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Relativistic Self-Consistent-Field Theory for Closed-Shell Atoms*†

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The relativistic Hartree-Fock-Roothaan equation for closed-shell configurations of atoms is derived. The relativistic Hamiltonian consists of the sum of the Dirac Hamiltonians and the interelectronic Coulomb repulsion terms. The atomic wave function is assumed to be an antisymmetrized product of 4-component orbitals whose radial functions are expanded in terms of the Slater-type basis functions. The Breit interaction operator is used as the relativistic interelectronic interaction term, and is treated as the first-order perturbation. Expressions for the matrix elements of the Breit interaction operator are given for the closed-shell configurations. Numerical results for the ground states of He, Be, and Ne atoms computed according to this formalism are also presented.

INTRODUCTION

THE Dirac theory of the electron, combined with quantum electrodynamics, has been very successful for the relativistic treatment of the hydrogen atom, but it is difficult to extend such a theory to many-electron atoms and develop a practical relativistic theory of complex atoms. The first obstacle to such an extension is the difficulty of finding a Lorentz-invariant Hamiltonian operator to describe all relativistic interactions of atomic electrons among themselves and with the nucleus. Since the Hartree-Fock self-consistent-field (SCF) theory[1] starts from a Hamiltonian operator (or the corresponding Schrödinger equation), the extension of the SCF theory to the relativistic case starts with an approximation to the relativistic Hamiltonian operator to be used, in addition to other approximations on which the nonrelativistic SCF theory is based.

The first-order relativistic effects, however, such as the spin-orbit coupling, magnetic interaction, and the retardation of the Coulomb repulsion between electrons, may be approximated by the sum of the Dirac Hamiltonians[2] and the Breit interaction operators[3] (referred to as the Breit operator hereafter). In the nonrelativistic limit, these operators are reduced to the terms denoted by Bethe and Salpeter[4] as H_1 through H_6, which include, among others, spin-orbit, spin-spin, and spin-other-orbit couplings. The hyperfine structure and the nuclear motion are not included in these operators. At present, however, it is impossible to express the higher order relativistic effects, which contribute to the Lamb shift, in terms of some operators suitable for the extension of the SCF formalism.[5]

There is a theoretical difficulty associated even with the use of the Breit operator in the relativistic Hartree-Fock scheme. As was pointed out by Breit,[3] and later by Bethe and Salpeter,[6] the Breit operator should be treated as the first-order perturbation to the relativistic Hamiltonian which is the sum of the Dirac Hamiltonians for the one-electron part and the nonrelativistic Coulomb repulsion terms for the electron-electron interaction. Inclusion of the Breit operator in the unperturbed Hamiltonian would lead to a result inconsistent with quantum electrodynamics.

The Breit operator accounts for the magnetic interaction and the retardation of the Coulomb repulsion; both these terms are of the order $(v/c)^2$ compared to the nonrelativistic two-electron interaction term, where v is some average speed of the electrons and c is the speed of light. In the hydrogenic case, the ratio v/c is of the order of $Z\alpha$, where Z and α are the nuclear charge and the fine-structure constant, respectively. The nonrelativistic expectation value of the nuclear potential is of the order of $Z^2\alpha^2 m_0c^2$, where m_0 is the rest mass of the electron, and the nonrelativistic expectation value of the interelectronic repulsion term should be of the order of $Z\alpha^2 m_0c^2$. Therefore, the change in the one-electron energy due to the Dirac Hamiltonian is expected to be of

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[1] For the nonrelativistic SCF theory of atoms, see, for instance, D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957). It is customary to reserve the term "Hartree-Fock wave function" for the exact solution of the Hartree-Fock integro-differential equation. We shall use the terms SCF and Hartree-Fock interchangeably.

[2] We follow the conventions of M. E. Rose, *Relativistic Electron Theory* (John Wiley & Sons, Inc., New York, 1961) except for the units. We use atomic units.

[3] G. Breit, Phys. Rev. **34**, 553 (1929). The derivation and discussion of the Breit operator, from the veiwpoint of the *S*-matrix theory, can be found in A. I. Akhiezer and V. B. Berestetsky, *Quantum Electrodynamics* (Interscience Publishers, Inc., New York, 1965). See also H. A. Bethe and E. Fermi, Z. Physik **77**, 296 (1932).

[4] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Julius Springer-Verlag, Berlin, 1957), p. 181.

[5] For the computation of the Lamb shift correction, it is necessary to include contributions from the unperturbed wave functions of all the excited states, which is impractical for complex atoms. See, for instance, K. Y. Kim [Phys. Rev. **140**, A1498 (1965)] for calculations of higher order relativistic corrections for the helium atom; also G. E. Brown *et al.* [Proc. Roy. Soc. (London) **A251**, 92 (1959); **A251**, 105 (1959)], and D. F. Mayers *et al.* [Phys. Rev. Letters, **3**, 90 (1959)] for the Lamb shift corrections for heavy atoms.

[6] Reference 4, p. 170.

the order $Z^4\alpha^4m_0c^2$, whereas the change in the interelectronic interaction terms (including those from the Breit operator) would be of the order of $Z^3\alpha^4m_0c^2$.

The first attempt to formulate a relativistic SCF theory was made by Swirles.[7] She tabulated the relativistic equivalent of the Slater coefficients arising from the Coulomb repulsion term, but no serious application of this scheme was made at the time. Later, some relativistic SCF calculations were made by various authors, but most of these calculations either omitted the exchange term or made some approximations to avoid the numerical difficulties. For instance, Schonfelder computed for various atoms numerical wave functions without the exchange terms,[8] and Liberman and his coworkers calculated numerical wave functions for the closed-shell configurations of some atoms by approximating the exchange term by Slater's method.[9] A significant theoretical advance was made a few years ago by Grant,[10] who derived more general expressions for the relativistic Slater coefficients computed by Swirles as well as for those arising from the magnetic interaction. In addition, Grant presented the relativistic Hartree-Fock equations for closed-shell atoms including the magnetic interaction term in the unperturbed Hamiltonian. More recently, Synek[11] proposed a relativistic SCF scheme in which the orbitals are expanded in terms of 4-component basis spinors, but he did not make use of Grant's results for the relativistic Slater coefficients.

In this paper, we present a relativistic SCF theory for closed-shell atoms based on an uperturbed Hamiltonian which is the sum of the Dirac Hamiltonians and the Coulomb repulsion terms. The complete Breit operator, which contains both the magnetic interaction and the retardation terms, is treated as the first-order perturbation. The total wave function is a Slater determinant of four-component, one-electron orbitals. The radial functions of the orbitals are expanded in terms of Slater-type functions with *nonintegral* principal quantum numbers. The expansion coefficients for the large and small components are determined by solving the variational problem as a pseudo-eigenvalue problem in a method similar to that developed by Roothaan,[12] but no *a priori* relationships between the large and small component radial functions are assumed. A nonintegral principal quantum number occurs in the relativistic wave function of the hydrogenic atom. Similarly, for many-electron atoms, it is necessary to introduce nonintegral principal quantum numbers to satisfy the relativistic Hartree-Fock equations near the origin [cf. Appendix III and Eq. (129)]. Such principal quantum numbers also, as a bonus, provide additional variational parameters for the orbitals.[13]

The applicability of the formulas presented in this paper is limited to closed-shell configurations of neutral atoms and atomic ions. A relativistic shell is specified by the total angular momentum and the space-inversion parity of the electrons in the shell. For instance, $(p_{1/2})^2$ and $(p_{3/2})^4$ in conventional spectroscopic notation are relativistically closed shells, although their nonrelativistic counterparts, $(p)^2$ and $(p)^4$, are not. A relativistically closed shell forms a $J=0$ state, where J is the total angular momentum, but not all $J=0$ states are relativistically closed shells.

The numerical results for the ground states of He, Be, and Ne atoms, computed from the formalism presented here, are given at the end of this paper.

HAMILTONIAN AND WAVE FUNCTION

The unperturbed Hamiltonian H for an N-electron atom of nuclear charge Z is, in atomic units,

$$H=\sum_{\mu} H_D(\mu)+\tfrac{1}{2}\sum_{\mu}\sum_{\nu\neq\mu}(1/r_{\mu\nu}), \tag{1}$$

where the summations are from 1 to N, $r_{\mu\nu}$ is the distance between the μth and νth electrons, and $H_D(\mu)$ is the Dirac Hamiltonian of the μth electron, namely,

$$H_D(\mu)=\boldsymbol{\alpha}_\mu\cdot\mathbf{p}_\mu c+\beta_\mu c^2-Z/r_\mu. \tag{2}$$

In Eq. (2), $\mathbf{p}$ is the momentum operator, and r_μ the distance from the nucleus to the μth electron, and $\boldsymbol{\alpha}$ and β are the Dirac matrices in conventional representation, i.e.,

$$\boldsymbol{\alpha}=\begin{pmatrix}0 & \boldsymbol{\sigma}\\ \boldsymbol{\sigma} & 0\end{pmatrix},\quad \beta=\begin{pmatrix}I & 0\\ 0 & -I\end{pmatrix},$$

where the $\boldsymbol{\sigma}$ are 2×2 Pauli matrices and I is a 2×2 unit matrix.

The Breit operator H_B is given by

$$H_B(\mu,\nu)=-\left\{\frac{\boldsymbol{\alpha}_\mu\cdot\boldsymbol{\alpha}_\nu}{r_{\mu\nu}}+\frac{[(\boldsymbol{\alpha}_\mu\cdot\boldsymbol{\nabla}_\mu)(\boldsymbol{\alpha}_\nu\cdot\boldsymbol{\nabla}_\nu)r_{\mu\nu}]}{2}\right\}, \tag{3}$$

where the gradient operators $\boldsymbol{\nabla}_\mu$ and $\boldsymbol{\nabla}_\nu$ operate on $r_{\mu\nu}$ only, and not on the wave function when the expectation value of H_B is taken. The first term on the right-hand side of Eq. (3) is the magnetic interaction term, and the second is the retardation term. The matrices $\boldsymbol{\alpha}_\mu$ operate only on the spinor containing the coordinates of the μth electron.[14]

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[7] B. Swirles, Proc. Roy. Soc. (London) **A152**, 625 (1935).

[8] J. L. Schonfelder, Proc. Phys. Soc. (London) **87**, 163 (1966).

[9] D. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. **137**, A27 (1965).

[10] I. P. Grant, Proc. Roy. Soc. (London) **A262**, 555 (1961). We get the relativistic Hartree-Fock integro-differential equation for our formalism by neglecting the magnetic interaction term in the equation given in this reference.

[11] M. Synek, Phys. Rev. **136**, A1552 (1964).

[12] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

[13] R. G. Parr and H. W. Joy, J. Chem. Phys. **26**, 424 (1957).

[14] The last term of Eq. (3) reduces to the more conventional form $-(\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2)/(2r_{12})-(\boldsymbol{\alpha}_1\cdot\mathbf{r}_{12})(\boldsymbol{\alpha}_2\cdot\mathbf{r}_{12})/(2r_{12}^3)$ when the differentiation is carried out. In our form, however, each term has a clear physical meaning, and it is easier to apply the Racah algebra to the retardation term.

The Dirac Hamiltonian contains the rest-mass energy c^2 of the electron. To get the binding energy, we subtract this energy from the Dirac Hamiltonian and obtain

$$H_D'(\mu)=\boldsymbol{\alpha}_\mu\cdot\mathbf{p}_\mu c+\beta_\mu' c^2-Z/r_\mu\,, \tag{4}$$

where

$$\beta_\mu'=\begin{pmatrix}0 & 0\\ 0 & -2I\end{pmatrix}.$$

Therefore, the unperturbed binding energy is given by

$$E=\langle\Psi|H'|\Psi\rangle\,, \tag{5}$$

where

$$H'=\sum_\mu H_D'(\mu)+\tfrac{1}{2}\sum_\mu\sum_{\nu\neq\mu}(1/r_{\mu\nu})\,, \tag{6}$$

and Ψ is the normalized total wave function.

The relativistic correction to the binding energy due to the Breit operator is given by

$$E_B=\tfrac{1}{2}\sum_\mu\sum_{\nu\neq\mu}\langle\Psi|H_B(\mu,\nu)|\Psi\rangle. \tag{7}$$

The total wave function Ψ is determined by applying the variational principle to the binding energy E. The wave function is an antisymmetrized combination of one-electron orbitals defined as

$$\psi_{n\kappa m}(r,\theta,\varphi)=\begin{pmatrix}r^{-1}P_{n\kappa}(r)\chi_{\kappa m}(\theta,\varphi)\\ ir^{-1}Q_{n\kappa}(r)\chi_{-\kappa m}(\theta,\varphi)\end{pmatrix}, \tag{8}$$

where $P_{n\kappa}(r)/r$ and $Q_{n\kappa}(r)/r$ are the large and small radial wave functions, respectively, and satisfy the orthonormality condition

$$\int_0^\infty dr\,[P_{n\kappa}(r)P_{n'\kappa}(r)+Q_{n\kappa}(r)Q_{n'\kappa}(r)]=\delta_{nn'}\,, \tag{9}$$

where $\delta_{nn'}$ is the Kronecker delta. The choice of the phase in Eq. (8) enables us to take real radial functions both for the large and small components.

The angular functions $\chi_{\kappa m}(\theta,\varphi)$ are given by

$$\chi_{\kappa m}(\theta,\varphi)=\sum_{\sigma=\pm 1/2}C(l\tfrac{1}{2}j,\,m-\sigma,\,\sigma)Y_{l,m-\sigma}(\theta,\varphi)\phi_\sigma\,, \tag{10}$$

where the $C(l\frac{1}{2}j;\,m-\sigma,\,\sigma)$ are Clebsch-Gordan coefficients, the $Y_{l,m-\sigma}(\theta,\varphi)$ are normalized spherical harmonics, both in Rose's notation,[15] and the ϕ_σ are the two-component spinors

$$\phi_{1/2}=\begin{pmatrix}1\\0\end{pmatrix},\quad \phi_{-1/2}=\begin{pmatrix}0\\1\end{pmatrix}.$$

The orbitals given by Eq. (8) are orthonormal to each other.

The quantum number κ classifies the orbitals according to their symmetry species analogous to the orbital angular momentum in the nonrelativistic case. This is a consequence of the fact that the Hamiltonian H' [cf. Eq. (6)] is invariant under the spatial rotation, and an irreducible representation of the rotation operator with half-integer angular momentum j can be uniquely determined only if the space-inversion parity along with j is specified.[16] In Eq. (8), the orbitals are chosen in such a way that the orbitals of same κ form the basis vectors for the $(2j+1)$-dimensional irreducible representation of the unitary, unimodular group $SU(2j+1)$. With this choice, the magnetic quantum number m labels the subspecies, namely, the component of $\mathbf{j}$ along one of the coordinate axes. The index n labels orbitals which cannot be distinguished by κ and m. Although we are free to choose an arbitrary labeling system for n (e.g., the system used in the nuclear shell model), we adopted the convention used by Swirles[7] (cf. Table I), i.e., $1s$, $2s,\cdots$, $2\bar{p}$, $3\bar{p},\cdots$, $2p$, $3p,\cdots$, $3d$, $4d,\cdots$ etc. The total angular momentum j and the orbital angular momenta l and $\bar{l}$ of the large and small components, respectively, are related to κ by

$$\begin{aligned} j&=|\kappa|-\tfrac{1}{2}\,,\\ l&=|\kappa+\tfrac{1}{2}|-\tfrac{1}{2}\,,\\ \bar{l}&=|-\kappa+\tfrac{1}{2}|-\tfrac{1}{2}\,. \end{aligned} \tag{11}$$

TABLE I. Relativistic shells and their parameters.

Shell	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$
κ	-1	1	-2	2	-3
j	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{5}{2}$
l	0	1	1	2	2
$\bar{l}$	1	0	2	1	3
$\mathcal{G}$[a]	+	−	−	+	+
Shell[b]	s	$\bar{p}$	p	$\bar{d}$	d

[a] The space-inversion parity $\mathcal{G}=(-)^l$.
[b] B. Swirles's notation for the relativistic shells. (Reference 7.)

In principle, we could have chosen radial functions depending on n, κ, and m; that is, different radial functions for different angular-momentum orientations, but in order to keep the computational complexity within reason, we have foregone the use of such functions.

The symmetry species κ is the eigenvalue of the operator

$$K=\beta(\boldsymbol{\sigma}'\cdot\mathbf{l}+1)\,,$$

where

$$\boldsymbol{\sigma}'=\begin{pmatrix}\boldsymbol{\sigma} & 0\\ 0 & \boldsymbol{\sigma}\end{pmatrix}$$

and $\mathbf{l}$ is the angular momentum operator; that is,

$$K\psi_{n\kappa m}=-\kappa\psi_{n\kappa m}.$$

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[15] See Ref. 2, and, also M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

[16] M. Hamermesh, *Group Theory* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1962), p. 348.

The operator K commutes with the Dirac Hamiltonian and $\mathbf{j}$. The values of various parameters for some relativistic shells are given in Table I.

