

# Relativistic Pseudopotential Incorporating Core/Valence Polarization and Nonlocal Effects

M. M. Marino<sup>†</sup>

Department of Chemistry and Chemical Biology, Stevens Institute of Technology,  
Hoboken, New Jersey 07030

Received June 21, 2000

A relativistic pseudopotential (RPP) for use in *ab initio* molecular electronic structure calculations is derived in the context of the relativistic effective core potential (REP) method of Lee et al. The resulting atom-specific RPP has salient features of the REP imbedded within it while retaining the form of a functional that is dynamically defined at runtime when used in calculations on molecules. The RPP is determined from Dirac–Fock wave functions for the isolated atom. Outer core two-electron interactions are incorporated into the RPP by means of variable coefficients that are defined in the context of the final molecular wave function. This form permits polarization of the outer core shells analogous to that occurring in all-electron molecular Hartree–Fock calculations while retaining these shells as part of the atomic pseudopotential. Use of the RPP in post-Hartree–Fock molecular calculations permits the incorporation of core/valence correlation effects.

## I. INTRODUCTION

Procedures based on the use of relativistic effective core potentials (REPs) derived from all-electron *ab initio* numerical Dirac–Fock (DF) atomic wave functions afford the ability to reduce the number of electrons that must be treated explicitly to a small enough number that in many instances large basis set full-CI calculations incorporating spin–orbit coupling and other relativistic effects become feasible.<sup>1</sup> The REP method is grounded in the fundamental tenet that atomic core and valence electrons can be formally distinguished and, in fact, treated rigorously from first principles as identifiable sets.<sup>2</sup> This subject, generally categorized as pseudopotential theory,<sup>3</sup> has been studied for many years since being proposed by Hellmann in the 1930s and has evolved into a rigorous method for the treatment of the electronic structure of polyatomic many-electron systems.<sup>4</sup> One type of *ab initio* REP that accounts for relativistic effects is defined by using shape-consistent nodeless pseudospinors<sup>5</sup> extracted from numerical two-component DF atomic spinors<sup>6</sup> following the procedure of Lee et al.<sup>2</sup>

Since REP-based methods rely on the principle of core/valence separability, a choice must be made regarding the number of electrons to be treated explicitly. In the procedure developed by Lee et al.,<sup>2</sup> this choice is arbitrary. For example, in the case of cesium the most practical REP would correspond to a one-electron valence space. However, the same atom may also be described by 9-electron and 19-electron valence spaces, where the former REP assigns the 5s and 5p Cs electrons to the valence space and the latter has a valence space comprised of the 5s, 5p, and 4d electrons. A REP having a one-electron valence space would allow the minimum number of electrons to be treated explicitly and, therefore, would render calculations at, say, the full-CI level of theory possible for clusters of two or more Cs atoms.

However, such an REP yields inaccurate excitation and ionization energies for Cs because of the large effects of core/valence polarization in this atom.<sup>7</sup>

It is possible to remain within the REP approximation, which is essential to guarantee tractability at a high level of theory while accounting for relativistic effects in all but the smallest systems, and reduce core/valence polarization errors. One approach is to increase the number of valence electrons treated explicitly. In the case of Cs, for example, a REP having a nine-electron valence space may be used instead of the REP requiring only one valence electron. Since the electrons in the  $n = 5$  shell are now part of the valence space, the interaction between these electrons and the Cs 6s electron can be described more accurately.

Two major disadvantages arise, however, with using REPs that require more than the minimum number of valence electrons. First, full-CI calculations, or even procedures that incorporate modest levels of electron correlation, would be rendered more difficult as the number of valence electrons increases, and for larger systems and/or systems containing heavy elements, the calculations would be intractable. A second disadvantage lies in the neglect of relativistic effects. Because the REPs are generated by using DF theory, relativistic effects are incorporated into REP-based calculations via the core electrons. Relativistic effects in the valence region, which is treated by using a nonrelativistic Hamiltonian, result from the propagation of these effects to the valence electrons from the core.<sup>2</sup> Thus, a reduction in the number of core electrons results in a neglect of direct relativistic effects, leading to decreased accuracy for calculations of heavy-element systems, where such effects are increasingly important. It is possible to account for core/valence polarization effects within the minimum-valence-electron REP approximation by adding a correction to the potential.<sup>8</sup> Christiansen showed that a high level of accuracy may be achieved with the minimum-valence-electron REP

<sup>†</sup> Telephone: (201) 659-5443. E-mail: mmarino@stevens-tech.edu.

if a core/valence polarization potential (CVPP) is included in the calculations.<sup>9</sup> Marino and Ermler later extended Christiansens's method to an REP-based CVPP derived in  $j$ - $j$  coupling.<sup>10</sup>

Despite the success and widespread use of REPs, there are still problems associated with these procedures. First, the use of methods based on the current REPs plus CVPPs, while leading to higher accuracy for systems containing heavy atoms, still results in significant errors. Molecules containing alkali metal and alkaline earth metal elements (LiMg, LiBa, Cs<sub>2</sub>, etc.) are examples.<sup>7</sup> Second, no REP method to date can account explicitly for outer core correlation, which may be especially significant in heavy-element systems because the number of core electrons is large. Third, large-core REPs are not accurate, and their shortcomings are well-known.<sup>4</sup> The error results primarily from the neglect of nonlocal, polarization, and correlation phenomena due to outer core electrons interacting with atomic and molecular valence electrons. While nonlocal errors can be significantly reduced by using improved pseudospinors,<sup>11</sup> polarization and correlation effects require an extension to the formalism.

In this work, a relativistic pseudopotential (RPP) is derived. When the RPP is used in molecular calculations, outer core polarization (at the Hartree–Fock or Dirac–Fock level) and outer core/valence correlation (via post-Hartree–Fock procedures) are incorporated, and local errors present in the large-core REP procedure are removed. The form of the RPP also allows, when used in post-Hartree–Fock procedures, the calculation of outer core correlation effects. This new method is based on the REP procedure as defined by Lee, Ermler, and Pitzer<sup>2</sup> and Christiansen, Lee, and Pitzer,<sup>5</sup> Roothaan's LCAO method,<sup>12</sup> and the nodeless-valence-spinor (NVS) procedure of Ermler and Marino.<sup>11</sup> The RPP is defined for each individual element, but its final form is established in the molecular environment corresponding to each specific application. It formally reduces to the large-core nodeless-valence REPs<sup>11</sup> in the limit where the outer core does not polarize (i.e., is truly corelike). Since the proposed method is grounded in pseudopotential theory and uses the procedure of Lee et al. as the starting point, it will be presented in terms of Dirac–Fock theory. The RPP is similar in form to the REP of Lee et al., but it responds in each separate molecular environment through coefficients that are self-consistently determined. The RPP is therefore analogous to generating a new REP for every molecular environment. Because the form of the RPP changes depending on the system being treated, it is a functional rather than a function, thus the name *pseudopotential*.

## II. DERIVATION OF THE RELATIVISTIC PSEUDOPOTENTIAL

Having established the nodeless valence spinor procedure, the derivation of the RPP will now be presented. Three logical realms of atomic electron occupancy will be defined: (a) inner core, (b) outer core, and (c) valence. Region b could also logically be termed the inner valence region. *Outer core* is the preferable term because this region will be incorporated into the RPP and remains characteristic of the parent atom but includes an improved representation of

the outer core orbitals, thus leading to a significant reduction in the local error present in other pseudopotential procedures. Regions a and b are therefore characteristic of the atom and are encoded into the RPP. Region c accommodates those electrons that lose the knowledge of their atomic parentage in the process of excitation or ionization or as a result of interatomic interactions. Earlier pseudopotential approaches have assumed the existence of the two regions a and c only.<sup>12,13</sup> Those cases in which changes in the electrons in region b are of clear importance were dealt with, as discussed above, by either expanding region c or by adding a CVPP.<sup>8,9,14</sup> The latter requires the a priori inclusion of the atomic outer core polarizability. The comprehensive inclusion of relativistic effects and the flexibility to account for correlation/polarization effects in the RPP will allow the accurate procedures of ab initio quantum chemistry to be extended to polyatomic systems that include atoms of any atomic number.

