Projector augmented wave 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 pseudopotential-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 able to 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.

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 wave functions together with norm-conserving pseudopotentials to represent the effects of the core electrons. In this paper, we develop a projected augmented wave (PAW) (Refs. 7–12) formulation of Hartree-Fock theory. Previous work by the VASP group[13] 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 theory[14] 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 focuses on the treatment of spherical atoms; application of the Hartree-Fock PAW formalism to nonspherical, spin polarized, and/or multicomponent 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 (AE) formalisms, comparing Kohn-Sham and Hartree-Fock equations. In Sec. III we examine the accuracy of various frozen-core (FC) 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

$$\Psi_p(\mathbf{r}) \equiv \Psi_{n_p l_p m_p}(\mathbf{r}) \equiv \frac{\psi_p(r)}{r} Y_{l_p m_p}(\hat{\mathbf{r}}), \qquad (1)$$

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. $Y_{l_p m_p}(\hat{\mathbf{r}})$ is the spherical harmonic function and $\psi_p(r)$ denotes the radial portion of the wave function. 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 $\rho(\mathbf{r}) \equiv \rho(r)$ is spherically symmetric

$$\rho(r) \equiv \frac{n(r)}{4\pi r^2} \quad \text{where} \quad n(r) = \sum_p N_p |\psi_p(r)|^2. \qquad (2)$$

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

$$E_{\text{tot}} = E_K + E_N + E_H + E_{xc}. \qquad (3)$$

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

$$E_H = \frac{e^2}{2} \int \int d^3 r \, d^3 r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \qquad (4)$$

We note that this definition of the Hartree energy includes the so-called electron self-interaction[15] 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) (Ref. 16) or generalized gradient approximation (GGA) (Ref. 17), the exchange-correlation functional is assumed to have an explicit dependence on the electron density $\rho(\mathbf{r})$ which is usually written in the form

$$E_{xc} = \int d^3 r f_{xc}(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|). \qquad (5)$$

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

$$\mathcal{H}^{\text{KS}}\Psi_p^{\text{KS}}(\mathbf{r}) = \varepsilon_p \Psi_p^{\text{KS}}(\mathbf{r}), \tag{6}$$

where the Kohn-Sham Hamiltonian takes the form

$$\mathcal{H}^{\text{KS}} = \mathcal{K} + V^{\text{KS}}(\mathbf{r}). \tag{7}$$

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

$$V^{\text{KS}}(\mathbf{r}) = V_N(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}). \tag{8}$$

For a spherical atom the potential components take the form

$$V_N(r) \equiv -\frac{Ze^2}{r}, \quad V_H(r) \equiv e^2 \int d^3 r' \frac{\rho(r')}{|\mathbf{r} - \mathbf{r}'|} \tag{9}$$

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

$$V_{xc}(r) \equiv \frac{\delta E_{xc}}{\delta \rho(r)}. \tag{10}$$

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 $\Psi_p^{\text{KS}}(\mathbf{r})$ are eigenstates of the Kohn-Sham Hamiltonian (7). Since the Kohn-Sham Hamiltonian is Hermitian, the eigenstates $\Psi_p^{\text{KS}}(\mathbf{r})$ 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

$$E_x \equiv -\frac{e^2}{2} \sum_{pq}{}' \int \int d^3 r d^3 r' \frac{\Psi_p^*(\mathbf{r})\Psi_q(\mathbf{r})\Psi_q^*(\mathbf{r}')\Psi_p(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{11}$$

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

$$E_x = -\sum_{pq} \sum_{L=|l_p - l_q|}^{l_p + l_q} \frac{1}{2} \Theta_{pq}^L R_{pq;qp}^L. \tag{12}$$

This exchange expression uses radial integrals similar to those introduced by Condon and Shortley[18]

$$R_{pq;st}^L \equiv e^2 \int \int dr\, dr' \frac{r_<^L}{r_>^{L+1}} \psi_p^*(r)\psi_q(r)\psi_s^*(r')\psi_t(r'). \tag{13}$$

The Fock weight factor for the moment L for the spherically averaged atom is given by[19–21]

$$\Theta_{pq}^L \equiv \begin{cases} \dfrac{1}{2} N_p N_q \begin{pmatrix} l_p & L & l_q \\ 0 & 0 & 0 \end{pmatrix}^2 & \text{for } p \neq q \\[2ex] \dfrac{1}{2} N_p (N_p - 1) \dfrac{4l_p + 2}{4l_p + 1} \begin{pmatrix} l_p & L & l_q \\ 0 & 0 & 0 \end{pmatrix}^2 & \text{for } p = q \text{ and } L \neq 0 \\[2ex] N_p & \text{for } p = q \text{ and } L = 0. \end{cases} \tag{14}$$

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

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

$$
\begin{aligned}
&F^{\text{HF}}(\{\psi_p^{\text{HF}}(r)\}, \{\lambda_{qp}\}) \\
&= E_{\text{tot}}(\{\psi_p^{\text{HF}}\}) - \sum_{qp} N_p \lambda_{qp}(\langle \Psi_p^{\text{HF}} | \Psi_q^{\text{HF}} \rangle - \delta_{qp}),
\end{aligned} \tag{15}
$$

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

$$\frac{\delta F^{\text{HF}}(\{\psi_p^{\text{HF}}(r)\}, \{\lambda_{qp}\})}{\delta \psi_p^{\text{HF}*}} = 0. \tag{16}$$

The Hartree-Fock equations take the form

$$H^{\text{HF}}(r)\psi_p^{\text{HF}}(r) + X_p(r) - \sum_{q;N_q > 0} \lambda_{qp}\psi_q^{\text{HF}}(r) = 0. \tag{17}$$

Here

$$H^{\text{HF}}(r) \equiv \mathcal{K} + V_N(r) + V_H(r). \tag{18}$$

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

$$X_p(r) \equiv \frac{1}{N_p} \frac{\delta E_x}{\delta \psi_p^*} = -\sum_q \sum_{L=|l_p-l_q|}^{l_p+l_q} \frac{1}{N_p} \Theta_{pq}^L W_{qp}^L(r) \psi_q^{\mathrm{HF}}(r), \tag{19}$$

where

$$W_{qp}^L(r) \equiv e^2 \int dr' \frac{r_<^L}{r_>^{L+1}} \psi_q^{\mathrm{HF}*}(r') \psi_p^{\mathrm{HF}}(r'). \tag{20}$$

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 wave functions which diagonalize blocks of the λ_{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 $\{\psi_p^{\mathrm{HF}(0)}(r)\}$ the approximate form of the Hartree-Fock equations is a set of inhomogeneous differential equations for the updated radial components $\{\psi_p^{\mathrm{HF}(1)}(r)\}$ of the form

