ORBITAL DEPENDENT FUNCTIONALS: AN ATOM PROJECTOR AUGMENTED WAVE METHOD IMPLEMENTATION

BY

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Abstract

This thesis explores the formulation and numerical implementation of orbital dependent exchange-correlation functionals within electronic structure calculations. These orbital-dependent exchange-correlation functionals have recently received renewed attention as a means to improve the physical representation of electron interactions within electronic structure calculations. In particular, electron self-interaction terms can be avoided. In this thesis, an orbital-dependent functional is considered in the context of Hartree-Fock (HF) theory as well as the Optimized Effective Potential (OEP) method and the approximate OEP method developed by Krieger, Li, and Iafrate, known as the KLI approximation. In this thesis, the Fock exchange term is used as a simple well-defined example of an orbital-dependent functional.

The Projected Augmented Wave (PAW) method developed by P. E. Blöchl has proven to be accurate and efficient for electronic structure calculations for local and semi-local functions because of its accurate evaluation of interaction integrals by controlling multiple moments. We have extended the PAW method to treat orbital-dependent functionals in Hartree-Fock theory and the Optimized Effective Potential method, particularly in the KLI approximation. In the course of study we develop a frozen-core orbital approximation that accurately treats the core electron contributions for above three methods. The main part of the thesis focuses on the treatment of spherical atoms. We have investigated the behavior of PAW-Hartree Fock and PAW-KLI basis, projector, and pseudopotential functions for several elements throughout the periodic table. We have also extended the formalism to the treatment of solids in a plane wave basis and implemented PWPAW-KLI code, which will appear in future publications.
1 Introduction and Outline

Density Functional Theory (DFT) \cite{1} and the Kohn-Sham \cite{2} method are powerful quantum mechanical methods for calculating the electronic structure of atoms, molecules and solids \cite{3}. In principle, DFT is exact, assuming a knowledge of the exact exchange-correlation functional $E_{xc}[\rho(r)]$, where $\rho(r)$ denotes the electron density. Since the exact $E_{xc}[\rho(r)]$ is not known, a major challenge for using DFT to represent real materials is the construction of a suitable approximation of the exchange-correlation energy functional and the corresponding exchange correlation potential \cite{4}.

The Local-density approximation (LDA) \cite{5} is one kind of approximation to the exchange-correlation energy functional. It is expressed as a functional of electron density only:

$$E_{xc}^{\text{LDA}}[\rho] = \int \varepsilon_{xc}(\rho(r))\rho(r) dr.$$  \hspace{1cm} (1.1)

The Generalized gradient approximation (GGA) \cite{6} is another kind of exchange-correlation functional that takes into account the gradient of the density at the same coordinate.

$$E_{xc}^{\text{GGA}}[\rho] = \int dr f(\rho, \nabla \rho).$$  \hspace{1cm} (1.2)

In our previous investigations of cathode materials for Li ion batteries, we found that DFT using either LDA or GGA functionals fail to explain the structural energy difference of certain materials, particularly those containing transition metals. A likely source of this inaccuracy is described as the “self-interaction” error \cite{7}. There are many ways to correct for such errors \cite{7}. An orbital dependent exchange functional is one way to exactly cancel the self-interaction error, which can be viewed as a further approximation of exchange-correlation functionals as compared to LDA and GGA. It has also been called “third generation Density Functional Theory” \cite{8} \cite{3}. It constitutes an implicit functional of the density, in the sense that the exchange-correlation functional is expressed in terms of Kohn-Sham orbitals, rather than an explicit expression of the density \cite{9}.
To use orbital-dependent exchange functionals within the Kohn-Sham scheme, the fundamental problem to be solved is how to obtain the corresponding local exchange potential $V_x(r)$ [9]. This problem is solved by using the Optimized Effective Potential (OEP) method [10] [11], which is described in section (2.5) using three different ways [3] [12] [13]. In addition, a very efficient approximation to the OEP has been introduced by Krieger, Li, and Iafrate (KLI) [14] [15], which has been applied to molecules [16] and solids [17] within pseudopotential approximation. The KLI approximation formalism is elaborated in section (2.7).

In this thesis, we first review the all-electron formalisms, and then explore the use of Hartree-Fock approximation as a component of electronic structure calculations [18], followed by the OEP method and the KLI approximation. For all the schemes, we present our own algorithms and implementations. The results for spherical atoms serve as preparation for analogous calculations in solids, which will appear in future publications. As a part of this work, we develop accurate frozen-core schemes for all of the formations. The frozen-core orbital approximation is shown to be accurate for various elements across the periodic table within both Kohn-Sham and Hartree-Fock treatments. This frozen-core orbital approximation also serves as a guideline for solid calculations.

The Projector Augmented Wave (PAW) method was developed by Blöchl [19] and implemented by a number of authors [20] [21], [22]. The PAW method accurately treats important core-valence as well as valence-valence contributions to the exchange interaction [23]. It is a natural choice for implementing orbital-dependent functional within an efficient pseudopotential-like scheme.

In this thesis, after presenting atomic All-electron and frozen-core algorithms in Chapter (2), we present the analogous PAW formalisms for Hartree-Fock, OEP, and KLI within the PAW atom framework in Chapters (4, 5, 6).

In chapter (4), we modify PAW formalism to work with the integral-differential equations of Hartree-Fock theory. In particular, we show how the relationship between the basis and projector functions differs from those Kohn-Sham theory using LDA or GGA functionals, and also examine the role of the core electrons within the treatment.

In chapter (5) we present our analysis of the implementation of OEP within PAW based on experiences we had. It is our understanding that in order to unify OEP and PAW, we have to use more than the usual number of basis functions which is computationally prohibitive. However, the KLI formulation provides an excellent
approximation to the full OEP approach which is can be effectively implemented in the PAW formalism. Its detailed implementation within atom PAW framework is explained in chapter (6). The treatment of solids will be presented in the future publications.
All-electron Spherical Atom Calculations within Hartree-Fock (HF) and Optimized Effective Potential (OEP) theory, including the KLI Approximation
2.1 Notation for Spherical Atoms

This section presents the notation for basic terms that are used in this thesis. Since the goal of this work is to derive quantities suitable for general use in modeling materials within the context of the Projected Augmented Wave (PAW) formalism, it is sufficient to work with atoms in spherically averaged and spin averaged configurations.

The one electron orbital takes the form:

\[ \Psi_p(r) = \Psi_{nplpm_p}(r) = \frac{\psi_p(r)}{r} Y_{lpm_p}(\hat{r}), \]  

(2.1)

here the symbol \( p \) is used 2 ways. In contexts involving \( \Psi_p(r) \), it stands for the composite index \( nplpm_p \) with \( n_p \) denoting the principle quantum number, \( l_p \) denoting the angular momentum, and \( m_p \) denoting the magnetic quantum number. In contexts involving the radial function \( \psi_p(r) \), \( Y_{lpm_p}(\hat{r}) \) is the spherical harmonic function, \( p \) denotes the shell index and \( N_p \) with \( N_p \leq 2(2l_p + 1) \) denotes the number of electrons in the shell.

The electron density is spherically symmetric, and can be obtained by summing over all the occupied shells:

\[ \rho(r) = \frac{n(r)}{4\pi r^2}, \quad \text{where} \quad n(r) = \sum_p N_p |\psi_p(r)|^2. \]  

(2.2)

The total electronic energy of a spherical atom can be written as a sum of four terms:

\[ E_{tot} = E_k + E_N + E_H + E_{xc}. \]  

(2.3)

Its components are the kinetic energy \( E_k \):

\[ E_k = \sum_p \int \Psi_p^*(r) K \Psi_p(r) d^3r = \sum_p N_p \int \psi_p^*(r) K_p \psi_p(r) dr, \]  

(2.4)

where:

\[ K = -\frac{\hbar^2}{2m} \nabla^2 \quad \text{and} \quad K_p \psi_p(r) = -\frac{\hbar^2}{2m} \left( 1 \frac{d^2}{dr^2} - \frac{l_p(l_p + 1)}{r^2} \right) \psi_p(r). \]  

(2.5)

The nuclear energy is:

\[ E_N = \int d^3r V_N(r) \rho(r), \]  

(2.6)

where the nuclear potential:

\[ V_N(r) = -\frac{Ze^2}{r}. \]  

(2.7)

The Hartree Energy is defined by:

\[ E_H = \frac{e^2}{2} \int \int d^3r d^3r' \frac{\rho(r)\rho(r')}{|r - r'|}. \]  

(2.8)
and the Hartree Potential is defined by:

\[ V_H(r) = e^2 \int d^3r' \frac{\rho(r')}{|r - r'|}. \]  

(2.9)

The exchange-correlation energy \( E_{xc} \) will be discussed later, and the exchange-correlation potential is defined in terms of the functional derivatives of \( E_{xc} \) with respect to the electron density \( \rho(r) \):

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

(2.10)
2.2 All-Electron Hartree-Fock Theory

2.2.1 Hartree-Fock Equation

The Hartree-Fock integral-differential equation can be derived from a total energy minimization problem with orthonormality constraints. The energy is minimized over the variation of orbitals, and Lagrangian multipliers. The overall object function is given by:

\[
F_{\text{obj}}[\{\Psi_p\}, \{\lambda_{pq}\}] = E_{\text{tot}} - \sum_{qp} \lambda_{qp}(\langle \Psi_p | \Psi_q \rangle - \delta_{qp}), \tag{2.11}
\]

where \(\lambda_{qp}\) denotes a Lagrange multiplier. Furthermore, we simplify the notation of wavefunction \(\Psi^{HF}_p(r)\) to become \(\Psi_p(r)\), and superscript \(HF\) is going to be omitted, but assumed to be present throughout this section.

Within Hartree-Fock theory, the Fock exchange energy is given by:

\[
E_x = -\frac{e^2}{2} \sum_{pq} \delta_{\sigma_p,\sigma_q} \int d^3r \int d^3r' \frac{\Psi^{HF*}_p(r)\Psi^{HF}_q(r')\Psi^{HF*}_q(r')\Psi^{HF}_p(r')}{|r - r'|}, \tag{2.12}
\]

where \(\sigma_p, \sigma_q\) denote the electron spin orientation quantum number.

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

\[
E_x = -\sum_p q \sum_{L=|p-q|}^{l_p+l_q} \frac{1}{2} \Theta^L_{pq} R^L_{qp,qp}(r), \tag{2.13}
\]

where the radial integral takes the form:

\[
R^L_{qp,qp} = e^2 \int dr dr' \int_{r \leq r' \leq r} \psi^*_p(r)\psi_q(r)\psi^*_q(r')\psi_p(r'), \tag{2.14}
\]

here the weight factor \(\Theta^L_{pq}[24]\) represents the spherically averaged angular factor for the \(L^{th}\) moment.

\[
\Theta^L_{pq} = \begin{cases} 
\frac{1}{2}N_pN_q \left( \begin{array}{ccc} l_p & L & l_q \\ 0 & 0 & 0 \end{array} \right)^2 & \text{for } p \neq q \\
\frac{1}{2}N_p(N_p - 1)^{4l_p+2}_{4l_p+1} \left( \begin{array}{ccc} l_p & L & l_q \\ 0 & 0 & 0 \end{array} \right)^2 & \text{for } p = q, L \neq 0 \\
N_p & \text{for } p = q, L = 0 
\end{cases}. \tag{2.15}
\]
In order to find the radial Hartree-Fock orbitals $\psi_p(r)$, the total energy in (2.3) is minimized as a functional of orbitals with orthonormality constraints. By taking the derivatives of the object function with respect to the Hartree-Fock orbitals, at convergence:

$$\frac{\partial F_{obj}}{\partial \Psi_p} = 0. \quad (2.16)$$

As a result, (2.16) gives the Hartree-Fock integral-differential equation. In terms of the radial wavefunctions $\psi_q(r)$, it can be written as:

$$H_{HF} \psi_p(r) + X_p(r) - \sum_q \lambda_{qp} \psi_q(r) = 0, \quad (2.17)$$

which must be solved self-consistently. At self-consistency the Lagrangian multipliers satisfy:

$$\lambda^l_{qp} = \langle \psi_q | H_{HF} \psi_p + X_p \rangle \delta_{ll_p} \delta_{ll_q}, \quad (2.18)$$

where the Hartree-Fock Hamiltonian takes the form

$$H_{HF}^p(r) = K_p + V_N(r) + V_H(r). \quad (2.19)$$

We define the derivatives of the Fock exchange term with respect to the orbitals as the **Exchange Kernel Function**:

$$X_p(r) = \frac{1}{N_p} \frac{\partial E_x}{\partial \psi_p^*} = -\sum_q \sum_{L=|l_p-l_q|}^{l_p+l_q} \frac{1}{N_p} \Theta_{pq}^L W_{qp}^L(r) \psi_q(r), \quad (2.20)$$

where $W_{qp}^L(r)$ is the radial integral:

$$W_{qp}^L(r) = e^2 \int dr' \frac{r_L^<}{r_{L+1}^>} \psi_q^*(r') \psi_p(r'). \quad (2.21)$$

Furthermore, given (2.20), we define an important term $V_{HF,p}^x(r)$ which will be helpful for the future analysis. If we rewrite (2.20) to become:

$$X_p(r) = \frac{1}{N_p} \frac{\partial E_x}{\partial \psi_p^*} \equiv V_{HF,p}^x(r) \psi_p(r), \quad (2.22)$$

here $V_{HF,p}^x(r)$ can be defined as **Fock exchange potential** for orbital $p$.

Its meaning becomes more clear if we rewrite the radial part of Hartree-Fock equation (2.17) to become:

$$H_{HF} \psi_p(r) + V_p^x \psi_p(r) = \sum_q \lambda_{qp} \psi_q(r), \quad (2.23)$$

where we see that Fock exchange potential $V_{HF,p}^x(r)$ serves as an exchange potential similar to the form found in the Kohn-Sham equations. However, here the Hartree-Fock potential $V_{HF,p}^x(r)$ is non-local, and orbital specific.
2.3 All-electron Hartree-Fock Implementation

2.3.1 Block Diagonalization within Angular Channels

It is first of all necessary to realize that $\lambda_{pq}$ matrix formed on the left hand side of the (2.17) has a block diagonal feature as shown below because of the orthogonality of the angular part of the wavefunction.

![Lambda Matrix Diagram]

Figure 2.1: The $\Lambda$ matrix consists of blocks corresponding to each angular momentum channel $l$, and the off-diagonal block are zero because of orthogonality between different channels.

