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Multiconfiguration relativistic Hartree-Fock-Roothaan theory for atomic systems

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By using the expansion method, the multiconfiguration relativistic Hartree-Fock-Roothaan theory for atomic systems is presented. The matrix element for two-electron operators, such as $1/r_{12}$ or the Breit operator, is calculated by using tensor-recoupling-transformation techniques for the second-quantized operators. The theory is tested in the calculation of term energies for oxygenlike atomic systems (O, Fe^{18+}, and Hg^{72+}) and transition frequencies for K-hole states in Fe^{18+}. It is shown that calculated term energies and transition frequencies agree well with experiment. The role of the electron correlation effects and the relativistic effects in each system is also discussed.

I. INTRODUCTION

It has long been known that the relativistic effects in an atom give the characteristic multiplet structures for its energy levels. In the nonrelativistic treatment of the relativistic effects, a first-order perturbation theory is used. However, this treatment of the effects is somewhat complex and yields poor results as the atomic number increases because the nonrelativistic wave function is not a good approximation. Interest in the relativistic calculation of atomic structures has increased in recent years in connection with the observation of inner-hole states or highly ionized states in atomic systems by the experiments of beam-foil spectroscopy,[1] heavy-ion-atom collisions,[2] and nuclear fusion plasma.[3]

The relativistic formalism for many-electron atoms goes back to Swirles[4] who gave the self-consistent-field (SCF) equation based on the semirelativistic wave equation which was first obtained by Breit[5-7] for two-electron systems. Grant[8,9] has reformulated Slater's coefficients for the repulsive Coulomb operator $1/r_{12}$ in a concise form by use of the Racah algebra, and has derived the relativistic Hartree-Fock or the Dirac-Fock (DF) equation for closed-shell atoms. The same equation has been obtained by Smith and Johnson,[10] and Coulthard.[11] By extending the expansion method of Roothaan,[12-14] Kim[15] has given the relativistic Hartree-Fock-Roothaan (RHFR) equation for closed-shell atoms, where orbitals are expanded in terms of Slater-type orbitals (STO's) with a noninteger principal quantum number.

For either open- or closed-shell systems, Slater's approximation[16-18] or its modified form[19] for the exchange potentials have often been introduced to facilitate practical calculations. The average-of-configuration method by Slater[20] has also been used to calculate the energies for open-shell atoms.[21-25] This method leads to the closed-shell-like calculation for open-shell orbitals so that off-diagonal Lagrange multipliers (ODLM's) do not appear in the calculation. However, the averaging method is not unique. Because the relativistic effects for inner-shell electrons is larger than those for outer-shell electrons, one has to devise a way of averaging the configuration for each relativistic shell in a certain atomic system. In the averaging, information about the multiplet structures of the energy levels is lost. Kagawa[26] has extended the RHFR theory of Kim to open-shell atoms, where the ODLM's are replaced by coupling operators with which separate SCF equations for closed- and open-shell orbitals are obtained.

All of the formalism described above is based on a single configuration wave function for the states considered. When one treats multiply excited states containing vacancies in inner as well as outer shells (which are of importance in recent high-energy experiments such as the beam-foil spectroscopy), the coupling scheme and the relativistic effects must be included in the theory consistently, as inner- and outer-shell electrons require different treatments for their coupling and relativistic effects.

In order to introduce wave functions in intermediate coupling into the theory, the multiconfiguration Dirac-Fock (MCDF) theory has been developed by Grant[27] and Desclaux.[28] Grant and his co-workers[29,30] have studied the fine structure of the ground and lower excited states of various atoms including heavier elements such as Hf and Bi. Briançon and Desclaux[31] have satisfactorily applied the MCDF theory to the calculation of the KLL Auger-transition energies for rare gases, U and Am. Very recently, Cheng, Desclaux, and Kim[32] carried out the MCDF calculation of the fine-structure intervals of $1s2s2p\,^4P^0$ and $1s2p^2\,^4P$ states in Li-like ions which have been observed in the beam-foil spectra. They[33] have also calculated term energies for carbonlike atoms and have showed that the MCDF calculation combined with the correct treatment of the Breit interaction and the approximate estimate for the Lamb-shift correction agrees well with experiment. These calculations show that an adequate intermediate coupling between pure *LS* and pure *jj* limits for inner- and outer-shell electrons in each atomic system can be obtained by the MCDF method and that energy correction due to the Breit interaction plays an important role in the *ab initio* calculation of multiplet structures of energy levels.

The MCDF equation has so far been solved by use of the numerical integration method and no calculation of the MCDF equation with the expansion method has been reported. Generally speaking, the expansion method gives less accurate results than the numerical integration method because of the limited basis set used in the expansion method. However, the merits of using the expansion method can be found not only in orbitals in an analytical form which are easier to handle in a calculation of various physical quantities other than energy, but also in the treatment of systems such as molecules for which it is difficult to apply the numerical integration method. Even for atomic systems, the expansion method has the merit that it requires less computation time in dealing with ODLM's for general open-shell cases. In fact, there have been few investigations on the rigorous treatment of ODLM's for relativistic atoms with the numerical integration method. Although the difficulty in the use of the expansion method lies in obtaining a good basis set, this method can supplement the deficiencies in the numerical integration method.

The purpose of this paper is to present a multiconfiguration relativistic Hartree-Fock-Roothaan (MCRHFR) theory for atomic systems. The Breit interaction is treated as a first-order perturbation. The matrix elements for the two-electron operators such as the repulsive Coulomb interaction operator or the Breit operator between two configuration state functions (CSF) are calculated by using Sasaki's method.[34] Sasaki's method deals with a successive use of the tensor recoupling transformation techniques for a set of second-quantized operators. This will be described in the Appendix. A numerical application of the theory to highly ionized oxygenlike systems is presented.

II. THE TOTAL ENERGY IN THE MULTICONFIGURATION SCHEME

The Dirac one-electron theory and quantum electrodynamics (QED) have been successfully applied to one-electron atoms. However, difficulty arises in the construction of the relativistic Hamiltonian for many-electron atoms: One cannot obtain a fully Lorentz-invariant Hamiltonian for many-electron systems in a closed form, since the complete electron-electron interaction involves not only the instantaneous Coulomb interaction but also the interaction through the process of exchanging virtual photons between the participating electrons. As has already been mentioned, a practical relativistic treatment for many-electron atoms has been developed by extending the Breit equation for two-electron systems to many-electron cases. The Breit equation can be derived by applying a nonrelativistic approximation to the second-order scattering matrix in QED formalism.[35] Special attention must be paid to the Breit equation in its practical use. The Breit equation is not Lorentz-invariant because of the interelectronic distance r_{12} and the Breit operator should be treated as a first-order perturbation, since inclusion of the Breit operator in the unperturbed Hamiltonian or treatment of the operator as a higher-order perturbation than the first order leads to results inconsistent with QED. Problems concerning the Breit equation have been discussed by Bethe and Salpeter.[36]

The total Hamiltonian for many-electron atomic systems is divided into two parts, that is, unperturbed and perturbing ones written as

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

where

$$\hat{H} = \sum_i \hat{H}_D(i) + \sum_{i<j} 1/r_{ij} \tag{2}$$

and

$$\hat{H}_D(i) = c\vec{\alpha}_i \cdot \vec{p}_i + c^2(\beta_i - \underline{I}_4) + V_N(r_i) . \tag{3}$$

Here, c denotes the velocity of light and $\underline{I}_4$ is the 4×4 unit matrix. The Dirac operators α and β are expressed by the matrix

$$\vec{\alpha} = \begin{bmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{bmatrix}, \quad \beta = \begin{bmatrix} \underline{I}_2 & 0 \\ 0 & -\underline{I}_2 \end{bmatrix} , \tag{4}$$

where $\vec{\sigma}$ stands for the three Pauli matrices and $\underline{I}_2$ is the 2×2 unit matrix. $V_N(r)$ is the nuclear potential. By assuming a uniformly charged sphere for the nucleus, the effect of the finite nuclear size is included in $V_N(r)$ and is written as

$$V_N(r) = \begin{cases} -(Z/2R)(3 - r^2/R^2), & r<R \\ -Z/r , & r \geq R . \end{cases} \tag{5}$$

The radius of the nucleus R has the value of $2.3 \times 10^{-5} A^{1/3}$ a.u., where A is the atomic mass. The rest-mass energy is subtracted in the $\hat{H}_D(i)$ to get the binding energy.

The perturbing Hamiltonian H' is given by

$$\hat{H}' = \sum_{i<j} \hat{H}_B(i,j) + \hat{H}_{\text{QED}}\,, \tag{6}$$

where $\hat{H}_B(i,j)$ is the Breit operator and $\hat{H}_{\text{QED}}$ is the effective Hamiltonian which accounts for the QED effects included in the Lamb shift. The Breit operator $\hat{H}_B(i,j)$ consists of the magnetic interaction operator $\hat{H}_M(i,j)$ and the operator representing the retardation effect of the Coulomb interaction $\hat{H}_R(i,j)$. The Breit operator is given by

$$\hat{H}_B(i,j) = \hat{H}_M(i,j) + \hat{H}_R(i,j)\,, \tag{7}$$

where

$$\hat{H}_M(i,j) = -(\vec{\alpha}_i \cdot \vec{\alpha}_j)/r_{ij} \tag{8}$$

and

$$\hat{H}_R(i,j) = -\tfrac{1}{2}(\vec{\alpha}_i \cdot \vec{\nabla}_i)(\vec{\alpha}_j \cdot \vec{\nabla}_j) r_{ij}\,. \tag{9}$$

$\hat{H}'$ is treated as a first-order perturbation. $\hat{H}_{\text{QED}}$ is neglected in our theory because it is a higher-order perturbation.

