

21 dec, 2007

Uitsluitend voor persoonlijk gebruik / for personal use only



Technische Universiteit Delft

Bibliotheek
Prometheusplein 1
Postbus 98
2600 MG Delft
Tel: +31 (0) 15 27 85678
Fax: +31 (0) 15 27 85706
Email: library@tudelft.nl
www.library.tudelft.nl

Aan: J.A. STRIJKER
UITLEENBUREAU UB

POSTBUS 559
9700 AN GRONINGEN

NEDERLAND

Aanvraag nr: 1356437

Uw referentie(s): A086567926
J.A. STRIJKER-DE.VRIES

Artikelomschrijving:

Aantal kopieën: 38

Artikel:

Auteur:

Titel: MODERN TECHNIQUES IN COMPUTATIONAL CHEMISTRY : MOT

Jaar: Vol. Nr. Pag. 169-

Plaatsnummer: 2029.431.1 +

De bibliotheek is gesloten van maandag 24 december 2007 t/m dinsdag 1 januari 2008.

The library will be closed from 24 December 2007 until 1 January 2008.

Chapter 4.

Kinetically Balanced Geometric Gaussian Basis Set Calculations For Relativistic Many-Electron Atoms

A. Mohanty and E. Clementi

IBM Corporation
Scientific and Engineering Computations
Dept. 48B/428
Kingston, New York 12401, U.S.A.

1. Introduction

Recently there has been an increased interest in solving the Dirac equation for many-electron atoms using the method of basis set expansion. In spite of an earlier problem¹ of "variational collapse" or bound failure associated with the basis set methods, it is now generally agreed²⁻⁷ that, with proper boundary conditions imposed upon the basis set, Dirac-Fock (DF) self consistent field (SCF) calculations can be performed on many-electron atoms using techniques similar to nonrelativistic methods. Crucial to the success of basis set approach lies in imposing kinetic balance²⁻⁷ between the large and the small component basis. Grant et al.⁵⁻⁸ used kinetically balanced Slater type orbitals (STOs) to perform basis set calculations on H-, He-, Be and Ne-like atoms with low to moderately high atomic charge ($Z = 2 - 50$), and obtained results comparable in accuracy (one part in 10^8) to the numerical DF methods.^{9,10} The same authors have also reported⁸ calculations for mercury ($Z = 80$).

Although STOs have the correct functional behavior to describe the relativistic wave function of atoms at the origin, they are not particularly suitable for analytic SCF molecular calculations. On the other hand, Gaussian type orbitals (GTOs) are useful in the evaluation of multi-center integrals in molecules but they do not possess the correct functional behavior at the origin. However, with a finite nuclear size model,¹¹ the Gaussian basis sets provide a natural description of the relativistic wavefunction within the nucleus. Aerts et al.^{12,13} used Gaussian basis sets to solve DF equations for one- and many-electron systems. Malli¹⁴ proposed the use of GTOs with both integer and non-integer powers for r for the relativistic DF calculation of atomic properties for a wide range of atomic charge,

including Xenon, in the point nucleus approximation. Matsuoka et al.¹⁵⁻¹⁸ reported kinetically balanced well-tempered basis set calculations with the finite nucleus size approximation and gave configuration average Dirac-Hartree-Fock (DHF) energies of various atoms, comparable to the numerical DF limit, of Desclaux.¹⁹ Very recently, we have also performed²⁰ DF many-electron atomic structure calculations using geometric Gaussian basis sets,²¹ with kinetic balance²⁻⁷ between the large and small component spinors.

In this paper we give the details of our calculations for closed- and open-shell atoms. We also present new numerical results for atoms (He–Rn) which support our claim that the prescription of kinetic balance works well when Gaussian type orbitals with integer powers of radial distance are employed, particularly for the finite nucleus charge distribution. There is no “variational collapse” and the eigenvalues converge from above to the numerical Dirac-Hartree-Fock result^{8,9} as the number of basis functions increases.

The organization of the rest of the paper is as follows. In section 2 we describe the Dirac Hamiltonian and wavefunctions for the many-electron systems. In section 3 we give simple formulae for the one- and two-electron integrals which are needed for deriving the Dirac-Fock equation. In section 4 we present details of the basis set used in our calculation. In section 5 we give matrix elements of the unperturbed Hamiltonian in terms of our basis sets. In section 6 we discuss the angular coefficients needed in computing the Fock matrices. In section 7 the evaluation of one- and two-electron integrals, in terms of elementary functions, is presented. In section 8 we give details of our finite nucleus size approximation. In section 9 we present open-shell calculations and in section 10 we give some of the vector-coupling coefficients used in our calculation. In section 11 we present our numerical results and, finally, in section 12 we give our conclusions.

2. Preliminary

The total Dirac-Breit Hamiltonian for a many-electron system has two terms: a one-electron part consisting of kinetic, mass energy and nuclear attraction:

$$\hat{H}_D(i) = c\vec{\alpha}_i \cdot \vec{p}_i + c^2(\beta_i - 1) + V_{nuc}(r_i), \quad (1)$$

and the two-electron part H_{12} consisting of Coulomb repulsion and the Breit interaction

$$H_{12} = \sum_{\substack{ij \\ i < j}} \frac{1}{r_{ij}} + \sum_{\substack{ij \\ i < j}} B_{ij}. \quad (2)$$

In the low-frequency limit;²²

$$B_{12} = - \frac{1}{(2r_{12})} \{ \vec{\alpha}_1 \cdot \vec{\alpha}_2 + [(\vec{\alpha}_1 \cdot \vec{r}_{12})(\vec{\alpha}_2 \cdot \vec{r}_{12})/r_{12}^2] \}. \quad (3)$$

The notation and phase choices of Grant et al.⁹ will be adhered to as closely as possible and atomic units ($e = \hbar = m = 1$) will be used throughout unless explicitly mentioned. The value of the speed of light is taken as 137.0373 (for comparison purposes).

In eqn. (1) we have subtracted the rest mass energy to get the binding energy. Dirac operators $\vec{\alpha}$ and β are expressed by the matrices

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \quad (4)$$

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

In the central field approximation, the solution of the Dirac equation is given in terms of four component spinors

$$\Psi_{n\kappa m}(r, \theta, \phi) = r^{-1} \begin{pmatrix} P_{n\kappa}(r) & \chi_{\kappa m}(\theta, \phi) \\ iQ_{n\kappa}(r) & \chi_{-\kappa m}(\theta, \phi) \end{pmatrix}, \quad (5)$$

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

$$\int_0^\infty [P_{n\kappa}(r)P_{n'\kappa}(r) + Q_{n\kappa}(r)Q_{n'\kappa}(r)]dr = \delta_{nn'}. \quad (6)$$

The spinor $\chi_{\kappa m}(\theta, \phi)$ is given by

$$\chi_{\kappa m} = \sum_{\sigma} Y_{l, m-\sigma}(\theta, \phi) \phi^{\sigma} c(l\frac{1}{2}j; m-\sigma, \sigma). \quad (7)$$

The angular state is characterized by the quantum number κ given by

$$\kappa = -2(j-l)(j+\frac{1}{2}), \quad (8)$$

where l is the orbital quantum number and $j = l \pm \frac{1}{2}$ is the total angular momentum number, the $c(l\frac{1}{2}j; m-\sigma, \sigma)$ are the Clebsch-Gordan coefficients and ϕ^{σ} are the two-component spinors:

$$\phi_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \phi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (9)$$

We shall use the spectroscopic notation similar to that of Grant et al.,⁹ where a state with $j = l - \frac{1}{2}$ is distinguished from a state with $j = l + \frac{1}{2}$ by placing a bar

over the spectroscopic label corresponding to l , e.g., $\bar{p} \equiv (l = 1, j = 1/2, \kappa = +1)$ or $p \equiv (l = 1, j = 3/2, \kappa = -2)$.

3. Matrix Elements of the Hamiltonian

Following the nonrelativistic case, the wavefunction for the many-electron system will be taken to consist of the sum of antisymmetrized products of one-electron central field orbitals given by equation (5). The total energy E then reduces to the sum of one electron integral I_A and two types of two electron integrals, the direct integral J_{AB} and the exchange integral K_{AB} , where the subscripts A and B denote the set of orbitals (n, κ, m) , viz,

$$E = \sum_A I_A + 1/2 \sum_{A,B} (J_{AB} - K_{AB}). \quad (10)$$

Here we define

$$I_A \equiv \langle \psi_A | H_D | \psi_A \rangle, \quad (11)$$

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

and

$$K_{AB} \equiv \langle \psi_A(1) \psi_B(2) | r_{12}^{-1} | \psi_B(1) \psi_A(2) \rangle. \quad (13)$$

The one electron integrals involve the matrix elements $\langle n\kappa m | H_D(i) | n'\kappa'm' \rangle$, the angular parts of which can be easily evaluated to yield

$$I_A = \int_0^\infty dr \left\{ -2c^2 [Q_A(r)]^2 + V_{nuc}(r) ([P_A(r)]^2 + [Q_A(r)]^2) + cQ_A(r) \left[P_A'(r) + \frac{\kappa_A}{r} P_A(r) \right] - cP_A(r) \left[Q_A'(r) - \frac{\kappa_A}{r} Q_A(r) \right] \right\}, \quad (14)$$

where the prime denotes the differentiation with respect to radial coordinates.

A general expression for the two-electron integrals is given by²³

$$\begin{aligned} C_{ABCD} &= \langle \psi_A(1) \psi_B(2) | \frac{1}{r_{12}} | \psi_C(1) \psi_D(2) \rangle \\ &= \sum_v C_v(j_C m_C; j_A m_A) C_v(j_B m_B; j_D m_D) \\ &\quad \times R_v(AC; BD) \delta_{m_A + m_B, m_C + m_D} \end{aligned} \quad (15)$$

B5

where $R_v(AC; BD)$ is the relativistic radial integral and C_v are the angular coefficients. The sum over the magnetic quantum numbers m can be carried out explicitly and for the closed shell structure one can write²³

$$\sum_B J_{AB} = \sum_{n_B k_B} \bar{a}_0^c(j_A, j_B) (2j_B + 1) \int \int dr_1 dr_2 U_v(1, 2) \times \{[P_A(1)]^2 + [Q_A(1)]^2\} \times \{[P_B(2)]^2 + [Q_B(2)]^2\}. \quad (16a)$$

Similarly

$$\sum_B K_{AB} = \sum_v \sum_{n_B k_B} (2j_B + 1) \bar{b}_v^c(j_A j_B) \int_0^\infty \int_0^\infty dr_1 dr_2 U_v(1, 2) [P_A(1) P_B(1) + Q_A(1) Q_B(1)] \times [P_A(2) P_B(2) + Q_A(2) Q_B(2)], \quad (16b)$$

where

$$U_v(1, 2) = r_1^v / r_2^{v+1}, \quad \text{if } r_1 < r_2 \\ = r_2^v / r_1^{v+1}, \quad \text{if } r_1 > r_2. \quad (17)$$

The analysis of the two-electron integral for the Breit interaction is much more involved. We refer the reader to Kim²³ and Grant²² for more details. Following Kim²³ we write

$$M_{AB} = \langle \psi_A(1) \psi_B(2) \left| \frac{\vec{\alpha}_1 \cdot \vec{\alpha}_2}{r_{12}} \right| \psi_A(1) \psi_B(2) \rangle \quad (18)$$

and

$$N_{AB} = \langle \psi_A(1) \psi_B(2) \left| \frac{\alpha_1 \cdot \alpha_2}{r_{12}} \right| \psi_B(1) \psi_A(2) \rangle \quad (19)$$

as the direct and exchange matrix elements of the magnetic interaction term. The exchange matrix element of the retardation term (the second term in Eq. 3) can be written as²³

$$R_{AB} = \frac{1}{2} \langle \psi_A(1) \psi_B(2) \left| [(\vec{\alpha}_1 \cdot \vec{\nabla}_1) (\vec{\alpha}_2 \cdot \vec{\nabla}_2) \vec{r}_{12}] \right| \psi_B(1) \psi_A(2) \rangle. \quad (20)$$

It is worth noting that the direct part of the retardation term vanishes. Therefore, the relativistic correction arising from the Breit interaction can then be written as follows:²³

$$E_B = -\frac{1}{2} \sum_{A,B} (M_{AB} - N_{AB} - R_{AB}). \quad (21)$$

For a closed-shell system as has been shown by Kim²³

$$\sum_{AB} M_{AB} = 0. \quad (22)$$

Hence, we can write the combined exchange and retardation terms as²³

$$\begin{aligned} \sum_B [N_{AB} + R_{AB}] &= \sum_B \sum_v (2j_B + 1) \\ &\quad [\bar{e}_v^c(\kappa_A \kappa_B) \int_0^\infty \int_0^\infty dr_1 dr_2 U_v(1, 2) P_A(1) Q_B(1) P_A(2) Q_B(2) \\ &\quad + \bar{e}_v^c(\kappa_A \kappa_B) \int_0^\infty \int_0^\infty dr_1 dr_2 U_v(1, 2) P_B(1) Q_A(1) P_B(2) Q_A(2) \\ &\quad + 2\bar{d}_v^c(\kappa_A \kappa_B) \int_0^\infty \int_0^\infty dr_1 dr_2 U_v(1, 2) P_A(1) Q_B(1) P_B(2) Q_A(2) \\ &\quad + 2\bar{g}_v^c(\kappa_A \kappa_B) \int_0^\infty \int_{r_1}^\infty dr_1 dr_2 U_v(1, 2) P_A(1) Q_B(1) P_B(2) Q_A(2)] \end{aligned} \quad (23)$$

All these basic integrals can be expressed in terms of the basis functions in the form analogous to nonrelativistic calculations. The coefficients \bar{a}_v^c , \bar{b}_v^c , \bar{e}_v^c , \bar{d}_v^c , \bar{g}_v^c , can be obtained in terms of 3j- and 9j-symbols using Racah Algebra.^{8,23} We shall return to the discussion of these angular factors in section 7.

