Relativistic calculations of nuclear motional effects in many-electron atoms

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We assume that the nucleus is a relativistic point mass with no internal degrees of freedom and derive an expression for its motional contribution to the energies of atomic levels in *jj* coupling. Our formalism has been implemented in a computer program module SMS used in conjunction with the GRASP2 multiconfiguration Dirac-Fock package. Representative calculations are presented for some atoms and ions.

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I. INTRODUCTION

The relativistic theory of atoms is usually based on the Dirac-Coulomb Hamiltonian for the atomic electrons,

$$H^{\mathrm{DC}}=\sum_{i=1}^{n^{\mathrm{elec}}} H_i^{\mathrm{D}}+\sum_{i=1}^{n^{\mathrm{elec}}-1}\sum_{j=i+1}^{n^{\mathrm{elec}}} H_{ij}^{\mathrm{C}} , \tag{1.1}$$

where

$$H_i^{\mathrm{D}}=T_i^{\mathrm{D}}+V_i^{\mathrm{nuc}} \tag{1.2}$$

is the Dirac Hamiltonian for electron i in a central field with potential energy given by V^{nuc}, and

$$H_{ij}^{\mathrm{C}}=\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} \tag{1.3}$$

is the Hamiltonian for the Coulomb interaction between electrons i and j. We use the symbol e for the charge on the proton. The Dirac kinetic-energy operator T^{D} is given by

$$T^{\mathrm{D}}=c\boldsymbol{\alpha}\cdot\mathbf{p}+(\beta-1)m^{\mathrm{elec}}c^2 , \tag{1.4}$$

where c is the speed of light in the vacuum, $\boldsymbol{\alpha}$ and β are the Dirac matrices, and m^{elec} is the mass of the electron. An (approximate) atomic state function (ASF) for a level with energy E, angular momentum $J(J+1)\hbar^2$, and parity P, may be constructed from a linear combination of configuration state functions (CSF's) that share the same angular momentum and parity,

$$|EJ^PM\rangle=\sum_{\gamma}|\gamma J^PM\rangle . \tag{1.5}$$

The CSF's, in turn, are usually constructed from a set of orbitals—one-electron states with the angular symmetry appropriate to the one-electron Hamiltonian. A relativistic orbital, denoted $|n\kappa m\rangle$ is thus an eigenfunction of the total angular momentum operator $\mathbf{j}=\boldsymbol{l}+\mathbf{s}$ and the relativistic parity operator π,

$$\begin{aligned}&\mathbf{j}^2|n\kappa m\rangle=(\kappa^2-\tfrac{1}{4})|n\kappa m\rangle ,\\ &j_z|n\kappa m\rangle=m|n\kappa m\rangle ,\\ &\pi|n\kappa m\rangle=(-1)^{|\kappa|+\mathrm{sgn}(\kappa)}|n\kappa m\rangle .\end{aligned} \tag{1.6}$$

To each nonrelativistic orbital with orbital quantum number $l>0$, there correspond two relativistic orbitals with $j=l-\frac{1}{2}$ and $l+\frac{1}{2}$; for these the quantum number κ takes the values l and $-l-1$, respectively. When $l=0$, $j=\frac{1}{2}$ and $\kappa=-1$. We refer the reader to the review article of Grant [1] for the many details of relativistic atomic electronic structure theory that we have omitted; in particular, the use of Racah algebra in the reduction of matrix elements of many-body operators between CSF's to sums over matrix elements of one- and two-electron operators between orbitals.

An assumption that is implicit in the formalism summarized above is that the degrees of freedom of the nucleus make no appreciable contribution to the energies of atomic levels. There are circumstances in which this assumption is unacceptable; account must then be taken at least of nuclear translational motion. The first quantum-mechanical treatment of such effects in many-electron atoms is due to Hughes and Eckart [2], who showed that two additional terms appear in the nonrelativistic atomic Hamiltonian:

$$H^{\mathrm{NMS}}=\sum_{i=1}^{n^{\mathrm{elec}}}(\mathbf{p}^{\mathrm{elec}})^2/2m^{\mathrm{nuc}} , \tag{1.7}$$

the *normal-mass-shift* term, accounted for by using the reduced mass μ, where

$$\frac{1}{\mu}=\frac{1}{m^{\mathrm{elec}}}+\frac{1}{m^{\mathrm{nuc}}} , \tag{1.8}$$

in place of m^{elec} in the electronic Hamiltonian, and

$$H^{\mathrm{SMS}}=\sum_{i=1}^{n^{\mathrm{elec}}-1}\sum_{j=i+1}^{n^{\mathrm{nelec}}}\mathbf{p}_i^{\mathrm{elec}}\cdot\mathbf{p}_j^{\mathrm{elec}}/m^{\mathrm{nuc}} , \tag{1.9}$$

the *specific-mass-shift* or mass-polarization term. In Eqs. (1.7)–(1.9) m^{nuc} is the mass of the nucleus. Nonrelativistic estimates of the specific mass shift have been made by a number of authors [3]. Recent work [4] has focused on the role of correlation in this context.

An *ab initio* relativistic treatment of the interaction of the atomic electrons with the nucleus would be based upon quantum field theory. However, no practically useful models of the atomic nucleus have emerged from this

framework. Theoretical models of the atomic nucleus based upon the gross features of the interactions of the nucleons are, at present, too cumbersome for use in atomic calculations. Recourse must, therefore, be had to relatively simple models that accurately manifest the most important gross features of the nucleus: examples are its mass, angular momentum, spherically averaged charge distribution, exterior electric and magnetic multipole moments, and polarizability.

Our approach to a relativistic treatment of nuclear motional effects differs from earlier work [5,6] in that the kinematics of the nucleus is assumed to be that of a relativistic point mass with no internal structure. Further, we neglect retardation and assume that the interaction of the nucleus with electron i is completely specified by $V^{\rm nuc}(r_i)$, a function of the distance separating the electron and the nucleus. Clearly, corrections of higher order must be introduced to account for other aspects of the interaction of the nucleus with the electrons. We shall not study these corrections here.