A relativistic orbital is given by

$$\psi_{n\kappa m}(\vec{r}) = \frac{1}{r}\begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\theta,\varphi) \\ iQ_{n\kappa}(r)\chi_{-\kappa m}(\theta,\varphi) \end{pmatrix}, \tag{10}$$

where $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small components of the radial wave function, respectively. The spinor is written as

$$\chi_{\kappa m}(\theta,\varphi) = \sum_{\sigma=\pm 1/2} C(l\tfrac{1}{2}j; m-\sigma, \sigma) Y_{l,m-\sigma}(\theta,\varphi)\phi_\sigma^{1/2}\,, \tag{11}$$

where $C(l\frac{1}{2}j; m-\sigma,\sigma)$ is a Clebsh-Gordon coefficient and $Y_{l,m-\sigma}(\theta,\varphi)$ and $\phi_\sigma^{1/2}$ are a spherical harmonic and the two-component Pauli spinor, respectively. The relativistic quantum number κ is defined as

$$\kappa = \mp(j+\tfrac{1}{2}) \tag{12}$$

for $l = j \mp \frac{1}{2}$ and $\bar{l} = j \pm \frac{1}{2}$, where l and $\bar{l}$ are orbital angular momentum quantum numbers of the large and small components of the wave function, respectively. The orthonormality condition on the orbitals is written as

$$\int_0^\infty [P_{n\kappa}(r)P_{n'\kappa}(r) + Q_{n\kappa}(r)Q_{n'\kappa}(r)]dr = \delta_{nn'}\,. \tag{13}$$

In the multiconfiguration scheme, the total wave function is expressed as a linear combination of configuration state functions (CSF's) in the following form,

$$\Psi(\alpha JP) = \sum_{i=1}^{n} c_i \Phi_i(\alpha_i JP)\,, \tag{14}$$

where c_i is a CSF expansion coefficient which is assumed here to be real, and $\Phi_i(\alpha_i JP)$ is a CSF. Each CSF is constructed from a linear combination of antisymmetrized products of orbitals given in Eq. (10). The total wave function and a set of CSF's $\{\Phi_i(\alpha_i JP)\}$ are eigenfunctions of the total angular-momentum operator $\hat{J}^2$ and the parity operator $\hat{P}$ with eigenvalues $J(J+1)$ and π, respectively. α_i is a set of labels for explicitly omitted symmetry properties and the electron configuration indices which are needed to define orthonormal CSF's. As an orthonormal set of CSF's is used, the normalization condition of the total wave function leads to

$$\sum_i c_i^2 = 1\,. \tag{15}$$

Atomic shells are classified into two cases: One is the completely occupied shell denoted by $\mathfrak{C}$ and the other the fractionally occupied shell denoted by $\mathfrak{F}$. The completely occupied shell $\mathfrak{C}$ means a closed shell in all the CSF's considered and the fractionally occupied shell $\mathfrak{F}$ corresponds to an open or a vacant shell at least in one of the CSF's; for example, when $1s^2 2s^2 2p^2$ and $1s^2 2p^4$ are chosen as CSF, $1s$ orbitals belongs to $\mathfrak{C}$ and $2s$ and $2p$ orbitals are $\mathfrak{F}$.

The unperturbed energy is expressed as follows:

$$\begin{aligned} E &= \langle \Psi | \hat{H} | \Psi \rangle \\ &= \sum_{ij} c_i c_j \langle \Phi_i | \hat{H} | \Phi_j \rangle \\ &= \sum_i c_i^2 \Big(\sum_s N_s I_s + \tfrac{1}{2} \sum_{st\nu} [a_\nu^{s,t}(i) J_\nu^{s,t} - b_\nu^{s,t}(i) K_\nu^{s,t}(i)] \Big) + \sum_{i\neq j} c_i c_j \tfrac{1}{4} \sum_{stuv,\nu} d_\nu^{stuv}(i,j) G_\nu^{stuv}\,, \end{aligned} \tag{16}$$

where

$$I_s = \langle \psi_s(1) | \hat{H}_D(1) | \psi_s(1) \rangle = \int_0^\infty \Big[cQ_s(r)\Big(\frac{d}{dr} + \frac{\kappa_s}{r}\Big)P_s(r) - cP_s(r)\Big(\frac{d}{dr} - \frac{\kappa_s}{r}\Big)Q_s(r) + V_N(r)[P_s^2(r) + Q_s^2(r)] - 2c^2 Q_s^2(r) \Big] dr\,, \tag{17}$$

$$G_\nu^{stuv}=\int_0^\infty\int_0^\infty\{U_\nu(1,2)[P_s(1)P_u(1)+Q_s(1)Q_u(1)]\,[P_t(2)P_v(2)+Q_t(2)Q_v(2)]\}dr_1dr_2\,, \tag{18}$$

and

$$U_\nu(1,2)=r_<^\nu/r_>^{\nu+1}\,. \tag{19}$$

The direct $J_\nu^{s,t}$ and the exchange $K_\nu^{s,t}$ radial integrals are expressed in terms of G_ν^{stuv} in Eq. (18) as

$$J_\nu^{s,t}=G_\nu^{stst} \tag{20}$$

and

$$K_\nu^{s,t}=G_\nu^{stts}\,, \tag{21}$$

respectively. $N_s(i)$ is the occupation number of electrons in the sth shell of the ith CSF. $a_\nu^{s,t}(i)$ and $b_\nu^{s,t}(i)$ are the coefficients for the direct and exchange integrals, respectively. If either sth or tth shell is a closed shell in the ith CSF, $b_\nu^{s,t}(i)$ is written in a compact form as

$$b_\nu^{s,t}(i)=N_s(i)N_t(i)\frac{1}{2\nu+1}[C(j_sj_t\nu;\tfrac{1}{2},-\tfrac{1}{2})]^2\,, \tag{22}$$

while $a_\nu^{s,t}(i)$ is a product of $N_s(i)$ and $N_t(i)$. If both s and t are open shells, these coefficients become complicated. The coefficient $d_\nu^{stuv}(i,j)$ which comes from the off-diagonal matrix element between two CSF's are even more complicated. The calculation of these coefficients is carried out by using Sasaki's method[34] which will be described in the Appendix.

III. THE MULTICONFIGURATION RELATIVISTIC HARTREE-FOCK-ROOTHAAN EQUATION

As has been done in the RHFR theory,[15,26] the large $P(r)$ and the small $Q(r)$ components of orbitals in Eq. (10) are expanded in terms of Slater-type orbitals (STO's) as follows:

$$P_s(r)=\sum_p \xi_{sp}f_{\kappa_sp}(r)=\underline{f}_{\kappa_s}^\dagger\underline{\xi}_s \tag{23}$$

and

$$Q_s(r)=\sum_q \eta_{sq}f_{\kappa_s}q(r)=\underline{f}_{\kappa_s}^\dagger\underline{\eta}_s\,, \tag{24}$$

where ξ and η are the orbital expansion coefficients for the large and small components of orbitals, respectively. A STO $f_{\kappa p}$ is given by

$$f_{\kappa p}(r)=(2\zeta_{\kappa p})^{n'_{\kappa p}+1}[\Gamma(2n'_{\kappa p}+1)]^{-1/2}r^{n'_{\kappa p}}e^{-\zeta_{\kappa p}r}\,, \tag{25}$$

where $\Gamma(2n'_{\kappa p}+1)$ is a gamma function. $\zeta_{\kappa p}$ is an orbital exponent and $n'_{\kappa p}$ is a principal quantum number which is in general not an integer.

The total energy given in Eq. (16) can now be rewritten by using the orbital expansion coefficients ξ and η. The expression for the total energy contains various integrals over STO's. The one-electron integral in Eq. (17) is rewritten with the orbital expansion coefficient as

$$I_s=(\underline{\xi}_s^\dagger\underline{\eta}_s^\dagger)\underline{I}_{\kappa_s}\begin{bmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{bmatrix}\,, \tag{26}$$

where

$$\underline{I}_\kappa=\begin{bmatrix}\underline{V}_{N,\kappa} & -c\underline{T}_\kappa^- \\ c\underline{T}_\kappa^+ & \underline{V}_{N,\kappa}-2c^2\underline{S}_\kappa\end{bmatrix}\,. \tag{27}$$

$\underline{S}_\kappa$ is the overlap matrix whose elements are given by

$$(\underline{S}_\kappa)_{pq}=\int_0^\infty f_{\kappa p}(r)f_{\kappa q}(r)dr\,. \tag{28}$$

The kinetic energy matrix $\underline{T}_\kappa^\pm$ is defined as

$$(\underline{T}_\kappa^\pm)_{pq}=\int_0^\infty f_{\kappa p}(r)\left(\frac{d}{dr}\pm\frac{\kappa}{r}\right)f_{\kappa q}(r)dr\,. \tag{29}$$

The element of the nuclear potential matrix $V_{N,\kappa}$ is written as

$$(\underline{V}_{N,\kappa})_{pq}=\int_0^R f_{\kappa p}(r)\left[-\frac{Z}{2R}\left(3-\frac{r^2}{R^2}\right)\right]f_{\kappa q}(r)dr + \int_R^\infty f_{\kappa p}(r)\left(-\frac{Z}{r}\right)f_{\kappa q}(r)dr\,. \tag{30}$$

Numerical integration is useful in the calculation of elements of the nuclear potential matrix.