If we apply the variation principle to Eq. (5), we find that the radial functions $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ must satisfy coupled Hartree-Fock equations. If we want numerical wave functions, we must solve these coupled integro-differential equations (cf. Appendix III). If we want to find analytic expansion-type wave functions, the application of the variation principle to the expansion coefficients leads to a pseudo-eigenvalue equation, referred to as the Hartree-Fock-Roothaan equation in literature, to be satisfied by these coefficients.

Experience with nonrelativistic calculations shows that the numerical wave functions have more accurate asymptotic behavior than the analytic ones, though both give total energies of comparable accuracy. The analytic wave functions, however, are much easier to handle, for instance, in the calculations of various expectation values other than the total energy. The solutions of the Hartree-Fock integro-differential equations can be approximated by Roothaan's method to any degree of accuracy by increasing the number of basis functions to expand the radial functions, but the amount of numerical work increases very rapidly as the number of basis functions is increased. Actually, Roothaan's method enables us to find analytic wave functions of high accuracy with a relatively small number of basis functions provided the basis functions are chosen carefully.

The radial functions may be expanded in terms of any basis functions, i.e.,

$$\begin{aligned} P_{n\kappa}(r) &= \sum_p \xi_{n\kappa p} f_{\kappa p}(r)\,, \\ Q_{n\kappa}(r) &= \sum_q \eta_{n\kappa q} f_{\kappa q}(r)\,, \end{aligned} \tag{12a}$$

or in vector notation,

$$\begin{aligned} P_{n\kappa}(r) &= \mathbf{f}_\kappa \cdot \boldsymbol{\xi}_{n\kappa}\,, \\ Q_{n\kappa}(r) &= \mathbf{f}_\kappa \cdot \boldsymbol{\eta}_{n\kappa}\,, \end{aligned} \tag{12b}$$

where $\mathbf{f}_\kappa$ is a row vector of the basis functions $f_{\kappa i}$, and $\boldsymbol{\xi}_{n\kappa}$ and $\boldsymbol{\eta}_{n\kappa}$ are column vectors of the expansion coefficients $\xi_{n\kappa p}$ and $\eta_{n\kappa q}$, respectively.

Although we may choose any functions as basis functions, the Slater-type functions are the best ones for atomic calculations in the sense that a small number of these functions are sufficient to describe the radial functions to high accuracy. We use, therefore, the Slater-type functions

$$\begin{aligned} f_{\kappa i}(r) = {} & (2\zeta_{\kappa i})^{\gamma_{\kappa i}+1/2} \\ & \times [\Gamma(2\gamma_{\kappa i}+1)]^{-1/2} r^{\gamma_{\kappa i}} \exp(-\zeta_{\kappa i} r)\,, \end{aligned} \tag{13}$$

where the exponents γ and ζ are nonlinear variation parameters and γ need not be an integer. The standard notation for the gamma function $\Gamma(x)$ is used in Eq. (13). Since we chose the radial functions to be real, we may choose the expansion coefficients to be real also.

MATRIX ELEMENTS OF THE UNPERTURBED HAMILTONIAN IN TERMS OF THE RADIAL FUNCTIONS

As in the nonrelativistic case, the total energy E is reduced to the sum of one-electron integrals I_A, and two types of two-electron integrals, the direct integral[17] J_{AB} and the exchange integral K_{AB}, where the subscripts A and B denote the set of orbital labels (n,κ,m),

$$E = \sum_A I_A + \tfrac{1}{2} \sum_{A,B} (J_{AB} - K_{AB})\,. \tag{14}$$

Integrals I_A, J_{AB}, and K_{AB} are defined as

$$I_A \equiv \langle \psi_A | H_D' | \psi_A \rangle\,, \tag{15}$$

$$J_{AB} \equiv \langle \psi_A(1)\psi_B(2) | r_{12}^{-1} | \psi_A(1)\psi_B(2) \rangle\,, \tag{16}$$

and

$$K_{AB} \equiv \langle \psi_A(1)\psi_B(2) | r_{12}^{-1} | \psi_B(1)\psi_A(2) \rangle\,. \tag{17}$$

A straightforward derivation of Eq. (14) leads to a restriction $B \neq A$ on the summation over B, but such a restriction can be eliminated and the summation over B may be carried out to all orbitals including $B = A$ because $J_{AA} = K_{AA}$ by definition. The summation over all A and B simplifies the expressions for the Slater coefficients greatly.

One-Electron Integral

The angular part of the one-electron integral I_A can easily be integrated out,[2] and we have

$$\begin{aligned} I_A = \int_0^\infty dr\, \{ & -2c^2[Q_A(r)]^2 \\ & -(Z/r)([P_A(r)]^2 + [Q_A(r)]^2) \\ & + cQ_A(r)[P_A'(r) + (\kappa_A/r)P_A(r)] \\ & - cP_A(r)[Q_A'(r) - (\kappa_A/r)Q_A(r)]\}\,, \end{aligned} \tag{18}$$

where the prime indicates the differentiation with respcet to r. With our choice of radial functions, $P_A(r)$ and $Q_A(r)$ are specified by (n_A,κ_A) rather than (n_A,κ_A,m_A). For brevity, we shall not introduce new symbols for the labels of radial functions, and it should be understood that in what follows all radial integrals depend only on (n,κ). Inasmuch as Eq. (18) does not contain m_A, the sum of I_A over a closed shell can be obtained by multiplying I_A by the electron occupation number of the shell, namely, $2j_A+1$.

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[17] We call J_{AB} "the direct integral of the Coulomb repulsion term" to distinguish it from the direct integrals of the magnetic interaction and the retardation terms in the Breit operator. Obviously, J_{AB} is the relativistic counterpart of the nonrelativistic Coulomb integral.

Two-Electron Integrals

A general expression for the two-electron integrals of the Coulomb repulsion term

$$C_{ABCD}\equiv\langle\psi_A(1)\psi_B(2)|r_{12}^{-1}|\psi_C(1)\psi_D(2)\rangle \tag{19}$$

is, as was shown by Grant,[10]

$$C_{ABCD}=\sum_\nu C_\nu(j_Cm_C;\,j_Am_A)C_\nu(j_Bm_B;\,j_Dm_D)\times F_\nu(AC;\,BD)\delta_{m_A+m_B,m_C+m_D}, \tag{20}$$

where

$$C_\nu(jm;\,j'm')=(-)^{1/2-m'}[(2j+1)(2j'+1)]^{1/2}/(2\nu+1)\times C(jj'\nu;\,\tfrac{1}{2},\,-\tfrac{1}{2})C(jj'\nu;\,m,\,-m'), \tag{21}$$

$$F_\nu(AC;\,BD)=\int_0^\infty\int_0^\infty dr_1dr_2\;U_\nu(1,2)\times[P_A(1)P_C(1)+Q_A(1)Q_C(1)]\times[P_B(2)P_D(2)+Q_B(2)Q_D(2)], \tag{22}$$

and

$$U_\nu(1,2)=r_<^{\nu}/r_>^{\nu+1}, \tag{23}$$

where $r_<\equiv\min(r_1,r_2)$, and $r_>\equiv\max(r_1,r_2)$. The summation over ν in Eq. (20) is carried out in steps of 2. The range of ν is limited by the relations

$$\begin{gathered} l_A+l_C+\nu=\text{even}, \\ l_B+l_D+\nu=\text{even}, \\ \max(|j_A+j_C|,\,|j_B-j_D|)\leqslant\nu\leqslant\min(j_A+j_C,\,j_B+j_D). \end{gathered} \tag{24}$$

From Eqs. (16), (20), (21), (22), and (24), we get

$$J_{AB}=C_{ABAB}=\sum_\nu a_\nu(j_Am_A;\,j_Bm_B)F_\nu(AA;\,BB), \tag{25}$$

where

$$a_\nu(jm;\,j'm')=(-)^{1-m-m'}C(jj\nu;\,m,\,-m)\times C(j'j'\nu;\,m',\,-m')a_\nu(jj'), \tag{26}$$

and

$$a_\nu(jj')=(2j+1)(2j'+1)(2\nu+1)^{-2}\times C(jj\nu;\,\tfrac{1}{2},\,-\tfrac{1}{2})C(j'j'\nu;\,\tfrac{1}{2},\,-\tfrac{1}{2}). \tag{27}$$

The summation in Eq. (25) runs from $\nu=0$ to $\min(2j_A,2j_B)$.

Similarly, for the exchange integral, we get

$$K_{AB}=C_{ABBA}=\sum_\nu b_\nu(j_Am_A;\,j_Bm_B)F_\nu(AB;\,AB), \tag{28}$$

where

$$b_\nu(jm;\,j'm')=[C(jj'\nu;\,m,\,-m')]^2b_\nu(jj'), \tag{29}$$

and

$$b_\nu(jj')=(2j+1)(2j'+1)\times(2\nu+1)^{-2}[C(jj'\nu;\,\tfrac{1}{2},\,-\tfrac{1}{2})]^2. \tag{30}$$

The range of ν for the exchange integral is limited by the following conditions:

$$l_A+l_B+\nu=\text{even},$$

and

$$|j_A-j_B|\leqslant\nu\leqslant j_A+j_B. \tag{31}$$

The coefficients $C_\nu(jm;\,j'm')$, $a_\nu(jm;\,j'm')$, and $b_\nu(jm;\,j'm')$ are the relativistic counterparts of the nonrelativistic coefficients $c^k(lm;\,l'm')$, $a^k(lm;\,l'm')$, and $b^k(lm;\,l'm')$, respectively, of Condon and Shortley.[18]

The fact that the m dependence of $a_\nu(jm;\,j'm')$ and $b_\nu(jm;\,j'm')$ can be factored out as the product of two Clebsch-Gordan coefficients makes it very simple to sum them over a closed shell using sum rules of the Clebsch-Gordan coefficients. This feature is common to all the relativistic Slater coefficients discussed in this paper; the Racah algebra is to be thanked for the manifestation of such a simple result.

Before we proceed to write the radial integrals $F_\nu(AA;\,BB)$ and $F_\nu(AB;\,AB)$ in terms of the basis functions, it is convenient to carry out the summation of $a_\nu(jm;\,j'm')$ and $b_\nu(jm;\,j'm')$ over the magnetic quantum numbers m and m', taking both j and j' to be angular momenta of closed shells. Then we have[10]

$$\sum_{m,m'} a_\nu(jm;\,j'm')\equiv(2j+1)(2j'+1)\bar{a}_\nu(jj')=(2j+1)(2j'+1)\delta_{\nu0}, \tag{32}$$

and

$$\sum_{m,m'} b_\nu(jm;\,j'm')\equiv(2j+1)(2j'+1)\bar{b}_\nu(jj')=[(2j+1)(2j'+1)/(2\nu+1)]\times[C(jj'\nu;\,\tfrac{1}{2},-\tfrac{1}{2})]^2, \tag{33}$$

The symmetry relations and numerical tables of various Slater coefficients are given in Appendix II.

Now the sum over B in Eq. (14) becomes

$$\sum_B J_{AB}=\sum_{n_B\kappa_B}(2j_B+1)\bar{a}_0(j_Aj_B)\int_0^\infty\int_0^\infty dr_1dr_2\;r_>^{-1}\times\{[P_A(1)]^2+[Q_A(1)]^2\}\{[P_B(2)]^2+[Q_B(2)]^2\}, \tag{34}$$

and similarly,

$$\sum_B K_{AB}=\sum_\nu\sum_{n_B\kappa_B}(2j_B+1)\bar{b}_\nu(j_Aj_B)\int_0^\infty\int_0^\infty dr_1dr_2\times U_\nu(1,2)[P_A(1)P_B(1)+Q_A(1)Q_B(1)]\times[P_A(2)P_B(2)+Q_A(2)Q_B(2)]. \tag{35}$$

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[18] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935), pp. 175, 176.

MATRIX ELEMENTS OF THE UNPERTURBED HAMILTONIAN IN TERMS OF THE BASIS FUNCTIONS

One-Electron Integrals

If we substitute the expansion form of the radial functions [cf. Eqs. (12)] into Eq. (18), we get

$$
\begin{aligned}
I_{n\kappa}=\sum_{p,q}\big[&-2c^2\eta_{n\kappa p}S_{\kappa pq}\eta_{n\kappa q}\\
&-ZU_{\kappa pq}(\xi_{n\kappa p}\xi_{n\kappa q}+\eta_{n\kappa p}\eta_{n\kappa q})\\
&+c\eta_{n\kappa p}T^{+}{}_{\kappa pq}\xi_{n\kappa q}-c\xi_{n\kappa p}T^{-}{}_{\kappa pq}\eta_{n\kappa q}\big],
\end{aligned}\qquad(36)
$$

where $\mathbf{S}_\kappa$ is the overlap integral matrix whose elements are defined by

$$
\begin{aligned}
S_{\kappa pq}&\equiv\int_0^\infty dr\, f_{\kappa p}(r)f_{\kappa q}(r)\\
&=[V(2\gamma_{\kappa p},\zeta_{\kappa p})V(2\gamma_{\kappa q},\zeta_{\kappa q})]^{-1/2}\\
&\qquad\times V(\gamma_{\kappa p,\kappa q};\tfrac{1}{2}\zeta_{\kappa p,\kappa q}),
\end{aligned}\qquad(37)
$$

$\mathbf{U}_\kappa$ is the nuclear potential matrix defined as

$$
U_{\kappa pq}\equiv\int_0^\infty dr\, f_{\kappa p}(r)r^{-1}f_{\kappa q}(r)=S_{\kappa pq}(\zeta_{\kappa p,\kappa q}/\gamma_{\kappa p,\kappa q}),\qquad(38)
$$

$\mathbf{T}^{+}{}_{\kappa}$ and $\mathbf{T}^{-}{}_{\kappa}$ are the kinetic-energy matrices

$$
\begin{aligned}
T^{+}{}_{\kappa pq}&\equiv\int_0^\infty dr\, f_{\kappa p}(r)[f_{\kappa q}'(r)+(\kappa/r)f_{\kappa q}(r)]\\
&=U_{\kappa pq}[(\zeta_{\kappa p}\gamma_{\kappa q}-\zeta_{\kappa q}\gamma_{\kappa p})/\zeta_{\kappa p,\kappa q}+\kappa],
\end{aligned}\qquad(39)
$$

and

$$
\begin{aligned}
T^{-}{}_{\kappa pq}&\equiv\int_0^\infty dr\, f_{\kappa p}(r)[f_{\kappa q}'(r)-(\kappa/r)f_{\kappa q}(r)]\\
&=U_{\kappa pq}[(\zeta_{\kappa p}\gamma_{\kappa q}-\zeta_{\kappa q}\gamma_{\kappa p})/\zeta_{\kappa p,\kappa q}-\kappa].
\end{aligned}\qquad(40)
$$

The function $V(n,x)$ is defined as

$$
V(n,x)\equiv\Gamma(n+1)/x^{n+1},
$$

and the parameters $\gamma_{\kappa p,\kappa q}$ and $\zeta_{\kappa p,\kappa q}$ are defined as

$$
\begin{aligned}
\gamma_{\kappa p,\kappa q}&\equiv\gamma_{\kappa p}+\gamma_{\kappa q},\\
\zeta_{\kappa p,\kappa q}&\equiv\zeta_{\kappa p}+\zeta_{\kappa q},
\end{aligned}\qquad(41)
$$

respectively.

The elements of $\mathbf{T}^{+}{}_{\kappa}$ and $\mathbf{T}^{-}{}_{\kappa}$ satisfy the following relation:

$$
T^{+}{}_{\kappa qp}=-T^{-}{}_{\kappa pq}.\qquad(42)
$$

Equation (42) is equivalent to

$$
(\mathbf{T}^{+}{}_{\kappa})^\dagger=-\mathbf{T}^{-}{}_{\kappa}\qquad(42')
$$

and the sums over p and q of the last two terms in Eq. (36) are identical. The dagger in Eq. (42′) stands for the Hermitian conjugate.

Equation (36) may be written, using the usual convention for matrix multiplication, as

$$
I_{n\kappa}=-(\xi_{n\kappa}{}^\dagger\boldsymbol{\eta}_{n\kappa}{}^\dagger)\begin{pmatrix} Z\mathbf{U}_\kappa & c\mathbf{T}^{-}{}_{\kappa}\\ -c\mathbf{T}^{+}{}_{\kappa} & 2c^2\mathbf{S}_\kappa+Z\mathbf{U}_\kappa\end{pmatrix}\begin{pmatrix}\xi_{n\kappa}\\ \boldsymbol{\eta}_{n\kappa}\end{pmatrix}.\qquad(43)
$$

The 2×2 supermatrix in Eq. (43) is symmetric because $\mathbf{S}_\kappa$ and $\mathbf{U}_\kappa$ are symmetric by definition and Eq. (42′) holds. Note that the kinetic-energy matrices $\mathbf{T}^{+}{}_{\kappa}$ and $\mathbf{T}^{-}{}_{\kappa}$ are not symmetric by themselves.