4. Choice of Basis Sets

The radial functions are expanded in terms of the basis sets as

$$P_{n\kappa}(r) = \sum_p C_{\kappa p}^L g_{\kappa p}^L(r) \quad (24)$$

and

$$Q_{n\kappa}(r) = \sum_p C_{\kappa p}^S g_{\kappa p}^S(r), \quad (25)$$

where the summation index p runs over the number of basis functions, N , $g_{\kappa p}^L(r)$ and $g_{\kappa p}^S(r)$ are the basis functions belonging to the large and the small components respectively, and $C_{\kappa p}^L$ and $C_{\kappa p}^S$ are the corresponding expansion coefficients for

each type of orbital of symmetry κ . For brevity we have omitted the summation over various types of orbitals of a particular symmetry.

For the large component, we have chosen GTOs of the form:

$$g_{\kappa i}^L(r) = C_{N_{\kappa i}}^L r^{n_{\kappa}} e^{-\alpha_i r^2}, \quad (26)$$

where n_{κ} takes integer values 1, 2, 3, 4 for $s, \bar{p}, p; \bar{d}, d; \bar{f}, f$ symmetries respectively, and $C_{N_{\kappa i}}^L$ is the normalization factor given by

$$C_{N_{\kappa i}}^L = \left[\frac{\sqrt{\pi}}{2^{2n_{\kappa} + 3/2}} \frac{(2n_{\kappa} - 1)!!}{(\alpha_i)^{\frac{2n_{\kappa} + 1}{2}}} \right]^{-1/2}. \quad (27)$$

We have constrained our small component radial basis according to the kinetic balance condition⁴⁻⁷

$$g_{\kappa i}^S(r) = C_{N_{\kappa i}}^S \left(\frac{d}{dr} + \frac{\kappa}{r} \right) g_{\kappa i}^L(r), \quad (28a)$$

where

$$C_{N_{\kappa i}}^S = \left\{ \frac{\alpha_i}{(2n_{\kappa} - 1)} [(4\kappa^2 - 1) + 4(n_{\kappa} + \kappa)] \right\}^{-1/2}. \quad (28b)$$

Hence, the same set of exponents have been used for the large as well as the small component. The exponents α_i 's are generated according to

$$\alpha_i = \alpha_0 \beta^{i-1}, \quad i = 1, 2, \dots, N \quad (29)$$

where α_0 and β are parameters determined by the basis set size N and the particular atomic system being considered. For Xenon ($Z = 54$) N was taken to be of the order 30 for the $1s_{1/2}$ orbital. These geometric basis sets defined by Eq. (29) were introduced by Clementi et al.²¹ for nonrelativistic atomic and molecular computations.

5. Relativistic Hartree-Fock-Roothaan Equation

The derivation of relativistic Hartree-Fock-Roothaan equation in the basis set expansion form is familiar from the work of Kim²³ and Kagawa.²⁴ The inclusion of the Breit interaction in the SCF equation was studied by Grant et al.,⁷ whose formulation we shall adopt. For closed shell system, the equation takes the matrix form:

$$FC = \epsilon SC \quad (30)$$

In Eq. (30) the basis sets are used to parametrize the large- and small-component parts of the atomic spinors. If we choose our basis sets according to the kinetic balance prescription, the Fock matrix will be of $2N\kappa \times 2N\kappa$ dimension, where κ denotes the number of symmetry species being considered. The matrices are block diagonalized according to symmetry type κ :

$$F_{\kappa} C_{\kappa} = \varepsilon_{\kappa} S_{\kappa} C_{\kappa}, \quad (31)$$

where

$$C_{\kappa} = \begin{bmatrix} C_{\kappa}^L \\ C_{\kappa}^S \end{bmatrix}. \quad (32)$$

Equation (31) gives a set of coupled equations to be solved for the expansion coefficients C_{κ} as in the nonrelativistic equations.

The overlap matrix can be partitioned into $N \times N$ blocks of the form

$$S_{\kappa} = \begin{bmatrix} S_{\kappa}^{LL} & 0 \\ 0 & S_{\kappa}^{SS} \end{bmatrix}, \quad (33)$$

where the subscripts LL and SS denote the fact that large and small component wavefunctions are used.

The Fock operator has three contributions in general: viz,

$$F_{\kappa} = h_{\kappa} + g_{\kappa} + b_{\kappa}, \quad (34)$$

where

$$h_{\kappa} = \begin{bmatrix} V_{\kappa}^{LL} & c\Pi_{\kappa}^{LS} \\ c\Pi_{\kappa}^{SL} & V_{\kappa}^{SS} - 2c^2 S_{\kappa}^{SS} \end{bmatrix} \quad (35)$$

is the one-electron bare nucleus operator,

$$g_{\kappa} = \begin{bmatrix} J_{\kappa}^{LL} - K_{\kappa}^{LL} & -K_{\kappa}^{LS} \\ -K_{\kappa}^{SL} & J_{\kappa}^{SS} - K_{\kappa}^{SS} \end{bmatrix} \quad (36)$$

gives the Coulomb repulsion term and

$$b_{\kappa} = \begin{bmatrix} B_{\kappa}^{LL} & B_{\kappa}^{LS} \\ B_{\kappa}^{SL} & B_{\kappa}^{SS} \end{bmatrix} \quad (37)$$

denotes the contribution due to the Breit term. The matrix form of the one- and two-electron operators appearing in Eqs. (35)–(37) can be deduced from the

expressions for I_A , J_{AB} , K_{AB} and $N_{AB} + R_{AB}$ given by Eqs. (14), (16a), (16b), and (23) respectively.

If we write the general form of a single element of Gaussian function as

$$\psi_{\kappa i}(r) = \begin{bmatrix} g_{\kappa i}^L(r) \\ g_{\kappa i}^S(r) \end{bmatrix}, \quad (38)$$

the one-electron matrices given in eqn (35) have the elements

$$V_{\kappa ij}^{TT} = \int_0^\infty g_{\kappa i}^T(r) V_{nuc}(r) g_{\kappa j}^T(r) (r) dr, \quad (39)$$

$$S_{\kappa ij}^{TT} = \int_0^\infty g_{\kappa i}^T(r) g_{\kappa j}^T(r) dr, \quad (40)$$

where the superscript TT indicates LL or SS, and

$$\Pi_{\kappa ij}^{SL} = \int_0^\infty dr g_{\kappa i}^S(r) \left[\frac{d}{dr} + \frac{\kappa}{r} \right] g_{\kappa j}^L(r), \quad (41a)$$

$$\Pi_{\kappa ij}^{LS} = \int_0^\infty dr g_{\kappa i}^L(r) \left[-\frac{d}{dr} + \frac{\kappa}{r} \right] g_{\kappa j}^S(r). \quad (41b)$$

Integrating by parts we can see that Π^{LS} and Π^{SL} are matrix adjoints of each other, provided that boundary terms vanish which, of course, is true in case of spherical Gaussian functions.

The matrices J_{κ}^{TT} and K_{κ}^{TT} are given by

$$J_{\kappa pq}^{TT} = \sum_{\kappa' rs} \left[D_{\kappa' rs}^{TT} J_{\kappa pq, \kappa' rs}^{0TTTT} + D_{\kappa' rs}^{\bar{T}\bar{T}} J_{\kappa pq, \kappa' rs}^{0TT\bar{T}\bar{T}} \right] \quad (42)$$

and

$$K_{\kappa pq}^{TT'} = \sum_v \sum_{\kappa' rs} [\bar{b}_v^c(jj')] D_{\kappa' rs}^{TT'} K_{\kappa pq, \kappa' rs}^{vTT', TT'}. \quad (43)$$

The superscripts $T\bar{T}$ represent a pair of LS or SL and the superscripts T and T' are either L or S. The density matrices are defined as

$$D_{\kappa pq}^{TT'} = N_{\kappa} C_{\kappa p}^T C_{\kappa q}^{T'}. \quad (44)$$

For a closed shell $N_k = 2j + 1$. The Coulomb integrals $J_{\kappa pq, \kappa' rs}^{0TT, T'T'}$ and $K_{\kappa pq, \kappa' rs}^{vTT', TT'}$ are defined as usual

$$J_{\kappa pq, \kappa' rs}^{vTT, T'T'} = \int_0^\infty \int_0^\infty g_{\kappa p}^T(r_1) g_{\kappa q}^T(r_1) U_v(r_1, r_2) g_{\kappa' r}^{T'}(r_2) g_{\kappa' s}^{T'}(r_2) dr_1 dr_2 \quad (45)$$

where

$$U_v(r_1, r_2) \equiv U_v(1, 2) = r_1^v / r_2^{v+1}, \quad \text{if } r_1 < r_2 \\ r_2^v / r_1^{v+1}, \quad \text{if } r_1 > r_2 \quad (46)$$

and

$$K_{\kappa pq, \kappa' rs}^{vTT', TT'} = \int_0^\infty \int_0^\infty g_{\kappa p}^T(r_1) g_{\kappa' r}^{T'}(r_1) U_v(r_1, r_2) g_{\kappa q}^{T'}(r_2) g_{\kappa' s}^{T'}(r_2) dr_1 dr_2. \quad (47)$$

The general form of the Breit interaction matrices is:

$$B_{\kappa pq}^{TT} = \sum_v \sum_{\kappa' rs} \bar{e}_v^c(\kappa \kappa') D_{\kappa rs}^{\bar{T}\bar{T}} K_{\kappa pq, \kappa' rs}^{vTT\bar{T}\bar{T}} \quad (48)$$

and

$$B_{\kappa pq}^{T\bar{T}} = \sum_v \sum_{\kappa' rs} (\bar{d}_v^c(\kappa \kappa') D_{\kappa' rs}^{\bar{T}T} K_{\kappa pq, \kappa' rs}^{vT\bar{T}, \bar{T}T} + \bar{g}_v^c(\kappa \kappa') D_{\kappa rs}^{\bar{T}T} M_{\kappa pq, \kappa' rs}^{vT\bar{T}, \bar{T}T}), \quad (49)$$

where

$$K_{\kappa pq, \kappa' rs}^{vT\bar{T}, \bar{T}T} = \int_0^\infty \int_0^\infty g_{\kappa p}^T(r_1) g_{\kappa' r}^{\bar{T}}(r_1) U_v(r_1, r_2) g_{\kappa q}^{\bar{T}}(r_2) g_{\kappa' s}^T(r_2) dr_1 dr_2, \quad (50)$$

and

$$M_{\kappa pq, \kappa' rs}^{vT\bar{T}, \bar{T}T} = \int_0^\infty \int_{r_1}^\infty g_{\kappa p}^T(r_1) g_{\kappa' r}^{\bar{T}}(r_1) U_v(r_1, r_2) g_{\kappa q}^{\bar{T}}(r_2) g_{\kappa' s}^T(r_2) dr_1 dr_2 \quad (51)$$

The angular coefficients $\bar{e}_v^c(\kappa \kappa')$, $\bar{d}_v^c(\kappa \kappa')$ and $\bar{g}_v^c(\kappa \kappa')$ can be evaluated explicitly by using Grant's general angular⁹ package. Also, some closed-shell coefficients for low angular momentum orbitals such as s , \bar{p} and p are tabulated in Kim's paper.²³