By using the expressions of the relevant integrals in Eqs. (26)–(30), the unperturbed energy given by Eq. (16) is written in the following matrix form:

$$\begin{aligned}E=&\sum_s\overline{N}_s(\underline{\xi}_s^\dagger\underline{\eta}_s^\dagger)\underline{I}_s\begin{bmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{bmatrix}\\ &+\tfrac{1}{2}\sum_{s,t}(\underline{\xi}_s^\dagger\underline{\eta}_s^\dagger)\begin{bmatrix}\underline{J}^{s,t}-\underline{K}_{\xi\xi}^{s,t} & -\underline{K}_{\xi\eta}^{s,t}\\ -\underline{K}_{\eta\xi}^{s,t} & \underline{J}^{s,t}-\underline{K}_{\eta\eta}^{s,t}\end{bmatrix}\begin{bmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{bmatrix}\\ &+\tfrac{1}{4}\sum_{stuv}(\underline{\xi}_s^\dagger\underline{\eta}_s^\dagger)\begin{bmatrix}\underline{L}_{\xi\xi}^{stuv} & \underline{L}_{\xi\eta}^{stuv}\\ \underline{L}_{\eta\xi}^{stuv} & \underline{L}_{\eta\eta}^{stuv}\end{bmatrix}\begin{bmatrix}\underline{\xi}_t\\ \underline{\eta}_t\end{bmatrix},\end{aligned} \tag{31}$$

where

$$(\underline{J}^{s,t})_{kl}=\sum_{p,q}(\xi_{tp}\xi_{tq}+\eta_{tp}\eta_{tq})\sum_\nu\overline{a}_\nu^{s,t}R_\nu^{sk,tp;sl,tq}\,, \tag{32}$$

$$(\underline{K}_{\xi\xi}^{s,t})_{kl}=\sum_{pq}\xi_{tp}\xi_{tq}\sum_\nu\overline{b}_\nu^{s,t}R_\nu^{sk,tp;tq,sl}\,, \tag{33}$$

$$(\underline{L}^{stuv}_{\xi\xi})_{kl}=\sum_{p,q}\xi_{up}\xi_{vq}\sum_{\nu}\bar{d}^{stuv}_{\nu}R^{sk,tl;up,vq}_{\nu}\,, \tag{34}$$

and

$$R^{sk,tl;up,vq}_{\nu}=\int_0^{\infty}\int U_{\nu}(1,2)f_{\kappa_s k}(1)f_{\kappa_t l}(2)\times f_{\kappa_u p}(1)f_{\kappa_v q}(2)dr_1dr_2\,. \tag{35}$$

The coefficients $\bar{N}_s$, $\bar{a}^{s,t}_{\nu}$, $\bar{b}^{s,t}_{\nu}$, and $\bar{d}^{stuv}_{\nu}$ are given by

$$\bar{N}_s=\sum_i c_i^2 N_s(i)\,, \tag{36}$$

$$\bar{a}^{s,t}_{\nu}=\sum_i c_i^2 a^{s,t}_{\nu}(i)\,, \tag{37}$$

$$\bar{b}^{s,t}_{\nu}=\sum_i c_i^2 b^{s,t}_{\nu}(i)\,, \tag{38}$$

and

$$\bar{d}^{stuv}_{\nu}=\sum_{i\neq j}c_ic_jd^{stuv}_{\nu}(i,j)\,. \tag{39}$$

The matrices of $\underline{K}^{s,t}_{\xi\eta}$, $\underline{K}^{s,t}_{\eta\xi}$, $\underline{K}^{s,t}_{\eta\xi}$, $\underline{L}^{stuv}_{\eta\xi}$, $\underline{L}^{stuv}_{\xi\eta}$, and $\underline{L}^{s,t}_{\eta\eta}$ are obtained by replacing $\xi\xi$ in $\underline{K}^{s,t}_{\xi\xi}$ or $\underline{L}^{stuv}_{\xi\xi}$ by corresponding products of ξ and η. The orthonormality condition for orbitals in Eq. (13) is also rewritten as

$$(\underline{\xi}^{\dagger}_{n\kappa}\underline{\eta}^{\dagger}_{n\kappa})\begin{pmatrix}\underline{S}_{\kappa} & 0\\ 0 & \underline{S}_{\kappa}\end{pmatrix}\begin{pmatrix}\underline{\xi}_{n'\kappa}\\ \underline{\eta}_{n'\kappa}\end{pmatrix}=\delta_{nn'}\,. \tag{40}$$

The variation of the unperturbed energy with respect to orbital expansion coefficients ξ and η under the condition that orbitals are orthogonal leads to the SCF equation in the matrix form. If the orbitals belonging to the same symmetry are all completely occupied, i.e., all $s\subset \mathfrak{C}$, the SCF equation is reduced to a familiar SCF equation given by

$$\underline{F}_s\begin{pmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{pmatrix}=\epsilon_s\begin{pmatrix}\underline{S}_{\kappa_s} & 0\\ 0 & \underline{S}_{\kappa_s}\end{pmatrix}\begin{pmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{pmatrix}\,, \tag{41}$$

where

$$\underline{F}_s=(2j_s+1)\underline{I}_s+\sum_t\begin{pmatrix}\underline{J}^{s,t}-\underline{K}^{s,t}_{\xi\xi} & -\underline{K}^{s,t}_{\xi\eta}\\ -\underline{K}^{s,t}_{\eta\xi} & \underline{J}^{s,t}-\underline{K}^{s,t}_{\eta\eta}\end{pmatrix}. \tag{42}$$

For a general open-shell case, the SCF equation is obtained as

$$\sum_t\underline{F}_{s,t}\begin{pmatrix}\underline{\xi}_t\\ \underline{\eta}_t\end{pmatrix}=\sum_{s'}\epsilon_{s,s'}\begin{pmatrix}\underline{S}_{\kappa_s} & 0\\ 0 & \underline{S}_{\kappa_s}\end{pmatrix}\begin{pmatrix}\underline{\xi}_{s'}\\ \underline{\eta}_{s'}\end{pmatrix}\,, \tag{43}$$

where t represents all orbitals and s and s' stand for orbitals belonging to the same symmetry. The Fock operator matrix is given by

$$\underline{F}_{s,t}=\delta_{s,t}\left[\bar{N}_s\underline{I}_s+\sum_u\begin{pmatrix}\underline{J}^{s,u}-\underline{K}^{s,u}_{\xi\xi} & -\underline{K}^{s,u}_{\xi\eta}\\ -\underline{K}^{s,u}_{\eta\xi} & \underline{J}^{s,u}-\underline{K}^{s,u}_{\eta\eta}\end{pmatrix}\right]+\frac{1}{2}\sum_{u,v}\begin{pmatrix}\underline{L}^{stuv}_{\xi\xi} & \underline{L}^{stuv}_{\xi\eta}\\ \underline{L}^{stuv}_{\eta\xi} & \underline{L}^{stuv}_{\eta\eta}\end{pmatrix}. \tag{44}$$

In order to simplify the SCF equation, we modify the Fock matrix as follows

$$\tilde{\underline{F}}_s=\tfrac{1}{2}(\underline{X}_s\underline{Y}_s+\underline{Y}^{\dagger}_s\underline{X}^{\dagger}_s)\,, \tag{45}$$

where

$$\underline{X}_s=\sum_t\underline{F}_{s,t}\begin{pmatrix}\underline{\xi}_t\\ \underline{\eta}_t\end{pmatrix} \tag{46}$$

and

$$\underline{Y}_s=(\underline{\xi}^{\dagger}_s\underline{\eta}^{\dagger}_s)\begin{pmatrix}\underline{S}_{\kappa_s} & 0\\ 0 & \underline{S}_{\kappa_s}\end{pmatrix}. \tag{47}$$

By using the modified Fock matrix $\tilde{\underline{F}}_s$, the SCF equation for a general open-shell case is given by

$$\tilde{\underline{F}}_s\begin{pmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{pmatrix}=\sum_{s'}\epsilon_{s,s'}\begin{pmatrix}\underline{S}_{\eta_s} & 0\\ 0 & \underline{S}_{\eta_s}\end{pmatrix}\begin{pmatrix}\underline{\xi}_{s'}\\ \underline{\eta}_{s'}\end{pmatrix}. \tag{48}$$

Applying the variational principle to the SCF expansion coefficients $\{c_i\}$, we obtain the eigenvalue equation from Eq. (16) in the following form,

$$\underline{H}\underline{C}=\underline{C}\underline{E}\,, \tag{49}$$

where $\underline{H}$ is the Hamiltonian matrix whose element is given by

$$(\underline{H})_{ij}=\langle\Phi_i|\hat{H}|\Phi_j\rangle\,, \tag{50}$$

and $\underline{C}$ is the column matrix of the CSF expansion coefficients.

