A projector augmented wave (PAW) formulation of Hartree-Fock calculations of electronic structure

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The Projector Augmented Wave (PAW) formalism developed by Blöchl [Phys. Rev. B 50, 17953 (1994)] has been demonstrated to be an accurate and efficient pseudo-potential-like scheme for electronic structure calculations within density functional theory. We have extended this formalism to treat the integral-differential equations of Hartree-Fock (HF) theory, demonstrating that the PAW-HF method is to able calculate valence energies with the same accuracy as the frozen core orbital approximation. We show that for some elements, electrons in core states provide significant contributions to the valence exchange energy and we develop schemes for incorporating their effects into the PAW-HF formalism.

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I. INTRODUCTION

Recently, there has been renewed interest in using the Hartree-Fock approximation as a component of electronic structure calculations.1–6 Many of these calculations use plane-wave representations for the valence wavefunctions together with norm-conserving pseudopotentials to represent the effects of the core electrons. In this paper, we develop a projected augmented wave (PAW)7–12 formulation of Hartree-Fock theory. Previous work by the VASP group13 has shown that the PAW formalism is able to accurately evaluate the Fock operator, including all of its multipole moments. In this paper, we explore how the PAW formalism, developed for Kohn-Sham theory14 can be modified to work with the integral-differential equations of Hartree-Fock theory. In particular, we show how the relationship between the basis and projector functions should be modified, and also examine the role of the core electrons within the treatment. In this paper, the detailed analysis focusses on the treatment of spherical atoms; application of the Hartree-Fock PAW formalism to non-spherical, spin polarized, and/or multi-component systems can be obtained with a straightforward extension of the basic equations.

The paper is organized as follows. In Sec. II, we review the all-electron formalisms, comparing Kohn-Sham and Hartree-Fock equations. In Sec. III we examine the accuracy of various frozen core approximations within both Kohn-Sham and Hartree-Fock treatments. The PAW formalism is presented in Sec. IV and example functions are presented in Sec. V. The summary and conclusions are given in Sec. VI. Some additional details of the formalism are given in Appendices A and B.

II. ALL-ELECTRON FORMALISMS

In all of the treatments of the electronic structure of atoms, we will use one-electron orbitals which can be written in the form:

$$\Psi_p(r) = \Psi_{n_p m_p}(r) = \frac{\psi_p(r)}{r} Y_{l_p m_p}(\hat{r})$$  \hspace{1cm} (1)

where symbols $p$ (and $q, s, t \ldots$) denotes a shell index, with $n_p$ denoting the principle quantum number and $l_p$ denoting the angular momentum. $Y_{l_p m_p}(\hat{r})$ is the spherical harmonic function and $\psi_p(r)$ denotes the radial portion of the wavefunction. The number of electrons in a shell is given by $N_p \leq 2(2l_p+1)$. For simplicity, we consider only the averaged electronic configuration, so that the electron density $\rho(r) \equiv \rho(r)$ is spherically symmetric:

$$\rho(r) \equiv \frac{n(r)}{4\pi r^2}$$ \hspace{1cm} where $n(r) = \sum_p N_p |\psi_p(r)|^2$.  \hspace{1cm} (2)

The total electronic energy in all of the treatments can be written as a sum of four terms

$$E_{tot} = E_K + E_N + E_H + E_{xc}.$$ \hspace{1cm} (3)

Here the kinetic energy $E_K$ and the nuclear energy $E_N$ can be evaluated in terms of the one-electron orbitals and densities in the usual way. The Hartree energy can be expressed in terms of the electron density using the expression

$$E_H = \frac{e^2}{2} \int d^3r d^3r' \rho(r)\rho(r')[r - r']^{-1}.$$ \hspace{1cm} (4)

We note that this definition of the Hartree energy includes the so-called electron self-interaction15 which should in principle be corrected within the exchange-correlation contribution. The form of the exchange-correlation energy $E_{xc}$ or the exchange-only energy $E_x$ depends on the particular approximation scheme we are using and will be discussed in more detail below.

A. Kohn-Sham theory

Within the local density approximation (LDA)16 or generalized gradient approximation (GGA),17 the exchange-correlation functional is assumed to have an explicit dependence on the electron density $\rho(r)$ which is usually written in the form

$$E_{xc} = \int d^3 r f_{xc}(\rho(r), |\nabla \rho(r)|).$$ \hspace{1cm} (5)
For the case of GGA, the functional depends explicitly not only on the density but also on the gradient of the density. The one-electron orbitals are solutions of the Kohn-Sham equations of the form

$$\mathcal{H}^{KS} \Psi_p^{KS}(r) = \varepsilon_p \Psi_p^{KS}(r),$$

(6)

where the Kohn-Sham Hamiltonian takes the form

$$\mathcal{H}^{KS} = K + V^{KS}(r).$$

(7)

Here $K$ denotes the kinetic energy operator and $V^{KS}(r)$ denotes the Kohn-Sham potential which is determined from the density derivatives of the last three terms in Eq. (3), with

$$V^{KS}(r) = V_N(r) + V_H(r) + V_{xc}(r).$$

(8)

For a spherical atom the potential components take the form

$$V_N(r) \equiv -\frac{Ze^2}{r}, \quad V_H(r) \equiv e^2 \int d^3r' \rho(r') \frac{\rho(r')}{|r-r'|},$$

(9)

and the exchange-correlation potential is defined in terms of the functional derivative with respect to the electron density $\rho(r)$

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)}.$$  

(10)

The self-consistent solution of the Kohn-Sham equations is obtained by minimizing the total energy (Eq. (3)) with $E_{xc}$ defined by Eq. (5) subject to the constraint that Kohn-Sham orbitals $\Psi_p^{KS}(r)$ are eigenstates of the Kohn-Sham Hamiltonian (7). Since the Kohn-Sham Hamiltonian is Hermitian, the eigenstates $\Psi_p^{KS}(r)$ are unique up to normalization.

### B. Hartree-Fock formalism

Within Hartree-Fock theory, the total energy of a spherical atom is given by Eq. (3) with the replacement of “exchange-correlation” energy with the Fock exchange energy:

$$E_x = -\frac{e^2}{2} \sum_{pq} \int \int d^3r d^3r' \frac{\Psi_p^{*}(r)\Psi_q(r)\Psi_q^{*}(r')\Psi_p(r')}{|r-r'|},$$

(11)

where the notation implies that the summation is taken over all occupied states of the same spin. For a spin and configuration averaged atom, the Fock exchange energy can be evaluated by using a moment expansion of the Coulomb kernel,

$$E_x = -\sum_{pq} \sum_{L=|l_p-l_q|}^{l_p+l_q} \frac{1}{2} \Theta_{pq}^L \Theta_{pq}^{L*}.$$

(12)

This exchange expression uses radial integrals similar to those introduced by Condon and Shortley

$$\Theta_{pq}^{L*} = e^2 \int \int dr dr' \frac{r_p^L}{r_p^L+1} \psi_p^{*}(r)\psi_q(r)\psi_q^{*}(r')\psi_p(r').$$

(13)

The Fock weight factor for the moment $L$ for the spherically averaged atom is given by

$$\Theta_{pq}^{L} = \left\{
\begin{array}{ll}
\frac{1}{2} N_p N_q \left( \begin{array}{ccc}
l_p & L & l_q \\
n & 0 & 0 \\
0 & 0 & 0
\end{array} \right)^2 & \text{for } p \neq q \\
\frac{1}{2} N_p (N_p - 1) \frac{2L+2}{2L+1} \left( \begin{array}{ccc}
l_p & L & l_q \\
n & 0 & 0 \\
0 & 0 & 0
\end{array} \right)^2 & \text{for } p = q \text{ and } L \neq 0 \\
N_p & \text{for } p = q \text{ and } L = 0.
\end{array} \right.$$  

(14)

In addition to the Fock exchange, this weight factor includes the Hartree self-interaction correction.

