are best evaluated using the techniques of tensor operator algebra, which requires that the terms of the Hamiltonian operator be transformed first to tensor form. The resulting expressions (except for the appropriate mass-correction factors[9]) are the following:

$$H_{el}=\sum_\rho(T_\rho-Z/r_\rho)+\sum_k\sum_{\substack{\rho,\sigma\\(\rho<\sigma)}}(r_<^k/r_>^{k+1})[\mathbf{C}^{(k)}(\rho)\cdot\mathbf{C}^{(k)}(\sigma)],$$

$$H_{SM}=-(1/m_a)\sum_{\substack{\rho,\sigma\\(\rho<\sigma)}}\{[\mathbf{C}^{(1)}(\rho)\cdot\mathbf{C}^{(1)}(\sigma)]\partial_\rho\partial_\sigma-\sqrt{2}[\mathbf{C}^{(1)}(\rho)\cdot\mathbf{R}^{(1,1)}(\sigma)]r_\sigma^{-1}\partial_\rho-\sqrt{2}[\mathbf{R}^{(1,1)}(\rho)\cdot\mathbf{C}^{(1)}(\sigma)]r_\rho^{-1}\partial_\sigma+2[\mathbf{R}^{(1,1)}(\rho)\cdot\mathbf{R}^{(1,1)}(\sigma)]r_\rho^{-1}r_\sigma^{-1}\},$$

$$H_{MV}=-(\alpha^2/2)\sum_\rho T_\rho^2,$$

$$H_{D,1}=(\pi\alpha^2Z/2)\sum_\rho\delta(\mathbf{r}_\rho),$$

$$H_{D,2}=-(\alpha^2/4)\sum_{\substack{\rho,\sigma\\(\rho<\sigma)}}\left[r_\rho^{-2}\delta(r_{\rho\sigma})\sum_k(2k+1)[\mathbf{C}^{(k)}(\rho)\cdot\mathbf{C}^{(k)}(\sigma)]\right],$$

$$H_{SSC}=-(2\alpha^2/3)\sum_{\substack{\rho,\sigma\\(\rho<\sigma)}}\left[r_\rho^{-2}\delta(r_{\rho\sigma})[\mathbf{s}^{(1)}(\rho)\cdot\mathbf{s}^{(1)}(\sigma)]\sum_k(2k+1)[\mathbf{C}^{(k)}(\rho)\cdot\mathbf{C}^{(k)}(\sigma)]\right],$$

$$H_{OO}=(\alpha^2/2)\sum_{\substack{\rho,\sigma\\(\rho<\sigma)}}\sum_k h_{OO}^{(k)}(\rho,\sigma)$$