The final unperturbed energy can be obtained by solving Eqs. (41) or (48) for orbital expansion coefficients and Eq. (49) for CSF expansion coefficients alternately until the difference of the unperturbed energies between two equations becomes lower than a given threshhold value. In terms of orbital energies, the total unperturbed energy is expressed as follows:

$$E=\frac{1}{2}\sum_s\left[\epsilon_s+\bar{N}_s(\xi^{\dagger}_s\eta^{\dagger}_s)\underline{I}_s\begin{pmatrix}\underline{\xi}_s\\ \underline{\eta}_s\end{pmatrix}\right]. \tag{51}$$

IV. EVALUATION OF THE OFF-DIAGONAL LAGRANGE MULTIPLIERS

When fractionally occupied orbitals $\mathfrak{F}$ are contained in orbitals of the same symmetry, off-diagonal Lagrange multipliers (ODLM's) appear in the SCF equation [see Eq. (48)]. The general SCF equation has been discussed by Huzinaga[37] and Hirao *et al.*[38,39] Hinze[40] has proposed various methods to solve the general SCF equation, that is, methods to evaluate the ODLM's. Here, the two-by-two rotation method of Hinze is used in the numerical calculations. This method is to make the unitary transformation for a pair of orbitals having the same symmetry so that the Lagrange multiplier matrix becomes Hermitian, namely,

$$\epsilon_{ss'} - \epsilon_{s's} = (\underline{\xi}_s^\dagger \underline{\eta}_s^\dagger)(\underline{\tilde{F}}_s - \underline{\tilde{F}}_{s'})\begin{pmatrix} \underline{\xi}_{s'} \\ \underline{\eta}_{s'} \end{pmatrix} = 0 . \tag{52}$$

The unitary transformation for a pair of orbitals in the expansion method is written as

$$(\underline{\xi}_s^\dagger \underline{\eta}_s^\dagger)' = (\underline{\xi}_s^\dagger \underline{\eta}_s^\dagger)\cos\theta + (\underline{\xi}_{s'}^\dagger \underline{\eta}_{s'}^\dagger)\sin\theta \tag{53}$$

and

$$(\underline{\xi}_{s'}^\dagger \underline{\eta}_{s'}^\dagger) = -(\underline{\xi}_s^\dagger \underline{\eta}_s^\dagger)\sin\theta + (\underline{\xi}_{s'}^\dagger \underline{\eta}_{s'}^\dagger)\cos\theta , \tag{54}$$

where θ is an angle of rotation. The final angle of the rotation in the transformation matrix is obtained through the SCF-like calculation. The two-by-two rotation method starts with the initial set of orbital expansion coefficients $(\underline{\xi}_s^\dagger \underline{\eta}_s^\dagger)$ and $(\underline{\xi}_{s'}^\dagger \underline{\eta}_{s'}^\dagger)$ which are used to construct the initial Fock matrix $\underline{\tilde{F}}_s$ and $\underline{\tilde{F}}_{s'}$.

By using $\underline{\tilde{F}}_s$ and $\underline{\tilde{F}}_{s'}$ and the new set of orbital expansion coefficients $(\underline{\xi}_s^\dagger \underline{\eta}_s^\dagger)'$ and $(\underline{\xi}_{s'}^\dagger \underline{\eta}_{s'}^\dagger)'$ which are obtained as a result of the unitary transformation in Eqs. (53) and (54), Lagrange multiplier matrices $\epsilon'_{ss'}$ and $\epsilon'_{s's}$ are constructed. By substituting $(\underline{\xi}_s^\dagger \underline{\eta}_s^\dagger)$ and $(\underline{\xi}_{s'}^\dagger \underline{\eta}_{s'}^\dagger)$ for $(\underline{\xi}_s^\dagger \underline{\eta}_s^\dagger)'$ and $(\underline{\xi}_{s'}^\dagger \underline{\eta}_{s'}^\dagger)'$ in $\epsilon'_{ss'}$ and $\epsilon'_{s's}$ through the relations in Eqs. (53) and (54), the rotational angle θ is determined from the approximate condition $\epsilon'_{ss'} \simeq \epsilon'_{s's}$. If we assume that an angle of the rotation is small, then

$$\cos\theta \simeq 1 - \tfrac{1}{2}\sin^2\theta . \tag{55}$$

This relation leads to an equation for θ in the following way

$$A \sin^2\theta + B \sin\theta + C \simeq 0 , \tag{56}$$

where

$$A = \langle s' | s' | s \rangle + \langle s | s' | s' \rangle - \langle s | s | s' \rangle - \langle s' | s | s \rangle , \tag{57}$$

$$B = \langle s' | s' | s' \rangle + \langle s | s | s \rangle - \langle s' | s | s' \rangle - \langle s | s' | s \rangle , \tag{58}$$

$$C = \langle s' | s | s \rangle - \langle s | s' | s' \rangle , \tag{59}$$

and

$$\langle s | s' | s'' \rangle = (\underline{\xi}_s^\dagger \underline{\eta}_s^\dagger)\underline{F}_{s'}\begin{pmatrix} \underline{\xi}_{s''} \\ \underline{\eta}_{s''} \end{pmatrix} . \tag{60}$$

By using the θ obtained from the Eq. (56), the new set of orbital expansion coefficients are calculated and then used in the construction of the new Fock matrices. This procedure is continued until the rotational angle becomes zero. In the next step, a different pair of orbitals are picked from orbitals with the same symmetry and the unitary transformation is analogously applied to them. The calculation terminates when the Lagrange multiplier matrix becomes Hermitian.

This method requires an initial set of orbitals which may affect the accuracy of the calculated results. It may be reasonable in most cases to consider that the fractionally occupied orbitals $\mathfrak{F}$ deviate only a small amount from corresponding completely occupied orbitals $\mathfrak{C}$ in the closed-shell system. The two-step calculation is carried out in the SCF iteration when using the two-by-two rotation method. To get the initial set of orbitals, first the SCF iteration is carried out by using the SCF equations of Eqs. (41) and (48), where the ODLM's $\epsilon_{ss'}$ and the coefficients of $\bar{d}_\nu^{stuv}$ are neglected. In the last step, the SCF iteration is continued by using the orbitals obtained from the modified SCF calculation, in which the exact SCF equations and the two-by-two rotation method are used.

V. THE CALCULATION OF THE BREIT INTERACTION ENERGY

The energy correction due to the Breit interaction is small and has the order of $(Z\alpha)^2$ compared with the Coulomb interaction energy. However, this correction is important in an accurate calculation of multiplet structures and electron binding energies.

The Breit operator in Eqs. (7)–(9) is the two-electron operator. The expectation value for the operator between the two CSF's can be evaluated in the same way as that for the repulsive Coulomb interaction operator $1/r_{12}$. The matrix element for the Breit operator has been studied by Grant,[8,9] Kim,[15] and Mann and Johnson[41] for closed-shell atoms. Grant and Pyper,[42] and Doyle[43] have given the general expression for the matrix element in the multiconfigurational case. The numerical calculation of this interaction in the MCDF formalism has been carried out by Kim's group[32,33] for three-electron systems and carbonlike atoms.

Following Grant and Pyper,[42] we expand the magnetic operator $\hat{H}_M(1,2)$ in Eq. (8) and the retardation operator $\hat{H}_R(1,2)$ in Eq. (9) in terms of tensors as follows:

$$\hat{H}_M(1,2) = \sum_{\nu, L} (-1)^{\nu+L} \underline{T}^{(1\nu)L}(1) \cdot \underline{T}^{(1\nu)L}(2)\, U_\nu(1,2) , \tag{61}$$

and

$$\hat{H}_R(1,2) = -2\sum_{\nu}\left(\frac{\nu+1}{2\nu+3}\underline{T}^{(1\nu)\nu+1}(1)\cdot\underline{T}^{(1\nu)\nu+1}(2)+\frac{\nu}{2\nu-1}\underline{T}^{(1\nu)\nu-1}(1)\cdot\underline{T}^{(1\nu)\nu-1}(2)\right)U_\nu(1,2)$$

$$+\sum_{\nu}\left\{\left[\left(-\frac{[(\nu+1)(\nu+2)(2\nu+1)(2\nu+5)]^{1/2}}{2\nu+3}\underline{T}^{(1,\nu+2)\nu+1}(1)\cdot\underline{T}^{(1\nu)\nu+1}(2)\right.\right.\right.$$

$$\left.\left.\left.+\frac{[\nu(\nu-1)(2\nu+1)(2\nu-3)]^{1/2}}{2\nu-1}\underline{T}^{(1\nu)\nu-1}(1)\cdot\underline{T}^{(1,\nu-2)\nu-1}(2)\right)\frac{r_2^\nu}{r_1^{\nu+1}}\right]+[1\leftrightarrow 2]\right\}, \qquad (62)$$

where

$$\underline{T}^{(1\nu)L} = (\underline{\alpha}^{(1)}\underline{C}^{(\nu)})^L\,. \qquad (63)$$

The notation $1\leftrightarrow 2$ stands for the expression in which particle coordinates $\vec{r}_1$ and $\vec{r}_2$ are interchanged. The matrix elements for any two-electron operator such as $1/r_{12}$ or $\hat{H}_B(1,2)$ between two CSF's can be decomposed in terms of products of many-particle coefficients of the fractional parentage (CFP) and the reduced matrix element for the operator. The calculation of many particle CFP's will be described in the Appendix.