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

where

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

Here the parameters $\epsilon_p^{(0)} \approx \lambda_{pp}^{(0)}$ are introduced to further stabilize the solution.[22] At convergence $\{\psi_p^{\mathrm{HF}(0)}(r)\} \equiv \{\psi_p^{\mathrm{HF}(1)}(r)\}$. The results obtained in this way[25] are essentially identical to those obtained from the ATSP package developed by Fischer *et al.*[21] That is, the values of λ_{qp} from the two programs agree within 10^{-4} Ry and graphs the radial wave functions $\psi_q^{\mathrm{HF}}(r)$ 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 an all-electron calculation for an atom in a reference state, the shell indices $p, q, \ldots$ are divided in to core states (c) and valence states (v). The total electron density is partitioned into core and valence contributions

$$\rho(\mathbf{r}) = \rho_c(\mathbf{r}) + \rho_v(\mathbf{r}), \tag{23}$$

where

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

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 the valence electron energy in the form

$$E_{\mathrm{val}} = E_K^v + E_N^v + E_H^{cv} + E_H^{vv} + E_{xc}. \tag{25}$$

Here, the valence kinetic energy E_K^v and valence nuclear potential energy E_N^v 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

$$E_H^{cv} = e^2 \int \int d^3 r \, d^3 r' \frac{\rho_c(r) \rho_v(r')}{|\mathbf{r} - \mathbf{r}'|} \equiv \int dr V_H^c(r) n_v(r) \tag{26}$$

and a valence-valence interaction

$$E_H^{vv} = \frac{e^2}{2} \int \int d^3 r \, d^3 r' \frac{\rho_v(r) \rho_v(r')}{|\mathbf{r} - \mathbf{r}'|} \equiv \frac{1}{2} \int dr V_H^v(r) n_v(r). \tag{27}$$

The Kohn-Sham and Hartree-Fock treatments of the valence contributions to the exchange-correlation energy, E_{xc}, 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 $\rho_c(\mathbf{r})$ plus the self-consistent valence density $\rho_v(\mathbf{r})$. The self-consistent valence radial functions $\{\psi_v(r)\}$ are determined from solving the Kohn-Sham Eq. (6) while the frozen-core density $\rho_c(\mathbf{r})$ 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.

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 products of pairs of electron orbitals and can be divided into core-valence and valence-valence contributions

$$E_{xc} \rightarrow E_x^{(\mathrm{val})} \quad \text{where} \quad E_x^{(\mathrm{val})} = E_x^{cv} + E_x^{vv}. \tag{28}$$

Here

$$E_x^{cv} = -\sum_{vc} \sum_{L=|l_v-l_c|}^{l_v+l_c} \Theta_{vc}^L R_{vc;cv}^L \tag{29}$$
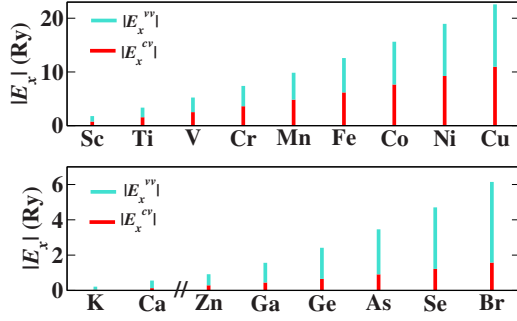
and

FIG. 1. (Color online) Plot of exchange energy magnitudes $|E_x^{cv}|$ and $|E_x^{vv}|$ defined in Eqs. (29) and (30), respectively, for spherically averaged ground-state atoms in the fourth row of the periodic table. In these plots, the configuration of Ar defines the core states. The energy values are given in Ry units.

$$E_x^{vv} = -\sum_{vv'}\sum_{L=|l_v-l_{v'}|}^{l_v+l_{v'}} \frac{1}{2}\Theta_{vv'}^L R_{vv';v'v}^L. \quad (30)$$

The magnitude of the valence exchange energy and the relative strength of core-valence and valence-valence contributions is strongly dependent on the atomic species in the calculation. For example, for elements in the second row of the periodic table, Li-F calculated in their ground states using the He configuration as core states, we find $E_x^{cv}/E_x^{vv} \approx 0.1$. For elements in the third row of the periodic table, Na-Cl calculated in their ground states using the Ne configuration as core states, we find $E_x^{cv}/E_x^{vv} \approx 0.2$. For the $4s4p$ materials in the fourth row of the periodic table, K-Ca and Zn-Br calculated in their ground states using the Ar configuration as core states, we find $E_x^{cv}/E_x^{vv} \approx 0.3$. On the other hand, for the $4s3d$ materials in the fourth row of the periodic table, Sc-Cu calculated in the $4s^2 3d^x$ state using the Ar configuration as core states, we find $E_x^{cv}/E_x^{vv} \approx 1$. In addition to these trends in the E_x^{cv}/E_x^{vv} ratios, the magnitudes of the exchange energies for the fourth row elements graphed in Fig. 1 show a monotonic increase with increasing numbers of electrons.

The self-consistent solution of the Hartree-Fock equations in the frozen-core orbital approximation corresponds to solving Eq. (17) only for the valence orbitals ($p \equiv v$) while leaving the core orbitals $\psi_c^{HF}(r)$ fixed to the functions found for the reference state. It is important to require that the valence orbitals $\Psi_v^{HF}(\mathbf{r})$ remain strictly orthogonal to each other as well as to the core orbitals

$$\langle \Psi_v^{HF} | \Psi_c^{HF} \rangle = 0 \quad (31)$$

in order to avoid spurious contributions to the valence-core exchange energy E_x^{cv} of Eq. (29).

For pseudopotential treatments of electronic structure, it is often desirable to eliminate the core wave functions and to represent their effects with contributions to the pseudopotential.[4–6] In principle, pseudopotential formulations are based on corresponding full wave function frozen-core potential approximations. The frozen-core potential $V_H^c(r)$ due to core electrons in the Hartree energy has already been defined in Eq. (26) and requires no additional approximation beyond the frozen-core orbital approximation. The
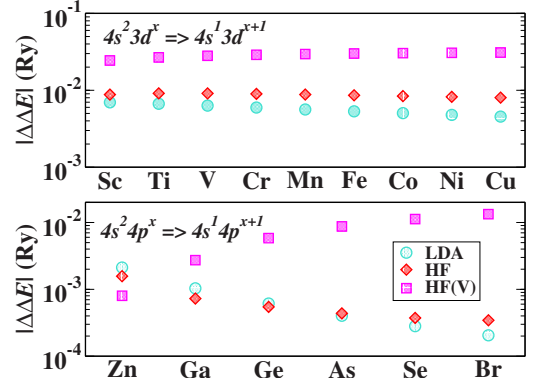

FIG. 2. (Color online) Plots of the magnitudes of $\Delta\Delta E$ [Eq. (39)] in Ry units for elements in the fourth row of the periodic table with the Ar core configuration. Three types of results are compared: "LDA" denotes the Kohn-Sham formalism using the local density approximation (Ref. 16); "HF" denotes the Hartree-Fock formalism using the frozen-core orbital approach using Eq. (17); "HF(V)" denotes the and Hartree-Fock formalism using the frozen-core potential approach using Eq. (33) and (36).

question is whether one can find a fixed potential $V_x^{cv}(r)$ which can accurately approximate the core-valence exchange interaction in the effective single-particle Hamiltonian

$$H^{HF(V)}(r) \equiv \mathcal{K} + V_N(r) + V_H^c(r) + V_H^v(r) + V_x^{cv}(r). \quad (32)$$

The corresponding integral-differential equations for the wave functions in the Hartree-Fock frozen-core potential approximation take the form

$$H^{HF(V)}(r)\bar{\psi}_v^{HF}(r) + X_v^{vv}(r) = \sum_{q;N_q>0} \lambda_{qv}\psi_q^{HF}(r), \quad (33)$$

where

$$X_v^{vv}(r) \equiv -\sum_{v'}\sum_{L=|l_v-l_{c'}|}^{l_v+l_{v'}} \frac{1}{N_v}\Theta_{vv'}^L W_{v'v}^L(r)\bar{\psi}_{v'}^{HF}(r). \quad (34)$$