The orthonormality constraint, Eq. (9), may be rewritten in 2×2 supermatrix form as

$$
(\xi_{n'\kappa}{}^\dagger\boldsymbol{\eta}_{n'\kappa}{}^\dagger)\begin{pmatrix}\mathbf{S}_\kappa & 0\\ 0 & \mathbf{S}_\kappa\end{pmatrix}\begin{pmatrix}\xi_{n\kappa}\\ \boldsymbol{\eta}_{n\kappa}\end{pmatrix}=\delta_{nn'}.\qquad(44)
$$

Two-Electron Integrals

The sum of the direct integrals J_{AB} [cf. Eq. (34)] now becomes, in terms of the basis functions,

$$
\sum_B J_{AB}=\sum_{p,q}(\xi_{Ap}J_{\kappa Apq}\xi_{Aq}+\eta_{Ap}J_{\kappa Apq}\eta_{Aq}),\qquad(45)
$$

where the elements of the Coulomb matrix $\mathbf{J}_\kappa$ are given by

$$
\begin{aligned}
J_{\kappa pq}=\sum_{n'\kappa'}(2j'+1)\sum_{s,t}&\mathcal{J}_{\kappa pq,\kappa' st,\nu}\\
&\times(\xi_{n'\kappa' s}\xi_{n'\kappa' t}+\eta_{n'\kappa' s}\eta_{n'\kappa' t}),
\end{aligned}\qquad(46)
$$

and the basic Coulomb supermatrix element $\mathcal{J}_{\kappa pq,\kappa' st,\nu}$ is defined as

$$
\begin{aligned}
\mathcal{J}_{\kappa pq,\kappa' st,\nu}&\equiv\int_0^\infty\int_0^\infty dr_1dr_2\, U_\nu(1,2)f_{\kappa p}(1)f_{\kappa q}(1)f_{\kappa' s}(2)f_{\kappa' t}(2)\\
&=\int_0^\infty du\int_u^\infty dv\,(u^\nu/v^{\nu+1})[f_{\kappa p}(u)f_{\kappa q}(u)f_{\kappa' s}(v)f_{\kappa' t}(v)+f_{\kappa p}(v)f_{\kappa q}(v)f_{\kappa' s}(u)f_{\kappa' t}(u)].
\end{aligned}\qquad(47)
$$

Equation (47) can be expressed in terms of the unnormalized incomplete beta function $B(\alpha,\beta;x)$ as

$$
\begin{aligned}
\mathcal{J}_{\kappa pq,\kappa' st,\nu}=2[&V(2\gamma_{\kappa p},\zeta_{\kappa p})V(2\gamma_{\kappa q},\zeta_{\kappa q})V(2\gamma_{\kappa' s},\zeta_{\kappa' s})V(2\gamma_{\kappa' t},\zeta_{\kappa' t})]^{-1/2}\{[\tfrac{1}{2}\zeta_{\kappa p,\kappa q}]^{-a}[\tfrac{1}{2}\zeta_{\kappa' s,\kappa' t}]^{-b}\\
&\times\Gamma(a+b)B[a,b;x/(1+x)]+[\tfrac{1}{2}\zeta_{\kappa p,\kappa q}]^{-a'}[\tfrac{1}{2}\zeta_{\kappa' s,\kappa' t}]^{-b'}\Gamma(a'+b')B[b',a';x'/(1+x')]\},
\end{aligned}\qquad(48)
$$

where

$$\begin{aligned} a&=\gamma_{\kappa p,\kappa q}+\nu+1\,, & a'&=\gamma_{\kappa p,\kappa q}-\nu\,,\\ b&=\gamma_{\kappa' s,\kappa' t}-\nu\,, & b'&=\gamma_{\kappa' s,\kappa' t}+\nu+1\,,\\ x&=\zeta_{\kappa p,\kappa q}/\zeta_{\kappa' s,\kappa' t}\,, & x'&=1/x. \end{aligned} \tag{49}$$

The unnormalized incomplete beta function[19] is defined as

$$B(\alpha,\beta;\,x)\equiv\int_0^x t^{\alpha-1}(1-t)^{\beta-1}dt\,, \tag{50}$$

where $0\leqslant x<1, \alpha>0$, and β may be an arbitrary real number. It is important that the integral (50) exists for negative values of β, because otherwise some of the matrix elements of the Breit operator can not be calculated with orbitals which satisfy the relativistic Hartree-Fock equations exactly near the origin. The matrix elements of the Breit operator are discussed later. Equation (45) may be written, in matrix notation, as

$$\sum_B J_{AB}=(\boldsymbol{\xi}_A{}^\dagger\boldsymbol{\eta}_A{}^\dagger)\begin{pmatrix}\mathbf{J}_{\kappa A} & 0\\ 0 & \mathbf{J}_{\kappa A}\end{pmatrix}\begin{pmatrix}\boldsymbol{\xi}_A\\ \boldsymbol{\eta}_A\end{pmatrix}. \tag{51}$$

Similarly, from Eq. (35), the sum over the exchange integrals of the Coulomb repulsion term may be written as

$$\sum_B K_{AB}=\sum_{p,q}(\xi_{Ap}K_{\xi\xi,\kappa Apq}\xi_{Aq}+\xi_{Ap}K_{\xi\eta,\kappa Apq}\eta_{Aq}+\eta_{Ap}K_{\eta\xi,\kappa Apq}\xi_{Aq}+\eta_{Ap}K_{\eta\eta,\kappa Apq}\eta_{Aq})\,, \tag{52}$$

where the elements of the exchange matrices **K** are given by

$$K_{\xi\xi,\kappa pq}=\sum_{n'\kappa'}\sum_{s,t}(2j'+1)\xi_{n'\kappa' s}\mathcal{K}^b{}_{\kappa pq,\kappa' st}\xi_{n'\kappa' t}\,, \tag{53}$$

$$K_{\xi\eta,\kappa pq}=\sum_{n'\kappa'}\sum_{s,t}(2j'+1)\xi_{n'\kappa' s}\mathcal{K}^b{}_{\kappa pq,\kappa' st}\eta_{n'\kappa' t}\,, \tag{54}$$

$$K_{\eta\xi,\kappa pq}=\sum_{n'\kappa'}\sum_{s,t}(2j'+1)\eta_{n'\kappa' s}\mathcal{K}^b{}_{\kappa pq,\kappa' st}\xi_{n'\kappa' t}\,, \tag{55}$$

$$K_{\eta\eta,\kappa pq}=\sum_{n'\kappa'}\sum_{s,t}(2j'+1)\eta_{n'\kappa' s}\mathcal{K}^b{}_{\kappa pq,\kappa' st}\eta_{n'\kappa' t}\,, \tag{56}$$

$$\mathcal{K}^b{}_{\kappa pq,\kappa' st}=\sum_\nu \bar{b}_\nu(jj')\mathcal{K}_{\kappa pq,\kappa' st,\nu}\,, \tag{57}$$

and the basic exchange supermatrix element $\mathcal{K}_{\kappa pq,\kappa' st,\nu}$ is defined as

$$\begin{aligned}\mathcal{K}_{\kappa pq,\kappa' st,\nu}&\equiv\int_0^\infty\int_0^\infty dr_1dr_2\;U_\nu(1,2)f_{\kappa p}(1)f_{\kappa q}(2)f_{\kappa' s}(1)f_{\kappa' t}(2)\\ &=\int_0^\infty du\int_u^\infty dv\;(u^\nu/v^{\nu+1})[f_{\kappa p}(u)f_{\kappa' s}(u)f_{\kappa q}(v)f_{\kappa' t}(v)+f_{\kappa p}(v)f_{\kappa' s}(v)f_{\kappa q}(u)f_{\kappa' t}(u)].\end{aligned} \tag{58}$$

In terms of the incomplete beta function, Eq. (58) becomes

$$\begin{aligned}\mathcal{K}_{\kappa pq,\kappa' st,\nu}=2[V(2\gamma_{\kappa p},\zeta_{\kappa p})V(2\gamma_{\kappa q},\zeta_{\kappa q})V(2\gamma_{\kappa' s},\zeta_{\kappa' s})V(2\gamma_{\kappa' t},\zeta_{\kappa' t})]^{-1/2}\{[\tfrac{1}{2}\zeta_{\kappa p,\kappa' s}]^{-c}[\tfrac{1}{2}\zeta_{\kappa q,\kappa' t}]^{-d}\\ \times\Gamma(c+d)B[c,d;\,y/(1+y)]+[\tfrac{1}{2}\zeta_{\kappa p,\kappa' s}]^{-c'}[\tfrac{1}{2}\zeta_{\kappa q,\kappa' t}]^{-d'}\Gamma(c'+d')B[d',c';\,y'/(1+y')]\}\,,\end{aligned} \tag{59}$$

where

$$\begin{aligned} c&=\gamma_{\kappa p,\kappa' s}+\nu+1\,, & c'&=\gamma_{\kappa p,\kappa' s}-\nu\,,\\ d&=\gamma_{\kappa q,\kappa' t}-\nu\,, & d'&=\gamma_{\kappa q,\kappa' t}+\nu+1\,,\\ y&=\zeta_{\kappa p,\kappa' s}/\zeta_{\kappa q,\kappa' t}\,, & y'&=1/y. \end{aligned} \tag{60}$$

In matrix notation, Eq. (52) can be written as

$$\sum_B K_{AB}=(\boldsymbol{\xi}_A{}^\dagger\boldsymbol{\eta}_A{}^\dagger)\begin{pmatrix}\mathbf{K}_{\xi\xi,\kappa A} & \mathbf{K}_{\xi\eta,\kappa A}\\ \mathbf{K}_{\eta\xi,\kappa A} & \mathbf{K}_{\eta\eta,\kappa A}\end{pmatrix}\begin{pmatrix}\boldsymbol{\xi}_A\\ \boldsymbol{\eta}_A\end{pmatrix}. \tag{61}$$

We note that the Coulomb supermatrix element is symmetric under the exchange of indices ($p\leftrightarrow q$) and/or ($s\leftrightarrow t$), but the exchange supermatrix element is symmetric only under the *simultaneous* exchange of indices ($p\leftrightarrow q$) and ($s\leftrightarrow t$). With this property of the exchange supermatrix element and from Eqs. (54) and (55) we get the relation

$$K_{\xi\eta,\kappa qp}=K_{\eta\xi,\kappa pq}. \tag{62}$$

Other matrices $\mathbf{J}$, $\mathbf{K}_{\xi\xi}$, and $\mathbf{K}_{\eta\eta}$ are symmetric by definition and the 2×2 supermatrix in Eq. (61) is also symmetric because Eq. (62) holds.

RELATIVISTIC HARTREE-FOCK-ROOTHAAN EQUATION

Now we proceed to derive the pseudo-eigenvalue equation (the Hartree-Fock-Roothaan equation) for the expansion coefficients $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$, in the same manner as that of Roothaan.[12]

From Eqs. (14), (43), (51), and (61) the unperturbed energy is given by

$$E=\sum_{n\kappa}(2j+1)(\boldsymbol{\xi}_{n\kappa}{}^\dagger\boldsymbol{\eta}_{n\kappa}{}^\dagger)\begin{pmatrix}\mathbf{E}_{\xi\xi,\kappa} & \mathbf{E}_{\xi\eta,\kappa}\\ \mathbf{E}_{\eta\xi,\kappa} & \mathbf{E}_{\eta\eta,\kappa}\end{pmatrix}\begin{pmatrix}\boldsymbol{\xi}_{n\kappa}\\ \boldsymbol{\eta}_{n\kappa}\end{pmatrix}, \tag{63}$$

---

[19] For details, see *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1964), Appl. Math. Ser. 55. For the derivation of Eq. (48) from Eq. (47), see H. W. Joy and R. G. Parr, J. Chem. Phys. **28**, 448 (1958).

where

$$\mathbf{E}_{\xi\xi,\kappa}=-Z\mathbf{U}_\kappa+\tfrac{1}{2}(\mathbf{J}_\kappa-\mathbf{K}_{\xi\xi,\kappa})\,, \tag{64}$$

$$\mathbf{E}_{\xi\eta,\kappa}=-c\mathbf{T}^-{}_\kappa-\tfrac{1}{2}\mathbf{K}_{\xi\eta,\kappa}\,, \tag{65}$$

$$\mathbf{E}_{\eta\xi,\kappa}=c\mathbf{T}^+{}_\kappa-\tfrac{1}{2}\mathbf{K}_{\eta\xi,\kappa}\,, \tag{66}$$

and

$$\mathbf{E}_{\eta\eta,\kappa}=-(Z\mathbf{U}_\kappa+2c^2\mathbf{S}_\kappa)+\tfrac{1}{2}(\mathbf{J}_\kappa-\mathbf{K}_{\eta\eta,\kappa})\,. \tag{67}$$

To get the relativistic Hartree-Fock-Roothaan equation, we vary $\boldsymbol{\xi}_{n\kappa}$ and $\boldsymbol{\eta}_{n\kappa}$ in Eq. (63) and the orthonormality constraint (44) and combine them with Lagrange multipliers. All the argument used by Roothaan[12] in his nonrelativistic theory can be applied here also, and we get a pseudo-eigenvalue equation in 2×2 supermatrix form in exactly the same manner. For instance, the Lagrange multiplier matrix is Hermitian, and for closed-shell configurations, can be diagonalized by a unitary transformation that, at the same time, keeps the matrices **J** and **K** invariant, so that the Hartree-Fock operator remains the same. The variation of $\boldsymbol{\xi}_{n'\kappa'}$ and $\boldsymbol{\eta}_{n'\kappa'}$ in the **J** and **K** matrices leads again to the same expression as the one obtained by varying $\boldsymbol{\xi}_{n\kappa}$ and $\boldsymbol{\eta}_{n\kappa}$, and doubles the contribution from the two-electron integrals.

Thus, the relativistic Hartree-Fock-Roothaan equation becomes

$$\begin{pmatrix}\mathbf{F}_{\xi\xi,\kappa} & \mathbf{F}_{\xi\eta,\kappa}\\ \mathbf{F}_{\eta\xi,\kappa} & \mathbf{F}_{\eta\eta,\kappa}\end{pmatrix}\begin{pmatrix}\boldsymbol{\xi}_{n\kappa}\\ \boldsymbol{\eta}_{n\kappa}\end{pmatrix}=\epsilon_{n\kappa}\begin{pmatrix}\mathbf{S}_\kappa & 0\\ 0 & \mathbf{S}_\kappa\end{pmatrix}\begin{pmatrix}\boldsymbol{\xi}_{n\kappa}\\ \boldsymbol{\eta}_{n\kappa}\end{pmatrix}, \tag{68}$$

where $\epsilon_{n\kappa}$ is the orbital energy of $(n\kappa)$ shell, and

$$\mathbf{F}_{\xi\xi,\kappa}=-Z\mathbf{U}_\kappa+\mathbf{J}_\kappa-\mathbf{K}_{\xi\xi,\kappa}\,, \tag{69}$$

$$\mathbf{F}_{\xi\eta,\kappa}=-c\mathbf{T}^-{}_\kappa-\mathbf{K}_{\xi\eta,\kappa}\,, \tag{70}$$

$$\mathbf{F}_{\eta\xi,\kappa}=c\mathbf{T}^+{}_\kappa-\mathbf{K}_{\eta\xi,\kappa}\,, \tag{71}$$

and

$$\mathbf{F}_{\eta\eta,\kappa}=-(Z\mathbf{U}_\kappa+2c^2\mathbf{S}_\kappa)+\mathbf{J}_\kappa-\mathbf{K}_{\eta\eta,\kappa}\,. \tag{72}$$

In view of Eqs. (63) and (68), we have

$$E=\sum_{n\kappa}(2j+1)\left\{\epsilon_{n\kappa}-\tfrac{1}{2}(\boldsymbol{\xi}_{n\kappa}{}^\dagger\boldsymbol{\eta}_{n\kappa}{}^\dagger)\begin{pmatrix}\mathbf{J}_\kappa-\mathbf{K}_{\xi\xi,\kappa} & -\mathbf{K}_{\xi\eta,\kappa}\\ -\mathbf{K}_{\eta\xi,\kappa} & \mathbf{J}_\kappa-\mathbf{K}_{\eta\eta,\kappa}\end{pmatrix}\begin{pmatrix}\boldsymbol{\xi}_{n\kappa}\\ \boldsymbol{\eta}_{n\kappa}\end{pmatrix}\right\}. \tag{73}$$

We note that both 2×2 supermatrices in Eq. (68) are symmetric and real. If we consider the expansion coefficients $\boldsymbol{\xi}_{n\kappa}$ and $\boldsymbol{\eta}_{n\kappa}$ to form a column vector, Eq. (68) becomes the same type of pseudo-eigenvalue equation as the nonrelativistic one derived by Roothaan.

The relative simplicity of our pseudo-eigenvalue equation and of the total energy expression was achieved by using the same set of basis functions for the large and small radial functions, a procedure which is consistent with the exact solutions of the Dirac equation for the hydrogenic atoms. In principle, we could modify our formalism so that the small radial function uses a different set of basis functions from that of the large radial function; this would require a modification of all matrices related to the small component. For instance, all off-diagonal elements of the 2×2 supermatrices become rectangular matrices if the numbers of basis functions for the large and small components differ, and the overlap matrices in the upper diagonal and lower diagonal position of the supermatrices must accordingly be defined. The practical value, however, of such a scheme is very doubtful.