The Breit interaction energy is expressed as

$$E_B=\sum_i c_i^2\left(\tfrac{1}{2}\sum_{st\nu}\sum_{\gamma=1}^{3}\{A_{\gamma,\nu}^{s,t}(i)\overline{M}_{\gamma,\nu}^{s,t}-B_{\gamma,\nu}^{s,t}\overline{N}_{\gamma,\nu}^{s,t}+[\tilde{a}_{\gamma,\nu}^{s,t}(R;i\,\|\,1>2)M_{\gamma,\nu}^{s,t}(1>2)-\tilde{b}_{\gamma,\nu}^{s,t}(R:i\,\|\,1>2)N_{\gamma,\nu}^{s,t}(1,2)+(1\leftrightarrow 2)]\}\right)$$

$$+\sum_{i\neq j}c_ic_j\left(\tfrac{1}{4}\sum_{stuv}\sum_{\gamma=1}^{3}\{D_{\gamma,\nu}^{stuv}(i,j)\overline{W}_{\gamma,\nu}^{stuv}+[\tilde{d}_{\gamma,\nu}^{stuv}(R;i,j\,\|\,1>2)W_{\gamma,\nu}^{stuv}(1>2)+(1\leftrightarrow 2)]\}\right), \qquad (64)$$

where

$$A_{\gamma,\nu}^{s,t}(i)=a_{\gamma,\nu}^{s,t}(M;i)+a_{\gamma,\nu}^{s,t}(R;i)\,, \qquad (65)$$

$$B_{\gamma,\nu}^{s,t}(i)=b_{\gamma,\nu}^{s,t}(M;i)+b_{\gamma,\nu}^{s,t}(R;i)\,, \qquad (66)$$

$$D_{\gamma,\nu}^{stuv}(i,j)=d_{\gamma,\nu}^{stuv}(M;i,j)+d_{\gamma,\nu}^{stuv}(R;i,j)\,, \qquad (67)$$

$$\overline{W}_{\gamma,\nu}^{stuv}=W_{\gamma,\nu}^{stuv}(1>2)+W_{\gamma,\nu}^{stuv}(1<2)\,, \qquad (68)$$

$$\overline{M}_{\gamma,\nu}^{s,t}=\overline{W}_{\gamma,\nu}^{stst}\,, \qquad (69)$$

$$\overline{N}_{\gamma,\nu}^{s,t}=\overline{W}_{\gamma,\nu}^{stts}\,, \qquad (70)$$

$$M_{\gamma,\nu}^{s,t}(x>y)=W_{\gamma,\nu}^{stst}(x>y)\,, \qquad (71)$$

and

$$N_{\gamma,\nu}^{s,t}(x>y)=W_{\gamma,\nu}^{stts}(x>y) \qquad (72)$$

for x, $y(\neq x)=1$, 2. The index γ indicates the type of the radial integral given by

$$W_{\gamma,\nu}^{stuv}(x>y)=\begin{cases}\displaystyle\int_0^\infty dr_x\int_0^{r_x}dr_y\frac{r_y^\nu}{r_x^{\nu+1}}[P_s(r_x)P_t(r_y)Q_u(r_x)Q_v(r_y)]\,,\quad \gamma=1 & (73)\\[2ex] \displaystyle\int_0^\infty dr_x\int_0^{r_x}dr_y\frac{r_y^\nu}{r_x^{\nu+1}}[Q_s(r_x)Q_t(r_y)P_u(r_x)P_v(r_y)]\,,\quad \gamma=2 & (74)\\[2ex] \displaystyle\int_0^\infty dr_x\int_0^{r_x}dr_y\frac{r_y^\nu}{r_x^{\nu+1}}[P_s(r_x)Q_t(r_y)Q_u(r_x)P_v(r_y)]\,,\quad \gamma=3\,. & (75)\end{cases}$$

$a_{\gamma,\nu}^{s,t}(M;i)$ and $b_{\gamma,\nu}^{s,t}(M;i)$ are the coefficients for the direct and the exchange terms of the magnetic interaction in the ith CSF, respectively. $a_{\gamma,\nu}^{s,t}(R;i)$ and $\tilde{a}_{\gamma,\nu}^{s,t}(R;i\,\|\,x>y)$, $b_{\gamma,\nu}^{s,t}(R;i)$ and $\tilde{b}_{\gamma,\nu}^{s,t}(R;i\,\|\,x>y)$ are the coefficients for the retardation term in the ith CSF. x and y stand for a label of coordinates of the two interacting electrons. $d_{\gamma,\nu}^{stuv}(M;i,j)$ and $d_{\gamma,\nu}^{stuv}(R;i,j)$ and $\tilde{d}_{\gamma,\nu}^{stuv}(R;i,j\,\|\,x>y)$ are the coefficients of the off-diagonal matrix element between ith and jth CSF's for the magnetic and the retardation operators, respectively. These coefficients are evaluated with the reduced matrix elements for the tensor operators in Eqs. (61) and (62) and many-particle CFP's described in the Appendix.

In the expansion method, the radial integral $W_{\gamma,\nu}^{stuv}(x>y)$ is expressed as

$$W_{\gamma,\nu}^{stuv}(x>y)=\begin{cases}\underline{\xi}_s^\dagger\underline{W}_{\xi\eta,\nu}^{stuv}(x>y)\underline{\eta}_u\,,\quad\gamma=1 & (76)\\ \underline{\eta}_s^\dagger\underline{W}_{\eta\xi,\nu}^{stuv}(x>y)\underline{\xi}_u\,,\quad\gamma=2 & (77)\\ \underline{\xi}_s^\dagger\underline{W}_{\eta\xi,\nu}^{stuv}(x>y)\underline{\eta}_u\,,\quad\gamma=3, & (78)\end{cases}$$

where

$$[\underline{W}^{stuv}_{\xi\eta,\nu}(x>y)]_{kl}=\sum_{p,q}\xi_{tp}\eta_{vq}Z^{sk,tp;ul,vq}_{\nu}(x>y)\,, \tag{79}$$

$$[\underline{W}^{stuv}_{\eta\xi,\nu}(x>y)]_{kl}=\sum_{p,q}\eta_{tp}\xi_{vq}Z^{sk,tp;ul,vq}_{\nu}(x>y)\,, \tag{80}$$

and

$$Z^{sk,tp;ul,vq}_{\nu}(x>y)=\int_0^\infty dr_x\int_0^{r_x}dr_y\frac{r_y^{\nu}}{r_x^{\nu+1}}[f_{\kappa_s k}(r_x)f_{\kappa_t p}(r_y)f_{\kappa_u l}(r_x)f_{\kappa_v q}(r_y)]\,. \tag{81}$$

VI. DETAILS OF THE NUMERICAL CALCULATION

The relativistic ground state, which is the lowest positive-energy state, corresponds to an excited state in the nonrelativistic case because of the infinite number of negative-energy states below the positive-energy states. The ground-state energy for atomic systems is obtained as the lowest stationary value among positive-energy values in the relativistic variational calculation. In the single configuration RHFR calculation,[15,26] the relativistic virial theorem[44] has been used to check whether an energy value obtained is stationary with respect to optimization of the exponents in the STO's. This situation is very different from the nonrelativistic case: In a nonrelativistic variational calculation, it is guaranteed by the variational principle that for an arbitrary wave function one cannot obtain a lower energy than the true ground-state energy. For excited states, MacDonald's theorem[45] can be used if one can construct an excited-state wave function which is orthogonal to all of wave functions for lower states belonging to the same symmetry than the state considered. However, it is impossible to apply this theorem to the calculation of inner-hole or autoionizing states in both the relativistic and the nonrelativistic calculations. In practice, one invokes an orbital picture for actual systems. As has been mentioned above, we cannot practically construct a variational function orthogonal to all the negative-energy functions: Most of them are continuum ones. It is probable that one has a lower energy than the corresponding exact energy for a system in a multiconfigurational calculation when increasing number of CSF's. This means that one must choose CSF's carefully in each calculation.

Two types of CSF's are considered in the relativistic multiconfiguration scheme. One is the coupling effect CSF and the other the correlation effect CSF.[29] The coupling effect CSF is defined as the set of jj configurations $(n\bar{l})^{m-r}(nl)^r$, J for $0\leq r\leq m$, where $\bar{l}$ and l correspond to orbital-angular-momentum quantum numbers for the shells of $j=l-\frac{1}{2}$ and $j=l+\frac{1}{2}$, respectively. The correlation effect CSF includes all the rest. The coupling effect CSF is used in the numerical calculation.

The electron correlation problem in the relativistic formalism is important. But the correlation energy is defined in the nonrelativistic framework. The concept of the electron correlation effect in the relativistic formalism is considered to be qualitative rather than quantitative because the relativistic energy cannot always be clearly divided into the nonrelativistic HF relativistic and correlation energies. The role of the coupling effect CSF will be discussed in connection with the correlation energy for the case of the *LS* limit in Sec. VII.

