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Relativistic Pseudopotential Incorporating
Core/Valence Polarization and Nonlocal Effects

by

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ABSTRACT

A relativistic pseudopotentional (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. Outercore 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 outercore shells analogous to that occurring in all-electron molecular Hartree-Fock calculations while retaining these shells as part of the atomic pseudopotentional. 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 [1]. 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 [2]. This subject, generally categorized as pseudopotential theory [3], 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 [4]. One type of ab initio REP that accounts for relativistic effects is defined by using shape-consistent nodeless pseudospinors [5] extracted from numerical two-component DF atomic spinors [6] following the procedure of Lee et al. [2].

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. [2], this choice is arbitrary. For example, in the case of cesium the most practical REP would correspond to a one-electron valence space. But 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 comprising the 5s, 5p, and 4d electrons. A REP having a 1-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 [7].

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 9-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 [2]. 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 [8]. Christiansen showed that a high level of accuracy may be achieved with the minimum valence-electron REP if a core/valence polarization potential (CVPP) is included in the calculations [9]. Marino and Ermler later extended Christiansens's method to an REP-based CVPP derived in j-j coupling [10].

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 alkaline and alkaline earth elements (LiMg, LiBa, Cs_2, etc.) are examples [7]. Second, no REP method to date can account explicitly for outercore 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 [4]. The error results primarily from to the neglect of nonlocal, polarization, and correlation phenomena due to outercore electrons interacting with atomic and molecular valence electrons. (In this work, the term *outercore* replaces the more conventional *outer core*. The new term is needed for clarity.) While nonlocal errors can be significantly reduced by using improved pseudospinors [11], 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, outercore polarization (at the Hartree-Fock or Dirac-Fock level) and outercore/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 outercore correlation effects. This new method is based on the REP procedure as defined by Lee, Ermler and Pitzer [2] and Christiansen, Lee and Pitzer [5], Roothaan's LCAO method [12], and the nodeless-valence-spinor (NVS) procedure of Ermler and Marino [11]. 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 [11] in the limit where the outercore 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 *pseudopotentional*.

II. Derivation of the Relativistic Pseudopotentional

Having established the nodeless valence spinor procedure, we now present the derivation of the RPP. Three logical realms of atomic electron occupancy will be defined: (a) inner core, (b) outercore, and (c) valence. Region (b) could also logically be termed the inner valence region. *Outercore* 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 outercore 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 [2, 13]. Those cases in which changes in the electrons in region (b) are of clear importance were dealt with, as discussed above, by either expanding the region (c) or by adding a CVPP [8, 9, 14]. The latter requires the a priori inclusion of the atomic outercore 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

$$H_{rel} = \Sigma_i \, h_D \, (i) + \Sigma_i \Sigma_j r_{ij}^{-1}, \tag{1}$$

where i and j index electrons. (Although the pseudopotential is developed by using the Dirac Hamiltonian, the formalism itself is not dependent on the form of the Hamiltonian used, and thus the Schroedinger Hamiltonian may also be used.) Many electron relativistic effects, which may be approximated by including the Breit interaction term [15], are omitted for now. The Dirac one-electron Hamiltonian is

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

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

$$\alpha = \begin{matrix} 0 & \sigma^p \\ \sigma^p & 0 \end{matrix} \quad \text{and} \quad \beta = \begin{matrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{matrix} . \tag{3}$$

Here, σ^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:

$$\Psi_{nkm} (r,\theta,\phi) = \begin{matrix} r^{-1} & P_{nk} (r) & \chi_{km} (\theta,\phi) \\ iQ_{nk} (r) & \chi_{km} (\theta,\phi) \end{matrix}, \tag{4}$$

where the angular factors are defined by

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

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, λ is an index defined as $|\gamma + 1/2|$ -1/2, and γ 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, outercore, and valence spaces. The corresponding wavefunction for this system is

$$\Psi = A \, [(\phi_1^c \, \phi_2^c \, \phi_3^c...\phi_l^c)(\phi_1^o \, \phi_2^o \, \phi_3^o...\phi_m^o) \, (\phi_1^v \, \phi_2^v \, \phi_3^v...\phi_n^v)], \tag{6}$$

where c, o, and v denote (inner) core, outercore, and valence, respectively. A is the antisymmetrization and normalization operator. The set of core, outercore, and valence spinors are assured to be orthogonal to one another, that is,

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} . \tag{7}$$

Each ϕ_i of Eq. (6) may be represented by a linear combination of m basis functions that are normalized but nonorthogonal [12]:

$$\phi_i = \Sigma_p C_{pi} \chi_p, \tag{8}$$

$$<\chi_p | \chi_p> = 1. \tag{9}$$

Because the χ_i are nonorthogonal, overlap integrals result:

$$<\chi_p | \chi_q> = S_{pq}. \tag{10}$$

Also, from Eq. (8) and Eq. (10) it is clear that

$$<\phi_i | \phi_j> = \mathbf{C}_i^{\dagger} \mathbf{S} \mathbf{C}_j = \delta_{ij} , \tag{11}$$

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

$$\begin{aligned} H^{rel} = &\Sigma_c h_c + \Sigma_c \Sigma_{c'} 1/r_{cc'} \\ &+ \Sigma_o h_o + \Sigma_o \Sigma_{o'} 1/r_{oo'} + \Sigma_c \Sigma_o 1/r_{co} \\ &+ \Sigma_v h_v + \Sigma_v \Sigma_{v'} 1/r_{vv'} + \Sigma_c \Sigma_v 1/r_{cv} + \Sigma_o \Sigma_v 1/r_{ov} , \end{aligned} \tag{12}$$

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

The total energy is then given by

$$E_t = <\Psi | H^{rel} | \Psi> = E_c + E_o + E_{co} + E_v + E_{cv} + E_{ov} , \tag{13}$$

which is a sum of core, outercore, core/outercore, valence, core/valence, and outercore/valence energies. The first term in Eq. (13) is given by

$$E_{core} = \Sigma_c <\phi_c | h_c | \phi_c> + \Sigma_c \Sigma_{c'} [J_{cc'} - K_{cc'}], \tag{14}$$

which is the standard form for a closed-shell determinantal wave function of singly occupied atomic spinors [15]. The $J_{cc'}$ and $K_{cc'}$ of Eq. (14) represent Coulomb and exchange energies, respectively, involving only core electrons and are defined by

$$J_{cc'} = <\phi_c \phi_{c'} | 1/r_{12} | \phi_c \phi_{c'}>, \tag{15}$$

and

$$K_{cc'} = <\phi_c \phi_{c'} | 1/r_{12} | \phi_{c'} \phi_c>. \tag{16}$$

Terms two and three in Eq. (13) may be combined to yield

$$E_o + E_{co} = <\phi_o | H^o | \phi_o>, \tag{17}$$

where

$$H^o = \Sigma_O \{ h_o + \Sigma_{o'} [J_{o'} - K_{o'}] + \Sigma_c [J_c - K_c] \} \qquad . \tag{18}$$

Here, H^o contains the one-electron and two-electron operators for the outercore electrons plus additional terms that represent the effects of the core on the outercore spinors. Consequently, H^o operates only on the outercore portion of the total wavefunction of Eq. (6). In Eq. (18) J_c and K_c are Coulomb and exchange operators, respectively, and are defined as

$$J_c \phi_o = <\phi_c \mid 1/r_{12} \mid \phi_c> \phi_o \qquad (19)$$

and

$$K_c \phi_o = <\phi_c \mid 1/r_{12} \mid \phi_o> \phi_c . \qquad (20)$$

These operators contain core orbitals while operating on the outercore wavefunctions, thereby representing the effects of the core on the outercore spinors. $J_{o'}$ and $K_{o'}$ are defined analogously:

$$J_{o'} \phi_o = <\phi_{o'} \mid 1/r_{12} \mid \phi_{o'}> \phi_o$$

(21)
and

$$K_{o'} \phi_o = <\phi_{o'} \mid 1/r_{12} \mid \phi_o> \phi_{o'}$$

(22)

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

$$E_o = \Sigma_o <\phi_o \mid h_o \mid \phi_o> + \Sigma_o\Sigma_{o'}[J_{oo'} - K_{oo'}] + \Sigma_o\Sigma_c[J_{oc} - K_{oc}] . \qquad (23)$$

In Eq. (23) $J_{oo'} = J_{o'}$ and $K_{oo'} = K_{o'}$ when $J_{o'}$ and $K_{o'}$ operate on outercore orbitals. Also, $J_{oc} = J_c$ and $K_{oc} = K_c$ when J_c and K_c operate on outercore orbitals, as shown in Eqs. (19)–(22).