An important difference between the relativistic Hartree-Fock scheme and the nonrelativistic one is that the negative energy states exist in the former. For negative energy solutions, the role of the large and small components is reversed. Since we have biased the one-electron energies in our calculation by $-m_0c^2$, the orbital energies of the negative energy states would be of the order of $-2m_0c^2$. Also, the variational principle will lead to a stationary value, but not necessarily to a minimum. The lowest minimum energy in the relativistic formalism is $-\infty$, in the continuum range of the negative energy states. The negative energy states are, however, of no physical interest, and in numerical application we use only trial functions corresponding to the positive energy states.

MATRIX ELEMENTS OF THE BREIT OPERATOR

Similarly to the electrostatic terms, the matrix elements of the Breit operator become the sum of direct and exchange matrix elements of the magnetic interaction and the retardation terms. As will be shown later, the sum of the direct matrix elements of the magnetic interaction term over a closed shell vanishes, and the direct matrix elements of the retardation term vanish identically for all configurations. The first result is readily understandable because a closed shell has no net angular momentum and, therefore, cannot have net magnetic moment to cause any mganetic interaction. The second result is a consequence of the fact that there is no time dependence in the charge distributions $\psi_A{}^\dagger(1)\psi_A(1)$ and $\psi_B{}^\dagger(2)\psi_B(2)$ and, therefore, no retardation for the Coulomb repulsion between static charge distributions. For the exchange matrix element of the retardation term, however, the charge distributions $\psi_A{}^\dagger(1)\psi_B(1)$ and $\psi_B{}^\dagger(2)\psi_A(2)$, when $A\neq B$, do have a sinusoidal time dependence and the Coulomb repulsion is retarded accordingly.[20]

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[20] This interpretation was suggested by G. Wentzel (private communication).

The direct and exchange matrix elements of the magnetic interaction term are defined, respectively, as

$$M_{AB}=\langle\psi_A(1)\psi_B(2)|\frac{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2}{r_{12}}|\psi_A(1)\psi_B(2)\rangle, \quad (74)$$

and

$$N_{AB}=\langle\psi_A(1)\psi_B(2)|\frac{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2}{r_{12}}|\psi_B(1)\psi_A(2)\rangle. \quad (75)$$

The exchange matrix element of the retardation term is defined as

$$R_{AB}=\tfrac{1}{2}\langle\psi_A(1)\psi_B(2)| \times[(\boldsymbol{\alpha}_1\cdot\boldsymbol{\nabla}_1)(\boldsymbol{\alpha}_2\cdot\boldsymbol{\nabla}_2)r_{12}]|\psi_B(1)\psi_A(2)\rangle. \quad (76)$$

Then, the relativistic correction E_B, due to the Breit operator, is given by

$$E_B=-\tfrac{1}{2}\sum_{A,B}(M_{AB}-N_{AB}-R_{AB}). \quad (77)$$

All relativistic SCF calculations carried out so far have neglected the contribution from the retardation term. However, no justification has been given for such a simplification, and in the case of the closed-shell configurations, when

$$\sum_{A,B}M_{AB}=0,$$

it is inconsistent to take only the second term and not the third term in Eq. (77). As can be seen from the numerical example of the Ne atom, the retardation term is not always negligible compared to the magnetic interaction term.

As was done for the matrix elements of the Coulomb repulsion term, the restriction $B\neq A$ was removed in Eq. (77) because $M_{AA}=N_{AA}$, and $R_{AA}=0$ for the same reason which made all direct matrix elements of the retardation term vanish.

Two-Electron Integrals of the Magnetic Interaction Term

According to Grant,[10] the general expression for the two-electron integral of the magnetic interaction term is

$$\begin{aligned}M_{ABCD}&\equiv\langle\psi_A(1)\psi_B(2)|\frac{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2}{r_{12}}|\psi_C(1)\psi_D(2)\rangle\\&=-2\sum_\nu\sum_J\delta_{m_A+m_B,m_C+m_D}\{M_{J\nu}(j_C\bar{l}_Cm_C;\,j_Al_Am_A)M_{J\nu}(j_Bl_Bm_B;\,j_D\bar{l}_Dm_D)G_\nu(AC;BD)\\&\qquad-M_{J\nu}(j_C\bar{l}_Cm_C;\,j_Al_Am_A)M_{J\nu}(j_B\bar{l}_Bm_B;\,j_Dl_Dm_D)G_\nu(AC;DB)\\&\qquad-M_{J\nu}(j_Cl_Cm_C;\,j_A\bar{l}_Am_A)M_{J\nu}(j_Bl_Bm_B;\,j_D\bar{l}_Dm_D)G_\nu(CA;BD)\\&\qquad+M_{J\nu}(j_Cl_Cm_C;\,j_A\bar{l}_Am_A)M_{J\nu}(j_B\bar{l}_Bm_B;\,j_Dl_Dm_D)G_\nu(CA;DB)\},\end{aligned} \quad (78)$$

where

$$M_{J\nu}(jlm;\,j'l'm)=(-)^{l'-j'-m'}[3(2l+1)(2l'+1)(2j+1)(2j'+1)/(2\nu+1)]^{1/2}\times\begin{Bmatrix}l&\frac{1}{2}&j\\l'&\frac{1}{2}&j'\\\nu&1&J\end{Bmatrix}C(ll'\nu;00)C(jj'J;m,-m'), \quad (79)$$

$$G_\nu(AB;CD)=\int_0^\infty\int_0^\infty dr_1dr_2\,U_\nu(1,2)P_A(1)Q_B(1)P_C(2)Q_D(2), \quad (80)$$

and

$$\begin{Bmatrix}l&\frac{1}{2}&j\\l'&\frac{1}{2}&j'\\\nu&1&J\end{Bmatrix}$$

is the 9-j symbol.[21] The integer J in Eqs. (78) and (79) takes only the values $\nu-1$, ν, $\nu+1$ to satisfy the triangular conditions of the 9-j symbols. The allowed values of ν are determined from those of the Clebsch-Gordan coefficient $C(ll'\nu;00)$ in Eq. (79):

$$l+l'+\nu=\text{even integer}, \quad (81)$$

and

$$|l-l'|\leqslant\nu\leqslant l+l'.$$

For the direct integral of the magnetic interaction term, we put $A=C$, $B=D$ in Eq. (78). Then, we note that Eq. (78) does not vanish only if $M_{J\nu}(jlm;\,j\bar{l}m)=-M_{J\nu}(j\bar{l}m;\,jlm)$. From Eq. (79), it is found that this is the case if J is an odd integer. Since $l+\bar{l}$ is odd and $l+\bar{l}+\nu$ must be even, ν must be odd. Hence $J=\nu$ is the only allowed value for the direct integral, and we have

$$M_{AB}=-8\sum_\nu d_\nu(\kappa_Am_A;\,\kappa_Bm_B)G_\nu(AA;BB), \quad (82)$$

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[21] For the definition and properties of the 9-j symbol, see A. de-Shalit and I. Talmi, *Nuclear Shell Theory* (Academic Press Inc., New York, 1963). The numerical tables prepared by H. Matsunobu and H. Takebe [Progr. Theoret. Phys. (Kyoto) 14, 589 (1955)] are very useful for our calculation.

where

$$d_\nu(\kappa m;\kappa' m')=M_{\nu\nu}(j\bar{l}m;\,jlm)M_{\nu\nu}(j'l'm';\,j'\bar{l}'m). \quad (83)$$

If we substitute Eq. (79) into (83), then we get

$$d_\nu(\kappa m;\kappa' m')=d_\nu(\kappa\kappa')C(j\nu j;\,m0)C(j'\nu j';\,m'0)\,, \quad (84)$$

where

$$d_\nu(\kappa\kappa')=(-)^{l+l'}12[j(j+1)j'(j'+1)]^{1/2}(2j+1)(2j'+1)$$
$$\times C(\bar{l}l\nu;00)C(l'\bar{l}'\nu;00)\begin{Bmatrix}\bar{l} & \frac{1}{2} & j\\ l & \frac{1}{2} & j\\ \nu & 1 & \nu\end{Bmatrix}\begin{Bmatrix}l' & \frac{1}{2} & j'\\ \bar{l}' & \frac{1}{2} & j'\\ \nu & 1 & \nu\end{Bmatrix}. \quad (85)$$

From Eq. (84) we note that

$$d_\nu(\kappa m;\kappa',-m')=-d_\nu(\kappa m;\kappa' m')\,,$$

because $C(j\nu j;\,m0)=(-)^\nu C(j\nu j;\,-m0)$ and ν is an odd integer. Hence the sum of $d_\nu(\kappa m;\kappa m')$ over a closed shell vanishes; that is,

$$\sum_m d_\nu(\kappa m;\kappa' m')=\sum_{m'} d_\nu(\kappa m;\kappa' m')=0. \quad (86)$$

For the exchange integral of the magnetic interaction term, we put $A=D$ and $B=C$ in Eq. (78) and get

$$N_{AB}=2\sum_\nu [e_\nu(j_Al_Am_A;\,j_B\bar{l}_Bm_B)G_\nu(AB;AB)$$
$$+e_\nu(j_A\bar{l}_Am_A;\,j_Bl_Bm_B)G_\nu(BA;BA)$$
$$+2f_\nu(\kappa_Am_A;\kappa_Bm_B)G_\nu(AB;BA)], \quad (87)$$

where

$$e_\nu(jlm;\,j'l'm')=\sum_J [M_{J\nu}(j'l'm';\,jlm)]^2, \quad (88)$$

and

$$f_\nu(\kappa m;\kappa' m')=-\sum_J M_{J\nu}(j'\bar{l}'m';\,jlm)$$
$$\times M_{J\nu}(j'l'm';\,j\bar{l}m). \quad (89)$$

The m dependence of Eqs. (88) and (89) may be separated out by substituting Eq. (79) into them. Then,

$$e_\nu(jlm;\,j'l'm')=\sum_J e_{J\nu}(jl;\,j'l')[C(jj'J;\,m,-m')]^2, \quad (90)$$

where

$$e_{J\nu}(jl;\,j'l')=\frac{3(2l+1)(2l'+1)(2j+1)(2j'+1)}{2\nu+1}\left[C(ll'\nu;00)\begin{Bmatrix}l & \frac{1}{2} & j\\ l' & \frac{1}{2} & j'\\ \nu & 1 & J\end{Bmatrix}\right]^2, \quad (91)$$

and

$$f_\nu(\kappa m;\kappa' m')=\sum_J f_{J\nu}(\kappa\kappa')[C(jj'J;\,m,-m')]^2, \quad (92)$$

where

$$f_{J\nu}(\kappa\kappa')=\frac{12(2j+1)(2j'+1)[j(j+1)j'(j'+1)]^{1/2}}{2\nu+1}C(l\bar{l}'\nu;00)C(\bar{l}l'\nu;00)\begin{Bmatrix}l & \frac{1}{2} & j\\ \bar{l}' & \frac{1}{2} & j'\\ \nu & 1 & J\end{Bmatrix}\begin{Bmatrix}\bar{l} & \frac{1}{2} & j\\ l' & \frac{1}{2} & j'\\ \nu & 1 & J\end{Bmatrix}. \quad (93)$$

The allowed values of J and ν for the exchange integral N_{AB} are

$$\left.\begin{array}{lr} J=\nu-1,\quad \nu,\quad \nu+1(\nu>0) & \\ =1 & (\nu=0)\\ =\nu & [(n_A\kappa_A)=(n_B\kappa_B)]\end{array}\right\},\quad |j_A-j_B|\leqslant J\leqslant j_A+j_B, \quad (94)$$

$$|l_A-\bar{l}_B|\leqslant\nu\leqslant l_A+\bar{l}_B \quad \text{for} \quad e_\nu(j_Al_Am_A;\,j_B\bar{l}_Bm_B),$$
$$|\bar{l}_A-l_B|\leqslant\nu\leqslant \bar{l}_A+l_B \quad \text{for} \quad e_\nu(j_A\bar{l}_Am_A;\,j_Bl_Bm_B),$$
$$\max(|l_A-\bar{l}_B|,|\bar{l}_A-l_B|)\leqslant\nu\leqslant\min(l_A+\bar{l}_B,\,\bar{l}_A+l_B) \quad \text{for} \quad f_\nu(\kappa_Am_A;\kappa_Bm_B), \quad (95)$$

and

$$\nu+j_A+j_B=\text{even}, \quad \text{if} \quad \kappa_A\kappa_B>0,$$
$$=\text{odd}, \quad \text{if} \quad \kappa_A\kappa_B<0,$$

for all coefficients in Eq. (87).

The summation of $e_\nu(jlm;\,j'l'm')$ and $f_\nu(\kappa m;\kappa' m')$ over m and m' is readily carried out with the use of the sum rule

$$\sum_{m,m'}[C(jj'J;\,m,-m')]^2=2J+1.$$

Hence,

$$\sum_{m,m'} e_\nu(jlm;\,j'l'm')\equiv\bar{e}_\nu(jl;\,j'l')(2j+1)(2j'+1)$$
$$=\sum_J(2J+1)e_{J\nu}(jl;\,j'l'), \quad (96)$$

and

$$\sum_{m,m'} f_\nu(\kappa m;\kappa' m') \equiv f_\nu(\kappa\kappa')(2j+1)(2j'+1)$$
$$=\sum_J (2J+1) f_{J\nu}(\kappa\kappa'). \tag{97}$$

Very recently, Grant has shown that the sum over J in Eqs. (96) and (97) may further be carried out in closed form by expanding the 9-j symbols in terms of the Racah coefficients and using sum rules of the Racah coefficients.[22] In this way, we get

$$\bar{e}_\nu(jl;j'l') = [2(j'+1)(2\nu+1)]^{-1}\{j'[C(jj'\nu;\tfrac{1}{2},-\tfrac{1}{2})]^2+(2j'+3)[C(j,j'+1,\nu;\tfrac{1}{2},-\tfrac{1}{2})]^2\}, \quad \text{if} \quad j'=l'-\tfrac{1}{2}, \tag{98}$$

$$\bar{e}_\nu(jl;j'l') = [2j'(2\nu+1)]^{-1}\{(2j'-1)[C(j,j'-1,\nu;\tfrac{1}{2},-\tfrac{1}{2})]^2+(j'+1)[C(jj'\nu;\tfrac{1}{2},-\tfrac{1}{2})]^2\}, \quad \text{if} \quad j'=l'+\tfrac{1}{2}, \tag{99}$$

and

$$2\bar{f}_\nu(\kappa\kappa') = \bar{b}_\nu(jj'). \tag{100}$$

The symmetry relations of these coefficients and their numerical values for some symmetry species are given in Appendix II.

Exchange Matrix Element of the Retardation Term

As is shown in Appendix I, the general expression for the matrix element of the retardation term is

$$R_{ABCD} \equiv \tfrac{1}{2}\langle\psi_A(1)\psi_B(2)|[(\boldsymbol{\alpha}_1\cdot\boldsymbol{\nabla}_1)(\boldsymbol{\alpha}_2\cdot\boldsymbol{\nabla}_2)r_{12}]|\psi_C(1)\psi_D(2)\rangle$$
$$\begin{aligned}=-\sum_\nu\sum_{\lambda,\mu}\delta_{m_A+m_B,m_C+m_D}\{&R_{\lambda\nu}(j_C\bar{l}_Cm_C;j_Al_Am_A)R_{\mu\nu}(j_Bl_Bm_B,j_D\bar{l}_Dm_D)G_{\lambda\mu\nu}(AC;BD)\\ &-R_{\lambda\nu}(j_C\bar{l}_Cm_C;j_Al_Am_A)R_{\mu\nu}(j_B\bar{l}_Bm_B;j_Dl_Dm_D)G_{\lambda\mu\nu}(AC;DB)\\ &-R_{\lambda\nu}(j_Cl_Cm_C;j_A\bar{l}_Am_A)R_{\mu\nu}(j_Bl_Bm_B;j_D\bar{l}_Dm_D)G_{\lambda\mu\nu}(CA;BD)\\ &+R_{\lambda\nu}(j_Cl_Cm_C;j_A\bar{l}_Am_A)R_{\mu\nu}(j_B\bar{l}_Bm_B;j_Dl_Dm_D)G_{\lambda\mu\nu}(CA;DB)\},\end{aligned} \tag{101}$$

where

$$R_{\omega\nu}(jlm;j'l'm') = (-)^{l'-j'-m'}[3(2l+1)(2l'+1)(2j+1)(2j'+1)/(2\nu+1)]^{1/2}$$
$$\times\begin{Bmatrix} l & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ \omega & 1 & \nu \end{Bmatrix} C(ll'\omega;00)C(\nu 1\omega;00)C(jj'\nu;m,-m'), \tag{102}$$

$$G_{\lambda\mu\nu}(AB;CD) = \int_0^\infty\int_0^\infty dr_1dr_2\, P_A(1)Q_B(1)P_C(2)Q_D(2)\partial_\lambda(1)\partial_\mu(2)W_\nu(1,2), \tag{103}$$

with

$$\begin{aligned}\partial_\omega(i) &= \frac{\partial}{\partial r_i}-\frac{\nu}{r_i} \quad \text{if} \quad \omega=\nu+1,\\ &= \frac{\partial}{\partial r_i}+\frac{\nu+1}{r_i} \quad \text{if} \quad \omega=\nu-1,\\ &= 0 \quad \text{otherwise},\end{aligned} \tag{104}$$

and

$$W_\nu(1,2) = U_\nu(1,2)[r_<^2/(2\nu+3)-r_>^2/(2\nu-1)]. \tag{105}$$

Obviously, from Eq. (104) the allowed values of λ and μ in Eq. (101) are limited to $\nu\pm1$. Equation (105) gives the radial part of the expansion of r_{12} in terms of $\mathbf{r}_1$ and $\mathbf{r}_2$.[23] The values of ν are restricted by the triangular condition of the 9-j symbol in Eq. (102), namely,

$$|j-j'| \leqslant \nu \leqslant j+j'.$$

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[22] I. P. Grant, Proc. Phys. Soc. (London) **86**, 523 (1965).