The accuracy of calculated results with the expansion method depends on a basis set used. When Salter-type orbitals (STO's) are taken as basis functions, the variation of orbital exponents in STO's is needed to get a good basis set. This requires much computation time. However, this difficulty can be dissolved to a certain degree by transferring a scaled basis set for an atom to other atoms and by using common basis functions not only between the large and small components of a radial wave function but between orbitals with the same orbital-angular-momentum quantum number such as $p_{1/2}$ and $p_{3/2}$ or $d_{3/2}$ and $d_{5/2}$ and so on.

Here, we calculate all states considered with a common basis set, which is obtained from the calculation of the single configuration RHFR method for the ground state in a system. Since difference of orbitals among the ground state, low-lying excited states, and the K-hole states is small, the orbitals can safely be represented by the same basis set.

VII. RESULTS AND DISCUSSIONS

A. Term energies

The MCRHFR method is first tested on term energies for oxygenlike systems, namely, O, Fe^{18+}, and Hg^{72+}. The highly ionized iron atom is impor-

TABLE I. Relativistic energies for the ground state and lower excited states in oxygen (a.u.).

Term	J	Unperturbed energy	Magnetic energy	Retardation energy	Total energy
$2s^2 2p^4$					
^3P	2	−74.858 424	0.007 846	−0.000 293	−74.850 871
	1	−74.857 666	0.007 713	−0.000 292	−74.850 245
	0	−74.857 487	0.007 817	−0.000 313	−74.849 983
^1D	2	−74.777 138	0.007 780	−0.000 290	−74.769 648
^1S	0	−74.656 213	0.007 794	−0.000 268	−74.648 687
$2s2p$					
$^3P^o$	2	−74.218 633	0.007 839	−0.000 319	−74.211 113
	1	−74.220 687	0.007 788	−0.000 315	−74.213 214
	0	−74.217 209	0.007 727	−0.000 319	−74.209 701
$^1P^o$	1	−73.902 753	0.007 837	−0.000 319	−73.895 235
$2p^6$					
^1S	0	−73.357 489	0.007 739	−0.000 340	−73.350 090

tant in fusion plasma diagnostics. Although no observation of the spectra for Hg^{72+} has been reported, this ion is picked as a representative system of the jj limit to see the effectiveness of the theory for such a system.

The calculated energies for the ground and low-lying excited states arising from configurations of type $1s^2 2s^n (2p_{1/2})^{n'} (2p_{3/2})^{n''}$ of oxygen are listed in Table I, where $n+n'+n''=6$. The CSF's used are coupling effect ones which are listed in Table II. The total wave function is constructed as a linear combination of two CSF's for all states except for $2s^2 2p^4\,{}^3P_1$, $2s2p^5\,{}^3P_{2,0}$, and $2p^6\,{}^1S_0$, where a single configuration is used. The core $1s^2$ is omitted in the notation of the configurations. The separate calculations are made for the $2s^2 2p^4\,{}^1S_0$ and $2p^6\,{}^1S_0$ states because these two configurations are correlation effects CSF's for each other in our classification scheme.

TABLE II. Configuration state functions (CSF's) used. $2\bar{p}$ and $2p$ mean $2p_{1/2}$ and $2p_{3/2}$, respectively.

Term	Configuration	J
^3P, ^1D, ^1S	$1s^2 2s^2 2\bar{p}^2 2p^2$	0, 2
	$1s^2 2s^2 2\bar{p}\ 2p^3$	1, 2
	$1s^2 2s^2 2p^4$	0
^1S	$1s^2 2\bar{p}^2 2p^4$	0
$^3P^o$, $^1P^o$	$1s^2 2s 2\bar{p}^2 2p^3$	1, 2
	$1s^2 2s 2\bar{p}\ 2p^4$	0, 1
$^3P^o$, $^1P^o$	$1s 2s^2 2\bar{p}^2 2p^3$	1, 2
	$1s 2s^2 2\bar{p}\ 2p^4$	0, 1
^3S, ^1S	$1s 2s 2\bar{p}^2 2p^4$	0, 1
^4P, ^2D, ^2P, ^2S	$1s 2s^2 2\bar{p}^2 2p^2$	$\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$
	$1s 2s^2 2\bar{p}\ 2p^3$	$\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$
	$1s 2s^2 2p^4$	$\frac{1}{2}$

The basis set is obtained from the single configuration RHFR calculation for the ground state $2s^2 2p^4\,{}^3P_2$. As the effect of the finite nucleus is included in the RHFR Hamiltonian, the principal quantum number in STO's can be taken as an integer to save computation time, while the point nucleus (the cusp condition at the origin) leads to the noninteger principal quantum number in the single-electron Dirac theory. However, noninteger STO's are used as basis functions here, since trial calculations showed that the noninteger STO's

TABLE III. Values of orbital exponents in STO's used in the RHFR calculations for O, Fe^{18+}, and Hg^{72+}.

Symmetry	n'[a]	Exponent O	Fe^{18+}	Hg^{72+}
s	$1s$	8.0	25.223	94.3225
	$1s$	12.105	38.1653	142.7218
	$2s$	6.805	21.4551	80.2331
	$2s$	3.39	10.6887	39.9692
	$2s$	1.698	5.3536	20.02
$p_{1/2}$ and $p_{3/2}$	$1p$[b]	8.0	26.0987	83.4604
	$2p$	5.598	18.2631	58.4014
	$2p$	3.592	11.7183	37.4737
	$2p$	2.015	6.5737	21.0216
	$2p$	1.205	3.9312	12.5712

[a] The principal quantum number in an STO is $n-[\kappa^2-(Z\alpha)^2]^{1/2}$.

[b] This STO is used only for a $2p_{1/2}$ orbital.

TABLE IV. Relativistic energies for the ground state and lower excited states in Fe^{18+} (a.u.).

Term	J	Unperturbed energy	Magnetic energy	Retardation energy	Total energy
$2s^22p^4$					
^3P	2	−1052.2526	0.4177	−0.0297	−1051.8646
	1	−1051.8382	0.3997	−0.0295	−1051.4680
	0	−1051.8843	0.4285	−0.0327	−1051.4885
^1D	2	−1051.4586	0.3976	−0.0296	−1051.0906
^1S	0	−1050.6209	0.4044	−0.0291	−1050.2456
$2s2p^5$					
$^3P^o$	2	−1047.9588	0.4246	−0.0334	−1047.5676
	1	−1047.6699	0.4191	−0.0330	−1047.2838
	0	−1047.4601	0.4110	−0.0330	−1047.0821
$^1P^o$	1	−1046.3091	0.4190	−0.0330	−1045.9231
$2p^6$					
^1S	0	−1042.4703	0.4319	−0.0370	−1042.0754

gave better convergence (especially for heavier elements) in the RHFR calculation. The number of STO's is 5 for the s shell, 5 for the $p_{1/2}$ shell, and 4 for the $p_{3/2}$ shell. These basis sets used in the MCRHFR calculations for O, Fe^{18+}, and Hg^{72+} are listed in Table III. The STO's for the $p_{1/2}$ shell are the same as those for the $p_{3/2}$ shell except that a $1p$ STO which is introduced to describe a node of the small component of the $p_{1/2}$ orbital.

In the calculation of states with two CSF's, the MCRHFR orbitals obtained by solving the SCF equation in Eqs. (41) or (48) are used to construct the two-dimensional Hamiltonian matrix. The two energies obtained by diagonalizing this Hamiltonian matrix are assigned to corresponding upper and lower levels.

The calculated energies for Fe^{18+} as a system in intermediate coupling and for Hg^{72+} as jj limit system are listed in Tables IV and V, respectively. In Table I, one sees an inversion of the unperturbed and total energies between the $^3P_2^o$ and $^3P_1^o$ states arising from the $2s2p^5$ configuration in oxygen. On the other hand this inversion of the energies between the $^3P_2^o$ and $^3P_1^o$ states is not observed for Fe^{18+} and Hg^{72+}, which is in agreement with experiment for Fe^{18+}.

The magnetic interaction energy is always positive, whereas the retardation energy which is about 10% of the magnetic energy in magnitude is negative. The Breit interaction energy increases rapidly when the atomic number increases. The energy correction due to this interaction is about 0.01, 0.04, and 0.12% of the unperturbed energy for all states considered for O, Fe^{18+}, and Hg^{72+}, respectively.

By using the energy values in Tables I, IV, and V, the term energies relative to the ground state are calculated and listed in Table VI together with

TABLE V. Relativistic energies for the ground state and lower excited states in Hg^{72+} (a.u.).

Term	J	Unperturbed energy	Magnetic energy	Retardation energy	Total energy
$2s^22p^4$					
^3P	2	−11 802.721	15.646	−1.144	−11 788.219
	1	−11 728.454	14.626	−1.148	−11 714.976
	0	−11 800.549	16.078	−1.147	−11 785.618
^1D	2	−11 727.387	14.874	−1.145	−11 713.658
^1S	0	−11 652.077	14.255	−1.140	−11 638.962
$2s2p^5$					
$^3P^o$	2	−11 710.986	15.743	−1.274	−11 696.517
	1	−11 707.606	15.886	−1.269	−11 692.989
	0	−11 636.226	14.905	−1.275	−11 622.596
$^1P^o$	1	−11 634.475	14.990	−1.274	−11 620.759
$2p^6$					
^1S	0	−11 614.690	16.027	−1.396	−11 600.059

TABLE VI. Comparative results for term energies relative to the ground state in O, Fe^{18+}, and Hg^{72+} (cm^{-1}).