6. Angular Coefficients

To evaluate the angular coefficients $\bar{b}_v^e(\kappa\kappa')$, $\bar{e}_v^e(\kappa\kappa')$, $\bar{g}_v^e(\kappa\kappa')$ and $\bar{d}_v^e(\kappa\kappa')$ that appear in the two-electron matrix elements, we follow Quincy et al.⁸ and write the general matrix element as

$$\langle \psi_a(1) \psi_b(2) | \frac{1}{r_{12}} | \psi_c(1) \psi_d(2) \rangle = \sum_{vq} \left\{ \begin{matrix} m_a & v & j_c \\ j_a & q & m_c \end{matrix} \right\} \left\{ \begin{matrix} m_b & v & j_d \\ j_b & q & m_d \end{matrix} \right\} X^v(abcd), \quad (52)$$

where m is the magnetic quantum number and $X^v(abcd)$ is the effective interaction strength. For the Coulomb interaction:

$$\frac{1}{r_{12}} = \sum_v U_v(r_1, r_2) C^v(1) \cdot C^v(2), \quad (53)$$

$$C_q^v(\theta, \phi) = \sqrt{4\pi/(2v+1)} Y_{vq}(\theta, \phi), \quad (54)$$

and the interaction strength can be written as follows:

$$X^v(abcd) = \{j_a j_c v\} \{j_b j_d v\} \pi^e(\kappa_a, \kappa_c, v) \pi^e(\kappa_b, \kappa_d, v) \\ (-1)^v \langle j_a \| C^{(v)} \| j_c \rangle \langle j_b \| C^{(v)} \| j_d \rangle R^v(ab; cd) \quad (55)$$

where

$$R^v(ab; cd) = \iint \rho_{ac}^e(r_1) \rho_{bd}^e(r_2) U^v(r_1, r_2) dr_1 dr_2, \quad (56)$$

$$\rho_{ac}^e(r) = P_a(r) P_c(r) + Q_a(r) Q_c(r), \quad (57)$$

$$\langle j \| C^v \| j' \rangle = (-1)^{j+1/2} [jj'] \begin{bmatrix} j & v & j' \\ 1/2 & 0 & -1/2 \end{bmatrix}, \quad (58)$$

$$\pi^e(\kappa, \kappa', v) = 1/2 [1 - \delta\delta'(-1)^{j+j'+v}] (\delta = -\text{sign}(\kappa)), \quad (59)$$

and the triangular factors $\{jj'v\}$ express the restriction

$$|j - j'| \leq v \leq j + j'. \quad (60)$$

By summing over the magnetic quantum number, the coefficients \bar{a}_v^e and \bar{b}_v^e for the closed shell case can be evaluated explicitly to give⁹

$$\bar{a}_v^e = \delta_{v0} \quad (61)$$

and

$$\bar{b}_v^c = \begin{bmatrix} j & v & j' \\ 1/2 & 0 & -1/2 \end{bmatrix}^2. \quad (62)$$

The matrix element of the Breit interaction has a more complicated structure. Here we follow the derivation of Grant et al.²² and give the equations for the sake of completeness. The effective interaction strength in the low frequency limit²² has the form

$$\begin{aligned} X_T^v(ab;cd) = & (-1)^v \langle j_a \| C^{(v)} \| j_c \rangle \langle j_b \| C^{(v)} \| j_d \rangle \{j_a j_c v\} \{j_b j_d v\} \\ & \times \left\{ \sum_{\lambda=v-1}^{v+1} \pi^0(\kappa_a, \kappa_c, \lambda) \pi^0(\kappa_b, \kappa_d, \lambda) \sum_{\mu=1}^4 r_{\mu}^{\lambda, v}(abcd) R_{\mu}^{\lambda}(ab;cd) \right. \\ & \left. + \pi^0(\kappa_a, \kappa_c, v-1) \pi^0(\kappa_b, \kappa_d, v+1) \sum_{\mu=1}^8 s_{\mu}^v(abcd) S_{\mu}^v(ab;cd) \right\} \end{aligned} \quad (63)$$

where $\pi^0(\kappa, \kappa', v) = 1 - \pi^e(\kappa, \kappa', v)$. The radial integrals $R_{\mu}^{\lambda}(ab;cd)$ and $S_{\mu}^v(ab;cd)$ are defined²² in terms of standard integrals

$$R^v(ac; bd) = \int \int \rho_{ac}^0(r_1) [U_v(r_1, r_2)] \rho_{bd}^0(r_2) dr_1 dr_2 \quad (64)$$

and

$$S^v(ac; bd) = \int \int \rho_{ac}^0(r_1) W_{v-1, v+1, v}(r_1, r_2) \rho_{bd}^0(r_2) dr_1 dr_2. \quad (65)$$

In Eqs. (64) and (65)

$$\rho_{ac}^0 = P_a(r_1) Q_c(r_2) \quad (66)$$

$$\rho_{bd}^0 = P_b(r_1) Q_d(r_2) \quad (68)$$

and

$$W_{v-1, v+1, v}(r_1, r_2) = -1/2[v][\bar{U}_{v-1}(r_1, r_2) - \bar{U}_{v+1}(r_1, r_2)], \quad (69)$$

where

$$\bar{U}_v(r_1, r_2) = \begin{cases} r_1^v/r_2^{v+1} & \text{if } r_1 < r_2 \\ 0 & \text{if } r_1 > r_2 \end{cases} \quad (70)$$

so that

$$U_v(r_1, r_2) = \bar{U}_v(r_1, r_2) + \bar{U}_v(r_2, r_1). \quad (71)$$

The coefficients $r_\mu^{l,v}$ and s_μ^l are given by Grant and McKenzie²¹ and can be further combined to give the coefficients $\bar{e}_v^c(\kappa\kappa')$, $\bar{g}_v^c(\kappa\kappa')$ and $\bar{d}_v^c(\kappa\kappa')$ in the matrix representation. It has recently been demonstrated by Quincy et al.⁷ that the Breit interaction can be readily incorporated in the SCF iterations. We shall, however, ignore the Breit interaction in the remaining discussion.

7. Evaluation of Matrix Elements

The expression for one-electron integrals is especially simple for Gaussian functions with integer powers of r .

The overlap integral has two parts

$$S_{\kappa ij}^{LL} = [V_{2n_{\kappa i}}(\alpha_{\kappa i}) V_{2n_{\kappa j}}(\alpha_{\kappa j})]^{-1/2} V_{n_{\kappa i} + n_{\kappa j}}(\alpha_{\kappa ij}) \quad (72a)$$

and

$$\begin{aligned} S_{\kappa ij}^{SS} = & C_{N_{\kappa i}}^S C_{N_{\kappa j}}^S [V_{2n_{\kappa i}}(\alpha_{\kappa i}) V_{2n_{\kappa j}}(\alpha_{\kappa j})]^{-1/2} \\ & \times [4(n_{\kappa i} + \kappa)(n_{\kappa j} + \kappa) V_{n_{\kappa i} + n_{\kappa j} - 2}(\alpha_{\kappa ij}) \\ & - 2\{\alpha_{\kappa j}(n_{\kappa i} + \kappa) + \alpha_{\kappa i}(n_{\kappa j} + \kappa)\} V_{n_{\kappa i} + n_{\kappa j}}(\alpha_{\kappa ij}) \\ & + \alpha_{\kappa i} \alpha_{\kappa j} V_{n_{\kappa i} + n_{\kappa j} + 2}(\alpha_{\kappa ij})], \end{aligned} \quad (72b)$$

where

$$\alpha_{\kappa ij} = \frac{1}{2}(\alpha_{\kappa i} + \alpha_{\kappa j}), \quad (73)$$

$$V_i(x) = \frac{(i-1)!!}{x^{\frac{i+1}{2}}}, \quad (74)$$

and $C_{N_{\kappa j}}^S$ is the normalization factor given by Eq. (28b).

The kinetic energy integral

$$\begin{aligned} \Pi_{\kappa ij}^{SL} &= \langle g_{\kappa i}^S | \vec{\sigma} \cdot \vec{p} | g_{\kappa j}^L \rangle \\ &= \int_0^\infty g_{\kappa i}^S(r) \left(\frac{d}{dr} + \frac{\kappa}{r} \right) g_{\kappa j}^L(r) dr \\ &= S_{\kappa ij}^{SS} / C_{N_{\kappa j}}^S = \Pi_{\kappa ji}^{LS}. \end{aligned} \quad (75)$$

The electron-nucleus Coulomb interaction integral for the point nucleus of charge Z also consists of two parts

$$V_{\kappa ij}^{LL} = (-Z) \frac{2\sqrt{2}}{\sqrt{\pi}} [V_{2n_{\kappa i}}(\alpha_{\kappa i}) V_{2n_{\kappa j}}(\alpha_{\kappa j})]^{-1/2} \\ \times V_{n_{\kappa i} + n_{\kappa j} - 1}(\alpha_{\kappa ij})$$

and

$$V_{\kappa ij}^{SS} = (-Z) \frac{2\sqrt{2}}{\sqrt{\pi}} C_{N_{\kappa i}}^S C_{N_{\kappa j}}^S [V_{2n_{\kappa i}}(\alpha_{\kappa i}) V_{2n_{\kappa j}}(\alpha_{\kappa j})]^{-1/2} \\ [4(n_{\kappa i} + \kappa)(n_{\kappa j} + \kappa) V_{n_{\kappa i} + n_{\kappa j} - 3}(\alpha_{\kappa ij}) \\ - 2\{\alpha_{\kappa i}(n_{\kappa j} + \kappa) + \alpha_{\kappa j}(n_{\kappa i} + \kappa)\} V_{n_{\kappa i} + n_{\kappa j} - 1}(\alpha_{\kappa ij}) \\ + \alpha_{\kappa i} \alpha_{\kappa j} V_{n_{\kappa i} + n_{\kappa j} + 1}(\alpha_{\kappa ij})].$$

The expressions for all the required two-electron Coulomb repulsion integrals be obtained in terms of the incomplete Beta functions as shown by Malli,¹⁴ have, however, adopted a different algorithm previously developed.²⁵

The two-electron integrals (due to Breit and Coulomb) can be evaluated in terms of the primitive integral

$$I_{\kappa p \kappa q, \kappa' r \kappa' s}^{vTT', T''T'''} = \int_0^\infty \int_0^\infty dr_1 dr_2 g_{\kappa p}^T(r_1) g_{\kappa q}^{T'}(r_1) U^v(r_1, r_2) \\ g_{\kappa' r}^{T''}(r_2) g_{\kappa' s}^{T'''}(r_2)$$

For example, the direct integral for the large component can be written as

$$J_{\kappa p q, \kappa' r s}^{vLL; LL} = I_{\kappa p q, \kappa' r s}^{vLL, LL} = \frac{2\sqrt{2}}{\sqrt{\pi}} \left[S_{\kappa p q}^{LL} S_{\kappa' r s}^{LL} / V_{n_{\kappa p} + n_{\kappa q}}(\alpha_{\kappa p q}) V_{n_{\kappa' r} + n_{\kappa' s}}(\alpha_{\kappa' r s}) \right] \\ \times V_{n_{\kappa p} + n_{\kappa q} - v - 1}(\alpha_{\kappa p q}) V_{n_{\kappa' r} + n_{\kappa' s} + v}(\alpha_{\kappa' r s}) \\ \times C_{n_{\kappa p} + n_{\kappa q} - v - 1, n_{\kappa' r} + n_{\kappa' s} + v} \left(\frac{\alpha_{\kappa p q}}{\alpha_{\kappa' r s}} \right),$$

where

$$C_{\alpha, \beta}(t) = (1+t)^{-1/2(\beta+1)} \sum_{\lambda=0}^{(\alpha-1)/2} \frac{(2\lambda + \beta - 1)!!}{(2\lambda)!!(\beta - 1)!!} \left(\frac{t}{1+t} \right)^\lambda.$$

Similarly, the basic exchange integral has the following symmetrized form

$$K_{\kappa p q, \kappa' r s}^{LL, LL} = 1/2 [I_{\kappa p \kappa' r, \kappa q \kappa' s}^{vLL, LL} + I_{\kappa q \kappa' s, \kappa p \kappa' r}^{vLL, LL} \\ + I_{\kappa p \kappa' s, \kappa q \kappa' r}^{vLL, LL} + I_{\kappa q \kappa' r, \kappa p \kappa' s}^{vLL, LL}],$$

where

$$\begin{aligned}
I_{\kappa p \kappa' r, \kappa q \kappa' s}^{vLL,LL} &= \frac{2\sqrt{2}}{\sqrt{\pi}} \frac{S_{\kappa p q} S_{\kappa' r s}}{V_{n_{\kappa p} + n_{\kappa' r}}(\alpha_{\kappa p r}) V_{n_{\kappa q} + n_{\kappa' s}}(\alpha_{\kappa q s})} \\
&\times V_{n_{\kappa p} + n_{\kappa' r} - v - 1}(\alpha_{\kappa p \kappa' r}) V_{n_{\kappa q} + n_{\kappa' s} + v}(\alpha_{\kappa q \kappa' s}) \\
&\times C_{n_{\kappa p} + n_{\kappa' r} - v - 1, n_{\kappa q} + n_{\kappa' s} + v} \left(\frac{\alpha_{\kappa p \kappa' r}}{\alpha_{\kappa q \kappa' s}} \right),
\end{aligned} \tag{82}$$

and

$$\alpha_{\kappa p \kappa' r} = \frac{1}{2}(\alpha_{\kappa p} + \alpha_{\kappa' r}), \tag{83}$$

$$\alpha_{\kappa q \kappa' s} = \frac{1}{2}(\alpha_{\kappa q} + \alpha_{\kappa' s}). \tag{84}$$

The M-type of integrals which occur in the matrix elements of Breit interaction are readily obtained from the primitive integral (K-type) given in Eq. (81) by retaining only half the terms. Since these integrals are analytic, they can be quite accurately evaluated which, of course is critical for the success of the analytic calculations.

