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Relativistic Hartree-Fock-Roothaan theory for open-shell atoms

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The expansion method for the nonrelativistic Hartree-Fock theory by Roothaan is extended to relativistic cases for general open-shell atoms. Numerical applications of the theory to the first transition elements are carried out. It is shown that the conventional approximation of the exchange potential shifts the energy value considerably, whereas the off-diagonal Lagrange multiplier has little effect on the energy. Some problems in the application of the theory to open-shell atoms are discussed.

I. INTRODUCTION

The recent relativistic Hartree-Fock (RHF) calculation[1] for all atoms in the periodic system has shown that a complete treatment of the exchange integrals of the repulsive Coulomb interaction term is important for the ground-state energy of open-shell atoms such as the transition elements.

The RHF theory derived by Swirles[2] and Grant[3-5] is based on the semirelativistic wave equation that is well known as the Breit equation.[6-8] Although not fully Lorentz invariant, it is used as an approximate wave equation. For either RHF or nonrelativistic Hartree-Fock (NRHF) theory, there are two alternative schemes to solve the Hartree-Fock equation. One is the numerical integration method of Hartree[9]; the other is the expansion method of Roothaan,[10-12] where orbitals are expanded in terms of analytical functions. In the application of the Hartree-Fock theory to open-shell systems, one cannot obtain a single closed pseudo-eigenvalue equation because of the off-diagonal Lagrange multipliers (ODLM). The Roothaan expansion method can give the separate pseudo-eigenvalue equations for closed- and open-shell orbitals.

Kim[13] has extended the expansion method to the relativistic closed-shell atoms. Although many relativistic calculations for atoms have been reported, no calculation using the relativistic Hartree-Fock-Roothaan (RHFR) theory, that is, the expansion method, has been carried out except that for helium, beryllium and neon by Kim. The purpose of this work is to present the RHFR theory for general open-shell atoms.

According to approximate ways for treating the exchange potential, relativistic calculations by the numerical integration method are classified into three types, namely, relativistic Hartree (RH),[14-16] Hartree-Fock-Slater or modified Slater (RHFS),[17-21] and Dirac-Hartree-Fock (DHF),[1,22-26] where the exchange integrals have been treated exactly for closed-shell atoms but approximately for open-shell atoms by the use of a value averaged over the shell. The DHF wave function has been obtained by neglecting the ODLM for open-shell atoms. Some of the DHF results concerning the ground-state configuration of atoms such as Cu or Cr are not consistent with experiment, whereas the NRHF calculation[27] for Cu, in which the ODLM has been treated rigorously, has given the same ground-state configuration as the experimental one. In the present work, the RHFR theory of Kim[13] is extended to general open-shell atoms. It is interesting to investigate the effect of the exchange potential and the ODLM on the energy.

In the present RHFR theory, we assume that states considered satisfy the following conditions: (a) The state has no more than one open shell for each symmetry species; (b) The wave function for the state is expressed by a single configuration; (c) When the configuration contains only one open shell, the state can be uniquely specified by the total angular-momentum quantum number J and the seniority number v; (d) When the configuration contains more than one open shell, the state can be uniquely specified by J only.

For the ground state or some lower excited states, it is assumed that the angular momentum j of each shell takes a value less than $\frac{9}{2}$. This assumption leads to a simple treatment of two-electron integrals, since the expectation value of any two-body interaction operator with a wave function constructed from orbitals with $j \leq \frac{7}{2}$, is diagonal in the seniority scheme[28,29] which is used in the present treatment. The Breit interaction and the effect of the finite nucleus are included in the theory as a first-order perturbation. Numerical applications of the theory to the first transition elements are made. Some problems in the application of the theory are discussed.

II. FORMULATION

A. Hamiltonian and wave function

The total Hamiltonian is divided into two parts, one unperturbed and the other perturbed:

$$\hat{H}_T = \hat{H} + \hat{H}' \,, \tag{1}$$

where

$$\hat{H} = \sum_{\mu} \hat{H}'_D(\mu) + \sum_{\mu<\nu} \frac{1}{r_{\mu\nu}} \tag{2}$$

and

$$\hat{H}' \equiv \hat{H}_{\rm B} + \hat{H}_{\rm FN} \,. \tag{3}$$

$\hat{H}'_D(\mu)$ is the modified Dirac Hamiltonian

$$\hat{H}'_D(\mu) = c\vec{\alpha}_\mu \cdot \vec{\mathrm{p}}_\mu + c^2\beta'_\mu - Z/r_\mu \,, \tag{4}$$

where the rest-mass energy is subtracted to get the binding energy. Dirac operators $\vec{\alpha}$ and β' are expressed by the matrices

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \quad \text{and} \quad \beta' = \begin{pmatrix} 0 & 0 \\ 0 & -2\underline{I} \end{pmatrix}, \tag{5}$$

where $\vec{\sigma}$ stands for the three Pauli matrices and $\underline{I}$ is the 2×2 unit matrix.

The perturbing Hamiltonian $\hat{H}'$ consists of the Breit operator $\hat{H}_{\rm B}$ and the operator containing the effect of the finite nucleus $\hat{H}_{\rm FN}$. Problems arising in the use of the Breit operator have been discussed in detail by Bethe and Salpeter.[30] The general expression for two-electron integrals of the Breit operator has been given elsewhere.[3,13,22,25] The Breit interaction energy is smaller than the unperturbed energy by a factor $(Z\alpha)^2$. Moreover, most of the contributions that are due to this interaction arise from K and L electrons. It can be expected that the total energy for open-shell atoms shifts very little whether this interaction between two open shells is calculated rigorously by tensor algebra or approximately by an average method such as the weighted-mean method of Slater.[31] The effect of the finite nucleus is important, especially for K electrons, but it is very small compared with the unperturbed energy. These two perturbation energies cause small energy shifts of an equal amount for every state with different J arising from a given configuration.

In the present work, H' is neglected because these two perturbation energies are small and also because they have almost no dependence on J.