The remaining terms in Eq. (13) may be combined to yield

$$E_v + E_{cv} + E_{ov} = <\phi_v \mid H^v \mid \phi_v> \qquad , \qquad (24)$$

where

$$H^v = \Sigma_v\{ h_v + \Sigma_c [J_c - K_c] + \Sigma_o [J_o - K_o]\} + \Sigma_{v>v'} 1/r_{vv'} . \qquad (25)$$

Here, H^v includes the one-electron Hamiltonian for the valence electrons plus additional terms that represent the effects of the core and outercore on the valence orbitals. Therefore, H^v operates only on the valence portion of the total wavefunction of Eq. (6). In Eq. (25) J_c, K_c, J_o, and K_o are one-electron operators involving the core and outercore orbitals but operating only on the valence orbitals.

In both Eq. (18) and Eq. (25), the term $\Sigma_c [J_c - K_c]$ can be replaced by a small-core relativistic effective potential U^{REP}[11]. The REP represents the interaction of the core orbitals with the orbitals comprising the outercore (designated by U_i^{REP}) and the valence (designated by $U_{i'}^{REP}$). The use of such an REP to represent these interactions is well understood [2]. The energy of the outercore and valence electrons relative to the energy of the core may then be expressed by

$$E = \{\Sigma_i [U_i^{REP} + H_i] + \Sigma_{ij} (J_{ij} - K_{ij}) \} + \{ \Sigma_{i'} [U_{i'}^{REP} + H_{i'}] + \Sigma_{i'}\Sigma_{j'} (J_{i'j'} - K_{i'j'})\}$$
$$+ \{\Sigma_{i'}\Sigma_j (J_{i'j} - K_{i'j})\} . \qquad (26)$$

Here, i and j index outercore electrons while i' and j' index valence electrons. In Eq. (26) the one-electron energies H_i and $H_{i'}$, the pseudopotential integrals U_i^{REP} and $U_{i'}^{REP}$, 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

$$\mathbf{H_i = H_i^{*}} = , <\phi_i \mid h_i \mid \phi_i> \qquad (27)$$

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and similarly for $H_{i'}$;

$$U_i^{REP} = U_i^{REP*} = <\phi_i |U_i^{REP}| \phi_i> \tag{28}$$

and similarly for $U_i'^{REP}$;

$$J_{ij} = J_{ji} = J_{ij}^* = J_{ji}^* = , <\phi_i\phi_j|1/r_{12}| \phi_i\phi_j> \tag{29}$$

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

$$K_{ij} = K_{ji} = K_{ij}^* = K_{ji}^* = , <\phi_i\phi_j|1/r_{12}| \phi_j\phi_i> \tag{30}$$

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 [12] becomes

$$\delta E = \{2 \Sigma_i [\delta U_i^{REP} + \delta H_i] + \Sigma_{ij} (2\delta J_{ij} - \delta K_{ij}) \} + \{ 2 \Sigma i' [\delta U_{i'}^{REP} + \delta H_{i'}] + \Sigma_{i'}\Sigma_{j'} (2\delta J_{i'j'} - \delta K_{i'j'})\}$$
$$+ \{\Sigma_{i'}\Sigma_j(2\delta J_{i'j} - \delta K_{i'j})\} . \tag{31}$$

In Eq. (31) variation of the atomic spinors is analogous to a variation of the outercore and valence spinors. Because the atomic spinors are expressed as linear combinations of basis functions, as defined in Eq. (8), Eq. (31) becomes

$$\delta E = \{2 \Sigma_i (\delta C_i^\dagger) [U_i^{REP} + H_i^o]C_i + \Sigma_{ij} [(\delta C_i^\dagger) (J_j - K_j)C_i + (\delta C_j^\dagger)(J_i - K_i)C_j]$$
$$+ 2 \Sigma_i C_i^\dagger [U_i'^{REP} + H_i^o]\delta C_i + \Sigma_{ij} [C_i^\dagger (J_j - K_j) (\delta C_i) + C_j^\dagger (J_i - K_i) (\delta C_j)]\}$$
$$+ \{2 \Sigma_{i'} (\delta C_{i'}^\dagger) [U_{i'}^{REP} + H_{i'}^v]C_{i'} + \Sigma_{i'j'} [(\delta C_{i'}^\dagger) (J_{j'} - K_{j'})C_{i'} + (\delta C_{j'}^\dagger) (J_{i'} - K_{i'})C_{j'}]$$
$$+ 2 \Sigma_{i'} C_{i'}^\dagger [U_{i'}'^{REP} + H_{i'}^v]\delta C_{i'} + \Sigma_{i'j'} [(C_{i'}^\dagger) (J_{j'} - K_{j'}) \delta C_{i'} + C_{j'}^\dagger (J_{i'} - K_{i'}) \delta C_{j'}]\}$$
$$+ \{\Sigma_{i'j} [(\delta C_{i'}^\dagger) (J_j - K_j)C_{i'} + (\delta C_j^\dagger) (J_{i'} - K_{i'})C_j]$$
$$+ \Sigma_{i'j} [(C_{i'}^\dagger) (J_j - K_j) \delta C_{i'} + C_j^\dagger (J_{i'} - K_{i'}) \delta C_j]\}, \tag{32}$$

where † and * correspond to the Hermitian conjugate and the complex conjugate, respectively, of C_i.

For cases in which there are two terms between brackets, the second term gives the same result as the first after complete summation over i, j, i', and j'. Equation (32) can be expressed in terms of matrices whereby

$$\chi_p = (\chi_1, \chi_2, \ldots \chi_m) \tag{33a}$$

$$C_i = \begin{matrix} C_{1i} \\ C_{2i} \\ : \\ C_{mi} \end{matrix} \tag{33b}$$

$$C = \begin{matrix} C_{11} & C_{12} & \ldots C_{1i} \\ C_{21} & C_{22} & \ldots C_{2i} \\ . & . & . \\ C_{m1} & C_{m2} & \ldots C_{mi} \end{matrix} \tag{33c}$$

Also,

$$M_{pq} = <\chi_p |M| \chi_q> \tag{34a}$$

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$$\mathbf{M} = \begin{matrix} M_{11}\,M_{12}\,..._{}M_{1i} \\ M_{21}\,M_{22}\,..._{}M_{2I} \\ .\quad.\quad.\quad.\quad. \\ \\ M_{m1}\,\,M_{m2}\,..._{}M_{mi}\,, \end{matrix} \tag{34b}$$

where $\mathbf{M}$ is a one-electron operator. Therefore,

$$<\phi_i\,|\mathbf{M}|\,\phi_j> = \mathbf{C}_i^\dagger\,\mathbf{M}\mathbf{C}_j\ . \tag{35}$$

From Eq. (27), Eq. (28), Eq. (29), Eq. (30), and Eq. (35), it is clear that

$$\mathbf{H}_i = \mathbf{C}_i^\dagger\,\mathbf{H}\mathbf{C}_j \tag{36}$$

$$U_i^{REP} = \mathbf{C}_i^\dagger\ U_i^{REP}\,\mathbf{C}_j \tag{37}$$

$$\mathbf{J}_{ij} = \mathbf{C}_i^\dagger\,\mathbf{J_j}\mathbf{C}_i = \mathbf{C}_i^\dagger\,\mathbf{J_i}\mathbf{C}_j \tag{38}$$

$$\mathbf{K}_{ij} = \mathbf{C}_i^\dagger\,\mathbf{K_j}\mathbf{C}_i = \mathbf{C}_i^\dagger\,\mathbf{K_i}\mathbf{C}_j\ . \tag{39}$$

