interaction of $3s3p^6\,{}^2S$ with both $3s^23p^43d\,{}^2S$ and $3s^23p^44d\,{}^2S$. This interpretation has now been confirmed by the recent work on Ar II by Werme *et al.*[9] in which the $3d$ and $4d$ satellite lines were resolved and their positions accurately measured. The theoretical analysis of Ar II by Luyken[10] shows that $3s3p^6\,{}^2S$ has a much stronger interaction with $3s^23p^43d\,{}^2S$ than with $3s^23p^44d\,{}^2S$, although the distribution of $3s3p^6\,{}^2S$ into the various excited states was not given explicitly. Nevertheless, the relative intensities of the $3d$ and $4d$ satellite lines observed by Werme *et al.* are at least qualitatively confirmed by Luyken's results.

The absence of any satellite structure near Na($2s$) in NaCl is undoubtedly due to the fact that there are no $2d$ electrons.

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Local Exchange Potential for the Relativistic Hartree–Fock Equations*

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An exact local representation of the relativistic Hartree–Fock exchange potential for electrostatic interactions is presented for closed-shell atoms. This single-particle potential depends upon all relativistic single-particle quantum numbers except the magnetic quantum number m. This exchange potential should be useful for relativistic atomic Hartree–Fock calculations.

I. INTRODUCTION

Several[1–10] relativistic atomic-structure calculations have appeared in the recent literature. Some[2,4,6] have used Slater[11]-type exchange approximations, while others[3,5,7–10] have attempted exact solutions of the complicated relativistic Hartree–Fock equations. The dilemma associated with these latter calculations is pointed out by Kim.[3] Exact treatments of the problem are costly, owing to the computer storage requirements of the relativistic calculation, while approximations to the exchange term may overshadow the accuracy gained by the treatment of relativistic effects. Thus a simple treatment of exchange is needed which still maintains the locality of the Hartree–Fock potential. Such a formalism (appropriate for closed-shell atoms or ions) is reported in this comment.

II. RELATIVISTIC EXCHANGE FORMALISM

In analogy to the nonrelativistic variational derivation, one obtains the relativistic Hartree–Fock equations (atomic units are used throughout);

$$[c\vec{\alpha}\cdot\vec{p}+\beta Mc^2]\,\phi_i(1)-\frac{2Z}{r_1}\,\phi_i(1)+\sum_j\left(\int\phi_j^\dagger(2)\,\frac{2}{r_{12}}\,\phi_j(2)\,d\tau_2\right)\phi_i(1)-\sum_j\left(\int\phi_j^\dagger(2)\,\frac{2}{r_{12}}\,\phi_i(2)\,d\tau_2\right)\phi_j(1)=\epsilon_i\phi_i(1),\quad(1)$$

where $\vec{\alpha}$ and β are the usual Dirac matrices, and the wave functions ϕ are the four-component Dirac spinors. The Breit magnetic and retardation terms of the electron-electron interaction are not included in Eq. (1), since it is inappropriate to include these terms in the Hartree–Fock potential.[3,10] The arguments of the wave functions are denoted 1 and 2 to represent the spatial locations $\vec{r}_1$ and $\vec{r}_2$. The symbol $d\tau$ represents a volume integral over all space. The exchange term may be viewed as a nonlocal potential; however, a local representation may be obtained by multiplying and dividing the exchange term by $[\phi_i^\dagger(1)\phi_i(1)]$,

$$V_i^{\rm ex}(1)=-[\phi_i^\dagger(1)\phi_i(1)]^{-1}\sum_j\left(\int\phi_j^\dagger(2)\,\frac{2}{r_{12}}\,\phi_i(2)\,d\tau_2\right)$$

$$\times[\phi_j(1)\phi_i^\dagger(1)]. \quad (2)$$

Note that the factor $[\phi_j(1)\phi_i^\dagger(1)]$ is a 4×4 matrix. Any 4×4 matrix M may be expanded[12] in the 16 linearly independent matrices γ^A formed from products of the Dirac matrices,