The sum over q in Eq. (33) includes both the frozen-core wave functions and the modified valence functions $\bar{\psi}_v^{HF}(r)$. The corresponding valence-core exchange energy is then given by

$$E_c^{cv} \approx \bar{E}_x^{cv} \equiv \int dr V_x^{cv}(r) n_v(r). \quad (35)$$

We have invested some effort in evaluating the frozen-core potential approximation. One of the frozen-core potential forms is chosen to be

$$V_x^{cv}(r) = \left.\frac{\sum_v N_v X_v^{cv}(r)\psi_v^{HF}(r)}{n_v(r)}\right|_{ref}, \quad (36)$$

where

$$X_v^{cv}(r) \equiv - \sum_c \sum_{L=|l_v-l_c|}^{l_v+l_c} \frac{1}{N_v} \Theta_{vc}^L W_{cv}^L(r) \psi_c^{\text{HF}}(r). \qquad (37)$$

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

$$E_x^{cv} = \int dr \sum_v N_v X_v^{cv}(r) \psi_v^{\text{HF}}(r), \qquad (38)$$

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 excitation energy calculated in an all-electron treatment to be

$$\Delta\Delta E \equiv (E_{\text{tot}}^{\text{excited}} - E_{\text{tot}}^{\text{ground}}) \rfloor_{\text{AE}} - (E_{\text{val}}^{\text{excited}} - E_{\text{val}}^{\text{ground}}) \rfloor_{\text{FC}}. \qquad (39)$$

Using this measure, results for excitation energies of elements in the fourth 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 9×10^{-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 (semicore states) as valence states. By contrast, 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 second and third 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[29] of the frozen-core potential $V_x^{cv}(r)$ 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 $V_x^{\text{OEP}}(r)$ for use in the Kohn-Sham Hamiltonian consistent with the Fock exchange functional. However, in the OEP formulation, the $V_x^{\text{OEP}}(r)$ potential is used only to determine the Kohn-Sham wave functions which are in turn used to determine the exchange energy using the functional form of Eq. (12). It will be in-

teresting 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 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 ultrasoft pseudopotential approach of Vanderbilt.[39] The formalism needs a set of basis and projector functions for each atom a which represent the valence states. Using the atomic shell nomenclature defined in Eq. (1), we will denote these as $\Phi_i^a(\mathbf{r})$ for an all-electron basis function, $\widetilde{\Phi}_i^a(\mathbf{r})$ for the corresponding pseudoelectron basis function, and $\widetilde{P}_i^a(\mathbf{r})$ 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 $0 \leq r \leq r_c^a$ (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 $\{\Phi_i^a(\mathbf{r})\}$ 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) (Ref. 40) with special consideration for continuum states.[41] The projector functions satisfy the relationship[42]

$$\langle \widetilde{P}_i^a | \widetilde{\Phi}_j^a \rangle = \delta_{ij} \qquad (40)$$

and the radial pseudofunctions have the property

$$\widetilde{\phi}_i^a(r) = \phi_i^a(r) \quad \text{for} \quad r > r_c^a. \qquad (41)$$

Here r_c^a denotes the matching radius for atom a. The radial function associated with the projector function $p_i^a(r)$ is constructed to be spatially localized within the augmentation sphere r_c^a.

A key idea of the PAW formalism is the transformation between a calculated pseudowave function $[\widetilde{\Psi}_v(\mathbf{r})]$ corresponding to a valence state of the system and the corresponding fully nodal wave function $[\Psi_v(\mathbf{r})]$ of that state which is given by[7]

$$\Psi_v(\mathbf{r}) = \widetilde{\Psi}_v(\mathbf{r}) + \sum_{ai} [\Phi_i^a(\mathbf{r} - \mathbf{R}^a) - \widetilde{\Phi}_i^a(\mathbf{r} - \mathbf{R}^a)]\langle \widetilde{P}_i^a | \widetilde{\Psi}_v \rangle. \tag{42}$$

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 pseudopotential-like contributions plus a sum of atom-centered corrections in the form

$$E_{\text{vale}} = \underbrace{\widetilde{E}_{\text{vale}}}_{\text{pseudoenergy}} + \sum_a \underbrace{(E_{\text{vale}}^a - \widetilde{E}_{\text{vale}}^a)}_{\text{atom-centered corrections}}. \tag{43}$$

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 in Eq. (43) is an explicit functional of the electron density which in turn is an explicit functional of the valence pseudowave functions, the Kohn-Sham equations in the PAW formalism can be evaluated[7] in terms of the functional derivative

$$\frac{\delta E_{\text{vale}}}{\delta \widetilde{\Psi}_v^{\text{KS}*}(\mathbf{r})} = \mathcal{H}_{\text{KS}}^{\text{PAW}}(\mathbf{r})\widetilde{\Psi}_v^{\text{KS}}(\mathbf{r}) = \varepsilon_v \mathcal{O}^{\text{PAW}}\widetilde{\Psi}_v^{\text{KS}}(\mathbf{r}). \tag{44}$$

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

$$\langle \widetilde{\Psi}_v^{\text{KS}} | \mathcal{O}^{\text{PAW}} | \widetilde{\Psi}_{v'}^{\text{KS}} \rangle = \delta_{vv'}. \tag{45}$$

Here the PAW Hamiltonian takes the form

$$\mathcal{H}_{\text{KS}}^{\text{PAW}}(\mathbf{r}) = \widetilde{\mathcal{H}}^{\text{KS}}(r) + \sum_{aij} |\widetilde{P}_i^a\rangle D_{ij}^a \langle \widetilde{P}_j^a| \tag{46}$$

and

$$\mathcal{O}^{\text{PAW}} = 1 + \sum_{aij} |\widetilde{P}_i^a\rangle O_{ij}^a \langle \widetilde{P}_j^a|. \tag{47}$$

Here the Kohn-Sham pseudo-Hamiltonian has the form

$$\widetilde{\mathcal{H}}^{\text{KS}}(r) \equiv \mathcal{K} + \widetilde{V}^{\text{KS}}(r). \tag{48}$$

The overlap matrix element is given by

$$O_{ij}^a = \langle \Phi_i^a | \Phi_j^a \rangle - \langle \widetilde{\Phi}_i^a | \widetilde{\Phi}_j^a \rangle. \tag{49}$$

The general form of $\widetilde{V}^{\text{KS}}(\mathbf{r})$ as well as of the one center matrix elements D_{ij}^a 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 pseudowave function basis according to

$$(\widetilde{\mathcal{H}}^{\text{KS}}(r) - \varepsilon_i^a)\widetilde{\Phi}_i^a(\mathbf{r}) = \sum_j \widetilde{P}_j^a(\mathbf{r})\langle \widetilde{\Phi}_j^a | \widetilde{\mathcal{H}}^{\text{KS}} - \varepsilon_i^a | \widetilde{\Phi}_i^a \rangle. \tag{50}$$

This relationship is consistent with the requirements that each pseudowave function basis function $\widetilde{\Phi}_i^a(\mathbf{r})$ must be a solution of the Kohn-Sham PAW Eqs. (44) of the reference state and with the special form of the one-center Hamiltonian matrix elements of the reference state

$$D_{ij}^a \rfloor_{\text{ref}} = \langle \Phi_i^a | \mathcal{H}^{\text{KS}} | \Phi_j^a \rangle \rfloor_{\text{ref}} - \langle \widetilde{\Phi}_i^a | \widetilde{\mathcal{H}}^{\text{KS}} | \widetilde{\Phi}_j^a \rangle \rfloor_{\text{ref}}. \tag{51}$$

In practice, the projector functions $\{\widetilde{P}_i^a(\mathbf{r})\}$ are determined by solving Eq. (50) from a knowledge of the reference pseudo-Hamiltonian $\widetilde{\mathcal{H}}^{\text{KS}}(r)$, the basis functions $\{\Phi_i^a(\mathbf{r}), \widetilde{\Phi}_i^a(\mathbf{r})\}$, and the eigenenergies $\{\varepsilon_i^a\}$, 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 form of the treatment of the Fock exchange term and in the representation of the frozen-core orbitals. From our analysis of the full wave function 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 $\widetilde{\Psi}_v^{\text{HF}}(\mathbf{r})$ 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 pseudofunctions $\{\widetilde{\Phi}_i^a(\mathbf{r})\}$ within the augmentation sphere.