Also, analogously to Roothaan [12], making use of the Hermitian property of the operators H_i, J_i, and K_i yields

$$\delta E = \{2\Sigma_i\ (\delta\mathbf{C}_i^\dagger)\ [\ U_i^{REP} + \mathbf{H}_i^{o} + \Sigma_j\ (\mathbf{J_j} - \mathbf{K_j})]\mathbf{C}_i + 2\ \Sigma_i\ \mathbf{C}_i^\dagger\ [U_i^{REP} + \mathbf{H}_i^{o} +\Sigma_j\ (\mathbf{J_j} - \mathbf{K_j})]\ (\delta\mathbf{C}_i)\}$$
$$+ \{2\Sigma_{i'}\ (\delta\mathbf{C}_{i'}^\dagger)\ [\ U_{i'}^{REP} + \mathbf{H}_{i'}^{v} + \Sigma_{j'}\ (\mathbf{J_{j'}} - \mathbf{K_{j'}})]\mathbf{C}_{i'} + 2\ \Sigma_{i'}\ \mathbf{C}_{i'}^\dagger\ [U_{i'}^{REP} + \mathbf{H}_{i'}^{v} + \Sigma_{j'}\ (\mathbf{J_{j'}} -\ \mathbf{K_{j'}})]\ (\delta\mathbf{C}_{i'})\}$$
$$+ \{2\Sigma_{i'j}\ [(\delta\mathbf{C}_{i'}^\dagger)\ (\mathbf{J_j} - \mathbf{K_j})\mathbf{C}_{i'} + (\mathbf{C}_{i'}^\dagger)\ (\mathbf{J_j} - \mathbf{K_j})(\delta\mathbf{C}_{i'})]\ , \tag{40}$$

which leads to

$$\delta E = \{2\Sigma_i\ (\delta\mathbf{C}_i^\dagger)\ [\ U_i^{REP} + \mathbf{H}_i^{o}+ \Sigma_j\ [(\mathbf{J_j} - \mathbf{K_j})]\mathbf{C}_i + 2\ \Sigma_i\ (\delta\mathbf{C}_i^{T})[U_i^{*REP} + \mathbf{H}_i^{*o} + \Sigma_j\ (\mathbf{J_j}^* - \mathbf{K_j}^*)]\mathbf{C}_i^*\}$$
$$+ \{2\Sigma_{i'}\ (\delta\mathbf{C}_{i'}^\dagger)\ [\ U_{i'}^{REP} + \mathbf{H}_{i'}^{v} + \Sigma_{j'}\ [(\mathbf{J_{j'}} - \mathbf{K_{j'}})]\mathbf{C}_{i'} + 2\ \Sigma_{i'}\ (\delta\mathbf{C}_{i'}^{T})[U_{i'}^{*REP} + \mathbf{H}_{i'}^{*v} + \Sigma_{j'}\ (\mathbf{J_{j'}}^* - \mathbf{K_{j'}}^*)]\mathbf{C}_{i'}^*\}$$
$$+ \{2\Sigma_{i'j}\ [(\delta\mathbf{C}_{i'}^\dagger)\ (\mathbf{J_j} - \mathbf{K_j})\mathbf{C}_{i'} + (\delta\mathbf{C}_{i'}^{T})\ (\mathbf{J_j}^* - \mathbf{K_j}^*)(\mathbf{C}_{i'}^*)]\}\ , \tag{41}$$

where ^{T} denotes the transpose of $\mathbf{C}_i$. Now, the following are defined:

$$\mathbf{F}^{RPP} = [U_i^{REP} + \mathbf{H}_i^{o} + \Sigma_j(\mathbf{J_j} - \mathbf{K_j})], \tag{42}$$

where $\mathbf{F}^{RPP}$ corresponds to the outercore, and

$$\mathbf{F}^{,RPP} = [U_{i'}^{REP} + \mathbf{H}_{i'} + \Sigma_{j'}(\mathbf{J_{j'}} - \mathbf{K_{j'}})], \tag{43}$$

where $F^{,RPP}$ corresponds to the valence. Now δE is written

$$\delta E = \{2\Sigma_i\ (\delta\mathbf{C}_i^\dagger)\ \mathbf{F}^{RPP}\ (\mathbf{C}_i\ ) + 2\ \Sigma_i\ (\delta\mathbf{C}_i^{T})\ \mathbf{F}^{*RPP}\ (\mathbf{C}_i^*)$$
$$+ \{2\Sigma_{i'}\ (\delta\mathbf{C}_{i'}^\dagger)\ F^{,RPP}\ (\mathbf{C}_{i'}\ ) + 2\ \Sigma_{i'}\ (\delta\mathbf{C}_{i'}^{T})\ \mathbf{F}^{,*RPP}\ (\mathbf{C}_{i'}^*)$$
$$+ \{2\Sigma_{i'j}\ [(\delta\mathbf{C}_{i'}^\dagger)\ (\mathbf{J_j} - \mathbf{K_j})\ (\mathbf{C}_{i'}) + (\delta\mathbf{C}_{i'}^{T})\ (\mathbf{J_j}^* - \mathbf{K_j}^*)(\mathbf{C}_{i'}^*)]\}\ . \tag{44}$$

However, there are resticting conditions resulting from the orthonormality of the MOs:

$$\langle\phi_i|\phi_j\rangle = \mathbf{C_i}^\dagger\mathbf{SC_j} = \delta_{ij} \tag{45}$$

$$\langle\phi_{i'}|\phi_{j'}\rangle = \mathbf{C_{i'}}^\dagger\mathbf{S"C_{j'}} = \delta_{i'j'} \tag{46}$$

and

$$\langle\phi_{i'}|\phi_{j'}\rangle = \langle\phi_i|\phi_{j'}\rangle = \mathbf{C_i}^\dagger\mathbf{S'C_{j'}} = \delta_{ij'} \tag{47}$$

The restricting conditions (shown below) are incorporated by varying the above equations as follows.

$$(\delta\mathbf{C_i}^\dagger)\mathbf{SC_j} + \mathbf{C_i}^\dagger\mathbf{S}(\delta\mathbf{C_j}) = 0 \quad\text{or}\quad (\delta\mathbf{C_i}^\dagger)\mathbf{SC_j} + (\delta\mathbf{C_j}^\tau)\mathbf{S*}(\delta\mathbf{C_i*}) = 0 \tag{48a,b}$$

$$(\delta\mathbf{C_{i'}}^\dagger)\mathbf{S"C_{j'}} + \mathbf{C_{i'}}^\dagger\mathbf{S"}(\delta\mathbf{C_{j'}}) = 0 \quad\text{or}\quad (\delta\mathbf{C_{i'}}^\dagger)\mathbf{S"C_{j'}} + (\delta\mathbf{C_{j'}}^\tau)\mathbf{S"*}(\delta\mathbf{C_{i'}*}) = 0 \tag{49a,b}$$

$$(\delta\mathbf{C_{i'}}^\dagger)\mathbf{S'C_j} + \mathbf{C_{i'}}^\dagger\mathbf{S'}(\delta\mathbf{C_j}) = 0 \quad\text{or}\quad (\delta\mathbf{C_{i'}}^\dagger)\mathbf{S'C_j} + (\delta\mathbf{C_j}^\tau)\mathbf{S'*}(\delta\mathbf{C_{i'}*}) = 0 \tag{50a,b}$$