$$M=\tfrac{1}{4}\sum_{A=1}^{16}\mathrm{Tr}(\gamma_A M)\gamma^A. \quad (3)$$

The 16 matrices γ^A may be grouped into five different categories according to the Lorentz transformation properties of the associated tensor density $\bar{\phi}(\vec{r})\gamma^A\phi(\vec{r})$, where $\phi(\vec{r})$ is any four-component Dirac wave function and $\bar{\phi}(\vec{r})=[\gamma^0\phi(\vec{r})]^\dagger$. The matrices in these five categories are I, γ^μ, $\gamma^5=\gamma^0\gamma^1\gamma^2\gamma^3$, $\gamma^5\gamma^\mu$, and $\gamma^\mu\gamma^\nu$ ($\mu,\nu=0,1,2,3$) and have tensor densities which transform as order-zero weight-zero (scalar or invariant), order-one weight-zero (vector), order-zero weight-one pseudoscalar), order-one weight-one (pseudovector), and order-two weight-zero (tensor) tensors under Lorentz transformations. Thus, in general, the exchange potential for the electrostatic interaction gives contributions to all possible types of Dirac interactions: (1) scaler, (2) vector, (3) pseudoscalar, (4) pseudovector, and (5) tensor. This expansion takes the form,

$$\begin{aligned}[\phi_j(1)\phi_i^\dagger(1)]&=\frac{1}{4}\sum_A\phi_i^\dagger(1)\gamma_A\phi_j(1)\gamma^A\\&=\tfrac{1}{4}[\phi_i^\dagger(1)\phi_j(1)+\phi_i^\dagger(1)\gamma_\mu\phi_j(1)\gamma^\mu+\phi_i^\dagger(1)\gamma_5\phi_j(1)\gamma^5\\&\quad+\phi_i^\dagger(1)\gamma_\mu\gamma_5\phi_j(1)\gamma^5\gamma^\mu+\phi_i^\dagger(1)\gamma_\mu\gamma_\nu\phi_j(1)\gamma^\nu\gamma^\mu],\end{aligned} \quad (4)$$

where the summation in the tensor term goes over the six independent elements of $\gamma^\nu\gamma^\mu$ only. This expansion leads to a relativistic Hartree–Fock equation with all possible types of local Dirac potentials:

$$\begin{aligned}\{c\vec{\alpha}\cdot\vec{p}+\beta[Mc^2+V_s(1)+\gamma^\mu V_v^\mu(1)+\gamma^5V_{ps}(1)\\+\gamma^5\gamma^\mu V_{pv}^\mu(1)+\gamma^\mu\gamma^\nu V_t^{\mu\nu}(1)]\}\phi_i(1)=\epsilon_i\phi_i(1).\end{aligned} \quad (5)$$

Note that the form of the Hartree–Fock equations has been chosen to yield an explicit diagonal form for the eigenvalue matrix ($\lambda_{ij}=\delta_{ij}\epsilon_i$). If one is restricted to atomic systems made up of closed shells, then the system will possess spherical symmetry and all the potential terms will commute with the total angular momentum operator $\vec{J}$ and with the relativistic parity operator ($P=\beta P_0$). This restriction has been shown to greatly simplify Eq. (5) because only four potential terms remain nonzero: (1) $V_s(1)$, (2) $V_v^0(1)$, (3) $V_v^r(1)$, and (4) $V_1^r(1)$.[13] The potentials V_s and V_v^0 are the scalar and zeroth component of the four-vector terms, respectively. The potential V_v^r is the radial component of the spacelike part of the four-vector potential. The potential V_1^r is the radial component of the three-vector obtained by setting one index equal to zero and letting the other range over the space indices in the tensor potential $V_t^{\mu\nu}$. For electrostatic interactions the direct potential of the Hartree–Fock equations contributes to the vector term (V_v^0) only. The exchange potential, however, contributes to all four Dirac potential terms. It is desirable to develop simple expressions for these contributions.

First of all, one may note that nonrelativistic versions of Eq. (2) contain singularities due to nodes in the denominator ($\phi_i^\dagger(1)\phi_i(1)$). For relativistic wave functions this denominator will have nodes due to the angular parts of the function, but not the radial parts, because the large and small components of the radial wave functions never vanish at the same point. Because of this inherent difference between the relativistic and nonrelativistic wave functions, the Slater averaging procedure will not be needed to remove singularities from the potential.