In Sec. II we give a brief resume of the kinematics of relativistic point masses to derive approximate expressions for the energy due to nuclear motion. The reduction of matrix elements of operators corresponding to certain important expressions of Sec. II is discussed in Sec. III. We have implemented the methods of Sec. III in a computer program; this program is briefly described in Sec. IV. Some estimates of energy-level shifts due to our specific mass shift Hamiltonian using relativistic models of atoms are given in Sec. V. We summarize our work in Sec. VI.

II. RELATIVITY AND THE MOTION OF THE ATOMIC NUCLEUS

The momentum $\mathbf{p}$ of a particle is related to its mass m and velocity $\mathbf{v}$ by the Einstein formula

$$\mathbf{p}=m\,\mathbf{v}(1-v^2/c^2)^{-1/2}\ , \tag{2.1}$$

where

$$v=|\mathbf{v}|\ . \tag{2.2}$$

The total energy E is given by

$$E=(p^2c^2+m^2c^4)^{1/2}\ , \tag{2.3}$$

where

$$p=|\mathbf{p}|\ . \tag{2.4}$$

Clearly, when $p=0$, then $E=mc^2$, the rest energy. The kinetic energy T is the total energy less the rest energy,

$$T=E-mc^2\ . \tag{2.5}$$

Substituting Eq. (2.1) in Eq. (2.3), we obtain with a little algebra,

$$E=mc^2(1-v^2/c^2)^{-1/2}\ . \tag{2.6}$$

We expand the rightmost term in powers of v^2/c^2 using the binomial theorem,

$$E=mc^2(1+\tfrac{1}{2}v^2/c^2+\tfrac{3}{8}v^4/c^4+\tfrac{5}{16}v^6/c^6+\cdots)\ . \tag{2.7}$$

Clearly, when v^2/c^2 is sufficiently small, Eqs. (2.5) and (2.7) yield

$$T\approx\tfrac{1}{2}mv^2\ , \tag{2.8}$$

the familiar nonrelativistic expression.

In the center of momentum frame,

$$\mathbf{p}^{\rm nuc}+\sum_{i=1}^{n^{\rm elec}}\mathbf{p}_i^{\rm elec}=\mathbf{0}\ , \tag{2.9}$$

or

$$\mathbf{p}^{\rm nuc}=-\sum_{i=1}^{n^{\rm elec}}\mathbf{p}_i^{\rm elec}\ . \tag{2.10}$$

Thus

$$(\mathbf{p}^{\rm nuc})^2=\sum_{i=1}^{N}(\mathbf{p}_i^{\rm elec})^2+2\sum_{i=1}^{n^{\rm elec}-1}\sum_{j=i+1}^{n^{\rm elec}}\mathbf{p}_i^{\rm elec}\cdot\mathbf{p}_j^{\rm elec}\ . \tag{2.11}$$

From Eq. (2.5),

$$E_i^{\rm elec}=T_i^{\rm elec}+m^{\rm elec}c^2\ ; \tag{2.12}$$

squaring both sides,

$$(E_i^{\rm elec})^2=(T_i^{\rm elec})^2+2m^{\rm elec}c^2T_i^{\rm elec}+(m^{\rm elec})^2c^4\ . \tag{2.13}$$

From Eq. (2.3),

$$(\mathbf{p}_i^{\rm elec})^2c^2=(E_i^{\rm elec})^2-(m^{\rm elec})^2c^4\ . \tag{2.14}$$

We substitute the right-hand side of Eq. (21.3) for $(E_i^{\rm elec})^2$ in Eq. (2.14) to obtain

$$(\mathbf{p}_i^{\rm elec})^2c^2=(T_i^{\rm elec})^2+2m^{\rm elec}c^2T_i^{\rm elec}\ . \tag{2.15}$$

We divide both sides of this formula by c^2 and use this result in place of the first term on the right-hand side of Eq. (2.11),

$$(\mathbf{p}^{\rm nuc})^2=\frac{1}{c^2}\sum_{i=1}^{n^{\rm elec}}[(T_i^{\rm elec})^2+2m^{\rm elec}c^2T_i^{\rm elec}]+2\sum_{i=1}^{n^{\rm elec}-1}\sum_{j=i+1}^{n^{\rm elec}}\mathbf{p}_i^{\rm elec}\cdot\mathbf{p}_j^{\rm elec}\ . \tag{2.16}$$

The motional energy of the nucleus,

$$T^{\rm nuc}=[(\mathbf{p}^{\rm nuc})^2c^2+(m^{\rm nuc})^2c^4]^{1/2}-m^{\rm nuc}c^2\ , \tag{2.17}$$

may thus be obtained from the motional energy and momenta of the electrons.

We shall now examine two important nonrelativistic limits of these expressions. In typical atomic problems,

$$(\mathbf{p}^{\rm nuc})^2c^2\ll(m^{\rm nuc})^2c^4\ . \tag{2.18}$$

We write Eq. (2.17) as

$$T^{\rm nuc}=\left[1+\frac{(\mathbf{p}^{\rm nuc})^2}{(m^{\rm nuc})^2c^2}\right]^{1/2}m^{\rm nuc}c^2-m^{\rm nuc}c^2\ , \tag{2.19}$$

and expand the term in the square brackets using the binomial theorem; it immediately follows that

$$T^{\rm nuc}=\frac{(\mathbf{p}^{\rm nuc})^2}{2m^{\rm nuc}}-\frac{(\mathbf{p}^{\rm nuc})^4}{8(m^{\rm nuc})^3c^2}+\cdots\ . \tag{2.20}$$

We begin by treating the nucleus as a nonrelativistic particle; its kinetic energy $T_{\rm nuc}$ is then given by the first term, or Eq. (2.8),

$$T^{\rm nuc}=\frac{(\mathbf{p}^{\rm nuc})^2}{2m^{\rm nuc}} . \tag{2.21}$$

We substitute for $(\mathbf{p}^{\rm nuc})^2$ from Eq. (2.16) to obtain

$$T^{\rm nuc}=\frac{1}{2m^{\rm nuc}c^2}\sum_{i=1}^{n^{\rm elec}}[(T_i^{\rm elec})^2+2m^{\rm elec}c^2T_i^{\rm elec}] +\frac{1}{m^{\rm nuc}}\sum_{i=1}^{n^{\rm elec}-1}\sum_{j=i+1}^{n^{\rm elec}}\mathbf{p}_i^{\rm elec}\cdot\mathbf{p}_j^{\rm elec} . \tag{2.22}$$

This result, derived from more fundamental principles, has appeared in the literature [6].