with

$$\begin{aligned}h_{OO}^{(k)}(\rho,\sigma)=&[\mathbf{C}^{(k)}(\rho)\cdot\mathbf{C}^{(k)}(\sigma)](\{[k(k+1)/(2k-1)](r_<^{k-1}/r_>^k)-[k(k+1)/(2k+3)](r_<^{k+1}/r_>^{k+2})\}\partial_\rho\partial_\sigma\\&+(k/2)[(r_\rho^{k-1}/r_\sigma^{k+1})\partial_\rho-(r_\sigma^{k-1}/r_\rho^{k+1})\partial_\rho]+[(k+1)/2][-(r_\rho^k/r_\sigma^{k+2})\partial_\rho+(r_\sigma^k/r_\rho^{k+2})\partial_\sigma])\\&+[\mathbf{C}^{(k)}(\rho)\cdot\mathbf{R}^{(k,k)}(\sigma)](\{[k(k+1)]^{1/2}/(2k+3)\}[-k(r_\rho^{k+1}/r_\sigma^{k+2})+(k+3)(r_\sigma^{k+1}/r_\rho^{k+2})]\\&+\{[k(k+1)]^{1/2}/(2k-1)\}[(k-2)(r_\rho^{k-1}/r_\sigma^k)-(k+1)(r_\sigma^{k-1}/r_\rho^k)])r_\sigma^{-1}\partial_\rho\\&+[\mathbf{R}^{(k,k)}(\rho)\cdot\mathbf{C}^{(k)}(\sigma)](\{[k(k+1)]^{1/2}/(2k+3)\}[(k+3)(r_\rho^{k+1}/r_\sigma^{k+2})-k(r_\sigma^{k+1}/r_\rho^{k+2})]\\&+\{[k(k+1)]^{1/2}/(2k-1)\}[(k+1)(r_\rho^{k-1}/r_\sigma^k)-(k-2)(r_\sigma^{k-1}/r_\rho^k)])r_\rho^{-1}\partial_\sigma\\&+[\mathbf{R}^{(k,k)}(\rho)\cdot\mathbf{R}^{(k,k)}(\sigma)]\{[k(k+3)/(2k+3)](r_<^{k+1}/r_>^{k+2})-[(k-2)(k+1)/(2k-1)](r_<^{k-1}/r_>^k)\}r_\rho^{-1}r_\sigma^{-1}\\&-[\mathbf{R}^{(k-1,k)}(\rho)\cdot\mathbf{R}^{(k-1,k)}(\sigma)]\{[2(2k-1)/(k+1)](r_<^k/r_>^{k+1})r_\rho^{-1}r_\sigma^{-1}\}\\&-[\mathbf{R}^{(k-1,k)}(\rho)\cdot\mathbf{C}^{(k)}(\sigma)][k(2k-1)/2]^{1/2}[(r_\rho^{k-2}/r_\sigma^{k+1})-(r_\sigma^k/r_\rho^{k+3})]\\&-[\mathbf{C}^{(k)}(\rho)\cdot\mathbf{R}^{(k-1,k)}(\sigma)][k(2k-1)/2]^{1/2}[(r_\rho^k/r_\sigma^{k+3})-(r_\sigma^{k-2}/r_\rho^{k+1})],\end{aligned}$$

$$H_{SO}=(Z\alpha^2/2)\sum_\rho r_\rho^{-3}[\mathbf{s}^{(1)}(\rho)\cdot\mathbf{l}^{(1)}(\rho)]+(\alpha^2/2)\sum_{\substack{\rho,\sigma\\(\rho<\sigma)}}(1+T'_{\rho\sigma})[\mathbf{s}^{(1)}(\rho)+2\mathbf{s}^{(1)}(\sigma)]\cdot\sum_k(-1)^{k+1}h_{SO}^{(k)}(\rho,\sigma)$$

with

$$h_{SO}^{(k)}=[\mathbf{C}^{(k)}(\rho)\times\mathbf{C}^{(k)}(\sigma)]^{(1)}[k(k+1)(2k+1)/3]^{1/2}[(r_\rho^{k-1}/r_\sigma^{k+1})+(r_\sigma^k/r_\rho^{k+2})]\partial_\rho$$
$$+[\mathbf{R}^{(k,k)}(\rho)\times\mathbf{C}^{(k)}(\sigma)]^{(1)}[(2k+1)/3]^{1/2}[k(r_\sigma^k/r_\rho^{k+3})-(k+1)(r_\rho^{k-2}/r_\sigma^{k+1})]$$
$$-[\mathbf{R}^{(k-1,k)}(\rho)\times\mathbf{C}^{(k-1)}(\sigma)]^{(1)}[(2k+1)/3]^{1/2}(2k-1)(r_\sigma^{k-1}/r_\rho^{k+2})$$
$$+[\mathbf{R}^{(k+1,k)}(\rho)\times\mathbf{C}^{(k+1)}(\sigma)]^{(1)}[(2k+1)/3]^{1/2}(2k+3)(r_\rho^{k-1}/r_\sigma^{k+2}),$$