[23] S.-S. Huang, Astrophys. J. **108**, 354 (1948).

Furthermore, the conditions on ω in $C(ll'\omega;00)$ and the fact that $\omega=\nu\pm1$ require ν to change in steps of 2 as does ω, which also satisfies the triangular condition $|l-l'|\leqslant\omega\leqslant l+l'$.

When we carry out the differentiation of $W_\nu(1,2)$ for the four possible combinations of λ and μ, they all reduce to combinations of $U_{\nu+1}(1,2)$ and $U_{\nu-1}(1,2)$ [cf. Eq. (23)] with different multiplicative constants. We can carry out the summation over λ and μ by substituting $\nu\pm1$ for λ and μ in Eq. (101). Then each radial integral $G_{\lambda\mu\nu}$ in Eq. (101) will be split into two parts, $G_{\nu+1}$ and $G_{\nu-1}$ [cf. Eq. (80)] with their own coefficients. The derivation of the general formulas for such coefficients is tedious and the expressions are very cumbersome. We shall, instead, give the expression for the exchange integral.

The direct integral of the retardation term vanishes identically because of the triangular conditions of the Clebsch-Gordan coefficients and the 9-j symbols of Eq. (102). For instance, $R_{\lambda\nu}(j_C\bar{l}_Cm_C;\, j_Al_Am_A)$, in the case of the direct integral, is

$$R_{\lambda\nu}(j_A\bar{l}_Am_A;\, j_Al_Am_A)=(-)^{l_A-j_A-m_A}[12j_A(j_A+1)/(2\nu+1)]^{1/2}(2j_A+1)$$

$$\times\begin{Bmatrix}\bar{l}_A & \frac{1}{2} & j_A\\ l_A & \frac{1}{2} & j_A\\ \lambda & 1 & \nu\end{Bmatrix}C(\bar{l}_Al_A\lambda;00)C(\nu1\lambda;00)C(j_Aj_A\nu;m_A,-m_A).$$

The triangular conditions for $C(\bar{l}_Al_A\lambda;00)$ and $C(\nu1\lambda;00)$ require that $\bar{l}_A+l_A+\lambda=\text{even}$ as well as $\nu+1+\lambda=\text{even}$. Since $l_A+\bar{l}_A$ is odd, and $2j_A$ is also odd,

$$\begin{Bmatrix}\bar{l}_A & \frac{1}{2} & j_A\\ l_A & \frac{1}{2} & j_A\\ \lambda & 1 & \nu\end{Bmatrix}=-\begin{Bmatrix}l_A & \frac{1}{2} & j_A\\ \bar{l}_A & \frac{1}{2} & j_A\\ \lambda & 1 & \nu\end{Bmatrix}.$$

Therefore, $R_{\lambda\nu}(j_A\bar{l}_Am_A;\, j_Al_Am_A)=R_{\lambda\nu}(j_Al_Am_A;\, j_A\bar{l}_Am_A)$ and the right-hand side of Eq. (101) vanishes identically when $A=C$, and $B=D$.

For the exchange integral, we put $A=D$ and $B=C$ in Eq. (101), carry out the differentiation of $W_\nu(1,2)$, sum over the allowed values of λ and μ, and get

$$\begin{aligned}R_{AB}=\sum_\nu\{&g_\nu(j_Al_Am_A;\, j_B\bar{l}_Bm_B)G_{\nu+1}(AB;AB)+g_\nu'(j_Al_Am_A;\, j_B\bar{l}_Bm_B)G_{\nu-1}(AB;AB)\\ &+g_\nu(j_A\bar{l}_Am_A;\, j_Bl_Bm_B)G_{\nu+1}(BA;BA)+g_\nu'(j_A\bar{l}_Am_A;\, j_Bl_Bm_B)G_{\nu-1}(BA;BA)\\ &+2[h_\nu(\kappa_Am_A;\,\kappa_Bm_B)G_{\nu+1}(AB;BA)+h_\nu'(\kappa_Am_A;\,\kappa_Bm_B)G_{\nu-1}(AB;BA)]\\ &+2k_\nu(\kappa_Am_A;\,\kappa_Bm_B)[H_{\nu-1}(AB;BA)-H_{\nu+1}(AB;BA)]\},\end{aligned}\tag{106}$$

where

$$g_\nu(jlm;\, j'l'm')=g_\nu(jl;\, j'l')[C(jj'\nu;m,-m')]^2,\tag{107a}$$

$$g_\nu'(jlm;\, j'l'm')=g_\nu'(jl;\, j'l')[C(jj'\nu;m,-m')]^2,\tag{107b}$$

$$h_\nu(\kappa m;\,\kappa'm')=h_\nu(\kappa\kappa')[C(jj'\nu;m,-m')]^2,\tag{108a}$$

$$h_\nu'(\kappa m;\,\kappa'm')=h_\nu'(\kappa\kappa')[C(jj'\nu,m,-m')]^2,\tag{108b}$$

$$k_\nu(\kappa m;\,\kappa'm')=k_\nu(\kappa\kappa')[C(jj'\nu;m,-m')]^2,\tag{109}$$

$$H_\nu(AB;BA)=\int_0^\infty dr_2\int_{r_2}^\infty dr_1\frac{{r_2}^\nu}{{r_1}^{\nu+1}}P_A(1)Q_B(1)P_B(2)Q_A(2),\tag{110}$$

with

$$\begin{aligned}g_\nu(jl;\, j'l')=3(2j+1)(2j'+1)(2l+1)(2l'+1)(2\nu+1)^{-1}\Bigg\{&-\frac{2(\nu+1)}{2\nu+3}\left[\begin{Bmatrix}l & \frac{1}{2} & j\\ l' & \frac{1}{2} & j'\\ \nu+1 & 1 & \nu\end{Bmatrix}C(ll'\nu+1;00)\right]^2\\ &+[\nu(\nu+1)]^{1/2}\begin{Bmatrix}l & \frac{1}{2} & j\\ l' & \frac{1}{2} & j'\\ \nu-1 & 1 & \nu\end{Bmatrix}\begin{Bmatrix}l & \frac{1}{2} & j\\ l' & \frac{1}{2} & j'\\ \nu+1 & 1 & \nu\end{Bmatrix}C(ll'\nu-1;00)C(ll'\nu+1;00)\Bigg\},\end{aligned}\tag{111a}$$

$$g_\nu'(jl;j'l')=-3(2j+1)(2j'+1)(2l+1)(2l'+1)(2\nu+1)^{-1}\left\{\frac{2\nu}{2\nu-1}\left[\begin{Bmatrix} l & \frac{1}{2} & j \\ l & \frac{1}{2} & j' \\ \nu-1 & 1 & \nu \end{Bmatrix} C(ll'\nu-1;00)\right]^2\right.$$

$$\left.+[\nu(\nu+1)]^{1/2}\begin{Bmatrix} l & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ \nu-1 & 1 & \nu \end{Bmatrix}\begin{Bmatrix} l & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ \nu+1 & 1 & \nu \end{Bmatrix} C(ll'\nu-1;00)C(ll'\nu+1;00)\right\}, \tag{111b}$$

$$h_\nu(\kappa\kappa')=-3(2j+1)(2j'+1)[(2l+1)(2\bar{l}+1)(2l'+1)(2\bar{l}'+1)]^{1/2}$$

$$\times\frac{2(\nu+1)}{(2\nu+1)(2\nu+3)}\begin{Bmatrix} l & \frac{1}{2} & j \\ \bar{l}' & \frac{1}{2} & j' \\ \nu+1 & 1 & \nu \end{Bmatrix}\begin{Bmatrix} \bar{l} & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ \nu+1 & 1 & \nu \end{Bmatrix} C(l\bar{l}'\nu+1;00)C(\bar{l}l'\nu+1;00), \tag{112a}$$

$$h_\nu'(\kappa\kappa')=-3(2j+1)(2j'+1)[(2l+1)(2\bar{l}+1)(2l'+1)(2\bar{l}'+1)]^{1/2}$$

$$\times\frac{2\nu}{(2\nu+1)(2\nu-1)}\begin{Bmatrix} l & \frac{1}{2} & j \\ \bar{l}' & \frac{1}{2} & j' \\ \nu-1 & 1 & \nu \end{Bmatrix}\begin{Bmatrix} \bar{l} & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ \nu-1 & 1 & \nu \end{Bmatrix} C(l\bar{l}'\nu-1;00)C(\bar{l}l'\nu-1;00), \tag{112b}$$

$$k_\nu(\kappa\kappa')=-3(2j+1)(2j'+1)[(2l+1)(2\bar{l}+1)(2l'+1)(2\bar{l}'+1)]^{1/2}$$

$$\times(2\nu+1)^{-1}[\nu(\nu+1)]^{1/2}\left[\begin{Bmatrix} l & \frac{1}{2} & j \\ \bar{l}' & \frac{1}{2} & j' \\ \nu+1 & 1 & \nu \end{Bmatrix}\begin{Bmatrix} \bar{l} & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ \nu-1 & 1 & \nu \end{Bmatrix} C(l\bar{l}'\nu+1;00)C(\bar{l}l'\nu-1;00)\right.$$

$$\left.+\begin{Bmatrix} \bar{l} & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ \nu+1 & 1 & \nu \end{Bmatrix}\begin{Bmatrix} l & \frac{1}{2} & j \\ \bar{l}' & \frac{1}{2} & j' \\ \nu-1 & 1 & \nu \end{Bmatrix} C(\bar{l}l'\nu+1;00)C(l\bar{l}'\nu-1;00)\right]. \tag{113}$$

The particular form of $k_\nu(\kappa\kappa')$ was chosen such that

$$k_\nu(\kappa\kappa')=k_\nu(\kappa'\kappa).$$

The sums over the magnetic quantum numbers m and m' of g's, h's, and k's can be obtained simply by multiplying Eqs. (111) through (113) by $2\nu+1$. Hence, if we define

$$\sum_{m,m'} g_\nu(jlm;j'l'm')\equiv(2j+1)(2j'+1)\bar{g}_\nu(jl;j'l'), \tag{114a}$$

etc., then we have, for instance,

$$\bar{g}_\nu(jl;j'l')=3(2l+1)(2l'+1)\left\{-\frac{2(\nu+1)}{2\nu+3}\left[\begin{Bmatrix} l & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ \nu+1 & 1 & \nu \end{Bmatrix} C(ll'\nu+1;00)\right]^2\right.$$

$$\left.+[\nu(\nu+1)]^{1/2}\begin{Bmatrix} l & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ \nu-1 & 1 & \nu \end{Bmatrix}\begin{Bmatrix} l & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ \nu+1 & 1 & \nu \end{Bmatrix} C(ll'\nu-1;00)C(ll'\nu+1;00)\right\}. \tag{114b}$$

The values of ν are limited by the conditions

$$|j-j'|\leqslant\nu\leqslant j+j', \tag{115a}$$

and

$$\begin{aligned} \nu+j+j' &= \text{odd}, \quad \text{if} \quad \kappa\kappa'>0, \\ &= \text{even}, \quad \text{if} \quad \kappa\kappa'<0. \end{aligned} \tag{115b}$$

We note that the conditions (115) are exactly the opposite of the conditions on ν for the exchange integral of the magnetic interaction term. [Cf. Eqs. (95).] Hence the allowed values of $\nu\pm1$ for R_{AB} will coincide with the allowed values of ν for N_{AB}. We may, therefore, combine the two exchange integrals, Eqs. (87) and (106), by absorbing g's and h's into e_ν's and f_ν's, respectively. Thus, the combined exchange matrix element of the Breit operator is given by

$$\begin{aligned} \sum_{m_A,m_B} N_{AB}' &= \sum_{m_A,m_B} (N_{AB}+R_{AB}) \\ &= (2j_A+1)(2j_B+1)\sum_\nu [\bar{e}_\nu'(j_Al_A;\, j_B\bar{l}_B)G_\nu(AB;\, BA) \\ &\qquad +\bar{e}_\nu'(j_A\bar{l}_A;\, j_Bl_B)G_\nu(BA;\, BA)+2\bar{f}_\nu'(\kappa_A\kappa_B)G_\nu(AB;\, BA)+2\bar{k}_\nu'(\kappa_A\kappa_B)H_\nu(AB;\, BA)], \end{aligned} \tag{116}$$

where

$$\bar{e}_\nu'(jl;\, j'l') = 2\bar{e}_\nu(jl;\, j'l')+\bar{g}_{\nu-1}(jl;\, j'l')+\bar{g}_{\nu+1}'(jl;\, j'l'), \tag{117}$$

$$\bar{f}_\nu'(\kappa\kappa') = 2\bar{f}_\nu(\kappa\kappa')+h_{\nu-1}(\kappa\kappa')+h_{\nu+1}(\kappa\kappa'), \tag{118}$$

and

$$\bar{k}_\nu'(\kappa\kappa') = \bar{k}_{\nu+1}(\kappa\kappa')-\bar{k}_{\nu-1}(\kappa\kappa'). \tag{119}$$

Then,

$$\begin{aligned} \sum_B N_{AB}' = \sum_B \sum_\nu (2j_B+1)\Bigg[& \bar{e}_\nu'(j_Al_A;\, j_B\bar{l}_B)\int_0^\infty\int_0^\infty dr_1dr_2\, U_\nu(1,2)P_A(1)Q_B(1)P_A(2)Q_B(2) \\ & +\bar{e}_\nu'(j_A\bar{l}_A;\, j_Bl_B)\int_0^\infty\int_0^\infty dr_1dr_2\, U_\nu(1,2)P_B(1)Q_A(1)P_B(2)Q_A(2) \\ & +2\bar{f}_\nu'(\kappa_A\kappa_B)\int_0^\infty\int_0^\infty dr_1dr_2\, U_\nu(1,2)P_A(1)Q_B(1)P_B(2)Q_A(2) \\ & +2\bar{k}_\nu'(\kappa_A\kappa_B)\int_0^\infty dr\int_{r_1}^\infty dr_2\, U_\nu(1,2)P_A(1)Q_B(1)P_B(2)Q_A(2)\Bigg]. \end{aligned} \tag{120}$$

In terms of the basis functions, this equation becomes

$$\sum_B N_{AB}' = \sum_{p,q} (\xi_{Ap}B_{\xi\xi,\kappa_Apq}\xi_{Aq}+\xi_{Ap}B_{\xi\eta,\kappa_Apq}\eta_{Aq}+\eta_{Ap}B_{\eta\xi,\kappa_Apq}\xi_{Aq}+\eta_{Ap}B_{\eta\eta,\kappa_Apq}\eta_{Aq}), \tag{121}$$

where

$$B_{\xi\xi,\kappa pq} = \sum_{n'\kappa'}(2j'+1)\sum_{s,t}\eta_{n'\kappa's}\eta_{n'\kappa't}[\sum_\nu \bar{e}_\nu(jl;\, j'\bar{l}')\mathcal{K}_{\kappa pq,\kappa'st,\nu}], \tag{122}$$

$$B_{\xi\eta,\kappa pq} = \sum_{n'\kappa'}(2j'+1)\sum_{s,t}\eta_{n'\kappa's}\xi_{n'\kappa't}\sum_\nu [f_\nu'(\kappa\kappa')\mathcal{K}_{\kappa pq,\kappa'st,\nu}+\bar{k}_\nu'(\kappa\kappa')\mathcal{L}_{\kappa pq,\kappa'st,\nu}], \tag{123}$$

$$B_{\eta\xi,\kappa pq} = \sum_{n'\kappa'}(2j'+1)\sum_{s,t}\xi_{n'\kappa's}\eta_{n'\kappa't}\sum_\nu [f_\nu'(\kappa\kappa')\mathcal{K}_{\kappa pq,\kappa'st,\nu}+\bar{k}_\nu'(\kappa\kappa')\mathcal{M}_{\kappa pq,\kappa'st,\nu}], \tag{124}$$

and

$$B_{\eta\eta,\kappa pq} = \sum_{n'\kappa'}(2j'+1)\sum_{s,t}\xi_{n'\kappa's}\xi_{n'\kappa't}[\sum_\nu \bar{e}_\nu'(j\bar{l};\, j'l')\mathcal{K}_{\kappa pq,\kappa'st,\nu}]. \tag{125}$$

The partial exchange supermatrix elements $\mathcal{L}_{\kappa pq,\kappa'st,\nu}$ and $\mathcal{M}_{\kappa pq,\kappa'st,\nu}$ are defined as

$$\mathcal{L}_{\kappa pq,\kappa'st,\nu} \equiv \int_0^\infty du\int_u^\infty dv\, \frac{u^\nu}{v^{\nu+1}} f_{\kappa p}(u)f_{\kappa's}(u)f_{\kappa q}(v)f_{\kappa't}(v), \tag{126a}$$

and

$$\mathcal{M}_{\kappa pq,\kappa'st,\nu} \equiv \int_0^\infty du\int_0^u dv\, \frac{v^\nu}{u^{\nu+1}} f_{\kappa p}(u)f_{\kappa's}(u)f_{\kappa q}(v)f_{\kappa't}(v), \tag{126b}$$

respectively. Equations (126) become, in terms of the unnormalized, incomplete beta functions,

$$\mathcal{L}_{\kappa pq,\kappa' st,\nu}=2[V(2\gamma_{\kappa p},\zeta_{\kappa p})V(2\gamma_{\kappa q},\zeta_{\kappa q})V(2\gamma_{\kappa' s},\zeta_{\kappa' s})V(2\gamma_{\kappa' t},\zeta_{\kappa' t})]^{-1/2} \times[\tfrac{1}{2}\zeta_{\kappa p,\kappa' s}]^{-c}[\tfrac{1}{2}\zeta_{\kappa q,\kappa' t}]^{-d}\Gamma(c+d)B[c,d;y/(1+y)], \quad (127a)$$

and

$$\mathfrak{M}_{\kappa pq,\kappa' st,\nu}=2[V(2\gamma_{\kappa p},\zeta_{\kappa p})V(2\gamma_{\kappa q},\zeta_{\kappa q})V(2\gamma_{\kappa' s},\zeta_{\kappa' s})V(2\gamma_{\kappa' t},\zeta_{\kappa' t})]^{-1/2} \times[\tfrac{1}{2}\zeta_{\kappa p,\kappa' s}]^{-c'}[\tfrac{1}{2}\zeta_{\kappa q,\kappa' t}]^{-d'}\Gamma(c'+d')B[d',c';y'/(1+y')], \quad (127b)$$

where the parameters c, d, y, c', d', and y' are given by Eqs. (60).