The starting point is the Dirac Coulomb Hamiltonian

$$H_{\text{rel}} = \sum_i h_D(i) + \sum_i \sum_j r_{ij}^{-1} \quad (1)$$

where  $i$  and  $j$  are index electrons. (It is noted that although the pseudopotential is developed using the Dirac Hamiltonian, the formalism itself is not dependent on the form of the Hamiltonian used, and thus the Schrodinger Hamiltonian may also be used.) Many-electron relativistic effects, which may be approximated by including the Breit interaction term<sup>15</sup> are omitted for now. The Dirac one-electron Hamiltonian is

$$h_D = c\alpha \cdot \mathbf{p} + \beta C^2 - Z/r \quad (2)$$

where  $\mathbf{p}$  is the momentum operator,  $Z$  the atomic number,  $r$  the electron–nucleus interparticle distance, and

$$\alpha = \begin{pmatrix} 0 & \sigma^p \\ \sigma^p & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{pmatrix} \quad (3)$$

Here,  $\sigma^p$  is the Pauli spin matrix and  $\mathbf{I}$  is the unit matrix of rank 2. The zero of the energy is that of the free electron. The eigenfunctions of  $h_D$  are four-component Dirac spinors:

$$\Psi_{nk}(r, \theta, \phi) = \begin{pmatrix} r^{-1} P_{nk}(r) \chi_{km}(\theta, \phi) \\ i Q_{nk}(r) \chi_{km}(\theta, \phi) \end{pmatrix} \quad (4)$$

where the angular factors are defined by

$$\chi_{km}(\theta, \phi) = \sum_{\sigma=-1/2}^{1/2} C(\lambda \ 1/2 \ j; \ m - \sigma, \ \sigma) Y_{\lambda}^{m-\sigma}(\theta, \phi) \phi_{1/2}^{\sigma} \quad (5)$$

and  $Y_{\lambda}^{m-\sigma}$  are the spherical harmonics,  $\phi_{1/2}^{\sigma}$  are the Pauli spinors;  $C(\lambda \ 1/2 \ j; \ m - \sigma, \ \sigma)$  are Clebsch–Gordan coefficients;  $\lambda$  is an index defined as  $|\gamma + 1/2| - 1/2$  and  $\gamma$  is  $+\kappa$  or  $-\kappa$ , where the relativistic quantum number,  $\kappa = \pm(j + 1/2)$  as  $j = l \pm 1/2$ ,  $j$  is the total angular momentum quantum number, and  $l$  is the orbital angular momentum quantum number.

It is assumed that the many-electron atom can be separated into core, outer core, and valence spaces. The corresponding

wave function for this system is

$$\Psi = A[(\phi_1^c \phi_2^c \phi_3^c \dots \phi_1^c)(\phi_1^o \phi_2^o \phi_3^o \dots \phi_m^o)(\phi_1^v \phi_2^v \phi_3^v \dots \phi_n^v)] \quad (6)$$

where c, o, and v denote (inner) core, outer core, and valence, respectively.  $A$  is the antisymmetrization and normalization operator. It is noted that the set of core, outer core, and valence spinors are assured to be orthogonal to one another, i.e.

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad (7)$$

Each  $\phi_i$  of eq 6 may be represented by a linear combination of  $m$  basis functions that are normalized but nonorthogonal:<sup>12</sup>

$$\phi_i = \sum_p C_{pi} \chi_p \quad (8)$$

$$\langle \chi_p | \chi_p \rangle = 1 \quad (9)$$

Because the  $\chi_i$  are nonorthogonal, overlap integrals result:

$$\langle \chi_p | \chi_q \rangle = S_{pq} \quad (10)$$

Also, from eq 8 and eq 10 it is clear that

$$\langle \phi_i | \phi_j \rangle = \mathbf{C}_i^\dagger \mathbf{S} \mathbf{C}_j = \delta_{ij} \quad (11)$$

where  $\mathbf{C}_j$  is a column vector and  $\mathbf{S}$  is the overlap matrix. The corresponding Dirac Coulomb Hamiltonian for the system may be written

$$H^{\text{rel}} = \sum_c h_c + \sum_c \sum_{c'} 1/r_{cc'} + \sum_o h_o + \sum_o \sum_{o'} 1/r_{oo'} + \sum_c \sum_o 1/r_{co} + \sum_v h_v + \sum_v \sum_{v'} 1/r_{vv'} + \sum_c \sum_v 1/r_{cv} + \sum_o \sum_v 1/r_{ov} \quad (12)$$

where  $h_c$ ,  $h_o$ , and  $h_v$  have the same form as the  $h_D$  of eq 2 but operate only on core, outer core, and valence electrons, respectively, and  $h_v$  is the Schroedinger one-electron Hamiltonian operator.

The total energy is then given by

$$E_t = \langle \Psi | H^{\text{rel}} | \Psi \rangle = E_c + E_o + E_{co} + E_v + E_{cv} + E_{ov} \quad (13)$$

which is a sum of core, outer core, core/outer core, valence, core/valence, and outer core/valence energies. The first term in eq 13 is given by

$$E_{\text{core}} = \sum_c \langle \phi_c | h_c | \phi_c \rangle + \sum_c \sum_{c'} [J_{cc'} - K_{cc'}] \quad (14)$$

which is the standard form for a closed-shell determinantal wave function of singly occupied atomic spinors.<sup>15</sup> The  $J_{cc'}$  and  $K_{cc'}$  of eq 14 represent Coulomb and exchange energies,

respectively, involving only core electrons and are defined by

$$J_{cc'} = \langle \phi_c \phi_{c'} | 1/r_{12} | \phi_c \phi_{c'} \rangle \quad (15)$$

and

$$K_{cc'} = \langle \phi_c \phi_{c'} | 1/r_{12} | \phi_{c'} \phi_c \rangle \quad (16)$$

Terms two and three in eq 13 may be combined to yield

$$E_o + E_{co} = \sum_o \langle \phi_o | H^o | \phi_o \rangle \quad (17)$$

where

$$H^o = \sum_i \{h_o(i) + \sum_{o'} [J_{oo'}(i) - K_{oo'}(i)] + \sum_c [J_{co}(i) - K_{co}(i)]\} \quad (18)$$

Here,  $\phi_o$  is the set of outer core orbitals and  $H^o$  contains the one-electron and two-electron operators associated with the outer core electrons plus additional terms involving the sum over c, which represent the effects of the core on the outer core spinors. Consequently,  $H^o$  is defined such that it is that part of the Hamiltonian that operates only on the outer core portion of the total wave function of eq 6. In eq 18  $J_c$  and  $K_c$  are Coulomb and exchange operators, respectively.

The one-electron Coulomb operator  $J_{o'}$  and one-electron exchange operator  $K_{o'}$  both contain outer core orbitals (designated by  $o'$ ). Thus, the outer core energy is given by

$$E_o + E_{co} = \sum_o \langle \phi_o | h_o | \phi_o \rangle + \sum_o \sum_{o'} [J_{oo'} - K_{oo'}] + \sum_o \sum_c [J_{oc} - K_{oc}] \quad (19)$$

In eq 19  $J_{oo'}$  and  $K_{oo'}$  represent integrals formed when  $J_{o'}$  and  $K_{o'}$  operate on outer core orbitals. Also,  $J_{oc}$  and  $K_{oc}$  represent integrals formed when  $J_c$  and  $K_c$  operate on outer core orbitals. The remaining terms in eq 13 may be combined to yield

$$E_v + E_{cv} + E_{ov} = \sum_v \langle \phi_v | H^v | \phi_v \rangle \quad (20)$$

where

$$H^v = \sum_j \{h_v(j) + \sum_c [J_{cj}(j) - K_{cj}(j)] + \sum_o [J_{oj}(j) - K_{oj}(j)]\} + \sum_{j>j'} 1/r_{jj'} \quad (21)$$

Here,  $H^v$  includes the one-electron Hamiltonian for the valence electrons plus additional terms, the sums over c and o, that represent the effects of the core and outer core on the valence electrons. Therefore,  $H^v$  is defined such that it is that part of the Hamiltonian that operates only on the valence portion of the total wave function of eq 6. In eq 21  $J_c$ ,  $K_c$ ,  $J_o$ , and  $K_o$  are one-electron operators involving the core and outer core orbitals but operating only on the valence orbitals.

In both eq 18 and eq 21, the term  $\sum_c [J_c - K_c]$  can be replaced by a small-core relativistic effective potential  $U^{\text{REP}}$ .<sup>11</sup> In this case, the REP represents the interaction of the core

orbitals with the orbitals comprising the outer core (designated by  $U_i^{\text{REP}}$ ) and the valence (designated by  $U_{i'}^{\text{REP}}$ ). In addition, use of the REP necessarily dictates that all integrals associated with both one-electron and two-electron interactions among core electrons have been completely integrated. The resulting constant can be set equal to zero. Thus, no terms specifically involving core electrons appear in eq 22. The use of such an REP to represent these interactions is well understood.<sup>2</sup> The energy of the outer core and valence electrons relative to the energy of the core may then be expressed by

$$E = \left\{ \sum_i [U_i^{\text{REP}} + H_i] + \sum_{ij} (J_{ij} - K_{ij}) \right\} + \left\{ \sum_{i'} [U_{i'}^{\text{REP}} + H_{i'}] + \sum_{i'j'} (J_{i'j'} - K_{i'j'}) \right\} + \left\{ \sum_{i'j} (J_{i'j} - K_{i'j}) \right\} \quad (22)$$