A four-component orbital is written as

$$\psi_{n\kappa m}(\vec{\mathrm{r}}) = r^{-1} \begin{pmatrix} P_{n\kappa}(r) & \chi_{\kappa m}(\theta,\varphi) \\ iQ_{n\kappa}(r) & \chi_{-\kappa m}(\theta,\varphi) \end{pmatrix} . \tag{6}$$

$P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small components of the radial wave function, and they satisfy the orthonormal condition

$$\int_0^\infty [P_{n\kappa}(r)P_{n'\kappa}(r) + Q_{n\kappa}(r)Q_{n'\kappa}(r)]\, dr = \delta_{nn'} \,. \tag{7}$$

The spinor $\chi_{\kappa m}(\theta,\varphi)$ is written as

$$\chi_{\kappa m}(\theta,\varphi) = \sum_{\sigma=\pm\frac{1}{2}} C(l\tfrac{1}{2}j;m-\sigma,\sigma)Y_{l,m-\sigma}(\theta,\varphi)\phi_\sigma^{1/2} \,, \tag{8}$$

where $C(l\frac{1}{2}j;m-\sigma,\sigma)$ is a Clebsch-Gordan coefficient, $Y_{lm}(\theta,\varphi)$ is a spherical harmonic, and $\phi_\sigma^{1/2}$ is the two-component Pauli spinor. The relativistic quantum number κ is given by

$$\kappa = \pm(j+\tfrac{1}{2}) \quad \text{for } l = j \pm \tfrac{1}{2} \text{ and } \bar{l} = j \mp \tfrac{1}{2} \,, \tag{9}$$

where l and $\bar{l}$ denote the orbital-angular-momentum quantum numbers of large and small components of the wave function, respectively.

B. Unperturbed energy

In general, the total wave function is a sum of several Slater determinants. The unperturbed energy for the state considered here is written as

$$\begin{aligned} E = {} & \sum_n \sum_\kappa N_{c\kappa} I_{n\kappa} + \sum_\kappa N_{o\kappa} I_{o\kappa} + \frac{1}{2}\sum_n \sum_\kappa \sum_{n'} \sum_{\kappa'} N_{c\kappa} N_{c\kappa'} \{J_{n\kappa,n'\kappa'} - K_{n\kappa,n'\kappa'}\} \\ & + \sum_n \sum_\kappa \sum_{\kappa'} N_{c\kappa} N_{o\kappa'} \{J_{n\kappa,o\kappa'} - K_{n\kappa,o\kappa'}\} + \frac{1}{2} \sum_\kappa \sum_{\kappa'} N_{o\kappa} N_{o\kappa'} \{J_{o\kappa,o\kappa'} - K_{o\kappa,o\kappa'}\} \,. \end{aligned} \tag{10}$$

$N_{c\kappa}$ and $N_{o\kappa}$ are the number of electrons in closed and open shells, respectively. $N_{c\kappa}$ always equals $2j+1$, whereas $N_{o\kappa}$ takes various values. The one-electron integral I_s is given by

$$I_s = \langle \psi_{sm}(1) | \hat{H}'_D(1) | \psi_{sm'}(1) \rangle \delta_{mm'} \,, \tag{11}$$

where s denotes $n\kappa$ or $o\kappa$, and m and m' are the magnetic quantum numbers associated with κ.

By using tensor algebra, the general two-electron integral involving $1/r_{12}$ has been given by Grant.[3] The three types of direct and exchange integrals have appeared in Eq. (10). The first two types are the interaction between closed shells and between a closed shell and an open shell. These are given by

$$J_{s,s'}=\frac{1}{(2j+1)(2j'+1)}\sum_m\sum_{m'}\left\langle\psi_{sm}(1)\psi_{s'm'}(2)\left|\frac{1}{r_{12}}\right|\psi_{sm}(1)\psi_{s'm'}(2)\right\rangle=\sum_\nu a_\nu^c(\kappa\kappa')F^\nu(ss;s's') \tag{12}$$

and

$$K_{s,s'}=\frac{1}{(2j+1)(2j'+1)}\sum_m\sum_{m'}\left\langle\psi_{sm}(1)\psi_{s'm'}(2)\left|\frac{1}{r_{12}}\right|\psi_{sm}(2)\psi_{s'm'}(1)\right\rangle=\sum_\nu b_\nu^c(\kappa\kappa')F^\nu(ss';ss')\ , \tag{13}$$

where

$$a_\nu^c(\kappa\kappa')=\delta_{\nu 0}\ , \tag{14}$$

$$b_\nu^c(\kappa\kappa')=[C(jj'\nu;\tfrac{1}{2},-\tfrac{1}{2})]^2/(2\nu+1)\ , \tag{15}$$

$$F^\nu(AC;BD)=\int\int dr_1dr_2U_\nu(1,2)[P_A(1)P_C(1)+Q_A(1)Q_C(1)][P_B(2)P_D(2)+Q_B(2)Q_D(2)]\ , \tag{16}$$

and

$$U_\nu(1,2)=r_<^\nu/r_>^{\nu+1}\ . \tag{17}$$

The last type is the interaction between two open shells, which is written in the following form:

$$J_{o\kappa,o\kappa'}=\sum_\nu a_\nu^o(\kappa\kappa'J)F^\nu(o\kappa,o\kappa;o\kappa',o\kappa') \tag{18}$$

and

$$K_{o\kappa,o\kappa'}=\sum_\nu b_\nu^o(\kappa\kappa'J)F^\nu(o\kappa,o\kappa';o\kappa,o\kappa')\ . \tag{19}$$

The coefficients $a_\nu^o(\kappa\kappa'J)$ and $b_\nu^o(\kappa\kappa'J)$ are determined so that the integrals represent the correct total energy for the state considered. In the present theory, it is assumed that more than one state with the same total angular-momentum quantum number J and the same seniority number v does not appear in a given configuration. The calculation of these coefficients by the seniority scheme will be described in the Appendix.

When $\kappa\neq\kappa'$, $a_\nu^o(\kappa\kappa'J)$ and $b_\nu^o(\kappa\kappa'J)$ are obtained from the off-diagonal matrix element involving $1/r_{12}$ for the case where two open-shells exist (see Appendix). When $\kappa=\kappa'$ in Eqs. (18) and (19), $a_\nu^o(\kappa\kappa J)$ and $b_\nu^o(\kappa\kappa J)$ are not independent of each other because $F^\nu(o\kappa,o\kappa;o\kappa,o\kappa)$ is the same in both $J_{o\kappa,o\kappa}$ and $K_{o\kappa,o\kappa}$. In our case,

$$a_\nu^o(\kappa\kappa J)=\delta_{\nu o} \tag{20}$$

is assumed. This leads to a simplification in the treatment of the coupling operator, which is described below.