The presence of angular functions in both the numerator and denominator of Eq. (2) still presents a computational problem. The exchange potential does not destroy the spherical symmetry of a system, and this fact causes the angular dependence to drop out of the nonrelativistic exchange potential. The situation is not so simple in the relativistic formalism; however, an analogous simplification is obtained by noting that the exchange potential V_i^{ex} must be independent of the magnetic quantum number m_i of the ith state. If this were not the case, then spherical symmetry would not be maintained. The potential of Eq. (2) is thus independent of m_i even though both the numerator and denominator depend upon m_i. This enables one to sum both the numerator and denominator independently over m_i and achieve a considerable simplification:

$$\begin{aligned}V_i^{ex}(1)=&-\Big(\sum_{m_i}\phi_i^\dagger(1)\,\phi_i(1)\Big)^{-1}\\&\times\sum_j\sum_{m_i}\Big(\int\phi_j^\dagger(2)\frac{2}{r_{12}}\,\phi_i(2)\,d\tau_2\,\phi_j(1)\,\phi_i^\dagger(1)\Big).\end{aligned} \quad (6)$$

The Dirac wave functions appropriate for spherical symmetry are

$$\phi(1)=\frac{1}{r_1}\begin{pmatrix}F(1)&\mathcal{Y}_{lm}^J(\Omega_1)\\iG(1)&\mathcal{Y}_{l'm}^J(\Omega_1)\end{pmatrix}, \quad (7)$$

where F and G are the large and small components, respectively, J and m are the total angular momentum and its z-projection quantum numbers, respectively, and l and l' are the orbital angular momentum quantum numbers of the large and small components, respectively. The functions $\mathcal{Y}_{lm}^J(\Omega)$ are Pauli central-field spinors formed by coupling a spherical harmonic $Y_{lm_l}(\Omega)$ with the two-component

Pauli spinors to obtain a function of good total angular momentum J and z projection m. Using these wave functions, the angular dependence of the denominator in Eq. (6) is removed;

$$\sum_{m_i=-J_i}^{J_i} \phi_i^\dagger(1)\,\phi_i(1) = \frac{2J_i+1}{4\pi r_1^2}\,[F_i^2(1)+G_i^2(1)]. \tag{8}$$

The exchange potential becomes

$$V_i^{\mathrm{ex}}(1) = -\left(\frac{(2J_i+1)\,[F_i^2(1)+G_i^2(1)]}{4\pi r_1^2}\right)^{-1} \times \sum_j \sum_{m_j} \left(\int \phi_j^\dagger(2)\,\frac{2}{r_{12}}\,\phi_i(2)\,d\tau_2\right)[\phi_j(1)\,\phi_i^\dagger(1)]. \tag{9}$$

Using the Dirac matrix expansion (Eq. 4), one obtains the contributions to the four spherically symmetric Dirac potentials:

$$V_s^i(1) = \frac{-1}{4}\left(\frac{(2J_i+1)\,[F_i^2(1)+G_i^2(1)]}{4\pi r_1^2}\right)^{-1} \sum_j \sum_{m_j} \left(\int \phi_j^\dagger(2)\,\frac{2}{r_{12}}\,\phi_i(2)\,d\tau_2\right)[\phi_i^\dagger(1)\gamma_0\phi_j(1)], \tag{10}$$

$$V_v^{0i}(1) = \frac{-1}{4}\left(\frac{(2J_i+1)\,[F_i^2(1)+G_i^2(1)]}{4\pi r_1^2}\right)^{-1} \sum_j \sum_{m_j} \left(\int \phi_j^\dagger(2)\,\frac{2}{r_{12}}\,\phi_i(2)\,d\tau_2\right)[\phi_i^\dagger(1)\,\phi_j(1)], \tag{11}$$

$$V_v^{ri}(1) = \frac{-1}{4}\left(\frac{(2J_i+1)\,[F_i^2(1)+G_i^2(1)]}{4\pi r_1^2}\right)^{-1} \sum_j \sum_{m_j} \left(\int \phi_j^\dagger(2)\,\frac{2}{r_{12}}\,\phi_i(2)\,d\tau_2\right)[\phi_i^\dagger(1)\gamma_r\gamma_0\phi_j(1)], \tag{12}$$