The radial matrix elements of Coulomb and low frequency Breit interactions for a particular set of indices $\{pqrs\}$ depend upon primitive integrals which differ in tensor order 'v' and on the labels T . The set of integral lists which are required to perform relativistic super matrix calculation have the labels $[LL,LL]$, $[LL,SS]$, $[SS,LL]$, $[SS,SS]$, $[SL,SL]$ and $[SL,LS]$ and hence can be generated easily with proper indexing structure.

8. Finite Nucleus Approximation

It is well known that Gaussians do not have the proper functional form for representing relativistic wavefunctions for atoms near the origin. For example, in the hydrogenic case the relativistic $1s_{1/2}$ wavefunctions behaves as²⁶

$$P_{1s}(r) \sim r^\gamma, \gamma = \sqrt{1 - Z^2 \alpha^2}. \tag{85}$$

Equation (85) clearly shows that the derivative of P_{1s} has a singularity at the origin and such type of cusp behavior is more pronounced for high Z value. In order to accurately represent this cusp behavior even for Xenon ($Z=54$), one needs to have exponents as high as 9×10^9 . This actually corresponds to a wavefunction which is highly localized in the nucleus region and the number of exponents needed for accurate results is dramatically large. However, in the extended nucleus approximation the $1s_{1/2}$ solution at the origin can be represented as¹¹

$$P_{1s_{1/2}}(r) = r + g_3^L r^3 + g_5^L r^5 + \dots \tag{86a}$$

and

$$Q_{1s\frac{1}{2}}(r) = g_2^S r^2 + g_4^S r^4 + \dots, \quad (86b)$$

so that

$$\frac{1}{r} \left(\frac{P_{nk}(r)}{Q_{nk}(r)} \right) \cong \left(\frac{\exp(-\alpha_L r^2)}{r \exp(-\alpha_S r^2)} \right). \quad (87)$$

Of course, in the matched basis set, $\alpha_L = \alpha_S$, and Eq. (87) shows that in this case Gaussians give a natural description of the wavefunction within the nucleus. Ishikawa et al.¹¹ had shown that by representing the nucleus by a uniform charge distribution, the cusp condition is automatically relaxed and one needs optimal exponents much smaller in number in those expansions in which finite nucleus size is considered than those in which the point nucleus is used.

Our results for Hg^{79+} were also obtained using even-tempered kinetically-balanced matched basis sets and we completely agree with the results of Ishikawa et al.¹¹ Furthermore, we have extended the calculations to many-electron systems up to Radon and we have shown²⁰ that a similar convergence pattern is observed for the finite-nucleus-size approximation.

The only part of the Fock matrix which needs modification due to the finite nuclear charge distribution is the nuclear potential matrix elements V_k^{LL} and V_k^{SS} .

Let $V_{nuc}(r)$ denote nuclear potential. By assuming a uniformly charged sphere for the nucleus, the effect of the finite nuclear size is included in $V_{nuc}(r)$ and is written as¹⁰

$$V_{nuc}(r) = \begin{cases} -(Z/2R)(3 - r^2/R^2), & \text{if } r < R \\ -Z/r, & \text{if } r \geq R. \end{cases} \quad (88)$$

For the radius of the nucleus we use $R = 2.2677 \times 10^{-5} A^{1/3}$ in atomic units²¹ where A is the atomic number.

The modification of the nuclear potential due to finite nuclear size introduces new terms in the electron-nucleus attraction integrals over GTOs. For the basis sets we have chosen, the bare nucleus matrix elements are given by (we are using the same type of notation as the point nucleus matrix element)

$$\begin{aligned} V_{kpq}^{LL} = & \int_0^R g_{kp}^L(r) \left[-\frac{Z}{2R} (3 - r^2/R^2) \right] g_{kq}^L(r) dr \\ & + \int_R^\infty g_{kp}^L(r) (-Z/r) g_{kq}^L(r) dr \end{aligned} \quad (89)$$

and

$$V_{\kappa pq}^{SS} = \int_0^R g_{\kappa p}^S(r) [-Z/2R (3 - r^2/R^2)] g_{\kappa q}^S(r) dr + \int_R^\infty g_{\kappa p}^S(r) (-Z/R) g_{\kappa q}^S(r). \quad (90)$$

The integrals in Eqs. (89) and (90) can be expressed in a straightforward manner in terms of elementary functions and error functions; viz,

$$V_{\kappa pq}^{LL} = (-Z) \frac{2\sqrt{2}}{\sqrt{\pi}} (2R)^{n_{\kappa pq}} [V_{2n_{\kappa p}}(\alpha_{\kappa p}) V_{2n_{\kappa q}}(\alpha_{\kappa q})]^{-1/2} \times [I(n_{\kappa pq}/2, t) + 3/2 F(n_{\kappa pq}/2, t) - 1/2 F((n_{\kappa pq} + 2)/2, t)] \quad (91)$$

where

$$t = (\alpha_{\kappa p} + \alpha_{\kappa q}) R^2, \quad (92)$$

$$n_{\kappa pq} = n_{\kappa p} + n_{\kappa q}, \quad (93)$$

$$I(v, t) = \int_1^\infty y^{2v-1} \exp(-ty^2) dy = \sum_{n=1}^v \frac{1}{(2t)^n} \frac{(2v-2)!!}{(2v-2n)!!} \exp(-t), \quad t > 0 \quad (94)$$

and $F_v(t)$ is the incomplete Gamma Function defined by

$$F_v(t) = \int_0^1 dx x^{2v} \exp(-tx^2). \quad (95)$$

Similarly,

$$V_{\kappa pq}^{SS} = \frac{2\sqrt{2}}{\sqrt{\pi}} (2R)^{n_{\kappa pq}} [V_{2n_{\kappa p}}(\alpha_{\kappa p}) V_{2n_{\kappa q}}(\alpha_{\kappa q})]^{-1/2} C_{N_{\kappa p}}^S C_{N_{\kappa q}}^S \times \left[(R^{-2}) (n_{\kappa p} + \kappa) (n_{\kappa q} + \kappa) \{ I(n_{\kappa pq} - 2, t) + 3/2 F((n_{\kappa pq} - 2)/2, t) - 1/2 F(n_{\kappa pq}/2, t) \} - \{ 2 \alpha_{\kappa p} (n_{\kappa p} + \kappa) + 2 \alpha_{\kappa q} (n_{\kappa q} + \kappa) \} \{ I(n_{\kappa pq}, t) + 3/2 F(n_{\kappa pq}/2, t) - 1/2 F((n_{\kappa pq} + 2)/2, t) \} + 4 \alpha_{\kappa p} \alpha_{\kappa q} R^2 \{ I(n_{\kappa pq} + 2, t) + 3/2 F((n_{\kappa pq} + 2)/2, t) - 1/2 F((n_{\kappa pq} + 4)/2, t) \} \right]. \quad (96)$$

It is easily seen from the definition of $I(v, t)$ and $F_v(t)$ that the extra terms arising from the integration inside the nucleus go to zero as $R \rightarrow 0$. Thus, the effect of finite nucleus is to add extra easily computable terms in the formulae for nuclear attraction integral. However, as we shall see later, the results differ considerably from point nucleus calculations and the convergence patterns are very much different.

9. Open-Shell Calculations

In section 5 we described the pseudo-eigenvalue equation for a closed-shell system which is to be solved for the expansion coefficients C_k (Eq. 31). However, it is well known from the work of Roothaan²⁷ that in the Hartree-Fock theory of open-shell systems one has to deal with two pseudo-eigenvalue equations, one for the closed- and the other one for the open-shell orbitals. The extension of the Relativistic Hartree-Fock (RHF) theory to open-shells was treated by LeClerc²⁷ and by Kagawa.²⁴ Here we shall follow Kagawa²⁴ to derive the Relativistic Hartree-Fock Roothaan (RHFR) theory for open-shell calculations, and we assume the following:

1. The state has no more than one open-shell for each symmetry species defined by κ .
2. The wavefunction for the state is expressed by a single configuration.
3. When the configuration contains only one open-shell, the state can be uniquely specified by the total angular momentum quantum number J and the seniority number V .
4. When the configuration contains more than one open-shell, the state can be uniquely specified by the total angular quantum number J .

The unperturbed energy for a single determinant is given by

$$\begin{aligned}
 E = & \sum_A N_A I_A + \sum_{A'} N_{A'} I_{A'} \\
 & + \frac{1}{2} \sum_A \sum_B N_A N_B \{J_{AB} - K_{AB}\} \\
 & + \sum_A \sum_{A'} N_A N_{A'} \{J_{AA'} - K_{AA'}\} \\
 & + \frac{1}{2} \sum_{A'} \sum_{B'} N_{A'} N_{B'} \{J_{A'B'} - K_{A'B'}\}.
 \end{aligned} \tag{97}$$

Here N_A and $N_{A'}$ are the number of electrons in the closed and open shell, respectively. N_A always equals to $2j_A + 1$, whereas $N_{A'} < 2j_{A'} + 1$. It should be noted that in Eq. (97) we have explicitly shown the sum over the number of electrons of each orbital type defined by the set of quantum numbers $A \equiv nkm$ or $A' = n'k'm'$. The interactions between the closed shells can be obtained from Eqs. (16a) and (16b). For the closed-open shell interaction, the sum over the m quantum numbers can be performed²⁴ to give

$$\begin{aligned} J_{ss'} &= \frac{1}{(2j+1)(2j'+1)} \sum_m \sum_{m'} \langle \psi_{sm}(1) \psi_{s'm'}(2) | \frac{1}{r_{12}} | \psi_{sm}(1) \psi_{s'm'}(2) \rangle \\ &= \sum_v \bar{a}_v^c(\kappa\kappa') R^v(ss'; s's') \end{aligned} \quad (98)$$

and

$$\begin{aligned} K_{s,s'} &= \frac{1}{(2j+1)(2j'+1)} \sum_m \sum_{m'} \langle \psi_{sm}(1) \psi_{s'm'}(2) | \frac{1}{r_{12}} | \psi_{sm}(2) \psi_{s'm'}(1) \rangle \\ &= \sum_v \bar{b}_v^c(\kappa\kappa') R^v(ss'; ss'). \end{aligned} \quad (99)$$

Here s and s' stand for either A or A' and denote the quantum numbers of the closed- and open-shell orbitals, respectively.

Similarly, the open-open shell interaction can be written in the form:

$$J_{A'B'} = \sum_v a_v^o(\kappa_{A'}\kappa_{B'}J) R^v(A'A'; B'B') \quad (100)$$

and

$$K_{A'B'} = \sum_v b_v^o(\kappa_{A'}\kappa_{B'}J) R^v(A'B'; A'B'). \quad (101)$$

In order to obtain the SCF equation for the open-shell system we add to the energy functional (97) the orthonormality constraint

$$C_{ikp} S C_{jkq}^\dagger = \delta_{ij} \quad (102)$$

multiplied by a lagrange multiplier θ_{ij} , (the index i or j denote the type of orbital $1s, 2s, 3s, \dots$, etc., for a particular symmetry κ) and minimize the entire expression with respect to the expansion coefficients C_{ikp} .