		O		Fe^{18+}			Hg^{72+}	
Term	J	MCRHFR	Expt.[a]	MCRHFR	RZD[c]	Expt.[b]	MCRHFR	RZD[c]
$2s^2 2p^4$								
^3P	2	0	0	0	0	0	0	0
	1	137	158.3	87 044	77 694	89 410	$0.160\,750\times 10^8$	$0.128\,00\times 10^8$
		155[d]		86 820[d]				
	0	195	227.0	82 544	75 719	75 290	$0.570\,853\times 10^6$	$0.584\,24\times 10^6$
		231		78 641[d]				
^1D	2	17 826	15 867.9	169 873	176 020	169 800	$0.163\,643\times 10^8$	$0.129\,54\times 10^8$
		17 780[d]		170 307[d]				
		17 593[e]						
^1S	0	44 374	33 792.6	355 329	343 040	326 160	$0.327\,581\times 10^8$	$0.259\,38\times 10^8$
		44 332[d]		351 545[d]				
		43 557						
$2s2p^5$								
$^3P^o$	2	140 411	126 266.8	943 082	1 092 500	922 770	$0.201\,263\times 10^8$	$0.167\,44\times 10^8$
	1	139 950	126 340.1	1 005 370	1 148 900	984 650	$0.209\,006\times 10^8$	$0.175\,08\times 10^8$
	0	140 721	126 383.8	1 049 550	1 187 600	1 029 830	$0.363\,500\times 10^8$	$0.296\,06\times 10^8$
$^1P^o$	1	209 738		1 304 010	1 468 300	1 268 400	$0.367\,534\times 10^8$	$0.299\,54\times 10^8$
$2p^6$								
^1S	0	329 383		2 148 480	2 525 100	2 134 800	$0.412\,963\times 10^8$	$0.345\,98\times 10^8$

[a] Reference 48.
[b] Reference 49.
[c] Values obtained with the relativistic Z-dependent theory (see Ref. 43).
[d] Reference 47.
[e] Reference 46.

those of the relativistic Z-dependent (RZD) theory of Doyle[43] and the nonrelativistic Hartree-Fock (NRHF) method[46,47] and experiment.[48,49] The MCRHFR values for O and Fe^{18+} agree well with experiment except even parity states of the $^3P_{2,1,0}$, $^1D_2$, and $^1S_0$ states in oxygen. The MCRHFR method with coupling effect CSF yields better results for heavier elements than for lighter ones in which the electron correlation effects are larger than the relativistic effects. This comes from the fact that the correlation energy is almost independent on atomic number, whereas the unperturbed energy increases in proportion to the square of the atomic number. Veillard and Clementi[46] have estimated the empirical correlation energy for the first- and the second-row elements in the periodic system. In oxygen the difference of the correlation energies between the ^1D and ^3P and between the ^1S and ^3P states arising from the configuration $1s^2 2s^2 2p^4$ are -0.0078 and -0.0446 a.u., respectively.

If the MCRHFR term energies are corrected by adding these correlation energies, the theoretical term energies are 16 114 cm^{-1} for the $^1D_2$ and 34 585 cm^{-1} for the $^1S_0$ state, which are close to the experimental values. The term energies for the $^3P_1$ and $^3P_0$ states which are smaller than experiment will be improved if the correlation energy and the higher-order QED effects are taken into account. In the calculated term energies for Fe^{18+}, the discrepancy between the calculated and experimental values for the $^1D_2$ and $^1S_0$ states is small, whereas the calculated values for $^1S_0$ state of oxygen is about 30% larger in magnitude than the experimental result. This means that the relativistic effects play an important role in Fe^{18+} compared with the correlation effects.

To compare our results with other relativistic ones, the calculated term energies by Doyle's relativistic Z-dependent (RZD) theory[43] are listed in Table VI. This theory is an Z^{-1}-expansion perturbation theory which has an advantage that the same formula of calculating a given energy level can be used for all the members of an isoelectronic sequence by varying the atomic number. Since this method does not yield the correct term energies for oxygen, only the RZD results for Fe^{18+} and Hg^{72+} are listed in Table VI. The RZD term energies are not as good as the MCRHFR ones for all the states in Fe^{18+} except the $^3P_0$ and $^1S_0$ states arising from the $2s^2 2p^4$ configuration. For Hg^{72+}, discrepancy between the RZD and the MCRHFR results is slightly large compared with that for Fe^{18+}. Although a trend of the term energies when atomic number increases can be easily obtained by the RZD method, this method should be carefully used since a wrong fine structure of energy levels is obtained in some cases.

The nonrelativistic term energies in Table VI have been obtained from a HF calculation[46,47] in which all the relativistic corrections are included. The NRHF term energies for both O and Fe^{18+} are almost the same as our results. This shows that the Pauli approximation for the Breit equation is fairly good even for highly ionized atoms such as Fe^{18+}.

It is interesting to compare the MCRHFR results for oxygen with the NRHF ones, since neutral oxygen is considered to be a system in the *LS* limit. Comparison of the MCRHFR energies for oxygen with two NRHF ones[46,47] are made in Table VII. The MCRHFR unperturbed energies are lower than the nonrelativistic Hartree-Fock-Roothaan (NRHFR) (Ref. 46) or the numerical NRHF (Ref. 47) ones because some of the relativistic effects such as the spin-orbit interaction are included in the MCRHFR unperturbed energy.

Our total energies in Table VII are little higher than the NRHFR and the NRHF ones. The small difference in the total energy between the relativistic and the nonrelativistic methods arises from the difference in orbitals which are used in the calculations of the energy correction due to the Breit interaction and the relativistic correction, respectively. However, the results in Table VII show that the MCRHFR method can be applied to the system in the *LS* limit with satisfactory accuracy.

From the theoretical values for Hg^{72+} in Table V, one is able to predict the trends in the relative values for the term energies in the *jj* limit. For Hg^{72+}, the unperturbed energies between the $^3P_2$ and $^3P_0$ states and between the $^3P_1$ and $^1D_2$ states in Table V are very close to each other. The reason is that the wave functions for $^3P_2$ and $^3P_0$ states can almost be expressed by $1s^22s^2(2p_{1/2})^2(2p_{3/2})^2$ and that the wave functions for $^3P_1$ and $^1D_2$ states by the $1s^22s^2(2p_{1/2})(2p_{3/2})^3$ configuration. In the *jj* limit, the energy difference between $(2p_{1/2})^2(2p_{3/2})^2$ and $(2p_{1/2})(2p_{3/2})^3$ configurations becomes large because the binding energy of $2p_{1/2}$ electrons is much larger than that of $2p_{3/2}$ ones. To examine this effect of the coupling scheme in more detail, the CSF expansion coefficients obtained from the calculation of the ground state for O, Fe^{18+}, and Hg^{72+} are listed in Table VIII. It can be seen that the MCRHFR method yields a wave function with appropriate intermediate coupling for each system. The term energy for $2s^22p^4\,{}^1S_0$ of Hg^{72+} is higher than that for $2s2p^5\,{}^3P^o_{2,1}$, contrary to oxygen and Fe^{18+}. This characteristic is also explained by looking at the CSF expansion coefficients and binding energies of each electron.

TABLE VIII. Values of the CSF expansion coefficients for the ground state ($1s^22s^22p^4$, $^3P_2$) of O, Fe^{18+}, and Hg^{72+}. Values in the parentheses are those in the LS limit. $2\bar{p}$ and $2p$ stand for $2p_{1/2}$ and $2p_{3/2}$, respectively.

CSF		CSF expansion coefficient O	Fe^{18+}	Hg^{72+}
$1s^22s^22\bar{p}^22p^2$	$(J=2)$	0.822 00 (0.816 50)	0.956 78	0.999 99
$1s^22s^22\bar{p}2p^3$	$(J=2)$	0.569 48 (0.577 35)	−0.290 81	0.010 07

B. Transition energies for the *K*-hole states in Fe^{18+}

The fine structure in inner-hole states is of interest when studying relativistic effects in inner-shell electrons. The calculated energies for all *K*-hole states arising from the configurations $1s2s^2(2p_{1/2})^n(2p_{3/2})^{n'}(n+n'=5)$ and $1s2s(2p_{1/2})^2(2p_{3/2})^4$ for Fe^{18+} are listed in Table IX together with those for Fe^{19+} whose configuration is $1s2s^2(2p_{1/2})^n(2p_{3/2})^{n'}(n+n'=4)$. It is seen from Table IX that not only the unperturbed energies but also magnetic energies are reduced in the *K*-hole states compared with those in corresponding valence states in Table IV. However, the retarda-

TABLE VII. Comparison of the MCRHFR results with nonrelativistic HF results for oxygen (a.u.).