In order to find the Hartree-Fock orbitals $\{\psi_p^{HF}(r)\}$, the total energy (3) is optimized as a function of the orbitals with orthonormalization constraints. The objective function of this optimization is given by

$$F^{HF}(\{\psi_p^{HF}(r)\}, \{\lambda_{qp}\}) = E_{tot}(\{\psi_p^{HF}\}) - \sum_{qp} N_p \lambda_{qp} \left( \langle \Psi_p^{HF} | \Psi_q^{HF} \rangle - \delta_{qp} \right),$$

(15)

where $\lambda_{qp}$ denotes a Lagrange multiplier. The minimization is obtained by self-consistently solving the integral-differential equations resulting from the functional derivative.

$$\frac{\delta E_{tot}(\{\psi_p^{HF}\}, \{\lambda_{qp}\})}{\delta \psi_p^{HF*}} = 0.$$  

(16)

The Hartree-Fock equations take the form:

$$H^{HF}(r)\psi_p^{HF}(r) + X_p(r) - \sum_{q,N_q>0} \lambda_{qp} \psi_q^{HF}(r) = 0.$$  

(17)

Here,

$$H^{HF}(r) \equiv K + V_N(r) + V_H(r).$$

(18)
The nuclear and Hartree potentials have the same form as given in Eq. (9). The exchange kernel function is given by

\[ X_p(r) \equiv \frac{1}{N_p} \frac{\delta E_x}{\delta \psi_p} = -\sum_q \sum_{L=|p-q|}^{L+1} \frac{1}{N_p} \Theta_{pq} W_{qp}^L(r) \psi_q^{HF}(r), \tag{19} \]

where

\[ W_{qp}^L(r) = e^2 \int dr' \frac{r^L}{r\geq r'} \psi_q^{HF*}(r') \psi_p^{HF}(r'). \tag{20} \]

Self-consistently solving the Hartree-Fock equations is equivalent to minimizing the total energy Eq. (3) with \( E_{xc} \) given by the Fock exchange energy defined by Eq. (12). In order to stabilize the numerical algorithm used to solve Eq. (17), it is convenient to use linear combinations of Hartree-Fock wavefunctions which diagonalize blocks of the \( \lambda_{qp} \) matrix which correspond to closed shells of the same angular momentum \( l_q = l_p \). For simplicity, rather than directly solving the integral-differential equations, we use an iterative technique.\(^{21-24}\) Starting with an initial guess for the radial components \( \{ \psi_p^{HF(0)}(r) \} \) the approximate form of the Hartree-Fock equations is a set of inhomogeneous differential equations for the updated radial components \( \{ \psi_p^{HF(1)}(r) \} \) of the form:

\[ \left( H^{HF(0)}(r) - \epsilon_p^{(0)} \right) \psi_p^{HF(1)}(r) = \mathcal{R}_p^{(0)}, \tag{21} \]

where

\[ \mathcal{R}_p^{(0)} = -X_p^{(0)}(r) + \sum_q \lambda_{qp}^{(0)} \psi_q^{HF(0)}(r) - \epsilon_p^{(0)} \psi_p^{HF(0)}(r). \tag{22} \]

Here the parameters \( \epsilon_p^{(0)} \approx \lambda_{qp}^{(0)} \) are introduced to further stabilize the solution.\(^{22}\) At convergence \( \{ \psi_p^{HF(0)}(r) \} \equiv \{ \psi_p^{HF(1)}(r) \} \). The results obtained in this way are essentially identical to those obtained from the ASAPS package developed by Fischer et al.\(^{21}\) That is, the values of \( \lambda_{qp} \) from the two programs agree within \( 10^{-4} \) Ry and graphs the radial wavefunctions \( \psi_q^{HF}(r) \) are superposable.

III. FROZEN CORE FORMALISMS

The notion of the frozen core approximation is that the inner shell electrons of any atom remain approximately constant and insensitive to a variety of atomic bonding and compositional environments. In practice, after all-electron calculation for an atom in a reference state, the shell indices \( p, q, \ldots \) are divided into core states (c) and valence states (v). The total electron density is partitioned into core and valence contributions:

\[ \rho(r) = \rho_c(r) + \rho_v(r), \tag{23} \]

where

\[ \rho_v(r) = \frac{n_v(r)}{4\pi r^2}, \quad \text{with} \quad n_v(r) = \sum_v N_v |\psi_v(r)|^2. \tag{24} \]

Here we are using the \( c \) and \( v \) labels to refer to both the category label and the label for the individual states in each category. In general, instead of calculating the “total” electron energy, it is convenient to define a valence electron energy in the form

\[ E_{val} = E_K + E_N + E_{H}^{\text{val}} + E_{xc}^{\text{val}}. \tag{25} \]

Here, the valence kinetic energy \( E_K^{\text{val}} \) and valence nuclear potential energy \( E_N^{\text{val}} \) can be evaluated in terms of the one-electron valence orbitals and the valence density respectively. The two contributions to the Hartree energy are divided into a core-valence interaction

\[ E_H^{\text{val}} = e^2 \int \int d^3r d^3r' \frac{\rho_c(r)\rho_c(r')}{|r-r'|} \equiv \int dr V_H(r)n_v(r) \tag{26} \]

and a valence-valence interaction

\[ E_{H}^{vv} = e^2 \int \int d^3r d^3r' \frac{\rho_v(r)\rho_v(r')}{|r-r'|} \equiv \frac{1}{2} \int dr V_H(r)n_v(r). \tag{27} \]

The Kohn-Sham and Hartree Fock treatments of the valence contributions to the exchange-correlation energy, \( E_{xc}^{\text{val}} \), are different as explained below.

A. Frozen core in Kohn-Sham theory

The frozen core approximation within Kohn-Sham theory has been well described in the literature.\(^{26}\) The local density and generalized gradient functionals are nonlinear functions of the density and therefore, it is not possible to determine a valence only contribution to \( E_{xc} \) in Eq. (25). In practice Eq. (5) is evaluated using the “frozen” core density \( \rho_c(r) \) plus the self-consistent valence density \( \rho_v(r) \). The self-consistent valence radial functions \( \{ \psi_v(r) \} \) are determined from solving the Kohn-Sham equations (6), while the frozen core density \( \rho_c(r) \) is not updated. The frozen core approximation comes from the fact that the core radial functions are generally not solutions of those Kohn-Sham equations as the valence states change from the reference configuration. Also, the valence orbitals are generally no longer exactly orthogonal to the core states. Our past experience\(^{27}\) shows this to be a very good approximation; some of the quantitative results are included in Fig. 2 below.

B. Frozen core in Hartree-Fock theory

There are at least two different methods of formulating a frozen core approximation within Hartree-Fock theory; we use the terminology of “frozen core orbital” and “frozen core potential” to distinguish the two schemes.

The frozen core orbital approximation within Hartree-Fock theory has been well described in the literature.\(^{24,28}\) Since the exchange energy is formed from the product of pairs of electron orbitals and can be divided into core-valence and valence-valence contributions:

\[ E_{xc} \rightarrow E_x^{\text{val}}, \quad \text{where} \quad E_x^{\text{val}} = E_x^{\text{core}} + E_x^{vv}. \tag{28} \]
The self-consistent solution of the Hartree-Fock equations form the core-valence exchange energy can be written
\[ E_{x}^{cv} \equiv \int dr V_{x}^{cv}(r)n_{v}(r). \] (35)

We have invested some effort in evaluating the frozen core potential approximation. One of the frozen core potential forms is chosen to be
\[ V_{x}^{cv}(r) = -\sum_{c} \frac{N_{v}X_{x}^{cv}(r)\psi_{v}^{HF}(r)}{n_{v}(r)} \]. (36)

where
\[ X_{x}^{cv}(r) = -\sum_{c} \frac{N_{v}X_{x}^{cv}(r)\psi_{v}^{HF}(r)}{n_{v}(r)} \]. (37)

This form is motivated by the fact that for any configuration, including the reference configuration, the exact expression for the core-valence exchange energy can be written
\[ E_{x}^{cv} = \int dr \sum_{v} N_{v}X_{x}^{cv}(r)\psi_{v}^{HF}(r). \] (38)

As a quantitative measure of the frozen core error, we define the difference of the excitation energy calculated in the frozen
core approximation relative to the exitation energy calculated in an all-electron treatment to be:

\[
\Delta \Delta E \equiv \left( E_{\text{tot}}^{\text{excited}} - E_{\text{tot}}^{\text{ground}} \right)_{AE} - \left( E_{\text{val}}^{\text{excited}} - E_{\text{val}}^{\text{ground}} \right)_{FC}.
\]  

(39)