In the closed shell case the orbitals can always be subjected to a unitary transformation,²⁷ which brings the matrix of Lagrange multipliers into diagonal form. We

then end up with the pseudo-eigenvalue equation given by Eq. (30). However, for the open-shell case, as discussed in Roothaan's paper,²⁷ there are only unitary transformations available which transform the open and closed shells within themselves. Such transformations can eliminate only the off-diagonal Lagrange multipliers, say θ_{AB} and $\theta_{A'B'}$ but not the multiplier $\theta_{AA'}$ which couple the closed and open shells. Only when closed and open-shell orbitals have no common symmetry, the off-diagonal multipliers vanish automatically and in that case one obtains two pseudo-eigenvalue equations, one for the closed and one for the open shells. We now review the derivations leading to these two pseudo-eigenvalue equations, which is very similar to the nonrelativistic approach.²⁷

We shall have Lagrangian multipliers between orbitals of closed-shells, between orbitals of open-shells, and between orbitals of closed- and open-shell. The latter type of multiplier will be eliminated by introducing new operators R_A and $R_{A'}$ for closed- and open-shells, respectively. The introduction of R_A and $R_{A'}$ in order to eliminate the Lagrangian multipliers is convenient because the R operators, called *coupling operators*, are expressed in terms of the orbitals as follows:

$$\hat{R}_s \psi_{s'm'} = \frac{N_s}{N_A} \sum_m [\langle \psi_{sm} | \hat{J}^{A'} - \hat{K}^{A'} | \psi_{s'm'} \rangle \psi_{sm} + \langle \psi_{sm} | \psi_{s'm'} \rangle (\hat{J}^{A'} - \hat{K}^{A'}) \psi_{sm}] \quad (103)$$

where, as before, both s and s' denote A or A' . Here $\hat{J}^{A'}$ and $\hat{K}^{A'}$ are the direct and exchange operators defined by Roothaan²⁷ as

$$\hat{J}^s(1)\psi_{s'}(1) = \int [\psi_s^\dagger(2) \frac{1}{r_{12}} \psi_s(2) d\vec{r}_2] \psi_{s'}(1) \quad (104a)$$

and

$$\hat{K}^s(1)\psi_{s'}(1) = \int [\psi_s^\dagger(2) \frac{1}{r_{12}} \psi_s(2) d\vec{r}_2] \psi_s(1). \quad (104b)$$

When $\kappa = \kappa'$, the $a_v^o(\kappa\kappa'J)$ and $b_v^o(\kappa\kappa'J)$ coefficients are not independent of each other because $R^o(A'A'; A'A')$ is the same in both $J_{A'A'}$ and $K_{A'A'}$. We assume, following Kagawa,²⁴

$$a_v^o(\kappa\kappa'J) = \delta_{v0}. \quad (105)$$

This leads to the simplification of the coupling operator (103) which we now describe.

By summing over m and m' we obtain

$$\begin{aligned} \frac{1}{N_A^2} \sum_{m, m'} < \psi_{sm} | \hat{J}^{A'} - \hat{K}^{A'} | \psi_{s'm'} > \\ = \frac{N_A}{N_A - N_{A'}} \left[\sum_v \{ \alpha_v(\kappa J) R^v(A' A'; ss') - \beta_v(\kappa J) R^v(A' s; A' s') \} \right] \end{aligned} \quad (106)$$

where

$$\alpha_v(\kappa J) = \bar{a}_v^c(\kappa J) - a_v^0(\kappa J) \quad (107a)$$

$$\beta_v(\kappa J) = \bar{b}_v^c(\kappa J) - b_v^0(\kappa J). \quad (107b)$$

The direct integral involving \hat{J}^{ok} vanishes because of Eq. (105) and Eq. (61).

By using Eq. (106) in Eq. (103) we obtain the two coupling operators R_A and $R_{A'}$ in terms of the supermatrices S , D and Q ,

$$R_A = [N_A / (N_A - N_{A'})] [S_\kappa D_{A'} Q_{A'} + Q_{A'} D_A S_\kappa] \quad (108a)$$

and

$$R_{A'} = [N_{A'} / (N_{A'} - N_A)] [S_\kappa D_A Q_{A'} + Q_{A'} D_{A'} S_\kappa], \quad (108b)$$

where the closed- and open-shell densities are defined respectively as

$$D_A = \sum_{i \in \text{closed}} D_{Ai} \quad (109a)$$

and

$$D_{A'} = \sum_{i \in \text{open}} D_{A'i} \quad (109b)$$

Further, we define

$$D_T = D_A + D_{A'} \quad (109c)$$

as the total density matrix.

The supermatrix Q in (108) is defined by

$$Q_{\kappa p q, \kappa r s}^{TT', TT'} = - \sum_{v=k_1, k_1+2, \dots}^{k_2} \beta_v(\kappa J') K_{\kappa p q, \kappa r s}^{vTT', TT'} \quad \text{when } \kappa = \kappa', \quad (110a)$$

and

$$Q_{\kappa pq, \kappa' rs}^{TT', TT'} = \sum_{v=0, 2, \dots}^{k_0} \alpha^v(\kappa \kappa' J) J_{\kappa pq, \kappa' rs}^{vTT', TT'} - \sum_{v=k_1, k_1+2, \dots}^{k_2} \beta^v(\kappa \kappa' J) K_{\kappa pq, \kappa' rs}^{vTT', TT'} \quad (110b)$$

when $\kappa \neq \kappa'$.

Here the vector-coupling coefficients $\alpha_v(\kappa \kappa' J)$ and $\beta_v(\kappa \kappa' J)$ for $\kappa \neq \kappa'$ are defined by the relation

$$\alpha_v(\kappa \kappa' J) = \begin{cases} 0, & v=0 \\ -a_v^0(\kappa \kappa' J), & v \neq 0 \end{cases} \quad (111a)$$

$$\beta_v(\kappa \kappa' J) = \bar{b}_v^c(\kappa \kappa' J) - b_v^0(\kappa \kappa' J). \quad (111b)$$

Further, we define supermatrix P as

$$P_{\kappa pq, \kappa' rs}^{TT', TT'} = J_{\kappa pq, \kappa' rs}^{oTT', TT'} - \sum_{v=k_1, k_1+2, \dots}^{k_2} \bar{b}_v^c(\kappa \kappa' J) K_{\kappa pq, \kappa' rs}^{vTT', TT'}. \quad (112)$$

In Eqs. (109a)–(109c)

$$\begin{aligned} \kappa_1 &= |j - j'|, \text{ if } \kappa \kappa' > 0, \\ &= |j - j'| + 1, \text{ if } \kappa \kappa' < 0, \\ \kappa_2 &= j + j', \text{ and } k_0 = (2j - 1, 2j' - 1)_{<}. \end{aligned} \quad (113)$$

In addition, let us designate by F_c and F_o the quantities

$$F_{c, \kappa pq} = h_{\kappa pq} + P_{\kappa pq} + R_{o, \kappa pq} \text{ and } F_{o, \kappa pq} = H_{\kappa pq} + P_{\kappa pq} - Q_{\kappa pq} + R_{c, \kappa pq}, \quad (114)$$

where we have used the notation $A \equiv c\kappa$ and $A' \equiv o\kappa$ to denote the quantum numbers of closed- and open-shells of symmetry κ and we have defined

$$P_{\kappa pq}^{TT'} = \sum_{\kappa' rs} P_{\kappa pq, \kappa' rs}^{TT', TT'} D_{\kappa' rs}^{TT'} \quad (115)$$

and

$$Q_{\kappa pq}^{TT'} = \sum_{\kappa' rs} Q_{\kappa pq, \kappa' rs}^{TT', TT'} D_{\kappa' rs}^{TT'}. \quad (116)$$

By making use of a unitary transformation on the closed and open shells separately, we can bring the matrices of Lagrangian multiplier into diagonal form. By

designating as ε_{sk} , the diagonal elements of the transformed Lagrangian matrices, we can finally write

$$\Sigma_q F_{c, \kappa p q} C_{k \kappa q} = \varepsilon_{c \kappa} \Sigma_q S_{q p q} C_{k \kappa q}, \quad (117)$$

$$\Sigma_q F_{o, \kappa p q} C_{m \kappa q} = \varepsilon_{o \kappa} \Sigma_q S_{q p q} C_{m \kappa q}, \quad (118)$$

where $k = i$ closed- and $m = i$ open-shell respectively or, in a more compact notation, we have

$$F_c C = \varepsilon S C, \quad (119)$$

$$F_o C = \varepsilon S C. \quad (120)$$

The Eqs. (119) and (120) are similar to the Hartree-Fock equations for closed and open shells as in the nonrelativistic case.²⁷ They are pseudo-eigenvalue equations, because the matrices F_c and F_o depend on the solution C .

The expression for DHF total energy is obtained in supervector and supermatrix notation

$$E_{DHF} = \frac{1}{2} D_T^\dagger P D_T - \frac{1}{2} D_o^\dagger Q D_o + h^\dagger D_T. \quad (121)$$

10. Vector Coupling Coefficients

The vector coupling coefficient $\beta_v(\kappa \kappa' J)$ given by Eq. (111) are evaluated using the coefficients of fractional parentage (CFP).²⁹ The computer program by Grant et al.⁸ has been used to generate the coefficients $\bar{b}_v^c(\kappa \kappa' J)$ and $b_v^o(\kappa \kappa' J)$ for the jj coupled configurations. In Table I we give coefficients $\bar{b}_v^c(\kappa \kappa')$ up to $J = 7/2$. These were obtained by Eq. (62).

For the open-shell coefficients $b_v^o(\kappa \kappa' J)$ one can have two types of terms, one consisting of diagonal terms which come from open-shells like p^n , d^m , f^n , etc., and the other consisting of off-diagonal terms resulting from open shells $p^n s$, $d^m f$, etc. General formulae for integrals of two-electron operator V_{12} and the vector coupling coefficients are given in Refs. 29 and 30. Even with more than two open shells involved, the general formula reduces to the following two open-shell cases^{23,29}

$$\begin{aligned} \langle j_1^{n_1}(V_1 J_1) j_2^{n_2}(V_2 J_2) J | \sum_{i < \kappa}^{n_1 + n_2} V_{i \kappa} | j_1^{n_1}(V_1 J_1) j_2^{n_2}(V_2 J_2) | J \rangle \\ = A_1 + A_2 + B, \end{aligned} \quad (122)$$

where the diagonal matrix elements A_λ is written as

Table I. $\bar{b}_\zeta(\kappa\kappa')$

κ	κ'	$v = 0$						
		0	1	2	3	4	5	6
∓ 1	∓ 1	1/2	—	—	—	—	—	—
∓ 1	± 1	—	1/6	—	—	—	—	—
∓ 2	∓ 1	—	1/6	—	—	—	—	—
∓ 2	± 1	—	—	1/10	—	—	—	—
∓ 2	∓ 2	1/4	—	1/20	—	—	—	—
∓ 2	± 2	—	1/60	—	9/140	—	—	—
∓ 3	∓ 1	—	—	1/10	—	—	—	—
∓ 3	± 1	—	—	—	1/14	—	—	—
∓ 3	∓ 2	—	1/10	—	1/35	—	—	—
∓ 3	± 2	—	—	1/70	—	1/21	—	—
∓ 3	∓ 3	1/6	—	4/105	—	1/63	—	—
∓ 3	± 3	—	1/210	—	4/315	—	25/693	—
-4	-1	—	—	—	1/14	—	—	—
-4	$+1$	—	—	—	—	1/18	—	—
-4	-2	—	—	9/140	—	5/252	—	—
-4	$+2$	—	—	—	1/84	—	5/132	—
-4	-3	—	1/14	—	1/42	—	5/462	—
-4	$+3$	—	—	1/210	—	5/462	—	25/858
-4	-4	1/8	—	5/168	—	9/616	—	25/3432

$$A_\lambda = \langle j_\lambda^{n_\lambda} V_\lambda J_\lambda | \sum_{i < \kappa} V_{i\kappa} | j_\lambda^{n_\lambda} V_\lambda J_\lambda \rangle \quad (123)$$

and the off-diagonal matrix element as

$$B = \langle j_1^{n_1}(V_1 J_1) j_2^{n_2}(V_2 J_2) | \sum_{i=1}^n \sum_{\kappa=n_1+1}^{n_1+n_2} V_{i\kappa} | j_1^{n_1}(V_1 J_1) j_2^{n_2}(V_2 J_2) | J \rangle, \quad (124)$$

where n_λ denotes the number of electrons in the J_λ shell, and V_λ and J_λ are the seniority and total angular momentum quantum numbers.

The diagonal elements A can be expressed²⁹ in terms of the coefficients of fractional parentage by use of seniority number V yielding

Table II. Values of $\beta_v(\kappa\kappa J)$.