The diagonal block matrices $\lambda_{qp}^l$ (where $l_p = l_q = l$) are usually symmetric. In those cases, an orthogonal transformation among the orbitals $\psi_p(r)$ in the block can diagonalize $\lambda_{qp}^l$. Working with the transformed orbitals helps to stabilize the self-consistent iterations. When an atom has both filled shells and partially filled shells for the same $l$, the block matrix $\lambda_{qp}^l$ has an asymmetry. In those cases, it is convenient to transform the orbitals in the block into linear combinations of themselves which diagonalize the related matrix $\Lambda_{pq}^l = \Lambda_{qp}^l = \frac{1}{2}(\lambda_{pq}^l + \lambda_{qp}^l)$. Our diagonalization procedure goes as follows.
Diagonalization within Blocks with the same l-value

\( (l_p = l_q = l) \)

1 **Orthonormalization** \( \langle \psi_q \mid \psi_p \rangle = \delta_{qp} \)

2 **Update** \( \{ \rho(r), V_H(r), X_p(r) \} \) Using \( \psi_p(r) \)

3 **Update** \( \lambda_{pq}^l \leftarrow \langle \psi_q(r) \mid H^{HF}(r)\psi_p(r) + X_p(r) \rangle \)

\[ \Lambda_{p}^{l} = \Lambda_{q}^{l} \leftarrow \frac{1}{2}(\lambda_{pq}^{l} + \lambda_{qp}^{l}) \]

4 **Diagonalize the Block** Diagonalize the Block matrices \( \Lambda_{pq}^{l} \)

   to determine eigenvalue \( \varepsilon_p \)

   obtaining transformed orbitals \( \psi_p(r) \)

5 **Normalization** \( \langle \psi_p \mid \psi_p \rangle = 1 \)

6 **Update** \( \{ \rho(r), V_H(r), X_p(r) \} \leftarrow \psi_p(r) \)

7 **Update** \( \lambda_{pq} \leftarrow \langle \psi_q \mid H^{HF} \mid \psi_p \rangle + \langle \psi_q \mid X_p \rangle \)

In practice, this algorithm is implemented similarly using both FORTRAN and Matlab codes. Within each self-consistent step, we first block diagonalize all the blocks that have the same l-value, even for non-full shell block, and then immediately after that, we use newly obtained wavefunction to update the block matrix element \( \lambda_{pq} \) using (2.18). It is important to notice that due to (2.18), the non-full shell block is not symmetric. This procedure is not identical to the Fischer’s implementation [25], however these algorithms are stable and both FORTRAN and Matlab results agrees well with those of Fischer as shown in Fig [2.3] and Table [2.1].
2.3.2 Adding Diagonal terms

Another important practical procedure we adopted was suggested by Cowan and co-workers [26]. Rather than solving the Hartree Fock equation (2.17) directly, we modified the equation by adding diagonal terms on both sides to become:

\[
(H_{HF}^{HF}(r) - \varepsilon_p^t)\psi_p^{HF}(r) = -X_p(r) + \sum_q \lambda_{pq}^t \psi_q^{HF}(r) - \varepsilon_p^t \psi_p^{HF}(r),
\]

(2.24)

where:

\[
\varepsilon_p = \lambda_p^l,
\]

(2.25)

and this procedure helps to stabilize the overall SCF calculations. To sum up, the overall self-consistent algorithm goes as follows:

---

**Hartree-Fock All Electron SCF Procedure**

1. \( t = 0 \)
2. do
3. \textbf{Orthonormalization} \( \langle \psi_q^t | \psi_p^t \rangle = \delta_{qp} \)
4. \textbf{Diagonalization within Blocks with the same l-value}
   - Obtain new \( \{ \lambda_{pq}^t, X_p^l(r)\psi_p^t, V_{HF}^t(r) \} \)
5. \textbf{Update} \( H_{HF}^t \leftarrow K + V_N(r) + V_{HF}^t(r) \)
6. \textbf{Solve} \( (H_{HF}^t(r) - \varepsilon_p^t)\psi_p^{t+1}(r) = -X_p^t(r) + \sum_q \lambda_{pq}^t \psi_q^t(r) - \varepsilon_p^t \psi_p^t(r) \)
   - to obtain \( \psi_p^{t+1}(r) \)
7. \textbf{Adjust} \( \psi_p^{t+1}(r) \)'s number of nodes = \( n_p - l_p - 1 \)
8. \textbf{Update} \( \psi_p^t \leftarrow a\psi_p^t + (1 - a)\psi_p^{t+1} \)
   - \( t \leftarrow t + 1 \)

---

In practice, Step (6) the differential equations solver is sensitive to the eigenenergy \( \varepsilon_p^t \). For most of the time, we can use \( \varepsilon_p \) from (2.25), however, it is sometime necessary to adjust \( \varepsilon_p^t \) in order to generate the appropriate wavefunction \( \psi_p^{t+1} \) with the correct number of nodes. For example, one possible adjustment for \( \varepsilon_L^t \) could be:

\[
\varepsilon_L^t = \frac{1}{2} \lambda_{L-1,L-1}^t,
\]

(2.26)
here L denotes the outer most orbital, and $L - 1$ denotes the second outer most orbital. By applying such adjustments (2.26) over the eigenvalues during the self-consistent calculations, the wavefunction $\psi_{t+1}^p$ determined from 2.17 would gradually achieve to have correct number of nodes, and eventually converge.
The following figure reproduced from [18] compares 4s and 4p wavefunction of Ge, results from Hartree-Fock and LDA calculations. The shapes of the Hartree-Fock wavefunctions are, in general, similar to the shapes of the corresponding Kohn-Sham wavefunctions:

Figure 2.2: Radial wavefunctions for Ge, comparing Kohn-Sham (LDA) and Hartree-Fock (HF)
The calculated eigenenergies and wavefunctions are in good agreements with the work and results published by C. F. Fischer [25]. Fig (2.3), Fig (2.4) and Fig (2.5) illustrate the comparisons of wavefunction generated with the Matlab code with that generated with atk2 program [25] which is documented in the reference [27] and shared on the website http://atoms.vuse.vanderbilt.edu/. For this comparison we used logarithmic grid with 2001 points. The numerical results are illustrated in Table [2.1] Table [2.1], Table [2.2], and Table [2.3] It should be noted that the degree of accuracy can be controlled by increasing the radial grid sampling.

Figure 2.3: Radial wavefunctions for C: Comparison between Matlab and atk2 codes

Figure 2.4: Radial wavefunctions for S: Comparison between Matlab and atk2 codes
Comparison of C.F. Fischer result and this work: Fe

Figure 2.5: Radial wavefunctions for Fe: Comparison between Matlab and atk2 codes
Fischer:

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Total Energy = -75.31939608 Kinetic Energy = 75.31939634
Ratio(P. E./K. E.) = -1.999999996 Potential Energy = -150.63879244

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Total Energy = -75.319147846664023 Kinetic Energy = 75.525472467072362
Ratio(P. E./K. E.) = -1.997268145253930 Potential Energy = -150.844620313736390

Table 2.1: Energy Comparison of C
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Total Energy = -794.95709892, Kinetic Energy = 794.95709908
Ratio(P. E./K. E.) = -2.000000000, Potential Energy = -1589.914198

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Total Energy = -794.9578783288450, Kinetic Energy = 795.243963580120520
Ratio(P. E./K. E.) = -1.999640255367681, Potential Energy = -1590.20184212959000

Table 2.2: Energy Comparison of S
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Total Energy = -2524.58172602
Kinetic Energy = 2524.58213896
Ratio(P. E./K. E.) = -1.999999836
Potential Energy = -5049.16386496

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Total Energy = -2524.58597596628800
Kinetic Energy = 2524.634867335707
Ratio(P. E./K. E.) = -1.999999836
Potential Energy = -5049.16386496

Table 2.3: Energy Comparison of Fe
2.4 Kohn-Sham Theory

Hartree-Fock theory is based on directly optimizing the expectation value of the Hamiltonian for a wavefunction expressed in terms of a single Slater determinant or sometimes as a sum of a few Slater determinants. Density Functional Theory, on the other hand, has been developed by directly replacing the many-body problem with an independent particle picture. It is based on Hohenberg-Kohn theorems [1], and has become the primary tool for calculation of electronic structure in condensed matter physics [28]. The Hohenberg-Kohn theorems can be stated as follows [1] [28]:

**Theorem I**

For any system of interacting particles with external potential $V_{ext}(r)$ up to a constant, there is one to one correspondence between $V_{ext}(r)$ and the system’s ground state electron density $\rho_0(r)$.

**Theorem II**

The ground state density $\rho_0(r)$ is a basic variable which determines the system’s properties. The total energy is a functional of the density. The global minimum of the total energy functional is the exact ground state energy.

The Kohn-Sham approach is to replace the difficult interacting many-body system with a non-interacting system that can be solved more easily. The ansatz of Kohn-Sham assumes that the ground state density of the original interacting system is equal to that of some chosen non-interacting system with all the difficult many-body terms incorporated into an exchange-correlational functional of the density [28]. In principle the non-interacting system can be evaluated with controlled numerical precision and can represent the many-body problem within the reliability of the exchange-correlation functional.

Solution of the non-interacting system ground state can be viewed as an optimization problem with orthonormalization constraints. The ground state energy can be written as a functional of density:

$$E_{KS} = E_k[\rho] + \int d^3r V_{ext}(r)\rho(r) + E_H[\rho] + E_{xc}[\rho].$$  \hspace{1cm} (2.27)

By incorporating the orthonormalization constraints, the overall objective function that
needs to be minimized takes the form:

\[ F_{\text{obj}} = E_{KS} + \sum_p \varepsilon_p (\langle \Psi_p^{KS} | \Psi_q^{KS} \rangle - \delta_{pq}), \]  

(2.28)

where \( \Psi_p^{KS}, \Psi_q^{KS} \) are Kohn-Sham orbitals. To achieve the ground state energy, one needs to vary the wavefunction to obtain the variational equation. At convergence, one ends up with:

\[ \frac{\partial F_{\text{obj}}}{\partial \Psi_p^*(r)} = 0, \]  

(2.29)

where the total energy derivative with respect to the wavefunction can be expressed using the chain rule:

\[ \frac{\partial E_{KS}}{\partial \Psi_p^*(r)} = \frac{\partial E_k[\rho]}{\partial \Psi_p^*(r)} + \left[ \frac{\partial E_{\text{ext}}[\rho]}{\partial \rho(r)} + \frac{\partial E_H[\rho]}{\partial \rho(r)} + \frac{\partial E_{xc}[\rho]}{\partial \rho(r)} \right] \frac{\partial \rho(r)}{\partial \Psi_p^*(r)}, \]  

(2.30)

where we denote:

\[ \frac{\partial E_k[\rho]}{\partial \Psi_p^*(r)} = -\frac{\hbar^2}{2m} \nabla^2 \Psi_p(r) = K \Psi_p(r). \]  

(2.31)

We also define exchange-correlation potential in terms of the exchange-correlation energy functional \( E_{xc} \) which, in principle, contains all the many body effects:

\[ \frac{\partial E_{xc}[\rho]}{\partial \rho(r)} = V_{xc}(r). \]  

(2.32)

We therefore can obtain the Kohn-Sham equation:

\((K + V_{\text{ext}}(r) + V_H(r) + V_{xc}(r) - \varepsilon_p) \Psi_p(r) = 0. \)  

(2.33)

with Kohn-Sham potential defined as:

\[ V_s(r) = V_{\text{ext}}(r) + V_H(r) + V_{xc}(r). \]  

(2.34)

For this thesis, the exchange-correlation functional is that of Fock-exchange. \( E_{xc} \rightarrow E_x \) and \( V_{xc}(r) \rightarrow V_x(r) \), therefore:

\[ V_s(r) = V_{\text{ext}}(r) + V_H(r) + V_x(r). \]  

(2.35)

The “external” potential \( V_{\text{ext}}(r) \) is the nuclear potential \( V_N(r) \), for most examples considered in this thesis. The single particle Hamiltonian can be described as:

\[ H = K + V_s(r). \]  

(2.36)
2.4.1 Hartree-Fock Optimized Effective Potential Comparison

Energy Minimization Discussion

In Hartree-Fock theory, the total energy functional is minimized without restrictions, except for orthogonality between the orbitals, which leads to Hartree-Fock differential-integral equation. The Hartree-Fock Differential-Integral equations is a single-particle Schrödinger equation with a non-local effective potential as shown in (2.17) [3].

By contrast, in the Optimized Effective Potential method, the total energy functional is minimized under the subsidiary conditions that the orbitals come from a local or multiplicative potential, while this local $V_x(r)$ is determined as a solution to an integral equation [3] [9].

The Hartree-Fock solution would give the lowest possible total energy, while the total energy calculated from solving OEP integral equation is slightly higher [11] [3] [9]. The wavefunctions $ψ^{HF}(r), ψ^{OEP}(r)$ are similar, however the differences between the eigenenergies of Hartree Fock and Kohn-Sham OEP are not always small [3].
2.5 All Electron Optimized Effective Potential Theory

There are several distinct ways to derive the basic equations which yield the Optimized Effective Potential. [3] [9] [29] [13]. Here we present 3 instructive ones, which are of equal importance. In practice, we adopt the scheme in section (2.5.3).

2.5.1 Direct functional derivative

Within the Optimized Effective Potential (OEP) formalism, the exchange energy \( E_x \) is defined as orbital-dependent-functional-Fock expression written in terms of KS orbitals.

\[
E_x = \frac{-e^2}{2} \sum_{pq} \delta_{\sigma\sigma'} \int d^3r \int d^3r' \frac{\Psi_{p}^{KS}(r)\Psi_{q}^{KS}(r')\Psi_{q}^{KS}(r')\Psi_{p}^{KS}(r')}{|r - r'|}, \tag{2.37}
\]

here \( p, q \) are the labels for all occupied states, super index \( KS \) stands for Kohn-Sham, and this is the most appropriate definition as it guarantees the exact cancelation of the self-interaction energy in (2.8) of Hartree Energy. This expression is identical to (2.12) except for the use of orbitals \( \Psi_{p}^{KS}(r) \) rather than the Hartree-Fock counter parts.

Thus the exchange only potential takes the form:

\[
V_x(r) = \frac{\delta E_x[\{\Psi_{p}\}]}{\delta \rho(r)}. \tag{2.38}
\]

We need to use chain rule for the functional derivatives, to transform (2.38) into derivatives with respect to \( \Psi_{p}(r) \):

\[
V_x(r) = \frac{\delta E_x[\{\Psi_{k}\}]}{\delta \rho(r)} = \int d^3r' \frac{\delta V_s(r')}{\delta \rho(r)} \sum_p \int d^3r'' \frac{\delta \Psi_{p}^{*}(r'')}{\delta V_{s}(r'')} \frac{\delta E_x}{\delta \Psi_{p}^{*}(r'')} + c.c. \tag{2.39}
\]

The functional derivatives of exact exchange energy \( E_x \) can be easily calculated:

\[
\frac{\delta E_x}{\delta \Psi_{p}^{*}(r')} = -e^2 \sum_q \delta_{\sigma\sigma'} \Psi_{q}(r') \int d^3r \frac{\Psi_{q}^{*}(r)\Psi_{p}(r)}{|r - r'|}. \tag{2.40}
\]

Also notice that the factor \( \frac{1}{2} \) within the expression of exact exchange energy \( E_x \) is eliminated because we are summing over all the occupied states twice.

Using first order perturbation theory one obtains:

\[
\delta \Psi_{p}^{*}(r) = -\sum_{q\neq p} \int \frac{\Psi_{q}(r')\delta V_s(r')\Psi_{p}^{*}(r')}{\varepsilon_q - \varepsilon_p} \Psi_{q}^{*}(r). \tag{2.41}
\]
yielding:
\[
\frac{\delta \Psi_p^* (r)}{\delta V_s (r')} = - \sum_{q \neq p} \frac{\Psi_q (r') \Psi_q^*(r')}{\varepsilon_q - \varepsilon_p} \Psi_q^* (r) = -G_p (r, r') \Psi_p^* (r').
\] (2.42)

with Green's function defined as:
\[
G_p (r, r') = \sum_{q \neq p} \frac{\Psi_q (r') \Psi_q^* (r)}{\varepsilon_q - \varepsilon_p}.
\] (2.43)

The inverse of \( \frac{\delta V_s (r')}{\delta \rho (r)} \) is the static response function \( \chi_s \) of the Kohn-Sham system [3]:
\[
\chi_s (r, r') = \frac{\delta \rho (r)}{\delta V_s (r')} = \frac{\delta \sum_q |\Psi_q (r)|^2}{\delta V_s (r')}.
\] (2.44)

This can be simplified to become:
\[
\chi_s (r, r') = - \sum_p (\Psi_p (r) G_p (r, r') \Psi_p^* (r') + c.c),
\] (2.45)

If we substitute (2.45), (2.43), into (2.39), (2.39) would become:
\[
V_x (r) = \int d^3r' \chi_s^{-1} (r, r') \Lambda_x (r'),
\] (2.46)

where:
\[
\Lambda_x (r) = - \sum_p (\int d^3r' \Psi_p^* (r') G_p (r, r') \frac{\delta E_x}{\delta \Psi_p^* (r')} + c.c).
\] (2.47)

If one multiplies both sides of (2.46) by \( \chi_s (r, r') \), and integrates over \( r \), making use of the fact that:
\[
\int d^3r'' \chi_s^{-1} (r, r'') \chi_s (r'', r') = \delta^3 (r - r').
\] (2.48)

One ends up with the OEP integral equations.
\[
\int d^3r' \chi_s (r, r') V_x (r') = \Lambda_x (r).
\] (2.49)
2.5.2 Total energy minimization

This approach relies on energy minimization, and the physical meaning of the Optimized Effective Potential integral equation would become more clear in this derivation \([9] [11]\). The Hohenberg-Kohn theorem points out that there is an unique relationship between \(\rho(r)\) and \(V_s(r)\), thus, we can also minimize the \(E_{tot}\) with respect to \(V_s(r)\).