$$H_{SSD}=(\alpha^2/\sqrt{5})\sum_{\substack{\rho,\sigma\\(\rho<\sigma)}}\sum_k(-1)^k[k(k+1)(2k-1)(2k+1)(2k+3)]^{1/2}$$
$$\times([\mathbf{s}^{(1)}(\rho)\times\mathbf{s}^{(1)}(\sigma)]^{(2)}\cdot\{(r_\rho^{k-1}/r_\sigma^{k+2})[\mathbf{C}^{(k-1)}(\rho)\times\mathbf{C}^{(k+1)}(\sigma)]^{(2)}$$
$$+(r_\sigma^{k-1}/r_\rho^{k+2})[\mathbf{C}^{(k+1)}(\rho)\times C^{(k-1)}(\sigma)]^{(2)}\}),$$

$$H_D=g_e\mu_B\sum_\rho(r_\rho^{-3}\{\mathbf{l}^{(1)}(\rho)-(10)^{1/2}[\mathbf{s}^{(1)}(\rho)\times\mathbf{C}^{(2)}(\sigma)]^{(1)}\}+\tfrac{2}{3}r_\rho^{-2}\delta(r_\rho)\mathbf{s}^{(1)}(\rho))\cdot\mathbf{N}^{(1)},$$

$$H_Q=-[\sqrt{6}Q/2I(2I-1)]\sum_\rho r_\rho^{-3}[\mathbf{C}^{(2)}(\rho)\cdot\mathbf{I}^{(2)}],$$

$$H_O=-(\tfrac{5}{3})^{1/2}\mu_B\sum_\rho r_\rho^{-5}\{[6-\tfrac{8}{7}r_\rho\delta(r_\rho)][\mathbf{s}^{(1)}(\rho)\times C^{(2)}(\rho)]^{(3)}-2[\mathbf{C}^{(2)}(\rho)\times\mathbf{l}^{(1)}(\rho)]^{(3)}\}\cdot\mathbf{N}^{(3)},$$

where the expressions for the interactions with the nuclear magnetic dipole (H_D), the nuclear electric quadrupole (H_Q), and the nuclear magnetic octupole (H_O) are those given by Armstrong.[10] In the above expressions, T stands for the kinetic energy operator, $r_<$ and $r_>$ are the lesser and the greater, ∂_ρ is an abbreviation for $\partial/\partial r_\rho$, μ_B is the Bohr magneton, and g_e is the electron g factor; $T'_{\rho\sigma}$ denotes the transposition of ρ and σ. The nuclear spin vector is denoted by $\mathbf{I}$ and the nuclear tensor operators $\mathbf{N}^{(k)}$ are characterized by the expectation values (for $M_I=I$)

$$\mu_I=(IM_I\,|\,\mathbf{N}^{(1)}\,|\,IM_I),$$
$$\Omega=-(IM_I\,|\,\mathbf{N}^{(3)}\,|\,IM_I),$$

where μ_I and Ω denote the nuclear magnetic dipole and octupole moments, respectively. (The nuclear electric quadrupole moment is represented by Q.) The modified spherical harmonic tensors have components

$$C_q^{(k)}=[4\pi/(2k+1)]^{1/2}Y_q^{(k)}$$

(where $Y_q^{(k)}$ denotes a spherical harmonic) and

$$\mathbf{R}^{(k,k')}=(\mathbf{C}^{(k)}\times\mathbf{l}^{(1)})^{(k')}.$$

Matrix elements

The matrix elements are evaluated for $|\,C\beta SM_SLM_L)$ functions (when only the electrostatic and SL-nonsplitting interactions are considered), $|\,C\beta SLJM_J)$ functions (when the fine-structure coupling is included), or $|\,C\beta JIFM_F)$ functions (when the hyperfine-structure interactions are included), where C denotes the configuration and S, M_S, L, M_L, J, M_J, I, F, and M_F are the usual quantum numbers, while β includes all the additional details needed in order to completely label the state.

Application of tensor algebra yields the expressions of the matrix elements as expansions of radial and angular integrals and SL-coupling coefficients, denoted in this work as $(\{l\}\{m\mu\}_u M_S M_L\,|\,\beta SL)$, where $\{l\}$ and $\{m\mu\}$ stand for the sets of quantum numbers $l_1,l_2,\ldots,l_N$ and $m_1\mu_1,m_2\mu_2,\ldots,m_N\mu_N$, N being the number of electrons and m_i and μ_i the orbital and spin angular momentum z-component quantum numbers.