Here,  $i$  and  $j$  index outer core electrons while  $i'$  and  $j'$  index valence electrons. Since no interactions in eq 22 involving core electrons appear explicitly due to the presence of the  $U^{\text{REP}}$  terms, the notation may be simplified such that the remaining subscripts are replaced by  $i$  and  $j$ , as explained previously. In eq 22 the one-electron energies  $H_i$  and  $H_{i'}$ , the pseudopotential integrals  $U_i^{\text{REP}}$  and  $U_{i'}^{\text{REP}}$ , the Coulomb integrals  $J_{ij}$ ,  $J_{i'j'}$ , and  $J_{i'j}$ , and the exchange integrals  $K_{ij}$ ,  $K_{i'j'}$ , and  $K_{i'j}$  are defined by

$$H_i = H_i^* = \langle \phi_i | h_i | \phi_i \rangle \quad (23)$$

similarly for  $H_{i'}$

$$U_i^{\text{REP}} = U_i^{\text{REP}*} = \langle \phi_i | U_i^{\text{REP}} | \phi_i \rangle \quad (24)$$

similarly for  $U_{i'}^{\text{REP}}$

$$J_{ij} = J_{ji} = J_{ij}^* = J_{ji}^* = \langle \phi_i \phi_j | 1/r_{12} | \phi_i \phi_j \rangle \quad (25)$$

similarly for  $J_{i'j'}$  and  $J_{i'j}$ , and, finally

$$K_{ij} = K_{ji} = K_{ij}^* = K_{ji}^* = \langle \phi_i \phi_j | 1/r_{12} | \phi_j \phi_i \rangle \quad (26)$$

and similarly for  $K_{i'j'}$  and  $K_{i'j}$ , where  $*$  denotes the complex conjugate. When each atomic spinor is varied by an infinitesimal amount, the variation of the energy<sup>12</sup> becomes

$$\delta E = \left\{ 2 \sum_i [\delta U_i^{\text{REP}} + \delta H_i] + \sum_{ij} (2\delta J_{ij} - \delta K_{ij}) \right\} + \left\{ 2 \sum_{i'} [\delta U_{i'}^{\text{REP}} + \delta H_{i'}] + \sum_{i'j'} (2\delta J_{i'j'} - \delta K_{i'j'}) \right\} + \left\{ \sum_{i'j} (2\delta J_{i'j} - \delta K_{i'j}) \right\} \quad (27)$$

In eq 27 variation of the atomic spinors is analogous to a variation of the outer core and valence spinors, both of which are expressed as linear combinations of basis functions, as defined in eq 8. The variation is carried out analogously to that of Roothaan.<sup>12</sup> Making use of the Hermitian properties

of the operators  $H_i$  and  $J_i$  and  $K_i$  yields

$$\begin{aligned} \delta E = & \left\{ 2 \sum_i (\delta C_i^\dagger) [U_i^{\text{REP}} + H_i^o + \sum_j (J_j - K_j)] C_i + \right. \\ & 2 \sum_i (\delta C_i^T) [U_i^{*\text{REP}} + H_i^{*o} + \sum_j (J_j^* - K_j^*)] C_i^* \left. + \right. \\ & \left\{ 2 \sum_{i'} (\delta C_{i'}^\dagger) [U_{i'}^{\text{REP}} + H_{i'}^v + \sum_{j'} (J_{j'} - K_{j'})] C_{i'} + \right. \\ & 2 \sum_{i'} (\delta C_{i'}^T) [U_{i'}^{*\text{REP}} + H_{i'}^{*v} + \sum_{j'} (J_{j'}^* - K_{j'}^*)] C_{i'}^* \left. + \right. \\ & \left. \left\{ 2 \sum_{i'j} [(\delta C_{i'}^\dagger)(J_j - K_j) C_{i'} + (\delta C_{i'}^T)(J_j^* - K_j^*)(C_{i'}^*)] \right\} \right\} \quad (28) \end{aligned}$$

where  $\dagger$ ,  $*$ , and  $T$  correspond to the Hermitian conjugate, the complex conjugate, and the transpose of  $C_i$ , respectively. Now, the following are defined:

$$F^{\text{RPP}} = [U_i^{\text{REP}} + H_i^o + \sum_j (J_j - K_j)] \quad (29)$$

where  $F^{\text{RPP}}$  corresponds to the outer core region, and

$$F'^{\text{RPP}} = [U_{i'}^{\text{REP}} + H_{i'}^v + \sum_{j'} (J_{j'} - K_{j'})] \quad (30)$$

where  $F'^{\text{RPP}}$  corresponds to the valence region. Equation 29 involves only the outer core spinors. The interaction of the core spinors with the outer core spinors is contained in  $U_i^{\text{REP}}$ . Also, the interaction of the core spinors with the valence spinors is contained in  $U_{i'}^{\text{REP}}$ . As stated previously, the interactions among core spinors have been integrated out. Consequently, no core spinors are explicitly contained in eqs 29 and 30. The interactions among outer core spinors are associated with the  $H_i^o + \sum_j (J_j - K_j)$  terms of eq 29. Analogously, the interactions among the valence spinors are associated with the  $H_{i'}^v + \sum_{j'} (J_{j'} - K_{j'})$  terms of eq 30.

Substitution of eqs 29 and 30 into eq 28 leads to

$$\begin{aligned} \delta E = & \left\{ 2 \sum_i (\delta C_i^\dagger) F^{\text{RPP}}(C_i) + 2 \sum_i (\delta C_i^T) F^{*\text{RPP}}(C_i^*) \right\} + \\ & \left\{ 2 \sum_{i'} (\delta C_{i'}^\dagger) F'^{\text{RPP}}(C_{i'}) + 2 \sum_{i'} (\delta C_{i'}^T) F'^{* \text{RPP}}(C_{i'}^*) \right\} + \\ & \left\{ 2 \sum_{i'j} [(\delta C_{i'}^\dagger)(J_j - K_j)(C_{i'}) + (\delta C_{i'}^T)(J_j^* - K_j^*)(C_{i'}^*)] \right\} \quad (31) \end{aligned}$$

where the first line of eq 31 contains terms associated with the outer core interactions, the second line contains terms associated with the valence interactions, and the third line contains terms associated with the interactions between the outer core and valence spaces.

Since, as stated above, variation of the spinors is carried out analogously to that of Roothaan,<sup>12</sup> a set of restricting conditions are imposed, and these are multiplied by a set of Lagrangian multipliers that are part of a Hermitian matrix. When the resulting variations are added to the variation of the energy,  $\delta C_i^\dagger$  and  $\delta C_i^T$  are factored out, and like terms are combined, the conditions  $\delta E = 0$  for any variation of



the vectors  $\delta C_i$  and  $\delta C_i^*$ ,  $\delta C_i^\dagger$ , and  $\delta C_i^T$  are given by the following two equations:

$$F^{\text{RPP}}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon \quad (32)$$

and

$$(F^{\text{RPP}} + (J_j - K_j))\mathbf{C}'' = \mathbf{S}''\mathbf{C}''\epsilon'' + \mathbf{S}'\mathbf{C}'\epsilon' \quad (33)$$

Equation 32 is related to the first line of eq 31 and is associated with that part of the Fock matrix containing interactions among the outer core electrons. It is also associated with the interactions between the core and outercore electrons via the  $U_i^{\text{REP}}$  operator imbedded in  $F^{\text{RPP}}$ . Here,  $\mathbf{C}$  is the outer core eigenvector matrix,  $\mathbf{S}$  is the outercore overlap matrix, and  $\epsilon$  is the outercore eigenvalue matrix. Similarly, eq 33 is related to the second and third lines of eq 31 and is associated with that part of the Fock matrix containing interactions among the valence electrons. It is also associated with the interactions between the core and valence electrons via the  $U_i^{\text{REP}}$  operator imbedded in  $F^{\text{RPP}}$  and with the interactions between the outer core and valence electrons via the  $J_j$  and  $K_j$  operators. Here,  $\mathbf{C}''$  is the valence eigenvector matrix,  $\mathbf{S}''$  is the valence overlap matrix, and  $\epsilon''$  is the valence eigenvalue matrix. The last term of eq 33 results from the exchange operator  $K_j$  and is associated with the outer core/valence interactions. The  $\epsilon'$  matrix here contains the off-diagonal Lagrange multipliers associated with the valence and the outer core.

The  $l$ th element of the  $J_j$  and  $K_j$  of eq 33 may be written as one-electron operators

$$J_l\phi_{i'} = \langle \phi_j | 1/r_{12} | \phi_j \rangle \phi_{i'} \quad (34)$$

where  $\phi_j$  may be expressed as a linear combination of basis functions as shown by eq 8. Keeping in mind eqs 7–10, eq 34 may be expressed as

$$J_l\phi_{i'} = \left( \sum_p C_{jp}^* \sum_q C_{jq} \right) J_{pq}\phi_{i'} \quad (35)$$

where

$$J_{pq}\phi_{i'} = \langle \chi_p | 1/r_{12} | \chi_q \rangle \phi_{i'} \quad (36)$$

Similarly

$$K_l\phi_{i'} = \left( \sum_p C_{jp}^* \sum_q C_{jq} \right) K_{pq}\phi_{i'} \quad (37)$$

where

$$K_{pq}\phi_{i'} = \langle \chi_p | 1/r_{12} | \phi_i \rangle \chi_q \quad (38)$$

From eqs 34–38, it follows that

$$(J_l - K_l) = \left( \sum_p C_{jp}^* \sum_q C_{jq} \right) (J_{pq} - K_{pq}) \quad (39)$$

Consequently, it is clear from eqs 34–39 that eq 33 may be written as

$$[(F^{\text{RPP}} + C^*C(J_l - K_l))\mathbf{C}'' = \mathbf{S}''\mathbf{C}''\epsilon'' + \mathbf{S}'\mathbf{C}'\epsilon' \quad (40)$$

where  $\mathbf{C}$  is the matrix of outer core eigenvectors, which also

appears in eq 32, and  $J_l$  and  $K_l$  contain the complete set of Coulomb and exchange operators, each of which is defined by either eqs 35 and 36 or eqs 37 and 38.