For the ground state, the following derivative should be zero at convergence:

\[
0 = \frac{\delta E_{tot}[\Psi_k]}{\delta V_s(r)}.
\] (2.50)

The functional derivatives can be evaluated using chain rule:

\[
\frac{\delta E_{tot}[\Psi_k]}{\delta V_s(r)} = \sum_p \int d^3r' \left[ \frac{\delta \Psi_p^*(r')}{\delta V_s(r)} \frac{\delta E_{tot}}{\delta \Psi_p^*(r')} + c.c \right].
\] (2.51)

According to Kohn-Sham equation, the derivative of total energy with respect to the \(\Psi_p^*(r)\) can be written as:

\[
\frac{\delta E_{tot}}{\delta \Psi_p^*(r)} = \left[ -\frac{\hbar^2 \nabla^2}{2m} + V_N(r) + V_H(r) \right] \Psi_p(r) + \frac{\delta E_x}{\delta \Psi_p^*(r)}.
\] (2.52)

Using Kohn-Sham Equation (2.33), one can further simplify the right hand side to become:

\[
\frac{\delta E_{tot}}{\delta \Psi_p^*(r)} = [\varepsilon_p - V_x(r)] \Psi_p(r) + \frac{\delta E_x}{\delta \Psi_p^*(r)}.
\] (2.53)

From (2.43) and (2.50) we obtain:

\[
0 = \sum_p \int d^3r' \left[ \Psi_p^*(r') G_p(r, r') \Psi_p(r) V_x(r') - \Psi_p^*(r') G_p(r, r') \Psi_p(r) \varepsilon_p 
+ \Psi_p^*(r') G_p(r, r') \frac{\delta E_x}{\delta \Psi_p^*(r')} + c.c \right].
\] (2.54)

One immediately identifies the first term is actually \(\int d^3r' \chi_s(r, r') V_x(r')\) as defined in (2.49), and the second term vanishes:
\[ \sum_p \int d^3r' \Psi_p^*(r) G_p(r, r') \Psi_p(r') \varepsilon_p = \sum_p \varepsilon_p \Psi_p(r') \int d^3r' \Psi_p^*(r) G_p(r, r') \Psi_p(r') = 0. \] (2.55)

Because of the orthogonality relation:
\[ \int d^3r \Psi_p^*(r) G_p(r, r') = \int d^3r' G_p(r, r') \Psi_p(r') = 0. \] (2.56)

and the third term is \( \Lambda_x(r) \). Therefore, one ends up with the OEP integral equation (2.49) again. This approach is instructive because it indicates that the search for Optimal Effective (Exact Exchange) Potential \( V_x(r) \) can be cast into an optimization problem.
2.5.3 Gradient Search Method

Given the fact that a direct solution $V_x(r)$ of the integral equation is very demanding [3] [11] [30], a better approach is to solve the integral equations iteratively. In practice we find the algorithm suggested by Hayman, Stiles and Zangwill [13] [30] to be quite effective.

The total energy functional that needs to be minimized can be written as:

$$E_{tot} = E_k + E_N + E_H + E_x.$$ 

In this section, we write explicit formalism in terms of radial functions of spherical atoms. When evaluating the Optimized Effective Potential for the exact exchange case, the exchange energy is expressed in terms of Kohn-Sham orbitals (2.37). Hayman, Stiles and Zangwill [13] suggest that this can be cast into a minimization problem with normalization and Kohn-Sham equation constraints, and these constraints are forced by adding Lagrange multipliers to the energy functional. This leads to the object functional $F$:

$$F[\{\psi_p(r)\}, \{\lambda_p\}, \{g_p\}] = E_{tot}(\{\psi_p(r)\}) - \sum_p \lambda_p(\langle \psi_p \mid \psi_p \rangle - 1)$$

$$- \sum_p N_p(\langle g_p \mid H_{KS} - \varepsilon_p \mid \psi_p \rangle + c.c)$$ 

with independent variables set $\{g_p^*(r), \lambda_p, \psi_p^*(r), \varepsilon_p, V_x(r)\}$. The gradient of (2.57) with respect to these independent variables are zero at convergence:

$$\frac{\delta F}{\delta g_p^*(r)} = (\varepsilon_p - H_{KS})\psi_p(r) = 0$$

$$\frac{\delta F}{\delta \lambda_p} = 1 - \int d^3r |\psi_p|^2 = 0$$

$$\frac{\delta F}{\delta \varepsilon_p} = \langle g_p \mid \psi_p \rangle + \langle \psi_p \mid g_p \rangle = 0$$

$$\frac{\delta F}{\delta \psi_p^*(r)} = \frac{1}{N_p \delta \psi_p^*(r)} - \lambda_p \psi_p - (H_{KS} - \varepsilon_p)g_p(r) = 0$$

$$\frac{\delta F}{\delta V_x(r)} = - \sum_p N_p(g_p^*(r)\psi_p(r) + g_p(r)\psi_p^*(r)) = 0$$ 

Notice that here $g_p(r)$ is introduced as a Lagrange function, which is also called auxiliary function. The derivative of $\frac{\delta F}{\delta \varepsilon_p} = 0$ requires this auxiliary function $g_p(r)$ to be orthogonal to the wavefunction $\psi_p(r)$. 

The Kohn-Sham equations and normalization constraints are automatically satisfied when we minimized the object function with respect to this Lagrange function $g_p(r)$ and also $\lambda_p$. Furthermore one can simplify $\frac{\delta F}{\delta \psi_p^*(r)}$ to obtain an inhomogeneous differential equation for auxiliary $g_p(r)$, the detailed derivation of (2.59) will be presented in the Appendix (A.1).

$$(H_{KS} - \varepsilon_p)g_p(r) = \frac{1}{N_p} \frac{\delta E_x}{\delta \psi_p^*(r)} - V_x(r)\psi_p(r) - U_p\psi_p(r).$$

(2.59)

The obtained differential equation (2.59) further verifies that $\langle g_p | \psi_p \rangle = 0$ is true, and such orthogonalization needs to be explicitly enforced, as $\psi_p(r)$ is the homogeneous solution to (2.59) where $U_p$ is defined as:

$$U_p = -\langle \psi_p | V_x | \psi_p \rangle + \left\langle \psi_p \left| \frac{1}{N_p} \frac{\delta E_x}{\delta \psi_p^*(r)} \right. \right\rangle.$$  

(2.60)

Equation (2.59) determines $g_p(r)$ which in turn provides a gradient according to

$$\frac{\delta F}{\delta V_x(r)} = -\sum_p N_p (g_p^*(r)\psi_p(r) + g_p(r)\psi_p^*(r))$$

to search for optimal $V_x(r)$ that yields the energy minimum.
2.5.4 Orbital Shift interpretation

In this section, we will verify that at convergence, the Gradient Search Method is equivalent to the OEP Integral Equation. Starting from (2.49):

$$\int d^3r' \chi_s(r, r') V_x(r') = \Lambda_x(r). \quad (2.61)$$

If we expand response function $\chi_s(r, r')$ and $\Lambda_x(r)$ using their definition, (2.49) becomes:

$$\sum_p \int d^3r' \Psi^*_p(r') G_p(r, r') \Psi_p(r) V_x(r') = \sum_p \int d^3r' [\Psi^*_p(r') G_p(r, r') \frac{\delta E_x}{\delta \Psi^*_p(r')} + c.c]. \quad (2.62)$$

It is convenient to define the derivative of exchange energy with respect to the wavefunction to become a potential like term times the wavefunction, similar to the definition (2.22):

$$\frac{\delta E_x}{\delta \Psi^*_p(r')} \equiv W_p(r' \Psi^*_p(r'), \quad (2.63)$$

therefore the OEP Integral Equation can be further transformed into:

$$\sum_p \int d^3r' \Psi^*_p(r') (V_x(r') - W_p(r')) G_p(r, r') \Psi_p(r) + c.c = 0. \quad (2.64)$$

It is convenient to define $\delta \Psi^*_p(r)$ as:

$$\delta \Psi^*_p(r) = \sum_p \int d^3r' (V_x(r') - W_p(r')) G_p(r, r') \Psi^*_p(r'), \quad (2.65)$$

with $g_p(r)$ representing its radial part:

$$\delta \Psi_p(r) = \delta \Psi_{nlm_p}(r) = \frac{g_p(r)}{r} Y_{lm_p}(\hat{r}). \quad (2.66)$$

Therefore the integral equation (2.49) becomes:

$$\sum_p (\delta \Psi^*_p(r) \Psi_p(r) + c.c) = 0. \quad (2.67)$$

It can be proved similarly according to (A.1), that the differential equation that $\delta \Psi^*_p(r)$ satisfies is:

$$(H_{KS} - \varepsilon_p)\delta \Psi^*_p(r) = (-V_x(r) + W_p(r) + (\overline{V_{xp}} - \overline{W_p})) \Psi_p(r), \quad (2.68)$$

with $\overline{V_{xp}}$ and $\overline{W_p}$ defined as:

$$\overline{V_{xp}} = \int d^3r' \Psi^*_p(r') V_x(r') \Psi_p(r') \quad (2.69)$$

$$\overline{W_p} = \int d^3r' \Psi^*_p(r') W_p(r') \Psi_p(r'). \quad (2.69)$$
For a spherically averaged atom, it’s radial part satisfies:

\[(H_{KS} - \varepsilon_p)\delta \psi_p^*(r) = (-V_x(r) + W_p(r) + (V_{x,p} - W_p))\psi_p(r), \tag{2.70}\]

where \(W_p(r)\) is defined as:

\[W_p(r)\psi_p(r) \equiv \frac{1}{N_p} \frac{\delta E_x}{\delta \psi_p^*(r)} \tag{2.71}\]

Now one can identify that (2.70) is indeed (2.59), with \(\delta \psi_p^*(r)\) corresponding to the Lagrange function, and \(U_p\) in (2.60) is actually \(W_p - V_{x,p}\).

The physical meaning of \(\delta \Psi_p^*(r)\) can be interpreted as **Orbital Shifts** due to perturbation [30] by noticing that (2.67) can be interpreted as charge density conservation when the system is under small perturbation:

\[\delta \rho(r) = \sum_p (\delta \Psi_p^*(r)\Psi_p(r) + c.c) = 0. \tag{2.72}\]

And the definition of \(\delta \Psi_p^*(r)\) can be cast into a first order perturbation form:

\[\delta \Psi_p^*(r) = \int d^3r'(V_x(r') - \frac{1}{\Psi_p(r')} \frac{\partial E_x}{\partial \Psi_p^*(r')})G_p(r, r')\Psi_p(r') \tag{2.73}\]

with the perturbation defined as:

\[\Delta V(r') = V_x(r') - \frac{1}{\Psi_p(r')} \frac{\partial E_x}{\partial \Psi_p^*(r')} = V_x(r') - W_p(r')\tag{2.74}\]

Therefore the auxiliary function can be viewed as variation of the orbital \(g_p(r) = \delta \psi_p(r)\) due to the perturbation of replacing the orbital dependent potential with a local potential [30].

The analysis contains two implications:

1. \(g(r)\) should be small intuitively, because changing from the optimized effective potential to the orbital-dependent potentials (2.22) should not change the density too much.

2. The \(V_x^{OEP}(r)\) is kind of average of the orbital-specific potential, using Kohn-Sham orbitals.
2.6 All Electron OEP Implementation

2.6.1 Basic All-Electron OEP Implementation

This section explains the basic algorithm to implement the Gradient Search Method, while in practice, other constraints are necessary, it is suitable for spherical atoms, and we are working with the radial part $\psi(r)$ of the $\Psi(r)$ only.

---

**Basic Gradient Search**

1. $\alpha = 0$

2. do

3. Construct $H_{KS}^\alpha$ matrix using $\left\langle K_p + V_N + V_H^2 + V_X^\alpha \right\rangle$

4. Solve Schrödinger Equation $\psi^{\alpha+1}_p(r) \leftarrow H_{KS}^\alpha \psi^{\alpha+1}_p = \epsilon^{\alpha+1}_p \psi^{\alpha+1}_p$

5. Update $\{V^{\alpha+1}_H, U^{\alpha+1}_p, E^{\alpha+1}_x\} \leftarrow \psi^{\alpha+1}_p(r)$

6. Update $H_{KS}^{\alpha+1} \leftarrow K_p + V_N + V^{\alpha+1}_H + V_X^\alpha$

7. Solve $\partial^{\alpha+1}_p(r)$ from $(H_{KS}^{\alpha+1} - \epsilon^{\alpha+1}_p) g^{\alpha+1}_p = \frac{\partial E^{\alpha+1}_x}{\partial \psi^{\alpha+1}_p} - V_x \psi^{\alpha+1}_p - U^{\alpha+1}_p \psi^{\alpha+1}_p$

8. Calculate: $\frac{\partial F}{\partial V_x^\alpha} = s^\alpha(r) \leftarrow - \sum_p N_p (g^{\alpha+1}_p \psi^{\alpha+1}_p + c.c.)$

    $\triangleright$ the gradient for updating $V_x^\alpha(r)$

9. Update $V_x^{\alpha+1} \leftarrow V_x^\alpha + s^\alpha(r) * Mixer$

    $\alpha = \alpha + 1$

---

The iteration number $\alpha$ denotes SCF sequence.
2.6.2 Practical Implementation of Gradient Search Method

Previous basic algorithm is generally not stable in practice because at step (6):

\[ H_{KS}^{α+1} = K_p + V_N + V_H^{α+1} + V_x^{α}, \]

an updated Hartree potential \( V_H^{α+1} \) is used here instead of \( V_H^{α} \). On the other hand, the wavefunctions we are using are still the solution of \( H_{KS}^{α} \psi_n = ε_n \psi_n \) with \( H_{KS}^{α} = K_p + V_N + V_H^{α} + V_x^{α} \), rather than using \( V_H^{α+1} \). We believe this subtle inconsistency introduces instability to our differential equation solver. Therefore we designed an inner loop to determine self-consistent values of \( ψ_n(r) \) which solves the Kohn-Sham equations with a fixed value of \( V_{xc}^{α}(r) \), here \( β \) is the iteration index of the inner loop:

**Update Hartree Algorithm**

1. \( β = 0 \)
2. **Update** \( V_H^{β} = e^2 \sum_p \int d^3 r' N_p |ψ_p(r')|^2 \frac{1}{|r-r'|} \)
3. **do** Construct: \( H_{KS}^{β} \leftarrow K_p + V_N + V_H^{β} + V_x^{α} \)
4. **Solve** \( \{ ψ_p^{β+1}(r) \} \) from \( (H_{KS}^{β} - ε_p^{β+1})ψ_p^{β+1} = 0 \) and corresponding \( V_H^{β+1}(r) \)
5. **if** \( |V_H^{β+1} - V_H^{β}| \leq ε \)
6. then **EXIT** \( ▷ \text{CONVERGED} \)
7. **else** **Update** \( V_H^{β+1} \)
   \[ β = β + 1 \]
2.6.3 Additional Constraints on $V_x(r)$

There is an additional condition on $V_x(r)$, derived by Grabo, Kreibich, Kurth, and Gross [3], who showed that the wavefunction $\psi_L(r)$ of the most extended orbital ($p \equiv L$) is such that $U_L = 0$. This condition will be imposed in the following way.

The basic idea is that for $0 \leq r \leq r_M$, the form of $V_x(r)$ is well determined by the equations. However for $r > r_M$, the unknowns are weighted by decaying functions and therefore are not mathematically well-determined. We choose this "matching" point $r_M$ as either the last maximum of $\psi_L(r)$ or the value of $\frac{2}{\sqrt{-\epsilon_L}}$. Denote the current value of the exchange-correlation potential by $V^0_x(r)$ and denote:

\[ u_x(r) \equiv \frac{1}{\psi_L(r)} \frac{\delta E_x}{\delta \psi_L^*}, \]  
\[ (2.75) \]

which we need only to evaluate in a region where $\psi_L(r)$ does not have any zeros. We also define some auxiliary functions:

\[ f_i(r) \equiv \{ u_x(r) + \frac{e^2}{r} \} \frac{1}{r^i}, \]
\[ (2.76) \]

where $n = 1, 2, \ldots$. We then set:

\[ V_x(r) = \begin{cases} 
V_x^0(r) + C_0 & \text{for } 0 \leq r \leq r_M \\
u_x(r) + \sum_{i=1}^{n} C_i f_i(r) & \text{for } r > r_M 
\end{cases}, \]
\[ (2.77) \]

here the constants $C_i$ are found by forcing $V_x$ to be continuous in the neighborhood of $r_M$ and by imposing the $U_L = 0$ condition. We find this procedure to be reasonably robust, although there is some sensitivity to the choice of the matching point $r_M$. 