The coupling operator $\hat{R}_s$ introduced by Roothaan[1] is defined by

$$\hat{R}_s\psi_{s'm'}=\frac{N_s}{N_{c\kappa}}\sum_m[\langle\psi_{sm}|\hat{J}^{o\kappa}-\hat{K}^{o\kappa}|\psi_{s'm'}\rangle\psi_{sm}+\langle\psi_{sm}|\psi_{s'm'}\rangle(\hat{J}^{o\kappa}-\hat{K}^{o\kappa})\psi_{sm}]\ , \tag{21}$$

where both s and s' denote $n\kappa$ or $o\kappa$, that is, orbitals of symmetry κ, and N_s denotes $N_{c\kappa}$ and $N_{o\kappa}$ when s represents $n\kappa$ and $o\kappa$, respectively. $\hat{J}^{o\kappa}$ and $\hat{K}^{o\kappa}$ are the direct and the exchange operators by the open-shell orbital, whose expectation value, after carrying out the sum over the shell, is given by

$$\frac{1}{N_{c\kappa}^2}\sum_m\sum_{m'}\langle\psi_{sm}|\hat{J}^{o\kappa}-\hat{K}^{o\kappa}|\psi_{s'm'}\rangle=\frac{N_{c\kappa}}{N_{c\kappa}-N_{o\kappa}}\sum_\nu[\alpha_\nu(\kappa J)F^\nu(o\kappa,o\kappa;s,s')-\beta_\nu(\kappa J)F^\nu(o\kappa,s;o\kappa,s')]\ . \tag{22}$$

The coefficients $\alpha_\nu(\kappa J)$ and $\beta_\nu(\kappa J)$ are given by

$$\alpha_\nu(\kappa J)=a_\nu^c(\kappa\kappa)-a_\nu^o(\kappa\kappa J) \tag{23}$$

and

$$\beta_\nu(\kappa J)=b_\nu^c(\kappa\kappa)-b_\nu^o(\kappa\kappa J)\ . \tag{24}$$

The direct integral involving $\hat{J}^{o\kappa}$ vanishes since $\alpha_\nu(\kappa J)$ is always zero because of relation (14) and assumption (20).

C. The relativistic Hartree-Fock-Roothaan equation

Following Kim,[13] we expand large $P(r)$ and small $Q(r)$ components of the radial wave function in terms of the same Slater-type orbitals (STO's) with nonintegral principal quantum number,[32] where the expansion coefficients are different for $P(r)$ and $Q(r)$. These are given by the matrix form

$$P_s(r)=\sum_p\xi_{sp}f_{\kappa p}(r)=\underline{f}_\kappa^\dagger\underline{\xi}_s \tag{25}$$

and

$$Q_s(r)=\sum_q \eta_{sq} f_{\kappa q}(r)=\underline{f}^{\dagger}_{\kappa}\eta_s\ , \tag{26}$$

where ξ_{sp} and η_{sp} are the expansion coefficients. A STO $f_{\kappa p}(r)$ is written

$$f_{\kappa p}(r)=(2\zeta_{\kappa p})^{n'_{\kappa p}+1/2}[\Gamma(2n'_{\kappa p}+1)]^{-1/2} r^{n'_{\kappa p}} e^{-\zeta_{\kappa p}\cdot r}\ , \tag{27}$$

where $\Gamma(2n'_{\kappa p}+1)$ is a gamma function, and

$$n'_{\kappa p}=n_{\kappa p}+(\kappa^2-Z^2\alpha^2)^{1/2},\quad n_{\kappa p}=0,1,\ldots\ . \tag{28}$$

The one-electron integral is written as

$$I_s=(\underline{\xi}^{\dagger}_s\underline{\eta}^{\dagger}_s)\underline{I}_{\kappa}\begin{pmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{pmatrix}\ , \tag{29}$$

where

$$\underline{I}_{\kappa}=-\begin{pmatrix} Z\underline{U}_{\kappa} & c\underline{T}^{-}_{\kappa}\\ -c\underline{T}^{+}_{\kappa} & 2c^2\underline{S}_{\kappa}+Z\underline{U}_{\kappa}\end{pmatrix}. \tag{30}$$

$\underline{S}_{\kappa}$ is the overlap matrix whose elements have the form

$$(\underline{S}_{\kappa})_{pq}=\int_0^{\infty} dr\, f_{\kappa p}(r) f_{\kappa q}(r)\ . \tag{31}$$

The nuclear potential matrix $\underline{U}_{\kappa}$ and the kinetic energy matrix $\underline{T}^{\pm}_{\kappa}$ are given by

$$(\underline{U}_{\kappa})_{pq}=\int_0^{\infty} dr \frac{f_{\kappa p}(r) f_{\kappa q}(r)}{r} \tag{32}$$

and

$$(\underline{T}^{\pm}_{\kappa})pq=\int_0^{\infty} dr\, f_{\kappa p}(r)\left(\frac{d}{dr}\pm\frac{\kappa}{r}\right) f_{\kappa q}(r)\ . \tag{33}$$

The direct and the exchange two-electron integrals are also written by the matrix

$$J_{s,s'}=(\underline{\xi}^{\dagger}_s\underline{\eta}^{\dagger}_s)\begin{pmatrix}\underline{J}^{s,s'} & 0\\ 0 & \underline{J}^{s,s'}\end{pmatrix}\begin{pmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{pmatrix} \tag{34}$$

and

$$K_{s,s'}=(\underline{\xi}^{\dagger}_s\underline{\eta}^{\dagger}_s)\begin{pmatrix}\underline{K}^{s,s'}_{\xi\xi} & \underline{K}^{s,s'}_{\xi\eta}\\ \underline{K}^{s,s'}_{\eta\xi} & \underline{K}^{s,s'}_{\eta\eta}\end{pmatrix}\begin{pmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{pmatrix}, \tag{35}$$

where

$$(\underline{J}^{s,s'})_{pq}=\sum_u\sum_v(\xi_{s'u}\xi_{s'v}+\eta_{s'u}\eta_{s'v})\times\left(\sum_{\nu} A^{s,s'}_{\nu} R^{\nu}(\kappa p,\kappa' u;\kappa q,\kappa' v)\right), \tag{36}$$

$$(\underline{K}^{s,s'}_{\xi\xi})_{pq}=\sum_u\sum_v \xi_{s'u}\xi_{s'v}\times\left(\sum_{\nu} B^{s,s'}_{\nu} R^{\nu}(\kappa p,\kappa' u;\kappa' v,\kappa q)\right), \tag{37}$$

and

$$R^{\nu}(AB;CD)=\iint_0^{\infty} dr_1\, dr_2\, U_{\nu}(1,2)\times f_A(r_1) f_B(r_2) f_C(r_1) f_D(r_2)\ . \tag{38}$$

The coefficients $A^{s,s'}_{\nu}$ and $B^{s,s'}_{\nu}$ are $a^c_{\nu}(\kappa\kappa')$ and $b^c_{\nu}(\kappa\kappa')$, respectively, when the interaction is between two closed shells or between a closed and an open shell. The coefficients become $a^o_{\nu}(\kappa\kappa' J)$ and $b^o_{\nu}(\kappa\kappa' J)$ between two open shells. $\underline{K}^{s,s'}_{\xi\eta}$, $\underline{K}^{s,s'}_{\eta\xi}$, and $\underline{K}^{s,s'}_{\eta\eta}$ are obtained by replacing $\xi_{s'u}\xi_{s'v}$ in Eq. (37) by $\xi_{s'u}\eta_{s'v}$, $\eta_{s'u}\xi_{s'v}$, and $\eta_{s'u}\eta_{s'v}$, respectively.