κ	j	n	V	J	$v=0$	$v=2$	$v=4$	$v=6$
∓ 1	1/2	1	1	1/2	-1/2	—	—	—
∓ 2	3/2	1	1	3/2	-3/4	1/20	—	—
		2	2	2	-1/4	-1/100	—	—
		3	1	3/2	-1/12	1/180	—	—
∓ 3	5/2	1	1	5/2	-5/6	0.0380952380952	0.015873015873	—
		2	2	4	-1/3	-0.01904761904769	0.0079365079365079	—
		3	3	9/2	-1/6	0.018503401360544	0.00075585789871	—
		4	2	4	-1/12	-0.0047619047619047	0.0019841269841269	—
		5	1	5/2	-1/30	0.0015238095238095	0.00063492063492063	—
± 4	7/2	1	1	7/2	-7/8	0.0297619047619	0.01461038961	0.00728438228
		2	2	6	-3/8	-0.00992063492206349	-0.0048701298701298	0.0065372661526507
		3	3	15/2	-5/24	-0.0231481481481	-0.003492719401810	0.003571441508504
		4	4	8	-1/8	-0.0184240362811790	-0.003731657952437	0.00134134130546997
		5	3	15/2	-3/40	-0.008333333333	-0.0012573789846516	0.0012857189430616
		6	2	6	-1/24	-0.0011022927689593	-0.000541125411254	0.00072636290585
		7	1	7/2	-1/56	0.00607385811467	0.00029817121653585	0.0001486608629465

$$A = \sum_v \bar{b}_v^o(\kappa\kappa J) R^v(o\kappa, o\kappa; o\kappa, o\kappa), \quad (125a)$$

The expression for the off-diagonal matrix elements B is much more involved. Details of the calculations can be found in the article by Grant.³⁰ After angular integration and by using CFPs we can write

$$B = \left[\sum_v \bar{a}_v^o(\kappa_1\kappa_2 J) R^v(o\kappa_1, o\kappa_1; o\kappa_2 o\kappa_2) - \bar{b}_v^o(\kappa_1\kappa_2 J) R^v(o\kappa_1, o\kappa_2; o\kappa_1, o\kappa_2) \right]. \quad (125b)$$

In Eqs. (125a) and (125b) the bar over $b_v^o(\kappa\kappa' J)$ and $a_v^o(\kappa\kappa' J)$ denotes the coefficient which includes the sum over a distinct pair of electrons.

Numerical values of coefficients $\bar{a}_v^o(\kappa_1\kappa_2 J)$ and $\bar{b}_v^o(\kappa_1\kappa_2 J)$ can be obtained by using the graphical techniques.³⁰ Using the general package by Grant et al.⁸ these coeffi-

Table III(a). Vector coupling coefficients for the $\bar{f}-\bar{d}$ interaction in some of the high spin, high total angular momentum states of $f^n\bar{d}^1$ configuration.

	$\alpha_2(\bar{f}\bar{d}J)$	$\beta_1(\bar{f}\bar{d}J)$	$\beta_3(\bar{f}\bar{d}J)$
$\bar{f}_{1/2}^1; 5/2; 5/2 \bar{d}_{1/2}^1; 3/2; 3/2 J=4$	0.071428571428571	-0.3	0.016326530612245
$\bar{f}_{3/2}^1; 4; 4 \bar{d}_{1/2}^1; 3/2; 3/2 J=11/2$	-0.0228571428527428	-0.18	0.007755102040816
$\bar{f}_{5/2}^1; 9/2; 9/2 \bar{d}_{1/2}^1; 3/2; 3/2 J=6$	-	-0.1	-
$\bar{f}_{7/2}^1; 4; 4 \bar{d}_{1/2}^1; 3/2; 3/2 J=11/2$	0.011428571428571	-0.05	-0.005102040816326
$\bar{f}_{9/2}^1; 5/2; 5/2 \bar{d}_{1/2}^1; 3/2; 3/2 J=4$	0.0114285714285714	-0.02	0.005714285714285

Table III(b). Vector coupling coefficients for the $f-\bar{d}$ interaction in some of the high spin, high total angular momentum states of $f^n\bar{d}^1$ configuration.

	$\alpha_2(f\bar{d}J)$	$\beta_3(f\bar{d}J)$	$\beta_5(f\bar{d}J)$
$f_{1/2}^1; 7/2; 7/2 \bar{d}_{1/2}^1; 3/2; 3/2 J=5$	0.0666666666666666	-0.0039682539682539	0.03696051423324
$f_{3/2}^1; 6; 6 \bar{d}_{1/2}^1; 3/2; 3/2 J=15/2$	-0.038095238095238	-0.0073696145124716	0.03558310376492
$f_{5/2}^1; 15/2; 15/2 \bar{d}_{1/2}^1; 3/2; 3/2 J=9$	-0.0158730158730158	-0.0085034013605442	0.033287419651056
$f_{7/2}^1; 8; 8 \bar{d}_{1/2}^1; 3/2; 3/2 J=19/2$	-	-0.0079365079365079	0.029843893480257
$f_{9/2}^1; 15/2; 15/2 \bar{d}_{1/2}^1; 3/2; 3/2 J=9$	0.0095238095238095	-0.006235827664399	0.0250229568411386
$f_{11/2}^1; 6; 6 \bar{d}_{1/2}^1; 3/2; 3/2 J=15/2$	0.0095238095238095	-0.0017006802721088	0.010330578512396
$f_{13/2}^1; 7/2; 7/2 5\bar{d}_{1/2}^1; 3/2; 3/2 J=5$	0.0126984126984126	-0.0039682539682539	0.0185950413223140

cients have been further combined with $\bar{b}_v^c(\kappa_1\kappa_2J)$ to obtain the vector coupling coefficients. For the LS-coupling scheme Malli and Olive³¹ have shown that the vector coupling coefficients can be generated from Slater coefficients. We use similar relation in the relativistic case, viz,

$$\left. \begin{aligned} \alpha^v(\kappa\kappa'J) &= -\bar{a}_v^0(\kappa\kappa'J)/N_A N_{A'}, v \neq 0 \\ \beta^v(\kappa\kappa'J) &= \bar{b}_v^c(\kappa\kappa'J) + \bar{b}_v^0(\kappa\kappa'J)/N_A N_{A'} \end{aligned} \right\}, \kappa \neq \kappa' \quad (126)$$

$$\beta^v(\kappa\kappa J) = \bar{b}_v^c(\kappa\kappa J) + 2\bar{b}_v^0(\kappa\kappa J)/N_A^2 \quad v \neq 0, \kappa = \kappa', \quad (127a)$$

$$\beta^v(\kappa\kappa J) = \bar{b}_v^c(\kappa\kappa J) - 1/N_A \quad v = 0, \kappa = \kappa'. \quad (127b)$$

Table IV. Fully relativistic Dirac-Hartree-Fock total energies (in a.u.).

Z	Atom	Atomic Weight	(a) State	(b) Configuration	(c) $-\epsilon_{\text{DHF}}$	(d) $-\epsilon_{\text{DHF}}$
2	He	4.0026	$1s^2$	$1s^2$	2.86181328	2.86181335
3	Li	6.939	$2s_{1/2}^1$	(He) $2s^1$	7.433532996	7.43353322
4	Be	9.0122	$2s^2$	(He) $2s^2$	14.5758915	14.5758919
5	B	10.811	$2p_{1/2}^1$	(He) $2s^2 2p^1$	24.5366160	24.5366169
6	C	12.01115	$2p^2$	(He) $2s^2 2p^2$	37.65741796	37.6574196
7	N	14.0067	$2p_{3/2}^1$	(He) $2s^2 2p^2 2p^1$	54.3169598	54.3169626
8	O	15.9994	$2p_{2,2}^2$	(He) $2s^2 2p^2 2p^2$	74.8393203	74.8393234
9	F	18.9984	$2p_{3/2}^3$	(He) $2s^2 2p^2 2p^3$	99.5022976	99.5023027
10	Ne	20.183	$2p^4$	(He) $2s^2 2p^2 2p^4$	128.691927	128.691938
11	Na	22.9898	$3s_{1/2}^1$	(Ne) $3s^1$	162.078089	162.078100
12	Mg	24.312	$3s^2$	(Ne) $3s^2$	199.935070	199.935083
13	Al	26.9815	$3p_{1/2}^1$	(Ne) $3s^2 3p^1$	242.331126	242.331141
14	Si	28.086	$3p^2$	(Ne) $3s^2 3p^2$	289.449851	289.449869
15	P	30.9738	$3p_{3/2}^1$	(Ne) $3s^2 3p^2 3p^1$	341.488940	341.488962
16	S	32.064	$3p_{2,2}^2$	(Ne) $3s^2 3p^2 3p^2$	398.608727	398.608749
17	CL	35.453	$3p_{3/2}^3$	(Ne) $3s^2 3p^2 3p^3$	460.939846	460.939870
18	Ar	39.948	$3p^4$	(Ne) $3s^2 3p^2 3p^4$	528.683800	528.683840
19	K	39.102	$4s_{1/2}^1$	(Ar) $4s^1$	601.526017	601.526048
20	Ca	40.08	$4s^2$	(Ar) $4s^2$	679.710239	679.710276
21	Sc	44.956	$3d_{3/2}^1$	(Ar) $3d^1 4s^2$	763.379306	763.379350
22	Ti	47.90	$3d_{2,2}^2$	(Ar) $3d^2 4s^2$	852.841025	852.841097
23	V	50.942	$3d_{3/2}^3$	(Ar) $3d^3 4s^2$	948.206618	948.206681
24	Cr	51.996	$3d^4$	(Ar) $3d^4 4s^2$	1049.67637	1049.67644

(Continued)

Table IV (cont.). Fully relativistic Dirac-Hartree-Fock total energies (in a.u.).

Z	Atom	Atomic Weight	(a) State	(b) Configuration	(c) $-\epsilon_{\text{DHF}}$	(d) $-\epsilon_{\text{DHF}}$
25	Mn	54.938	$3d_{1;5/2}^1 5s_{1/2}^2$	(Ar) $3d^4 3d^1 4s^2$	1157.35190	1157.35199
26	Fe	55.847	$3d_{2;4}^2 4s^2$	(Ar) $3d^4 3d^2 4s^2$	1271.44029	1271.44038
27	Co	58.9332	$3d_{3;9/2}^3 4s^2$	(Ar) $3d^4 3d^3 4s^2$	1392.06875	1392.06884
28	Ni	58.71	$3d_{2;4}^4 4s^2$	(Ar) $3d^4 3d^4 4s^2$	1519.34397	1519.34409
29	Cu	63.54	$4s_{1;1/2}^1 3d_{1/2}^1$	(Ar) $3d^4 3d^6 4s^1$	1653.46159	1653.46168
30	Zn	65.37	$4s^2$	(Ar) $3d^4 3d^6 4s^2$	1794.61331	1794.61340
31	Ga	69.72	$4p_{1;1/2}^1 3d_{1/2}^1$	(Ar) $3d^4 3d^6 4s^2 4p^1$	1942.56665	1942.56674
32	Ge	72.59	$4p^2$	(Ar) $3d^4 3d^6 4s^2 4p^2$	2097.46666	2097.46675
33	As	74.9216	$4p_{1;3/2}^1 3d_{1/2}^1$	(Ar) $3d^4 3d^6 4s^2 4p^2 4p^1$	2259.44457	2259.44468
34	Se	78.96	$4p_{2;2}^2 3d_{1/2}^1$	(Ar) $3d^4 3d^6 4s^2 4p^2 4p^2$	2428.60582	2428.60594
35	Br	79.909	$4p_{1;3/2}^3 3d_{1/2}^1$	(Ar) $3d^4 3d^6 4s^2 4p^2 4p^3$	2605.02986	2605.03002
36	Kr	83.80	$4p^4$	(Ar) $3d^4 3d^6 4s^2 4p^2 4p^4$	2788.86149	2788.86168
37	Rb	85.47	$5s_{1;1/2}^1 4p_{1/2}^1$	(Kr) $5s^1$	2979.80592	2979.80718
38	Sr	87.62	$5s^2$	(Kr) $5s^2$	3178.08115	3178.08133
39	Y	88.905	$4d_{1;3/2}^1 5s_{1/2}^1$	(Kr) $4d^1 5s^2$	3383.76421	3383.76461
40	Zr	91.22	$4d_{2;2}^2 5s_{1/2}^1$	(Kr) $4d^2 5s^2$	3597.10295	3597.10314
41	Nb	92.906	$4d_{3;3/2}^3 5s_{1/2}^1$	(Kr) $4d^3 5s^2$	3818.18956	3818.18977
42	Mo	95.94	$4d^4 5s^2$	(Kr) $4d^4 5s^2$	4047.17894	4047.17917
43	Tc	99.0	$4d_{2;4}^2 5s_{1;1/2}^1 4p_{1/2}^1$	(Kr) $4d^4 4d^2 5s^1$	4284.19183	4284.19211
44	Ru	101.07	$4d_{3;9/2}^3 5s_{1;1/2}^1 4p_{1/2}^1$	(Kr) $4d^4 4d^3 5s^1$	4529.33236	4529.33269
45	Rh	102.95	$4d_{2;4}^4 5s_{1;1/2}^1 4p_{1/2}^1$	(Kr) $4d^4 4d^4 5s^1$	4782.68776	4782.68805
46	Pd	106.4	$4d_{1;5/2}^5 5s_{1;1/2}^1 4p_{1/2}^1$	(Kr) $4d^4 4d^5 5s^1$	5044.40597	5044.40632

(Continued)

Table IV (cont.). Fully relativistic Dirac-Hartree-Fock total energies (in a.u.).