To sum up, the overall algorithm for finding the OEP potential $V_x(r)$ is as follows

**Practical OEP Gradient Search**

1. $\alpha = 0$
2. \hspace{0.5em} do
3. \hspace{1.5em} Adjust $V_x(r)$ for $U_L = 0$
4. \hspace{1.5em} Construct $H_{KS}^\alpha \leftarrow K + V_N + V_H^\alpha + V_X^\alpha$
5. \hspace{1.5em} $\psi^\alpha_p(r) \leftarrow \psi^\alpha_p(r)$
6. \hspace{1.5em} $\beta = 0$
7. \hspace{1.5em} Update Hartree Algorithm
   \[ V_H^\beta = e^2 \sum_p \int d^3r' \frac{N_p|\psi^\beta_p(r')|^2}{|r-r'|} \]
8. \hspace{1.5em} \hspace{0.5em} do Construct: $H_{KS}^\beta \leftarrow K + V_N + V_H^\beta + V_X^\alpha$
9. \hspace{1.5em} \hspace{1.5em} Solve $\{\psi^{\beta+1}_p(r)\}$ from $\left( H_{KS}^\beta - \varepsilon^{\beta+1}_p \right) \psi^{\beta+1}_p = 0$
10. \hspace{1.5em} \hspace{1.5em} and corresponding $V^{\beta+1}_H(r)$
11. \hspace{1.5em} \hspace{1.5em} if $|V^{\beta+1}_H - V_H^\beta| \leq \varepsilon$
12. \hspace{1.5em} \hspace{1.5em} then $\psi^{\beta+1}_p(r) \rightarrow \psi^\alpha_p(r)$ \hspace{1em} EXIT \hspace{1em} ▶ CONVERGED
13. \hspace{1.5em} \hspace{1.5em} else \hspace{1em} Update $V^{\beta+1}_H$ \hspace{1em} $\beta = \beta + 1$
14. \hspace{1.5em} Update $H_{KS}^{\alpha+1} \leftarrow T + V_N + V^{\alpha+1}_H + V_X^\beta$
15. \hspace{1.5em} Solve $g^{\alpha+1}_p(r)$ from $\left( H_{KS}^{\alpha+1} - \varepsilon^{\alpha+1}_p \right) g^{\alpha+1}_p = \frac{1}{N_p} \frac{\partial E^{\alpha+1}}{\partial \psi^{\alpha+1}_p} - V^\alpha_x \psi^{\alpha+1}_p - U^{\alpha+1}_p \psi^{\alpha+1}_p$
16. \hspace{1.5em} Calculate: $\frac{\partial F}{\partial V_x^\alpha} = s^\alpha(r) \leftarrow - \sum_p N_p (g^{\alpha+1}_p \psi^{\alpha+1}_p + \text{c.c.})$
17. \hspace{1.5em} Update $V^{\alpha+1}_x \leftarrow V_x^\alpha + s^\alpha(r) \ast Mixer$
18. \hspace{1.5em} $\alpha = \alpha + 1$
2.6.4 Alternative Algorithm

Motivation of Using Hartree Fock as starting point

Originally, the all-electron OEP calculation is started from using the hydrogen-like wavefunctions as initial guesses. We experienced some instabilities in the self-consistent calculation, and certain constraints have to be forced, which is computationally inconvenient.

On the other hand, based on the fact that Hartree-Fock orbitals and OEP orbitals are really similar according to Figure (2.6), it is intuitively appealing to make use of the rich information contained in the Hartree-Fock wavefunction to expedite the process. In the next section, we will go into detail of how to make use of these wavefunctions, and how to construct an initial exchange potential guess for the OEP.
Alternative Algorithms

There are three key points in order to make use of the wavefunctions from the Hartree Fock results:

1. **Initial guess of** $V_x(r)$ The first important fact is that the magnitude of the auxiliary functions are small at all ranges, and the overall shift times the mixing parameters are even smaller, so are the changes to the exchange potential at each iteration. So, the algorithm has limited space to recover local exchange potential’s shape at mid range and long range comparing to the core region. So an initial guess is vital to the convergence of the SCF calculation, from our experience, starting with shallow initial guess of exchange potential is always robust, which will be explained in detail in the next section.

2. **Recovering the Shape of** $V_x(r)$ After the initial guess of $V_x(r)$ is obtained, we use HF wavefunctions to help shape the basic structure of the local exchange potential. In the first few hundreds of iterations, we do not solve the Schrödinger equation, therefore there is no update on the wavefunction at this stage. The calculation done here is starting from an initial guess of the exchange potential, evaluate the auxiliary functions during the iterations, using the corresponding shift/gradient to update the exchange potential until the gradient is relatively small.

This procedure is similar to solving an inverse problem, which can be described as: Given the wavefunctions, and KS equations, how to evaluate the local exchange potential that generates these wavefunctions. As a comparison, a direct problem means solving Schrödinger equation with given local potential.

3. **Mix** $V_H(r)$ After the overall shift becomes relatively small (usually after hundreds of simple iterations), it is time to start the full self consistent calculation, to allow both wavefunctions and auxiliary functions to update. Another important procedure that needs to apply here is the mixing of Hartree potential between current iteration and the previous iterations. Numerical evidence shows that without this technique, most of the calculation would diverge quickly, even when local exchange potential is sufficiently close to the converged one. The reason for this instability has already been explained in previous section. The reason that mixing Hartree potential is an effective solution that leads to con-
vergence remains to be explored.
Details of constructing the initial exchange potential

The following formulation for initial guess \( V_x^0(r) \) proved to be effective to restore the correct mid range and long range local exchange potential:

\[
V_x^0(r) = \sum_p \frac{\partial E_x}{\partial \psi_p^*(r)} \psi_p(r) / \sum_n N_p \psi_p^*(r) \psi_p(r),
\]

(2.78)

The physical interpretation of such formula can be understood by noticing that \( \frac{1}{\psi(r)} \frac{\partial E_x}{\partial \psi^*(r)} \) is the effective nonlocal exchange potential of corresponding HF orbital, and so \( V_x(r) \) from (2.78) can be understood as the averaged non-local exchange potential of all the orbitals.

Taking Al for example:

![Al](image)

**Figure 2.7: Al \( V_x^0(r) \) using (2.78)**

Here the green curve represents \( V_x^0(r) \), compared with the blue one which is converged \( V_x(r) \). The converged \( V_x(r) \) from the alternative scheme is in excellent agreement with \( V_x(r) \) from the previous scheme.
We see that this initial guess for the exchange potential is good at long range, but is too attractive on the mid range. In practice, we further smooth the initial guess of $V_x(r)$ between $[0, r_M]$ to get a less attractive potential, this procedure proven to be very helpful for the convergence given all the elements we tested, including the transitional metal.

The process of obtaining the smooth version of the exchange potential can be represented as:

$$\tilde{V}_x^0(r) = \begin{cases} 
\sum_{m=0,1,2,3,4} C_m r^m & r \leq r_M \\
V_x^0(r) & r > r_M 
\end{cases}$$

where $C_m$ are unknowns, can be chosen to ensure that $\tilde{V}_x^0(r)$ is equal to $V_x^0(r)$ up to 4 derivatives. Again using Al for example, the smoothed initial exchange potential is shown below:

Figure 2.8: Al smoothed initial exchange potential
And the choice of such $r_M$ can be tabulated as following (bohr):

<table>
<thead>
<tr>
<th>$r_M$</th>
<th>2$^{nd}$ Row</th>
<th>3$^{rd}$ Row</th>
<th>4$^{th}$ Row</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0</td>
<td>2.3</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**Alternative: Using KLI**

Another alternative of constructing the initial $V_x(r)$ is to solve KLI equation using KLI exchange potential in the next section.

**Alternative Adjust $V$**

The alternative way to get rid of the shifting constant is by adding the constant

$$U_L = \langle \psi_L | \frac{\partial E_x}{\partial \psi^*_L} \rangle - \langle \psi_L | V_x | \psi_L \rangle.$$  

(2.80)

to the exchange potential $V_x(r)$ during the iteration to ensure:

$$\langle \psi_L | \frac{\partial E_x}{\partial \psi^*_L} \rangle - \langle \psi_L | V_x | \psi_L \rangle = 0.$$  

(2.81)

It is suggested by Perdew [29] that the constant should be added directly to the exchange potential in order to have correct asymptotic behavior, this approach, however, is not applicable here because starting from the beginning, we need to preserve the right asymptotic behavior of the initial exchange potential derived from Hartree-Fock all-electron result, and ensure its continuity. Therefore we construct a smooth-step function or smooth-envelop function:

$$f_1(r) = \frac{e^{2r} - 1}{e^{2r} + 1}.$$  

(2.82)

$$f_2(r) = \frac{e^{2(r-r_m)} - 1}{e^{2(r-r_m)} + 1} + 1.$$  

(2.83)

And

$$\text{SmoothStep}(r) = \frac{1}{2}(f_1(r) - f_2(r)).$$  

(2.84)

where $r_m$ can be set to be the same as $r_M$ before. The smoothstep function is shown below:
Figure 2.9: Smooth-Step Function

And the adjustV scheme can be constructed as:

\[ V_x(r) \leftarrow V_x(r) + U_L \times \text{SmoothStep}(r). \quad (2.85) \]

In practice, this modification procedure on the \( V_x(r) \) works well for all tested elements, including transition metals.
The algorithm of this alternative All-Electron OEP calculation can be described as follows:

**ALTERNATIVE AE OEP ALGORITHM**

1. **Initialize** \( \psi_p(r) \): use \( \psi_p^{\text{HF}}(r) \)
2. **Initialize** \( V_x(r) \): use smoothed averaged-HF-orbital-specific potential
3. **Update properties**
   4. \( \alpha = 1 \)
   5. **do**
      6. **Update** \( V_H(r) \): \( V_H(r) \leftarrow (1 - \text{Mixh})V_H^{\alpha-1}(r) + \text{Mixh} \ast V_H^\alpha(r) \)
      7. \( V_s(r) \leftarrow V_H(r) + V_x(r) + V_N(r) \)
      8. if \( \alpha < \text{updatewfn\_flag} \)
         9. then \( \triangleright \) Do not update \( \psi_p(r) \)
      10. else \( \triangleright \) Fully SCF calculation starts
         11. Perform **Basic Gradient Search**
             to update \( \psi_p(r) \) and exchange potential.
         12. **Adjust** \( V_x(r) \): \( V_x(r) \leftarrow V_x(r) + U_L \times \text{SmoothStep}(r) \)
         13. \( V_s(r) \leftarrow V_H(r) + V_x(r) + V_N(r) \)
         14. if \( \left| \sum_p N_p g_p^*(r) \psi_p(r) \right| \leq \varepsilon \)
            15. then **EXIT** \( \triangleright \) CONVERGED
2.7 All Electron KLI Theory

Krieger, Li and Iafrate proposed this approximation \[14\] \[15\] \[31\] \[32\] as an alternative to solve the integral equation of \(V_x^{OEP}(r)\) numerically. It no longer requires to calculate the auxiliary function \(g_p(r)\) from (2.70) or \(\delta \Psi_p^*(r)\) of (2.68), which is an highly accurate approximation for \(V_x^{OEP}(r)\). \[3\] \[9\]

Following Krieger, Li and Iafrate \[32\] \[33\], the algorithm also starts from the fact that at convergence, the overall orbital shift should equal to zero (2.67):

\[
\sum_p [N_p g_p^*(r) \psi_p(r) + c.c] = 0. \tag{2.86}
\]

In the previous sections, the auxiliary function was defined as (2.65) and (2.66), therefore the radial part can be written as:

\[
g_p^*(r) = \int d^3r' (V_x(r') - W_p(r')) G_p(r, r') \psi_p^*(r'). \tag{2.87}
\]

As a result, (2.67) becomes:

\[
\sum_p N_p \psi_p(r) \int d^3r' (V_x(r') - W_p(r')) G_p(r, r') \psi_p^*(r') + c.c = 0. \tag{2.88}
\]

If we multiply both sides by \(V_x(r)\)

\[
V_x(r) \sum_p N_p \psi_p(r) \int d^3r' (V_x(r') - W_p(r')) G_p(r, r') \psi_p^*(r') + c.c = 0. \tag{2.89}
\]

For the radial Green’s function, it has the following properties:

\[
\{K + V_x(r) - \varepsilon_p\} G_p(r, r') = \delta(r - r') - \psi_p(r) \psi_p^*(r'). \tag{2.90}
\]

This implies that (\[11\]):

\[
V_x(r) G_p(r, r') = \delta(r - r') - \psi_p(r) \psi_p^*(r') - \{K_p - \varepsilon_p\} G_p(r, r'). \tag{2.91}
\]

And consequently:

\[
0 = V_x(r) \sum_p N_p \psi_p(r) \int d^3r' (V_x(r') - W_p(r')) G_p(r, r') \psi_p^*(r') + c.c
\]
\[
= \sum_p N_p \psi_p(r) \int d^3r' (V_x(r') - W_p(r')) [\delta(r - r') - \psi_p(r) \psi_p^*(r') + \{K + \varepsilon_p\} G_p(r, r')] \psi_p^*(r') + c.c
\]
\[
= \sum_p N_p \psi_p(r) [\psi_p(r) V_x(r) - \frac{\partial E_x}{\partial \psi_p^*(r')} - (V_{x,p} - U_{x,p}) \psi_p^*(r')] + c.c.
\]
\[
- \{\sum_p N_p \psi_p(r) \int d^3r' (V_x(r') - W_p(r')) [K + \varepsilon_p] G_p(r, r') \psi_p^*(r') + c.c
\]
\[
= 0 \tag{2.92}
\]
here the unknown variable is $V_x(r)$. Move it to the LHS, and regroup the rest of the terms, and take into account of complex conjugate parts to obtain:

$$V_x(r) = \frac{1}{2n(r)} \left\{ \sum_p N_p \{ |\psi_p(r)|^2 [W_p(r) + (\nabla_{x,p} - \nabla_{x,x})] - \psi_p(r)[K + \varepsilon_p]g_p^*(r) \} + c.c. \right\}. \tag{2.93}$$

It can be proved [3] [33] in Appendix (A.2) that:

$$\sum_p N_p \psi_p(r)[-K_p + \varepsilon_p]g_p^*(r) = -\sum_p \frac{N_p}{m} \frac{d}{dr} (g_p^*(r) \frac{d}{dr} \psi_p(r)). \tag{2.94}$$

And one simplest possible approximation of KLI formalism is to completely neglect the terms involving $g_p(r)$ [3], which interpreted as a mean field approximation [33]. Hence the radial part of the equation known as KLI equation is given by:

$$V_x(r) = \frac{1}{2n(r)} \sum_p \left\{ N_p |\psi_p(r)|^2 [W_p(r) + (\nabla_{x,p} - \nabla_{x,x})] \right\} + c.c. \tag{2.95}$$
2.8 All Electron KLI Implementation

2.8.1 Working Formula

The working formula to solve for all-electron spherical atom KLI radial equation can be formally written as:

\[ V_x(r) = \frac{1}{n(r)} \sum_q N_q \psi_q(r) X_q(r) + \sum_q (\bar{V}_x - \bar{W}_q) \frac{N_q \psi^2_q(r)}{n(r)}. \]  (2.96)

here the relation between \( W_p(r) \) of (2.67) and \( X_p(r) \) of (2.96) is:

\[ W_p(r) \psi_p(r) = X_p(r). \]  (2.97)

As there are unknowns on both sides, the equation can be solved by multiplying both sides by the \( \psi^2_p(r) \) and integrate over the whole grid, yielding:

\[ \langle \psi_p | V_x | \psi_p \rangle = \sum_q N_q \int \frac{\psi^2_p(r) \psi_q(r) X_q(r)}{n(r)} dr + \sum_q N_q (\bar{V}_x - \bar{W}_q) \int \frac{\psi^2_q(r) \psi^2_p(r)}{n(r)} dr. \]  (2.98)

Then the \( \langle \psi_p | V_x | \psi_p \rangle \) are the unknown coefficients; regrouping the unknowns to the LHS:

\[ \sum_{pq} \left[ \delta_{qp} - N_q \int \frac{\psi^2_p(r) \psi_q(r) X_q(r)}{n(r)} dr \right] \bar{V}_x = \sum_q N_q \int \frac{\psi^2_p(r) \psi_q(r) X_q(r)}{n(r)} dr - \sum_q \int \frac{\psi^2_q(r) \psi^2_p(r)}{n(r)} dr. \]  (2.99)

here \( \bar{W}_q \) is defined as previously:

\[ \bar{W}_q = \left\langle \psi_q(r) \left| \frac{1}{N_q} \frac{\partial E_x}{\partial \psi_q(r)} \right. \right\rangle. \]  (2.100)

If we define:

\[ \Gamma_{pq} \equiv \int \frac{\psi^2_q(r) \psi^2_p(r)}{n(r)} dr, \]  (2.101)

and

\[ \Xi_p = \sum_q N_q \int \frac{\psi^2_q(r) \psi_p(r) X_q(r)}{n(r)} dr. \]  (2.102)

Equation (2.99) can be further rewritten as:

\[ \sum_{pq} \left[ \delta_{qp} - N_q \Gamma_{pq} \right] \bar{V}_x = \Xi_p - \sum_q N_q \Gamma_{pq} \bar{W}_q. \]  (2.103)

Grabo [3] pointed out that both OEP and KLI potential should satisfy some rigorous properties, namely, the constraints on exchange potential we applied during OEP implementation should also apply here in order to have one unique solution:

\[ \bar{V}_{xL} = \bar{W}_L. \]  (2.104)
It also should be noticed that during the SCF calculation, this shell index \( L \) can be determined by comparing the eigenenergy at run time. On the other hand, this dynamically determining the outermost orbital might introduces some artifacts when eigenenergy of two orbitals are really close for some transitional elements. One solution can be fixing the outermost orbitals index ahead of the calculation, another solution is set both orbitals(for example 3d and 4s) to be the outermost all, numerically, they are both stable, and no difference in terms of energy and shape of the exchange potential at convergence were observed.