Using this measure, results for excitation energies of elements in the 4th row of the periodic table, where the “frozen” core configuration is that of the Ar atom, are illustrated in Fig. 2. For the 4s4p materials, the Hartree-Fock frozen core orbital approximation has an error of \(2 \times 10^{-3}\) Ry or less which is similar to the frozen core density error obtained using LDA. For the 3d materials, the frozen core errors are \(9 \times 10^{-3}\) Ry or less for the Hartree-Fock frozen core orbital approximation which is similar (within a factor of 2) to the frozen core density error obtained using LDA. For the lighter elements, we have found HF frozen core orbital and LDA frozen core density errors to be \(10^{-4}\) Ry or less. Of course, all of these errors can be reduced by treating the upper core states (“semi-core states”) as valence states. By constrast, results for the frozen core error obtained by using the frozen core potential of Eq. (36) show the error in the valence energies of excited states to be larger by a factor of 5-10 than that of the frozen core orbital approximation as shown in Fig. 2. We have also examined the 2nd and 3rd row elements of the periodic table, finding the frozen core orbital error to be smaller than that of the frozen core potential approximation by a factor 10 or more. While for most materials that we have studied, the frozen core orbital error is considerably smaller than that of the frozen core potential, it is clear that the errors of both schemes are controllable. It is also quite possible that the frozen core potential error can be reduced by improving the form\(^35\) of the frozen core potential \(V_{\text{FC}}(r)\) over that given in Eq. (36). However, the fact remains that the functional forms of Eqs. (35) and (38) are different and it is not surprising that they should give different results as the valence configuration changes.

The optimized effective potential (OEP) method\(^{30,31}\) is designed to find a local potential \(V_{\text{OEP}}^{\text{loc}}(r)\) for use in the Kohn-Sham Hamiltonian consistent with the Fock exchange functional. However, in the OEP formulation, the \(V_{\text{OEP}}^{\text{loc}}(r)\) potential is used only to determine the Kohn-Sham wavefunctions which are in turn used to determine the exchange energy using the functional form of Eq. (12). It will be interesting to compare a frozen core potential approximation within the OEP formalism\(^32\) to this frozen core potential approximation of the Hartree-Fock formalism.

Despite the numerical error observed for frozen core potential treatments of the Fock functional discussed above, the corresponding norm conserving pseudopotential treatments within Hartree-Fock theory\(^4-6\) and exchange-only OEP theory\(^29\) have been quite successful. In fact the importance of core electron effects within exchange-only OEP theory has been a topic of debate in the recent literature,\(^33\) and several authors\(^34-36\) have shown that it is possible to get quite reasonable results with valence-only pseudopotentials. The PAW formulation of electronic structure calculations, provides a well-defined method for examining the core-electron effects more carefully in both Hartree-Fock and Kohn-Sham formalisms.\(^37\)

IV. PAW FORMALISM

The Projector Augmented Wave (PAW) formalism was developed by Blöchl\(^7\) and implemented by a number of authors.\(^7,9,11,12,27,38\) It is similar to the ultra-soft pseudopotential approach of Vanderbilt.\(^39\) The formalism needs a set of basis and projector functions for each atom \(\alpha\) which represent the valence states. Using the atomic shell nomenclature defined in Eq. (1), we will denote these as \(\Phi^\alpha_i(r)\) for an all-electron basis function, \(\tilde{\Phi}^\alpha_i(r)\) for the corresponding pseudo-electron basis function, and \(P^\alpha_i(r)\) for the corresponding projector function. For these functions, the “shell” indices \(i\) that enumerate the basis functions include the valence atomic states and may also include continuum and other states defined in the radial range \(0 \leq r \leq r_c^\alpha\) (the “augmentation” region) in order to increase the “completeness” of the basis set. For each formalism, it is required that the all-electron basis functions \(\{\Phi^\alpha_i(r)\}\) are solutions of the differential or differential integral equations corresponding to the reference configuration of the atom within the augmentation region. For the case of Kohn-Sham theory, they are eigenstates of the Kohn-Sham Hamiltonian (6). For the case of Hartree-Fock theory they are solutions of the Hartree-Fock Eq. (17)\(^40\) with special consideration for continuum states.\(^41\) The projector functions satisfy the relationship\(^52\)

\[
\langle \tilde{P}^\alpha_i | \tilde{\Phi}^\alpha_j \rangle = \delta_{ij},
\]

(40)

and the radial pseudo-functions have the property

\[
\tilde{\phi}^\alpha_i(r) = \phi^\alpha_i(r) \quad \text{for} \quad r > r_c^\alpha.
\]

(41)
Here \( r^a_c \) denotes the matching radius for atom \( a \). The radial function associated with the projector function \( P^a_i(r) \) is constructed to be spatially localized within the augmentation sphere \( r^a_c \).

A key idea of the PAW formalism is the transformation between a calculated pseudo-wavefunction \( \tilde{Ψ}_v(r) \) corresponding to a valence state of the system and the corresponding fully nodal wavefunction \( Ψ_v(r) \) of that state which is given by

\[
Ψ_v(r) = \tilde{Ψ}_v(r) + \sum_{a i} \left( \Phi^a_i(r - R^a) - \tilde{Φ}^a_i(r - R^a) \right) \langle \tilde{P}^a_i | \tilde{Ψ}_v \rangle.
\]

The sum \( ai \) is over atom center sites \( a \) and basis functions \( i \). With this transformation and a few additional terms, it is possible to evaluate the valence electron energy of the system as a combination of smooth pseudo-potential-like contributions plus a sum of atom-centered corrections in the form

\[
E_{\text{vale}} = \frac{\delta E_{\text{vale}}}{\delta \tilde{Ψ}^{KS}_v(r)} = \mathcal{H}^{\text{PAW}}_{KS}(r)\tilde{Ψ}^{KS}_v(r) = E_{\text{vale}} + \sum_a \left( E^a_{\text{vale}} - E_{\text{vale}}^a \right) \delta_{\text{atom-centered corrections}}.
\]

A. PAW formulation of Kohn-Sham theory

The detailed expression of the PAW valence energy in the local density approximation has been reported extensively in the literature and only the main points will be discussed here and a few additional details are given in Appendix A. Since the valence energy (43) is an explicit functional of the electron density which in turn is an explicit functional of the valence pseudowavefunctions, the Kohn-Sham equations in the PAW formalism can be evaluated in terms of the functional derivative

\[
\frac{\delta E_{\text{vale}}}{\delta \tilde{Ψ}^{KS}_v(r)} = \mathcal{H}^{\text{PAW}}_{KS}(r)\tilde{Ψ}^{KS}_v(r) = E_{\text{vale}} + \sum_a \left( E^a_{\text{vale}} - E_{\text{vale}}^a \right) \delta_{\text{atom-centered corrections}} = \mathcal{H}_{\text{KS}}^{\text{PAW}}(r)\tilde{Ψ}^{KS}_v(r) = \varepsilon_v O^{\text{PAW}}\tilde{Ψ}^{KS}_v(r).
\]

This equation must be solved self-consistently with the orthonormalization constraint

\[
\langle \tilde{Ψ}^{KS}_v | O^{\text{PAW}} | \tilde{Ψ}^{KS}_{v'} \rangle = \delta_{vv'}.
\]

Here the PAW Hamiltonian takes the form

\[
\mathcal{H}_{\text{KS}}^{\text{PAW}}(r) = \mathcal{H}_{\text{KS}}(r) + \sum_{a i j} |\tilde{P}^a_i| D^a_{ij} |\tilde{P}^a_j|,
\]

and

\[
O^{\text{PAW}} = 1 + \sum_{a i j} |\tilde{P}^a_i| O^a_{ij} |\tilde{P}^a_j|.
\]

Here the Kohn-Sham pseudo-Hamiltonian has the form

\[
\tilde{H}_{\text{KS}}(r) = K + \tilde{V}_{\text{KS}}(r).
\]

The overlap matrix element is given by

\[
O^a_{ij} = \langle \tilde{Φ}^a_i | \tilde{Φ}^a_j \rangle - \langle \tilde{Φ}^a_i | \tilde{Ψ}^a_i \rangle.
\]

The general form of \( \tilde{V}_{\text{KS}}(r) \) as well as of the one center matrix elements \( D^a_{ij} \) has been given in many references.\(^7,^{11,27,38}\) For convenience the contributions from terms other than exchange and correlation are given in Appendix A.