Z	Atom	Atomic Weight	(a) State	(b) Configuration	(c) $-\epsilon_{\text{DHF}}$	(d) $-\epsilon_{\text{DHF}}$
47	Ag	107.87	$5s_{1/2}^1$	(Kr) $4d^4 4d^6 5s^1$	5314.63638	5314.63674
48	Cd	112.40	$5s^2$	(Kr) $4d^4 4d^6 5s^2$	5593.32242	5593.32286
49	In	114.82	$5p_{1/2}^1$	(Kr) $4d^4 4d^6 5s^2 5p^1$	5880.44109	5880.44152
50	Sn	118.69	$5p^2$	(Kr) $(4d^4) 4d^6 5s^2 5p^2$	6176.14055	6176.14105
51	56	121.75	$5p_{1/2}^1$	(Kr) $(4d^4) 4d^6 5s^2 5p^2 5p^1$	6480.53566	6480.53622
52	Te	127.60	$5p_{2/2}^2$	(Kr) $(4d^4) 4d^6 5s^2 5p^2 5p^2$	6793.72960	6793.73021
53	I	126.9044	$5p_{1/2}^3$	(Kr) $4d^4 4d^6 5s^2 5p^2 5p^3$	7115.80947	7115.81005
54	Xe	131.30	$5p^4$	(Kr) $4d^4 4d^6 5s^2 5p^2 5p^4$	7446.89956	7446.90018
55	Cs	132.905	$6s_{1/2}^1$	(Xe) $6s^1$	7786.77523	7786.77603
56	Ba	137.34	$6s^2$	(Xe) $6s^2$	8135.64919	8135.65006
57	La	138.91	$5d_{1/2}^1$	(Xe) $5d^1 6s^2$	8493.65223	8493.65318
58	Ce	140.12	$4f_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1$	(Xe) $4f^1 5d^1 6s^2$	8861.09775	8861.09872
59	Pr	140.907	$4f_{2/2}^2 5d_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1$	(Xe) $4f^2 5d^1 6s^2$	9238.27995	9238.28055
60	Nd	144.24	$4f_{3/2}^3 5d_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1$	(Xe) $4f^3 5d^1 6s^2$	9625.30609	9625.30702
61	Pm	145.0	$4f_{2/2}^4 5d_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1$	(Xe) $4f^4 5d^1 6s^2$	10122.2764	10022.2774
62	Sm	150.35	$4f_{1/2}^5 5d_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1$	(Xe) $4f^5 5d^1 6s^2$	10429.3605	10429.3616
63	Eu	151.96	$5d_{1/2}^1$	(Xe) $4f^6 5d^1 6s^2$	10846.7569	10846.7582
64	Gd	157.25	$4f_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1$	(Xe) $4f^6 4f^1 5d^1 6s^2$	11274.4393	11274.4405
65	Tb	158.924	$4f_{2/2}^2 5d_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1$	(Xe) $4f^6 4f^2 5d^1 6s^2$	11712.7263	11712.7275
66	Dy	162.50	$4f_{3/2}^3 5d_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1$	(Xe) $4f^6 4f^3 5d^1 6s^2$	12161.7420	12161.7431
67	Ho	164.930	$4f_{4/2}^4 5d_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1$	(Xe) $4f^6 4f^4 5d^1 6s^2$	12621.6044	12621.6056
68	Er	167.26	$4f_{3/2}^5 5d_{1/2}^1 5d_{1/2}^1 5d_{1/2}^1$	(Xe) $4f^6 4f^5 5d^1 6s^2$	13092.4173	13092.4186

(Continued)

Table IV (cont.). Fully relativistic Dirac-Hartree-Fock total energies (in a.u.).

Z	Atom	Atomic Weight	(a) State	(b) Configuration	(c) $- \epsilon_{\text{DHF}}$	(d) $- \epsilon_{\text{DHF}}$
69	Tm	168.934	$4f_{2,6}^6 5d_{1,3/2}^1 15/2$	(Xe) $4f^6 4f^6 5d^1 6s^2$	13574.3815	13574.4383
70	Yb	173.04	$4f_{1,7/2}^7 7/2; 5d_{1,3/2}^1 5$	(Xe) $4f^6 4f^7 5d^1 6s^2$	14067.6852	14067.6889
71	Lu	174.97	$5d_{1,3/2}^1 3/2$	(Xe) $4f^6 4f^8 5d^1 6s^2$	14572.5330	14572.5346
72	Hf	178.49	$5d_{2,2}^2 2$	(Xe) $4f^6 4f^8 5d^2 6s^2$	15088.8152	15088.8166
73	Ta	180.948	$5d_{1,3/2}^3 3/2$	(Xe) $4f^6 4f^8 5d^3 6s^2$	15616.6609	15616.6625
74	W	183.85	$5d^4$	(Xe) $4f^6 4f^8 5d^4 6s^2$	16156.2463	16156.2484
75	Re	186.2	$5d_{1,5/2}^1 5/2$	(Xe) $4f^6 4f^8 5d^4 5d^1 6s^2$	16707.6792	16707.6814
76	Os	190.2	$5d_{2,4}^2 4$	(Xe) $4f^6 4f^8 5d^4 5d^2 6s^2$	17271.1551	17271.1573
77	Ir	192.2	$5d_{3,9/2}^3 9/2$	(Xe) $4f^6 4f^8 5d^4 5d^3 6s^2$	17846.8566	17846.8590
78	Pt	195.09	$5d_{1,5/2}^5 5/2 6s_{1,1/2}^1 1/2 3$	(Xe) $4f^6 4f^8 5d^4 5d^5 6s^1$	18434.9109	18434.9133
79	Au	196.967	$6s_{1,1/2}^1 1/2$	(Xe) $4f^6 4f^8 5d^4 5d^6 6s^1$	19035.5586	19035.5612
80	Hg	200.59	$6s^2$	(Xe) $4f^6 4f^8 5d^4 5d^6 6s^2$	19648.8665	19648.8692
81	Tl	204.37	$6p_{1,1/2}^1 1/2$	(Xe) $4f^6 4f^8 5d^4 5d^6 6s^2 6p^1$	20274.8261	20274.8278
82	Pb	207.19	$6p^2$	(Xe) $4f^6 4f^8 5d^4 5d^6 6s^2 6p^2$	20913.7151	20913.7184
83	Bi	208.98	$6p_{1,3/2}^1 3/2$	(Xe) $4f^6 4f^8 5d^4 5d^6 6s^2 6p^2 6p^1$	21565.6930	21565.6960
84	Po	209.0	$6p_{2,2}^2 2$	(Xe) $4f^6 4f^8 5d^4 5d^6 6s^2 6p^2 6p^2$	22230.9946	22230.9978
85	At	210.0	$6p_{1,3/2}^3 3/2$	(Xe) $4f^6 4f^8 5d^4 5d^6 6s^2 6p^2 6p^3$	22909.7492	22909.7526
86	Rn	222.0	$6p^4$	(Xe) $4f^6 4f^8 5d^4 5d^6 6s^2 6p^2 6p^4$	23601.9706	23601.9742

(a) For open shell cases, we adopt a notation similar to that of Grant et al.⁹ For a single open shell case we denote the state by $n/q_j x$, where n is the principal quantum number, l labels the orbital quantum number, q denotes the occupation number, v denotes the seniority number, j denotes the resultant quantum number of the open shell, and x is the total quantum number of the state. Where there are two open shells, the state is defined by its total angular momentum number J . The closed shell structures are denoted by the last shell and its occupation number.

(b) The configurations are defined with respect to the nearest closed shell structure.

(c) Numerical DHF value⁹ obtained with the average level (AL) option (Breit interaction not included).

(d) This work using nonrelativistic optimized geometric gaussian basis sets (see Chapter 3, Table VIII).

We have used the above relations with the Slater coefficients from Grant's program.⁸ Some of the vector coupling coefficients for the case $\kappa = \kappa'$ are given in Table II and for the case $\kappa \neq \kappa'$ ($\bar{d} - \bar{f}$ interaction and $\bar{d} - f$ interactions) are given in Table III(a) and III(b).

Table V. Radial Expectation Values (in a.u.) for Ar. Numerical DF values⁹ obtained with the average level (AL) option are given in the bracket.

Orbital	$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
1s	17.70262598 (17.702650)	0.08562456 (0.08562454)	0.009863280 (0.009863278)
2s	3.58895526 (3.5889538)	0.40995835 (0.40995755)	0.19911321 (0.19911223)
3s	0.96793412 (0.96791243)	1.41613721 (1.4161612)	2.33104982 (2.3311181)
2 \bar{p}	3.48009481 (3.4801113)	0.37305593 (0.37305400)	0.17243040 (0.17242876)
3 \bar{p}	0.81876081 (0.81882635)	1.65570617 (1.6556346)	3.28238157 (3.2821931)
2p	3.45150000 (3.4514977)	0.37533778 (0.37533790)	0.17440355 (0.17440356)
3p	0.81333962 (0.81333304)	1.66538020 (1.6653913)	3.32155645 (3.3216004)

11. Numerical Results

Calculations were performed for the neutral states of all atoms up to $Z=86$ using kinetically balanced GTOs with integer powers of r . The results are presented in Tables IV through VIII. All values are given in atomic units. The Breit interaction is not included in our calculations.

For all atoms up to $Z=86$ it was possible to find a basis set which gave energies within a few milli-Hartrees, or less, of the numerical values. The initial basis set was taken as the one optimized to the closest nonrelativistic configuration. The value of the total DHF energy was always found to approach the true value from above.

The relativistic virial theorem³²

$$\langle T \rangle = - \langle V \rangle \quad (128)$$

Table VI. Convergence Pattern for the Ground State of Xenon.

$N_{s_{1/2}}^a$	$N_{p_{1/2}}^b$	$-E_{DHF}^c$	$-E_{DHF}^d$
28	26	7446.852770	7447.066014
31	26	7446.897507	7447.142336
33	26	7446.897690	7447.151981
33	28	7446.899177	7447.153555
33	30	7446.899510	7447.153975
34	30	7446.899511	7447.155759
35	30	7446.899512	7447.156711
35	31	7446.899548	7447.156787
35	32	7446.899556	7447.156827
35	33	7446.899557	7447.156848
E_{DHF} (by Grant et al. ⁹)		(7446.90018)	(7447.15856)

(a) $N_{s_{1/2}}$ is the number of geometric basis functions used for the large component of $s_{1/2}$ symmetry.

(b) $N_{p_{1/2}}$ is the number of geometric basis functions used for the large component of $p_{1/2}$ symmetry.

(c) This work with finite nucleus size approximation.

(d) This work with point nucleus calculation.

(e) In this calculation we have kept the following as constant: $N_{p_{3/2}} = 26$; $N_{d_{3/2}} = 20$; $N_{d_{5/2}} = 20$. The exponents were generated by using $\alpha_0 = 0.0143013$ and $\beta = 1.9778445$.

was tested in all point nucleus cases and was satisfied at least to one part in 10^5 .

In Table IV we present the total atomic DHF energies (in a.u.) for He-Rn and compare them with the numerical DHF energies computed by using the program of Grant et al.¹² The results indicate that even with Gaussian basis sets, one can produce energies and orbital eigenvalues close to the numerical limits. Some of the important points about our results are:

1. It was possible to obtain the DHF total energy which is accurate to within a few milli-Hartrees or less for all cases up to $Z=86$.

Table VII. Orbital and Total DHF Energies of Xe Ground State (in a.u.).