Now, we can write the relativistic correction due to the Breit operator in 2×2 supermatrix notation, and Eq. (77) becomes

$$E_B=\sum_{n\kappa}(2j+1)(\xi_{n\kappa}{}^{\dagger}\boldsymbol{\eta}_{n\kappa}{}^{\dagger})\begin{pmatrix}\mathbf{B}_{\xi\xi,\kappa} & \mathbf{B}_{\xi\eta,\kappa}\\ \mathbf{B}_{\eta\xi,\kappa} & \mathbf{B}_{\eta\eta,\kappa}\end{pmatrix}\begin{pmatrix}\xi_{n\kappa}\\ \boldsymbol{\eta}_{n\kappa}\end{pmatrix}. \quad (128)$$

The 2×2 supermatrix in Eq. (128) is symmetric, because $\mathbf{B}_{\xi\xi,\kappa}$ and $\mathbf{B}_{\eta\eta,\kappa}$ are symmetric by definition, and the relation $B_{\xi\eta,\kappa pq}=B_{\eta\xi,\kappa qp}$ follows from the fact that

$$\mathcal{L}_{\kappa pq,\kappa' st,\nu}=\mathfrak{M}_{\kappa qp,\kappa' ts,\nu}.$$

NUMERICAL APPLICATION

Peculiarities of the Relativistic Calculation

Much of the numerical technique developed for the electronic computation of the nonrelativistic, analytic expansion type wave function[24] may be used in our scheme also. All of the basic mathematical manipulations, such as the variation of the basis functions [see paragraph (e) below], orthonormalization of the orbitals, and the solution of the pseudo-eigenvalue equation (68) may also be used with very little modification.

There are, however, properties peculiar to the relativistic formalism which complicate the computational procedure. These peculiarities are discussed below.

(*a*) *Numerical accuracy.* In the nonrelativistic case, the numerical accuracy (within the framework of the theory used) is normally limited by the accuracy of the computer used. In the relativistic case however, the velocity of light, which is equal to the inverse of the fine-structure constant α in the atomic units, enters into the total energy expression. Hence the numerical value of α affects the accuracy of the final result. Although it is difficult to express the α dependence of the total energy explicitly without using an additional approximation, it is found that a small change of the value of α in the sixth significant figure results in a minor change of the total energy in the eighth significant figure. This type of difficulty *cannot* be overcome by simply using higher precision in the numerical calculation, and the numerical accuracy for the relativistic SCF calculations is limited probably to nine significant figures with the current knowledge of the fine-structure constant.

(*b*) *Computation speed.* The use of nonintegral principal quantum numbers in our basis functions slows down the computation of all matrix elements with respect to the basis functions. Factorials become gamma functions in our case, and to some extent we lose either speed or accuracy.

(*c*) *Computer memory.* The dimension of most of our matrices will be twice that of the corresponding nonrelativistic matrices. In addition, the matrices $\mathbf{K}_{\xi\eta}$, $\mathbf{K}_{\eta\xi}$, $\mathbf{B}_{\xi\eta}$, and $\mathbf{B}_{\eta\xi}$ are not symmetric and we cannot symmetrize our exchange supermatrix elements as was done by Roothaan *et al.*[25] for the nonrelativistic calculations. These conditions increase the computer memory storage required for the relativistic computation.

(*d*) *Small component.* Although the nonrelativistic radial functions are very good starting points for the large component, some care must be taken in finding the trial values of the small component. The properties of the small component of the hydrogenic solution of the Dirac equation[2] seem to be a good guide in the case of light atoms. In general, the ratios of the expansion coefficients of large and small radial functions are of the order $Z\alpha$. The numbers of nodes of the large and small radial functions are the same if $\kappa<0$, and the small component has one more node if $\kappa>0$. For instance, the small radial function of the $2\bar{p}$ orbital can be constructed from the linear combination of basis functions with $\gamma\approx1$ and $\gamma\approx2$ whereas the large radial function will depend very little on the basis function with $\gamma\approx1$. (Cf. Table V.) Also, near the origin the sign of the ratio of the large and small radial functions agrees with the sign of κ.

(*e*) *The ground state.* To improve the numerical accuracy, we have shifted the energy scale by $-m_0c^2$ by using β' matrix instead of β matrix [cf. Eq. (4)]. However, as was mentioned earlier, the ground state of the positive energy spectrum, which corresponds to the nonrelativistic ground state, is a stationary value, but not the lowest minimum. In the nonrelativistic case, the variational calculation will not give a total energy lower than the true ground-state energy. In the relativistic case, however, a poor approximation to the

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[24] C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. II, p. 47.

[25] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

TABLE II. Comparison of total energies (atomic units).

Atom $(^1S_0)$	Nonrelativistic calculations[a]			This calculation Breit operator			Other relativistic calculations	
	Total energy	Relativistic correction	Unperturbed energy	Magnetic interaction	Retardation	Total relativistic energy[b]	Hartree[c]	Hartree-Slater[d]
He	−2.861680	−0.000070	−2.861838	0.000080	0	−2.861758	−2.862	−2.965150
Be	−14.57302	−0.00220	−14.57590	0.00116	−0.000004	−14.57474		−14.31500
Ne	−128.5470	−0.1312	−128.6919	0.0131	−0.0012	−128.6800	−126.547	−127.7752

[a] Reference 29. Sum of the first two columns should be compared with the total relativistic energy.
[b] Total relativistic energy = unperturbed energy + expectation value of the Breit operator.
[c] Reference 8. This and the last columns should be compared with the unperturbed relativistic energy.
[d] D. A. Liberman, D. Cromer, and J. Waber (private communication). The exchange terms were approximated by the modified Slater approximation discussed by R. D. Cowan *et al.*, Phys. Rev. **144**, 5 (1966).

correct solution may give an energy lower than the ground-state energy, because an approximate energy value may be on either side of the correct stationary value. Other quantities such as the virial theorem value [cf. (g) below] may be used in finding the "correct" solution. The total energy of He in the Hartree-Slater approximation quoted in Table II is an example of the "less accurate" case. The fact that it is lower than the experimental value is insignificant in the relativistic calculation. What matters is the accuracy with which the conditions for the stationary property of the energy value is fulfilled. The numerical technique needed in computing the nonrelativistic wave functions of the excited states must be used for the computation of the relativistic ground state.[26]

(*f*) *Singularity at the origin* (*the cusp condition*). In the nonrelativistic case, we ruled out the radial solution which has singularity at the origin because it violated the condition that the wave function be *continuous and finite* at all points in the space.[27] In the relativistic case, however, for s shells, the Dirac theory introduces a weak singularity at the origin in order to satisfy the relativistic wave equation there. This condition restricts the lowest power of r of a radial function to be exactly

$$\gamma_{\min}=(\kappa^2-Z^2\alpha^2)^{1/2}, \tag{129}$$

so that in the Dirac equation the kinetic-energy term and the nuclear potential term cancel each other for small values of r. (Cf. Appendix III.) Equation (129) is equivalent to both the nonrelativistic *cusp condition*[25] and the requirement that the lowest power of r of an orbital be equal to $l+1$.

(*g*) *The virial theorem.* In our formulation, the unperturbed energy is not only the sum of kinetic and potential energies, but also has the contribution from the mass term, $\beta' c^2$. Let

$$E=\langle H'\rangle=\langle M\rangle+\langle T\rangle+\langle V\rangle,$$

where $\langle\ \rangle$ denotes the time average,

$$\langle M\rangle=\text{mass energy}$$
$$=\langle\sum_\mu \beta_\mu' c^2\rangle,$$
$$\langle T\rangle=\text{kinetic energy}$$
$$=\langle\sum_\mu \boldsymbol{\alpha}_\mu\cdot\mathbf{p}_\mu c\rangle,$$

and

$$\langle V\rangle=\text{potential energy}$$
$$=E-\langle M\rangle-\langle T\rangle.$$

Then, in analogy to the nonrelativistic virial theorem,[28] we get

$$\langle T\rangle/\langle V\rangle=n, \tag{130}$$

if the potential-energy operator is a homogeneous function of radial parameters, i.e., if

$$V=\sum_\mu (r_\mu)^n+\tfrac{1}{2}\sum_\mu \sum_{\nu\neq\mu}(r_{\mu\nu})^n.$$

Furthermore, if the potential is Coulombic ($n=-1$), then

$$E=\langle M\rangle. \tag{131}$$

Results

An IBM 7094 computer was used for the computation of the ground states $(^1S_0)$ of He, Be, and Ne atoms. These results have not yet been fully optimized, but further optimization is expected to affect the total energies

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[26] For instance, the method described by B. J. Ransil, Rev. Mod. Phys. **32**, 239 (1960) was found to be useful for small atoms.

[27] The basis functions used by Parr and Joy, Refs. 13 and 19, seem to violate this condition. They have used basis functions of principal quantum numbers less than 1 in the nonrelativistic radial functions of He atom and H_2 molecule, and their radial wave functions (radial function/r) are not finite at the origin. The amount of singularity allowed in their calculation is larger than that allowed in the relativistic theory. For a general discussion, see T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[28] For a classical treatment, see H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1950), p. 69. Equation (130) may be derived by using the methods described by L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 140, and by H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 355. Equation (131) is given by M. E. Rose and T. A. Welton, Phys. Rev. **86**, 432 (1952). A general discussion of the virial theorem is given by R. M. Schectman and R. H. Good, Am. J. Phys. **25**, 219 (1957).

TABLE III. Orbital energies (atomic units).

Atom	This calculation				Nonrelativistic[a]		
($^1S_0$)	$1s$	$2s$	$2\bar{p}$	$2p$	$1s$	$2s$	$2p$
He	−0.91803				−0.91796		
Be	−4.73349	−0.30932			−4.73267	−0.30927	
Ne	−32.81745	−1.93599	−0.85284	−0.84848	−32.77276	−1.93048	−0.85048

[a] Reference 31.

TABLE IV. Exponents of the Slater-type basis functions.

Atom	He		Be		Ne	
Basis function \ Exponent	γ	ζ	γ	ζ	γ	ζ
$s1$	0.9998935	1.444107	0.9995739	3.4703	0.997334	9.5735
$s2$	1.9998935	2.710702	0.9995739	6.3681	0.997334	15.4496
$s3$	1.9998935	1.731053	1.9995739	0.7516	1.997334	1.9550
$s4$			1.9995739	0.9084	1.997334	2.8462
$s5$			1.9995739	1.4236	1.997334	4.7746
$s6$			1.9995739	2.7616	1.997334	7.7131
$\bar{p}1$					0.997334	9.5735
$\bar{p}2$					1.997334	1.6663
$\bar{p}3$					1.997334	3.0315
$\bar{p}4$					1.997334	4.7746
$\bar{p}5$					1.997334	7.7131
$p1$					1.998668	10.5420
$p2$					1.998668	4.9450
$p3$					1.998668	2.7935
$p4$					1.998668	1.6230

only in their sixth and higher significant figures, and will not change any qualitative conclusions presented below.

The energies computed by various methods are presented in Table II, and the orbital energies are given in Table III. Our calculation clearly shows improvement over the corresponding nonrelativistic Hartree-Fock-Roothaan calculations,[29] except for the orbital energy of the $2p$ orbital of Ne, which is expected to improve when the orbitals are fully optimized. The nonrelativistic total energies after the relativistic corrections (computed by the first-order perturbation) agree remarkably well with our relativistic total energies. This agreement is not surprising at all because the Hamiltonian operators for the relativistic corrections were derived from the relativistic operators we have used. This agreement should, rather, be interpreted as a support for the Pauli approximation procedure used by Bethe and Salpeter[4] to reduce the Breit operator into the operators H_1 through H_6 in their notation.

Also, it is interesting to see that the magnetic interaction increases the total energy, whereas the retardation effect decreases it. It is difficult, however, to explain these effects in terms of classical electrodynamics because they all come from exchange matrix elements, which have no classical analogy.

The retardation term amounts to approximately 10% of the magnetic interaction term for Ne, although it is negligible for Be. The retardation term vanishes for He because both electrons belong to the same shell, and there is no retardation between the electrons belonging to the same shell. Our result indicates that, for atoms with p-shells, the retardation effect is by no means negligible compared to the magnetic interaction.

The exponents for the Slater-type basis functions are given in Table IV. The γ exponents were not varied in the present calculation, although we expect that the number of basis functions may be reduced when γ's are optimized as well. The basis functions for the He atom were adopted from those used by Bagus and Gilbert[30] for their nonrelativistic calculation, and the basis functions for the Be atom are those used by Clementi.[31] The basis functions for the Ne atom are a *cross-breed* of those used by Bagus[32] and Clementi.[31] It was found that the nonrelativistic Hartree-Fock-Roothaan wave functions of high accuracy[30–32] provide an excellent starting point for the relativistic calculation. In fact, Clementi's basis set for the Be atom was used without any optimization, except for adjusting the values of the γ exponents to satisfy the relativistic cusp condition (129). A more accurate relativistic calculation, based on the present formalism, for some isoelectronic series and closed-shell configurations of small atoms ($Z \leqslant 18$) is in progress.

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[29] H. Hartmann and E. Clementi, Phys. Rev. **133**, A1295 (1964).

[30] P. S. Bagus and T. L. Gilbert (private communication).

[31] E. Clementi, IBM J. Res. Develop. Suppl. **9**, 2 (1965).

[32] P. S. Bagus, Phys. Rev. **139**, A619 (1965).

TABLE V. Expansion coefficients of the radial functions.

Atom	He		Be		Ne	
Basis function \ Coefficient	ξ	$\eta\times10^2$	ξ	$\eta\times10^2$	ξ	$\eta\times10^2$
$(1s)$						
$s1$	1.37099	−1.00300	0.91784	−1.15951	0.93040	−3.20705
$s2$	−0.09597	0.10309	0.08737	−0.20322	0.04595	−0.26276
$s3$	−0.30310	0.31589	0.00144	−0.00041	−0.00088	−0.00004
$s4$			−0.00262	0.00089	0.00329	−0.00136
$s5$			0.00217	−0.00117	−0.00193	0.00038
$s6$			0.00602	−0.00473	0.03550	−0.08292
$(2s)$						
$s1$			0.17051	−0.20914	−0.23196	0.81387
$s2$			0.01475	−0.04005	−0.00445	0.03363
$s3$			−0.11676	0.02096	0.18078	−0.12231
$s4$			−0.67647	0.20611	0.66154	−0.52675
$s5$			−0.30353	0.02285	0.32444	−0.21934
$s6$			0.09262	−0.14454	−0.14229	0.52730
$(2\bar{p})$						
$\bar{p}1$					−0.00147	0.50594
$\bar{p}2$					0.41897	−0.12567
$\bar{p}3$					0.47190	0.02062
$\bar{p}4$					0.16635	0.28941
$\bar{p}5$					0.04285	0.41291
$(2p)$						
$p1$					0.00940	−0.03622
$p2$					0.24188	−0.43676
$p3$					0.47964	−0.48906
$p4$					0.36757	−0.21772

The expansion coefficients for the large and small component radial functions are tabulated in Table V, and the radial functions of the Ne atom are plotted in Figs. 1 and 2. It is obvious from the values of the expansion coefficients that one *should not* assume a constant ratio between the large and small radial functions. Such an assumption will force the large and small radial functions to have not only an equal number of nodes, but also to have them at exactly the same values of r. Such a property does not hold, in general, for the hydrogenic solutions of the Dirac equation, and it is not expected to hold for more complex atoms.[33] (Cf. Appendix IV.) The ordinate of Fig. 2 is amplified compared to that of Fig. 1 because absolute values of the small radial functions are too small to be shown on the same scale as the large radial functions. The large radial functions $P_{2\bar{p}}(r)$ and $P_{2p}(r)$ are so close to each other that they cannot be distinguished on the scale used in Fig. 1.[34] We found that maxima of the large radial functions occur at the same points (e.g., $\Delta r<0.02$ a.u. for the $1s$ orbital of Ne) as those of the nonrelativistic radial functions.