The ultimate goal of this derivation is to define a pseudopotential for use in atomic and molecular calculations in which only the valence electrons are treated explicitly, thus negating the necessity to include core and outer core spinors into the calculations. This can be accomplished analogously to the REP theory of Lee/Ermiler/Pitzer<sup>2</sup> by back-solving eq 40 for the term  $C^*C(J_l - K_l)$ , which describes the interactions between the outer core and valence spaces. However, the exchange operator of eq 40 does not allow the exclusion of outer core spinors because  $K_l$  exchanges an outer core spinor for a valence one—as given by eq 38. This can be addressed by defining a set of pseudovalence spinors  $\mathbf{C}_{\text{pv}}''$  such that the end result of operating on  $\mathbf{C}_{\text{pv}}''$  with  $K_l$  does not include the introduction of outer core spinors into the valence region. In other words, the orthogonality between the outer core and valence spinors must be removed. This may be accomplished by removing any nodes present in the valence spinor. However, the number of nodes in the set of eigenvectors comprising  $\mathbf{C}''$  of eq 40 have been eliminated in many cases and reduced to one in all others because the small core REP is imbedded in  $F^{\text{RPP}}$ . (Refer to eqs 29 and 30.) Removal of the remaining node is accomplished using the nodeless valence method of Ermiler and Marino.<sup>11</sup>

The nodeless valence method removes the orthogonality between the outer core and valence spinors as follows: a valence eigenvector that is orthogonal to an outer core eigenvector will contain coefficients corresponding to outer core basis functions. The orthogonality between the valence and outer core spinors is removed by setting these coefficients to zero. Once rendered nodeless, both eigenvectors are then self-consistently optimized with the restriction that they remain nodeless, i.e., nonorthogonal. It is this set of optimized nodeless valence eigenvectors that comprises  $\mathbf{C}_{\text{pv}}''$ . Since  $\mathbf{C}_{\text{pv}}''$  is orthogonal to the outer core eigenvectors, substitution of  $\mathbf{C}_{\text{pv}}''$  for  $\mathbf{C}''$  in eq 40 results in the removal of the second term on the right-hand side of the equation. In other words, the exchange operator  $K_l$  cannot project out an outer core spinor due to the form of  $\mathbf{C}_{\text{pv}}''$ . (For a more detailed description of the nodeless valence method, the reader is referred to the article by Ermiler and Marino in this journal.<sup>11</sup>) Substitution of  $\mathbf{C}_{\text{pv}}''$  for  $\mathbf{C}''$  in eq 40 yields

$$[(F^{\text{RPP}} + C^*C(J_l - K_l))\mathbf{C}_{\text{pv}}'' = \mathbf{S}''\mathbf{C}_{\text{pv}}''\epsilon'' \quad (41)$$

which can also be written as

$$[F^{\text{RPP}} + C^*CU^{\text{RPP}}]\mathbf{C}_{\text{pv}}'' = \mathbf{S}''\mathbf{C}_{\text{pv}}''\epsilon'' \quad (42)$$

where  $C^*CU^{\text{RPP}}$  is that part of the pseudopotential that represents both the outer core/valence interactions and, through  $\mathbf{C}_{\text{pv}}''$ , the outer core/valence orthogonality operator. Equation 42 can now be back-solved for  $CU^{\text{RPP}}$  as follows:

$$C^*CU^{\text{RPP}} = \mathbf{S}''\epsilon'' - F^{\text{RPP}}\mathbf{C}_{\text{pv}}''/\mathbf{C}_{\text{pv}}'' \quad (43)$$

The complete pseudopotential contains an outer core term given by eq 32, which is the solution to the outer core region of the atom. It also contains the  $C^*CU^{\text{RPP}}$  of eq 43,

a one-electron operator that operates on the valence spinors of the molecule. This form now allows outer core spinor relaxation via the participation of the outer core eigenvector matrixes,  $\mathbf{C}$  in eq 32 and  $\mathbf{C}^*\mathbf{C}$  in eq 43, in the SCF procedure; i.e., both the outer core and valence eigenvectors are involved in the self-consistent optimization of the total energy. It is noted, however, that although both spaces participate in the SCF procedure, they must remain distinct from one another during optimization because the final valence wave function cannot contain coefficients corresponding to outer core spinors and vice versa. Use of the RPP in atomic and in molecular calculations will be discussed in detail in sections III and IV, respectively.

Analogously to the Lee/Ermiler/Pitzer REP method<sup>2</sup>,  $\mathbf{C}^*\mathbf{C}U^{\text{RPP}}$  may be expressed as products of angular projection operators and radial functions:

$$C_{lj}U_{lj}^{\text{RPP}} = \sum_{l=0}^{\infty} \sum_{j=l+1/2}^{l+1/2} \sum_j^{m=-j} C_{lj}^*U_{lj}^{\text{RPP}}(r)|ljm\rangle\langle lj m| \quad (44)$$

In eq 44 the indices  $lj$  may be replaced by  $\kappa$ , the relativistic quantum number (refer to the definitions given below eq 5), because orbitals with different total angular momenta  $j$  but with the same orbital angular momentum  $l$  are nondegenerate in Dirac–Fock theory. Also,  $|ljm\rangle$  and  $\langle lj m|$  are two-component angular bases that are eigenfunctions of the Dirac Hamiltonian (refer to eqs 1, 2, and 12).

### III. THE RELATIVISTIC PSEUDOPOTENTIAL IN ATOMIC CALCULATIONS

The development of a pseudopotential is necessary because of the inability of currently available relativistic effective potentials to describe the outer core region of atoms properly and thus account for core/valence correlation effects in both atomic and molecular environments. These errors arise from the fact that REPs constrain the outer core orbitals to remain those of the ground-state atom, thereby preventing outer core relaxation and polarization upon valence electron excitation, ionization, and bonding. Since the degree of correlation and polarization is dependent on molecular environment, only a molecule-specific REP would account for these effects. Clearly, it is not practical to derive such a REP. The RPP, on the other hand, responds in each molecular environment through coefficients that are self-consistently determined and is therefore capable of properly describing outer core relaxation and polarization in atoms and molecules. Before discussing in detail the process by which the RPP is used in molecular calculations, it is important to describe the Fock matrix ( $\mathbf{F}$ ) in an all-electron calculation and in a REP calculation.

Let us assume that the electrons in an atom could be “frozen” at a given point in time and then labeled *core*, *outer core*, and *valence*, depending on their locations within the atom. Once tagged, the electrons are then “unfrozen” and allowed to interact as they normally would. (It is noted that the “labels” do not indicate the presence of either a pseudopotential or pseudopotential; they are merely a name given to each electron indicating its position at the moment that all motion was frozen.) The all-electron  $\mathbf{F}$  matrix for such an atom would contain the following interactions:

core/core interactions	core/outer core interactions	core/valence interactions
core/outer core interactions	outer core/outer core interactions	outer core/valence interactions
core/valence interactions	outer core/valence interactions	valence/valence interactions

REP calculations assume the existence of only two spaces: the core region and the valence region. The outer core region, therefore, is made either part of the core or part of the valence space. In both cases, the  $\mathbf{F}$  matrix has the following form:

0	0	0
0	0	0
0	0	valence/valence interactions

The core/core interactions are integrated out of the calculation, and the core energy is calculated to be a constant, independent of molecular geometry, which is set equal to zero. All core/valence interactions are represented by the REP, a one-electron operator which is present in that part of the  $\mathbf{F}$  matrix containing the valence/valence interactions.<sup>16</sup> Therefore, solution of the Hartree–Fock–Roothaan or Dirac–Fock–Roothaan equations in this case involves diagonalization of the block containing the valence/valence interactions.

RPP calculations, on the other hand, assume the existence of three spaces: core, outer core, and valence. Consequently, the  $\mathbf{F}$  matrix in a calculation containing a RPP has the following form:

0	0	0
0	outer core/outer core interactions	0
0	0	valence/valence interactions

As in a REP calculation, the core/core interactions are integrated out, and the core energy is calculated to be a constant, independent of molecular geometry, which is set equal to zero. All core/valence and outer core/valence interactions are represented by one-electron operators (refer to eqs 43 and 44), which are present in that part of the  $\mathbf{F}$  matrix containing the valence/valence interactions.

The outer core/outer core block corresponds to the  $F^{\text{RPP}}$  of eq 32 and contains both intraatomic outer core/outer core and intraatomic core/outer core interactions, the latter of which are included via the REP present in the  $F^{\text{RPP}}$  (see eq 29). Solution of the Hartree–Fock–Roothaan or Dirac–Fock–Roothaan equations in this case involves diagonalization of both the block containing the valence/valence interactions and that containing the outer core/outer core interactions. Although both of these blocks make up the  $\mathbf{F}$  matrix and are mathematically treated in the same manner, they are very different chemically and physically. The valence/valence interaction block, as the name implies, deals

only with valence electrons, the energy of which varies considerably depending on whether the **F** matrix in question corresponds to the ground-state atom or to one of a multitude of possible excited states (including Rydberg states and higher energy states corresponding to the ions of said atom). Because of the wide degree of variability that characterizes valence electronic motion, it is necessary to use a wide variety of basis functions to describe the valence electrons. Thus the basis functions contained in the valence/valence interaction block need to be changed depending on the atomic electronic state in which the atom finds itself. The block containing these interactions will therefore be different for different atomic electronic states. Alternatively, a basis set large enough to define the full range of electronic motion may be used; however, such a basis set can be so large as to render the calculations intractable, especially those including electron correlation.