There are several alternative schemes\(^7,^{39}\) to construct the basis and projector functions for the PAW-Kohn-Sham formalism. In terms of the pseudo Hamiltonian of the reference state, the projector functions are related to the pseudowavefunction basis according to

\[
\tilde{Ψ}^a_i(r) = \sum_j \tilde{P}^a_i(r) \langle \tilde{Ψ}^a_j | \tilde{Ψ}^{KS}_v(r) \rangle - \varepsilon^a_i \langle \tilde{Ψ}^a_i | \tilde{Ψ}^{KS}_v(r) \rangle.
\]

This relationship is consistent with the requirements that each pseudowavefunction basis function \( \tilde{Φ}^a_i(r) \) must be a solution of the Kohn-Sham PAW equations (44) of the reference state and with the special form of the one-center Hamiltonian matrix elements of the reference state:

\[
D^a_{ij} = \langle \tilde{Φ}^a_i | \tilde{Ψ}^{KS}_v(r) | \tilde{Φ}^a_j \rangle - \langle \tilde{Φ}^a_i | \tilde{Ψ}^{KS}_v(r) \rangle \langle \tilde{Ψ}^a_j | \tilde{Ψ}^{KS}_v(r) \rangle.
\]

In practice, the projector functions \( \{ \tilde{P}^a_i(r) \} \) are determined by solving Eq. (50) from a knowledge of the reference pseudo Hamiltonian \( \tilde{H}_{\text{KS}}(r) \), the basis functions \( \{ \tilde{Φ}^a_i(r) \} \), and the eigenenergies \( \{ \varepsilon^a_i \} \), following a similar procedure developed by Vanderbilt.\(^39\)

B. PAW formulation of Hartree-Fock theory

For Hartree-Fock theory, the PAW valence energy expression can be put in the form of Eq. (43) as in the case of Kohn-Sham theory. The main differences come in the from of the treatment of the Fock exchange term and in the representation of the frozen core orbitals. From our analysis of the full wavefunction frozen core approximation discussed in Sec. III B, we decided to use the frozen core orbital approach for our PAW implementation.

For the purpose of this formulation, the valence pseudo-orbitals \( \tilde{Ψ}^{HF}_v(r) \) are treated separately from the core orbitals. As in the case of the Kohn-Sham formulation, it is assumed that they are spanned by the basis pseudo-functions \( \{ \tilde{Φ}^a_i(r) \} \) within the augmentation sphere.

Most of the core wavefunctions \( Ψ^{HF}_v(r) \) are contained within the augmentation sphere and for those we can define a trivial core pseudowavefunction \( \tilde{Ψ}^{HF}_v(r) \equiv 0 \). For some materials it is possible that at most one core orbital per \( l \) channel will have a non-trivial amplitude for \( r > r^a_c \). In such a case, it is convenient to define a continuous pseudo-core orbital \( \tilde{ψ}^a_c(r) \) with \( \tilde{ψ}^a_c(r) \equiv \psi^a_c(r) \) for \( r > r^a_c \), in a similar spirit to the pseudo-core functions defined for the so-called non-linear core corrections in norm-conserving pseudopotentials.\(^43\) In our case, we define

\[
\tilde{ψ}^a_c(r) \equiv \begin{cases} r^{l+1} P_n(r) & \text{for } r \leq r^a_c, \\ \psi^a_c(r) & \text{for } r > r^a_c. \end{cases}
\]

The \( n^{th} \) order polynomial \( P_n(r) \) is chosen to ensure that \( \tilde{ψ}^a_c(r) \) is continuous up to \( n-1 \) derivatives. An example of
FIG. 3. (Color online.) Radial Hartree-Fock wavefunction \( \tilde{\psi}_c(r) \) for the 3d core state of Ge compared with the constructed pseudo-wavefunction \( \tilde{\psi}_c(r) \).

This construction is shown for the 3d core state of Ge in Fig. 3.

In order to define localized contributions from Coulombic interactions, it is necessary to define “compensation” charge moments of the form

\[
\tilde{m}_{ij}^{L}(r) = \frac{m_{ij}^{L}}{\int_{0}^{\infty} r^2 s_L(u) \, du} = m_{ij}^{L} q_{ij}^{L}(r). \tag{53}
\]

Here \( s_L(r) \) is a smooth shape function:

\[
s_L(r) = r^L k(r), \tag{54}
\]

or it could be similar smooth function such as one involving a spherical Bessel function \( s_L(r) \equiv j_{\ell}(nr) \). More often we have chosen

\[
k(r) = \begin{cases} \left[ \frac{\sin(\pi r/r_c^n)}{\pi r/r_c^n} \right]^2 & \text{for } r < r_c^n, \\ 0 & \text{for } r \geq r_c^n. \end{cases} \tag{55}
\]

The charge moment coefficient is given by

\[
m_{ij}^{L} = \int dr \, r^L \left( \phi_i^{a}(r) \phi_j^{a}(r) - \phi_i^{c}(r) \phi_j^{c}(r) \right). \tag{56}
\]

The appropriate values of \( L \) are given by \( |l_i - l_j| \leq L \leq l_i + l_j \). These compensation charge terms were used by Blöchl' to evaluate the Hartree energy contributions and are embedded in the PAW-Kohn-Sham formalism discussed above. They are also important for evaluating the Fock exchange terms so that they can be written in the PAW form (43):

\[
E_{x}^{\text{cov}} = \tilde{E}_{x} + \sum_{a} \left( E_{x}^{\text{cov}} - E_{x}^{\text{a cov}} \right),
\]

\[
E_{x}^{\text{cov}} = \tilde{E}_{x} + \sum_{a} \left( E_{x}^{\text{cov}} - E_{x}^{\text{a cov}} \right), \tag{57}
\]

The trick\(^{13}\) is to use the compensation charge components to ensure that the long-range behavior of individual contributions to the Fock integrals are correct, while using the grouping of the smooth pseudo terms and the one-center terms to cancel out the unphysical pseudo contributions near the atom centers.

Below, explicit expressions are given for a spherical atom in which case there is only one atomic center \( a \). The ideas are easily generalized to multicenter systems.

For a given product of two valence states, \( \psi_{v}^{\text{HF}}(r) \psi_{v'}^{\text{HF}}(r) \), we can define a compensation charge moment of order \( L \)

\[
\tilde{M}_{uv}^{L}(r) = \sum_{aIJ} \langle \tilde{\Psi}_{v}^{L} | \tilde{P}_{IJ}^{a} | \tilde{\Psi}_{v'}^{L} \rangle m_{ij}^{L}(r) \tag{58}
\]

The significance of this moment is that, within the accuracy of the PAW transformation, the \( L^{th} \) moment of \( \psi_{v}^{\text{HF}}(r) \psi_{v'}^{\text{HF}}(r) \) is the same as the \( L^{th} \) moment of \( \psi_{v}^{\text{HF}}(r) \psi_{v'}^{\text{HF}}(r) + \tilde{M}_{uv}^{L}(r) \). For the moment representing core-valence wavefunction products, the moment coefficient \( m_{ij}^{L} \) corresponding to valence-core contributions is defined by an expression similar to Eq. (56) with \( \phi_{a}^{v} \rightarrow \psi_{c}^{v} \) and \( \phi_{a}^{c} \rightarrow \psi_{c}^{c} \). Because of orthogonality properties of core and valence states of the reference system and because \( \psi_{c}^{v} = 0 \) for many cases, there are several simplifications of the terms involving the core functions as discussed in more detail in Appendix B.