The nonrelativistic charge density differs little from the relativistic one except that the relativistic charge density is slightly larger near the nucleus (e.g., $\Delta\rho\approx1\%$ at $r=0.02$ a.u. for the $1s$ orbital of Ne) than in the nonrelativistic case. Lower leading powers of the radial variable, which are necessary to satisfy the Dirac equation, lead to higher charge density near the nucleus, and consequently to larger binding energy for the electrons than in the nonrelativistic case.

CONCLUDING REMARKS

Comparison of our result on the He atom with the experimental value, $E_{\mathrm{expt}}=-2.903571(\pm0.7\times10^{-6})$

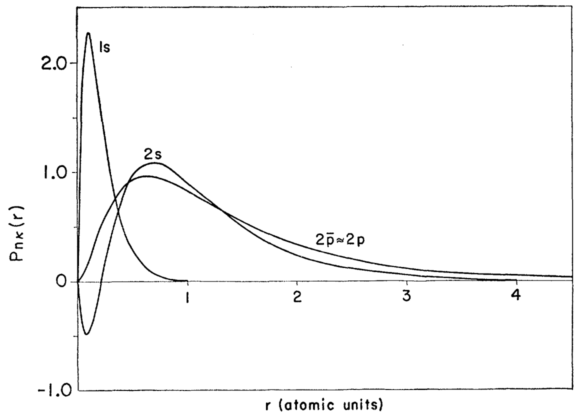

FIG. 1. The large-component radial functions of the neon atom.

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[33] For the trial input it is not necessary to use elaborate formulas for the ratio η/ξ as was done by M. Synek (Ref. 11). The SCF process will automatically adjust the expansion coefficients to satisfy Eq. (68). A simple formula such as $\eta=-\alpha Z'\xi$, where $Z'=Z-$(total number of electrons in the inner shells), is adequate for the orbitals with negative κ. For the orbitals with positive κ, the trial input must be chosen to represent the number of nodes properly. [Cf. paragraph (d) of previous section.]

[34] The numerical tabulation of the relativistic radial functions and the charge densities will be included in the Technical Report, Laboratory of Molecular Structure and Spectra, The University of Chicago, 1966 (unpublished).

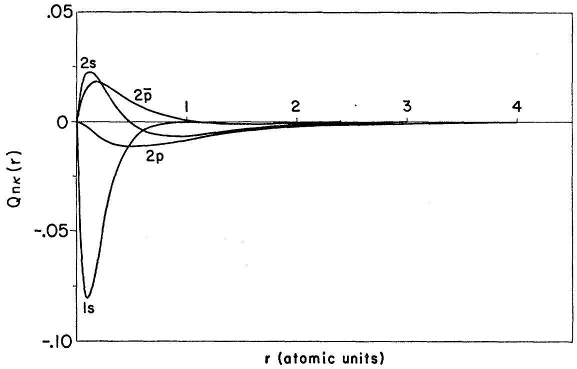

FIG. 2. The small-component radial functions of the neon atom.

atomic units,[35] indicates that a significant part of the total energy is yet to be explained by many-body theory. According to Pekeris,[36] the relativistic correction corresponding to ours ($E_J-2\alpha^2$ atomic units in his notation) computed from his correlated wave function for the ground state of He is $-23\ \text{cm}^{-1}$ whereas ours is $-17\ \text{cm}^{-1}$. This shows, as expected, that many-body effects also contribute a substantial amount to the relativistic correction. On the other hand, for small, closed-shell atoms, all the relativistic energy corrections that can be computed in terms of the relativistic Hartree-Fock model can also be computed with equal accuracy by applying the perturbation method to the operators given by Bethe and Salpeter[4] with accurate, nonrelativistic Hartree-Fock-Roothaan wave functions.

The numerical results presented in Table II speak for themselves on the importance of the correct treatment of the exchange terms in any relativistic calculation, as is also the case for the nonrelativistic one. In fact, our experience shows that the so-called *minimum basis set* relativistic wave functions lead to results so bad that it makes no sense to do any relativistic calculation with them. It is the great advantage of the analytic expansion method that it can handle the exchange matrix elements as easily as the direct matrix elements. Even in the nonrelativistic case, the exchange terms cause a great deal of difficulty in the numerical solution of the Hartree-Fock equation, and the situation is worse in the relativistic case.

Our formalism will be more valuable when it is extended to open-shell configurations. This can be done for configurations containing only one or two open-shell electrons, and for corresponding *hole* configurations because, in such cases, we know how to couple the orbitals in *j-j* coupling to construct the total wave function which is an eigenfunction of J, L, S, and M, where J is the total angular momentum, L is the orbital angular momentum, S is the spin angular momentum, and M is a projection of J.[37] Such an extension of this theory, although of limited scope, will greatly increase the variety of atoms and configurations which can be treated relativistically. The formulas for the relativistic Slater coefficients presented here can be used for the coupling of open-shell electrons also. To treat the open-shell configurations, the theory should also be extended to include *configuration mixing*. The ground state of the carbon atom ($^3P_0$) will serve as an example. The eigenfunction of the $^3P_0$ state is constructed from a linear combination (in a definite way) of $(2\bar{p})^2$ and $(2p)^2$ configurations. The formalism to handle such open-shell cases can easily be extended to include other configurations. Extension of our formalism to general cases of open-shell configurations will require a considerable amount of work on the theory of angular momentum coupling, including the introduction of a seniority scheme, to construct an eigenfunction of J, L, S, M, and the seniority number(s) by *j-j* coupling.

At present, the outlook for the application of our method to large atoms ($Z\gtrsim 50$) or molecules is not bright. The computers currently available are too slow and short on memory storage to handle the large number of basis functions needed to represent the Hartree-Fock solutions to an accuracy which makes any relativistic calculation meaningful.

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APPENDIX I: THE MATRIX ELEMENT OF THE RETARDATION TERM

Let u be the large component and v the small component of an orbital, that is,

$$\psi_A=\begin{pmatrix} u_A \\ v_A \end{pmatrix}.$$

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[35] G. Herzberg, Proc. Roy. Soc. (London) **A248**, 309 (1958).

[36] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

[37] Reference 18, p. 291.

Then,

$$\begin{aligned}2R_{ABCD}&\equiv\langle\psi_A(1)\psi_B(2)|[(\boldsymbol{\alpha}(1)\cdot\boldsymbol{\nabla})(1)(\boldsymbol{\alpha}(2)\cdot\boldsymbol{\nabla}(2))r_{12}]|\psi_C(1)\psi_D(2)\rangle\\&=\langle u_A(1)u_B(2)|R|v_C(1)v_D(2)\rangle+\langle u_A(1)v_B(2)|R|v_C(1)u_D(2)\rangle\\&\qquad+\langle v_A(1)u_B(2)|R|u_C(1)v_D(2)\rangle+\langle v_A(1)v_B(2)|R|u_C(1)u_D(2)\rangle,\end{aligned}\tag{A1}$$

where

$$R=(\boldsymbol{\sigma}(1)\cdot\boldsymbol{\nabla}(1))(\boldsymbol{\sigma}(2)\cdot\boldsymbol{\nabla}(2))r_{12},\tag{A2}$$

and $\boldsymbol{\sigma}$'s are the 2×2 Pauli spin matrices. The gradient operator $\boldsymbol{\nabla}(i)$ and $\boldsymbol{\sigma}(i)$ operate on the orbitals containing the coordinates of the ith electron. The interelectronic distance r_{12} may be expanded as[23]

$$\begin{aligned}r_{12}&=\sum_\nu W_\nu(1,2)\mathbf{C}_\nu(1)\cdot\mathbf{C}_\nu(2)\\&=\sum_\nu W_\nu(1,2)\sum_m(-)^mC_{\nu,-m}(1)C_{\nu m}(2),\end{aligned}\tag{A3}$$

where

$$C_{\nu m}(i)\equiv[4\pi/(2\nu+1)]^{1/2}Y_{\nu m}(\theta_i,\varphi_i)$$

is the unnormalized spherical harmonic, and $W_\nu(1,2)$ is given by Eq. (105).

Furthermore, we note that[38]

$$\nabla_p(i)C_{\nu m}(i)=\sum_\lambda C(\nu1\lambda;00)C(\nu1\lambda;mp)C_{\lambda,m+p}(i)\partial_\lambda(i),\tag{A4}$$

where ∂_λ is defined by Eqs. (104), and $C(\nu1\lambda;00)$ and $C(\nu1\lambda;mp)$ are the Clebsch-Gordan coefficients. If we substitute Eqs. (A3) and (A4) into (A2), we get

$$\begin{aligned}R=\sum_\nu\sum_m\sum_{p,q}\sum_{\lambda,\mu}&(-)^{p+q+m}C(\nu1\lambda;00)C(\nu1\lambda;-m,p)\\&\times\sigma_{-p}(1)C_{\lambda,p-m}(1)\partial_\lambda(1)C(\nu1\mu;00)C(\nu1\mu;mq)\sigma_{-q}(2)C_{\mu,q+m}(2)\partial_\mu(2)W_\nu(1,2).\end{aligned}\tag{A5}$$

From Eqs. (8) and (A5), we have

$$\begin{aligned}\langle u_A(1)u_B(2)|R|v_C(1)v_D(2)\rangle=&\sum_\nu\sum_m\sum_{p,q}\sum_{\lambda,\mu}\sum_{\sigma_A,\sigma_C}\sum_{\sigma_B,\sigma_D}(-)^{p+q+m}\\&\times C(l_A\tfrac{1}{2}j_A;m_A-\sigma_A,\sigma_A)C(\bar{l}_C\tfrac{1}{2}j_C;m_C-\sigma_C,\sigma_C)C(\nu1\lambda;00)C(\nu1\lambda;-m,p)\\&\times C(l_B\tfrac{1}{2}j_B;m_B-\sigma_B,\sigma_B)C(\bar{l}_D\tfrac{1}{2}j_D;m_D-\sigma_D,\sigma_D)C(\nu1\mu;00)C(\nu1\mu;mq)\\&\times\langle Y_{l_A,m_A-\sigma_A}(1)\phi_{\sigma_A}(1)|\sigma_{-p}(1)C_{\lambda,p-m}(1)|Y_{\bar{l}_C,m_C-\sigma_C}(1)\phi_{\sigma_C}(1)\rangle\\&\times\langle Y_{l_B,m_B-\sigma_B}(2)\phi_{\sigma_B}(2)|\sigma_{-q}(2)C_{\mu,q+m}(2)|Y_{\bar{l}_D,m_D-\sigma_D}(2)\phi_{\sigma_D}(2)\rangle\\&\times i^2\int_0^\infty\int_0^\infty dr_1dr_2\,P_A(1)P_B(2)Q_C(1)Q_D(2)\partial_\lambda(1)\partial_\mu(2)W_\nu(1,2),\end{aligned}\tag{A6}$$

where $\langle Y|A|Y'\rangle$ is the matrix element of A with respect to the spherical harmonics. With the help of the Wigner-Eckart theorem,[39] we get

$$\begin{aligned}\langle Y_{l_A,m_A-\sigma_A}(1)\phi_{\sigma_A}(1)&|\sigma_{-p}(1)C_{\lambda,p-m}(1)|Y_{\bar{l}_C,m_C-\sigma_C}(1)\phi_{\sigma_C}(1)\rangle\\&=\langle\phi_{\sigma_A}|\sigma_{-p}|\phi_{\sigma_C}\rangle\langle Y_{l_A,m_A-\sigma_A}|C_{\lambda,p-m}|Y_{\bar{l}_C,m_C-\sigma_C}\rangle\\&=C(\tfrac{1}{2}1\tfrac{1}{2};\sigma_C,-p,\sigma_A)(\tfrac{1}{2}\|\boldsymbol{\sigma}\|\tfrac{1}{2})C(\bar{l}_C\lambda l_A;m_C-\sigma_C,p-m,m_A-\sigma_A)(l_A\|\mathbf{C}_\lambda\|\bar{l}_C),\end{aligned}\tag{A7}$$

where

$$(\tfrac{1}{2}\|\boldsymbol{\sigma}\|\tfrac{1}{2})=\sqrt{3}$$

together with

$$(l_A\|\mathbf{C}_\lambda\|\bar{l}_C)=C(\bar{l}_C\lambda l_A;00)[(2l_A+1)/(2\bar{l}_C+1)]^{1/2}$$

gives the reduced matrix elements.

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[38] H. Horie, Progr. Theoret. Phys. (Kyoto) **10**, 296 (1953).

[39] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), p. 85.

The summation over p and m may immediately be carried out in Eq. (A6) because the triangular conditions of the Clebsch-Gordan coefficients in Eq. (A7) limit the values of p and m to

$$p=\sigma_C-\sigma_A\,,$$

and

$$m=m_C-m_A\,.$$

Similarly,

$$\langle Y_{l_B,m_B-\sigma_B}(2)\phi_{\sigma_B}(2)\,|\,\sigma_{-q}(2)C_{\mu,q+m}(2)\,|\,Y_{\bar{l}_D,m_D-\sigma_D}(2)\phi_{\sigma_D}(2)\rangle$$
$$=C(\tfrac{1}{2}1\tfrac{1}{2};\sigma_D,-q,\sigma_B)(\tfrac{1}{2}\|\boldsymbol{\sigma}\|\tfrac{1}{2})C(\bar{l}_D\mu l_B;m_D-\sigma_D,q+m,m_B-\sigma_B)(l_B\|\mathbf{C}_\mu\|\bar{l}_D)\,,$$

and the values of q and m are limited to

$$q=\sigma_D-\sigma_B\,,$$

and

$$m=m_B-m_D\,.$$

Hence, Eq. (A6) reduces to

$$\begin{aligned}\langle u_A(1)u_B(2)|R|v_C(1)v_D(2)\rangle={}&2\sum_\nu\sum_{\lambda,\mu}\sum_{\sigma_A,\sigma_C}\sum_{\sigma_B,\sigma_D}(-)^{l_A-j_A-m_A+\bar{l}_D-j_D-m_D}\\
&\times[(2l_A+1)(2l_B+1)(2\bar{l}_C+1)(2\bar{l}_D+1)]^{1/2}[(2\nu+1)^2(2\lambda+1)(2\mu+1)]^{-1/2}\\
&\times C(\tfrac{1}{2}\,\tfrac{1}{2}1;\sigma_C,-\sigma_A)C(\bar{l}_Cl_A\lambda;m_C-\sigma_C,\sigma_A-m_A)C(l_A\tfrac{1}{2}j_A;\sigma_A-m_A,\sigma_A)\\
&\times C(\bar{l}_C\tfrac{1}{2}j_C;m_C-\sigma_C,\sigma_C)C(\lambda1\nu;\sigma_A-\sigma_C+m_C-m_A,\sigma_C-\sigma_A)C(\tfrac{1}{2}\,\tfrac{1}{2}1;\sigma_B,-\sigma_D)\\
&\times C(l_B\bar{l}_D\mu;m_B-\sigma_B,\sigma_D-m_D)C(l_B\tfrac{1}{2}j_A;m_B-\sigma_B,\sigma_B)C(\bar{l}_D\tfrac{1}{2}j_D;\sigma_D-m_D,-\sigma_D)\\
&\times C(\mu1\nu;-\sigma_B+\sigma_D-m_D+m_B,-\sigma_D+\sigma_B)(-)^{\mu+1-\nu}C(\nu1\lambda;00)C(\bar{l}_Cl_A\lambda;00)\\
&\times C(\nu1\mu;00)C(l_B\bar{l}_D\mu;00)\delta_{m_A+m_B,m_C+m_D}\int_0^\infty\int_0^\infty dr_1dr_2\,P_A(1)Q_C(1)P_B(2)Q_D(2)\partial_\lambda(1)\partial_\mu(2)W_\nu(1,2)\,.\end{aligned}\tag{A8}$$