Most of the core wave functions $\Psi_c^{\text{HF}}(\mathbf{r})$ are contained within the augmentation sphere and for those we can define a trivial core pseudowave function $\widetilde{\Psi}_c^{\text{HF}}(\mathbf{r}) \equiv 0$. For some materials it is possible that at most one core orbital per l channel will have a nontrivial amplitude for $r > r_c^a$. In such a case, it is convenient to define a continuous pseudocore orbital $\widetilde{\psi}_c^a(r)$ with $\widetilde{\psi}_c^a(r) \equiv \psi_c^a(r)$ for $r > r_c^a$, in a similar spirit to the pseudocore functions defined for the so-called nonlinear core corrections in norm-conserving pseudopotentials.[43] In our case, we define

$$\widetilde{\psi}_c^a(r) \equiv \begin{cases} r^{l_c+1}P_n(r) & \text{for } r \leq r_c^a \\ \psi_c^a(r) & \text{for } r > r_c^a. \end{cases} \tag{52}$$

The nth order polynomial $P_n(r)$ is chosen to ensure that $\widetilde{\psi}_c^a(r)$ is continuous up to $n-1$ derivatives. An example of 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[7] moments of the form

$$\hat{m}_{ij}^{aL}(r) \equiv m_{ij}^{aL} \frac{r^2 s_L(r)}{\displaystyle\int du \, u^{L+2} s_L(u)} \equiv m_{ij}^{aL} g_L^a(r). \tag{53}$$

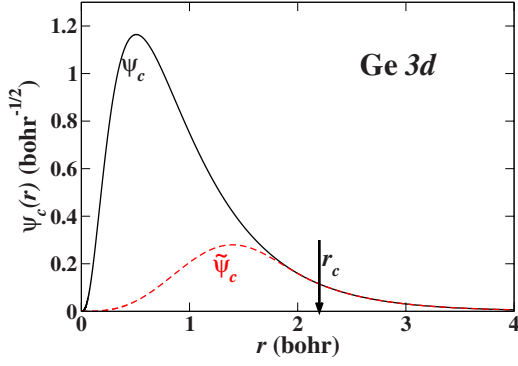Here $s_L(r)$ is a smooth shape function

FIG. 3. (Color online) Radial Hartree-Fock wave function $\psi_c(r)$ for the $3d$ core state of Ge compared with the constructed pseudo-wave function $\tilde{\psi}_c(r)$.

$$s_L(r) = r^L k(r) \tag{54}$$

or it could be similar smooth function such as one involving a spherical Bessel function $s_L(r) \equiv j_L(\kappa r)$. More often we have chosen

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

The charge moment coefficient is given by

$$m_{ij}^{aL} \equiv \int dr \; r^L [\phi_i^a(r)\phi_j^a(r) - \tilde{\phi}_i^a(r)\tilde{\phi}_j^a(r)]. \tag{56}$$

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[7] 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[13] so that they can be written in the PAW form (43)

$$E_x^{vv} = \tilde{E}_x^{vv} + \sum_a (E_x^{avv} - \tilde{E}_x^{avv}),$$

$$E_x^{cv} = \tilde{E}_x^{cv} + \sum_a (E_x^{acv} - \tilde{E}_x^{acv}). \tag{57}$$

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 pseudoterms and the one-center terms to cancel out the unphysical pseudocontributions 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, $\psi_v^{\mathrm{HF}*}(r)\psi_{v'}^{\mathrm{HF}}(r)$, we can define a compensation charge moment of order L

$$\hat{M}_{vv'}^L(r) \equiv \sum_{aij} \langle \tilde{\Psi}_v^{\mathrm{HF}}|\tilde{P}_i^a\rangle\langle\tilde{P}_j^a|\tilde{\Psi}_{v'}^{\mathrm{HF}}\rangle \hat{m}_{ij}^{aL}(r),$$

$$\hat{M}_{vc}^L(r) \equiv \sum_{ai} \langle \tilde{\Psi}_v^{\mathrm{HF}}|\tilde{P}_i^a\rangle \hat{m}_{ic}^{aL}(r). \tag{58}$$

The significance of this moment is that, within the accuracy of the PAW transformation, the Lth moment of $[\psi_v^{\mathrm{HF}*}(r)\psi_{v'}^{\mathrm{HF}}(r)]$ is the same as the Lth moment of $[\tilde{\psi}_v^{\mathrm{HF}*}(r)\tilde{\psi}_{v'}^{\mathrm{HF}}(r) + \hat{M}_{vv'}^L(r)]$. For the moment representing core-valence wave-function products, the moment coefficient m_{ic}^{aL} corresponding to valence-core contributions is defined by an expression similar to Eq. (56) with $\phi_j^a \rightarrow \psi_c^a$ and $\tilde{\phi}_j^a \rightarrow \tilde{\psi}_c^a$. Because of orthogonality properties of core and valence states of the reference system and because $\tilde{\psi}_c^a \equiv 0$ 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 pseudoexchange integrals take the form

$$\tilde{E}_x^{vv} = -\sum_{vv'} \sum_{L=|l_v - l_{v'}|}^{l_v + l_{v'}} \frac{1}{2}\Theta_{vv'}^L \tilde{R}_{vv';v'v}^L,$$

$$\tilde{E}_x^{cv} = -\sum_{vc} \sum_{L=|l_v - l_c|}^{l_v + l_c} \Theta_{vc}^L \tilde{R}_{vc;cv}^L, \tag{59}$$

where

$$\tilde{R}_{vv';v'v}^L \equiv e^2 \int\int dr \; dr' \frac{r_<^L}{r_>^{L+1}}[\tilde{\psi}_v^{\mathrm{HF}*}(r)\tilde{\psi}_{v'}^{\mathrm{HF}}(r) + \hat{M}_{vv'}^L(r)]$$

$$\times [\tilde{\psi}_{v'}^{\mathrm{HF}*}(r')\tilde{\psi}_v^{\mathrm{HF}}(r') + \hat{M}_{v'v}^L(r')] \tag{60}$$

with an identical expression for $v' \rightarrow c$. The corresponding one-center contributions take the form

$$E_x^{avv} - \tilde{E}_x^{avv} = -\sum_{vv'} \sum_{L=|l_v - l_v'|}^{l_v + l_v'} \frac{1}{2}\Theta_{vv'}^L \sum_{ijkl} \langle\tilde{\Psi}_v^{\mathrm{HF}}|\tilde{P}_i^a\rangle\langle\tilde{P}_j^a|\tilde{\Psi}_{v'}^{\mathrm{HF}}\rangle$$