By using these compensation charge moments, the pseudo exchange integrals take the form

\[
\tilde{E}_{x}^{\text{cov}} = - \sum_{vv' L=|l_{v'}-l_{v}|}^{l_{v}+l_{v}'} \frac{1}{2} \Theta_{vv'}^{L} \tilde{R}_{v'v vv'}^{L} \tag{59}
\]

\[
\tilde{E}_{x}^{\text{cov}} = - \sum_{vv' L=|l_{v'}-l_{v}|}^{l_{v}+l_{v}'} \Theta_{vv'}^{L} \tilde{R}_{v'v vv'}^{L}, \tag{59}
\]

where

\[
\tilde{R}_{v'v vv'}^{L} = e^{2} \int dr \, dr' \sum_{\nu \nu' \delta_{\nu \nu'}} r_{\nu}^{L} \left( \psi_{v}^{\text{HF}}(r) \psi_{v'}^{\text{HF}}(r') + \tilde{M}_{v'v}^{L}(r') \right)
\]

\[
\times \left( \tilde{\psi}_{v}^{L}(r) \tilde{\psi}_{v'}^{L}(r) + \tilde{M}_{v'v}^{L}(r) \right), \tag{60}
\]

with an identical expression for \( \nu' \rightarrow c \). The corresponding one-center contributions take the form

\[
E_{x}^{\text{cov}} - \tilde{E}_{x}^{\text{cov}} = - \sum_{vv' L=|l_{v'}-l_{v}|}^{l_{v}+l_{v}'} \frac{1}{2} \Theta_{vv'}^{L} \]

\[
\times \sum_{ijkl} \langle \tilde{\Psi}_{v}^{L} | \tilde{P}_{ij}^{aL} | \tilde{\Psi}_{v'}^{L} \rangle \langle \tilde{\Psi}_{v}^{L} | \tilde{P}_{j}^{aL} | \tilde{\Psi}_{v'}^{L} \rangle
\]

\[
\times \left( R_{ij,kl}^{aL} - \tilde{R}_{ij,kl}^{aL} \right), \tag{61}
\]

and

\[
E_{x}^{\text{cov}} - \tilde{E}_{x}^{\text{cov}} = - \sum_{vv' L=|l_{v'}-l_{v}|}^{l_{v}+l_{v}'} \Theta_{vv'}^{L} \]

\[
\times \sum_{ij} \langle \tilde{\Psi}_{v}^{L} | \tilde{P}_{ij}^{aL} | \tilde{\Psi}_{v'}^{L} \rangle \left( R_{ic,ij}^{aL} - \tilde{R}_{ic,ij}^{aL} \right) \tag{62}
\]
Here
\[ R_{ij;kl}^{nL} \equiv e^2 \int dr \, dr' \, \frac{r_L}{r_{r,1}^L} \phi_k^*(r) \phi_j^*(r') \phi_i^*(r') \phi_i^*(r). \]  
(63)
and
\[ \tilde{R}_{ij;kl}^{nL} \equiv e^2 \int dr \, dr' \, \frac{r_L}{r_{r,1}^L} \left( \phi_k^*(r) \tilde{\phi}_j^*(r) + \tilde{m}_{ij}^{nL}(r) \right) \times \left( \phi_k^*(r') \tilde{\phi}_j^*(r') + \tilde{m}_{kl}^{nL}(r') \right). \]  
(64)

These expressions for the valence electron contributions to the exchange energy are equivalent to results given by previous workers. \(^{13,44}\)

From the PAW representations of the exchange energies and of the other energy terms, the PAW Hartree-Fock equations can be derived by taking the functional derivative the energy with respect to the valence pseudo-orbitals. The self-consistent Hartree-Fock equations for the PAW formulation take the form
\[ \Psi_{HF}^{PAW}(r) \psi_{HF}(r) + X_{HF}^{PAW}(r) - \sum_q \lambda_{qv} O_{HF}^{PAW} \psi_{HF}(r) = 0. \]  
(65)
These equations must be solved self-consistently, with orthonormalization constraint
\[ \langle \psi_{HF}(r) | O_{HF}^{PAW} | \psi_{HF}(r) \rangle = \delta_{eq}. \]  
(66)
This differs slightly from the orthonormalization constraint in the Kohn-Sham case (Eq. 45) since the index \( q \) can refer to either a valence state \( v \) or a (frozen) core state \( c \) for which the relevant matrix elements take the form:
\[ \langle \psi_{HF}^c | O_{HF}^{PAW} | \psi_{HF}^c \rangle = \langle \psi_{HF}^c | \psi_{HF}^c \rangle + \sum_{a} \langle \psi_{HF}^c | \tilde{P}_a^c \rangle O_{a}^c, \]  
(67)
where \( O_{a}^c \equiv m_{ac}^0 \). In general, these terms are very small if not identically zero. The single particle term of Eq. (65) takes the form
\[ \mathcal{H}_{HF}^{PAW}(r) \equiv \tilde{\mathcal{H}}_{HF}^{PAW} + \sum_{a, j} |P_a^c| D_{ij}^{aHF}(P_a^j), \]  
(68)
where the pseudo Hamiltonian-like terms depend on the pseudopotentials due to the nuclear and Hartree interactions:
\[ \tilde{\mathcal{H}}_{HF}(r) \equiv \mathcal{K} + \tilde{V}_X(r) + \tilde{V}_H(r). \]  
(69)
The exchange function term takes the form
\[ X_{HF}^{PAW}(r) \equiv \tilde{X}_v(r) + \sum_{a} |P_a^c| X_{a}^v, \]  
(70)
where the pseudo-exchange kernel function takes the form:
\[ \tilde{X}_v(r) \equiv -\sum_q \sum_{L=|u_q-L_q|}^{l_v+l_q} \frac{1}{N_v} \Theta_{eq}^L \tilde{W}_{vq}^L(r) \psi_q^v(r). \]  
(71)
In this expression, the summation over \( q \) includes both valence orbitals which are updated self-consistently and core orbitals which are “frozen”. The interaction function \( \tilde{W}_{vq}^L(r) \) is the pseudo analogue of Eq. (20):
\[ \tilde{W}_{vq}^L(r) \equiv e^2 \int dr' \, \frac{r_L}{r_{r,1}^L} \left( \psi_{HF}^v(r') \tilde{\psi}_{HF}^q(r') + M_{vq}^L(r') \right). \]  
(72)
The one center matrix element for the pseudo-exchange kernel function takes the form:
\[ X_{a}^v = -\sum_q \sum_{L=|u_q-L_q|}^{l_v+l_q} \frac{1}{N_v} \Theta_{ev}^L \tilde{Z}_{aL}^{ev}, \]  
(73)
where
\[ \tilde{Z}_{aL}^{ev} \equiv \int dr \tilde{W}_{vq}^L(r) \tilde{m}_{ij}^{aL}(r). \]  
(74)
The relationship between the projector and basis functions is somewhat different from that of the Kohn-Sham formalism, taking the form:
\[ \tilde{H}_{HF}(r) \tilde{\Phi}_j^a(r) + \tilde{X}_i^a(r) - \sum_{q:N_q>0} \lambda_{qi} \tilde{\psi}_{HF}^q(r) = \sum_j P_{ij}^a(r) A_{ji}^a \]  
(75)
Here the matrix coefficients are given by
\[ A_{ji}^a \equiv \langle \tilde{\Phi}_j^a | \tilde{H}_{HF} | \tilde{\Phi}_i^a \rangle + \langle \tilde{\Phi}_j^a | \tilde{X}_i \rangle - \sum_{q:N_q>0} \lambda_{qi} \langle \tilde{\Phi}_j^a | \tilde{\psi}_{HF}^q \rangle, \]  
(76)
where the differential \( \tilde{H}_{HF}(r) \) and integral \( \tilde{X}_i(r) \) operators as well as the Lagrange multipliers \( \lambda_{qi} \) are all evaluated for the reference configuration. Analogous to Eq. (50) for the PAW-Kohn-Sham formalism, for the PAW-Hartree-Fock formalism Eq. (75) is used to determine the projector functions \( \{ P_{ij}^a(r) \} \). Equation (75) is consistent with the requirement that the pseudowavefunction basis functions \( \tilde{\Phi}_j^a(r) \) must be a solution of the PAW Hartree-Fock equations (65) for the reference configuration of the atom and the following identities. For the reference state, the single particle terms satisfy the relationship
\[ D_{ij}^{aHF} \big|_{\text{ref}} = \langle \tilde{\Phi}_i^a | \mathcal{H}_{HF}^{PAW} | \tilde{\Phi}_j^a \rangle \big|_{\text{ref}} - \langle \tilde{\Phi}_i^a | \tilde{H}_{HF}^a | \tilde{\Phi}_j^a \rangle \big|_{\text{ref}}, \]  
(77)
and the two-particle terms satisfy the relationship:45

\[ X_{iv}^a |_{\text{ref}} = \langle \Phi^a_v | X_v^c \rangle |_{\text{ref}} - \langle \tilde{\Phi}^a_v | \tilde{X}_v^c \rangle |_{\text{ref}}. \] (78)