The summation over the σ's can be carried out by using Eq. (14.41) of de Shalit and Talmi,[21] and we have

$$\begin{aligned}\sum_{\sigma_A,\sigma_C}&C(\bar{l}_C\tfrac{1}{2}j_C;m_C-\sigma_C,\sigma_C)C(l_A\tfrac{1}{2}j_A;\sigma_A-m_A,-\sigma_A)C(\bar{l}_Cl_A\lambda;m_C-\sigma_C,\sigma_A-m_A)\\
&\times C(\tfrac{1}{2}\,\tfrac{1}{2}1;\sigma_C,-\sigma_A)C(\lambda1\nu;m_C-m_A+\sigma_A-\sigma_C,\sigma_C-\sigma_A)\\
&=[3(2j_A+1)(2j_C+1)(2\lambda+1)]^{1/2}C(j_Cj_A\nu;m_C,-m_A)\begin{Bmatrix}\bar{l}_C&\tfrac{1}{2}&j_C\\l_A&\tfrac{1}{2}&j_A\\\lambda&1&\nu\end{Bmatrix}.\end{aligned}$$

A similar relation also holds for the sum over σ_B and σ_D. With these results, Eq. (A8) becomes

$$\begin{aligned}\langle u_A(1)u_B(2)|R|v_C(1)v_D(2)\rangle={}&6\sum_\nu\sum_{\lambda,\mu}(-)^{l_A-j_A-m_A+\bar{l}_D-j_D-m_D}\\
&\times[(2j_A+1)(2j_C+1)(2j_B+1)(2j_D+1)(2l_A+1)(2\bar{l}_C+1)(2l_B+1)(2\bar{l}_D+1)]^{1/2}\\
&\times(2\nu+1)^{-1}C(\bar{l}_Cl_A\lambda;00)C(l_B\bar{l}_D\mu;00)C(\nu1\lambda;00)C(\nu1\mu;00)\\
&\times C(j_Cj_A\nu;m_C,-m_A)C(j_Bj_D\nu;m_B,-m_D)\begin{Bmatrix}\bar{l}_C&\tfrac{1}{2}&j_C\\l_A&\tfrac{1}{2}&j_A\\\lambda&1&\nu\end{Bmatrix}\begin{Bmatrix}l_B&\tfrac{1}{2}&j_B\\\bar{l}_D&\tfrac{1}{2}&j_D\\\mu&1&\nu\end{Bmatrix}\\
&\times i^2\int_0^\infty\int_0^\infty dr_1dr_2\,P_A(1)Q_C(1)P_B(2)Q_D(2)\partial_\lambda(1)\partial_\mu(2)W_\nu(1,2)\,,\end{aligned}\tag{A9}$$

where the fact that $\mu=\nu\pm1$ was used to eliminate $(-)^{\mu-\nu+1}$. The rest of the matrix element of the retardation term, Eq. (A1), may now easily be deduced from Eq. (A9). The general expression for the matrix element of the retardation term is

$$R_{ABCD}=-\sum_{\nu}\sum_{\lambda,\mu}\{R_{\lambda\nu}(j_C\bar{l}_Cm_C;\,j_Al_Am_A)R_{\mu\nu}(j_Bl_Bm_B;\,j_D\bar{l}_Dm_D)G_{\lambda\mu\nu}(AC;BD)$$
$$-R_{\lambda\nu}(j_C\bar{l}_Cm_C;\,j_Al_Am_A)R_{\mu\nu}(j_B\bar{l}_Bm_B;\,j_Dl_Dm_D)G_{\lambda\mu\nu}(AC;DB)$$
$$-R_{\lambda\nu}(j_Cl_Cm_C;\,j_A\bar{l}_Am_A)R_{\mu\nu}(j_Bl_Bm_B;\,j_D\bar{l}_Dm_D)G_{\lambda\mu\nu}(CA;BD)$$
$$+R_{\lambda\nu}(j_Cl_Cm_C;\,j_A\bar{l}_Am_A)R_{\mu\nu}(j_B\bar{l}_Bm_B;\,j_Dl_Dm_D)G_{\lambda\mu\nu}(CA;DB)\}\,,\quad\text{(A10)}$$

where $R_{\omega\nu}(jlm;\,j'l'm')$ is given by Eq. (102), and $G_{\lambda\mu\nu}$ by Eq. (103).

APPENDIX II: THE SYMMETRY RELATIONS AND THE TABLES OF THE RELATIVISTIC SLATER COEFFICIENTS

(a) *Symmetry relations.* The following symmetry relations can easily be verified from the symmetry properties of the Clebsch-Gordan coefficients and the 9-j symbols. Let $s_\nu(\kappa m;\kappa m')$ be any of the relativistic Slater coefficients

$$a_\nu(jm;\,j'm')\,,\quad b_\nu(jm;\,j'm')\,,\quad d_\nu(\kappa m;\,\kappa'm')\,,$$
$$e_\nu(jlm;\,j'l'm')\,,\quad f_\nu(\kappa m;\,\kappa'm')\,,\quad g_\nu(jlm;\,j'l'm')\,,$$
$$g_\nu'(jlm;\,j'l'm')\,,\quad h_\nu(\kappa m;\,\kappa'm')\,,\quad h_\nu'(\kappa m;\,\kappa'm')\,,$$

and

$$k_\nu(\kappa m;\,\kappa'm')\,.$$

Then

$$s_\nu(\kappa m;\,\kappa'm')=s_\nu(\kappa,\,-m;\,\kappa',\,-m')\quad\text{(A11)}$$
$$=s_\nu(\kappa'm';\,\kappa m)\,.\quad\text{(A12)}$$

When the summation over m and m' is carried out, we get from Eq. (A12)

$$\bar{s}_\nu(\kappa\kappa')=\bar{s}_\nu(\kappa'\kappa)\,.\quad\text{(A13)}$$

Note that Eq. (A13) means, for instance,

$$\bar{e}_\nu(jl;\,j'\bar{l}')=\bar{e}_\nu(j'\bar{l}';\,jl)\neq\bar{e}_\nu(j'l';\,j\bar{l})\,,\quad\text{(A14)}$$

and similar relations for $\bar{g}_\nu(jl;\,j'l')$, $\bar{g}_\nu'(jl;\,j'l')$, and $\bar{e}_\nu'(jl;\,j'l')$.

Additional symmetry relations exist for the relativistic Slater coefficients arising from the direct integrals, namely, $a_\nu(jm;\,j'm')$ and $d_\nu(\kappa m;\,\kappa'm')$:

$$a_\nu(jm;\,j'm')=a_\nu(jm;\,j',\,-m')\,,\quad\text{(A15)}$$

and

$$d_\nu(\kappa m;\,\kappa'm')=-d_\nu(\kappa m;\,\kappa',\,-m')\,.\quad\text{(A16)}$$

(b) *Tables of the relativistic Slater coefficients.* We present tables of the coefficients which are summed over the magnetic quantum numbers m and m'.

TABLE VI. The values of the coefficients $\bar{b}_\nu(jj')$.

κ	κ'	$\nu=0$	$\nu=1$	$\nu=2$
s	s	1/2	0	0
$\bar{p}$	s	0	1/6	0
$\bar{p}$	$\bar{p}$	1/2	0	0
p	s	0	1/6	0
p	$\bar{p}$	0	0	1/10
p	p	1/4	0	1/20

For $\bar{a}_\nu(jj')$ and $\bar{d}_\nu(\kappa\kappa')$, simple relations exist. [Cf. Eqs. (32) and (86).]

$$\bar{a}_\nu(jj')=\delta_{\nu 0}\quad\text{(A17)}$$

and

$$\sum_{m,m'}d_\nu(\kappa m;\,\kappa'm')\equiv(2j+1)(2j'+1)\bar{d}_\nu(\kappa\kappa')=0\,.\quad\text{(A18)}$$

From Eq. (33), we have

$$\bar{b}_\nu(jj')=(2\nu+1)^{-1}[C(jj'\nu;\,\tfrac{1}{2},\,-\tfrac{1}{2})]^2,\quad\text{(A19)}$$

and the expressions for the coefficients of the Breit operator can be obtained from Eqs. (98), (99), (100), (111), (112), (113), and (114).

TABLE VII. The values of the coefficients $\bar{e}_\nu'(jl;\,j'\bar{l}')$, $\bar{e}_\nu'(j\bar{l};\,j'l')$, $\bar{f}_\nu'(\kappa\kappa')$, and $\bar{k}_\nu'(\kappa\kappa')$.

				$\bar{e}_\nu'(jl;\,j'\bar{l}')$				$\bar{e}_\nu'(j\bar{l};\,j'l')$				$\bar{f}_\nu'(\kappa\kappa')$				$\bar{k}_\nu'(\kappa\kappa')$	
κ	κ'	ν	$2\bar{e}_\nu$	$\bar{g}_{\nu-1}$	$\bar{g}_{\nu+1}'$	$\bar{e}_\nu'$	$2\bar{e}_\nu$	$\bar{g}_{\nu-1}$	$\bar{g}_{\nu+1}'$	$\bar{e}_\nu'$	$2\bar{f}_\nu$	$\bar{h}_{\nu-1}$	$\bar{h}_{\nu+1}'$	$\bar{f}_\nu'$	$\bar{k}_{\nu-1}$	$\bar{k}_{\nu+1}$	$\bar{k}_\nu'$
s	s	1	1/2	−1/6	0	1/3	1/2	−1/6	0	1/3	1/3	1/6	0	1/2	0	0	0
$\bar{p}$	s	0	1/6	0	−1/6	0	3/2	0	−1/2	1	1	0	−1/6	5/6	0	−1/3	−1/3
		2	4/15	−1/15	0	1/5	0	0	0	0	0	0	0	0	−1/3	0	1/3
$\bar{p}$	$\bar{p}$	1	1/2	−1/6	0	1/3	1/2	−1/6	0	1/3	1/3	1/6	0	1/2	0	0	0
p	s	0	2/3	0	−1/6	1/2	0	0	0	0	0	0	0	0	0	−1/6	−1/6
		2	1/6	−1/15	0	1/10	3/10	−1/10	0	1/5	1/5	−1/30	0	1/6	−1/6	0	1/6
p	$\bar{p}$	1	1/2	0	−1/6	1/3	1/10	0	−1/15	1/30	1/3	0	−1/30	3/10	0	−3/10	−3/10
		3	0	0	0	0	6/35	−3/70	0	9/70	0	0	0	0	−3/10	0	3/10
p	p	1	1/4	−1/12	1/60	11/60	1/4	−1/12	1/60	11/60	1/30	1/12	1/75	39/300	0	−3/50	−3/50
		3	3/28	−3/70	0	9/140	3/28	−3/70	0	9/140	9/70	9/700	0	99/700	−3/50	0	3/50

We have tabulated the values of these coefficients up to $p(j=\frac{3}{2})$ symmetry in Tables VI and VII. The values of the coefficients which make up $\bar{e}_\nu'(jl;j'l')$ and $\bar{f}_\nu'(\kappa\kappa')$ [cf. Eqs. (117) and (118)] are also given in Table VII so that the coefficients from the exchange matrix elements of the magnetic interaction term ($2\bar{e}_\nu$ and $2\bar{f}_\nu$) and those from the retardation term ($\bar{g}_{\nu-1}$, $\bar{g}_{\nu+1}'$, $\bar{h}_{\nu-1}$, and $\bar{h}_{\nu+1}'$) may be compared directly.

As is mentioned in the main text, the direct integral of the retardation term vanishes identically. We expect, therefore, that the contributions from the exchange matrix elements of the retardation term will cancel each other when the orbitals in the radial integrals of Eq. (120) are identical, i.e., if $A=B$. This can easily be checked to be true from Table VII, using the identity

$$\int_0^\infty du\int_u^\infty dv\frac{u^\nu}{v^{\nu+1}}P_A(u)Q_A(u)P_A(v)Q_A(v)$$

$$\equiv\int_0^\infty du\int_0^u dv\frac{v^\nu}{u^{\nu+1}}P_A(u)Q_A(u)P_A(v)Q_A(v)$$

$$=\frac{1}{2}\int_0^\infty\int_0^\infty dr_1dr_2\,U_\nu(1,2)$$

$$\times P_A(1)Q_A(1)P_A(2)Q_A(2). \quad \text{(A20)}$$

APPENDIX III: THE RELATIVISTIC HARTREE-FOCK EQUATIONS

The relativistic Hartree-Fock equations for the closed-shell configurations are[10]

$$P_A'(r)+(\kappa_A/r)P_A(r)-(cr)^{-1}Q_A(r)[r(2c^2+\epsilon_A)+Z$$

$$-\sum_B(2j_B+1)U_0(BB;r)]-(cr)^{-1}\sum_\nu\sum_B(2j_B+1)$$

$$\times\bar{b}_\nu(j_Aj_B)U_\nu(AB;r)Q_B(r)=0, \quad \text{(A21)}$$

$$Q_A'(r)-(\kappa_A/r)Q_A(r)+(cr)^{-1}P_A(r)[r\epsilon_A+Z$$

$$-\sum_B(2j_B+1)U_0(BB;r)]+(cr)^{-1}\sum_\nu\sum_B(2j_B+1)$$

$$\times\bar{b}_\nu(j_Aj_B)U_\nu(AB;r)P_B(r)=0, \quad \text{(A22)}$$

where the prime stands for the derivative with respect to r. The allowed values of ν are specified by Eqs. (31), and

$$U_\nu(AB;r)\equiv\int_0^r ds\,(s/r)^\nu[P_A(s)P_B(s)+Q_A(s)Q_B(s)]$$

$$+\int_r^\infty ds\,(r/s)^{\nu+1}[P_A(s)P_B(s)+Q_A(s)Q_B(s)]. \quad \text{(A23)}$$

The condition on the cusp at the origin [cf. Eq. (129)] is found as follows. Let, near the origin,

$$\begin{aligned}P_A(r)&=r^{\gamma_A}(p_{A0}+p_{A1}r+p_{A2}r^2+\cdots),\\ Q_A(r)&=r^{\gamma_A}(q_{A0}+q_{A1}r+q_{A2}r^2+\cdots),\end{aligned} \quad \text{(A24)}$$

where the p_{Ai} and q_{Ai} are constants. For small r, low powers of r in Eqs. (A21) and (A22) dominate, and we need keep only terms of the lowest power in r, namely, of r^{γ_A-1}. Then, we have

$$\begin{aligned}P_A'(r)+(\kappa_A/r)P_A(r)-(Z/cr)Q_A(r)&=0,\\ Q_A'(r)-(\kappa_A/r)Q_A(r)+(Z/cr)P_A(r)&=0,\end{aligned} \quad \text{(A25)}$$

to be satisfied simultaneously. Using an argument similar to that given by Hartree[1] for the nonrelativistic case, it can be shown that the leading powers of r in the relativistic two-electron integrals are higher than that retained in Eqs. (A25). If we substitute Eqs. (A24) into Eqs. (A25), then, after factoring out r^{γ_A}, we get

$$\begin{aligned}(\gamma_A+\kappa_A)p_{A0}-(Z/c)q_{A0}&=0,\\ (Z/c)p_{A0}+(\gamma_A-\kappa_A)q_{A0}&=0.\end{aligned} \quad \text{(A26)}$$

To have a nontrivial solution for p_{A0} and q_{A0} from Eqs. (A26), the determinant of their coefficients must vanish, viz.,

$$\gamma_A^2-\kappa_A^2+(Z/c)^2=0$$

from which Eq. (129) follows.

APPENDIX IV: NONRELATIVISTIC LIMIT OF THE RELATIVISTIC HARTREE-FOCK-ROOTHAAN EQUATION

Equation (68) can be written as a pair of coupled linear equations for ξ and η as

$$\mathbf{F}_{\xi\xi}\xi+\mathbf{F}_{\xi\eta}\eta=\epsilon\mathbf{S}\xi, \quad \text{(A27)}$$

$$\mathbf{F}_{\eta\xi}\xi+\mathbf{F}_{\eta\eta}\eta=\epsilon\mathbf{S}\eta. \quad \text{(A28)}$$

For brevity orbital labels n and κ are omitted in above equations. The leading terms in $\mathbf{F}_{\eta\xi}$ and $\mathbf{F}_{\eta\eta}$ are $c\mathbf{T}^+$ and $-2c^2\mathbf{S}$, respectively, [cf. Eqs. (71) and (72)]. Hence, by neglecting the terms of lower orders in Eq. (A28), we get

$$\mathbf{T}^+\xi\cong 2c\mathbf{S}\eta,$$

or

$$\eta\cong(\mathbf{S}^{-1}\mathbf{T}^+/2c)\xi. \quad \text{(A29)}$$

Equation (A29) is the approximate relation between the large and small components. It also confirms our expectation that $\eta\sim(v/c)\xi$, because $\mathbf{T}^+$ comes from the momentum operator in the Dirac Hamiltonian and the denominator of Eq. (A29) from the rest-mass term. Hence, $\langle\mathbf{T}^+/(2m_0c\mathbf{S})\rangle_{\text{av}}\approx p/2m_0c=v/2c$.

If we retain only $-c\mathbf{T}^-$ in $\mathbf{F}_{\xi\eta}$, then from Eqs. (A27) and (A29) we get

$$(\mathbf{F}_{\xi\xi}+\boldsymbol{\tau})\xi=\epsilon\mathbf{S}\xi, \quad \text{(A30)}$$

where

$$\boldsymbol{\tau}=-\mathbf{T}^-\mathbf{S}^{-1}\mathbf{T}^+/2. \quad \text{(A31)}$$

In Eq. (A31) $\boldsymbol{\tau}$ corresponds to the matrix of the nonrelativistic kinetic-energy operator.