$$\times \langle\tilde{\Psi}_{v'}^{\mathrm{HF}}|\tilde{P}_k^a\rangle\langle\tilde{P}_l^a|\tilde{\Psi}_v^{\mathrm{HF}}\rangle(R_{ij;kl}^{aL} - \tilde{R}_{ij;kl}^{aL}) \tag{61}$$

and

$$E_x^{acv} - \tilde{E}_x^{acv} = -\sum_{vc} \sum_{L=|l_v - l_c|}^{l_v + l_c} \Theta_{vc}^L \sum_{ij} \langle\tilde{\Psi}_v^{\mathrm{HF}}|\tilde{P}_i^a\rangle\langle\tilde{P}_j^a|\tilde{\Psi}_v^{\mathrm{HF}}\rangle$$

$$\times (R_{ic;cj}^{aL} - \tilde{R}_{ic;cj}^{aL}). \tag{62}$$

Here

$$R_{ij;kl}^{aL} \equiv e^2 \int\int dr \; dr' \frac{r_<^L}{r_>^{L+1}} \phi_i^{a*}(r)\phi_j^a(r)\phi_k^{a*}(r')\phi_l^a(r') \tag{63}$$

and

$$\tilde{R}_{ij;kl}^{aL} \equiv e^2 \int\int dr \; dr' \frac{r_<^L}{r_>^{L+1}} [\tilde{\phi}_i^{a*}(r)\tilde{\phi}_j^a(r) + \hat{m}_{ij}^{aL}(r)]$$

$$\times [\tilde{\phi}_k^{a*}(r')\tilde{\phi}_l^a(r') + \hat{m}_{kl}^{aL}(r')]. \tag{64}$$

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

$$\mathcal{H}^{\mathrm{PAW}}_{\mathrm{HF}}(\mathbf{r})\widetilde{\Psi}^{\mathrm{HF}}_{v}(r) + X^{\mathrm{PAW}}_{v}(\mathbf{r}) - \sum_{q}\lambda_{qv}\mathcal{O}^{\mathrm{PAW}}_{\mathrm{HF}}\widetilde{\Psi}^{\mathrm{HF}}_{q}(\mathbf{r}) = 0. \tag{65}$$

These equations must be solved self-consistently with orthonormalization constraint

$$\langle \widetilde{\Psi}^{\mathrm{HF}}_{v}|\mathcal{O}^{\mathrm{PAW}}|\widetilde{\Psi}^{\mathrm{HF}}_{q}\rangle = \delta_{vq}. \tag{66}$$

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

$$\langle \widetilde{\Psi}^{\mathrm{HF}}_{v}|\mathcal{O}^{\mathrm{PAW}}_{\mathrm{HF}}|\widetilde{\Psi}^{\mathrm{HF}}_{c}\rangle \equiv \langle \widetilde{\Psi}^{\mathrm{HF}}_{v}|\widetilde{\Psi}^{\mathrm{HF}}_{c}\rangle + \sum_{ai}\langle \widetilde{\Psi}^{\mathrm{HF}}_{v}|\widetilde{P}^{a}_{i}\rangle O^{a}_{ic}, \tag{67}$$

where $O^{a}_{ic} \equiv m^{a0}_{ic}$. In general, these terms are very small if not identically zero. The single particle term of Eq. (65) takes the form

$$\mathcal{H}^{\mathrm{PAW}}_{\mathrm{HF}}(\mathbf{r}) = \widetilde{\mathcal{H}}^{\mathrm{HF}} + \sum_{aij}|\widetilde{P}^{a}_{i}\rangle D^{a\mathrm{HF}}_{ij}\langle \widetilde{P}^{a}_{j}|, \tag{68}$$

where the pseudo Hamiltonian-type terms depend on the pseudopotentials due to the nuclear and Hartree interactions

$$\widetilde{\mathcal{H}}^{\mathrm{HF}}(\mathbf{r}) \equiv \mathcal{K} + \widetilde{V}_{N}(\mathbf{r}) + \widetilde{V}_{H}(\mathbf{r}). \tag{69}$$

The exchange function term takes the form

$$X^{\mathrm{PAW}}_{v}(\mathbf{r}) = \widetilde{X}_{v}(\mathbf{r}) + \sum_{ai}|\widetilde{P}^{a}_{i}\rangle X^{a}_{iv}, \tag{70}$$

where the pseudoexchange kernel function takes the form

$$\widetilde{X}_{v}(r) \equiv -\sum_{q}\sum_{L=|l_{v}-l_{q}|}^{l_{v}+l_{q}}\frac{1}{N_{v}}\Theta^{L}_{vq}\widetilde{W}^{L}_{qv}(r)\widetilde{\psi}^{\mathrm{HF}}_{q}(r). \tag{71}$$

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 $\widetilde{W}^{L}_{qv}(r)$ is the pseudoanalog of Eq. (20)

$$\widetilde{W}^{L}_{qv}(r) \equiv e^{2}\int dr'\frac{r^{L}_{<}}{r^{L+1}_{>}}[\widetilde{\psi}^{\mathrm{HF}*}_{q}(r')\widetilde{\psi}^{\mathrm{HF}}_{v}(r') + M^{L}_{qv}(r')]. \tag{72}$$

The one center matrix element for the pseudoexchange kernel function takes the form

$$X^{a}_{iv} = -\sum_{v'}\sum_{L=|l_{v}-l_{v'}|}^{l_{v}+l_{v'}}\frac{1}{N_{v}}\Theta^{L}_{vv'}[\sum_{jkl}\langle \widetilde{P}^{a}_{j}|\widetilde{\Psi}^{\mathrm{HF}}_{v'}\rangle\langle \widetilde{\Psi}^{\mathrm{HF}}_{v'}|\widetilde{P}^{a}_{k}\rangle\langle \widetilde{P}^{a}_{l}|\widetilde{\Psi}^{\mathrm{HF}}_{v}\rangle$$

$$\times (R^{aL}_{ij;kl} - \widetilde{R}^{aL}_{ij;kl})] + \sum_{j}\langle \widetilde{P}^{a}_{j}|\widetilde{\Psi}^{\mathrm{HF}}_{v'}\rangle Z^{aL}_{v'v;ij}$$

$$-\sum_{c}\sum_{L=|l_{v}-l_{c}|}^{l_{v}+l_{c}}\frac{1}{N_{v}}\Theta^{L}_{vc}[\sum_{j}\langle \widetilde{P}^{a}_{j}|\widetilde{\Psi}^{\mathrm{HF}}_{v}\rangle(R^{aL}_{ic;cj} - \widetilde{R}^{aL}_{ic;cj}) + Z^{aL}_{cv;ic}], \tag{73}$$

where

$$Z^{aL}_{qv;ij} \equiv \int dr\widetilde{W}^{L}_{qv}(r)\hat{m}^{aL}_{ij}(r). \tag{74}$$

The relationship between the projector and basis functions is somewhat different from that of the Kohn-Sham formalism, taking the form

$$\widetilde{H}^{\mathrm{HF}}(\mathbf{r})\widetilde{\Phi}^{a}_{i}(\mathbf{r}) + \widetilde{X}_{i}(\mathbf{r}) - \sum_{q;N_{q}>0}\lambda_{qi}\widetilde{\Psi}^{\mathrm{HF}}_{q}(\mathbf{r}) = \sum_{j}\widetilde{P}^{a}_{j}(\mathbf{r})\Lambda^{a}_{ji}. \tag{75}$$