The resulting expressions are as follows.

a. Electronic and SL-nonsplitting terms. The one- and two-electron tensor operators in the electronic and nonsplitting terms of the Hamiltonian operator may be expressed, in a general fashion, as

$$\mathbf{T}^{(0)}(\rho)=[\mathbf{S}^{(0)}(\rho)\cdot\mathbf{L}^{(0)}(\rho)],$$
$$\mathbf{T}^{(0)}(\rho,\sigma)=[\mathbf{S}^{(\kappa\kappa 0)}(\rho,\sigma)\cdot\mathbf{L}^{(kk0)}(\rho,\sigma)],$$

where $\mathbf{S}^{(\kappa\kappa 0)}$ and $\mathbf{L}^{(kk0)}$ denote composite spin and orbital angular tensor operators. Denoting by $f(r_\rho)$ and $f(r_\rho,r_\sigma)$ the corresponding one- and two-electron radial components, the corresponding matrix elements may then be written, respectively, as

$$\left(C\beta SM_SLM_L\left|\sum_\rho f(r_\rho)\mathbf{T}^{(0)}(\rho)\right|C'\beta'S'M'_SL'M'_L\right)$$
$$=\delta(SM_SLM_L,S'M'_SL'M'_L)\sum_u\sum_v\left[(\{l\}\{m\mu\}_u M_S M_L\,|\,\beta SL)(\{l'\}\{m'\mu'\}_v M_S M_L\,|\,\beta' SL)\right.$$
$$\left.\times\sum_i\epsilon_i R(n_il_i;n'_il'_i)\delta(l_im_i\mu_i,l'_im'_i\mu'_i)\right],$$

$$\left[C\beta SM_S LM_L \left| \sum_{\substack{\rho,\sigma \\ (\rho<\sigma)}} f(r_\rho,r_\sigma)\mathbf{T}^{(0)}(\rho,\sigma) \right| C'\beta'S'M'_S L'M'_L \right]$$

$$=\delta(SM_S LM_L,S'M'_S L'M'_L)\sum_u\sum_v \Bigg[(\{l\}\{m\mu\}_u M_S M_L \mid \beta SL)(\{l'\}\{m'\mu'\}_v M_S M_L \mid \beta' SL)$$

$$\times \sum_{\substack{i,j \\ (i<j)}} \omega_{ij}P'_{ij}R(n_i l_i,n_j l_j;n'_i l'_i,n'_j l'_j)(\tfrac{1}{2}\mu_i \tfrac{1}{2}\mu_j \mid \mathbf{S}_0^{(\kappa\kappa 0)}(1,2) \mid \tfrac{1}{2}\mu'_i \tfrac{1}{2}\mu'_j)$$

$$\times (l_i m_i l_j m_j \mid L_0^{(kk0)}(1,2) \mid l'_i m'_i l'_j m'_j) \Bigg] ,$$

where the summations over i and j extend to the spin orbitals and the summations over u and v extend over the sets of quantum numbers $\{m\mu\}$. The coefficient ϵ_i may take the values 1 (for all i, when the two configurations are identical), δ_{ip} (if the two configurations differ only in the spin orbitals at the p position), and 0 (if the two configurations differ in two or more spin orbitals). The coefficient ω_{ij} takes the values 1 (for any i,j, if the two configurations are identical), δ_{jq} (if the two configurations differ in the spin orbitals at the q position), $\delta_{ip}\delta_{jq}$ (if the two configurations differ in the spin orbitals at the p and q positions), and 0 (if the two configurations differ in more than two spin orbitals). P'_{ij} stands for $1-T'_{ij}$, where T'_{ij} denotes the transposition of the spin orbitals $\mid n'_i l'_i m'_i \mu'_i)$ and $\mid n'_j l'_j m'_j \mu'_j)$ The symbol δ represents the usual Kronecker delta.