Analogously to Roothaan [12], the restricting conditions are multiplied by the Lagrangian multiplier $-2\varepsilon_{ij}$:

$$-2\Sigma_{ij}(\delta\mathbf{C_i}^\dagger)\mathbf{SC_j}\boldsymbol{\varepsilon}_{ji} - 2\Sigma_{ij}(\delta\mathbf{C_j}^\tau)\mathbf{S*C_i*}\boldsymbol{\varepsilon}_{ji} = 0 \tag{51a}$$

or

$$-2\Sigma_{ij}(\delta\mathbf{C_i}^\dagger)\mathbf{SC_j}\boldsymbol{\varepsilon}_{ji} - 2\Sigma_{ij}(\delta\mathbf{C_j}^\tau)\mathbf{S*C_j*}\boldsymbol{\varepsilon}_{ij} = 0 \tag{51b}$$

$$-2\Sigma_{i'j'}(\delta\mathbf{C_{i'}}^\dagger)\mathbf{S"C_{j'}}\boldsymbol{\varepsilon}_{j'i'} - 2\Sigma_{i'j'}(\delta\mathbf{C_j}^\tau)\mathbf{S"*C_{i'}*}\boldsymbol{\varepsilon}_{j'i'}) = 0 \tag{52a}$$

or

$$-2\Sigma_{i'j'}(\delta\mathbf{C_{i'}}^\dagger)\mathbf{S"C_{j'}}\boldsymbol{\varepsilon}_{j'i'} - 2\Sigma_{i'j'}(\delta\mathbf{C_{i'}}^\tau)\mathbf{S"*C_{j'}*}\boldsymbol{\varepsilon}_{i'j'} = 0 \tag{52b}$$

$$-2\Sigma_{i'j}(\delta\mathbf{C_{i'}}^\dagger)\mathbf{S'C_j}\boldsymbol{\varepsilon}_{ji'} - 2\Sigma_{i'j}(\delta\mathbf{C_j}^\tau)\mathbf{S'*C_{i'}*}\boldsymbol{\varepsilon}_{ji'} = 0 \tag{53a}$$

or

$$-2\Sigma_{i'j}(\delta\mathbf{C_{i'}}^\dagger)\mathbf{S'C_j}\boldsymbol{\varepsilon}_{ji'} - 2\Sigma_{i'j}(\delta\mathbf{C_{i'}}^\tau)\mathbf{S'*C_j*}\boldsymbol{\varepsilon}_{i'j} = 0 \tag{53b}$$

Adding the above to the variation of the energy yields δE^{new}, which is given by

$$\delta E^{new} = \{2\Sigma_i(\delta\mathbf{C_i}^\dagger)\mathbf{F^{RPP}}(\mathbf{C_i}) - 2\Sigma_{ij}(\delta\mathbf{C_i}^\dagger)\mathbf{SC_j}\boldsymbol{\varepsilon}_{ji} + 2\Sigma_i(\delta\mathbf{C_i}^\tau)\mathbf{F*^{RPP}}(\mathbf{C_i*}) - 2\Sigma_{ij}(\delta\mathbf{C_i}^\tau)\mathbf{S*C*_j}\boldsymbol{\varepsilon}_{ij}\}$$
$$+ \{2\Sigma_{i'}(\delta\mathbf{C_{i'}})\mathbf{F'^{RPP}}(\mathbf{C_{i'}}) - 2\Sigma_{i'j'}(\delta\mathbf{C_{i'}}^\dagger)\mathbf{S"C_{j'}}\boldsymbol{\varepsilon}_{j'i'} + 2\Sigma_{i'}(\delta\mathbf{C_{i'}}^\tau)\mathbf{F'*^{RPP}}(\mathbf{C_{i'}*}) - 2\Sigma_{i'j'}(\delta\mathbf{C_{i'}}^\tau)\mathbf{S"*C_{j'}*}\boldsymbol{\varepsilon}_{i'j'}$$
$$+ \{2\Sigma_{i'j}(\delta\mathbf{C_{i'}}^\dagger)(\mathbf{J_j} - \mathbf{K_j})(\mathbf{C_{i'}}) - 2\Sigma_{i'j}(\delta\mathbf{C_{i'}}^\dagger)\mathbf{S'C_j}\boldsymbol{\varepsilon}_{ji'} + 2\Sigma_{i'j}(\delta\mathbf{C_{i'}}^\tau)(\mathbf{J_j*} - \mathbf{K_j*})(\mathbf{C_{i'}*}) - 2\Sigma_{i'j}(\delta\mathbf{C_{i'}}^\tau)\mathbf{S'*C_j}\boldsymbol{\varepsilon}_{i'j}\}. \tag{54}$$

Factoring out $\delta\mathbf{C_i}\dagger$ and $\delta\mathbf{C_i}^T$ and combining like terms yield

$$\delta E^{new} = \{2\Sigma_i(\delta\mathbf{C_i}^\dagger)[\mathbf{F^{RPP}C_i} - 2\Sigma_j\mathbf{SC_j}\boldsymbol{\varepsilon}_{ji}] + 2\Sigma_i(\delta\mathbf{C_i}^\dagger)[\mathbf{F*^{RPP}C_i*} - \Sigma_j\mathbf{S*C_j*}\boldsymbol{\varepsilon}_{ij}]\}$$
$$+ \{2\Sigma_{i'}(\delta\mathbf{C_{i'}}^\dagger)[(\mathbf{F'^{RPP}} + (\mathbf{J_j} - \mathbf{K_j}))\mathbf{C_{i'}} - \Sigma_{j'}\mathbf{S"C_{j'}}\boldsymbol{\varepsilon}_{j'i'} - \Sigma_j\mathbf{S'C_j}\boldsymbol{\varepsilon}_{ji'}]$$
$$+ 2\Sigma_{i'}(\delta\mathbf{C_{i'}}^\tau)[(\mathbf{F'*^{RPP}} + (\mathbf{J_j*} - \mathbf{K_j*}))\mathbf{C_{i'}*} - \Sigma_{j'}\mathbf{S"*C_{j'}*}\boldsymbol{\varepsilon}_{i'j'} - \Sigma_j\mathbf{S'*C_j*}\boldsymbol{\varepsilon}_{i'j}]\} . \tag{55}$$

The conditions $\delta E^{new} = 0$ for any variation of the vectors $\delta\mathbf{C_i}$ and $\delta\mathbf{C_i*}$, $\delta\mathbf{C_i}^\dagger$, and $\delta\mathbf{C_i}^\tau$ are given by

$$\mathbf{F^{RPP}C_i} = \Sigma_j\mathbf{SC_j}\boldsymbol{\varepsilon}_{ji} \tag{56}$$

$$\mathbf{F*^{RPP}C_i*} = \Sigma_j\mathbf{S*C_j*}\boldsymbol{\varepsilon}_{ij} \tag{57}$$

$$[\mathbf{F'^{RPP}} + (\mathbf{J_j} - \mathbf{K_j})]\mathbf{C_{i'}} = \Sigma_{j'}\mathbf{S"C_{j'}}\boldsymbol{\varepsilon}_{j'i'} - \Sigma_j\mathbf{S'C_j}\boldsymbol{\varepsilon}_{ji'} \tag{58}$$

and

$$[\mathbf{F'*^{RPP}} + (\mathbf{J_j*} - \mathbf{K_j*})]\mathbf{C_i*} = \Sigma_{j'}\mathbf{S"*C_{j'}*}\boldsymbol{\varepsilon}_{i'j'} - \Sigma_j\mathbf{S'*C_j*}\boldsymbol{\varepsilon}_{i'j} . \tag{59}$$