According to (2.104), this equation gives the exact value of \( \bar{V}_{xL} \), which reduce rank of the coefficient matrix on the LHS (2.103) by one, one way to modify the coefficient matrix is to directly reduce the rank of the matrix by recognizing that \( \sum_q N_q \Gamma_{pq} = 1 \), another way which works equally well, is directly enforcing these constraints to the equations, by replacing the row corresponding to the outermost orbital with its known value \( \bar{W}_L \), so the equations become:

\[
\begin{bmatrix}
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
\bar{V}_{xL}
\end{bmatrix}
= \begin{bmatrix}
\bar{W}_L
\end{bmatrix}
\]

(2.105)

In the above equation, the coefficient matrix on the LHS is \( N \times N \), where \( N \) represents the total number of orbitals. It should be noticed that it is not always the case that the outermost orbital corresponds to the last row of the matrix, depending on how the shell blocks are arranged in the program.
2.8.2 Practical Implementation

In practice, we would like to start all-electron atom KLI calculation with some reasonable initial guess, here we are using orbitals from Hartree-Fock calculation, making use of the fact that Hartree-Fock orbitals, and KLI ground state wavefunction are really similar according to Fig (2.10)

The procedure of making use of Hartree-Fock orbitals is more simple than the OEP case, as for OEP case, we will need to construct a reasonable $V^0_x(r)$, in order to generate the orbital shift to update the $V_x(r)$. Here for KLI, $V^0_x(r)$ can be obtained by solving KLI equation (2.96) directly. This procedure, as mentioned before, can also serve as a pre-step for the OEP calculation, and therefore, save the effort of constructing the exchange potential initial guess, which involves averaging the Fock orbital specific exchange potential.
To sum up, the algorithm of KLI approximation to OEP Method can be written as:

**ALL-ELECTRON KLI SCF PROCEDURE**

1. $\alpha = 0$

2. Solve KLI Equations to obtain initial $V_{x=0}^\alpha(r)$
   
   $$V_x^0(r) = \frac{1}{n(r)} \sum_q N_q \psi_q'(r) X_q(r) + \sum_q (V_{zq} - \bar{U}_{zq}) \frac{N_q \psi_q^2(r)}{n(r)}$$

3. do

4. Solve Schrödinger $(H_{KS}^\alpha - \varepsilon_p^\alpha) \psi_p^\alpha(r) = 0$

5. Gram Schmidt $\langle \psi_p | \psi_q \rangle = \delta_{pq}$

6. Update $\{ \rho(r), V_H(r), X_p(r) \}$ using $\psi_p(r)$

7. Solve KLI equations

8. Construct KLI Equations (2.103)

9. Find Outermost Orbitals $L = \text{zeroindex}$

10. Replace $V_L = U_L$

11. Solve KLI equations (2.103)

12. Obtain $V_{x}^{\alpha+1}(r)$

13. if

14. then $|V_{x}^{\alpha+1} - V_{x}^\alpha| < \xi$ \hspace{1cm} $\triangleright$ CONVERGED

15. else Update $V_{x}^{\alpha+1} = \alpha V_x^\alpha + (1 - \alpha) V_{x}^{\alpha+1}$

16. $\alpha = \alpha + 1$
Figure 2.10: AE wavefunction of Fe: KLI vs HF
Figure 2.11: Comparison of OEP KLI of $V_x(r)$ for Fe ground states

Figure 2.12: Comparison of OEP KLI of $V_x(r)$ for Ni ground states
3 Frozen Core Calculation of Hartree-Fock, OEP and KLI

3.1 Frozen Core Approximation Overview

After all-electron atom calculations, the next necessary step is to test Frozen Core approximations. This is important in the subsequent solid calculations. The fundamental notion of the frozen-core approximation is that: the inner shell electrons of any atom remains approximately constant and insensitive to a variety of atomic bonding and compositional environments. In practice, after an all-electron atom calculation 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:

$$
\rho(r) = \rho_v(r) + \rho_c(r),
$$

where

$$
\rho_v(r) = \frac{n_v(r)}{4\pi r^2},
$$

$$
\rho_c(r) = \frac{n_c(r)}{4\pi r^2}.
$$

Here we are using the $c$ and $v$ labels to refer to both the category (core or valence) and the individual states in each category.

The Coulomb potential can be divided into core and valence contributions, either in Hartree-Fock picture or Kohn-Sham scheme:

$$
V^c_H(r) = e^2 \int d^3r' \frac{\rho_c(r')}{|r - r'|},
$$

and

$$
V^v_H(r) = e^2 \int d^3r' \frac{\rho_v(r')}{|r - r'|}.
$$

The Hartree energy can also be divided into the interactions between core and valence. For example, core-valence interaction:

$$
E^{cv}_H = \frac{e^2}{2} \int \int d^3r d^3r' \frac{\rho_c(r)\rho_v(r')}{|r - r'|} = \int d^3r V^v_H(r)\rho_v(r).
$$
and a valence-valence interaction:

$$E_{vv}^H = \frac{e^2}{2} \int \int d^3r d^3r' \frac{\rho_v(r)\rho_v(r')}{|r - r'|} = \int d^3r V_{vv}^H(r)\rho_v(r). \quad (3.7)$$

On the other hand, for orbital dependent exchange correlation functionals scheme, how we can define a core exchange potential is a complicated problem, together with how to calculate the exchange energy $E_{xc}$ will be elaborated in the next sections.

In general, instead of calculating the “total” electron energy, we define a valence electron energy in the form of:

$$E_{val} = E_{vK} + E_{vN} + E_{vH}^v + E_{vH}^{vv} + E_{xc}, \quad (3.8)$$

here the valence kinetic energy $E_{vK}$ and valence nuclear potential energy $E_{vN}$ can be evaluated in terms of the one-electron valence orbitals and the valence density respectively.
3.2 Hartree Fock Frozen Core Theory and Implementation

3.2.1 Frozen Core Orbital Theory

The frozen-core wavefunction approximation within Hartree-Fock theory has been well described in the literature [25] [34]. In this case, the exchange energy is formed from products of pairs of electron orbitals and can be divided into core-valence and valence-valence contributions:

\[ E_{\text{val}} = E_{\text{cv}}^x + E_{\text{vv}}^x, \]  

(3.9)

here

\[ E_{x}^{\text{cv}} = -\sum_{cv} \sum_{L=|l_v-L_c|} \Theta_{vc}^{L} R_{vc,vc}^{L}, \]  

(3.10)

and

\[ E_{x}^{\text{vv}} = -\sum_{cv} \sum_{L=|l_v-L_v'|} \Theta_{vv'}^{L} R_{vv',vv'}^{L}, \]  

(3.11)

To get an idea of the magnitude of the core-valence and valence-valence contributions to the exchange energy, results are presented in Fig. (3.1) for elements in the fourth row of the periodic table. From this example, we see that the ratio \( E_{x}^{\text{cv}} / E_{x}^{\text{vv}} \) varies with each element, having a value between \( \frac{1}{4} \) and \( \frac{1}{3} \) for the 4s4p materials and roughly \( \frac{1}{2} \) for the 3d materials.

The self-consistent solution of the Hartree-Fock equations in the frozen-core orbital approximation corresponds to solving Eq. (2.17) only for the valence orbitals \( (p \equiv v) \) while leaving the core orbitals \( \psi_c(r) \) fixed to the functions found for the reference state. It is important to require that the valence orbitals \( \Psi_v(r) \) remain strictly orthogonal to each other as well as to the core orbitals

\[ \langle \Psi_v | \Psi_c \rangle = 0, \]  

(3.12)

in order to avoid spurious contributions to the valence-core exchange energy \( E_{x}^{\text{cv}} \) of Eq. (3.10).

3.2.2 Frozen Core Potential Theory

For frozen-core potential theory, it is computationally advantageous to eliminate the core wavefunctions, if it can be done without sacrificing accuracy [35, 36, 37]. The Hartree Frozencore potential \( V_{H}^c(r) \) has already been defined in Eq. (3.7) and requires
Figure 3.1: Plot of exchange energy contributions $E_{x}^{cv}$ and $E_{x}^{vv}$ defined in Eqs. (3.10) and (3.11), respectively, for spherically averaged ground state atoms in the 4th row of the periodic table. In these plots, the configuration of Ar defines the core states. The energy values are given in Ry units.

no additional approximation beyond the frozen-core orbital approximation. The question is whether one can find a fixed potential $V_{cv}^{v}(r)$ which can accurately approximate the core-valence exchange interaction in the effective single-particle Hamiltonian to result in a good approximation of the valence wavefunction.

$$H_{HF} = K + V_N(r) + V_{H}^{c}(r) + V_{H}^{v}(r) + V_{x}^{cv}(r).$$  \hspace{1cm} (3.13)

And also provide accurate approximate core-valence exchange energy:

$$E_{x}^{cv} \simeq \int V_{x}^{cv}(r)\rho_v(r)dr.$$  \hspace{1cm} (3.14)

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

$$H_{FC}^{v} \psi_v(r) + X_v(r) = \sum_q \lambda_{qv} \psi_q(r),$$  \hspace{1cm} (3.15)

where sum over $q$ includes both the core and valence wavefunctions. And the Frozen-core Hamiltonian contains the core exchange contribution:

$$H_{FC} = K + V_N(r) + V_{H}^{c}(r) + V_{H}^{v}(r) + V_{x}^{cv}(r).$$  \hspace{1cm} (3.16)

And the valence exchange kernel is:

$$X_{vv}^{v}(r) = -\sum_{v'} \frac{1}{N_v} \sum_{L=|l_{v}-l_{v'}|} \Theta_{vv'}^{L} W_{vv'}^{L}(r) \psi_{v'}(r).$$  \hspace{1cm} (3.17)
We have invested a small effort in evaluating the frozen-core potential approximation and the results are included in Fig. (3.2). These results were obtained by choosing the frozen-core potential to take the form

$$V^c_v(r) = \left. \frac{\sum_v N_v X_v^c(r) \psi_v(r)}{n_v(r)} \right|_{\text{ref}}, \quad (3.18)$$

where

$$X^c_v(r) = - \sum_{v'} \sum_{L=|l_v-l_c|} \frac{1}{N_v} \Theta^L_{v'v} W^L_{vc}(r) \psi_c(r). \quad (3.19)$$

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

$$E^c_v = \int dr \sum_{v'} X^c_{v'}(r) \psi_{v'}(r). \quad (3.20)$$
Figure 3.2: Plots of the magnitudes of $\Delta \Delta E$ (Eq. (3.21)) in Ry units for elements in the 4th 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; “HF” denotes the Hartree-Fock formalism using the frozen-core orbital approach using Eq. (2.17); “HF(V)” denotes the Hartree-Fock formalism using the frozen-core potential approach using Eq. (3.15).

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:

$$\Delta \Delta E \equiv \left( E_{\text{excited}}^{\text{tot}} - E_{\text{ground}}^{\text{tot}} \right)_{\text{AE}} - \left( E_{\text{excited}}^{\text{val}} - E_{\text{ground}}^{\text{val}} \right)_{\text{FC}}$$  \hspace{1cm} \text{(3.21)}

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. (3.2).

For the $4s\,4p$ 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 contrast, results for the frozen-core error obtained by using the frozen-core potential of Eq. (3.18) 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.(3.2).

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 [12] of the frozen-core potential $V_{\text{cf}}(r)$ over that given in Eq. (3.18). However, the fact remains that the functional forms of Eqs. (3.10) and(3.14) are different and it is not surprising that they should give different results as the valence configuration changes.
3.2.3 Hartree Fock Frozen Core Orbital Implementation

The Hartree Fock frozen-core orbital implementation can be trivially applied by fixing the core wavefunctions while only updating the valence wavefunctions. The overall algorithm goes as follows:

HARTREE-FOCK FROZEN CORE SCF PROCEDURE

1. \( t = 0 \)
2. \textbf{do}
3. \textbf{Orthonormalization} \( \langle \psi_v^t \mid \psi_v^{t'} \rangle = \delta_{vv'} \) and \( \langle \psi_v^t \mid \psi_c^t \rangle = \delta_{vc} \)
4. \textbf{Diagonalization within Blocks with the same l-value} \( \rightarrow \{ \lambda_{vc}, \lambda_{vv'}, X_v(r) \} \)
5. \textbf{Update} \( H_{HF}^t \leftarrow K + V_N(r) + V_H(r) \)
6. \textbf{Solve} \( (H_{HF}^t - \varepsilon_v^t)\psi_v^{t+1}(r) = -X_v^t(r) + \sum_q \lambda_{vq} \psi_q(r) - \varepsilon_v^t \psi_v^t(r) \rightarrow \psi_v^{t+1}(r) \)
7. \textbf{Adjust} \( \psi_v^{t+1}(r) \)'s number of nodes = \( n_v - l_v - 1 \)
8. \textbf{Update} \( \psi_v^t \leftarrow a\psi_v^t + (1-a)\psi_v^{t+1} \)
9. \( t + 1 \leftarrow t \)
3.3 OEP Frozen Core Theory and Implementation

3.3.1 Gradient Search with valence electron only

Given the fact that Gradient Search Implementation of OEP method starting with optimization of total energy with respect to several independent variables, it is natural to design a frozen-core Gradient Search scheme that minimize the valence total energy. The results should be equivalent to frozen potential approximation method we introduced at section(3.2.2). During all-electron calculation, the orbitals and local exchange potential are independent variables, and total energy were obtained by performing minimization with respect to those variables. For frozen-core calculation, one intuitive way is to assume that valence orbitals and valence auxiliary functions are independent variables.