		This work		NRHFR[a]		NRHF[b]	
Term	J	Unperturbed energy	Total energy	HF	Total energy[c]	HF	Total energy[c]
^3P	2	−74.858 424	−74.850 871	−74.809 37	−74.856 23	−74.809 47	−74.856 26
	1	−74.857 666	−74.850 245				−74.855 55
	0	−74.857 487	−74.849 982				−74.855 21
^1D	2	−74.777 138	−74.769 648	−74.726 67	−74.776 07		−74.775 25
^1S	0	−74.656 213	−74.648 687	−74.608 42	−74.657 77		−74.654 27

[a] Reference 46.

[b] Reference 47.

[c] All the relativistic corrections are included.

TABLE IX. Relativistic energies for K-hole states in Fe^{18+} and Fe^{19+} (a.u.).

Term	J	Unperturbed energy	Magnetic energy	Retardation energy	Total energy
$1s2s^2 2p^5$					
$^3P^o$	2	−814.006 53	0.144 26	−0.022 34	−813.884 61
	1	−813.749 75	0.152 87	−0.012 45	−813.609 33
	0	−813.460 73	0.132 35	−0.022 39	−813.350 77
$^1P^o$	1	−813.017 77	0.138 66	−0.018 70	−812.897 81
$1s2s2p^6$					
^3S	1	−809.667 23	0.146 46	−0.022 03	−809.542 80
^1S	0	−809.536 83	0.146 93	−0.017 93	−809.407 83
$1s2s^2 2p^4$					
^4P	$\frac{5}{2}$	−759.246 86	0.119 83	−0.020 01	−759.147 04
	$\frac{3}{2}$	−759.054 33	0.128 12	−0.009 55	−758.935 76
	$\frac{1}{2}$	−758.617 39	0.137 23	−0.018 45	−758.498 61

tion energies are almost the same. This is because most of contributions of the magnetic interaction comes from the interaction between two 1s electrons, whereas the retardation energy between electrons in a closed shell vanishes. The basis set used in the calculation of K-hole states is the same as that for valence states, which is listed in Table III. The CSF's used are also listed in Table II.

By using energy values in Tables IV and IX for Fe^{18+}, all the possible transition frequencies except the singlet-triplet ones for the radiative transition when a 2p electron fills a 1s vacancy are calculated and are listed in Table X together with experiment.[49] It is seen from the table that the multiplet structure effect on the transition frequencies for all the transitions considered here is relatively small. The radiative transitions between various states arising from the configurations $1s^2 2s^2 2p^4$ and $1s2s^2 2p^5$, and $1s^2 2s2p^5$ and $1s2s2p^6$ are expected to exhibit structure if the resolution of the spectrometer is good enough.

TABLE X. Transition frequencies for Fe^{18+} (cm^{-1}).

Transition			Calc.
$1s^2 2s^2 2p^4$	-	$1s2s^2 2p^5$	
^3P		$^3P^o$	
2		2	52 231 000
2		1	52 291 000
1		2	52 144 000
1		1	52 204 000
1		0	52 261 000
0		1	52 208 000
$^1D_2$		$^1P^o_1$	52 277 000
$^1S_0$		$^1P^o_1$	52 092 000
$1s^2 2s2p$	-	$1s2s2p^6$	
$^3P^o$		^3S	
2		1	52 241 000
1		1	52 178 000
0		1	52 134 000
$^1P^o_1$		$^1S_0$	51 909 000
			Expt.[a]
$1s^2 2s^2 2p$	-	$1s2s^2 2p^5$	52 138 00

[a] Reference 49.

VIII. CONCLUDING REMARKS

By using the expansion method, the MCRHFR theory for atomic systems is presented. The ODLM's for open-shell cases are calculated by use of the two-by-two rotation method of Hinze. The Breit interaction is treated as a first-order perturbation. The calculation of the matrix elements for two-electron operators such as the repulsive Coulomb interaction operator and the Breit operator is carried out by Sasaki's method, where the tensor recoupling transformation techniques are used to calculate many-particle CFP's for second-quantized operators.

Numerical application of the theory to term energies for low-lying excited states in oxygenlike systems (O, Fe^{18+}, and Hg^{72+}) and to the transition energies for K-hole states in Fe^{18+} are presented. The calculated term energies are in agreement with experiment for heavier elements in which the relativistic effects are larger than the correlation effect. It is shown that the MCRHFR method yields the wave function in appropriate intermediate coupling for each system. The fixed basis set calculation is economical and useful in the calculations for highly ionized atomic systems with or without inner-shell vacancies although the truncation error of the basis set inherently exists in the MCRHFR method compared with the numerical MCDF method.

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APPENDIX: CALCULATION OF THE MATRIX ELEMENT FOR TWO-ELECTRON OPERATORS

By using tensor algebra, techniques of calculating the matrix element for two-body operators have been developed by various authors.[50-54] Here, we extend Sasaki's method[34] of calculating the matrix element to the *jj* coupling case.

The creation $a^\dagger$ and the annihilation a operators for an electron in the *nljm* shell satisfy the following fermion anticommutation relations:

$$[a_s, a_t^\dagger]_+ = \delta_{st}\,, \quad [a_s^\dagger, a_t^\dagger]_+ = [a_s, a_t]_+ = 0\,. \tag{A1}$$

It can easily be shown that $a_{nljm}^\dagger$ and $\tilde{a}_{nljm}$ defined as

$$\tilde{a}_{nljm} = (-1)^{j-m} a_{nlj,-m}\,, \tag{A2}$$

are irreducible tensors in the second-quantized form.

Any CSF in a second-quantized form can be constructed by use of creation operators such as

$$|\alpha J\rangle = [\cdots[(a_2^\dagger)^{N_2}, v_2 T_2 [(a_1^\dagger)^{N_1}, v_1 T_1]^{J_1}]^{J_2}\cdots]^{J}|0\rangle\,, \tag{A3}$$

where $|0\rangle$ denotes the vacuum state. N_s is the occupation number and v_s and T_s are the seniority number and the subtotal angular-momentum quantum number in the *s*th shell, respectively. J_s is the resultant angular momentum as a result of the recoupling of J_{s-1} and T_s, where $J_1 = T_1$. If there are shells with $j > \frac{7}{2}$ which contain more than two electrons, an additional label other than the seniority number v is needed to distinguish a state of T in the shell.

The two-electron operator is also written in a second-quantized form as

$$G = \frac{1}{2}\sum_{stuv} \langle st|g_\nu(1,2)|uv\rangle a_s^\dagger a_t^\dagger a_v a_u\,. \tag{A4}$$

The calculation of the matrix element for two-electron operators such as the repulsive Coulomb and the Breit interaction operators is essentially reduced to the expectation values of the operator having a form;

$$g_\nu(1,2) = \underline{g}^{(\nu)}(1)\cdot\underline{g}^{(\nu)}(2)\,. \tag{A5}$$

In this case, G is rewritten as

$$G = \sum_{stuv} (-1)^\nu (2\nu+1)^{-1/2} \langle s\|\underline{g}^{(\nu)}\|u\rangle\langle t\|\underline{g}^{(\nu)}\|v\rangle \times :[(a_s^\dagger \tilde{a}_u)^{(\nu)}(a_t^\dagger \tilde{a}_v)^{(\nu)}]^{(0)}:\,, \tag{A6}$$

where : : means the normal product.

The many-particle CFP is evaluated through the calculation of the expectation values between two CSF's for recoupled operators concerning participating electrons, i.e.,

$$I = \langle \alpha' J'\|[(a_s^\dagger \tilde{a}_u)^{(\nu)}(a_t^\dagger \tilde{a}_v)^{(\nu)}]^{(0)}|\alpha J\rangle \delta_{JJ'}\,. \tag{A7}$$

The essence of Sasaki's method consists of the use of alternative equations for recoupling transformation. Those equations are Eqs. (8) and (9) in his paper.[34]

Before applying these formulas, one has to arrange the operators in the two-electron operator with correct order from the innermost shell to the outermost one. This has already been done when constructing CSF's in Eq. (A3). The final form of operators in I of Eq. (A7) is given by

$$I = \sum_{\bar{J}} A_{\bar{J}} \langle \alpha' J'|(\cdots(q_2, v_2'' T_2''(q_1, v_1'' T_1'')^{J_1''})^{J_2''}\cdots)^{(0)} \times|\alpha J\rangle \delta_{JJ'}\,, \tag{A8}$$

where $q_s = a_s^\dagger$, $q_t = a_t^\dagger$, $q_u = \tilde{a}_u$, $q_v = \tilde{a}_v$, and $q_k = 1$ if k is other than s, t, u, and v. $A_{\bar{J}}$ is the coefficient arising from the recoupling for the operators of participating electrons in the two-electron operator, where $\bar{J}$ is one of resultant total-angular-momentum quantum numbers $\{J_i''\}$ in Eq. (A8). If there is more than one participating electron in the same shell, q means a set of these operators.

Applying the tensor recoupling transformation techniques given by Sasaki for a set of second-quantized operators, we obtain the many-electron CFP which is combined with the reduced matrix element for the operator to get the final result for the matrix element.

Note added. After this manuscript was submitted for publication, a paper on a computer program which calculates the Breit interaction energy has appeared in print.[55]

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