The one- and two-electron radial integrals are given by

$$R(n_i l_i;n_j l_j)=\int r^2 dr\, R_i(r)f(r)R_j(r) ,$$

$$R(n_i l_i,n_j l_j;n'_i l'_i,n'_j l'_j)$$

$$=\int r_1^2 dr_1 \int r_2^2 dr_2 R_i(r_1)R'_i(r_1)f(r_{1,2})R_j(r_2)R'_j(r_2) ,$$

respectively, where R_i denotes the radial function of the orbital $n_i l_i$.

b. Fine-structure coupling. The one- and two-electron tensor operators in the fine-structure terms are of the general form

$$\mathbf{T}^{(0)}(\rho)=[\mathbf{S}^{(K)}(\rho)\cdot\mathbf{L}^{(K)}(\rho)] ,$$

$$\mathbf{T}^{(0)}(\rho,\sigma)=[\mathbf{S}^{(\kappa\kappa' K)}(\rho,\sigma)\cdot\mathbf{L}^{(kk' K)}(\rho,\sigma)] ,$$

and the elements of the interaction matrix are given by

$$\left[C\beta SLJM_J \left| \sum_\rho f(r_\rho)\mathbf{T}^{(0)}(\rho) \right| C'\beta'S'L'J'M'_J \right]$$

$$=\delta(M_S M_L JM_J,M'_S M'_L J'M'_J)(-1)^{S'+L+J}[(2S+1)(2L+1)]^{1/2}\,[(L'M_L K0 \mid LM_L)(S'M_S K0 \mid SM_S)]^{-1}\begin{Bmatrix} S' & L' & J \\ L & S & K \end{Bmatrix}$$

$$\times\sum_u\sum_v \Bigg[(\{l\}\{m\mu\}_u M_S M_L \mid \beta SL)(\{l'\}\{m'\mu'\}_v M_S M_L \mid \beta' S'L')$$

$$\times \sum \epsilon_i R(n_i l_i;n'_i l'_i)(\tfrac{1}{2}\mu_i \mid S_0^{(K)}(1) \mid \tfrac{1}{2}\mu'_i)(l_i m_i \mid L_0^{(K)}(1) \mid l'_i m'_i) \Bigg] ,$$

$$\left[C\beta SLJM_J \left| \sum_{\substack{\rho,\sigma \\ (\rho<\sigma)}} f(r_\rho,r_\sigma)\mathbf{T}^{(0)}(\rho,\sigma) \right| C'\beta'S'L'J'M'_J \right]$$

$$=\delta(M_S M_L JM_J,M'_S M'_L J'M'_J)(-1)^{S'+L+J}[(2S+1)(2L+1)]^{1/2}\,[(L'M_L K0 \mid LM_L)(S'M_S K0 \mid SM_S)]^{-1}\begin{Bmatrix} S' & L' & J \\ L & S & K \end{Bmatrix}$$

$$\times\sum_u\sum_v \Bigg[(\{l\}\{m\mu\}_u M_S M_L \mid \beta SL)(\{l'\}\{m'\mu'\}_v M_S M_L \mid \beta' S'L')$$

$$\times \sum \omega_{ij}P'_{ij}R(n_i l_i,n_j l_j;n'_i l'_i,n'_j l'_j)(\tfrac{1}{2}\mu_i \tfrac{1}{2}\mu_j \mid S_0^{(\kappa\kappa' K)}(1,2) \mid \tfrac{1}{2}\mu'_i \tfrac{1}{2}\mu'_j)(l_i m_i l_j m_j \mid L_0^{(kk' K)}(1,2) \mid l'_i m'_i l'_j m'_j) \Bigg] ,$$

where the standard notation has been used for the Clebsch-Gordan coefficients and the 6-j symbols.