Orbital	$-\varepsilon^a$	$-\varepsilon^b$
1s	1277.2588019	1277.2586115
2s	202.4650992	202.4650254
3s	43.0104331	43.0104285
4s	8.4298806	8.4298898
5s	1.0101234	1.0101354
2 \bar{p}	189.6795387	189.6794723
3 \bar{p}	37.6598865	37.6598869
4 \bar{p}	6.4524449	6.4524608
5 \bar{p}	0.4925637	0.4925662
2p	177.7046897	177.7045060
3p	35.3253609	35.3252341
4p	5.9828279	5.9827651
5p	0.4398111	0.4397988
3 \bar{d}	26.0234451	26.0233447
4 \bar{d}	2.7113564	2.7113095
3d	25.5372327	25.5370856
4d	2.6338201	2.6337404
DHF Total	7446.900181	7446.899558

(a) Same as in footnote (c) of Table IV (the DHF energy given by Desclaux is -7446.9006 a.u.).

(b) This work.

Table VIII. Orbital and Total DHF Energies of Ground State of Radon (in a.u.).

Orbital	$- \epsilon^a$	$- \epsilon^b$
1s	3641.152594	3641.151683
2s	668.803231	668.803240
3s	166.831068	166.831296
4s	41.312994	41.313174
5s	8.408858	8.408980
6s	1.071426	1.074159
2 \bar{p}	642.327556	642.327511
3 \bar{p}	154.894066	154.894288
4 \bar{p}	36.019227	36.019414
5 \bar{p}	6.408880	6.408966
6 \bar{p}	0.540362	0.540372
2p	541.103035	541.102712
3p	131.73119	131.731021
4p	30.120838	30.120712
5p	5.175965	5.175900
6p	0.384038	0.384019
3 \bar{d}	112.567303	112.567168
4 \bar{d}	21.548307	21.548232
5 \bar{d}	2.189770	2.189705
3d	107.759555	107.759278
4d	20.439131	20.438872
5d	2.016730	2.016597
4 \bar{f}	9.194232	9.194121
4f	8.928566	8.928415
DHF Total	23601.97421	23601.97060

(a) Same as in footnote (c) of Table IV (the DHF energy given by Desclaux is -23601.978 a.u.).

(b) This work.

2. We have used nonrelativistic optimized basis sets as inputs for the relativistic calculation and the agreement with numerical results⁹ is excellent (one part in 10^8).
3. We also tried a universal basis set for atoms $Z=72$ to $Z=86$ and obtained results within a few milli-Hartrees of the numerical DF limit. However, the results improved consistently when we used the basis sets with each one independently optimized to the closest nonrelativistic ground state.
4. We calculated $\langle r^n \rangle$, $n = -1, 1, 2$ with our atomic orbitals and compared them with the expectation values obtained by numerical methods. One example of these expectation values is given for Argon in Table V. There is excellent agreement between the values calculated using the numerical DF wavefunctions and our basis set wavefunctions.

In Table VI we present an example of our improved basis set for Xenon (this is different from the one given in our earlier work²⁰) and show the convergence pattern for Xenon in the finite nucleus case. Indeed, our results for Xenon confirm the conclusion drawn by Ishikawa et al.¹¹ from their results for H-like Mercury ion that the convergence is much faster in the finite nucleus case than the point nucleus calculation. From Table VI we see that by the time we have reached $N_{s_{1/2}} = 33$ (number of basis functions for the symmetry $s_{1/2}$) and $N_{p_{1/2}} = 28$ (number of basis functions for the $p_{1/2}$ symmetry), the DHF energy has saturated and we have the limiting DHF total energy of -7446.8996 a.u. compared to the numerical value of -7446.9002 a.u. If we go beyond $N_{s_{1/2}} = 33$ and $N_{p_{1/2}} = 28$ the result for the DHF energy does not change to any appreciable degree. In contrast to this, even with $N_{s_{1/2}} = 35$ and $N_{p_{1/2}} = 28$, we cannot get close to the numerical limit of the DHF total energy⁹ for Xenon in the point nucleus approximation, which is -7447.15856 a.u. We think that the kinetic balance condition given by (5), along with proper boundary conditions imposed upon the basis set, contribute to the accelerated convergence and to the variational stability, as has been demonstrated by earlier workers.^{4-13,16} This type of convergence pattern seems to be a simple generalization of the result of Ishikawa et al.¹¹ to the many-electron case.

In Table VII we have given the DHF energy and the orbital energies for Radon (the heaviest atom reported by us) with an improved basis set. It is seen that the orbital energies of the inner shell as well as outer shells can be calculated to an accuracy comparable with the numerical method; the maximum discrepancy is ~ 0.0001 a.u. which occurs for $1s_{1/2}$ orbital. We also predict the energy difference between the $4\bar{f}$ and $4f$ orbitals to be within 0.0001 a.u. of numerical DF method. In passing, we should mention that convergence pattern for all heavy atoms is similar to that presented in Table VI for Xenon in the finite nucleus approximation, although we do not present the results explicitly.

To summarize our results, we state that the prescription of kinetic balance works extremely well for GTOs, particularly for a nucleus with finite size. Moreover, the

accuracy of our result up to Radon is comparable to that of numerical methods and "variational collapse" does not occur even when exponents as large as several hundred million are used. With a finite nucleus size convergence is faster to the numerical DHF value from above with fewer number of exponents, which is consistent with the results of Ishikawa et al.¹¹

12. Conclusions

In conclusion, we have demonstrated that the use of kinetically balanced geometric Gaussian basis sets for Dirac-Fock SCF calculations in many-electron atoms (He – Rn) can yield results comparable in accuracy to that of numerical DF methods, particularly in the finite nucleus model. Our results show that "variational collapse" does not occur if we use a matched basis set satisfying kinetic balance and proper boundary conditions for bound state orbitals – a point which has been emphasized by Grant et al. previously.⁵⁻⁸ Also, our calculations support the viewpoint that finite-size nucleus approximation facilitates the use of GTOs in the DF calculation for heavy atoms: the DHF total energy converges more rapidly to the true value from above and, therefore, one avoids the necessity for a very large basis set. The development of these compact Gaussian basis sets within the DF approach has potential applications in the study of molecules containing heavy elements.

Acknowledgments

The authors would like to express their sincere thanks to Dr. S. Chakravorty for providing us with his optimized nonrelativistic geometric Gaussian basis sets. Thanks are also due to Prof. G. Malli and Dr. Daniel Frye for their helpful comments and useful suggestions during the course of the preparation of this article.

References

1. For a review, see W. Kutzelnigg, *Int. J. Quantum Chem.*, **25**, 107 (1984).
2. Y. Ishikawa, R.C. Binning and K.M. Sando, *Chem. Phys. Letters*, **101**, 111 (1983).
3. K.G. Dyall, I.P. Grant and S. Wilson, *J. Phys.*, **B17**, 493 (1984); *ibid* **L45**; *ibid* **B17**, 1201.
4. R.E. Stanton and S. Havriliak, *J. Chem. Phys.*, **81**, 1910 (1984).
5. I.P. Grant, *J. Phys.*, **B19**, 3187 (1986).
6. I.P. Grant and H.M. Quiney, *Adv. in Atom. and Mol. Phys.*, **23**, 37 (1988).
7. H.M. Quiney, I.P. Grant and S. Wilson, *J. Phys.*, **B20**, 1413 (1987).
8. H.M. Quiney, I.P. Grant and S. Wilson, "On the Relativistic Many-Body Perturbation Theory of Atomic and Molecular Electronic Structure," to be published in *Lecture Notes in Chemistry*, U. Kaldor, Ed., Springer Verlag, Berlin.

9. I.P. Grant, B.J. McKenzie, P.H. Norrington, D.F. Mayers and N.C. Pyper, *Comput. Phys. Communication*, **21**, 207 (1980).
10. J.P. Desclaux, *Comput. Phys. Communication*, **9**, 31 (1975).
11. Y. Ishikawa, R. Barety and R.C. Binning, Jr., *Chem. Phys. Letters*, **121**, 130 (1985).
12. P.J.C. Aerts and W.C. Nieuwpoort, *Chem. Phys. Letters*, **113**, 165 (1985).
13. O. Visser, P.J.C. Aerts, D. Hegarty and W.C. Nieuwpoort, *Chem. Phys. Letters*, **134**, 34 (1987).
14. G. Malli, *Chem. Phys. Letters*, **68**, 529 (1979).
15. O. Matsuoka, M. Klobukowski and S. Huzinaga, *Chem. Phys. Letters*, **113**, 395 (1985).
16. O. Matsuoka and S. Huzinaga, *Chem. Phys. Letters*, **140**, 567 (1987).
17. S. Okada and O. Matsuoka, "Relativistic well-tempered Gaussian basis sets for Helium through Mercury," *Chem. Phys. Letters* (in press).
18. O. Matsuoka and S. Okada, "Dirac-Fock-Roothaan Calculation on the sixth row elements Tl-Rn," *Chem. Phys. Letters* (in press).
19. J.P. Desclaux, *Atomic and Nuclear Data Tables*, **12**, 311 (1973).
20. A.K. Mohanty and E. Clementi, *Chem. Phys. Letters*, **157**, 348 (1989).
21. E. Clementi and G. Corongiu, *Chem. Phys. Letters*, **90**, 359 (1982).
22. I.P. Grant and N.C. Pyper, *J. Phys. B.*, **9**, 761 (1976); I.P. Grant and B.J. McKenzie, *J. Phys. B. Atom. Molec. Phys.*, **13**, 2671 (1980).
23. Y.K. Kim, *Phys. Rev.*, **154**, 17 (1967); **159**, 190 (1967).
24. T. Kagawa, *Phys. Rev. A.*, **12**, 2245 (1975); **22**, 2340 (1980).
25. B. Roos, C. Salez, A. Veillard and E. Clementi, *Tech. Rep. RJ518*, IBM Research (August 12, 1968).
26. H.A. Bethe and E.S. Salpeter, *Quantum Mechanics of one- and two-electron atoms*, Springer Verlag, 70 (1957).
27. C.C.J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); **32**, 179 (1960).
28. J.M. Leclercq, *Phys. Rev. A.*, **1**, 1358 (1970).
29. S. DeShalit and I. Talmi, *Nuclear Shell Theory*, Academic Press (1961).
30. I. Grant, *Relativistic effects in atoms and molecules*, S. Wilson, Ed., Plenum Press (1988).
31. G.L. Malli and J.P. Olive, "Vector Coupling Coefficients for Atomic Self-Consistent Field Calculations," *Laboratory of Molecular Structure, Technical Report 1962-3, Part 2*, University of Chicago, 258 (1963).
32. For a discussion of relativistic virial theorem see Ref. 23; Also, P.J.C. Aerts, *Towards Relativistic Quantum Chemistry*, Ph.D. Thesis, University of Groningen (1986). If we scale the coordinates of N -electron wavefunction $\Phi(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N)$ by a parameter λ , then

$$\Phi(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) \rightarrow \Phi(\lambda\vec{r}_1, \lambda\vec{r}_2, \dots \lambda\vec{r}_N),$$

and

$$\langle H \rangle = \langle T \rangle + \langle V \rangle + \langle M \rangle \rightarrow \lambda(T + V) + M.$$

This is because $T = c\vec{\alpha} \cdot \vec{p}$ contains the first derivative with respect to the position coordinate r , operator V contains only terms with inverse power r , and the operator $M = \beta'c^2$ does not depend upon r . For any correct eigenfunction the infinitesimal variation of H with respect to scale parameter λ gives the relativistic virial theorem

$$\frac{\partial \langle H \rangle}{\partial \lambda} = (\langle T \rangle + \langle V \rangle) = 0$$

$$\text{or } \langle T \rangle = -\langle V \rangle \quad \text{or } \langle E \rangle = \langle M \rangle$$

In order to see the correspondence between the relativistic and nonrelativistic virial theorem, we calculate $\langle T \rangle$ and $\langle M \rangle$ by using the free particle spinors in the momentum representation, viz,

$$\psi_r = \sqrt{\frac{mc^2}{E\tau}} u^r(p) \exp(i\vec{p} \cdot \vec{x} - \frac{iEt}{\hbar})$$

with

$$u^r(p) = \sqrt{\frac{E + mc^2}{2mc}} \begin{pmatrix} \phi^\sigma \\ \frac{(\vec{\sigma} \cdot \vec{p})c}{E + mc^2} \phi^\sigma \end{pmatrix}.$$

Here ϕ^σ are the two-component Pauli spinors, p is the momentum, and τ is the volume over which the integration is performed.

And then taking the limit $c \rightarrow \infty$ one obtains the smooth nonrelativistic limit

$$\langle T \rangle = 2 \langle T_{nr} \rangle$$

$$\text{or } \langle M \rangle = -\langle T_{nr} \rangle = \langle E \rangle.$$