If the electrons are also treated as nonrelativistic particles,

$$T^{\rm elec}=\frac{(\mathbf{p}^{\rm elec})^2}{2m^{\rm elec}} , \tag{2.23}$$

and we may neglect the contribution of the first term in the square brackets in Eq. (2.22); we obtain the familiar nonrelativistic expression [2] for the nuclear motional contribution,

$$\frac{1}{2m^{\rm nuc}}\sum_{i=1}^{n^{\rm elec}}(\mathbf{p}_i^{\rm elec})^2+\frac{1}{m^{\rm nuc}}\sum_{i=1}^{n^{\rm elec}-1}\sum_{j=i+1}^{n^{\rm elec}}\mathbf{p}_i^{\rm elec}\cdot\mathbf{p}_j^{\rm elec} . \tag{2.24}$$

In the approximation represented by Eq. (2.22), the relativistic normal mass shift—the first term on the right-hand side of Eq. (2.22)—cannot be completely accounted for by using the reduced mass instead of the true electron mass in the Dirac-Coulomb Hamiltonian (1.1). The distinction between the normal and specific mass shifts can no longer be made in a meaningful manner as the higher-order terms in Eq. (2.20) are examined.

III. MATRIX ELEMENTS IN *jj* COUPLING

We write $\mathbf{p}$ in coupled-tensor-operator form,

$$\mathbf{p}=-i\left[\mathbf{C}^{(1)}\frac{\partial}{\partial r}-\frac{\sqrt{2}}{r}(\mathbf{C}^{(1)}\boldsymbol{l})^{(1)}\right] . \tag{3.1}$$

From the Wigner-Eckart theorem in the form

$$\langle\alpha J\|(\mathbf{T}^{(k_1)}\mathbf{U}^{(k_2)})^{(K)}\|\alpha'J'\rangle=(-1)^{J+K+J'}\sqrt{2K+1}\sum_{\alpha'',J''}\begin{Bmatrix}k_1 & k_2 & K\\ J' & J & J''\end{Bmatrix}\langle\alpha J\|\mathbf{T}^{(k_1)}\|\alpha''J''\rangle\langle\alpha''J''\|\mathbf{U}^{(k_2)}\|\alpha'J'\rangle , \tag{3.2}$$

with $J\to l$, $\mathbf{T}^{(k_1)}\to\mathbf{C}^{(1)}$, $\mathbf{U}^{(k_2)}\to\boldsymbol{l}$, and $J'\to l'$, we have

$$\langle\alpha l\|(\mathbf{C}^{(1)}\boldsymbol{l})^{(1)}\|\alpha'l'\rangle=(-1)^{l+1+l'}\sqrt{3}\sum_{\alpha'',l''}\begin{Bmatrix}1 & 1 & 1\\ l' & l & l''\end{Bmatrix}\langle\alpha l\|\mathbf{C}^{(1)}\|\alpha''l''\rangle\langle\alpha''l''\|\boldsymbol{l}\|\alpha'l'\rangle . \tag{3.3}$$

The second reduced matrix element on the right-hand side may be calculated from the formula

$$\langle\alpha J\|\mathbf{J}\|\alpha'J'\rangle=\delta_{\alpha\alpha'}\delta_{JJ'}\sqrt{J(J+1)(2J+1)} , \tag{3.4}$$

with $\alpha\to\alpha''$, $J\to l''$, $\mathbf{J}\to\boldsymbol{l}$, and $J'\to j'$, we have

$$\langle\alpha''l''\|\boldsymbol{l}\|\alpha'l'\rangle=\delta_{\alpha''\alpha'}\delta_{l''l'}\sqrt{l''(l''+1)(2l''+1)} . \tag{3.5}$$

Using this in Eq. (3.3), we obtain

$$\langle\alpha l\|(\mathbf{C}^{(1)}\boldsymbol{l})^{(1)}\|\alpha'l'\rangle=(-1)^{l+1+l'}\sqrt{3l'(l'+1)(2l'+1)}\times\begin{Bmatrix}1 & 1 & 1\\ l' & l & l'\end{Bmatrix}\langle\alpha l\|\mathbf{C}^{(1)}\|\alpha'l'\rangle . \tag{3.6}$$

Exploiting the symmetries of the $6j$ symbol (any interchange of columns, any interchange of pairs of row elements), we may use the formula

$$\begin{Bmatrix}a & b & c\\ 1 & c & b\end{Bmatrix}=(-1)^{a+b+c+1}\times\frac{b(b+1)+c(c+1)-a(a+1)}{2\sqrt{b(b+1)(2b+1)c(c+1)(2c+1)}} , \tag{3.7}$$

with $a=l$, $b=l'$, $c=1$ to obtain

$$\begin{Bmatrix}1 & 1 & 1\\ l' & l & l'\end{Bmatrix}=(-1)^{l+l'}\frac{l'(l'+1)+2-l(l+1)}{2\sqrt{6l'(l'+1)(2l'+1)}} . \tag{3.8}$$

Substituting this expression in Eq. (3.6) yields an important result:

$$\langle\alpha l\|(\mathbf{C}^{(1)}\boldsymbol{l})^{(1)}\|\alpha'l'\rangle=\frac{l(l+1)-2-l'(l'+1)}{2\sqrt{2}}\times\langle\alpha l\|\mathbf{C}^{(1)}\|\alpha'l'\rangle . \tag{3.9}$$