The coupling operator matrix $\underline{R}_s$ is given by

$$\underline{R}_s=N_s[\underline{X}^{o\kappa,s}(\underline{Y}^{\kappa,s})^{\dagger}+\underline{Y}^{\kappa,s}(\underline{X}^{o\kappa,s})^{\dagger}]\ , \tag{39}$$

where

$$\underline{X}^{o\kappa,s}=-\frac{N_{c\kappa}}{N_{c\kappa}-N_{o\kappa}}\begin{pmatrix}\underline{\bar{K}}^{o\kappa}_{\xi\xi} & \underline{\bar{K}}^{o\kappa}_{\xi\eta}\\ \underline{\bar{K}}^{o\kappa}_{\eta\xi} & \underline{\bar{K}}^{o\kappa}_{\eta\eta}\end{pmatrix}\begin{pmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{pmatrix}, \tag{40}$$

$$\underline{Y}^{\kappa,s}=\begin{pmatrix}\underline{S}_{\kappa} & 0\\ 0 & \underline{S}_{\kappa}\end{pmatrix}\begin{pmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{pmatrix}, \tag{41}$$

and

$$(\underline{\bar{K}}^{o\kappa}_{\xi\xi})_{pq}=\sum_u\sum_v \xi_{o\kappa,u}\,\xi_{o\kappa,v}\times\sum_{\nu}\beta_{\nu}(\kappa J) R^{\nu}(\kappa p,\kappa u;\kappa v,\kappa q). \tag{42}$$

The matrix elements for $\underline{\bar{K}}^{o\kappa}_{\xi\eta}$, $\underline{\bar{K}}^{o\kappa}_{\eta\xi}$, and $\underline{\bar{K}}^{o\kappa}_{\eta\eta}$ can be expressed in the same way as for $\underline{\bar{K}}^{o\kappa}_{\xi\xi}$ by replacing the expansion coefficients appropriately.

We obtain the RHFR equations to determine the expansion coefficients of large and small components by applying the variational principle under the condition that all orbitals are orthogonal to each other. The derivation is the same as that for the NRHF theory of Roothaan, where the coupling operator has been introduced in place of the off-diagonal Lagrange multipliers. The final equations are the following pseudo-eigenvalue equations for closed- and open-shell vectors of expansion coefficients

$$\underline{F}_{c\kappa}\begin{pmatrix}\underline{\xi}_{n\kappa}\\ \underline{\eta}_{n\kappa}\end{pmatrix}=\epsilon_{n\kappa}\begin{pmatrix}\underline{S}_{\kappa} & 0\\ 0 & \underline{S}_{\kappa}\end{pmatrix}\begin{pmatrix}\underline{\xi}_{n\kappa}\\ \underline{\eta}_{n\kappa}\end{pmatrix} \tag{43}$$

and

$$\underline{F}_{o\kappa}\begin{pmatrix}\underline{\xi}_{o\kappa}\\ \underline{\eta}_{o\kappa}\end{pmatrix}=\epsilon_{o\kappa}\begin{pmatrix}\underline{S}_{\kappa} & 0\\ 0 & \underline{S}_{\kappa}\end{pmatrix}\begin{pmatrix}\underline{\xi}_{o\kappa}\\ \underline{\eta}_{o\kappa}\end{pmatrix}, \tag{44}$$

where

$$\underline{F}_{c\kappa}=\underline{I}_{\kappa}+\underline{P}_{c\kappa}+\underline{R}_{o\kappa}\ , \tag{45}$$

$$\underline{F}_{o\kappa}=\underline{I}_{\kappa}+\underline{P}_{o\kappa}+\sum_{n}\underline{R}_{n\kappa}\ , \tag{46}$$

and

$$\underline{P}_{s}=\sum_{s'}N_{s'}\begin{pmatrix}\underline{J}^{s,s'}-\underline{K}^{s,s'}_{\xi\xi} & -\underline{K}^{s,s'}_{\xi\eta}\\ -\underline{K}^{s,s'}_{\eta\xi} & \underline{J}^{s,s'}-\underline{K}^{s,s'}_{\eta\eta}\end{pmatrix}. \tag{47}$$

By use of the Hartree-Fock (HF) orbital energies, the total energy is expressed in the following form:

$$E=\frac{1}{2}\left(\sum_{n}\sum_{\kappa}N_{c\kappa}(I_{n\kappa}+\epsilon_{n\kappa})+\sum_{\kappa}N_{o\kappa}(I_{o\kappa}+\epsilon_{o\kappa})\right). \tag{48}$$

The RHFR equation is solved by iteration for the closed- and open-shell equations until the self-consistency is obtained. The solutions for negative energy states are not used, since we are concerned with positive energy states.

III. DETAILS OF THE CALCULATION

The relativistic ground state, which is the lowest positive energy state, corresponds to an excited state in the nonrelativistic case, since there are negative energy states below the state in consideration. In the nonrelativistic variational calculation, it is guaranteed by the variational principle that one cannot obtain a lower energy than the true ground-state energy. This is not the case in the relativistic calculation. In the RHF calculation, the ground-state energy is obtained as the lowest stationary value among positive energy states.

As Bagus[33] has mentioned in his NRHF calculation for hole states of rare gases, a stationary value may be found by the use of the virial theorem. Kim[13] has also used the virial theorem in the RHFR calculation to obtain a stationary value for the energy.

For a system interacting with a Coulombic force, the relativistic virial theorem is given by[34]

$$\langle T\rangle=-\langle V\rangle \quad\text{and}\quad E=\langle M\rangle\ , \tag{49}$$

where $\langle T\rangle$, $\langle V\rangle$, and $\langle M\rangle$ are the expectation values for kinetic, potential, and rest-mass energy operators, respectively. However, satisfying the relativistic virial theorem is not a sufficient condition for the energy obtained to be the lowest stationary value. In the RHFR calculation, optimization of orbital exponents of STO's is important to obtain a good result, since the lowest stationary value for the energy with a wave function obtained by the expansion method would be found with respect to variation both of the expansion coefficients and the orbital exponents. However, this is difficult, because too much time is needed for the computation.