$$V_1^{ri}(1) = \frac{-1}{4}\left(\frac{(2J_i+1)\,[F_i^2(1)+G_i^2(1)]}{4\pi r_1^2}\right)^{-1} \sum_j \sum_{m_j} \left(\int \phi_j^\dagger(2)\,\frac{2}{r_{12}}\,\phi_i(2)\,d\tau_2\right)[\phi_i^\dagger(1)\gamma_r\phi_j(1)], \tag{13}$$

where the γ^r is the radial component of the Dirac matrix ($\vec{\gamma} = \beta\vec{\alpha}$). Equations (10)–(13) may be simplified by using wave functions of the form shown in Eq. (7) and performing the sums over magnetic quantum numbers m_i and m_j. Full details of this reduction are given in Ref. 13, where applications to the more complicated nucleon-nucleon interaction are presented. For the electrostatic interaction of Eqs. (10)–(13) the following results are obtained:

$$V_s^i(1) = -\tfrac{1}{2}\{(2J_i+1)\,[F_i^2(1)+G_i^2(1)]\}^{-1} \sum_{J_j\text{-shells}} \sum_l (2l+1)^{-1}\,[Z(l_i J_i l_j J_j;\tfrac{1}{2}l) \times F_i(1)F_j(1) - (-)^{(\tilde{\omega}_j-\tilde{\omega}_i)/2}\,Z(l_i' J_i l_j' J_j;\tfrac{1}{2}l)\,G_i(1)G_j(1)]\left(Z(l_i J_i l_j J_j;\tfrac{1}{2}l) \times \int_0^\infty F_i(2)\,F_j(2)\,\frac{r_<^l}{r_>^{l+1}}\,dr_2 + (-)^{(\tilde{\omega}_j-\tilde{\omega}_i)/2}\,Z(l_i' J_i l_j' J_j;\tfrac{1}{2}l)\int_0^\infty G_i(2)\,G_j(2)\,\frac{r_<^l}{r_>^{l+1}}\,dr_2\right), \tag{14}$$

$$V_v^{0i}(1) = -\tfrac{1}{2}\{(2J_i+1)\,[F_i^2(1)+G_i^2(1)]\}^{-1} \sum_{J_j\text{-shells}} \sum_l (2l+1)^{-1}\,[Z(l_i J_i l_j J_j;\tfrac{1}{2}l) \times F_i(1)\,F_j(1) + (-)^{(\tilde{\omega}_j-\tilde{\omega}_i)/2}\,Z(l_i' J_i l_j' J_j;\tfrac{1}{2}l)\,G_i(1)G_j(1)]\left(Z(l_i J_i l_j J_j;\tfrac{1}{2}l) \times \int_0^\infty F_i(2)\,F_j(2)\,\frac{r_<^l}{r_>^{l+1}}\,dr_2 + (-)^{(\tilde{\omega}_j-\tilde{\omega}_i)/2}\,Z(l_i' J_i l_j' J_j;\tfrac{1}{2}l)\int_0^\infty G_i(1)\,G_j(1)\,\frac{r_<^l}{r_>^{l+1}}\,dr_2\right), \tag{15}$$

$$V_1^{ri}(1) = \tfrac{1}{2}i\{(2J_i+1)\,[F_i^2(1)+G_i^2(1)]\}^{-1} \sum_{J_j\text{-shells}} \sum_l (2l+1)^{-1}\,[Z(l_i J_i l_j J_j;\tfrac{1}{2}l) \times F_i(1)\,G_j(1) - (-)^{(\tilde{\omega}_j-\tilde{\omega}_i)/2}\,Z(l_i' J_i l_j' J_j;\tfrac{1}{2}l)\,F_j(1)G_i(1)]\left(Z(l_i J_i l_j J_j;\tfrac{1}{2}l) \times \int_0^\infty F_i(2)\,F_j(2)\,\frac{r_<^l}{r_>^{l+1}}\,dr_2 + (-)^{(\tilde{\omega}_j-\tilde{\omega}_i)/2}\,Z(l_i' J_i l_j' J_j;\tfrac{1}{2}l)\int_0^\infty G_i(2)\,G_j(2)\,\frac{r_<^l}{r_>^{l+1}}\,dr_2\right), \tag{16}$$