Here the matrix coefficients are given by

$$\Lambda^{a}_{ji} \equiv \langle \widetilde{\Phi}^{a}_{j}|\widetilde{H}^{\mathrm{HF}}|\widetilde{\Phi}^{a}_{i}\rangle + \langle \widetilde{\Phi}^{a}_{j}|\widetilde{X}_{i}\rangle - \sum_{q;N_{q}>0}\lambda_{qi}\langle \widetilde{\Phi}^{a}_{j}|\widetilde{\Psi}^{\mathrm{HF}}_{q}\rangle, \tag{76}$$

where the differential $\widetilde{H}^{\mathrm{HF}}(\mathbf{r})$ and integral $\widetilde{X}_{i}(\mathbf{r})$ operators as well as the Lagrange multipliers λ_{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 $\{\widetilde{P}^{a}_{j}(\mathbf{r})\}$. Equation (75) is consistent with the requirement that the pseudowave function basis functions $\widetilde{\Phi}^{a}_{i}(\mathbf{r})$ must be a solution of the PAW Hartree-Fock Eq. (65) for the reference configuration of the atom and the following identities. For the reference state, the single-particle terms satisfy the relationship

$$D^{a\mathrm{HF}}_{ij}\rfloor_{\mathrm{ref}} = \langle \Phi^{a}_{i}|\mathcal{H}^{\mathrm{HF}}|\Phi^{a}_{j}\rangle\rfloor_{\mathrm{ref}} - \langle \widetilde{\Phi}^{a}_{i}|\widetilde{\mathcal{H}}^{\mathrm{HF}}|\widetilde{\Phi}^{a}_{j}\rangle\rfloor_{\mathrm{ref}} \tag{77}$$

and the two-particle terms satisfy the relationship[45]

$$X^{a}_{iv}\rfloor_{\mathrm{ref}} = \langle \Phi^{a}_{i}|X_{v}\rangle\rfloor_{\mathrm{ref}} - \langle \widetilde{\Phi}^{a}_{i}|\widetilde{X}_{v}\rangle\rfloor\mathrm{ref}. \tag{78}$$

Once the basis and projector functions are determined, the solution of self-consistent PAW-Hartree-Fock Eqs. (65) can be obtained using an iterative method similar to that of the all-electron or frozen core Eqs. (17). For any guess of the valence pseudowave functions $\{\widetilde{\psi}^{\mathrm{HF}(0)}_{v}(r)\}$, the Lagrange multipliers $\lambda^{(0)}_{v'v}$ can be estimated by multiplying both sides of Eq. (65) by $\widetilde{\Psi}^{\mathrm{HF}(0)}_{v'}(\mathbf{r})$ and integrating over all space. The Lagrange multipliers $\lambda^{(0)}_{cv}$ corresponding to the interaction between core states and valence states can be estimated from the form
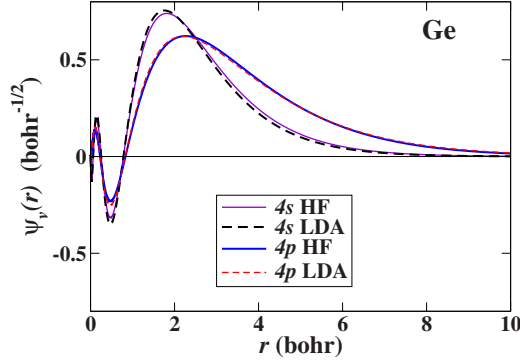
FIG. 4. (Color online) Radial valence wave functions for Ge, comparing Kohn-Sham (LDA) and HF.

$$\lambda_{cv}^{(0)} = \langle \widetilde{\Psi}_c^{\mathrm{HF}} | \widetilde{\mathcal{H}}^{\mathrm{HF}} | \widetilde{\Psi}_v^{\mathrm{HF}(0)} \rangle + \sum_j D_{cj}^{a\mathrm{HF}} \langle \widetilde{P}_j^a | \widetilde{\Psi}_v^{\mathrm{HF}(0)} \rangle$$

$$+ \langle \widetilde{\Psi}_c^{\mathrm{HF}} | \widetilde{X}_v^{(0)} \rangle + X_{cv}^{a(0)}. \tag{79}$$

Having derived the form of the PAW-HF equations, we are now in a position to examine the role of the core and pseudocore orbitals. It is clear that from the way that the pseudocore orbitals have been defined, $\widetilde{\psi}_c^a(r) \approx 0$, so that the main contributions of the core orbitals are expressed in the atom centered radial Coulomb integrals $R_{ic;cj}^{aL}$ similar to the expression defined in Eq. (63). When $\widetilde{\psi}_c^a(r) \equiv 0$, 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 $R_{ic;cj}^{aL}$ integrals which contribute to the core-valence exchange energy E_x^{cv} as defined in Eqs. (57) and (62). They also contribute to the pseudoexchange kernel function X_{iv}^a defined in Eq. (73). Since all of these core-valence contributions depend on constant matrix elements or functions that can be precalculated 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-wave functions in one-to-one correspondence with the fully nodal frozen-core wave functions for the range of electronic configurations of interest. In fact, the shapes of the Hartree-Fock valence wave functions are, in general, similar to the shapes of the corresponding Kohn-Sham valence wave functions. 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 $\widetilde{\phi}_i^a(r)$ from all-electron basis functions $\phi_i^a(r)$ using the polynomial form introduced by Vanderbilt in the construction of the ultrasoft pseudopotential scheme.[39] [This also is the scheme for constructing the nontrivial pseudocore functions $\widetilde{\psi}_c(r)$ of Eq. (52).] The other adjustable function in this construction is the localized potential $\widetilde{V}_{\mathrm{loc}}^a(r)$ defined in Eq. (A4). It is often efficient to choose this potential[11] as an unscreened norm-conserving pseudopotential derived from the Troullier-Martins[50] 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 $\widetilde{V}_{\mathrm{loc}}^a(r)$. A simple, but reasonable choice is

$$\widetilde{V}_{\mathrm{loc}}^a(r) = \mathcal{V}_0 k(r) \tag{80}$$

using the shape function defined in Eq. (55) and an adjustable amplitude $\mathcal{V}_0$. 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

TABLE I. Hartree-Fock valence energies for several configuration averaged atoms calculated with the frozen core *orbital* approximation (FC) and the PAW formalism. Results including ($|\widetilde{\psi}_c| > 0$) and excluding ($|\widetilde{\psi}_c| \equiv 0$) pseudocore orbitals are compared. The augmentation radii (r_c^a) are given in bohr units, the local potential amplitudes ($\mathcal{V}_0$) 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.