Once the basis and projector functions are determined, the solution of self-consistent PAW-Hartree-Fock equations (65) can be obtained using an iterative method similar to that of the all-electron or frozen core equations (17). For any guess of the valence pseudowavefunctions \( \{ \tilde{\psi}_v^{HF(0)}(r) \} \), the Lagrange multipliers \( \lambda_{iv}^{(a)} \) can be estimated by multiplying both sides of Eq. (65) by \( \tilde{\psi}_v^{HF(0)}(r) \) and integrating over all space. The Lagrange multipliers \( \lambda_{iv}^{(a)} \) corresponding to the interaction between core states and valence states can be estimated from the form

\[
\lambda_{iv}^{(a)} = \langle \tilde{\Phi}^a_v | \tilde{P}^{HF} | \tilde{\psi}_v^{HF(0)}(r) \rangle + \sum_j D_{ij}^{(a)} \langle \tilde{P}^{HF}_{ij} | \tilde{\psi}_v^{HF(0)}(r) \rangle + \langle \tilde{\psi}_v^{HF} | \tilde{X}_i^c(0) \rangle + X_{iv}^a |_{\text{ref}}.
\] (79)

Having derived the form of the PAW-HF equations, we are now in a position to examine the role of the core and pseudo-core orbitals. It is clear that from the way that the pseudo-core orbitals have been defined, \( \tilde{\psi}_v^a(r) \approx 0 \), so that the main contributions of the core orbitals are expressed in the atom centered radial Coulomb integrals \( R_{i|c\rightarrow j}^{aL} \) similar to the expression defined in Eq. (63). When \( \tilde{\psi}_v^a(r) \equiv 0 \), many of the matrix elements and Hamiltonian terms simplify as discussed in appendix B. In practice, the main contributions can be expressed in terms of the \( R_{i|c\rightarrow j}^{aL} \) integrals which contribute to the core-valence exchange energy \( E^{cv}_x \) as defined in Eqs. (57) and (62). They also contribute to the pseudo-exchange kernel function \( X_{iv}^c \) defined in Eq. (73). Since all of these core-valence contributions depend on constant matrix elements or functions that can be pre-calculated and stored, they should not substantially increase the computational requirements of PAW-Hartree-Fock over that of PAW-Kohn-Sham. (Of course the plane-wave treatment of the Fock operator and other numerical considerations of the Hartree-Fock equations must be taken into account as well.)

V. EXAMPLE PAW FUNCTIONS

There are many adjustable parameters in the construction of the PAW basis and projector functions which may be used to find a set of functions that “span” the space of pseudo wavefunctions in one-to-one correspondence with the fully nodal frozen core wavefunctions for the range of electronic configurations of interest. In fact, the shapes of the Hartree-Fock valence wavefunctions are, in general, similar to the shapes of the corresponding Kohn-Sham valence wavefunctions. This is illustrated in Fig. 4 for the example of Ge. Therefore, it should be possible to construct PAW-HF basis and projector sets with the help of the large literature describing the process for Kohn-Sham calculations.7,11,39,46–49

In constructing the pseudobasis functions, for each atom we vary only the augmentation radius \( r_c^a \) and construct the pseudobasis functions \( \tilde{\phi}_v^a(r) \) from all-electron basis functions \( \phi_v^a(r) \) using the polynomial form introduced by Vanderbilt in the construction of the ultra-soft pseudopotential scheme.39 (This also is the scheme for constructing the non-trivial pseudo-core functions \( \tilde{\psi}_v(r) \) of Eq. (52).) The other adjustable function in this construction is the localized potential \( V_{loc}^a(r) \) defined in Eq. (A4). It is often efficient to choose this potential as an unscreened norm-conserving pseudopotential derived from the Troullier-Martins construction for a high angular-momentum scattering state. Since the integral form of the Hartree-Fock equations slightly complicates the Troullier-Martins construction, we chose another method of constructing \( V_{loc}^a(r) \). A simple, but reasonable choice is

\[
V_{loc}^a(r) = V_0 \ k(r),
\] (80)

using the shape function defined in Eq. (55) and an adjustable amplitude \( V_0 \). Table I lists the Hartree-Fock valence energies of several atoms comparing the PAW energies with the corresponding frozen core results and also comparing the the effects of including or excluding the pseudo-core orbitals. In these cases, we have been able to achieve excellent agreement between the valence energies calculated with PAW and the frozen core orbital schemes. The convergence of the PAW-HF equations are sensitive to the choices of \( r_c^a \) and \( V_0 \), but the energies obtained including or excluding the smooth core functions are very close.

Our results provide information on the role of the pseudo-core orbitals of the upper core states. Of the materials presented in Table I, the core effects are most prominent for Ge. In Fig. 5 two examples of projector functions for the 4p states of Ge are presented, comparing the effects of including or excluding the pseudo-core functions and also comparing with the analogous LDA projector function. We see that the projector obtained by including the pseudo-core functions is quite similar in shape to that the LDA formulation. On the other hand, by setting the pseudo-core functions to zero, the projector function extends considerably beyond \( r_c^a \). The reason for this behavior can be explained from the defining Eq. (75).
TABLE I. Hartree-Fock valence energies for several configuration averaged atoms calculated with the frozen core orbital approximation (FC), and the PAW formalism (PAW). Results including ($|\tilde{\psi}_c| > 0$) and excluding ($|\tilde{\psi}_c| \equiv 0$) pseudo-core orbitals are compared. The augmentation radii ($r^a_c$) are given in bohr units, the local potential amplitudes ($V_0$) are given in Ry units, and the valence energies for the ground and excited states are given in Ry units. The core configurations are He for C, Ne for Si, and Ar for Ge.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Type</th>
<th>$r^a_c$</th>
<th>$V_0$</th>
<th>$E_{val}(ns^2np^2)$</th>
<th>$E_{val}(ns^1np^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>FC</td>
<td>-</td>
<td>-</td>
<td>-10.5990</td>
<td>-9.9542</td>
</tr>
<tr>
<td>C</td>
<td>PAW $&gt; 0$</td>
<td>1.3 2.0</td>
<td>-10.5990</td>
<td>-9.9541</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>PAW $\equiv 0$</td>
<td>1.3 2.0</td>
<td>-10.5990</td>
<td>-9.9541</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>FC</td>
<td>-</td>
<td>-</td>
<td>-7.3147</td>
<td>-6.8070</td>
</tr>
<tr>
<td>Si</td>
<td>PAW $&gt; 0$</td>
<td>2.0 3.0</td>
<td>-7.3147</td>
<td>-6.8066</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>PAW $\equiv 0$</td>
<td>2.0 3.0</td>
<td>-7.3147</td>
<td>-6.8070</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>FC</td>
<td>-</td>
<td>-</td>
<td>-7.2257</td>
<td>-6.6800</td>
</tr>
<tr>
<td>Ge</td>
<td>PAW $&gt; 0$</td>
<td>2.2 3.0</td>
<td>-7.2258</td>
<td>-6.6796</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>PAW $\equiv 0$</td>
<td>2.2 3.0</td>
<td>-7.2258</td>
<td>-6.6800</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 6. (Color on line.) Plots of the radial basis and projector functions for the 4s and 3d states of Fe. The parameters of the construction are described in the text. Label “I” refers to $|\tilde{\psi}_c| > 0$ and $V_0 = -2$ Ry and label “II” refers to $|\tilde{\psi}_c| \equiv 0$ and $V_0 = -6$ Ry, affecting only the shapes of the projector functions.

Fig. 5. (Color on line.) Radial PAW projector functions for 4p states of Ge, comparing effects of including and excluding pseudo-core orbital functions $\tilde{\psi}_c(r)$ within the Hartree-Fock (HF) formulation and also comparing the corresponding LDA projector. These projectors where used to obtain the results presented in Table I.

By construction, when the smooth core wavefunctions are included in Eq. (75), for $r \geq r^a_c$ the left hand side becomes identical to the left hand side of the all-electron Hartree-Fock Eq. (17) and therefore vanishes. When the smooth core functions are omitted, the two equations become equal only when core wavefunction amplitudes have become negligible so that the left hand side of Eq. (75) and therefore $\tilde{p}^a_i(r)$, remains non-zero beyond $r = r^a_c$. The example shown in Fig. 5 illustrates one of the more extreme cases of this effect, which is related to the extended shape of the Ge 3d core state shown in Fig. 3. However, the results in Table I show that the corresponding results on the valence energy of the atom are negligible. How these extended projectors behave when used to describe multiatomic systems will be an interesting question to study in future work.