In the present calculation, full optimization of the exponents is not carried out. By starting from the NRHF exponents,[27] improvement is made by carrying out some trial calculations with other values of the exponents to test whether or not the shift of the exponents yields a lower energy and a good virial coefficient $\langle V\rangle/\langle T\rangle$. Then, when it is found that number of basis functions is too small to construct reasonable orbitals, new functions are added. The exponents of old functions are adjusted if the overlap integral between new and old functions has a value greater than 0.95.

IV. CALCULATED RESULTS

The RHFR unperturbed energies of the ground and excited states of the first transition elements are listed in Table I together with DHF(TE),[1] RHFS,[17] and NRHF[27] ones. The calculations are carried out for all the states of the configuration $[\mathrm{Ar}]3d^{n}4s^{2}$, where [Ar] means the electronic configuration of the argon atom. For the configuration $[\mathrm{Ar}]3d^{n+1}4s^{1}$, only a state with the highest J is calculated with and without the ODLM, i.e., the coupling operator to examine the effect of the ODLM on the energy. The Breit interaction and the effect of the finite nucleus are neglected both because they are small and depend on J very little.

The orbital exponents of STO's used are listed in Table II. The relativistic shells are described by the notations of $nl+$ and $nl-$ for $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$, respectively, where l and j are the orbital and a total angular-momentum quantum numbers for the shell under consideration. The same STO's, except for the 1s STO for the $p-$ shell and the 2p STO for the $d-$ shell, are used for $nl\pm$ shells, since the large components of the radial wave functions for these shells can be expected to be nearly equal. It is also expected that the use of the same STO's for these shells has little effect on the energy because the eigenvectors for the small-component function are smaller by a factor 10^{-2} than those for the large-component one. For $p-$ and $d-$ shells, 1s and 2p STO's are needed, respectively, since the small-component function for the $nl-$ shell has one more node than the large-component function.

TABLE I. Comparison of the RHFR and other relativistic and nonrelativistic energies for the first transition elements (in a.u.). Values without the ODLM are in parentheses. The ground-state configuration obtained from experiment (Ref. 35) and the lowest RHFR energy are underlined. The configuration without core electrons [Ar] is given in the third column.

Atom	Z	Number of electrons			J	Virial Theorem	RHFR	DHF(TE)[a]	RHFS[b]	NRHF[c]
		$3d-$	$3d+$	$4s+$						
Sc	21	1		2	$\frac{3}{2}$	−0.999 98	763.377	763.3895	760.496	759.736
		2		1	$\frac{5}{2}$	−0.999 98	763.268	763.3150		
Ti	22	2		2	2	−0.999 99	852.841	852.8392	849.791	848.405
					0	−0.999 98	852.749			
		3		1	2	−0.999 98	852.728	852.7797		
						(−0.999 98	852.726)			
V	23	3		2	$\frac{3}{2}$	−0.999 99	948.217	948.2191	945.016	942.883
		4		1	$\frac{1}{2}$	−0.999 98	948.156	948.1693		
						(−0.999 95	948.117)			
Cr	24	4		2	0	−1.000 01	1049.67	1049.6820	1046.299	1043.306
		4	1	1	3	−0.999 99	1049.73	1049.6319		
						(−1.000 00	1049.70)			
Mn	25	4	1	2	$\frac{5}{2}$	−0.999 98	1157.34	1157.3673	1153.867	1149.865
		4	2	1	$\frac{9}{2}$	−0.999 97	1157.49	1157.3251		
						(−0.999 98	1157.47)			
Fe	26	4	2	2	4	−0.999 99	1271.44	1271.4370	1267.795	1262.443
					2	−1.000 00	1271.40			
					0	−1.000 00	1271.30			
		4	3	1	5	−0.999 99	1271.61	1271.4017		
						(−0.999 99	1271.60)			
Co	27	4	3	2	$\frac{9}{2}$	−0.999 98	1392.09	1392.0441	1388.264	1381.414
					$\frac{3}{2}$	−0.999 98	1391.99			
					$\frac{5}{2}$	−0.999 98	1391.98			
		4	4	1	$\frac{9}{2}$	−0.999 94	1391.11	1392.0155		
						(−0.999 98	1392.19)			
Ni	28	4	4	2	4	−0.999 98	1519.32	1519.3420	1515.425	1506.869
					2	−0.999 98	1519.28			
					0	−0.999 98	1519.15			
		4	5	1	3	−0.999 97	1519.40	1519.3194		
						(−0.999 98	1519.42)			
Cu	29	4	5	2	$\frac{5}{2}$	−0.999 97	1653.44	1653.4852		1638.949
		4	6	1	$\frac{1}{2}$	−0.999 97	1653.44	1653.4679	1649.474	1638.961
						(−0.999 97	1653.43)			

[a] Reference 1.
[b] Reference 17.
[c] Reference 27.

TABLE II. Optimum values of orbital exponents of STO's used in the RHFR calculation for the first transition elements.

Shell			*s*+		*p*− and *p*+		*d*− and *d*+
Atom \ STO	1*s*	2*s*	3*s*	4*s*	2*p*	3*p*	3*d*
Sc	20.8791^{a}	18.007	7.3798	3.2266	9.5892^{b}	9.0	5.5469
	36.0	8.6	4.7354	1.5278	16.476	5.0	4.57
			3.2087	0.96		4.1417	3.57
						2.8391	2.25
						1.8	1.6
							0.9
Ti	21.7832^{a}	18.7059	8.2372	3.4877	10.0056^{b}	9.5	9.1
	37.0	9.3846	4.8316	1.5391	16.7923	6.0	5.4
			3.3793	0.9385		4.7353	3.3
						2.9246	2.15
						1.3418	1.3
							0.95
V	22.7763^{a}	23.0	9.5	3.75	10.6236^{b}	8.0449	9.971
	40.0	9.374	6.7	1.6576	16.6889	5.367	4.7919
			3.7	0.9947		3.2011	3.5249
						1.475	2.5756
						0.9947	1.572
							1.172
Cr	23.5354^{a}	21.2835	10.5	3.2839	10.6674^{b}	6.6401	8.3587
	41.0	10.5	6.5	1.7226	16.3625	3.5474	5.2264
			4.0251	1.0567	7.6	2.0	3.47
						1.2	2.7
							1.8
							1.2645
Mn	24.6096^{a}	21.1177	8.7566	3.65	9.5894^{b}	9.0	11.1772
	40.0	10.6685	5.7335	1.816	16.2699	5.88	5.6157
			4.148	1.0811		4.28	4.5
						3.13	3.7239
						2.1	2.4849
							1.3718
Fe	25.8782^{a}	21.333	9.5002	3.8	10.092^{b}	12.0	7.5
	41.0	11.0123	6.0	1.8	17.0237	6.4765	5.0041
			4.5	1.0		4.4681	3.5954
						3.4539	2.6169
						2.5518	1.8488
							1.2
Co	26.8272^{a}	22.0	10.547	4.55	12.0^{b}	11.5	10.703
	40.0	12.1605	6.6822	2.0159	19.7	6.0	6.5802
			5.2084	1.1973		4.7	4.5541
						3.5319	2.7482
						2.7084	1.534
							0.9
Ni	27.781^{a}	22.6667	12.0	4.8023	12.3^{b}	11.3575	12.6791
	40.0	12.65	7.5	2.8	18.2	6.3026	6.8718
			4.5	1.2653		4.1333	4.63
						3.0	2.9253
						2.3286	2.2
							1.6098
Cu	28.7426^{a}	23.333	11.4199	5.0328	12.2857^{b}	11.8919	13.0023
	42.1133	13.1453	6.6632	2.1422	19.0591	7.2841	7.3857
			5.8397	1.2525		4.5745	5.0748
						2.8669	3.0723
						1.5	1.7192
							0.8