The formula

$$\langle\alpha j_1j_2;J\|\mathbf{T}^{(k_1)}\|\alpha'j_1'j_2';J'\rangle=(-1)^{j_1+j_2+k_1+J'}\sqrt{(2J+1)(2J'+1)}\times\begin{Bmatrix}j_1 & k_1 & j_1'\\ J' & j_2 & J\end{Bmatrix}\langle\alpha j_1\|\mathbf{T}^{(k_1)}\|\alpha'j_1'\rangle\delta_{j_2j_2'} , \tag{3.10}$$

with $j_1\to l$, $j_2\to\frac{1}{2}$, $J\to j$, $j_1'\to l'$, $j_2'\to\frac{1}{2}$, and $J'\to j'$, yields

$$\langle\alpha l\tfrac{1}{2};j\|\mathbf{T}^{(k_1)}\|\alpha'l'\tfrac{1}{2};j'\rangle=(-1)^{l+1/2+k_1+j'}\sqrt{(2j+1)(2j'+1)}\times\begin{Bmatrix}l & k_1 & l'\\ j' & \frac{1}{2} & j\end{Bmatrix}\langle\alpha l\|\mathbf{T}^{(k_1)}\|\alpha'l'\rangle . \tag{3.11}$$

Setting $\mathbf{T}^{(k_1)}=\mathbf{C}^{(1)}$ in Eq. (3.11),

$$\langle \alpha l\tfrac{1}{2};j\|\mathbf{C}^{(1)}\|\alpha' l'\tfrac{1}{2};j'\rangle = (-1)^{l+1/2+1+j'}\sqrt{(2j+1)(2j'+1)} \begin{Bmatrix} l & 1 & l' \\ j' & \frac{1}{2} & j \end{Bmatrix} \langle \alpha l\|\mathbf{C}^{(1)}\|\alpha' l'\rangle \ . \tag{3.12}$$

We again use Eq. (3.11), but with $\mathbf{T}^{(k_1)}=(\mathbf{C}^{(1)}\boldsymbol{l})^{(1)}$:

$$\langle \alpha l\tfrac{1}{2};j\|(\mathbf{C}^{(1)}\boldsymbol{l})^{(1)}\|\alpha' l'\tfrac{1}{2};j'\rangle = (-1)^{l+1/2+k_1+j'}\sqrt{(2j+1)(2j'+1)} \begin{Bmatrix} l & k_1 & l' \\ j' & \frac{1}{2} & j \end{Bmatrix} \langle \alpha l\|(\mathbf{C}^{(1)}\boldsymbol{l})^{(1)}\|\alpha' l'\rangle \ . \tag{3.13}$$

Combining this with Eq. (3.9), with a minor rearrangement, we have

$$\langle \alpha l\tfrac{1}{2};j\|(\mathbf{C}^{(1)}\boldsymbol{l})^{(1)}\|\alpha' l'\tfrac{1}{2};j'\rangle = (-1)^{l+1/2+k_1+j'}\sqrt{(2j+1)(2j'+1)} \begin{Bmatrix} l & k_1 & l' \\ j' & \frac{1}{2} & j \end{Bmatrix} \langle \alpha l\|\mathbf{C}^{(1)}\|\alpha' l'\rangle \times \frac{l(l+1)-2-l'(l'+1)}{2\sqrt{2}} \ . \tag{3.14}$$

Comparing Eqs. (3.12) and (3.14), we obtain our second important result:

$$\langle \alpha l\tfrac{1}{2};j\|(\mathbf{C}^{(1)}\boldsymbol{l})^{(1)}\|\alpha' l'\tfrac{1}{2};j'\rangle = \frac{l(l+1)-2-l'(l'+1)}{2\sqrt{2}} \langle \alpha l\tfrac{1}{2};j\|\mathbf{C}^{(1)}\|\alpha' l'\tfrac{1}{2};j'\rangle \ . \tag{3.15}$$

Combining this with Eq. (3.1),

$$\langle \alpha l\tfrac{1}{2};j\|\mathbf{p}\|\alpha' l'\tfrac{1}{2};j'\rangle = -i\langle \alpha l\tfrac{1}{2};j\|\mathcal{D}(l,l')\mathbf{C}^{(1)}\|\alpha' l'\tfrac{1}{2};j'\rangle \ , \tag{3.16}$$

where

$$\mathcal{D}(l,l')=\frac{\partial}{\partial r}-\frac{l(l+1)-2-l'(l'+1)}{2r} \ . \tag{3.17}$$

We may write our atomic orbitals as

$$\langle n\kappa m|\mathbf{r}\rangle=\frac{1}{r}\begin{bmatrix} P_{n\kappa}(r) & \langle \hat{\mathbf{r}}|l\tfrac{1}{2};j\rangle \\ iQ_{n\kappa}(r) & \langle \hat{\mathbf{r}}|\bar{l}\tfrac{1}{2};j\rangle \end{bmatrix} , \tag{3.18}$$

where

$$j=|\kappa|-\tfrac{1}{2} \ , \tag{3.19}$$

and

$$l=j+\tfrac{1}{2}\mathrm{sgn}(\kappa), \quad \bar{l}=j-\tfrac{1}{2}\mathrm{sgn}(\kappa) \ . \tag{3.20}$$

Thus

$$\langle n\kappa\|\mathbf{p}\|n'\kappa'\rangle=-i\langle l\tfrac{1}{2};j\|\mathbf{C}^{(1)}\|l'\tfrac{1}{2};j'\rangle[P_{n\kappa}/r|\mathcal{D}(l,l')|P_{n'\kappa'}/r]-i\langle \bar{l}\tfrac{1}{2};j\|\mathbf{C}^{(1)}\|\bar{l}'\tfrac{1}{2};j'\rangle[Q_{n\kappa}/r|\mathcal{D}(\bar{l},\bar{l}')|Q_{n'\kappa'}/r] \ . \tag{3.21}$$

We define the relativistic Vinti [7] integral,

$$\mathcal{V}(n\kappa,n'\kappa')=\int_0^\infty dr\, P_{n\kappa}(r)\left[\frac{d}{dr}-\frac{\kappa(\kappa+1)-\kappa'(\kappa'+1)}{2r}\right]P_{n'\kappa'}(r) + \int_0^\infty dr\, Q_{n\kappa}(r)\left[\frac{d}{dr}-\frac{-\kappa(-\kappa+1)+\kappa'(-\kappa'+1)}{2r}\right]Q_{n'\kappa'}(r) \ , \tag{3.22}$$

and exploit the relations

$$l(l+1)=\kappa(\kappa+1) \tag{3.23}$$

and

$$\bar{l}(\bar{l}+1)=-\kappa(-\kappa+1) \ , \tag{3.24}$$

and the fact [1] that the reduced matrix elements of $\mathbf{C}$ are independent of l to obtain

$$\langle n\kappa\|\mathbf{p}\|n'\kappa'\rangle=-i\langle j\|\mathbf{C}^{(1)}\|j'\rangle\mathcal{V}(n\kappa,n'\kappa') \ . \tag{3.25}$$

Note that the operators in the parentheses in Eq. (3.22) are different from the operators defined in (3.17): we have eliminated the factors $1/r$ in Eq. (3.21) in arriving at Eq. (3.22).