A more strenuous test of the PAW-HF formalism is the ionization of Fe based on an Ar core configuration and valence configurations $4s^23d^6 \rightarrow 4s^13d^6$. The augmentation radius was chosen to be $r^a_c = 2.0$ bohr and the valence orbital matching radii were chosen to be 2.0 and 1.6 bohr for the 4s and 3d states respectively. The reference state was constructed from the configuration averaged ground state of $4s^23d^6$. The shapes of the corresponding PAW basis and projector functions are shown in Fig. 6. Compared to the example of Ge discussed above, the effects of the pseudo-core orbitals on the shapes of the projector functions are small, as shown in these plots. For Fe and the other transition metal atoms, we find that the local potential amplitude $V_0$ plays an important role in stabilizing the PAW-HF integral-differential equations. Table II lists the computed ionization energies, comparing the all-electron, frozen core orbital, and PAW results for various choices of the local potential amplitude $V_0$ and the inclusion or exclusion of the smooth core orbital functions. For some of these choices, the calculation diverges or converges to a result with significant deviation from the frozen core ionization energy. For the two best choices of parameters shown in Table II – PAW (I) corresponding to $|\tilde{\psi}_c| > 0$ and $V_0 = -2$ Ry and PAW (II) corresponding to $|\tilde{\psi}_c| \equiv 0$ and $V_0 = -6$ Ry, the calculated 4s orbital for configuration averaged Fe in its ground and ionized states are very close to the frozen core orbital results as shown in Fig. 7.

In this Fe example, the 3d radial wavefunctions for Fe in its ionized configuration changes very little compared with that of the reference configuration. In order to extend this study of...
TABLE II. Hartree-Fock ionization energies (in Ry units) for configuration averaged Fe \((E(4s^13d^6) − E(4s^23d^6))\) calculated using all-electron (AE), frozen core orbital (FC), and PAW methods. The FC and PAW results are based on the Ar core configuration as described in the text. The amplitude of local potential \(V_0\) is specified in Ry. Results including \(|\tilde{\psi}_v| > 0\) and excluding \(|\tilde{\psi}_v| ≡ 0\) the pseudo-core wavefunctions are compared. “x” indicates that the calculation diverged.

| \(V_0\) | AE | FC | PAW \(|\tilde{\psi}_v| > 0\) | PAW \(|\tilde{\psi}_v| ≡ 0\) |
|------|---|----|-------------------|-------------------|
| -6   |   |    |                   |                   |
| -4   |   |    |                   |                   |
| -2   |   |    |                   |                   |
| 0    |   |    |                   |                   |

transition metal atoms to include configurations which alter the occupancy of the 3d shell, we find that it will be necessary to start with the Ne core configuration and use twice as many basis and projector functions.

VI. SUMMARY AND CONCLUSIONS

In this manuscript, we have derived the necessary equations and demonstrated examples of the PAW-HF formalism for atoms across the periodic table. For these examples, we have shown that with the proper choice of augmentation radii, local pseudopotentials, etc. atomic PAW calculations achieve the same numerical accuracy as the frozen core orbital approximation within Hartree-Fock theory. More generally, we have demonstrated that exchange contributions from interactions of core and valence electron states are significant for some elements and that they can be treated accurately within the integral-differential equations of the PAW-HF formalism (Eq. 65).

In addition, we have numerically compared the frozen core orbital and the frozen core potential approximations for atoms across the periodic table. For our choice of potential form, the frozen core orbital approximation gave results closer to the all-electron Hartree-Fock treatment. Further work may give additional insight on this issue.

At the end of Sec. III we posed the question of how core electrons are folded into norm-conserving pseudopotential treatments of Hartree-Fock and related formalisms. Within the PAW-HF formulation based on the frozen core orbital approximation, we see that most of the core electron effects are treated with stored matrix elements. However, we have seen for some atoms such as Ge, the upper core states have significant extension beyond the augmentation sphere. For these cases, we introduced the smooth pseudo-core functions \(\tilde{\psi}_v^c(r)\). We have explored how these extended core orbital functions affect the extent of the PAW-HF projector functions as defined by Eq. (75). In particular, we have shown several examples which show that by including \(|\tilde{\psi}_v^c(r)| > 0\), we can ensure that the projector functions are strictly contained within the augmentation sphere as suggested by the original formulation of the PAW theory. However if we set \(|\tilde{\psi}_v^c(r)| ≡ 0\), the effects of the extended core functions are incorporated into extended parts of the projector functions \(\tilde{P}_v^c(r)\). For cases we studied, the excitation energies of the two approaches were very similar. It remains to be determined whether these extended projector functions can be successfully used to calculate the electronic structure of multicenter systems.

In addition to further study of the question of extended core states, further work needs to be done to optimize the choice of PAW parameters such as the augmentation radii \(r_0\) and the optimal form of the local potential \(V_{\text{loc}}^a(r)\). In addition, the use of continuum functions within Hartree-Fock theory for the purpose of augmenting the “span” of the pseudo basis functions is somewhat more complicated than within Kohn-Sham theory. In the latter case, the continuum states are solutions of a Hermitian differential operator. In the case of the Hartree-Fock equations of spherically averaged atoms, the unoccupied continuum states are not as well-defined. In addition to these issues, the next step will be to extend the analysis to multicenter and spin polarized systems. Another interesting extension of this work will be to treat some of the many new hybrid Hartree-Fock and generalized gradient exchange-correlation functionals that have reported in the recent literature. In addition, there have been several groups who are developing methods to evaluate Hartree-Fock energies augmented with various types of correlation energy formalisms, using orbitals derived from Kohn-Sham calculations. At the
Hartree-Fock level, since a self-consistent Hartree-Fock calculation determines an unconstrained minimum of the energy, the energy determined from Kohn-Sham orbitals is an overestimate. Conceivably, self-consistent PAW-Hartree-Fock approach along the lines developed in the present manuscript could improve these energy estimates.

**Appendix A: Additional PAW expressions**

The non-exchange (correlation) contributions to the valence energy and Hamiltonian equations take the same form in both PAW-Kohn-Sham and PAW-Hartree-Fock formulations. There are various ways of evaluating the terms as described in several publications.\(^7,9,27,49\) For completeness we give the formulations that we have used in the present work on spherical atoms. The non-exchange (correlation) contributions to the pseudo-energy of Eq. (43) takes the form

\[
\tilde{E}_{\text{vale}}|_{\text{nX}} = \tilde{E}_K^v + \tilde{E}_N^v + \tilde{E}_H^v + \tilde{E}_{H\text{val}}^v. \tag{A1}
\]

Here the kinetic energy contribution is given by

\[
\tilde{E}_K^v = \sum_v N_v \langle \tilde{\Psi}_v | \hat{K} | \tilde{\Psi}_v \rangle.
\]

The interaction of the valence electron pseudo-orbitals with the pseudo nuclear and core electron potentials can be combined into a term of the form

\[
\tilde{E}_N^v + \tilde{E}_H^v = \int dr \tilde{V}_f^v(r) \tilde{n}_v(r), \tag{A3}
\]

where

\[
\tilde{V}_f^v(r) = \tilde{V}_{\text{loc}}^v(r) + \tilde{V}_{\text{core}}^v(r) + \left( -Z^a + Q^a_{\text{core}} - \bar{Q}^a_{\text{core}} \right) \tilde{g}_0^a(r), \tag{A4}
\]

and

\[
\tilde{n}_v(r) = \sum_v N_v |\tilde{\psi}_v(r)|^2. \tag{A5}
\]

Here \(\tilde{V}_{\text{loc}}^v(r)\) is a localized potential defined in the range \(0 \leq r < r_a\). The potential due to extended core states is given by

\[
\tilde{V}_{\text{core}}^v(r) = e^2 \int dr' \frac{\tilde{g}_c^a(r')}{r_\infty}, \text{ with } \tilde{g}_c^a(r) = \sum_c N_c |\tilde{\psi}_c^a(r)|^2. \tag{A6}
\]

The long range contribution of the nuclear and core electron charges is given by the last term of Eq. (A4), where the compensation charge potential is defined in terms of the functional form defined in Eq. (53)

\[
\tilde{g}_0^a(r) = e^2 \int dr' \frac{\tilde{g}_0^a(r')}{r_\infty}, \tag{A7}
\]

with

\[
Q^a_{\text{core}} = \int dr \psi_c^a(r) \text{ and } \bar{Q}^a_{\text{core}} = \int dr \tilde{\psi}_c^a(r). \tag{A8}
\]

The Coulomb interaction between valence electron pseudo-orbitals can be expressed in terms of radial integrals similar to those of the exchange contributions in Eq. (60)

\[
\tilde{E}_{H\text{val}}^v = \frac{1}{2} \sum_{v'v} N_v N_{v'} \tilde{R}^0_{vv'v'v'}'. \tag{A9}
\]