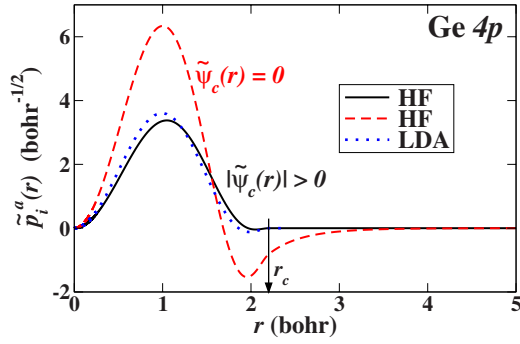| Atom	Type	$|\widetilde{\psi}_c|$	r_c^a	$\mathcal{V}_0$	$E_{\mathrm{val}}(ns^2np^2)$	$E_{\mathrm{val}}(ns^1np^3)$
C	FC				−10.5990	−9.9542
C	PAW	>0	1.3	2.0	−10.5990	−9.9541
C	PAW	≡0	1.3	2.0	−10.5990	−9.9541
Si	FC				−7.3147	−6.8070
Si	PAW	>0	2.0	3.0	−7.3147	−6.8066
Si	PAW	≡0	2.0	3.0	−7.3147	−6.8070
Ge	FC				−7.2257	−6.6800
Ge	PAW	>0	2.2	3.0	−7.2258	−6.6796
Ge	PAW	≡0	2.2	3.0	−7.2258	−6.6800

FIG. 5. (Color online) Radial PAW projector functions for $4p$ states of Ge, comparing effects of including and excluding pseudocore orbital functions $\widetilde{\psi}_c(r)$ within the HF formulation and also comparing the corresponding LDA projector. These projectors where used to obtain the results presented in Table I.

effects of including or excluding the pseudocore 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 $\mathcal{V}_0$ but the energies obtained including or excluding the smooth core functions are very close.

Our results provide information on the role of the pseudocore 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 pseudocore functions and also comparing with the analogous LDA projector function. We see that the projector obtained by including the pseudocore functions is quite similar in shape to that the LDA formulation. On the other hand, by setting the pseudocore 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). By construction, when the smooth core wave functions are included in Eq. (75), for $r \geq r_c^a$ 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 wave function amplitudes have become negligible so that the left-hand side of Eq. (75) and therefore $\widetilde{p}_i^a(r)$, remains nonzero beyond $r=r_c^a$. 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 $4s^2 3d^6 \rightarrow 4s^1 3d^6$. The augmentation radius was chosen to be $r_c^a=2.0$ bohr and the valence orbital matching radii were chosen to be 2.0 and 1.6 bohr for the $4s$ and $3d$ states, respectively.[51] The reference state was constructed from the configuration averaged ground state of
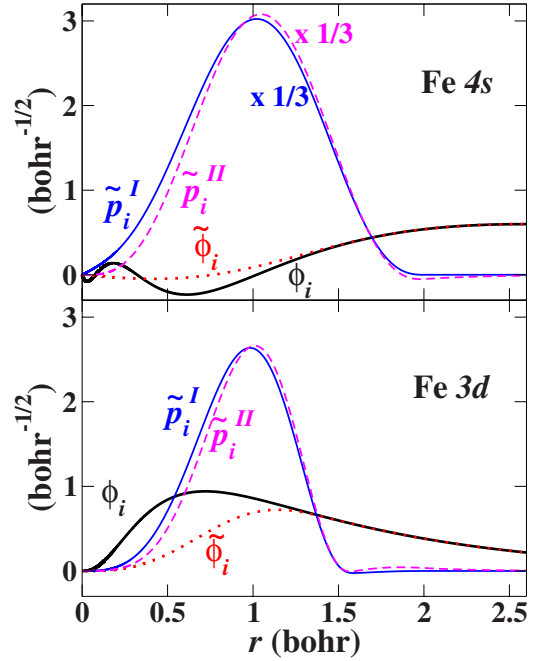

FIG. 6. (Color online) Plots of the radial basis and projector functions for the $4s$ and $3d$ states of Fe. The parameters of the construction are described in the text. Label "I" refers to $|\widetilde{\psi}_c|>0$ and $V_0=-2$ Ry and label "II" refers to $|\widetilde{\psi}_c|\equiv 0$ and $V_0=-6$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

$4s^2 3d^6$. 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 pseudocore 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 $\mathcal{V}_0$ 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 $\mathcal{V}_0$ 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

TABLE II. Hartree-Fock ionization energies (in Ry units) for configuration averaged Fe$[E(4s^1 3d^6)-E(4s^2 3d^6)]$ calculated using AE, FC orbital, 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 $\mathcal{V}_0$ is specified in Ry. Results including $(|\widetilde{\psi}_c|>0)$ and excluding $(|\widetilde{\psi}_c|\equiv 0)$ the pseudocore wave functions are compared. "x" indicates that the calculation diverged.

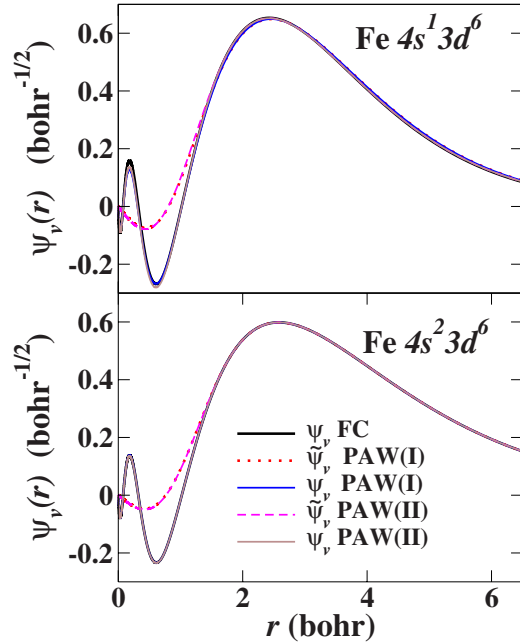| $\mathcal{V}_0$	AE	FC	PAW $(|\widetilde{\psi}_c|>0)$	PAW $(|\widetilde{\psi}_c|\equiv 0)$
	0.4991	0.4992		
-2			0.5002	x
-4			0.4904	0.6288
-6			x	0.4992

FIG. 7. (Color online) Plots of the Hartree-Fock radial 4s orbitals for Fe, comparing results for the ground-state configuration (lower panel) and ionized configuration (upper panel) and the FC orbital results. The PAW results are based on the calculation of the pseudofunctions $\widetilde{\psi}_v(r)$ and using the PAW transformation Eq. (42). The results for the fully nodal 4s wave functions are virtually indistinguishable on this scale.

$|\widetilde{\psi}_c| > 0$ and $\mathcal{V}_0 = -2$ Ry and PAW (II) corresponding to $|\widetilde{\psi}_c| \equiv 0$ and $\mathcal{V}_0 = -6$ 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 wave functions for Fe in its ionized configuration changes very little compared with that of the reference configuration. In order to extend this study of 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 pseudocore functions $\widetilde{\psi}_c^a(r)$. 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 $|\widetilde{\psi}_c^a(r)| > 0$, we can ensure that the projector functions are strictly contained within the augmentation sphere as suggested by the original formulation of the PAW theory.[7] However if we set $|\widetilde{\psi}_c^a(r)| \equiv 0$, the effects of the extended core functions are incorporated into extended parts of the projector functions $\widetilde{p}_i^a(r)$. 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 calculated 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_c^a and the optimal form of the local potential $\widetilde{V}_{\text{loc}}^a(r)$. In addition, the use of continuum functions within Hartree-Fock theory for the purpose of augmenting the span of the pseudobasis 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 recent hybrid Hartree-Fock and generalized gradient exchange-correlation functionals that have reported in the recent literature.[52] In addition, there have been several groups[1,2] 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 nonexchange (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 nonexchange (correlation) contributions to the pseudoenergy of Eq. (43) takes the form

$$\widetilde{E}_{\text{vale}} \rfloor_{\text{nX}} = \widetilde{E}_K^v + \widetilde{E}_N^v + \widetilde{E}_H^{cv} + \widetilde{E}_H^{vv}. \qquad \text{(A1)}$$