In atomic units, the operator for the Coulomb interaction between two electrons may be written as

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}=\sum_{k=0}^{\infty}(\mathbf{C}_1^{(k)}\mathbf{C}_2^{(k)})^{(0)}\frac{r_<^k}{r_>^{k+1}} \ . \tag{3.26}$$

From the form of Eq. (3.21), for any pair of electrons,

$$\mathbf{p}_1\cdot\mathbf{p}_2=-(\mathbf{C}_1^{(1)}\mathbf{C}_2^{(1)})^{(0)}\mathcal{D}_1\mathcal{D}_2 \ . \tag{3.27}$$

For a many-electron atom [1],

$$\left\langle \gamma_r J^P\left\|\sum_{i=1}^{n^{\mathrm{elec}}-1}\sum_{j=i+1}^{n^{\mathrm{elec}}}H_{ij}^C\right\|\gamma_s J^P\right\rangle = \sum_j V_{rs}^{k_j}(a_jb_jc_jd_j)R^{k_j}(a_jb_jc_jd_j) \ , \tag{3.28}$$

where $R^{k_j}(a_jb_jc_jd_j)$ is the relativistic Slater integral. We have adopted the abbreviation $a=(n_a,\kappa_a)$ in Eq. (3.28). On comparing (3.26) and (3.27), it follows that

$$\left\langle \gamma_r J^P \left\| \sum_{i=1}^{n^{\text{elec}}-1} \sum_{j=i+1}^{n^{\text{elec}}} \mathbf{p}_i \cdot \mathbf{p}_j \right\| \gamma_s J^P \right\rangle = -\sum_j \delta_{k_j 1} V_{rs}^{k_j}(a_j b_j c_j d_j) \mathcal{V}(a_j c_j) \mathcal{V}(b_j d_j) \ . \quad (3.29)$$

The nonrelativistic counterpart of this formula has appeared in the literature [8].

The kinetic-energy operator (1.4) is of rank zero and even parity. The reduced matrix elements of the square of T^{D} are obtained as a sum of the reduced matrix elements of T^{D} using Eq. (3.2):

$$\langle \alpha J \| (T^{\mathrm{D}})^2 \| \alpha' J' \rangle = (-1)^{J+J'} \sum_{\alpha'', J''} \begin{Bmatrix} 0 & 0 & 0 \\ J' & J & J'' \end{Bmatrix} \langle \alpha J \| T^{\mathrm{D}} \| \alpha'' J'' \rangle \times \langle \alpha'' J'' \| T^{\mathrm{D}} \| \alpha' J' \rangle \ . \quad (3.30)$$

Using

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & 0 \end{Bmatrix} = \frac{(-1)^{j_1+j_2+j_3}}{\sqrt{(2j_1+1)(2j_2+1)}} \delta_{j_1 l_2} \delta_{j_2 l_1} \ , \quad (3.31)$$

with $j_1 \to 0$, $j_2 \to J$, $j_3 \to J''$, $l_1 \to J'$, and $l_2 \to 0$, we have

$$\langle \alpha J \| (T^{\mathrm{D}})^2 \| \alpha' J' \rangle = \delta_{JJ'} \frac{1}{\sqrt{2J+1}} \sum_{\alpha''} \langle \alpha J \| T^{\mathrm{D}} \| \alpha'' J \rangle \times \langle \alpha'' J \| T^{\mathrm{D}} \| \alpha' J \rangle \ . \quad (3.32)$$

We have effectively presented expressions that permit the evaluation of the operator given by Eq. (2.16). It is now, in principle, possible to evaluate the terms of the expansion (2.20) to any order.

IV. THE COMPUTER PROGRAM PACKAGE

The formalism of Sec. III has been partially implemented in a FORTRAN 77 package, SMS, used in conjunction with Version 2.10 of the GRASP2 multiconfiguration Dirac-Fock computer program [9].

The angular coefficients $V_{rs}^{k}(abcd)$ required in Eq. (3.29) are obtained from the MCP package [10]. All coefficients with $k \neq 1$ are discarded. The requisite relativistic Vinti integrals (3.22) are calculated, and the contribution accumulated to obtain

$$\langle \gamma_r J^P \| H^{\mathrm{DC}} + H^{\mathrm{NMS}} + H^{\mathrm{SMS}} \| \gamma_s J^P \rangle \ , \quad (4.1)$$

the matrix of the composite operator between CSF's. The matrix (4.1) is then diagonalized to obtain new estimates of the ASF's and energies of interest. The user may eliminate the contribution of either the normal-mass-shift operator or the specific-mass-shift operator by setting options in the input to GRASP2.

The mass-shift operators in Eq. (4.1) are those of Eq. (2.22) without the first term in the square bracket. Future releases of SMS will be based upon Eqs. (2.20) and (2.16) and will yield more accurate estimates of nuclear motional effects within the domain of applicability of the approximations described in Sec. I.