The intraatomic outer core/outer core interaction block, on the other hand, corresponds only to the outer core electronic energy. Since the motion of an outer core electron is much more limited than that of a valence electron, a much smaller number of states are involved. Thus, this block could comprise an **F** matrix that corresponds to a ground-state atom or to one of a variety of excited states. In this case, however, the highest energy state would be that in which the outer core is polarized to its maximum degree. By definition, no higher-order excitations or ionizations are possible in this region. Such higher-energy electronic states are confined solely to the valence area. It is emphasized that outer core electrons themselves do not participate directly in excitations. However, these electrons polarize as a response to excitations involving the valence electrons. Because the number of electronic states associated with the outer core region is much smaller than the number associated with the valence one, the number of basis functions needed to describe the outer core electrons is also much smaller than that needed to describe the valence electrons. It is possible, then, to use a basis set large enough to describe the full range of outer core electronic motion and still maintain tractability even for correlated calculations. The **F**<sup>RPP</sup> of eq 32, which corresponds to the outer core of the atom in question, is thus the same regardless of the electronic state to which the total **F** matrix corresponds. The outer core energy, however, is not a constant despite the fact that the same basis functions are always present because the corresponding eigenvector matrix is allowed to change via the SCF step. In other words, the **F**<sup>RPP</sup> of eq 32 remains the same for every atomic (neutral and ionic) electronic state, but its corresponding eigenvector matrix **C** does not, and consequently, there is one corresponding outer core energy for every electronic state of the atom. The total energy of the system therefore reflects changes not only in the valence region but also in the outer core. Put more succinctly, the outer core spinors are allowed to relax in the presence of valence electron participation in bonding, excitation, and so forth, but the outer core electrons themselves, by definition, do not participate directly in these processes. The outer core region merely polarizes. The extent of the polarization corresponds to the type of process in which the valence electrons are involved. This is in sharp contrast to REP calculations, where only changes in the valence region affect the total energy. Energy changes caused by polarization of outer core orbitals can be calculated only

by using REPs if this region is labeled “valence”. Labeling it as such, however, requires incorporation of outer core basis functions into the calculation, which would dramatically increase the number of configurations required in a correlated calculation.

In an atomic RPP calculation, the all-electron Hamiltonian of eq 12 is replaced by the following: the Fock equation for the outer core, eq 32, and by the valence Hamiltonian, which is now given by

$$H^{\text{rel}} = \sum_v [h_v + C^*CU^{\text{RPP}}] + \sum_v \sum_{v'} 1/r_{vv'} \quad (45)$$

Terms three, four, and five on the right-hand side (rhs) of eq 12 are replaced by eq 32, while terms eight and nine on the rhs of eq 12 are replaced by the  $C^*CU^{\text{RPP}}$  of eqs 43 and 45. Terms six and seven on the rhs of eq 12 remain the same and are represented by the  $C^*CU^{\text{RPP}}$  term contained in eq 45. The first and second terms on the rhs of eq 12 have been indirectly incorporated via the REP, which is present in both eqs 32 and 45. (The reader is reminded that the REP is contained in eq 32 via  $F^{\text{RPP}}$  [refer to eq 29] and in eq 45 via  $U^{\text{RPP}}$ , which contains the  $F^{\text{RPP}}$  that has the  $U^{\text{REP}}$  imbedded within it [refer to eqs 43 and 30].) Equation 45 defines an operator that operates over the valence spinors to yield ultimately the valence Fock equation. On the other hand, eq 32 is the Fock equation over the outer core spinors. Once the valence Fock equation is generated, the total energy can be optimized self-consistently by varying the outer core eigenvectors constituting the matrix **C** of eq 32 and both the outer core and valence eigenvectors of the valence Fock equation. Optimization of the total energy yields a new Fock equation for the outer core because the resulting eigenvector matrix **C** will be different from the initial one. Therefore, a new eq 32 will be generated for every system treated, as well as for every state of a particular system. Since **C** also appears in eq 45, a new valence Hamiltonian will also be defined. The final form of the total pseudopotential, given by eqs 32 and 43 (the latter as contained in eq 45), is consequently generated at runtime. It is therefore a functional rather than a function, thus the name *pseudopotential* as opposed to *pseudopotential*.

One more point needs to be made: restrictions are imposed on the SCF procedure for calculations using RPPs. This is best explained by comparing the final wave function in an all-electron calculation and the final wave function in a small-core REP calculation to the final wave function generated in the presence of a RPP. In the first case, the final wave function extends over the entire molecule. Consequently, it contains contributions from all of the basis functions: core, outer core, and valence. In the second case, the outer core is treated explicitly as part of the valence space. The final wave function thus contains contributions from all of the valence basis functions, which includes those corresponding to the outer core region. In an RPP calculation, the outer core region is kept separate from the valence region. This prevents outer core “electron leakage” into the valence region. Each space is optimized in the presence of the other, but the spaces are not allowed to mix. This results in a valence wave function that contains contributions from basis functions corresponding solely to the valence region and in an outer core wave function that contains contributions solely from the outer core

region. This is equivalent to stating that the matrix of valence eigenvectors (which arises once the valence Fock equation is generated using the valence operator of eq 45) and the matrix of outer core eigenvectors  $\mathbf{C}$  are varied as distinct blocks, with no off-diagonal elements that connect the two spaces appearing in the total wave function. The effects of these off-diagonal elements are taken into account via the RPP (refer to the discussion corresponding to  $\mathbf{C}_{pv}''$  of eq 41).

#### IV. THE RELATIVISTIC PSEUDOPOTENTIAL IN MOLECULAR CALCULATIONS

Now, let us look at the RPP in a molecular calculation. The Hamiltonian of eq 12 corresponds to an atom. For molecules,  $H^{\text{rel}}$  becomes

$$H^{\text{rel}} = \sum_{\mathbf{c}} h_{\mathbf{c}} + \sum_{\mathbf{c}} \sum_{\mathbf{c}'} 1/r_{\mathbf{cc}'} + \sum_{\mathbf{o}} h_{\mathbf{o}} + \sum_{\mathbf{o}} \sum_{\mathbf{o}'} 1/r_{\mathbf{oo}'} + \sum_{\mathbf{c}} \sum_{\mathbf{o}} 1/r_{\mathbf{co}} + \sum_{\mathbf{v}} h_{\mathbf{v}} + \sum_{\mathbf{v}} \sum_{\mathbf{v}'} 1/r_{\mathbf{vv}'} + \sum_{\mathbf{c}} \sum_{\mathbf{v}} 1/r_{\mathbf{cv}} + \sum_{\mathbf{o}} \sum_{\mathbf{v}} 1/r_{\mathbf{ov}} + \sum_{\alpha} \sum_{\beta} Z_{\alpha} Z_{\beta} / r_{\alpha\beta} \quad (46)$$

where

$$h_{\mathbf{v}} = -1/2 \nabla_{\mathbf{v}}^2 - \sum_{\alpha} Z_{\alpha} / r_{\mathbf{iv}} \quad (47)$$

and  $h_{\mathbf{c}}$  and  $h_{\mathbf{o}}$  have the same form as  $h_{\mathbf{D}}$  in eq 2.  $Z_{\alpha}$  is the effective nuclear charge on atom  $\alpha$ , and  $r_{\alpha\beta}$  is the internuclear distance between atoms  $\alpha$  and  $\beta$ . The total energy is then given by

$$E_{\text{t}}^{\text{R}} = \langle \Psi^{\text{r}} | H^{\text{rel}} | \Psi^{\text{r}} \rangle = E_{\mathbf{c}}^{\text{R}} + E_{\mathbf{o}}^{\text{R}} + E_{\mathbf{co}}^{\text{R}} + E_{\mathbf{v}}^{\text{R}} + E_{\mathbf{cv}}^{\text{R}} + E_{\mathbf{ov}}^{\text{R}} + E_{\alpha\beta}^{\text{R}} \quad (48)$$

which is a sum of core, outer core, core/outer core, valence, core/valence, and outer core/valence interaction energies plus the nuclear repulsion energy. The first term on the right-hand side of eq 48 is a constant if the core region of each atom is not perturbed relative to the molecule. This, of course, is assumed to be the case. In the REP method, this constant is set equal to 0. Analogously for the RPP method, the core energy will be set equal to 0. The second and third terms on the right-hand side of eq 48 do not involve valence electrons. These terms are analogous to terms three, four, and five on the right-hand side of the Hamiltonian of eq 12 and are thus associated with the same type of interactions, but for the atom. For the molecule, these energies arise by operating on outer core basis functions with the operators shown in terms three, four, and five on the right-hand side of eq 46. Tagging the terms in eq 46 such that their atomic parentage is clearly understood yields

$$\sum_{\mathbf{o}} h_{\mathbf{o}}^{\alpha} + \sum_{\mathbf{o}} \sum_{\mathbf{o}'} 1/r_{\mathbf{oo}'}^{\alpha\alpha} + \sum_{\mathbf{c}} \sum_{\mathbf{o}} 1/r_{\mathbf{co}}^{\alpha\alpha} \quad (49)$$

where the unconventional use of the superscript  $\alpha$  denotes the atom from which the electrons originated. As labeled, the operators of eq 49 operate only on basis functions centered on atom  $\alpha$ . Interactions between electrons on different centers are not considered in eq 49. Because the pseudopotential is calculated from the atom, it is important

to the derivation that a distinction be made between inter-center and intracenter interactions. The benefits of this labeling scheme will be shown later.