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Since the ε_{ij} are part of a Hermitian matrix, $\boldsymbol{\varepsilon}$, the two corresponding equations are equivalent. Therefore, the above equations become

$$\mathbf{F^{RPP}C = SC\boldsymbol{\varepsilon}} \tag{60}$$

and

$$[\mathbf{F'^{RPP} + (J_o - K_o)]\ C''= S''C''\boldsymbol{\varepsilon''} + S'C'\boldsymbol{\varepsilon'}} \ , \tag{61}$$

where $\mathbf{J_o}$ and $\mathbf{K_o}$ correspond to the outercore and valence interactions. The jth element of $\mathbf{J_o}$ and $\mathbf{K_o}$ may be written as one-electron operators

$$\mathbf{J_j}\phi_{i'} = <\phi_j|\ 1/r_{12}|\ \phi_j>\phi_{i'} \ , \tag{62}$$

where ϕ_j may be expressed as a linear combination of basis functions as shown by Eq. (8). Keeping in mind Eqs. (7)–(10), one may express Eq. (62) as

$$\mathbf{J_j}\phi_{i'} = (\Sigma_p\ C_{jp}\ \Sigma_q\ C_{jq})J_{pq}\phi_{i'} \ , \tag{63}$$

where

$$\mathbf{J_{pq}}\phi_{i'} = <\chi_p|\ 1/r_{12}|\ \chi_q>\phi_{i'} \ . \tag{64}$$

Similarly

$$\mathbf{K_j}\phi_{i'} = (\Sigma_p\ C_{jp}\ \Sigma_q\ C_{jq})K_{pq}\phi_{i'} \ , \tag{65}$$

where

$$\mathbf{K_{pq}}\phi_{i'} = <\chi_p|\ 1/r_{12}|\ \phi_i >\chi_q \ . \tag{66}$$

From Eqs. (62) through (66), it follows that

$$(\mathbf{J_j - K_j}) = (\Sigma_p\ C_{jp}\ \Sigma_q\ C_{jq})(\mathbf{J_{pq} - K_{pq}}) \ . \tag{67}$$

Consequently, it is clear from Eqs. (62) through (67) that Eq. (61) may be written as

$$[(\mathbf{F'^{RPP} + C(J_{oc} - K_{oc})]\ C''= S''C''\boldsymbol{\varepsilon''} + S'C'\boldsymbol{\varepsilon'}} \ , \tag{68}$$

where $\mathbf{C}$ is the matrix of outercore eigenvectors, which also appears in Eq. (60), and $\mathbf{J_{oc}}$ and $\mathbf{K_{oc}}$ contain the complete set of Coulomb and exchange operators, each of which is defined by either Eqs. (63) and (64) or Eqs. (65) and (66).

The ultimate goal of this derivation is to define a pseudopotentional for use in atomic and molecular calculations in which only the valence electrons are treated explicitly, thus negating the necessity to include core and outercore spinors into the calculations. However, the operator of Eq. (68) does not allow this because $\mathbf{K_{oc}}$ exchanges an outercore spinor for a valence one, as given by Eq. (66). This can be addressed by defining a set of pseudospinors $\mathbf{C_v''}$ such that the end result of operating on $\mathbf{C_v''}$ with $\mathbf{K_{oc}}$ does not include the introduction of outercore spinors into the valence region. In other words, the orthogonality between the outercore and valence spinors must be removed. However, the number of nodes in the set of eigenvectors comprising $\mathbf{C''}$ of Eq. (68) has been eliminated in many cases and reduced to one in all others because the small core REP is imbedded in $\mathbf{F'^{RPP}}$. [Refer to Eqs. (42) and (43)]. Removal of the remaining node can be accomplished in a number of ways, and the effects of the chosen method on the final expression for the RPP will be discussed in Section V. For now, it is assumed that the node is removed by using the nodeless valence method [11].

The nodeless valence method removes the orthogonality between the outercore and valence spinors as follows: a valence eigenvector that is orthogonal to an outercore eigenvector will contain coefficients

corresponding to outercore basis functions. The orthogonality between the valence and outercore 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, that is, nonorthogonal. It is this set of nodeless, optimized valence eigenvectors that makes up C_v".

Analogously to the shape consistent method of Christiansen et al. [5], a nodeless, optimized valence eigenvector is related to the original noded valence eigenvector by a vector c_{vi} such that

$$C_i" = C_{vi}" - c_{vi} \,. \tag{69}$$

Substituting Eq. (69) into Eq. (68) yields

$$[(F'^{RPP} + C(J_{oc} - K_{oc})] \, C_v" - [(F'^{RPP} + C(J_{oc} - K_{oc})] \, c_v = S"C_v"\varepsilon" + S'C'\varepsilon' - S"c_v\varepsilon", \tag{70a}$$

which can also be written as

$$[F'^{RPP} + CU^{RPP}] \, C_v" = S"C_v"\varepsilon" \,, \tag{70b}$$

where CU^{RPP} is that part of the pseudopotentional that represents both the outercore/valence interaction and the outercore/valence orthogonality operator. Equation (70b) can now be back-solved for CU^{RPP} as follows:

$$CU^{RPP} = S"\varepsilon" - F'^{RPP} C_v"/ C_v" \,. \tag{71}$$

The complete pseudopotentional contains an outercore term given by Eq. (60), which is the solution to the outercore region of the atom, and, as such, is fully integrated. It also contains the CU^{RPP} of Eq. (71), a one-electron operator that operates on the valence spinors of the molecule. This form now allows outercore spinor relaxation through participation of the outercore eigenvector matrix C in the SCF procedure; that is, both the outercore and valence eigenvectors are involved in the self-consistent optimization of the total energy. Although both spaces participate in the SCF procedure, however, they remain distinct from one another because the final valence wavefunction does not contain coefficients corresponding to outercore spinors and vice versa. The details of this procedure are discussed in Sections III and IV.

Analogously to the REP method [2], CU^{RPP} may be expressed as products of angular projection operators and radial functions:

$$C_{lj}U_{lj}{}^{RPP} = \Sigma_{l=0}^{\infty} \, \Sigma_{j=|l+1/2|}^{11/2} \, \Sigma_{m=-j}^{j} \, C_{lj}U_{lj}{}^{RPP} \, (\, r \,)| \, ljm > < ljm| \,. \tag{72}$$

In Eq. (72) the indices lj may be replaced by κ, 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, $| \, ljm >$ and $< ljm \, |$ are two-component angular bases that are eigenfunctions of the Dirac Hamiltonian [refer to Eqs. (1), (2) and (12)].

III. The Relativistic Pseudopotentional in Atomic Calculations

The development of a pseudopotentional is necessary because of the inability of currently available relativistic effective potentials to describe the outercore 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 outercore orbitals to remain those of the ground-state atom, thereby preventing outercore 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 an 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 outercore 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 (F) in an all-electron calculation and in an REP calculation.

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Let us assume that the electrons in an atom could be "frozen" at a given point in time and then labeled *core*, *outercore* 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 pseudopotentional; they are merely a name given to each electron indicating its position at the moment that all motion was frozen.) The all-electron F matrix for such an atom would contain the following interactions:

core/core interactions	core/outercore interactions	core/valence interactions
core/outercore interactions	outercore/outercore interactions	outercore/valence interactions
core/valence interactions	outercore/valence interactions	valence/valence interactions

REP calculations assume the existence of only two spaces: the core region and the valence region. The outercore region, therefore, is made either part of the core or part of the valence space. In both cases, the 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 F matrix containing the valence/valence interactions [16]. 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, outercore, and valence. Consequently, the F matrix in a calculation containing an RPP has the following form:

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

As in an 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 outercore/valence interactions are represented by one-electron operators [refer to Eqs. (71) and (72)], which

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are present in that part of the F matrix containing the valence/valence interactions.