V. RELATIVISTIC SPECIFIC MASS SHIFTS

We have used the SMS package described in the previous section to compare specific-mass estimates from similar relativistic and nonrelativistic models of atoms and ions. In Table I we present some calculations for the most abundant isotopes of the rare-gas atoms Ne, Ar, Kr, Xe, and Rn. The nonrelativistic limit tabulated in column 3 in each case is obtained by setting c to a much higher value (than the normally used value of 137.035 989 5 in atomic units) in GRASP2; $c \to 10^4 c$ was found to suffice to obtain the nonrelativistic limit of the specific-mass-shift contribution, although a higher value would be required to obtain the nonrelativistic limit of the total energy. This is seen to compare well with Hartree-Fock calculations that are nonrelativistic from the outset [8,11]. Two different nuclear models have been used in the GRASP2 calculations. The potential energy of an electron in the field of a point nucleus is given by

$$V_{\text{point}}^{\text{nuc}}(r) = -\frac{Ze^2}{r} \ . \quad (5.1)$$

The potential for a "Fermi nucleus" is obtained from the charge distribution

$$\rho_{\text{Fermi}}^{\text{nuc}}(r) = \frac{\rho_0}{1+e^{(r-c)/a}} \ . \quad (5.2)$$

Here c is the radius at which $\rho_{\text{Fermi}}^{\text{nuc}}(r) = \rho_0/2$, and a is related to the skin thickness t through

$$t/a = 4 \ln 3 \ . \quad (5.3)$$

The reader may easily verify that $\rho_{\text{Fermi}}^{\text{nuc}}(c - t/2) = 0.9\rho_0$, and $\rho_{\text{Fermi}}^{\text{nuc}}(c + t/2) = 0.1\rho_0$. It is a little more difficult (see [12], for instance) to prove that

$$\langle r^2 \rangle \approx \tfrac{3}{5} c^2 + \tfrac{7}{5} \pi^2 a^2 \ . \quad (5.4)$$

Unless otherwise specified, we use the parametrization

$$\sqrt{\langle r^2 \rangle} = 0.836(A)^{1/3} + 0.570 \quad (5.5)$$

of Johnson and Soff [13], and

$$t = 2.30 \ . \quad (5.6)$$

The nuclear root-mean-square radius from Eq. (5.5) and the skin thickness from Eq. (5.6) are in femtometers. We denote the nucleon number (or baryon number) by A.

Upon comparing column 3 with column 4, and column 5 and column 6, in Table I, it is immediately apparent that the choice of nuclear model has negligible importance in the computation of specific mass effects in the Dirac-Fock approximation. The Dirac-Fock energies $\langle H^{\mathrm{DC}} \rangle_{\mathrm{DF}}$ corresponding to the entries in column 6 of Table I are, respectively, 128.691 930 52, 528.683 762 43, 2 788.860 581 9, 7 446.894 386 2, and 23 602.023 300 hartree. The relative contribution of the specific-mass-shift operator is seen to diminish very gradually for the rare-gas atoms. From the data in Table I, relativistic corrections to the specific mass contribution are seen to grow roughly as Z^4/m^{nuc}. Assuming that the specific mass contribution can be written approximately as

TABLE I. Comparison of nonrelativistic (Hartree-Fock) and relativistic (Dirac-Fock) specific-mass-shift contributions $\langle H^{\mathrm{SMS}}\rangle_{\mathrm{DF}}$ for some rare-gas atoms. The nuclear mass in each case is assumed to be A in atomic mass units (u). The "Fermi nucleus" is the charge distribution given by Eqs. (5.2) and (5.3); the parameters c and a are given by Eqs. (5.5) and (5.6). Our procedure for the determination of the nonrelativistic limits in columns 2 and 3 is described in the text. Energies are given in hartrees. Entries of the form $a[b]$ are to be interpreted as $a\times 10^{b}$.

	MCHF	GRASP2			
	point nucleus	point nucleus	Fermi nucleus	point nucleus	Fermi nucleus
Atom	$c\to\infty$	$c\to\infty$	$c\to\infty$	$c=1/\alpha$	$c=1/\alpha$
$^{20}_{10}$Ne	−4.109 2[−4]	−4.108 3[−4]	−4.108 3[−4]	−4.114 1[−4]	−4.114 2[−4]
$^{40}_{18}$Ar	−1.318 37[−3]	−1.318 08[−3]	−1.318 08[−3]	−1.327 26[−3]	−1.327 27[−3]
$^{84}_{36}$Kr	−4.896 83[−3]	−4.895 8[−3]	−4.895 8[−3]	−5.026 8[−3]	−5.026 8[−3]
$^{132}_{54}$Xe	9.632 08[−3]	−9.630 1[−3]	−9.630 1[−3]	−1.023 38[−2]	−1.023 40[−2]
$^{222}_{86}$Rn	−2.037 6[−2]	−2.037 2[−2]	−2.037 3[−2]	−2.412 5[−2]	−2.412 4[−2]

$$\Delta^{\mathrm{SMS}}(Z)/m^{\mathrm{nuc}}\ , \tag{5.7}$$

whence the specific mass shift between two isotopes with nuclear masses m_1^{nuc} and m_2^{nuc} is

$$\Delta^{\mathrm{SMS}}(Z)\left[\frac{1}{m_1^{\mathrm{nuc}}}-\frac{1}{m_2^{\mathrm{nuc}}}\right]=\Delta^{\mathrm{SMS}}(Z)\frac{m_2^{\mathrm{nuc}}-m_1^{\mathrm{nuc}}}{m_2^{\mathrm{nuc}}m_1^{\mathrm{nuc}}}\ , \tag{5.8}$$

the relativistic correction to the specific mass shift thus varies roughly as Z^4/A^2.

We have used the rough estimate $m^{\mathrm{nuc}}=A$ in the calculations presented in Table I. The mass of the nucleus in atomic mass units u is more accurately obtained from the atomic mass using the formula

$$m^{\mathrm{nuc}}(\mathrm{u})=m^{\mathrm{atom}}(\mathrm{u})-5.485\,799\,03\times10^{-4}\times[n^{\mathrm{elec}}-\alpha^2|E^B(\mathrm{a.u.})|] \tag{5.9}$$

(we have ignored the uncertainty in the conversion constant [14]). The use of Dirac-Fock binding energies as estimates for E^B introduces an error into our calculation of m^{nuc}. However, this error, usually negligible because the contribution of E^B itself is negligible, is a systematic error. All measurable effects of the specific mass shift are differences of energies including specific mass terms. Systematic errors tend to cancel when differences are taken.