When the operators of eq 49 operate on the basis functions centered on atom  $\alpha$ , the following equation results:

$$F_{\alpha}^{\text{RPP}} C_{\alpha} = S_{\alpha} C_{\alpha} \epsilon_{\alpha} \quad (50)$$

Equation 50 corresponds to intraatomic (for atom  $\alpha$ ) outer core/outer core interactions in a molecule and is analogous to eq 32, which corresponds to atomic outer core/outer core interactions.

For a heteronuclear diatomic molecule, which will now be used as an illustration, the Hamiltonian terms associated with the electrons on the second center,  $\beta$ , are

$$\sum_{\mathbf{o}} h_{\mathbf{o}}^{\beta} + \sum_{\mathbf{o}} \sum_{\mathbf{o}'} 1/r_{\mathbf{oo}'}^{\beta\beta} + \sum_{\mathbf{c}} \sum_{\mathbf{o}} 1/r_{\mathbf{co}}^{\beta\beta} \quad (51)$$

The terms in eq 51 are associated with the following variant of eq 50:

$$F_{\beta}^{\text{RPP}} C_{\beta} = S_{\beta} C_{\beta} \epsilon_{\beta} \quad (52)$$

For  $N$  noninteracting atoms,  $N$  equations of this type would result:

$$\begin{aligned} F_{\alpha}^{\text{RPP}} C_{\alpha} &= S_{\alpha} C_{\alpha} \epsilon_{\alpha} \\ F_{\beta}^{\text{RPP}} C_{\beta} &= S_{\beta} C_{\beta} \epsilon_{\beta} \\ &\vdots \\ F_N^{\text{RPP}} C_N &= S_N C_N \epsilon_N \end{aligned} \quad (53)$$

In the case of a heteronuclear diatomic molecule, the two-electron operators corresponding to the interaction between electrons on different centers are

$$\sum_{\mathbf{o}} \sum_{\mathbf{o}'} 1/r_{\mathbf{oo}'}^{\alpha\beta} + \sum_{\mathbf{c}} \sum_{\mathbf{o}} 1/r_{\mathbf{co}}^{\alpha\beta} \quad (54)$$

For an  $N$ -atom system,  $N(N-1)/2$  relations of this type result.

The matrix equations in eq 53 must be solved simultaneously by representing them as part of a larger matrix, the molecular Fock matrix, which has the following form for an  $N$ -atom molecule (relative to an all-electron  $\mathbf{F}$  matrix):

0	0	0	0
0	outer core/outer core interactions for atom $\alpha$ ...	0	0
.	.	.	.
.	.	.	.
.	.	.	.
0	0	outer core/outer core interactions for atom $N$	0
0	0	0	valence/valence interactions

**Matrix A**

As in a REP calculation, the core/core interactions are integrated out and the core energy is calculated to be a constant, which is set equal to zero. All core/outer core interactions within a center are represented by  $N$  atom-



specific RPPs, each of which is present along the diagonal of the molecular **F** matrix (see eq 53, and also eqs 32 and 29).

Outer core/outer core interactions among centers are more difficult to calculate directly because the RPP is generated for the atom and these interactions are molecular. However, it is possible to calculate these interactions very accurately because the intercenter Coulomb and exchange integrals can be easily generated from the outer core basis functions that are already contained in the calculation via eq 53. Consequently, all of the necessary two-electron integrals can be constructed for all known interatomic distances of the system with the exception of the two-electron exchange integrals that involve both outer core and valence spinors. No integrals of this type can be included as a consequence of the outer core–valence orthogonality operator that is contained in  $U^{\text{RPP}}$ . (Refer to eq 42 and accompanying discussion.) In other words, the outer core and valence regions must remain distinct from one another. All interactions between the two are incorporated into  $U^{\text{RPP}}$ , a one-electron operator that operates only on the valence spinors. Therefore, the RPP results in a very significant reduction in the total number of integrals and thus in the level of complexity. Inclusion of these off-diagonal terms into the above matrix yields the following.

0	0	0	0
0	outer core/outer core interactions for atom $\alpha$ ...	interactions between (outer core) $\alpha$ /(outer core) $N$	0
.	.	.	.
.	.	.	.
0	interactions between (outer core) $N$ /(outer core) $\alpha$ ...	outer core/outer core interactions for atom $N$	0
0	0	0	valence/valence interactions

**Matrix B**

At this point, the Fock matrix has been completed; however, the eigenvector matrix associated with it, the molecular eigenvector matrix, still does not contain the off-diagonal elements because the only solutions calculated to date correspond to the individual atoms. The molecular Fock matrix therefore corresponds to matrix B, while the molecular eigenvector matrix (at least at this point) corresponds to matrix A. In other words, the integrals corresponding to the interatomic interactions are present, but the coefficients associated with the basis functions in these integrals are zero. This molecular eigenvector is used as the initial guess: the initial set of coefficients that will be varied self-consistently to find the lowest energy of the system. The variation of these coefficients is carried out with the restriction that no resulting eigenvector contain coefficients associated with both outer core and valence spinors; that is, all of the coefficients in the resulting eigenvectors must correspond either to the valence basis functions or to the outer core basis functions. Thus these two blocks remain diagonal because of the restriction imposed on the variation. This results in the calculation of two molecular eigenvectors, one for the outer core space and one for the valence space, and these two are connected via the  $U^{\text{RPP}}$ . (Note that both eqs 32 and 43 contain **C**, the matrix of outer core eigenvectors.) Once the self-consistent variation is completed, the resulting outer core/outer core interaction blocks will be associated with sets of

eigenvectors that are different from the sets at the start of the calculation. In other words, each block will correspond to a relaxed, or polarized, outer core for each atom comprising the molecule.

## V. THE RELATIVISTIC PSEUDOPOTENTIAL AND VERY LARGE SYSTEMS

The RPP method assumes that the outer core electrons exhibit behavior that is more closely associated with the atom-like core spinors than with the molecular-like valence spinors (hence the label of *outer core* rather than of *inner valence*). Therefore, as previously stated, the perturbations to the outer core resulting from bond formation propagate to the outer core region from the valence space. In other words, when the valence space is altered during bonding, these changes are propagated to the outer core via the valence/outer core interaction terms, which cause the outer core space to polarize. However, these changes (i.e., the degree of polarization) never exceed the maximum degree of polarization of which the atom is capable. Thus, this behavior is rooted in the atomic nature of the atoms comprising the molecule rather than in the actual molecular nature of the system. If the outer core electrons are truly more corelike than valencelike, the interaction energies associated with the operators of eqs 49, 51, and 54 are equal to terms that represent the polarization of the outer core space arising from the interaction of valence electrons (without regard to a specific center of origin) and propagation of the effects of these interactions into the outer core region of each atom comprising the molecule. Therefore, the outer core/outer core interactions can be approximated accurately by assuming that each polarized atomic outer core represents a “charge” and that each of these “charges” can interact with all of the other “charges” comprising the outer core portion of the molecule. In other words, the intercenter outer core/outer core interaction energy can be calculated from the following set of integrals:

$$\langle \phi_\alpha \phi_\beta | 1/r_{12} | \phi_\alpha \phi_\beta \rangle \quad (55)$$

which are the two-center Coulomb integrals. These are analogous to integrating over the electronic charge distributions:

$$\int |\phi_\alpha|^2 |\phi_\beta|^2 (1/r_{12}) d\tau_\alpha d\tau_\beta \quad (56)$$

where  $\alpha$  and  $\beta$  represent the two centers and  $r_{12}$  is the distance between electron 1 on center  $\alpha$  and electron 2 on center  $\beta$ . (Note: eqs 55 and 56 are written in terms of spinors, but it is straightforward to rewrite these in terms of basis functions using eqs 8 and 9.)

By definition the electrons labeled *outer core* are restricted to reside in the outer core region; that is, no outer core electron is allowed to excite into the valence space. (If this type of excitation occurred in significant numbers, these electrons would have to be relabeled *valence*.) Also, the maximum polarization allowed in the outer core region of a given atom is dictated by its atomic polarizability. Consequently, the outer core spinors are expected to be significantly tighter than the valence ones. Moreover,  $r_{12}$  is, of course, larger when the electrons are on different centers. These two facts lead to the following approximation: all two-electron

integrals involving only outer core orbitals and not of the type given by eq 56 are assumed to make only small contributions to the total energy and may thus be omitted from the calculation. This results in a great reduction in complexity and would be a highly compelling option in cases where very heavy elements and/or very large systems (e.g., clusters, surfaces) are to be treated.

The pseudopotential method is therefore a highly flexible type of pseudopotential, allowing a range of inter-center two-electron interactions to be incorporated into the calculation via the off-diagonal elements of the molecular Fock matrix (matrix B). The treatment of very large systems would require only those integrals given by eq 56. Although this is expected to be a good approximation in general, it is always possible to encounter systems for which an accurate description of the outer core electronic structure would require the inclusion of additional Coulomb—and exchange—interactions, for example, systems having highly polarized outer cores and small interatomic distances. In these cases, all of the two-electron integrals (with the exceptions of those already noted in section IV) can be included in the molecular Fock matrix. These two cases are extremes, of course. It is also possible to include an intermediate number of two-electron integrals, for example, those given by eq 56 plus all two-center exchange integrals, and so forth. The number of integrals included is dictated by the level of accuracy desired.