The non-exchange (correlation) contributions to the atom-centered contributions to the valence energy can be written in the form

\[
\left( \tilde{E}_{\text{vale}}^a - \tilde{E}_{\text{vale}}^a \right) |_{\text{nX}} = \sum_{ij} \sum_v N_v \langle \tilde{\Psi}_v | \tilde{P}_{ij}^a | \tilde{\Psi}_v \rangle \times \left( K_{ij}^a + |V_{ij}^a| + \frac{1}{2} |V_{H\text{val}}^a|_{ij} \right). \tag{A10}
\]

The kinetic energy contribution is

\[
K_{ij}^a \equiv \langle \Phi_i | \hat{K} | \Phi_j \rangle - \langle \tilde{\Phi}_i | \hat{K} | \tilde{\Phi}_j \rangle. \tag{A11}
\]

The nuclear and core electron contribution is given by

\[
[V_{ij}^a]_{ij} = \langle \Phi_i | V_{ij}^a | \Phi_j \rangle - \langle \tilde{\Phi}_i | V_{ij}^a | \tilde{\Phi}_j \rangle, \tag{A12}
\]

where

\[
V_{ij}^a(r) \equiv \frac{Z^a e^2}{r} + V_H^a(r). \tag{A13}
\]

The valence-valence Hartree interactions may be evaluated

\[
[V_{H\text{val}}^a]_{ij} = \sum_{kl} \sum_{v'} N_{v'} \langle \tilde{\Psi}_{v'} | \tilde{P}_{ij}^a | \tilde{\Psi}_{v'} \rangle \left( R_{ij;kl} - \bar{R}_{ij;kl}^0 \right), \tag{A14}
\]

where the interaction integrals were defined in Eq. (63) and (64).

For evaluating the non exchange (correlation) terms in the smooth Hamiltonian, the pseudopotential contributions for the nuclear and Hartree interactions in both the Kohn-Sham (Eq. (48)) and Hartree-Fock (Eq. (69)) Hamiltonians can be written in the form

\[
\tilde{V}_N(r) + \tilde{V}_H(r) = \tilde{V}_f^v(r) + \sum_v N_v \tilde{W}_{\text{val}}^0(r), \tag{A15}
\]

where the fixed pseudopotential was defined in Eq. (A4) and the interaction function \(\tilde{W}_{\text{val}}^0(r)\) was defined in Eq. (72).

The non-exchange (correlation) contributions to the Hamiltonian matrix elements appropriate for both the PAW-Kohn-Sham and PAW-Hartree-Fock formalism is

\[
D_{ij}^a = K_{ij}^a + [V_{ij}^a]_{ij} + [V_{H\text{val}}^a]_{ij} + [V_0^a]_{ij}, \tag{A16}
\]

where the last term comes from the compensation charge contributions in Eq. (A9):

\[
[V_0^a]_{ij} \equiv m_{ij}^0 \int dr \tilde{v}_0^a(r) \left( \tilde{n}_v(r) + \sum_v N_v \tilde{M}_{vv}(r) \right). \tag{A17}
\]
Appendix B: Simplified expressions for core matrix elements.

When the core orbital is localized so that the corresponding pseudo-core orbital can be set to zero: \( \tilde{\psi}_c(r) \equiv 0 \), many of the expressions presented in Sect. IV simplify. For example, the charge moment coefficient (56) takes the form

\[
m_{ic}^{aL} = \int dr \, r^L \tilde{\phi}_i^a(r) \psi_c(r).
\]

The pseudo-core-valence contributions to exchange energy defined after Eq. (60) can be written

\[
\tilde{R}_{vccv}^{L} = \sum_{ij} \langle \tilde{\psi}_v^\text{HF} | \tilde{P}_{i}^a | \tilde{P}_{j}^a | \tilde{\psi}_v^\text{HF} \rangle \mathcal{M}_{ic;ij}^{aL},
\]

where

\[
\mathcal{M}_{ic;ij}^{aL} = e^2 \int \int dr \, dr' \frac{r^L}{r^L + r'^L} \tilde{m}_{ic}^a(r) \tilde{m}_{ij}^a(r')
\]

represents the interaction of two compensation charge contributions on site \( a \).

The analogous one-center contribution which appears in the one-center valence-core energy of Eq. (62) as defined by extending Eq. (64) to core states becomes

\[
\tilde{E}_{x}^{acv} = \sum_a \left( E_{x}^{acv} - \tilde{E}_{x}^{acv} \right) =
\]

\[
- \sum_{vc} \sum_{L=|l_v-l_c|}^{L_v+L_c} \Theta_{vc}^{L} \sum_{aij} \langle \tilde{\psi}_v^\text{HF} | \tilde{P}_{i}^a | \tilde{P}_{j}^a | \tilde{\psi}_v^\text{HF} \rangle R_{ic;ij}^{aL},
\]

representing a sum of single-site valence core-electron exchange energy contributions evaluated with the all-electron core and valence basis functions. Of course, in the complete extension of this formalism to multicenter systems, the occupancy-angular factor \( \Theta_{vc}^{L} \) defined in Eq. (14) will also be modified.

The self-consistent PAW-Hartree-Fock equations (65) can, in principle contain a contribution from localized core states if the Lagrange multiplier \( |\lambda_{vc}| > 0 \), since the extended overlap operator reduces to

\[
O_{ic}^{\text{PAW}} \tilde{\psi}_c \rightarrow \sum_{ai} \tilde{P}_{i}^a O_{ic}^a,
\]

where \( O_{ic}^a \equiv m_{ic}^{0a} \). If the PAW basis function \( \tilde{\Phi}_i^a \) corresponds to an occupied valence state, it is constructed to be orthogonal to the core orbitals so that \( O_{ic}^a = 0 \), otherwise \( O_{ic}^a \) may be non-zero.

While the pseudo-exchange kernel function \( \tilde{X}_c(r) \) defined in Eq. (71) has no contributions from localized core states, the one-center matrix element for the pseudo-exchange kernel function \( X_{ac}^a \) defined in Eq. (73) does have localized core state contributions. While the valence-valence terms of Eq. (73) remain as stated, if all of the core states were localized, their contributions can be expressed in terms of the atom-centered all-electron integrals.

\[
X_{ac}^a = - \sum_{cv} \sum_{L=|l_v-l_c|}^{L_v+L_c} \frac{1}{N_v} \Theta_{vc}^{L} \sum_{j} \langle \tilde{P}_{j}^a | \tilde{\psi}_v^\text{HF} \rangle R_{ic;j}^{aL}.
\]

One final point regarding pseudo-core orbitals needs clarification. That is, when \( |\tilde{\psi}_c(r)| > 0 \), Gram-Schmidt orthogonalization with the generalized overlap operator defined in Eq. (67), is used to orthogonalize the valence states to the core states. This process violates the notion that core and valence orbital functions reside in separate function spaces, but it can be consistently implemented provided that Eq. (67) is used also to calculate the denominator term \( \langle \tilde{\psi}_v^\text{HF} | O_{ic}^{\text{PAW}} | \tilde{\psi}_v^\text{HF} \rangle \).

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Note that the Kohn-Sham pseudopotential calculations using the so-called nonlinear core corrections developed by Louie et al., are analogous to a frozen core density approximation rather than a frozen core potential approximation in the sense of Eq. (35).


In order to augment the Hartree-Fock basis set with continuum states as is done for the Kohn-Sham formulation, we need to use Eq. (17) in slightly modified form. In practice, we have found that it is convenient to solve the equation for an unbound state \( \psi_{\lambda}^{(0)} \) by fixing \( \lambda_{\psi} \) at the positive energy of choice.


While all calculations are performed in terms of the radial functions, the bra and ket operators are written in terms of the full 3-dimensional functions defined in Eq. (1) in order to simplify the relationships involving the angular momenta \( l_{\mu}, l_{\nu}, \) etc.


In terms of the radial integrals, the notation is meant to imply \( \langle x_{\psi} | \psi^{(0)}(x) \rangle \equiv \delta_{\ell \mu} \int d \varphi \varphi^{*}(r) x_{\psi}(r) \).


Basis and projector functions for $l = 1$ channel were constructed from a continuum state since the $4p$ state is not bound. Although important for multicenter calculations, these functions have no effect on the atomic calculation.