The outercore/outercore block corresponds to the F^{RPP} of Eq. (60) and contains both intra-atomic outercore/outercore and intra-atomic core/outercore interactions, the latter of which are included via the REP present in the F^{RPP} [see Eq. (42)]. 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 outercore/outercore interactions. Although both of these blocks make up the 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 intra-atomic outercore/outercore interaction block, on the other hand, corresponds only to the outercore electronic energy. Since the motion of an outercore 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 outercore 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 outercore 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 outercore region is much smaller than the number associated with the valence one, the number of basis functions needed to describe the outercore 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 outercore electronic motion and still maintain tractability even for correlated calculations. The F^{RPP} of Eq. (60), which corresponds to the outercore of the atom in question, is thus the same regardless of the electronic state to which the total F matrix corresponds. The outercore 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^{RPP} of Eq. (60) remains the same for every atomic (neutral and ionic) electronic state, but its corresponding eigenvector matrix $\mathbf{C}$ does not, and, consequently, there is one corresponding outercore 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 outercore. Put more succinctly, the outercore spinors are allowed to relax in the presence of valence electron participation in bonding, excitation, and so forth; but the outercore electrons themselves, by definition, do not participate directly in these processes. The outercore 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 outercore orbitals can be calculated only by using REPs if this region is labeled "valence". Labeling it as such, however, requires incorporation of outercore 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 Fock equation for the outercore Eq. (60) and by the valence Hamiltonian, which is now given by

$$H^{rel} = \Sigma_V [h_V + \mathbf{C}U^{RPP}] + \Sigma_V\Sigma_{V'} 1/r_{VV'} . \tag{73}$$

Terms three, four, and five on the right-hand side (rhs) of Eq. (12) are replaced by Eq. (60), while terms eight and nine on the rhs of Eq. (12) are replaced by the $\mathbf{C}U^{RPP}$ of Eq. (73). Terms six and seven on the rhs of Eq. (12) remain the same and are contained in Eq. (73). The first and second terms on the rhs of Eq. (12) have been indirectly incorporated via the REP, which is present in both Eqs. (60) and (73). (The reader is

reminded that the REP is contained in Eq. (60) via $\mathbf{F}^{RPP}$ [refer to Eq. (42)] and in Eq. (73) via U^{RPP}, which contains the $\mathbf{F'}^{RPP}$ that has the U^{REP} imbedded within it [refer to Eqs. (71) and (43)].) Equation (73) defines an operator that operates over the valence spinors to yield ultimately the valence Fock equation. On the other hand, Eq. (60) is the Fock equation over the outercore spinors. Once the valence Fock equation is generated, the total energy can be optimized self-consistently by varying the outercore eigenvectors constituting the matrix $\mathbf{C}$ of Eq. (60) and the eigenvectors of the valence Fock equation. Optimization of the total energy yields a new Fock equation for the outercore because the resulting eigenvector matrix $\mathbf{C}$ will be different from the initial one. Therefore, a new equation (60) will be generated for every system treated, as well as for every state of a particular system. Since $\mathbf{C}$ also appears in Eq. (73), a new valence Hamiltonian will also be defined. The final form of the total pseudopotential, given by Eqs. (60) and (73), 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 wavefunction in an all-electron calculation and the final wavefunction in a small core REP calculation to the final wavefunction generated in the presence of a RPP. In the first case, the final wavefunction extends over the entire molecule. Consequently, it contains contributions from all of the basis functions: core, outercore, and valence. In the second case, the outercore is treated explicitly as part of the valence space. The final wavefunction thus contains contributions from all of the valence basis functions, which includes those corresponding to the outercore region. In an RPP calculation, the outercore region is kept separate from the valence region. This prevents outercore "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 wavefunction that contains contributions from basis functions corresponding solely to the valence region and in an outercore wavefunction that contains contributions solely from the outercore 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. (73)] and the matrix of outercore eigenvectors $\mathbf{C}$ are varied as distinct blocks, with no off-diagonal elements that connect the two spaces appearing in the total wavefunction. The effects of these off-diagonal elements are taken into account via the RPP [refer to Eqs. (70a) and (70b)].

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^{rel} becomes

$$H^{rel} = \Sigma_c h_c + \Sigma_c \Sigma_{c'} 1/r_{cc'}$$
$$+ \Sigma_o h_o + \Sigma_o \Sigma_{o'} 1/r_{oo'} + \Sigma_c \Sigma_o 1/r_{co}$$
$$+ \Sigma_v h_v + \Sigma_v \Sigma_{v'} 1/r_{vv'} + \Sigma_c \Sigma_v 1/r_{cv} + \Sigma_o \Sigma_v 1/r_{ov}$$
$$+ \Sigma_\alpha \Sigma_\beta Z_\alpha Z_\beta/r_{\alpha\beta}, \tag{74}$$

where

$$h_v = -1/2 \, \nabla_v^2 - \Sigma_\alpha Z_\alpha/r_{iv} \tag{75}$$

and h_c and h_o have the same form as h_D in Eq. (2). Z_α is the effective nuclear charge on atom α, and $r_{\alpha\beta}$ is the internuclear distance between atoms α and β. The total energy is then given by

$$E_t^R = <\Psi^r | H^{rel} | \Psi^r> = E_c^R + E_o^R + E_{co}^R + E_v^R + E_{cv}^R + E_{ov}^R + E_{\alpha\beta}^R, \tag{76}$$

which is a sum of core, outercore, core/outercore, valence, core/valence, and outer/core-valence interaction energies plus the nuclear repulsion energy. The first term on the right-hand side of Eq. (76) 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 to 0. The second and third terms on the right-hand side of Eq. (76) 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 outercore basis functions with the operators shown in terms three, four, and five on the right-hand side of Eq. (74). Tagging the terms in Eq. (74) such that their atomic parentage is clearly understood yields

$$\Sigma_o h_o{}^\alpha + \Sigma_o \Sigma_{o'} 1/r_{oo'}{}^{\alpha\alpha} + \Sigma_c \Sigma_o 1/r_{co}{}^{\alpha\alpha} , \tag{77}$$

where the unconventional use of the superscript α denotes the atom from which the electrons originated. As labeled, the operators of Eq. (77) operate only on basis functions centered on atom α. Interactions between electrons on different centers are not considered in Eq. (77). Because the pseudopotential is calculated from the atom, it is important to the derivation that a distinction be made between intercenter and intracenter interactions. The benefits of this labeling scheme will be shown later.

When the operators of Eq. (77) operate on the basis functions centered on atom α, the following equation results:

$$F_\alpha{}^{RPP} C_\alpha = S_\alpha\, C_\alpha\, \varepsilon_\alpha \tag{78}$$

Equation (78) corresponds to intra-atomic (for atom α) outercore/outercore interactions in a molecule and is analogous to Eq. (60), which corresponds to atomic outercore/outercore 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, β, are

$$\Sigma h{}^\beta{}_o + \Sigma_o \Sigma_{o'} 1/r_{oo'}{}^{\beta\beta} + \Sigma_c \Sigma_o 1/r_{co}{}^{\beta\beta} . \tag{79}$$

The terms in (79) are associated with the following variant of Eq. (78):

$$F_\beta{}^{RPP} C_\beta = S_\beta\, C_\beta\, \varepsilon_\beta . \tag{80}$$

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

$$F_\alpha{}^{RPP} C_\alpha = S_\alpha\, C_\alpha\, \varepsilon_\alpha$$

$$F_\beta{}^{RPP} C_\beta = S_\beta\, C_\beta\, \varepsilon_\beta \tag{81}$$

$$.$$
$$.$$
$$.$$

$$F_N{}^{RPP} C_N = S_N\, C_N\, \varepsilon_N .$$

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

$$\Sigma_o \Sigma_{o'} 1/r_{oo'}{}^{\alpha\beta} + \Sigma_c \Sigma_o 1/r_{co}{}^{\alpha\beta} . \tag{82}$$

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

The matrix equations in Eq. (81) 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

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all-electron F matrix):

0	0	0	0
0	outercore/outercore interactions for atom α...	0	0
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
0	0	outercore/outercore 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/outercore 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. (81), and also Eqs. (60) and (42)].