We have used Eq. (5.9) in conjunction with tabulated atomic mass data [15] to estimate isotope-dependent effects at the Dirac-Fock level in xenon. The two most abundant isotopes of Xe were selected. Our results are presented in Table II. Entries in the second column in the rows labeled "Difference" give estimates of the *nu-*

TABLE II. Calculation of isotope-dependent effects for Xe. The atomic mass of $^{129}_{54}$Xe has been taken to be 128.904 780 u, that of $^{132}_{54}$Xe, 131.904 144 u. The corresponding nuclear masses have been determined from Eq. (5.9).

	$\langle H^{\mathrm{DC}}\rangle_{\mathrm{DF}}$	$\langle H^{\mathrm{DC+NMS+SMS}}\rangle_{\mathrm{DF}}$
	$c=1/\alpha$	
$^{129}_{54}$Xe	−7 446.897 686 8	−7 446.874 458 6
$^{132}_{54}$Xe	−7 446.894 386 2	−7 446.871 686 4
Difference	0.003 300 6	0.002 722 2
	$c\to10^4c$	
$^{129}_{54}$Xe	−7 232.035 969 2	−7 232.015 017 4
$^{132}_{54}$Xe	−7 232.034 582 2	−7 232.014 106 9
Difference	0.001 387 0	0.000 910 5

TABLE III. Multiconfiguration Dirac-Fock calculation of the specific mass shift for $^4_2$He. $n_{\max}$ is the maximum principal quantum number in the expansion (5.10). The abbreviation "ex5" denotes the extrapolated [16] values for $n_{\max}$ up to 5; "ex6" with $n_{\max}$ up to 6. Both relativistic and nonrelativistic cases are shown. The nucleus has been taken to be a point charge. All energies are in hartrees. Estimated errors in the final digits are given by the entries in parentheses.

$n_{\max}$	$\langle H^{\mathrm{DC}}\rangle_{\mathrm{MCDF}}$	$\langle H^{\mathrm{DC+SMS}}\rangle_{\mathrm{MCDF}}$	$10^5\,\langle H^{\mathrm{SMS}}\rangle_{\mathrm{MCDF}}$
		$c=1/\alpha$	
1	−2.861 813 340 2	−2.861 813 340 2	
2	−2.897 808 460 1	−2.897 785 111 3	2.334 88
3	−2.901 974 647 1	−2.901 952 248 9	2.239 82
4	−2.903 042 972 4	−2.903 020 900 6	2.207 18
5	−2.903 433 572 0	−2.903 411 630 6	2.194 14
6	−2.903 609 177 9	−2.903 587 293 3	2.188 46
ex5	−2.903 855 2	−2.903 833 4	2.179
ex6	−2.903 856 8	−2.903 834 9	2.183
	−2.903 856 8(16)	−2.903 834 9(15)	2.183(4)
		$c\to10^4c$	
1	−2.861 679 993 6	−2.861 679 993 6	
2	−2.897 673 558 7	−2.897 650 214 2	2.334 45
3	−2.901 840 494 0	−2.901 818 129 7	2.236 43
4	−2.902 909 289 6	−2.902 887 273 7	2.201 59
5	−2.903 300 188 4	−2.903 278 312 5	2.187 59
6	−2.903 475 995 5	−2.903 454 180 9	2.181 46
ex5	−2.903 722 3	−2.903 700 6	2.172
ex6	−2.903 724 0	−2.903 702 3	2.175
	−2.903 724 0(17)	−2.903 702 3(17)	2.175(3)

TABLE IV. Multiconfiguration Dirac-Fock calculations of the specific mass shift for $^{20}_{10}Ne^{8+}$. The nuclear mass is taken to be 19.986 95 u. n_{max} is the maximum principal quantum number in expansion (5.10). The abbreviation "ex5" denotes the extrapolated [16] values for n_{max} up to 5; "ex6" with n_{max} up to 6. In the relativistic case, the nucleus is described by a Fermi charge distribution (5.2), whereas in the nonrelativistic case the nucleus is treated as a point charge. All energies are in hartrees. Estimated errors in the final digits are given by the entries in parentheses.

n_{max}	$\langle H^{DC}\rangle_{MCDF}$	$\langle H^{DC+SMS}\rangle_{MCDF}$	$10^5\ \langle H^{SMS}\rangle_{MCDF}$
		$c=1/\alpha$	
1	−93.982 756 778	−93.982 756 778	
2	−94.019 348 433	−94.019 315 451	3.2982
3	−94.025 268 909	−94.025 235 250	3.3659
4	−94.026 971 293	−94.026 937 626	3.3667
5	−94.027 627 276	−94.027 593 641	3.3635
6	−94.027 929 725	−94.027 896 109	3.3616
ex5	−94.028 372	−94.028 338	3.356
ex6	−94.028 364	−94.028 330	3.360
	−94.028 364(8)	−94.028 330(8)	3.360(4)
		$c\to 10^4 c$	
1	−93.861 113 505	−93.861 113 505	
2	−93.897 683 184	−93.897 650 400	3.2784
3	−93.903 636 786	−93.903 603 321	3.3465
4	−93.905 361 421	−93.905 327 950	3.3471
5	−93.906 032 020	−93.905 998 581	3.3439
6	−93.906 344 585	−93.906 311 164	3.3421
ex5	93.906 805	−93.906 772	3.336
ex6	−93.906 806	−93.906 773	3.341
	−93.906 806(1)	−93.906 773(1)	3.341(5)

clear volume or *field shift*. The field shift in the nonrelativistic limit is less than half that in the relativistic calculation. This reflects the well-known relativistic increase of electron density in the neighborhood of the nucleus. The total *isotope shift* in the binding energy of xenon, that is, the sum of the volume shift, the normal mass shift, and the specific mass shift appears in the third column in the same rows.

The calculations summarized in Tables I and II do not include estimates of correlation effects. To obtain some insight into the latter, a series of multiconfiguration Dirac-Fock (MCDF) calculations have been performed for three heliumlike ions.