$$V_1^{ri}(1) = -\tfrac{1}{2}i\{(2J_i+1)\,[F_i^2(1)+G_i^2(1)]\}^{-1} \sum_{J_j\text{-shells}} \sum_l (2l+1)^{-1}\,[Z(l_i J_i l_j J_j;\tfrac{1}{2}l) \times F_i(1)\,G_j(1) + (-)^{(\tilde{\omega}_j-\tilde{\omega}_i)/2}\,Z(l_i' J_i l_j' J_j;\tfrac{1}{2}l)\,F_j(1)G_i(1)]\left(Z(l_i J_i l_j J_j;\tfrac{1}{2}l) \times \int_0^\infty F_i(2)\,F_j(2)\,\frac{r_<^l}{r_>^{l+1}}\,dr_2 + (-)^{(\tilde{\omega}_j-\tilde{\omega}_i)/2}\,Z(l_i' J_i l_j' J_j;\tfrac{1}{2}l)\int_0^\infty G_i(2)\,G_j(2)\,\frac{r_<^l}{r_>^{l+1}}\,dr_2\right). \tag{17}$$

The Z's in Eqs. (14)–(17) are the Z coefficients of Blatt and Biedenharn,[14] which have been used extensively in nuclear-reaction theory. The phase conventions for the Z coefficient used here correspond to Appendix C of Ref. 12. The quantities $\tilde{\omega}_i$ and $\tilde{\omega}_j$ are single-particle quantum numbers which determine the relation between J, l, and l' for the single-particle wave functions;

$$J = l - \tfrac{1}{2}\tilde{\omega} = l' + \tfrac{1}{2}\tilde{\omega}\,; \quad \tilde{\omega} = \pm 1. \tag{18}$$

The symbols $r_<$ and $r_>$ are used to denote the lesser and greater, respectively, of the radii r_1 and r_2. Note that V_s and V_v^0 differ only by an internal sign. The same is true of the pair V_v^r and V_1^r. Note the expression involving the radial integrals is common to all four potentials. These properties simplify numerical calculations even though a different set of exchange potentials must be calculated for each J shell.

It remains to show how these four potentials enter into the radial Dirac equation. The role of the potential V_v^0 is, of course, familiar from use of the Dirac equation for the electrostatic interaction. The scalar potential V_s and the two vector potentials V_v^r and V_1^r have been investigated for the nuclear-physics problem[13,15]; however, their use in atomic physics with electrostatic interactions is new. It is interesting to note their appearance in the radial Dirac equations,

$$\frac{dF}{dr} = -\left(\frac{i(V_v^r - V_1^r)}{\hbar c} + \frac{\tilde{\omega}(J+\frac{1}{2})}{r}\right)F + \left(\frac{2Mc^2 + V_s - V_v^0 + E}{\hbar c}\right)G, \tag{19}$$

$$\frac{dG}{dr} = \left(\frac{V_s + V_v^0 - E}{\hbar c}\right)F - \left(\frac{i(V_v^r + V_1^r)}{\hbar c} - \frac{\tilde{\omega}(J+\frac{1}{2})}{r}\right)G. \tag{20}$$

These latter two potentials enter into the Dirac equation in an essentially different way than the more familiar potentials V_s and V_v^0. It would be interesting to study the form of their nonrelativistic reductions.

III. CONCLUSIONS

A local exchange potential has been developed for the relativistic Hartree–Fock problem of electrostatic interactions in closed-shell atoms. Unlike the direct potential, the exchange potential divides into terms which transform like all possible forms of Dirac tensors. The potential is state dependent and must be calculated separately for each J shell of single-particle orbitals. These characteristics make the method more complicated than statistical-exchange methods, such as the Slater approximation; however, the method should represent a simplification with respect to other exact treatments of exchange which rely upon solving Dirac equations with nonlocal potentials or with nonhomogeneous parts. Furthermore, the quantities needed for calculation of the exchange potentials are also needed as intermediate steps in the calculation of the exchange contributions to the total binding energy. It thus seems likely that this treatment of exchange can yield important simplifications in relativistic Hartree–Fock calculations of atomic structure.

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