c. Hyperfine-structure corrections. The one-electron tensor operators in the hyperfine-structure terms are of the general form

$$\mathbf{T}^{(0)}(\rho)=\{[\mathbf{S}^{(\kappa)}(\rho)\times\mathbf{L}^{(k)}(\rho)]^{(K)}\cdot\mathbf{N}^{(K)}\}$$

and the elements of the interaction matrix are given by

$$\left(C\beta JIFM_F\left|\sum_\rho f(r_\rho)\mathbf{T}^{(0)}(\rho)\right|C'\beta'J'IF'M_F'\right)$$

$$=\delta(M_SM_LFM_F,M_S'M_L'F'M_F')(-1)^{I+J+F}[(2I+1)(2J+1)(2J'+1)(2L+1)(2S+1)(2K+1)]^{1/2}$$

$$\times[(IM_IK0\,|\,IM_I)(L'M_Lk0\,|\,LM_L)(S'M_S\kappa0\,|\,SM_S)]^{-1}(IM_I\,|\,N_0^{(K)}\,|\,IM_I)\begin{Bmatrix}I & J' & F\\ J & I & K\end{Bmatrix}\begin{Bmatrix}S & L & J\\ S' & L' & J'\\ \kappa & k & K\end{Bmatrix}$$

$$\times\sum_u\sum_v\left[(\{l\}\{m\mu\}_uM_SM_L\,|\,\beta SL)(\{l'\}\{m'\mu'\}_vM_SM_L\,|\,\beta'S'L')\right.$$

$$\left.\times\sum\epsilon_iR(n_il_i;n_i'l_i')(\tfrac{1}{2}\mu_i\,|\,S_0^{(\kappa)}(1)\,|\,\tfrac{1}{2}\mu_i')(l_im_i\,|\,L_0^{(k)}(1)\,|\,l_i'm_i')\right],$$

where the standard notation has been used for the $9-j$ symbol.

The specific expressions for the matrix elements of the individual components of the Hamiltonian operator may be easily generated from these general relationships by evaluating the integrals for $S_0^{(\kappa)}$, $L_0^{(k)}$, and $N_0^{(K)}$ for each case, as exemplified below for some chosen interactions.

(i) For the electrostatic interaction one has

$$\mathbf{T}^{(0)}(\rho,\sigma)=r_{\rho\sigma}^{-1}=\sum_k(r_<^k/r_>^{k+1})[\mathbf{C}^{(k)}(\rho)\cdot\mathbf{C}^{(k)}(\sigma)]$$

so that

$$\mathbf{S}^{(\kappa\kappa0)}(\rho,\sigma)=1\,,$$

$$\mathbf{L}^{(kk0)}(\rho,\sigma)=[\mathbf{C}^{(k)}(\rho)\cdot\mathbf{C}^{(k)}(\sigma)]\,,$$

and

$$(\tfrac{1}{2}\mu_i\,\tfrac{1}{2}\mu_j\,|\,S_0^{(\kappa\kappa0)}(1,2)\,|\,\tfrac{1}{2}\mu_i'\,\tfrac{1}{2}\mu_j')=\delta(\mu_i,\mu_i')\delta(\mu_j,\mu_j')\,,$$

$$(l_im_il_jm_j\,|\,L_0^{(kk0)}(1,2)\,|\,l_i'm_i'l_j'm_j')$$

$$=\delta(m_i+m_j,m_i'+m_j')(-1)^q$$

$$\times[(2l_i'+1)(2l_j'+1)/(2l_i+1)(2l_j+1)]^{1/2}$$

$$\times\{l_i'm_i'k-q\,|\,l_im_i\}\{l_j'm_j'kq\,|\,l_jm_j\}$$

with $q=m_i-m_i'=m_j'-m_j$ and where

$$\{l_j'm_j'kq\,|\,l_jm_j\}=(l_j'm_j'kq\,|\,l_jm_j)(l_j'0k0\,|\,l_j0)\,.$$

(ii) For the spin-own-orbit interaction one has

$$\mathbf{T}^{(0)}(\rho)=[\mathbf{s}^{(1)}(\rho)\cdot\mathbf{l}^{(1)}(\rho)]$$

so that

$$(\tfrac{1}{2}\mu_i\,|\,s_0^{(1)}(1)\,|\,\tfrac{1}{2}\mu_i')(l_im_i\,|\,l_0^{(1)}(1)\,|\,l_i'm_i')=\delta(\mu,\mu_i')(1/\sqrt{2})(\tfrac{1}{2}\mu_i10\,|\,\tfrac{1}{2}\mu_i)(\tfrac{1}{2}||\mathbf{s}^{(1)}||\tfrac{1}{2})$$