The total energy still takes the form (3.8):

\[ E_{\text{val}} = E^v_k + E^v_N + E^v_H + E^{\text{avw}}_H + E_x. \] (3.22)

The object function is still defined as total energy together with constraints. For the frozen-core approximation, the independent variables are \( g_v(r), \varepsilon_v, \psi_v(r) \). In the spirit of frozen potential method the core exchange contribution can be represented as \( V^\text{core}_x(r) \), which is fixed at reference state, the previously independent variable \( V_x(r) \) has now becomes \( V^\text{vale}_x(r) \), so the goal of optimization is to minimize the object function given these variables:

\[
F[\{\psi_v(r)\}, \{\lambda_v\}, \{g_v\}] = E_{\text{val}}[\{\psi_v(r)\}] - \sum_v \lambda_v (\langle \psi_v | \psi_v \rangle - 1) \\
- \sum_v N_v (\langle g_v | H_{KS} - \varepsilon_v | \psi_v \rangle + \text{c.c})
\] (3.23)

The following gradient should achieve zero when the valence total energy is at its minimum.

\[
\frac{\delta F}{\delta g_v(r)} = (\varepsilon_v - H_{KS})\psi_v(r) = 0.
\] (3.24)

\[
\frac{\delta F}{\delta \lambda_v} = 1 - \int d^3r |\psi_v|^2 = 0.
\] (3.25)

\[
\frac{\delta F}{\delta \varepsilon_v} = \langle g_v | \psi_v \rangle + \text{c.c.} = 0.
\] (3.26)
As we mentioned before, the $V_{x}^{\text{vale}}(r)$ is unknown, so the derivative of $F$ with respect to $V_{x}^{\text{vale}}$ provides gradient for its update:

$$\frac{\partial F}{\partial V_{x}^{\text{vale}}(r)} = - \sum_{v} N_{v} (g_{v}^{*}(r)\psi_{v}(r) + C.C). \quad (3.27)$$

The derivation of differential equation that valence $g_{v}(r)$ needs to satisfy requires more details:

$$\frac{\delta F}{\delta \psi_{v}^{*}(r)} = \frac{\delta E_{\text{val}}}{\delta \psi_{v}^{*}(r)} - \lambda_{v} \psi_{v} - (H_{KS} - \varepsilon_{v}) g_{v}(r) = 0. \quad (3.28)$$

The valence energy can also be written as:

$$E_{\text{val}} = \sum_{v} (\langle \psi_{v} | T + V_{N} + V_{x}^{\text{core}} | \psi_{v} \rangle) + E_{x}^{v-u} + E_{H}. \quad (3.29)$$

This expression explicitly includes the $V_{x}^{\text{core}}(r)$ term, that represents the core contribution. Taking the derivatives of (3.29) with respect to valence orbital:

$$\frac{\partial E_{\text{val}}}{\partial \psi_{v}^{*}(r)} = (T + V_{N} + V_{H} + V_{x}^{\text{core}}) \psi_{v}(r) + \frac{\partial E_{x}^{v-u}}{\partial \psi_{v}^{*}(r)}. \quad (3.30)$$

Given Kohn-Sham equation (2.33):

$$H_{KS} \psi_{v}(r) = (T + V_{N} + V_{x}^{\text{core}} + V_{x}^{\text{vale}}) \psi_{v}(r) = \varepsilon_{v} \psi_{v}(r). \quad (3.31)$$

Therefore $(T + V_{N} + V_{H} + V_{x}^{\text{core}}) \psi_{v}(r)$ can be replaced with $(\varepsilon_{v} - V_{x}^{\text{vale}}) \psi_{v}(r)$ as:

$$(T + V_{N} + V_{H} + V_{x}^{\text{core}}) \psi_{v}(r) = (\varepsilon_{v} - V_{x}^{\text{vale}}) \psi_{v}(r). \quad (3.32)$$

Therefore the differential equation for valence $g_{v}(r)$ can be transformed into:

$$(H_{KS} - \varepsilon_{v}) g_{v}(r) = (\varepsilon_{v} - \lambda_{v}) \psi_{v}(r) - V_{x}^{\text{vale}} \psi_{v}(r) + \frac{\partial E_{x}^{v-u}}{\partial \psi_{v}^{*}(r)}. \quad (3.33)$$

One can multiply both sides by $\psi_{v}(r)$ and integrate over the whole grid:

$$-U_{v} = \langle \psi_{v} | V_{x}^{\text{vale}} | \psi_{v} \rangle - \langle \psi_{v} \left| \frac{\partial E_{x}^{v-u}}{\partial \psi_{v}^{*}(r)} \right. \rangle = \varepsilon_{v} - \lambda_{v}. \quad (3.34)$$

One ends up with the equation for valence $g_{v}(r)$

$$(H_{KS} - \varepsilon_{v}) g_{v}(r) = \frac{\partial E_{x}^{v-u}}{\partial \psi_{v}^{*}(r)} - V_{x}^{\text{vale}} \psi_{v}(r) - U_{v} \psi_{v}. \quad (3.35)$$

The core exchange potential can be defined as:

$$V_{x}^{\text{core}}(r) = V_{x}(r) - V_{x}^{\text{vale}}(r). \quad (3.36)$$

And the valence-core exchange energy can be written as:

$$E_{x}^{vc} = \int V_{x}^{\text{core}}(r)n_{v}(r)d^{3}r. \quad (3.37)$$
Disadvantages

In this scheme, starting from a spirit of general principle of optimization, and
intuitively how frozen-core calculation should be done in the LDA and GGA
case, the treatment is that not only the core orbitals are replaced by the poten-
tial, but also the core auxiliary function disappeared in the formalism. Some
careful scrutiny reveals drawbacks of this treatment.

• This scheme is not able to treat configuration with only one valence or-
bital, because the overall convergence relies on the sum of orbitals shifts
equal to zero (2.67). For configuration with only one valence orbital, the
 corresponding valence auxiliary function would need to be zero at whole
range in order to converge, namely \( g_v(r) = 0 \), which is a trivial solution of
the differential equation.

• \( g_v(r) \) is different from AE auxiliary function of the same orbital, because
the differential equation (3.3.1) is not the same as the AE’s (2.66), while
this seems no problem mathematically, the idea that auxiliary function
depends on how the valence and core labels are set up is non-physical.

• This scheme introduces un-physical structures to the exchange potential.
Although this is not noticeable for the lighter element Fig (3.3) and Fig
(3.4), it is becoming more and more unacceptable for the heavier elements.
The reason for this un-physical structure on the exchange potential is that
this method requires a reasonable starting guess on \( V_x^{\text{vale}}(r) \), and use the
update from (3.3.1), while at first it seems reasonable, further investigation
reveals that this scheme would create un-physical node structure on the
gradients, primarily from the nodes of the wavefunctions. Over the itera-
tions, those nodal points on the exchange potential would stay the same as
the initial guess, while its surrounding area were updated to develop lots
of structures, which is obviously non-physical.

• Unsatisfied valence-core interaction energy. The important criterion for
FC accuracy is valence energy, and core-valence exchange interaction is
certainly an important part of it. Depending on our numerical experience,
\( V_x^{\text{core}}(r) \) can hardly reproduce the exchange core-valence interaction energy
based on (3.37)

Insights and Conclusions
• Orbital shift cancelation: Part of the physical meaning of $g_n(r)$ is the orbital shift due to perturbation exchange potential, and the convergence of the gradient relies heavily on the cancelation between each channels, excluding the core electrons while relying on the valence shift from each channels to cancel out each other is not optimal choice.

• Treat $g_c(r)$ the same as $\psi_c(r)$: The underlying principle of FC approximation is expecting inner orbitals are inert to the changes of chemical environment, so that one do not have to update the core orbitals, and still expecting relative good result, this should be the same case for auxiliary functions.
Sample of Frozen Core Exchange Potential

Figure 3.3: Valence and Core exchange potential partition: N (core states: 1s²)
Figure 3.4: Valence and Core exchange potential partition: \( P \) (core states: \( 1s^22s^22p^6 \))
Figure 3.5: Valence and Core exchange potential partition: Fe (core states: 1s^22s^22p^63s^23p^6)
Figure 3.6: Valence and Core exchange potential partition: Cu (core states: $1s^2 2s^2 2p^6 3s^2 3p^6$)
3.3.2 Gradient Search with core electrons contribution

Based on the understanding that FC approximation’s goal is to expect every variables associated with the core are inert to the chemical environment changes, on the other hand, the OEP method has an extra auxiliary function, not only introduced as a Lagrangian multiplier, but also have physical meaning, as suggested by Kümmel and Perdew [30], in this scheme, we treat this $g_n(r)$ as if they also behave like wavefunctions at FC approximation. This approach eventually turns out equivalent to frozen-core orbital approximation mentioned in section(3.2.1). Below are the details of frozen-core orbital approximation implemented within OEP method.

Solve the Schrödinger equation for the valence electrons only, for system different from reference state, using the reference exchange potential as the initial guess:

$$H_{KS}\psi_v(r) = \varepsilon_v\psi_v(r).$$ (3.38)

Repeat the same process for the $g_v(r)$, but only solve for the valence states:

$$(H_{KS} - \varepsilon_v)g_v(r) = \frac{\partial E_x}{\partial \psi_v(r)} - V_x(r)\psi_v(r) - U_v\psi_v.$$ (3.39)

The updates on the exchange potential must include the core shift from reference states:

$$\frac{\partial F}{\partial V_x} = -\sum_v n_v g_v^*(r)\psi_v(r) + S_{\text{core}}(r),$$ (3.40)

where:

$$S_{\text{core}}(r) = -\sum_c n_c g_c^*(r)\psi_c(r).$$ (3.41)
Frozen-core Gradient Search

\[ \alpha = 0 \]

\[ \text{do} \]

\[ \text{Construct } H_{KS}^\alpha \leftarrow T + \nabla N + \nabla H + \nabla X \]

\[ \text{Solve } \phi_v^{\alpha+1}(r) \leftarrow H_{KS}^\alpha \phi_v^{\alpha+1} = e_v^{\alpha+1} \phi_v^{\alpha+1} \]

\[ \text{Update } \{ \nabla H^{\alpha+1}, \nabla U^{\alpha+1}, \nabla E^{\alpha+1} \} \leftarrow \phi_v^{\alpha+1}(r) \]

\[ \text{Update } H_{KS}^{\alpha+1} \leftarrow T + \nabla N + \nabla H^{\alpha+1} + \nabla X \]

\[ \text{Solve } g_v^{\alpha+1}(r) \text{ from } (H_{KS}^{\alpha+1} - \epsilon_v^{\alpha+1}) g_v^{\alpha+1} = \frac{\partial E_{\alpha+1}}{\partial \phi_v} - \nabla x \phi_v^{\alpha+1} - \nabla v \phi_v^{\alpha+1} \]

\[ \text{Calculate: } \frac{\partial E}{\partial v_x} = -\sum_v g_v^{\alpha+1}(r) \psi_v^{\alpha+1}(r) + S_{\text{core}}(r) \]

\[ \triangleright \text{the gradient for updating } V_x^{\alpha}(r) \]

\[ \text{Update } V_x^{\alpha+1} \leftarrow V_x^{\alpha} + s^\alpha(r) \ast \text{Mixer } \alpha = \alpha + 1 \]
3.4 KLI Frozen Core Theory and Implementation

The KLI Frozen-core orbital formalism can be trivially applied, based on our experience from Hartree Fock and OEP frozen-core implementation, in order to achieve high accuracy of calculated exchange potential, the key principle is that the exchange potential should always remain as full exchange potential, which means it should contain both the core and valence contributions. The attempt of trying to split the exchange into core and valence exchange contribution – the frozen-core potential approximation, would introduce artifacts into the potential and inaccuracy when evaluating the total exchange energy. Furthermore, in the frozen-core orbital approximation scheme, the algorithm should only update the valence wavefunction.

The procedure of Frozen-core KLI is simple, we use the exchange potential from reference states as initial guess, solve the Schrödinger equations for valence electrons only, and use obtained orbitals to solve for KLI equation (2.95) to update the exchange potential. The valence electrons should always remain orthogonal to the frozen-core orbitals.
To sum up, the algorithm of Frozen-core approximation of KLI can be written as:

**Frozen Core KLI SCF Procedure**

1. \( \alpha = 0 \)
2. **Initial Guess of** \( V_x(r) \) **Use All-electron reference state** \( V_x(r) \)
3. do
   4. Gram Schmidt \( \langle \psi_v | \psi_q \rangle = \delta_{vq} \)
   5. Update \( \{ \rho(r), V_H(r), \chi_v(r), \} \leftarrow \psi_v(r) \)
   6. Solve KLI equations
   7. Construct KLI Equations
   8. Find Outermost Orbitals \( L = \text{zeroindex} \)
   9. Replace \( V_L = U_L \)
   10. Obtain \( V_x^{\alpha+1}(r) \)
   11. if
       12. \( |V_x^{\alpha+1} - V_x^\alpha| < \xi \) ▶ CONVERGED
       13. else Update \( V_x^{\alpha+1} = \alpha V_x^\alpha + (1 - \alpha)V_x^{\alpha+1} \)
4 Atompaw Hartree Fock Implementation
4.1 PAW formalism

The Projector Augmented Wave (PAW) formalism was developed by Blöchl [38] and implemented by a number of authors [38, 22, 20, 21, 39]. It is similar to the ultra-soft pseudopotential approach of Vanderbilt [40]. The formalism needs a set of basis and projector functions for each atom \( a \) which represent the valence states.

A key idea of the PAW formalism is the transformation between a calculated pseudo-wavefunction \( \tilde{\Psi}_v(r) \) corresponding to a valence state of the system and the corresponding fully nodal wavefunction \( \Psi_v(r) \) of that state which is given by [38]

\[
\Psi_v(r) = \tilde{\Psi}_v(r) + \sum_{ai} [\Phi^a_i(r-R^a) - \tilde{\Phi}^a_i(r-R^a)] \left\langle \tilde{P}^a_i \right| \tilde{\Psi}_v \rangle .
\] (4.1)

Using the atomic shell nomenclature defined in Eq. (2.1), we will denote these as \( \Phi^a_i(r) \) for an all-electron basis function, \( \tilde{\Phi}^a_i(r) \) for the corresponding pseudo-electron basis function

\[
\Phi^a_i(r) = \frac{\phi^a_i(r)}{r} Y_{l_i m_i}(\hat{r}).
\] (4.2)

\[
\tilde{\Phi}^a_i(r) = \frac{\tilde{\phi}^a_i(r)}{r} Y_{l_i m_i}(\hat{r}).
\] (4.3)

and \( \tilde{P}^a_i(r) \) for the corresponding projector function, which contains both radial part and angular part

\[
\tilde{P}^a_i(r) = \frac{P^a_i(r)}{r} Y_{l_i m_i}(\hat{r}).
\] (4.4)

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 \( 0 \leq r \leq r^a_c \) (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 \( \{\Phi^a_i(r)\} \) 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 (2.36). For the case of Hartree-Fock theory they are solutions of the Hartree-Fock Equation (2.17) with special consideration for continuum states [41].

The valence electron density can be defined as:

\[
n^a_v(r) = \sum_{v,ij} N_v \left\langle \tilde{P}^a_i \right| \Psi_v \right\rangle \left\langle \tilde{P}^a_j \right| \Psi_v \right\rangle |\Phi^a_i(r-R^a)|^2.
\] (4.5)
And it is also necessary to define the atom center density and pseudodensity which only exist inside of the augmentation region:

\[
\tilde{n}^a(r) = \sum_{v,ij} N_v \langle \tilde{P}_i^a | \tilde{\Psi}_v \rangle \langle \tilde{P}_j^a | \tilde{\Psi}_v \rangle \tilde{\Phi}_i^a(r-R^a). \tag{4.6}
\]

and

\[
\tilde{n}^a_j(r) = \sum_v N_v \langle \tilde{P}_i^a | \tilde{\Psi}_v \rangle \langle \tilde{P}_j^a | \tilde{\Psi}_v \rangle \tilde{\Phi}_i^a(r-R^a). \tag{4.7}
\]

The projector functions satisfy the relationship

\[
\langle \tilde{P}_i^a | \tilde{\Psi}_j^a \rangle = \delta_{ij}, \tag{4.8}
\]

and the radial pseudo-functions have the property

\[
\tilde{\phi}_i^a(r) = \phi_i^a(r) \quad \text{for} \quad r > r_c. \tag{4.9}
\]

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 \( r_c^a \).

The sum \( a, i \) is over atom center sites \( a \) and basis functions \( i \). With this transformation and a few additional terms (Appendix (A.3)), 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:

\[
E_{\text{vale}} = \tilde{E}_{\text{vale}}^{\text{pseudoenergy}} + \sum_a \left( E_{\text{vale}}^a - \tilde{E}_{\text{vale}}^a \right). \tag{4.10}
\]
4.2 PAW formulation of Hartree-Fock theory

For Hartree-Fock theory, the PAW valence energy expression can be put in the form of Eq. (A.34) 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 wavefunction frozen-core approximation discussed in Sec. 3.2, we decided to use the frozen-core orbital approach for our PAW implementation.

For the purpose of this formulation, the valence pseudo-orbitals $\widetilde{\Psi}_v^\text{HF}(r)$ 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 $\{\tilde{\Phi}_a(r)\}$ within the augmentation sphere.

Most of the core wavefunctions $\Psi_c^\text{HF}(r)$ are contained within the augmentation sphere and for those we can define a trivial core pseudowavefunction $\widetilde{\Psi}_c^\text{HF}(r) \equiv 0$. For some materials it is possible that at most one core orbital per $l$ channel will have a non-trivial amplitude for $r > r_c^a$. In such a case, it is convenient to define a continuous pseudo-core orbital $\tilde{\psi}_c^a(r)$ with $\tilde{\psi}_c^a(r) \equiv \psi_c^a(r)$ for $r > r_c^a$, in a similar spirit to the pseudo-core functions defined for the so-called non-linear core corrections in norm-conserving pseudopotentials [42]. In our case, we define

$$\tilde{\psi}_c^a(r) \equiv \begin{cases} r_{l+1}^a P_n(r) & \text{for } r \leq r_c^a \\ \psi_c^a(r) & \text{for } r > r_c^a \end{cases}.$$  \tag{4.11}

The $n^{th}$ order polynomial $P_n(r)$ is chosen to ensure that $\tilde{\psi}_c^a(r)$ is continuous up to $n - 1$ derivatives. An example of this construction is shown for the 3$d^3$ core state of Ge in Fig 4.1.