Outercore/outercore 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 outercore basis functions that are already contained in the calculation via Eq. (81). 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 outercore and valence spinors. No integrals of this type can be included as a consequence of the outercore-valence orthogonality operator that is contained in U^{RPP}. [Refer to Eqs. (70a) and (70b).] In other words, the outercore and valence regions must remain distinct from one another. All interactions between the two are incorporated into U^{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	outercore/outercore interactions for atom α...	interactions between (outercore)$_\alpha$/(outercore)$_N$	0
.	.	.	.
.	.	.	.
.	.	.	.
0	interactions between (outercore)$_N$ /(outercore)$_\alpha$...	outercore/outercore 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 outercore and valence spinors; that is, all of the coefficients in the resulting eigenvectors must correspond either to the valence basis functions or to the outercore 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 outercore space and one for the valence space, and these two are connected via the U^{RPP}. [Note that both Eqs. (60) and (70b) contain $\mathbf{C}$, the matrix of outercore eigenvectors.] Once the self-consistent variation is completed, the resulting outercore/outercore 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, outercore for each atom comprising the molecule.

V. The Relativistic Pseudopotentional and Very Large Systems

The RPP method assumes that the outercore 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 *outercore* rather than of *inner valence*). Therefore, as previously stated, the perturbations to the outercore resulting from bond formation propagate to the outercore region from the valence space. In other words, when the valence space is altered during bonding, these changes are propagated to the outercore via the valence/outercore interaction terms, which cause the outercore 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 outercore electrons are truly more corelike than valencelike, the interaction energies associated with the operators of Eqs. (77), (79), and (82) are equal to terms that represent the polarization of the outercore 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 outercore region of each atom comprising the molecule. Therefore, the outercore/outercore interactions can be approximated accurately by assuming that

each polarized atomic outercore represents a "charge" and that each of these "charges" can interact with all of the other "charges" comprising the outercore portion of the molecule. In other words, the intercenter outercore/outercore interaction energy can be calculated from the following set of integrals:

$$\langle \phi_\alpha \phi_\beta | 1/r_{12} | \phi_\alpha \phi_\beta \rangle \ , \tag{83}$$

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

$$\int |\phi_\alpha|^2 \, |\phi_\beta|^2 \, 1/r_{12} \, d\tau_\alpha \, d\tau_\beta \ , \tag{84}$$

where α and β represent the two centers and r_{12} is the distance between electron 1 on center α and electron 2 on center β. [Note: Eqs. (83) and (84) 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 *outercore* are restricted to reside in the outercore region; that is, no outercore 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 outercore region of a given atom is dictated by its atomic polarizability. Consequently, the outercore 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 outercore orbitals and not of the type given by Eq. (84) 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 sytems (e.g., clusters, surfaces) are to be treated.

The pseudopotential method is therefore a highly flexible type of pseudopotential, allowing a range of intercenter 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. (84). Although this is expected to be a good approximation in general, however, it is always possible to encounter systems for which an accurate description of the outercore electronic structure would require the inclusion of additional Coulomb–and exchange–interactions, for example, systems having highly polarized outercores 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. (84) plus all two-center exchange integrals, and so forth. The number of integrals included is dictated by the level of accuracy desired.

VI. The Relativisitic Pseudopotential Approximation

The approximations involved in the RPP method are best understood in the context of the three electronic regions that it describes in both atomic and molecular systems. These regions are named core, outercore, and valence. The RPP method mathematically differentiates among the three in recognition of the fact that they are physically and chemically distinct from one another. This applies to both atoms and molecules. To understand the nature of these differences, it is helpful to consider an all-electron treatment in which the electronic space has been partitioned into core, outercore, 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 to r, where r is a radial distance (r equals zero at the nucleus). Outercore spinors are defined as those spinors whose maxima occur in the region from r to r', where r' > r. The valence spinors, on the other hand, maximize somewhere in the region from r' to infinity. These three types of spinors differ both radially and

energetically. Hence, core spinors, by definition the lowest-energy spinors, occupy an energy region that is distinct from outercore spinors. The latter, in turn, occupy an energy region that is distinct from the valence spinors, which are highest in energy. These physical separations result in chemical differences (which will become clearer as the discussion progresses). 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"; that is, although they extend from zero to infinity, they are situated overwhelmingly in the core region, with only a small percentage of the spinor extending outwardly into the outercore and valence regions. The outercore electrons are associated with spinors that are more diffuse. 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; that is, they are not as "tight". Although the outercore spinors are radially positioned predominantly in the outercore 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. These are the electrons of maximum interest to the chemist because they are the ones that participate in processes such as ionization and bonding.   Since core, outercore, and valence spinors are predominantly separated from each other, the electrons corresponding to these spinors will also be separated from each other. Consequently, the following two-electron exchange interactions,

$$<\phi_i\phi_j|1/r_{12}|\phi_j\phi_i> \qquad\qquad (85)$$

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. As noted earlier, this approximation is somewhat less accurate when these interactions are between outercore and valence electrons because outercore 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; that is, the spinors are, to a large degree, "situated" within their respective spaces. This is called the local approximation and is a foundation of pseudopotential theory. Exchange interactions among electrons occupying the same region of space–namely, core-core, outercore-outercore, and valence-valence interactions–cannot be neglected, however, because these electrons are closer to one another, making the operator of Eq. (85) larger and thus the integral significant.

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

$$<\phi_i\phi_j|1/r_{12}|\phi_i\phi_j> . \qquad\qquad (86)$$

Equation (86) may be written in terms of the charge densities of electrons 1 and 2:

$$\int |\phi_i|^2 \, |\phi_j|^2 \, 1/r_{12} \, d\tau_1 \, d\tau_2 \; . \qquad\qquad (87)$$

To understand the nature of the outercore region, it is more useful to consider the interregion Coulomb interactions in terms of Eq. (87). Thus, Equation (87) 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," and their maxima occur deep within the atom. Consequently, the probability of finding a core electron is highest in the core region; in other words, the core-electron density is highest in the core. The same can be said of a valence electron in the valence region. The charge densities of Eq. (87) 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 distance results 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, the 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 (the core spinors are "tight"). 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 outercore-valence interactions, the results are significantly different. This is due to the chemical nature of the outercore. The spinors in this region are more diffuse than

those of the core but less so than those of the valence. The outercore spinors correspond to electrons that are not held as closely to the nucleus because of 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 outercore 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 outercore electrons are lower in energy and correspond to spinors whose maxima lie in a distinct region of space. The probability of finding an outercore electron in the valence region is thus much lower than the probability of finding a valence electron in the same region. The outercore electrons are predominantly "localized" in the outercore 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, because the valence-like part of their nature.

This valence-like nature can be understood by examining Eq. (87) in the case where electron 1 is an outercore electron and electron 2 is a valence one. The highest probability of finding an outercore electron occurs in the outercore region. The same can be said of the probability of finding a valence electron in the valence region. In both cases, the distance between the electrons is large, making the $1/r_{12}$ operator of Eq. (87) small and thus the integral small. Since the outercore spinors are more diffuse than the core spinors, a greater portion of the outercore spinor–which, like the core ones, also extend radially from zero to infinity– resides in the valence region. In this case, r_{12} is small because both electrons occupy the valence region, making the operator of Eq. (87) large. In addition, the probability of finding the outercore electron in the valence region is not negligible (unlike the case of a core electron in the valence region) because the outercore spinors are more diffuse. Thus $|\phi_i|^2$ is no longer small enough to cause the integral of Eq. (87) to disappear.