We follow the procedure of Parpia and Grant [16], based upon a theorem of Fischer [17]. The approximate atomic wave function for the ground state is expressed as the superposition

$$|0^+\rangle=\sum_{n=1}^{n_{max}}\sum_{\kappa=-1,1,-2,2,\ldots}^{-n} c_{n\kappa}|(n\kappa)^2 J=0\rangle\ . \tag{5.10}$$

Thus, for each value of the quantum number n, all possible values of κ are included. Six sets of MCDF calculations are carried out for each of two values of the speed of light for ^4_2He, $^{20}_{10}Ne$, $^{22}_{10}Ne$, and $^{40}_{18}Ar$. The extrapolation procedure of Parpia and Grant [16], based on the assumption

TABLE V. As in Table IV, except that values are for $^{22}_{10}Ne^{8+}$, whence the nuclear mass is taken to be 21.985 90 u.

n_{max}	$\langle H^{DC}\rangle_{MCDF}$	$\langle H^{DC+SMS}\rangle_{MCDF}$	$10^5\ \langle H^{SMS}\rangle_{MCDF}$
		$c=1/\alpha$	
1	−93.982 758 749	−93.982 758 749	
2	−94.019 350 404	−94.019 320 420	2.9984
3	−94.025 270 880	−94.025 240 280	3.0600
4	−94.026 973 264	−94.026 942 657	3.0607
5	−94.027 629 247	−94.027 598 669	3.0578
6	−94.027 931 696	−94.027 901 136	3.0560
ex5	−94.028 374	−94.028 344	3.051
ex6	−94.028 366	−04.028 336	3.054
	−94.028 366(8)	−94.028 336(8)	3.054(3)
		$c\to 10^4 c$	
1	−93.861 113 505	−93.861 113 505	
2	−93.897 683 184	−93.897 653 379	2.9805
3	−93.903 636 786	−93.903 606 363	3.0423
4	−93.905 361 421	−93.905 330 992	3.0429
5	−93.906 032 020	−93.906 001 620	3.0400
6	−93.906 344 585	−93.906 314 202	3.0383
ex5	−93.906 805	−93.906 775	3.033
ex6	−93.906 806	−93.906 776	3.037
	−93.906 806(1)	−93.906 775(1)	3.037(4)

$$E_n-E_{n-1}\approx a/(n-\tfrac{1}{2})^4\ , \tag{5.11}$$

is used to estimate the exact Dirac-Coulomb energy, that is, the eigenenergy of the Hamiltonian (1.1). These calculations are summarized in column 2 of Tables III–VI. Differences in the Dirac-Coulomb energies in Tables IV and V arise from the difference in the nuclear volumes of the two isotopes $^{20}_{10}Ne$ and $^{22}_{10}Ne$.

TABLE VI. As in Table IV, except that values are for $^{40}_{18}Ar^{16+}$. The nuclear mass is taken to be 39.952 525 u.

n_{max}	$\langle H^{DC}\rangle_{MCDF}$	$\langle H^{DC+SMS}\rangle_{MCDF}$	$10^5\ \langle H^{SMS}\rangle_{MCDF}$
		$c=1/\alpha$	
1	−314.199 524 34	−314.199 524 34	
2	−314.236 239 02	−314.236 207 96	
3	−314.242 273 84	−314.242 241 94	
4	−314.244 000 71	−314.243 968 75	
5	−314.244 656 60	−314.244 624 64	
6	−314.244 952 82	−314.244 920 87	
ex5	−314.245 360	−314.245 328	3.195
ex6	−314.245 365	−314.245 334	3.194
	−314.245 365(6)	−314.245 334(6)	3.194(1)
		$c\to 10^4 c$	
1	−312.861 063 27	−312.861 063 27	
2	−312.897 709 83	−312.897 679 39	
3	−312.903 856 95	−312.903 825 66	
4	−312.905 659 75	−312.905 628 39	
5	−312.906 365 36	−312.906 334 01	
6	−312.906 695 55	−312.906 664 21	
ex5	−312.907 122	−312.907 091	3.135
ex6	−312.907 156	−312.907 124	3.133
	−312.907 156(34)	−312.907 124(34)	3.133(2)

Next, for each value of n_{max}, a larger basis than the "diagonal" form in Eq. (5.10) is generated from all possible CSF's with $J=0$ and even parity using the available set of orbitals. (That is, we carry out "complete active space" calculations for each n_{max}. The CSF list is generated using the JJCAS package of Parpia, Wijesundera, and Grant [18].) The lowest eigenvalue of the matrix (4.1) determined from this new basis is tabulated in column 3 of Tables II–VI.

Relativistic corrections to the specific-mass-shift contributions for this isoelectronic sequence increase with Z more rapidly than Z^3/m^{nuc}. The formula (5.8) is seen to hold accurately for all the two-electron ions studied here: the quantity Δ^{SMS} is not affected by variations in the nuclear charge distribution. A perusal of Tables III–VI shows that the relativistic contribution to the correlation differs from the nonrelativistic contribution only for $n_{max}=2$.

Unlike the systems of Tables I and II, the heliumlike ions exhibit positive specific-mass-shift contributions. The reasons for this unexpected behavior have been discussed by Krause, Morgan III, and Berry [19]. Quite generally, closed-shell atoms and ions that are well described by orbitals of only s symmetry exhibit positive specific-mass-shift contributions (cf. the paper of Aspect *et al.* [4]).

It is interesting to observe the trends in the last column of each of Tables III–VI. The specific mass shift of the He atom decreases monotonically for $n_{max}>2$. For the Ne and Ar atoms, the mass polarization contribution first increases and then decreases relatively slowly.

VI. CONCLUSION

We have derived expressions for the translational motion of the atomic nucleus to obtain the contribution of this motion to the level energy of the atom. The nucleus has been modeled as a relativistic point mass with no internal degrees of freedom. The electrons are assumed to be relativistic fermions. In the nonrelativistic limit ($c\rightarrow\infty$), our expressions reduce to the mass-shift Hamiltonian of Hughes and Eckart.

Our formalism has been implemented in a computer program SMS that forms part of a new version of the GRASP2 multiconfiguration Dirac-Fock atomic-structure program. Calculations have been carried out using SMS. In neutral atoms, the relativistic corrections to the specific mass shifts increase roughly as Z^4/A^2, where Z is the atomic number and A is the number of nucleons (protons and neutrons together). Relativistic corrections increase roughly as Z^3/A^2 along isoelectronic sequences.

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