## VI. THE RELATIVISTIC PSEUDOPOTENTIAL APPROXIMATION

The approximations involved in the RPP method are best understood in the context of the three electronic regions, the core, outer core, and valence, that it describes in both atomic and molecular systems. The method mathematically differentiates among the three in recognition of the fact that they are physically and chemically distinct from one another. To study the nature of these differences more carefully, it is helpful to consider an all-electron treatment in which the electronic space has been partitioned into core, outer core, and valence regions. (It is noted that the following discussion is made in the context of systems that include relativistic effects, hence the use of the term *spinor*. However, the same argument applies to nonrelativistic treatments, which would involve *orbitals*. In addition, the discussion is presented only with respect to the radial portion of the spinors.) Such a treatment is considered, first for an atom and then for a molecule.

All atomic spinors have a radial range from zero to infinity. However, their maxima reside in different spatial regions. Core spinors are defined as those spinors whose radial maxima occur in the region from zero (at the nucleus) to  $r$ , where  $r$  is a radial distance. Outer core spinors are defined as those spinors whose maxima occur in the region from  $r$  to  $r'$ , where  $r' > r$ . The valence spinors maximize somewhere in the region from  $r'$  to infinity. The three types of spinors differ both radially and energetically. The maxima of the core orbitals are imbedded deep within the atom. They correspond to electronic motion closest to the nucleus. Consequently they are “tight”. The outer core electrons are associated with spinors that are more diffuse because these electrons are partially sheltered from the nuclear charge by

the presence of the core electrons. Thus, their corresponding spinors have a larger radial extent and are not as “tight”. Although the outer core spinors are radially positioned predominantly in the outer core region, a portion extends into the valence space, and this portion is larger than that due to the core spinors. The valence spinors are the most diffuse because they correspond to the outermost electrons, which are the most sheltered from the “pull” of the nucleus. The following two-electron exchange interactions

$$\langle \phi_i \phi_j | 1/r_{12} | \phi_j \phi_i \rangle \quad (57)$$

for the case where electrons 1 and 2 occupy different regions (e.g., one is a core electron and the other is a valence electron), may be considered to be negligible because  $r_{12}$  is large. This approximation is somewhat less accurate when these interactions are between outer core and valence electrons because outer core spinors are more diffuse than core ones. However, the resulting errors are not expected to be large, because these spaces are, to a large degree, distinct from one another. This is called the local approximation and is a foundation of pseudopotential theory. Exchange interactions among electrons occupying the same region of space cannot be neglected, however, because these electrons are closer to one another, making the operator of eq 57 larger and thus the integral significant.

The spaces are still allowed to interact via the two-electron Coulomb integrals. These integrals are given by

$$\langle \phi_i \phi_j | 1/r_{12} | \phi_i \phi_j \rangle \quad (58)$$

Equation 58 may be written in terms of the charge densities of electrons 1 and 2:

$$\int |\phi_i|^2 |\phi_j|^2 (1/r_{12}) d\tau_1 d\tau_2 \quad (59)$$

The interregion Coulomb interactions of the outer core region are best considered in terms of eq 59, which describes the core–valence Coulomb interactions if electron 1 is a core electron and electron 2 is a valence one. As stated previously, the core spinors are very “tight”, making the core-electron density highest in the core. The same applies to a valence electron in the valence region. The charge densities of eq 59 are thus largest for core and valence electrons that reside far from each other (large  $r_{12}$ ) in their respective spaces; specifically,  $|\phi_i|^2$  and  $|\phi_j|^2$  are greatest when the operator  $1/r_{12}$  is very small. Thus, the large interelectron distances result in small core–valence Coulombic interactions. Conversely, when the core and valence electrons occupy the same region of space, the operator  $1/r_{12}$  is large because the distance between the electrons,  $r_{12}$ , is small. However, core-electron charge density in the valence region is very small because only a very small part of the spinor extends into the valence region. In this case, it is the small core-electron charge density in the valence region that is causing the core–valence Coulomb interactions to be small.

If the same argument is applied to the outer core–valence interactions, the results are significantly different due to the chemical nature of the outer core. The spinors in this region are more diffuse than those of the core because they are not held as closely to the nucleus due to the presence of the core electrons. However, they cannot diffuse to the same extent as those in the valence region because their motion is

limited by the presence of the higher-energy valence electrons. Since the outer core defines this intermediate area, the electrons in this region have both core and valence characteristics. Their “parentage” can still be traced to the atom, however, because they are not directly involved in bonding. The outer core electrons are predominantly “localized” in the outer core region and thus can be described by a potential. However, the potential must be flexible, since these spinors cannot be “frozen” at their ground-state atomic values due to the valencelike part of their nature.

This valencelike nature becomes clearer by examining eq 59 in the case where electron 1 is an outer core electron and electron 2 is a valence one. In this case, the distance between the electrons is large, making the  $1/r_{12}$  operator of eq 59 small and thus the integral small. Since the outer core spinors are more diffuse than the core spinors, a greater portion of each outer core spinor resides in the valence region, increasing the probability of finding the outer core electron in the valence region. In this case,  $r_{12}$  is small because both electrons occupy the same region. Thus,  $|\phi_i|^2$  is no longer small enough to cause the integral of eq 59 to disappear.

Equation 57 will now be discussed in terms of multicenter interactions. The core region is chemically inert. The core of a gas-phase atom A is therefore physically and chemically indistinguishable from the core of atom A in molecule AB. Since the maxima of the core spinors occur nearer the atomic nuclei than to the atomic valence,  $r_{12}$  is very large between core electrons on different centers, making multicenter core-electron interactions negligible. The outer core region, on the other hand, polarizes in response to valence electronic motion. This occurs due to the presence of two-electron Coulomb integrals between core and valence electrons (i.e., only the corresponding exchange integrals have been neglected). The outer core region, on the other hand, is not completely chemically inert. Two-electron, one-center Coulomb interactions between outer core and valence electrons of atom A in molecule AB result in a polarization of the outer core electrons of A in response to the valence electronic motion of AB via eq 59. If this polarization occurs in such a way as to shift the outer core electron density of A toward the outer core electron density of B, multicenter outer core–outer core interactions in AB cannot be neglected because the operator of eq 57, which defines these interactions, becomes large (i.e.,  $r_{12}$  becomes smaller). Finally, the valence region is the most chemically active since it contains the most diffuse spinors. As such, all two-electron interactions are significant and must be included for accuracy.

Having discussed two-electron interactions in the context of a partitioned electronic space, it is now possible to compare the REP to the RPP. REPs involve two spaces, the core and the valence. Since the outer core region is not explicitly labeled, these electrons must be treated either as part of the core or as part of the valence. When the outer core electrons are included in the valence space, the resulting REPs are small core, SCREPs. SCREPs correspond to a core region that is atomic-like in all chemical environments and a valence region that is treated explicitly. Since only the true core electrons are labeled *core*, SCREPs are accurate pseudopotentials. When the outer core electrons are included in the core space, the resulting REPs are large core, LCREPs. The outer core electrons, as previously discussed, are not chemically inert like the core ones. Thus, incorporation of

these electrons into the core space leads to sizable errors. Specifically, LCREPs include all two-electron one-center outer core Coulomb interactions. However, in addition to the neglect of exchange interactions as dictated by the local approximation, LCREPs neglect all two-electron multicenter interactions between outer core electrons. Furthermore, for molecules and excited-state atoms, all one-center Coulomb interactions between outer core and valence electrons are also erroneous, since the outer core spinors cannot be self-consistently optimized because they are frozen at their ground-state atomic values. Consequently, only the valence spinors participate in the SCF optimization. In other words, LCREPs do not allow outer core relaxation or polarization. This leads to sizable errors. RPPs, on the other hand, define the outer core region and at the most rigorous limit (refer to section V) include all one-center and multicenter interactions among outer core electrons. Moreover, the outer core spinors participate in the SCF optimization, thereby yielding accurate one-center Coulomb interactions between outer core and valence electrons. In other words, RPPs allow outer core relaxation and polarization.

Table 1, which summarizes all possible two-electron interactions and corresponds to an electronic space that has been divided into core, outer core, and valence regions, presents a comparison of SCREPs, LCREPs, and RPPs with respect to the two-electron interactions included and neglected in each procedure. Obviously, all-electron methods include all possible interactions because the electrons are treated explicitly. The presence of each type of interaction is indicated by the term *yes* in the column labeled *all electron*. The last set of interactions, labeled 21–24, are mentioned first because they are the simplest to consider with respect to all four procedures. Simply put, these interactions are identical in all four cases because the valence electrons are treated explicitly in all four cases. Interactions involving core electrons must be considered in light of the fact that both the RPP and REP methods recognize the core to be chemically inert. Therefore, the core spinors are frozen such that they correspond to those of the ground-state atom and no interatomic (multicenter) interactions among core electrons are considered, making the SCREP, LCREP, and RPP columns the same for interactions 1–4. Interactions 5–8 exist between core and outer core electrons. For these, the LCREP differs from the SCREP and RPP in that it includes core–outer core one-center exchange interactions because the outer core electrons are included in the core space, and thus interactions 1–4 and interactions 5–8 are equivalent for LCREPs. With SCREPs the outer core electrons are treated explicitly as part of the valence space, making interactions 5–8 equivalent to interactions 9–12. Since RPPs differentiate among the three regions, interactions 1–4 are distinct from interactions 5–8 and 9–12. The difference between the RPP and the REP for interactions 5–12 lies in the method by which the outer core and valence spinors are optimized. Since the REP does not differentiate between the outer core and valence spinors, no restrictions are placed on the optimization process, making the resulting valence wave function include outer core spinors; that is, the total valence wave function extends over the outer core space. RPPs, on the other hand, distinguish between outer core and valence electrons. Thus, the outer core and valence spinors are optimized such that the total valence wave function includes