[a] This 1*s* STO is also used for the *p*−shell in the calculation.

[b] This 2*p* STO is also used for the *d*−shell.

TABLE III. Comparison of orbital energies for copper ($Z = 29$) (in a.u.).

Shell	RHFR ($J = \frac{1}{2}$)	RHFS[a]	NRHF[b] (^2S)	Experiment[a]
$1s+$	332.661	328.67	328.793	330.14
$2s+$	41.664	39.92	40.820	40.48
$2p-$	36.302	35.23	35.619	35.11
$2p+$	35.548	34.45		34.38
$3s+$	3.149	4.458	5.013	4.57
$3p-$	3.421	2.960	3.326	2.87
$3p+$	3.322	2.861		
$3d-$	0.478	0.372	0.492	0.39
$3d+$	0.466	0.361		
$4s+$	0.244	0.261	0.236	0.284
E	1653.44	1649.47	1638.96	
$V.T.$	−0.999 97		−2.000 00	

[a] Reference 20.

[b] Reference 27.

The number of STO's used in the calculation is 10 for $s+$, 8 for $p-$, 7 for $p+$, 7 for $d-$, and 6 for $d+$ shells, respectively. The optimum exponents are obtained in the calculation of the state with the configuration $[\mathrm{Ar}]\,3d^n 4s^2$ and are transferred for the calculation of the state with the configuration $[\mathrm{Ar}]\,3d^{n+1}4s^1$.

The RHFR energy is obtained so as to satisfy the virial theorem. The maximum deviation of $\langle V\rangle / \langle T\rangle$ from the best value of $-1.000\,00$ is $\pm 0.000\,03$ in these calculations, so that the maximum energy deviation owing to incomplete optimization of the exponents is considered to be within ±1 in magnitude at the fifth figure, whereas the numerical error of the single precision calculation lies at the sixth figure within ±1.

The electronic configuration of the ground state as determined by experiment[35] is underlined in the columns labeled "Number of electrons" in Table I. The lowest energy obtained by the RHFR calculation is also underlined in that table. Agreement of the ground-state configuration obtained from the RHFR and experiment is obtained for Sc, Ti, V, Cr, and Cu, whereas the DHF(TE)[1] results are in agreement with experiment for all atoms considered here except for Cr and Cu. The discrepancies probably arise from inaccuracy of prediction of the ground-state configuration for these atoms by various Hartree-Fock schemes. Since $3d$ and $4s$ orbital energies are approximately the same, the energy difference between the configurations $[\mathrm{Ar}]\,3d^n 4s^2$ and $[\mathrm{Ar}]\,3d^{n+1}4s^1$ is small.

The DHF energies obtained by Maly *et al.*[1] have been calculated by two methods with the same wave function that was obtained by neglecting ODLM's in the Hartree-Fock equation. One is the method denoted by TE (total energy), in which the exact coefficient $N_{o\kappa} b_\nu^o(\kappa\kappa J)$ is replaced by $N_{o\kappa} b_\nu^c(\kappa\kappa)$. The other is denoted by AE (average energy), in which $(N_{o\kappa}-1)\,[(2j+1)/2j\,]\,b_\nu^c(\kappa\kappa)$ is used. The latter is the weighted-mean method of Slater.[31] The AE method gives the exact coefficient of the

TABLE IV. Energy difference by the RHFR calculation between the ground state and excited states arising from the same configuration as the ground state for Ti, Fe, Co, and Ni (in a.u.). $\Delta E = E\,(\text{excited}) - E\,(\text{ground})$.

		Number of electrons			RHFR			Experiment[a]		
Atom	Z	$3d-$	$3d+$	$4s+$	Ground state	Excited state	ΔE	Ground state	Excited state	$\Delta E \times 10^2$
Ti	22	2		2	$J=2$	$J=0$	0.092	$^3F_2$	$^3F_3$	0.077 559 6
									$^3F_4$	0.176 368
Fe	26	4	2	2	$J=4$	$J=2$	0.04	$^5D_4$	$^5D_3$	0.189 615
						$J=0$	0.14		$^5D_2$	0.320 940
									$^5D_1$	0.404 881
									$^5D_0$	0.445 884
Co	27	4	3	2	$J=\frac{9}{2}$	$J=\frac{5}{2}$	0.11	$^4F_{9/2}$	$^4F_{7/2}$	0.372 00
						$J=\frac{3}{2}$	0.10		$^4F_{5/2}$	0.641 349
									$^4F_{3/2}$	0.824 836
Ni	28	4	4	2	$J=4$	$J=2$	0.04	$^3F_4$	$^3F_3$	0.607 301
						$J=0$	0.17		$^3F_2$	1.010 46

[a] Reference 35. $1\ \mathrm{cm}^{-1} = 4.558\,79 \times 10^{-6}$ a.u. is used.

exchange integrals for the ground state of a closed-shell atom and an open-shell atom which has one electron or one hole in the open shell. Comparing these coefficients, we expect that TE is lower than AE for any open-shell atom if the same wave function is used, since $N_{o\kappa} > (N_{o\kappa} - 1)[(2j+1)/2j]$. This, however, is not so in the DHF results obtained by Maly *et al.*[1] In Table I, TE's in the DHF results are listed.

The RHFR orbital energies for Cu are listed in Table III together with the RHFS[17] and the NRHF[27] ones and the experimental binding energies.[35] The RHFS and the NRHF orbital energies are closer to the experimental binding energies than are the RHFR ones. Because Koopmans's theorem does not hold in this case[36, 37] and, moreover, the experimental energy contains various energies that are due to electron correlation effect, quantum electrodynamic effects,[38] etc., it cannot be concluded that the RHFR result is not valid.