$$\times\delta(m_i,m_i')(2l_i+1)^{-1/2}(l_i'm_i10\,|\,l_im_i)(l_i||\mathbf{l}^{(1)}||l_i')$$

$$=\delta(l_i,l_i')\delta(m_i,m_i')\delta(\mu_i,\mu_i')m_i\mu_i\,.$$

(iii) In the case of the nuclear electric quadrupole interaction one obtains

$$(C\beta JIFM_F\,|\,H_Q\,|\,C'\beta'J'IF'M_F')$$

$$=-(Q/2)\delta(SM_SM_LFM_F,S'M_S'M_L'F'M_F')(-1)^{I+S+L'+F}$$

$$\times[(I+1)(2I+1)(2I+3)(2J+1)(2J'+1)(2L+1)/I(2I-1)]^{1/2}(L'M_L20\,|\,LM_L)^{-1}\begin{Bmatrix}I & J' & F\\ J & I & 2\end{Bmatrix}\begin{Bmatrix}J' & L' & S\\ L & J & 2\end{Bmatrix}$$

$$\times\sum\left[(\{l\}\{m\mu\}_uM_SM_L\,|\,\beta SL)(\{l'\}\{m'\mu'\}_vM_SM_L\,|\,\beta'SL')\right.$$

$$\left.\times\sum\epsilon_iR_Q(n_il_i;n_i'l_i')\delta(m_i,m_i')\delta(\mu_i,\mu_i')\{l_i'm_i20\,|\,l_im_i\}[(2l_i'+1)/(2l_i+1)]^{1/2}\right]$$

with

$$I_0^{(2)}=[\mathbf{I}^{(1)}\times\mathbf{I}^{(1)}]_0^{(2)}$$

$$=-\left[\frac{1}{2\sqrt{6}}\right]I_+I_--\left[\frac{1}{2\sqrt{6}}\right]I_-I_++(2/\sqrt{6})I_z^2\,,$$

$$(IM_I\,|\,I_0^{(2)}\,|\,IM_I)=I(2I-1)/\sqrt{6}\quad(\text{for } M_I=I)$$

and where

$$R_Q(n_il_i;n_i'l_i')=\langle n_il_i\,|\,r^{-3}\,|\,n_i'l_i'\rangle\,.$$

PRACTICAL IMPLEMENTATION

The expressions given above for the matrix elements between SL functions are appropriate for calculations within the framework of a configuration-interaction treatment. The general organization of the calculations could be summarized as follows.

(a) The configurations to be included are selected and the common set of atomic orbitals listed.

(b) The radial functions are determined, as accurately as possible (see below), for the atomic orbitals listed above, with the condition (imposed by the formulation) that those corresponding to orbitals of the same symmetry designation be orthogonal. Although, in principle, any method that yields such functions is acceptable, it may be convenient to carry out the calculations within the framework of a multiconfigurational self-consistent-field approach (e.g., using the Hartree-Fock program of Froese Fischer[11]).

(c) The SL-coupling coefficients for the interacting monoconfigurational states are determined (using, e.g., the program of Nussbaumer[12]). In this connection, it should be mentioned that care should be exercised in choosing the M_S and M_L (and, therefore, the corresponding vector coupling coefficients) for which the matrix element is to be evaluated.

(d) The energy matrix representation of the chosen Hamiltonian operator is constructed, in the set of appropriate states of the configurations under consideration, for each symmetry designation. The contributions to its elements must be corrected by the appropriate factors needed in order to account for the relativistic mass correction.[9]

(e) Each energy matrix is diagonalized, yielding the eigenvalues for the corresponding symmetry designations.

(f) The final energy-level prediction is then obtained by referring all the energy values to the lowest one, taken as ground state, and correcting for the normal mass effect.

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