In order to define localized contributions from Coulombic interactions, it is necessary to define “compensation” charge [38] moments of the form

$$\hat{m}_{ij}^{aL} \equiv m_{ij}^{aL} \frac{r^2 s_L(r)}{\int du u^{L+2}s_L(u)} \equiv m_{ij}^{aL} g_L^a(r).$$  \tag{4.12}

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

$$s_L(r) = r^L k(r),$$  \tag{4.13}

or it could be similar smooth function such as one involving a spherical Bessel function.
Figure 4.1: (Color online.) Radial Hartree-Fock wavefunction $\psi_c(r)$ for the 3$d$ core state of Ge compared with the constructed pseudo-wavefunction $\tilde{\psi}_c(r)$.

$s_L(r) \equiv j_L(\kappa r)$. More often we have chosen

$$k(r) = \begin{cases} 
\left[ \frac{\sin(\pi r/r_a^c)}{(\pi r/r_a^c)} \right]^2 & \text{for } r < r_{a}^c \\
0 & \text{for } r \geq r_{a}^c
\end{cases} \quad (4.14)$$

The charge moment coefficient is given by

$$m_{ij}^{aL} \equiv \int dr r^L [\phi_i^a(r)\phi_j^a(r) - \tilde{\phi}_i^a(r)\tilde{\phi}_j^a(r)]. \quad (4.15)$$

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 [38] 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 [43] so that they can be written in the PAW form (A.34):

$$E_{xv}^{cv} = \tilde{E}_{xv}^{cv} + \sum_a \left( E_{xv}^{av} - \tilde{E}_{xv}^{av} \right),$$

$$E_{xv}^{uv} = \tilde{E}_{xv}^{uv} + \sum_a \left( E_{xv}^{av} - \tilde{E}_{xv}^{av} \right), \quad (4.16)$$

The trick [43] 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, \( \psi_v^{HF}(r)\psi_v^{HF}(r) \), we can define a compensation charge moment of order \( L \)

\[
\hat{M}^{L}_{vv'}(r) = \sum_{aij} \langle \hat{\psi}_v^{HF} | \hat{\rho}_a^{i} \rangle \langle \hat{\rho}_a^{j} | \hat{\psi}_{v'}^{HF} \rangle \hat{m}_{ij}^{iL}(r)
\]

\[
\hat{M}^{L}_{vc}(r) = \sum_{aij} \langle \hat{\psi}_v^{HF} | \hat{\rho}_a^{i} \rangle \hat{m}_{ic}^{iL}(r)
\]

(4.17)

The significance of this moment is that, within the accuracy of the PAW transformation, the \( L^{th} \) moment of \( (\psi_v^{HF}(r)\psi_v^{HF}(r)) \) is the same as the \( L^{th} \) moment of \( (\tilde{\psi}_v^{HF}(r)\tilde{\psi}_v^{HF}(r) + \hat{M}^{L}_{vv'}(r)) \). For the moment representing core-valence wavefunction products, the moment coefficient \( M^{iL}_{vc} \) corresponding to valence-core contributions is defined by an expression similar to Eq. (4.15) with \( \phi^a_j \rightarrow \psi^a_c \) and \( \phi^a_j \rightarrow \tilde{\psi}^a_c \). Because of orthogonality properties of core and valence states of the reference system and because \( \tilde{\psi}^a_c \equiv 0 \) for many cases, there are several simplifications of the terms involving the core functions as discussed in more detail in Appendix A.3.

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

\[
\tilde{E}^{vv}_{x} = - \sum_{vv',L=|v_v-L_{v'}|}^{l_v+l_{v'}} \frac{1}{2} \Theta^{L}_{vv'} R^{L}_{vv',v'}
\]

\[
\tilde{E}^{vv}_{x} = - \sum_{vc,L=|v_v-L_{c}|}^{l_v+l_c} \Theta^{L}_{vc} R^{L}_{vc,cv}
\]

(4.18)

where

\[
R^{L}_{vv',v'} \equiv e^2 \int dr dr' \int_{r_L}^{r_{L+1}} \int_{r_L}^{r_{L+1}} [\tilde{\psi}_v^{HF}(r)\tilde{\psi}_v^{HF}(r') + \hat{M}^{L}_{vv'}(r)][\tilde{\psi}_v^{HF}(r')\tilde{\psi}_v^{HF}(r') + \hat{M}^{L}_{vv'}(r')]
\]

(4.19)

with \( R^{L}_{vc,cv} \) has similar expression with \( v' \rightarrow c \). The corresponding one-center contributions take the form

\[
E^{vv}_{x} - \tilde{E}^{vv}_{x} = - \sum_{vv',L=|v_v-L_{v'}|}^{l_v+l_{v'}} \frac{1}{2} \Theta^{L}_{vv'} \sum_{ijkl} \langle \hat{\psi}_v^{HF} | \hat{\rho}_a^{i} \rangle \langle \hat{\rho}_a^{j} | \hat{\psi}_{v'}^{HF} \rangle \langle \hat{\psi}_v^{HF} | \hat{\rho}_a^{k} \rangle \langle \hat{\rho}_a^{l} | \hat{\psi}_{v'}^{HF} \rangle (R^{L}_{ijkl} - \tilde{R}^{L}_{ijkl})
\]

(4.20)

and

\[
E^{vc}_{x} - \tilde{E}^{vc}_{x} = - \sum_{vc,L=|v_v-L_{c}|}^{l_v+l_c} \frac{1}{2} \Theta^{L}_{vc} \sum_{ij} \langle \hat{\psi}_v^{HF} | \hat{\rho}_a^{i} \rangle \langle \hat{\rho}_a^{j} | \hat{\psi}_{c}^{HF} \rangle (R^{L}_{iccj} - \tilde{R}^{L}_{iccj})
\]

(4.21)
Here
\[ R_{ijkl}^a \equiv e^2 \int \int dr dr' \frac{r_L^L}{r_{L+1}^L} \phi^a_i(r) \phi^a_j(r') \phi^a_k(r') \phi^a_l(r'), \quad (4.22) \]
and
\[ \tilde{R}_{ijkl}^a \equiv e^2 \int \int dr dr' \frac{r_L^L}{r_{L+1}^L} [\tilde{\phi}^a_i(r) \tilde{\phi}^a_j(r) + \tilde{m}_{ij}^a L(r)] [\tilde{\phi}^a_k(r') \tilde{\phi}^a_l(r')] + \tilde{m}_{kl}^a L(r'). \quad (4.23) \]
These expressions for the valence electron contributions to the exchange energy are equivalent to results given by previous workers [43, 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 of the energy with respect to the valence pseudo-orbitals. The self-consistent Hartree-Fock equations for the PAW formulation take the form
\[ H_{HF}^{PAW}(r) \tilde{\Psi}_{HF}(r) + X_{v}^{PAW}(r) - \sum_q \lambda_{qv} O_{HF}^{PAW} \tilde{\Psi}_{q}(r) = 0. \quad (4.24) \]
These equations must be solved self-consistently, with orthonormalization constraint
\[ \left\langle \tilde{\Psi}_{HF}^v \left| O^{PAW} \right| \tilde{\Psi}_{HF}^q \right\rangle = \delta_{vq}. \quad (4.25) \]
This differs slightly from the orthonormalization constraint in the Kohn-Sham case (Eq. 5.3) 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:
\[ \left\langle \tilde{\Psi}_{HF}^v \left| O^{PAW} \right| \tilde{\Psi}_{HF}^c \right\rangle \equiv \left\langle \tilde{\Psi}_{HF}^v \left| \tilde{\Psi}_{HF}^c \right\rangle + \sum_{ai} \left\langle \tilde{\Psi}_{HF}^v \left| \tilde{P}_i^a \right\rangle \right\langle \tilde{P}_i^a \right| O_{ic}^a, \quad (4.26) \]
where \( O_{ic}^a \equiv m_{ic}^a0 \). In general, these terms are very small if not identically zero. The single particle term of Eq. (4.24) takes the form
\[ H_{HF}^{PAW}(r) = \tilde{H}_{HF} + \sum_{aij} \left\langle \tilde{P}_i^a \right\rangle D_{ij}^{aHF} \left\langle \tilde{P}_j^a \right\rangle. \quad (4.27) \]
where the pseudo Hamiltonian-like terms depend on the pseudopotentials due to the nuclear and Hartree interactions:
\[ \tilde{H}_{HF}(r) \equiv K + \tilde{V}_N(r) + \tilde{V}_H(r). \quad (4.28) \]
The exchange function term takes the form
\[ X_{v}^{PAW}(r) = \tilde{X}_v(r) + \sum_{ai} \left\langle \tilde{P}_i^a \right\rangle X_{iv}^a. \quad (4.29) \]
where the pseudo-exchange kernel function takes the form:

\[
\tilde{X}_v(r) = - \sum_q \sum_{L=|l_v-l_q|} \frac{1}{N_v} \Theta_{eq}^L \tilde{W}^L_{qv} \tilde{\psi}^H (r).
\]  

(4.30)

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 \( \tilde{W}^L_{qv}(r) \) is the pseudo analogue of Eq. (2.20):

\[
\tilde{W}^L_{qv}(r) \equiv e^2 \int dr' \frac{r_L^{<}}{r_L^{>}} [\tilde{\psi}_q^H (r') \tilde{\psi}_v^H (r') + M^L_{qv}(r')].
\]  

(4.31)

The one center matrix element for the pseudo-exchange kernel function takes the form:

\[
X_{iv}^a = - \sum_{v'} |l_v+l_q| \frac{1}{N_v} \Theta_{vv'}^L \sum_{jkl} \langle \tilde{P}_j^a | \tilde{\psi}_v^H \rangle \langle \tilde{\psi}_{v'}^H | \tilde{\psi}_k^H \rangle \langle \tilde{\psi}_l^H \rangle \left( R_{ijkl}^a - \tilde{R}_{ijkl}^a \right),
\]  

(4.32)

where

\[
Z_{qviij}^a \equiv \int dr \tilde{W}^L_{qv}(r) \tilde{\psi}_v^H (r).
\]  

(4.33)

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

\[
\tilde{H}^H F (r) \Phi_i^a (r) + \tilde{X}_i (r) - \sum_{q,N_q>0} \lambda_q \tilde{\psi}_q^H (r) = \sum_j \tilde{P}_j^a (r) \Lambda_j^a.
\]  

(4.34)

Here the matrix coefficients are given by

\[
\Lambda_j^a \equiv \langle \Phi_j^a | \tilde{H}^H F | \Phi_i^a \rangle + \langle \Phi_j^a | \tilde{X}_i \rangle - \sum_{q,N_q>0} \lambda_q \langle \tilde{\psi}_j^a | \tilde{\psi}_q^H \rangle.
\]  

(4.35)

where the differential \( \tilde{H}^H F (r) \) and integral \( \tilde{X}_i (r) \) operators as well as the Lagrange multipliers \( \lambda_q \) are all evaluated for the reference configuration. Analogous to Eq. (5.8) for the PAW-Kohn-Sham formalism, for the PAW-Hartree-Fock formalism Eq. (4.34) is used to determine the projector functions \( \{ \tilde{P}_j^a (r) \} \). Equation (4.34) is consistent...
with the requirement that the pseudowavefunction basis functions \( \tilde{\Phi}^a_i(r) \) must be a solution of the PAW Hartree-Fock equations (4.24) for the reference configuration of the atom and the following identities. For the reference state, the single particle terms satisfy the relationship

\[
D^a_{ij} \bigg|_{\text{ref}} = \langle \Phi^a_i \mid H^{HF} \mid \Phi^a_j \rangle \bigg|_{\text{ref}} - \langle \tilde{\Phi}^a_i \mid \tilde{H}^{HF} \mid \tilde{\Phi}^a_j \rangle \bigg|_{\text{ref}}.
\]

(4.36)

and the two-particle terms satisfy the relationship:

\[
X^a_{iv} \bigg|_{\text{ref}} = \langle \Phi^a_i \mid X_v \rangle \bigg|_{\text{ref}} - \langle \tilde{\Phi}^a_i \mid \tilde{X}_v \rangle \bigg|_{\text{ref}}.
\]

(4.37)

Once the basis and projector functions are determined, the solution of self-consistent PAW-Hartree-Fock equations (4.24) can be obtained using an iterative method similar to that of the all-electron or frozen-core equations counterparts. For any guess of the valence pseudowavefunctions \( \{ \tilde{\psi}^{HF(0)}_v(r) \} \), the Lagrange multipliers \( \lambda^{(0)}_{cv} \) can be estimated by multiplying both sides of Eq. (4.24) by \( \tilde{\Psi}^{HF(0)}_c(r) \) 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

\[
\lambda^{(0)}_{cv} = \langle \tilde{\psi}^{HF}_c \mid \tilde{H}^{HF} \mid \tilde{\Psi}^{HF(0)}_v \rangle + \sum_j D^a_{cj} \langle \tilde{P}^a_j \mid \tilde{\Psi}^{HF(0)}_v \rangle + \langle \tilde{\psi}^{HF}_c \mid \tilde{X}^{(0)}_c \rangle + X^a_{cv}.
\]

(4.38)

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, \( \tilde{\psi}^a_c(r) \approx 0 \), so that the main contributions of the core orbitals are expressed in the atom centered radial Coulomb integrals \( R^{aL}_{ic} \) similar to the expression defined in Eq. (4.22). When \( \tilde{\psi}^a_c(r) \equiv 0 \), many of the matrix elements and Hamiltonian terms simplify as discussed in Appendix (A.3). In practice, the main contributions can be expressed in terms of the \( R^{aL}_{ic} \) integrals which contribute to the core-valence exchange energy \( E^{cv}_x \) as defined in Eqs. (4.21) and Eqs. (A.34). They also contribute to the pseudo-exchange kernel function \( X^a_{iv} \) defined in Eq. (4.32). Since all of these core-exchange 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.)
4.3 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. (4.2) 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 [45, 46, 47, 21, 38, 40].

![Graph showing radial valence wavefunctions for Ge, comparing Kohn-Sham (LDA) and Hartree-Fock (HF).](image)

Figure 4.2: Radial valence wavefunctions for Ge, comparing Kohn-Sham (LDA) and Hartree-Fock (HF).

In constructing the pseudobasis functions, for each atom we vary only the augmentation radius $r_a$ and construct the pseudobasis functions $\tilde{\phi}_i^a(r)$ from all-electron basis functions $\phi_i^a(r)$ using the polynomial form introduced by Vanderbilt in the construction of the ultra-soft pseudopotential scheme [40]. The other adjustable function in this construction is the localized potential $\tilde{V}_{loc}^a(r)$ defined in Appendix (A.3). It is often efficient to choose this potential as an unscreened norm-conserving pseudopotential derived from the Troullier-Martins [48] 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 $\tilde{V}_{loc}^a(r)$. A simple, but reasonable choice is
Table 4.1: Hartree-Fock valence energies for several configuration averaged atoms calculated with the frozen-core orbital approximation (FC), and the PAW formalism (PAW). Results including ($\hat{\psi}_c > 0$) and excluding ($\hat{\psi}_c \equiv 0$) 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.

| Atom | Type | $|\hat{\psi}_c|$ | $r^a_c$ | $V_0$ | $E_{val}(ns^2np^2)$ | $E_{val}(ns^4np^3)$ |
|------|------|----------------|--------|------|----------------|----------------|
| C    | FC   | -              | -      | -    | -10.5990       | -9.9542       |
| C    | PAW  | > 0            | 1.3    | 2.0  | -10.5990       | -9.9541       |
| C    | PAW  | $\equiv 0$    | 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  | $\equiv 0$    | 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  | $\equiv 0$    | 2.2    | 3.0  | -7.2258        | -6.6800       |

Using the shape function defined in Eq. (4.14) and an adjustable amplitude $V_0$, Table 4.1 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 $r^a_c$ 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 4.1, the core effects are most prominent for Ge. In Fig. (4.3) 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 of the LDA formulation. On the other hand, by setting the pseudo-core functions to zero, the projector function extends considerably beyond $r^a_c$. The reason
for this behavior can be explained from the defining Eq. (4.34). By construction, when the smooth core wavefunctions are included in Eq. (4.34), for \( r \geq r_c^a \), the left hand side becomes identical to the left hand side of the all-electron Hartree-Fock Eq. (2.17) 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. (4.34) and therefore \( \tilde{p}_i^\alpha (r) \), remains non-zero beyond \( r = r_c^a \). The example shown in Fig. (4.3) 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. (4.1). However, the results in Table 4.1 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.

![Figure 4.3](image)

Figure 4.3: Radial PAW projector functions for 4\( p \) 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 4.1.

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 \( r_c^a = 2.0 \) bohr and the valence orbital matching radii were chosen to be 2.0 and 1.6 bohr for the 4s and 3d states respectively. \(^1\) 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. \(^1\)Basis and projector functions for \( l = 1 \) channel were constructed from a continuum state since the 4\( p \) state is not bound. Although important for multicenter calculations, these functions have no effect on the atomic calculation.
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 4.2 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 4.2 — 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. (4.5).