The orbital energy of the $3d+$ shell is higher than that of the $3d-$ shell in the RHFR results for the state with the highest J of Cr, Mn, Fe, and Ni, whose configurations are $[\mathrm{Ar}]3d^{n+1}4s^1$, and of Co, in which it arises from both $[\mathrm{Ar}]3d^{n+1}4s^1$ and $[\mathrm{Ar}]3d^n4s,^2$ i.e., Cr($J=3$), Mn($J=\frac{9}{2}$), Fe($J=5$), Ni($J=3$), and Co(two $J=\frac{9}{2}$) states (see Table I). The inversion of the orbital energy between $nl-$ and $nl+$ shells will be discussed later in connection with problems in the RHFR calculation.

V. DISCUSSION

In Table I, the difference of the energy values between the RHFR and the DHF(TE)[1] calculations is due not only to incomplete optimization of the exponents in the RHFR calculation and the difference of numerical technique, but also to the approximation of the exchange potential in the DHF(TE) calculation.

The effect of the exchange potential on the energy can be examined by comparing the energy value between the states with various J values arising from the same configuration. By using the energy values in Table I, energy differences between various states for Ti, Fe, Co, and Ni and corresponding experimental values are listed in Table IV.

For Ti, the energy difference between the ground ($J=2$) and the excited ($J=0$) states arising from the configuration $[\mathrm{Ar}]3d-^2 4s+^2$ is 0.092 a.u., which is 0.01% of the ground-state energy. For other atoms, the magnitude of the energy differences between the ground and the highest excited states are also about 0.01% of the ground-state energy. This means that energy value could shift at the fifth figure by the approximation of the exchange potential in the worst case. As has been mentioned before, the RHFR energies for all the states considered here are obtained by using the same STO's, since the difference in the wave function between the ground and lower excited states is very small. Regarding the energy difference between these states, it will be expected that the RHFR values in Table IV shift little if the RHFR energies are obtained by carrying out the complete optimization of the exponents in each calculation. It is concluded that the approximation of the exchange potential shifts the energy value considerably. However, the RHFR energy difference is too large when compared with experiment. The former is several hundred times larger than the latter. The reason for this is that a single configuration wave function by pure jj coupling cannot give an adequate description for these atoms.

By comparing the energies obtained with and without the ODLM, that is, the coupling operator for the configuration $[\mathrm{Ar}]3d^{n+1}4s^1$, it is found from Table I that the ODLM has little effect on the energy. In Table I, the RHFR energies obtained without the ODLM are in parentheses. The exceptional result for Co may be due to the inappropriate basis functions which gave a bad virial coefficient of -0.99994.

Sometimes convergence is not obtained in the RHFR calculation. Even if the convergence is obtained, it happens in some cases that the orbital energy of the $nl+$ shell is lower than that of the $nl-$ shell, which contradicts the experiment. Such an inversion of the orbital energy has occurred in the calculation for atoms from Cr through Ni, whose configuration is $[\mathrm{Ar}]3d-^4 3d+^{n+1}4s^1$, and for Co in the ground state. This has already been mentioned. For excited states with lower J, this inversion of the orbital energy does not appear. The reason for the inversion of the $nl\pm$ orbital energies is that the electronic states of small atoms or outer electrons of heavier atoms are described substantially by the LS or intermediate coupling. In other words, $nl\pm$ orbitals are nearly degenerate. The single-configuration wavefunction by the RHFR theory is written in pure jj coupling and is not adequate for describing these states.

The inversion of the $nl\pm$ orbital energies will disappear if we use the average method. However, the description of the state with the rigorous total angular momentum J is discarded in this case. Proper improvement of the RHFR scheme would be made by constructing the wave function as a linear combination of some configurations, i.e., by taking configuration mixing into account. However, this leads to the multiconfiguration Hartree-Fock scheme, which will be difficult to solve and is not described here.

One of the merits of using the expansion method is that the wave function obtained is easy to use in other calculations in related fields. The difficulty of this method lies in the optimization of the orbital exponents in terms of a small number of basis functions. This requires a large amount of time for computation. However, the application of the RHFR theory to heavier atoms is now possible as high-speed computers with large memory are coming into existence.

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APPENDIX: THE MATRIX ELEMENT OF $1/r_{12}$ BY USE OF THE SENIORITY SCHEME

Even if more than two open shells are involved in the configuration, the integrals for a general two-electron operator V_{12} are reduced to the following two open-shell cases[29]:

$$\left\langle j_1^{n_1}(v_1J_1)j_2^{n_2}(v_2J_2)J\left|\sum_{i<k}^{n_1+n_2} V_{ik}\right|j_1^{n_1}(v_1J_1)j_2^{n_2}(v_2J_2)J\right\rangle = A_1 + A_2 + B\ , \tag{A1}$$

where the diagonal matrix element A_λ is written

$$A_\lambda = \left\langle j_\lambda^{n_\lambda} v_\lambda J_\lambda\left|\sum_{i<k}^{n_\lambda} V_{ik}\right|j_\lambda^{n_\lambda} v_\lambda J_\lambda\right\rangle \tag{A2}$$

and the off-diagonal matrix element B is

$$B = \left\langle j_1^{n_1}(v_1J_1)j_2^{n_2}(v_2J_2)J\left|\sum_{i=1}^{n_1}\sum_{k=n_1+1}^{n_1+n_2} V_{ik}\right|j_1^{n_1}(v_1J_1)j_2^{n_2}(v_2J_2)J\right\rangle ;$$

n_λ is the number of electrons in the j_λ shell, and v_λ and J_λ are the seniority and the total angular-momentum quantum numbers for the configuration, respectively. The diagonal matrix element A is expressed by use of the seniority number v as follows:

$$A = \left\langle j^v vJ\left|\sum_{i<k}^{v} V_{ik}\right|j^v vJ\right\rangle + \frac{n-v}{2}V_0 + \frac{(n-v)(n+v-2)}{2(2j-1)}(E_0 - V_0)\ , \tag{A4}$$

where

$$E_0 = \frac{2}{2j+1}\sum_{J'(\text{even})}(2J'+1)V_{J'} \tag{A5}$$

and

$$V_J = \langle j^2J|V_{12}|\,j^2J\rangle\ . \tag{A6}$$

Recently, Grant[39] has made a computer program to calculate the coefficients of two-electron radial integrals involving $1/r_{12}$ for the jj configuration-

TABLE V. Values of $d_\nu\,(j^n vJ)$.