Here the kinetic energy contribution is given by

$$\widetilde{E}_K^v = \sum_v N_v \langle \widetilde{\Psi}_v | \mathcal{K} | \widetilde{\Psi}_v \rangle. \qquad \text{(A2)}$$

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

$$\widetilde{E}_N^v + \widetilde{E}_H^{cv} = \int dr \widetilde{V}_f^a(r) \widetilde{n}_v(r), \qquad \text{(A3)}$$

where

$$\widetilde{V}_f^a(r) \equiv \widetilde{V}_{\text{loc}}^a(r) + \widetilde{v}_{\text{core}}^a(r) + (-Z^a + Q_{\text{core}}^a - \widetilde{Q}_{\text{core}}^a)\hat{v}_0^a(r) \qquad \text{(A4)}$$

and

$$\widetilde{n}_v(r) \equiv \sum_v N_v |\widetilde{\psi}_v(r)|^2. \qquad \text{(A5)}$$

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

$$\widetilde{v}_{\text{core}}^a(r) \equiv e^2 \int dr' \frac{\widetilde{n}_c^a(r')}{r_>} \quad \text{with} \quad \widetilde{n}_c^a(r) \equiv \sum_c N_c |\widetilde{\psi}_c^a(r)|^2. \qquad \text{(A6)}$$

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)

$$\hat{v}_0^a(r) \equiv e^2 \int dr' \frac{g_0^a(r')}{r_>} \qquad \text{(A7)}$$

with

$$Q_{\text{core}}^a = \int dr \, n_c^a(r) \quad \text{and} \quad \widetilde{Q}_{\text{core}}^a = \int dr \, \widetilde{n}_c^a(r). \qquad \text{(A8)}$$

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)

$$\widetilde{E}_H^{vv} = \frac{1}{2} \sum_{vv'} N_v N_{v'} \widetilde{R}_{vv;v'v'}^0. \qquad \text{(A9)}$$

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

$$(E_{\text{vale}}^a - \widetilde{E}_{\text{vale}}^a) \rfloor_{\text{nX}} = \sum_{ij} \sum_v N_v \langle \widetilde{\Psi}_v | \widetilde{P}_i^a \rangle \langle \widetilde{P}_j^a | \widetilde{\Psi}_v \rangle$$

$$\times \left(K_{ij}^a + [V_f^a]_{ij} + \frac{1}{2} [V_H^{avv}]_{ij} \right). \qquad \text{(A10)}$$

The kinetic energy contribution is

$$K_{ij}^a \equiv \langle \Phi_i | \mathcal{K} | \Phi_j \rangle - \langle \widetilde{\Phi}_i | \mathcal{K} | \widetilde{\Phi}_j \rangle. \qquad \text{(A11)}$$

The nuclear- and core-electron contribution is given by

$$[V_f^a]_{ij} \equiv \langle \Phi_i | V_f^a | \Phi_j \rangle - \langle \widetilde{\Phi}_i | \widetilde{V}_f^a | \widetilde{\Phi}_j \rangle, \qquad \text{(A12)}$$

where

$$V_f^a(r) \equiv -\frac{Z^a e^2}{r} + V_H^c(r). \qquad \text{(A13)}$$

The valence-valence Hartree interactions may be evaluated

$$[V_H^{avv}]_{ij} \equiv \sum_{kl} \sum_{v'} N_{v'} \langle \widetilde{\Psi}_{v'} | \widetilde{P}_k^a \rangle \langle \widetilde{P}_l^a | \widetilde{\Psi}_{v'} \rangle (R_{ij;kl}^{a0} - \widetilde{R}_{ij;kl}^{a0}), \qquad \text{(A14)}$$

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

For evaluating the nonexchange (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

$$\widetilde{V}_N(r) + \widetilde{V}_H(r) = \widetilde{V}_f^a(r) + \sum_v N_v \widetilde{W}_{vv}^0(r), \qquad \text{(A15)}$$

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

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

$$D_{ij}^a \rfloor_{\text{nX}} = K_{ij}^a + [V_f^a]_{ij} + [V_H^{avv}]_{ij} + [V_0^a]_{ij}, \qquad \text{(A16)}$$

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

$$[V_0^a]_{ij} \equiv m_{ij}^{a0} \int dr \, \hat{v}_0^a(r) (\widetilde{n}_v(r) + \sum_v N_v \hat{M}_{vv}^0(r)). \qquad \text{(A17)}$$

APPENDIX B: SIMPLIFIED EXPRESSIONS FOR CORE MATRIX ELEMENTS

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

$$m_{ic}^{aL} = \int dr \, r^L \phi_i^a(r) \psi_c^a(r). \tag{B1}$$

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

$$\tilde{R}_{vc;cv}^L = \sum_{aij} \langle \tilde{\Psi}_v^{HF} | \tilde{P}_i^a \rangle \langle \tilde{P}_j^a | \tilde{\Psi}_v^{HF} \rangle \mathcal{M}_{ic;cj}^{aL}, \tag{B2}$$

where

$$\mathcal{M}_{ic;cj}^{aL} \equiv e^2 \int \int dr \, dr' \frac{r_<^L}{r_>^{L+1}} \hat{m}_{ic}^{aL}(r) \hat{m}_{cj}^{aL}(r') \tag{B3}$$

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

$$\tilde{R}_{ic;cj}^{aL} = \mathcal{M}_{ic;cj}^{aL} \tag{B4}$$

ensuring that the unphysical compensation charge contributions on a single site cancel out of the calculation. If all the core states were localized, the complete expression for the valence-core exchange energy would be given by

$$\tilde{E}_x^{cv} + \sum_a (E_x^{acv} - \tilde{E}_x^{acv}) = - \sum_{vc} \sum_{L=|l_v-l_c|}^{l_v+l_c} \Theta_{vc}^L \sum_{aij} \langle \tilde{\Psi}_v^{HF} | \tilde{P}_i^a \rangle$$
$$\times \langle \tilde{P}_j^a | \tilde{\Psi}_v^{HF} \rangle R_{ic;cj}^{aL} \tag{B5}$$

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 Θ_{vq}^L defined in Eq. (14) will also be modified.

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

$$\mathcal{O}_{HF}^{PAW} \tilde{\Psi}_c^{HF} \rightarrow \sum_{ai} |\tilde{P}_i^a\rangle O_{ic}^a, \tag{B6}$$

where $O_{ic}^a \equiv m_{ic}^{a0}$. If the PAW basis function $|\tilde{\Phi}_i^a\rangle$ 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 nonzero.

While the pseudoexchange kernel function $\tilde{X}_v(r)$ defined in Eq. (71) has no contributions from localized core states, the one-center matrix element for the pseudoexchange kernel function X_{iv}^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.

$$X_{iv}^a \rfloor_{vc} = - \sum_c \sum_{L=|l_v-l_c|}^{l_v+l_c} \frac{1}{N_v} \Theta_{vc}^L \sum_j \langle \tilde{P}_j^a | \tilde{\Psi}_v^{HF} \rangle R_{ic;cj}^{aL}. \tag{B7}$$

One final point regarding pseudocore 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 $\langle \tilde{\Psi}_c^{HF} | \mathcal{O}_{HF}^{PAW} | \tilde{\Psi}_c^{HF} \rangle$.

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