**Table 1.** Two-Electron Interactions in SCREPs, RPPs, and LCREPs

two-electron interactions <sup>a</sup>	all-electron	SCREP <sup>b,c</sup>	RPP <sup>b,d</sup>	LCREP <sup>b,e</sup>
1. core—core one-center Coulomb	yes	yes	yes	yes
2. core—core multicenter Coulomb	yes	no	no	no
3. core—core one-center exchange	yes	yes	yes	yes
4. core—core multicenter exchange	yes	no	no	no
5. core—outer core one-center Coulomb	yes	yes	yes	yes
6. core—outer core multicenter Coulomb	yes	yes <sup>f</sup>	yes <sup>f</sup>	no
7. core—outer core one-center exchange	yes	no	no	yes
8. core—outer core multicenter exchange	yes	no	no	no
9. core—valence one-center Coulomb	yes	yes	yes	yes
10. core—valence multicenter Coulomb	yes	yes <sup>f</sup>	yes <sup>f</sup>	yes <sup>f</sup>
11. core—valence one-center exchange	yes	no	no	no
12. core—valence multicenter exchange	yes	no	no	no
13. outer core—outer core one-center Coulomb	yes	yes	yes	yes
14. outer core—outer core multicenter Coulomb	yes	yes	yes	no
15. outer core—outer core one-center exchange	yes	yes	yes	yes
16. outer core—outer core multicenter exchange	yes	yes	yes	no
17. outer core—valence one-center Coulomb	yes	yes	yes	yes
18. outer core—valence multicenter Coulomb	yes	yes	yes	yes <sup>f</sup>
19. outer core—valence one-center exchange	yes	yes	no	no
20. outer core—valence multi-center exchange	yes	yes	no	no
21. valence—valence one-center Coulomb	yes	yes	yes	yes
22. valence—valence multicenter Coulomb	yes	yes	yes	yes
23. valence—valence one-center exchange	yes	yes	yes	yes
24. valence—valence multicenter exchange	yes	yes	yes	yes

<sup>a</sup> The term *multicenter* refers to two-center, three-center, and four-center interactions. <sup>b</sup> All interactions involving the core region are calculated using core spinors that correspond to the ground-state atom (REP approximation). <sup>c</sup> Outer core electrons are treated explicitly as part of the valence space; their corresponding spinors are self-consistently optimized. <sup>d</sup> Outer core electrons are treated as part of the outer core space; their corresponding spinors are self-consistently optimized within this space (RPP approximation). <sup>e</sup> Outer core electrons are treated as part of the core space; their corresponding spinors are optimum for the ground-state atom and are not self-consistently optimized (REP approximation). <sup>f</sup> Three-center interactions are restricted to include contributions from only one core spinor (REP approximation). Four-center interactions are not included.

only valence spinors and the total outer core wave function includes only outer core spinors; that is, the spaces are distinct. Neither the RPP nor the REP procedure allows optimization of core spinors. (In fact, the core spinors do not appear explicitly due to the presence of either the REP or the RPP operator.) All-electron procedures impose no optimization restrictions on any of the spinors. Because of the nature of the core, outer core, and valence spaces, interactions 1–12 are expected to be equivalent among all four procedures despite the mathematically different methods used to describe them. In other words, interactions explicitly calculated via all-electron procedures but not included via SCREPs, LCREPs, or RPPs are expected to contribute insignificantly to the total energy. That is, all-electron procedures include every two-electron integral explicitly, regardless of whether the contribution of some of these integrals is negligible. Conversely, REP and RPP procedures mathematically describe the chemical and physical characteristics of the core, outer core, and valence regions such that the explicit inclusion of insignificant integrals is not required.

LCREPs describe interactions 13–20 differently from SCREPs, RPPs, and all-electron methods. LCREPs include the outer core electrons in the core region, making interactions 13–16 and 17–20 analogous to interactions 1–4 and 9–12, respectively. SCREPs and all-electron methods, on the other hand, incorporate the outer core electrons into the valence space, making interactions 13–20 analogous to interactions 21–24. RPPs include interactions 13–16, as do SCREPs and all-electron calculations. However, as has been pointed out, the optimization of the outer core region is carried out separately from that of the valence region in RPPs, whereas in SCREPs and all-electron procedures the outer core is optimized as part of the valence region. Despite

these differences, all three procedures include multicenter Coulomb and multicenter exchange interactions (interactions 14 and 15). LCREPs do not include these interactions because the outer core orbitals are treated as core orbitals and are thus frozen at their atomic values; no interactions are considered among different cores. The outer core orbitals are thus kept from polarizing. The omission of interactions 14 and 15 results in errors when LCREPs are used in molecular calculations. Since RPPs include these interactions, they recover these errors. In addition, since outer core basis functions are not needed in molecular calculations using RPPs, use of the RPPs result in significant computational savings relative to SCREPs and all-electron procedures. Hence RPPs provide the accuracy of SCREP and all-electron procedures while retaining the savings comparable with procedures using LCREPs.

## VII. CONCLUSIONS

A relativistic pseudopotential (RPP) has been derived for use in molecular calculations. The RPP incorporates relativistic effects corresponding to the Dirac Coulomb Hamiltonian and intermediate angular momentum coupling. In addition, it contains essentially no local error.<sup>11</sup> At the Dirac–Fock and Hartree–Fock levels of theory, these RPPs account for outer core polarization effects. Core and outer core relativistic effects present in the atomic Dirac–Fock Hamiltonian will be consistently carried over to molecular environments and be deposited into the resulting polyatomic wave function. The RPP is derived for each individual element, but its final form is established in the molecular environment corresponding to each specific application through coefficients that are self-consistently determined. Solution of the Hartree–Fock–Roothaan or Dirac–Fock–Roothaan equations using a RPP involves diagonalization of two Fock



matrices, one corresponding to the outer core and the other to the valence region. This leads to a relaxation or polarization of the outer core region as a consequence of the valence interactions and is possible because all of the coefficients corresponding to the outer core atomic basis functions for each atom are present in each of the matrix equations. Although the outer core eigenvectors are self-consistently optimized, outer core–valence separability is maintained because no outer core coefficients contribute to the valence wave functions. Thus, only valence electrons are treated explicitly. This permits highly accurate calculations of electronic properties of large and/or heavy-element-containing molecules, clusters, and surfaces by the explicit treatment of the smallest possible number of valence electrons.

#### ACKNOWLEDGMENT

The author thanks Walter C. Ermler for invaluable suggestions and discussions. The referee is also cordially thanked for providing comments and suggestions resulting in a significantly improved manuscript. A faculty fellowship at Pacific Northwest National Laboratory was granted by Associated Western Universities, Incorporated.

#### REFERENCES AND NOTES

- (1) Marino, M. M.; Ermler, W. C.; Kern, C. W.; Bondybey, V. E. *J. Chem. Phys.* **1992**, *96*, 3756.
- (2) Lee, Y. S.; Ermler, W. C.; Pitzer, K. S. *J. Chem. Phys.* **1977**, *67*, 5861.
- (3) Szasz, L. *Pseudopotential Theory of Atoms and Molecules*; Wiley: New York, 1985.
- (4) Schwerdtfeger, P.; Fischer, T.; Dolg, M.; Igel-Mann, G.; Nicklass, A.; Stoll, H.; Haaland, A. *J. Chem. Phys.* **1995**, *102*, 2050, and private communication.
- (5) Christiansen, P. A.; Lee, Y. S.; Pitzer, K. S. *J. Chem. Phys.* **1979**, *71*, 4445.
- (6) Desclaux, J. P. *Comput. Phys. Commun.* **1975**, *9*, 3.
- (7) Ermler, W. C.; Marino, M. M. *Relativistic and Electron Correlation Effects in Molecules and Solids*; Malli, G., Ed.; Plenum: New York, 1994.
- (8) Stoll, H.; Fuentealba, P.; Schwerdtfeger, P.; Flad, J.; Szentpaly, L. V.; Preuss, H. *J. Chem. Phys.* **1984**, *81*, 2732.
- (9) Christiansen, P. A. *Chem. Phys. Lett.* **1986**, *127*, 50.
- (10) Marino, M. M.; Ermler, W. C. *Chem. Phys. Lett.* **1993**, *206*, 271.
- (11) Ermler, W. C.; Marino, M. M. *New Methods in Quantum Theory*; Tsipis, C. A.; Popov, V. S.; Herschbach, D. R.; Avery, J. S., Eds.; Kluwer Academic: Dordrecht, 1996. Ermler, W. C.; Marino, M. M. *J. Chem. Inf. Comput. Sci.* **2000**, *41*, 77.
- (12) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.
- (13) LaJohn, L. A.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. *J. Chem. Phys.* **1987**, *87*, 2812.
- (14) Muller, W.; Flesch, J.; Meyer, W. *J. Chem Phys.* **1984**, *80*, 3297.
- (15) Grant, I. P. *Adv. Phys.* **1970**, *19*, 747.
- (16) Ermler, W. C.; Ross, R. B.; Christiansen, P. A. *Adv. Quantum Chem.* **1988**, *19*, 139.

CI0000676