Equation (85) 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. This is due to the fact that the core electrons are deeply imbedded within the atom, near the nucleus, and their corresponding spinors are "tight". Since the maxima of these spinors occur nearer to 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 outercore 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 outercore region, on the other hand, is not completely chemically inert. As mentioned, this is an intermediate regime where the spinors are not as tight as those in the core but are tighter than those in the valence.   Since all outercore spinors, regardless of center, occupy the same energy regime (i.e., that region in which the electrons polarize during ionization and bonding), their maxima lie in approximately the same region of space. Among electrons in this region, multicenter interactions of the type given by Eq. (85) are significant because r_{12} is small. The following example makes this point clearer. Two-electron, one-center Coulomb interactions between outercore and valence electrons of atom A in molecule AB result in a polarization of the outercore electrons of A in response to the valence electronic motion of AB via Eq, (87). If this polarization occurs in such a way as to shift the outercore electron density of A toward the outercore electron density of B, multicenter outercore-outercore interactions in AB cannot be neglected because the operator of Eq. (85), 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 (i.e., the maxima of these spinors have a very large radial extent). 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, we can now compare the REP with the RPP. REPs involve two spaces, the core and the valence. Since the outercore region is not explicitly labeled, these electrons must be treated either as part of the core or as part of the valence. When the outercore electrons are included in the valence space, the resulting REPs are small core, SCREPs. SCREPs correspond to a core region that is atomiclike 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 outercore electrons are included in the core space, the resulting REPs are large core, LCREPs. The outercore electrons, as previously discussed, are not chemically inert like the core ones. Thus, incorporation of these electrons into the core space leads to sizeable errors. Specifically, LCREPs include all two-electron one-center outercore 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 outercore electrons. Furthermore, for molecules and excited-state atoms, all one-center

Coulomb interactions between outercore and valence electrons are also erroneous, since the outercore 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 outercore relaxation or polarization. This leads to sizable errors. RPPs, on the other hand, define the outercore region and at the most rigorous limit (refer to Section V) include all one-center and multicenter interactions among outercore electrons. Moreover, the outercore spinors participate in the SCF optimization, thereby yielding accurate one-center Coulomb interactions between outercore and valence electrons. In other words, RPPs allow outercore relaxation and polarization.

Table I, which summarizes all possible two-electron interactions and corresponds to an electronic space that has been divided into core, outercore, 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 through 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 one through four. Interactions five through six exist between core and outercore electrons. For these, the LCREP differs from the SCREP and RPP in that it includes core-outercore one-center exchange interactions because the outercore electrons are included in the core space, and thus interactions one through four and interactions five through eight are equivalent for LCREPs. With SCREPs the outercore electrons are treated explicitly as part of the valence space, making interactions five through eight equivalent to interactions nine through twelve. Since RPPs differentiate among the three regions, interactions one through four are distinct from interactions five through eight and nine through twelve. Tbe difference between the RPP and the REP for interactions five through twelve lies in the method by which the outercore and valence spinors are optimized. Since the REP does not differentiate between the outercore and valence spinors, no restrictions are placed on the optimization process, making the resulting valence wavefunction include outercore spinors; that is, the total valence wavefunction extends over the outercore space. RPPs, on the other hand, distinguish between outercore and valence electrons. Thus, the outercore and valence spinors are optimized such that the total valence wavefunction includes only valence spinors and the total outercore wavefunction includes only outercore 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, outercore, and valence spaces, interactions one through twelve 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, outercore, and valence regions such that the explicit inclusion of insignificant integrals is not required.

LCREPs describe interactions thirteen through twenty differently from SCREPs, RPPs, and all-electron methods. LCREPs include the outercore electrons in the core region, making interactions thirteen through sixteen and seventeen through twenty analogous to interactions one through four and nine through twelve, respectively. SCREPs and all-electron methods, on the other hand, incorporate the outercore electrons into the valence space, making interactions thirteen through twenty analogous to interactions twenty-one through twenty-four. RPPs include interactions thirteen through sixteen, as do SCREPs and all-electron calculations. However, as has been pointed out, the optimization of the outercore region is carried out separately from that of the valence region in RPPs, whereas in SCREPs and all-electron procedures the outercore is optimized as part of the valence region. Despite these differences, all three procedures include multicenter Coulomb and multicenter exchange interactions (interactions fourteen and fifteen). LCREPs do not include these interactions because the outercore orbitals are treated as core orbitals and are thus frozen at their atomic values; no interactions are considered among different cores. The outercore orbitals are thus kept from

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polarizing. The omission of interactions fourteen and fifteen results in errors when LCREPs are used in molecular calculations. Since RPPs include these interactions, they recover these errors. In addition, since outercore 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.

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

TWO-ELECTRON INTERACTIONS[a]	ALL-ELECTRON	SCREP[b,c]	RPP[b,d]	LCREP[b,e]
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-outercore one-center Coulomb	yes	yes	yes	yes
6. Core-outercore multicenter Coulomb	yes	yes[f]	yes[f]	no
7. Core-outercore one-center exchange	yes	no	no	yes
8. Core-outercore multicenter exchange	yes	no	no	no
9. Core-valence one-center Coulomb	yes	yes	yes	yes
10. Core-valence multicenter Coulomb	yes	yes[f]	yes[f]	yes[f]
11. Core-valence one-center exchange	yes	no	no	no
12. Core-valence multicenter exchange	yes	no	no	no
13. Outercore-outercore one-center Coulomb	yes	yes	yes	yes
14. Outercore-outercore multicenter Coulomb	yes	yes	yes	no
15. Outercore-outercore one-center exchange	yes	yes	yes	yes
16. Outercore-outercore multicenter exchange	yes	yes	yes	no
17. Outercore-valence one-center Coulomb	yes	yes	yes	yes
18. Outercore-valence multicenter Coulomb	yes	yes	yes	yes[f]
19. Outercore-valence one-center exchange	yes	yes	no	no
20. Outercore-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

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

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[11]. At the Dirac-Fock and Hartree-Fock levels of theory, these RPPs account for outercore polarization effects. Core and outercore relativistic effects present in the atomic Dirac-Fock hamiltonian will be consistently carried over to molecular environments and be deposited into the resulting polyatomic wavefunction. 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 outercore and the other to the valence region. This leads to a relaxation or polarization of the outercore region as a consequence of the valence interactions and is possible because all of the coefficients corresponding to the outercore atomic basis functions for each atom are present in each of the matrix equations. Although the outercore eigenvectors are self-consistently optimized, outercore-valence separability is maintained because no outercore coefficients contribute to the valence wavefunctions. 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.

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REFERENCES

1. M. M. Marino, W. C. Ermler, C. W. Kern, and V. E. Bondybey, J. Chem. Phys. 96, 3756 (1992).
2. Y. S. Lee, W. C. Ermler, and K. S. Pitzer, J. Chem. Phys. 67, 5861 (1977).
3. L. Szasz, *Pseudopotential Theory of Atoms and Molecules*, Wiley, New York (1985).
4. P. Schwerdtfeger, T. Fischer, M. Dolg, G. Igel-Mann, A. Nicklass, H. Stoll, and A. Haaland, J. Chem. Phys. 102, 2050 (1995), and private communication.
5. P. A. Christiansen, Y. S. Lee, and K. S. Pitzer, J. Chem. Phys. 71, 4445 (1979).
6. J. P. Desclaux, Computer Phys. Commun. 9, 31 (1975).
7. W. C. Ermler and M. M. Marino, *Relativistic and Electron Correlation Effects in Molecules and Solids*, ed. G. Malli, Plenum, N.Y. (1994).
8. H. Stoll, P. Fuentealba, P. Schwerdtfeger, J. Flad, L. V. Szentpaly, and H. J. Preuss, Chem. Phys. 81, 2732 (1984).
9. P. A. Christiansen, Chem. Phys. Lett. 127, 50 (1986).
10. M. M. Marino and W. C. Ermler, Chem. Phys. Lett. 206, 271 (1993).
11. W. C. Ermler and M. M. Marino, New Methods in Quantum Theory, ed. C. A. Tsipis, V. S. Popov, D. R. Herschbach, and J. S. Avery, Kluwer Academic, Dordrecht (1996).
12. C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).
13. L. A. LaJohn, P. A. Christiansen, R. B. Ross, T. Atashroo, and W. C. Ermler, J. Chem. Phys. 87, 2812 (1987).
14. W. Muller, J. Flesch, and W. Meyer, J. Chem Phys. 80, 3297 (1984).
15. I. P. Grant, Adv. Phys. 19, 747 (1970).
16. W. C. Ermler, R.B. Ross and P.A. Christiansen, Adv. Quantum Chem. 19, 139 (1988).