κ	j	n	v	J	$d_\nu\,(j^n vJ)$ $\nu=2$	$\nu=4$	$\nu=6$
±2	$\frac{3}{2}$	3	1	$\frac{3}{2}$	$-\frac{1}{15}$		
±3	$\frac{5}{2}$	3	1	$\frac{5}{2}$	0	0	
			3	$\frac{3}{2}$	$-\frac{4}{245}$	$-\frac{17}{441}$	
				$\frac{9}{2}$	$-\frac{104}{1225}$	$-\frac{10}{441}$	
		4	0	0	0	0	
			2	2	$-\frac{6}{175}$	$-\frac{1}{42}$	
				4	$-\frac{2}{35}$	$-\frac{1}{54}$	
		5	1	$\frac{5}{2}$	$-\frac{8}{175}$	$-\frac{2}{105}$	
±4	$\frac{7}{2}$	3	1	$\frac{7}{2}$	$\frac{5}{189}$	$\frac{1}{77}$	$\frac{25}{3861}$
			3	$\frac{3}{2}$	$-\frac{17}{441}$	$\frac{1}{539}$	$-\frac{25}{1287}$
				$\frac{5}{2}$	$\frac{1}{27}$	$-\frac{13}{363}$	$-\frac{575}{42471}$
				$\frac{9}{2}$	$-\frac{79}{1323}$	$-\frac{31}{5929}$	$-\frac{2714}{181083}$
				$\frac{11}{2}$	$-\frac{5}{189}$	$-\frac{73}{2541}$	$-\frac{425}{42471}$
				$\frac{15}{2}$	$-\frac{5}{63}$	$-\frac{23}{847}$	$-\frac{1025}{184041}$

TABLE VI. Values of $b_\nu^0(\kappa_1\kappa_2 J)$ for the configuration $\psi=|\, j_1^{n_1}(v_1 J_1),\ j_2=\frac{1}{2}, J\rangle^{\text{a}}$.

Shell	κ_1	j_1	n_1	v_1	J_1	ν	J	$b_\nu^0(\kappa_1\kappa_2 J)$	J	$b_\nu^0(\kappa_1\kappa_2 J)$
$p-$	1	$\frac{1}{2}$	1	1	$\frac{1}{2}$	1	0	$\frac{1}{3}$	1	$\frac{1}{9}$
$p+$	-2	$\frac{3}{2}$	1	1	$\frac{3}{2}$	1	1	$-\frac{1}{9}$	2	$\frac{1}{3}$
			2	0	0	1	$\frac{1}{2}$	$\frac{1}{6}$		
				2	2	1	$\frac{3}{2}$	0	$\frac{5}{2}$	$\frac{5}{18}$
			3	1	$\frac{3}{2}$	1	1	$\frac{2}{27}$	2	$\frac{2}{9}$
$d-$	2	$\frac{3}{2}$	1	1	$\frac{3}{2}$	2	1	$\frac{1}{5}$	2	$\frac{1}{25}$
			2	0	0	2	$\frac{1}{2}$	$\frac{1}{10}$		
				2	2	2	$\frac{3}{2}$	$\frac{4}{25}$	$\frac{5}{2}$	$\frac{3}{50}$
			3	1	$\frac{3}{2}$	2	1	$\frac{2}{15}$	2	$\frac{2}{25}$
$d+$	-3	$\frac{5}{2}$	1	1	$\frac{5}{2}$	2	2	$-\frac{1}{25}$	3	$\frac{1}{5}$
			2	0	0	2	$\frac{1}{2}$	$\frac{1}{10}$		
				2	2	2	$\frac{3}{2}$	$\frac{1}{25}$	$\frac{5}{2}$	$\frac{7}{50}$
				2	4	2	$\frac{7}{2}$	0	$\frac{9}{2}$	$\frac{9}{50}$
			3	3	$\frac{3}{2}$	2	1	$\frac{1}{15}$		
				3	$\frac{9}{2}$	2	4	$\frac{2}{75}$	5	$\frac{4}{25}$
			4	0	0	2	$\frac{1}{2}$	$\frac{1}{10}$		
				2	2	2	$\frac{3}{2}$	$\frac{7}{100}$	$\frac{5}{2}$	$\frac{3}{25}$
				2	4	2	$\frac{7}{2}$	$\frac{1}{20}$	$\frac{9}{2}$	$\frac{7}{50}$
			5	1	$\frac{5}{2}$	2	2	$\frac{9}{125}$	3	$\frac{3}{25}$

[a] j_2 is for the $s+$ shell.

mixing method, where the seniority scheme is used. The integral of Eq. (A1) is included as the single-configuration case in the program. After carrying out the angular integration and by using the coefficients of fractional parentage (cfp),[40] the diagonal integral A for $1/r_{12}$ is given in the following form:

$$A=\frac{n(n-1)}{2}\sum_{\nu} d_\nu(j^n vJ)F(o\kappa,o\kappa;o\kappa,o\kappa). \tag{A7}$$

From Eqs. (20), (21), (22) and (A7), $b_\nu^o(\kappa\kappa J)$ is obtained as

$$\begin{aligned} b_\nu^o(\kappa\kappa J) &= 1/n, \quad \nu=0\ , \\ &= -(n-1/n)d_\nu(j^n vJ), \quad \nu>0\ , \end{aligned} \tag{A8}$$

where $n=N_{o\kappa}$. The values of $d_\nu(j^n vJ)$ are calculated by use of Eqs. (A4), (A5), and (A6), and are listed in Table V.

The expression for the off-diagonal matrix element B is complex for general open-shell cases. As has been noted, we consider the cases where more than one state with the same J does not appear in a given configuration which contains more than one open shell. Detailed expressions for the matrix element B are given elsewhere.[29, 39] After evaluation of the angular integration and by use of cfp's, the matrix element B can be expressed with $a_\nu^o(\kappa_1\kappa_2 J)$ and $b_\nu^o(\kappa_1\kappa_2 J)$ as follows:

$$\begin{aligned} B = n_1 n_2 \sum_{\nu} \,[& a_\nu^o(\kappa_1\kappa_2 J)F^\nu(o\kappa_1,o\kappa_1;o\kappa_2,o\kappa_2) \\ & - b_\nu^o(\kappa_1\kappa_2 J)F^\nu(o\kappa_1,o\kappa_2;o\kappa_1,o\kappa_2)]\ , \end{aligned} \tag{A9}$$

where $a_\nu^o(\kappa_1\kappa_2 J)=\delta_{\nu 0}$. Numerical values of $b_\nu^o(\kappa_1\kappa_2 J)$ in which j_2 is for the $s+$ shell, are listed in Table VI.

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