![Figure 4.4](image-url)

**Figure 4.4:** 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.

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 transition metal atoms to include configurations which alter the
Table 4.2: 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 \(|\tilde{\psi}_c| > 0\) and excluding \(|\tilde{\psi}_c| \equiv 0\) the pseudo-core wavefunctions
are compared. “x” indicates that the calculation diverged.

| \(V_0\) | AE     | FC     | PAW \( (|\tilde{\psi}_c| > 0) \) | PAW \( (|\tilde{\psi}_c| \equiv 0) \) |
|---------|--------|--------|-------------------------------|-------------------------------|
| -       | 0. 4991| 0. 4992| -                             | -                             |
| -2      | -      | -      | 0. 5002                       | x                             |
| -4      | -      | -      | 0. 4904                       | 0. 6288                       |
| -6      | -      | -      | x                             | 0. 4992                       |

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.
Figure 4.5: 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 frozen-core orbital (FC) results. The PAW results are based on the calculation of the pseudofunctions $\tilde{\psi}_v(r)$ and using the PAW transformation Eq. (4.1). The results for the fully nodal 4s wavefunctions are virtually indistinguishable on this scale.
5 Atompaw OEP Implementation
5.1 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.3). Since the valence energy (4.10) is an explicit functional of the electron density which in turn is an explicit functional of the valence pseudowavefunctions, the Kohn-Sham Hamiltonian in the PAW formalism can be evaluated [38] in terms of the functional derivative

$$\frac{\partial E_{\text{vale}}}{\partial \tilde{\Psi}_v^{K}}(r) = H_{\text{PAW}}^{K}(r) \tilde{\Psi}_v^{K}(r).$$

(5.1)

Therefore the PAW Schrödinger Equation can be expressed as:

$$H_{\text{PAW}}^{K}(r) \tilde{\Psi}_v^{K}(r) = \varepsilon_v O_{\text{PAW}} \tilde{\Psi}_v^{K}(r).$$

(5.2)

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

$$\left\langle \tilde{\Psi}_v^{K} \right| O_{\text{PAW}} \left| \tilde{\Psi}_v^{K} \right\rangle = \delta_{vv'},$$

(5.3)

Here the PAW Hamiltonian takes the form

$$H_{\text{PAW}}^{K}(r) = \tilde{H}_v^{K} + \sum_{aij} \left| \tilde{P}_i^a \right| D_{ij} \left| \tilde{P}_j^a \right|,$$

(5.4)

and

$$O_{\text{PAW}} = 1 + \sum_{aij} \left| \tilde{P}_i^a \right| O_{ij} \left| \tilde{P}_j^a \right|,$$

(5.5)

Here the Kohn-Sham pseudo-Hamiltonian has the form:

$$\tilde{H}_v^{K} = K + \tilde{V}_v^{K}(r).$$

(5.6)

The overlap matrix element is given by

$$O_{ij}^a = \left\langle \Phi_i^a \right| \Phi_j^a \right\rangle - \left\langle \tilde{\Phi}_i^a \right| \tilde{\Phi}_j^a \right\rangle.$$

(5.7)

The general form of $\tilde{V}_v^{K}(r)$ as well as of the one center matrix elements $D_{ij}^a$ has been given in many references [38, 22, 21, 39]. For convenience the contributions from terms other than exchange and correlation are given in Appendix (A.3).

There are several alternative schemes suggested by Vanderbilt and Blöchl [40, 38] 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:

\[(\tilde{H}^{KS}(r) - \varepsilon_i)\tilde{\Phi}_i^a = \sum_j \tilde{P}_j^a \langle \tilde{\Phi}_i^a | \tilde{H}^{KS}(r) - \varepsilon_i | \tilde{\Phi}_j^a \rangle. \tag{5.8}\]

This relationship is consistent with the requirements that each pseudowavefunction basis function \(\tilde{\Phi}_i^a(r)\) must be a solution of the Kohn-Sham PAW equations (5.1) of the reference state and with the special form of the one-center Hamiltonian matrix elements of the reference state:

\[D_{ij}^a|_{\text{ref}} = \langle \Phi_i^a | H^{KS} | \Phi_j^a \rangle|_{\text{ref}} - \langle \tilde{\Phi}_i^a | \tilde{H}^{KS} | \tilde{\Phi}_j^a \rangle|_{\text{ref}}. \tag{5.9}\]

In practice, the projector functions \(\{\tilde{P}_i^a(r)\}\) are determined by solving Eq. (5.8) from a knowledge of the reference pseudo Hamiltonian \(\tilde{H}^{KS}(r)\), the basis functions \(\{\Phi_i^a(r), \tilde{\Phi}_i^a(r)\}\), and the eigenenergies \(\{\varepsilon_i^a\}\), following a similar procedure developed by Vanderbilt [40].
5.2 Basic Idea

The original intent of this thesis was to develop a PAW-OEP scheme. In the course of the study, we realized the original idea was more demanding on the PAW’s bases than anticipated. In this section, we summarize our findings which provide insight into future work and motivations for the KLI work in the future chapters.

According to the discussion in section(2.5.4), the physical meaning of the auxiliary function \( g_p(r) \) or \( \delta \Psi(r) \) is the orbital response to the variation of exchange potential. Therefore, it is conceivable and necessary to demand that \( g_p(r) \) function also follows the key idea of PAW formalism, which is the transformation between a calculated pseudo-wavefunction and full nodal wavefunction, and using the same notation given by (4.1).

For example, the transformation of the radial part of the orbital shift can be assumed to be:

\[
\tilde{g}^\alpha_a(r) = \tilde{g}_p(r) + \sum_i \langle \tilde{p}_i^\alpha | \tilde{g}_p \rangle \delta_{l_{itp}} (\phi_i^\alpha(r) - \tilde{\phi}_i^\alpha(r)),
\]

where \( \tilde{p}_i(r) \) is the radial part of the projector \( \tilde{P}_i(r) \) defined in(4.4). Here \( \delta_{l_{itp}} \) implies that the integral \( \langle \tilde{p}_i | \tilde{g}_p \rangle \) should only be carried out within the same \( l \)-channel. This \( \delta_{l_{itp}} \) will be assumed to be present throughout this chapter, even if not explicitly included.

A close inspection of (5.10) would suggest that, (5.10) requires for \( r \leq r_c^\alpha \):

\[
\tilde{g}_p^\alpha(r) = \sum_i \langle \tilde{p}_i^\alpha | \tilde{g}_p \rangle \tilde{\phi}_i^\alpha(r),
\]

and

\[
g_p^\alpha(r) = \sum_i \langle p_i^\alpha | g_p \rangle \phi_i^\alpha(r),
\]

to be true for the ground state as well as excited states. We expect this would be a sufficient approximation for the excited states also. The methods to generate smooth orbital shift \( \tilde{g}(r) \) will be discussed later.

The necessity for such assumption is based on the following: Upon convergence at reference state, the orbital shift or the gradient to update the exchange potential should be essentially zero or below convergence criterion at all region:

\[
S(r) = \frac{\partial F}{\partial V_x(r)} = \sum_p n_p g_p(r) \psi_p(r) \to 0,
\]
and if (5.12) and (5.11) are good approximation, the PAW counterparts of (5.13) will be automatically satisfied. To write out the corresponding version of orbital shift in PAW formalism, one needs to start from PAW version of the object function.
5.3 General Scheme of OEP PAW

According to (2.57), the PAW object function can be accordingly written as the total energy with constraints:

\[ F = E_{tot} - \sum_p \lambda_p \langle \tilde{\psi}_p | \hat{O} | \tilde{\psi}_p \rangle - 1 - \sum_p N_p \langle \hat{g}_p | H^{PAW} - \varepsilon_p \hat{O} | \tilde{\psi}_p \rangle + c.c. \]  

(5.14)

We first tried to treat \( \tilde{V}_x(x), [V_x]_{ij} \) as independent variables, namely they are the terms being updated during SCF, so initially:

\[ \frac{\partial F}{\partial \tilde{V}_x(r)} = - \sum_p N_p \tilde{g}_p(r) \tilde{\psi}_p(r) \]  

(5.15)

\[ \frac{\partial F}{\partial [V_x]_{ij}} = - \sum_p N_p \langle \tilde{g}_p | P^a_i \rangle \langle P^a_j | \tilde{\psi}_p \rangle \]  

(5.16)

The above scheme would immediately introduces conflicts: while the system is at reference states, the corresponding convergence criterions are no longer met. Furthermore, the convergence of (5.16) requires \( \langle \tilde{g}_p | P^a_i \rangle \) to have certain cancelation relationships between each states, which can not be directly derived.

Consequently, we therefore treat \( \tilde{V}_x(x), V_x(r) \) as the unknowns. Instead of writing out the orbital shift of PAW scheme, it is more convenient to inspect the derivatives of object function with respect to both \( \tilde{V}_x(x) \) and \( V_x(r) \) to scrutinize the possible working formalisms. One of the two parts is:

\[ \frac{\partial F}{\partial \tilde{V}_x(r)} = - \sum_p N_p \tilde{g}_p(r) \tilde{\psi}_p(r) + \sum_p \sum_{ij} N_p \langle \tilde{g}_p | P^a_i \rangle \langle P^a_j | \tilde{\psi}_p \rangle \phi^a_i(r) \phi^a_j(r). \]  

(5.17)

One important property this treatment has is that outside of \( r_c \), \( \tilde{g}_p(r) = g_p(r) \). For reference state, \( \frac{\partial F}{\partial \tilde{V}_x(r)} \rightarrow 0 \) is automatically satisfied for reference state. The properties inside of the augmentation region will be discussed in detail in later sections.

Inside of the augmentation region, \( V_x(r) \) is the independent variable, and its derivative with respect to the object function can be written as:

\[ \frac{\partial F}{\partial V_x(r)} = - \sum_p \sum_{ij} N_p \langle \tilde{g}_p | P^a_i \rangle \langle P^a_j | \tilde{\psi}_p \rangle \phi^a_i(r) \phi^a_j(r). \]  

(5.18)

(5.18) provides a way to update \( V_x \) inside of the augmentation region.
5.3.1 Sample of auxiliary function

This subsection gives samples of radial part of the auxiliary function from all-electron OEP calculations, both reference state and excited states. The purpose is to demonstrate the auxiliary function has more complicated nodal structures which can be anticipated from (2.73). Taking into account of all the spectrum, and changes drastically from reference states to excited states, and within one particular channel, would require more bases than wavefunction does to be represented. In the next subsection, we are going to explore and present our preliminary investigations on whether it is possible to find the proper bases and projectors to satisfy PAW transformation of such auxiliary function.

![Figure 5.1: Complex nodal structure of carbon reference state $g(r)$](image-url)
Figure 5.2: Drastic changes between excited ('x') and reference (solid) state \( g(r) \) of carbon. In this case, the ground state corresponds to the configuration \( 1s^22s^22p^2 \) and the excited state has the configuration \( 1s^22s^12p^3 \).

Figure 5.3: S All-electron reference state \( g(r) \)
Figure 5.4: S All-electron excited (‘x’) compared with reference (solid) state $g(r)$. In this case the ground state configuration is $3s^23p^4$ and the excited state configuration is $3s^13p^5$. 

\begin{figure}
\begin{center}
\includegraphics[width=0.5\textwidth]{s_all-electron_excited}
\end{center}
\end{figure}
5.4 The construction of $\tilde{g}_p(r)$: I

One approach to construct the smooth version of the orbital shift is to directly pseudize the $g_p(r)$ inside of the augmentation region to obtain $\tilde{g}_p(r)$:

$$\tilde{g}_p(r) = \tilde{g}_{nlp}(r) = \begin{cases} \sum_{m=0}^{r_{l+1}} C_m r^m & r \leq r_c \\ g_{nlp}(r) & r > r_c \end{cases}.$$  \hspace{1cm} (5.19)

Here, $C_m$ are unknowns and are chosen to ensure that $\tilde{g}_p(r)$ is equal to $g_p(r)$ up to 4th derivative. Therefore, starting with (5.11):

$$\tilde{g}_p(r) = \sum_i \langle p_i | \tilde{g}_p \rangle \tilde{\phi}_i(r).$$ \hspace{1cm} (5.20)

As mentioned in the previous section Fig (5.1), since $g_p(r)$ has more complicated nodal structure, we are required to use more bases and projectors in each channel to represent them accurately, here $\tilde{g}_p(r)$ is from (5.19). For the $\tilde{g}_p(r)$, it is conceivable that more bases would be helpful to make (5.11) more accurate, however, $g_p(r)$ expansion has less freedom, whether is is sufficient enough to use the $\tilde{g}_p(r)$ expansion parameters, which is $\langle p_i | \tilde{g}_p \rangle$ and the all-electron bases $\phi_i(r)$ to represent all-electron $g_p(r)$ is unknown.

$$g_p(r) = \sum_i \langle p_i | g_p \rangle \phi_i(r).$$ \hspace{1cm} (5.21)

And overall, the scheme relies on the following transformation (5.10) to be valid in order to work: The major short coming of this method is that the pseudization process of constructing the $\tilde{g}(r)$ can not guarantee the accuracy of (5.12).
5.5 The construction of $\tilde{g}_p(r)$: II

Another approach is to start with expanding the all-electron auxiliary function first, using all-electron bases:

$$g_p(r) = \sum_i c_i \phi_i(r). \quad (5.22)$$

Here $c_i$ are the unknowns, it is chosen to minimize the reconstruction error, which is defined as:

$$R_p = \min c_i [g_p(r) - \sum_i c_i \phi_i(r)]^2. \quad (5.23)$$

The obtained coefficients $c_i$ are then used to construct $\tilde{g}_p(r)$, which is an exact relation, and continuous on the $r_c$ boundary:

$$\tilde{g}_p(r) = \sum_i c_i \tilde{\phi}_i(r). \quad (5.24)$$

Schematically, after $\tilde{g}_p(r)$ is obtained, $\tilde{V}_x(r)$ can be obtained by solving the PAW counterparts of (2.70), the next step is unscreening procedure, which will be elaborated in the next chapter. Here an important fact is that this approach still requires more than usual number of bases to construct a spatially quickly varying function $g_p(r)$, which is computationally expensive.
5.6 Demonstration of PAW auxiliary transformation

Fig (5.5), Fig (5.6) and Fig (5.7) are the basis, projectors used in order to test the auxiliary function’s expansion of carbon reference state. Fig (5.8) plots of all-electron auxiliary function, against the $\tilde{g}(r)$, and PAW transformed $g^\text{PAW}_p(r)$ of (5.10). For the Carbon case, we have 1 extra basis in each channel, for $S$ channel, we set the energy for continuous states to be 10 Rydberg for $P$ channel, 20 Rydberg correspondingly.

Figure 5.5: C basis in s and p channel

Figure 5.6: C smoothed basis (black) compared with basis (colored) in s and p channel
The observation is that by including more bases, the accuracy of approximation on the auxiliary function was not improving significantly, whether poor quality of PAW transformation would affect the overall SCF results remain to be investigated.

This level of accuracy of $g_P^{PAW}(r)$ would eventually affect the updates on $V_x(r)$ to deviate from All-electron exchange potential $V_x(r)$ and make the subsequent calculation less reliable. In the next Chapter (6), we will adopt KLI approximation ([14]), which is the first order approximation of OEP method, and implement it in the Atompaw framework.
Figure 5.8: PAW transformation demo of s and p channel
6 Atompaw KLI Implementation
This chapter aimed at providing programming notes for AtompawKLI program, which is implemented using MATLAB and independently from the Fortran AtompawKLI program which provides inputs for the PWPAWKLI. The notations in this chapter is slightly different than PWPAWKLI formalism that going to be appeared in the future publications. Appendix provides the complete notes for Atompaw program including the expression for the AtompawKLI energy Appendix (A.5) and Hamiltonian Appendix(A.6), and working formalism for solving the Schrödinger Equation self consistently Appendix (A.7).

6.1 Atompaw KLI Basic Formalism

To work out the Atompaw KLI equation, we first start with the radial part of the AE KLI equation (2.96):

\[ V_x(r) \rho(r) = \sum_q N_q \Psi_q(r) X_q(r) + \sum_q (\tilde{V}_{xzq} - \tilde{U}_{xzq}) N_q \Psi_q^2(r). \]  

(6.1)

The PAW form of exchange potential should be written as:

\[ V_x(r) = \tilde{V}_x(r) + \sum_a (V_{xa}(r) - \tilde{V}_{xa}(r)). \]  

(6.2)

Here in the working notes, we use notation single underscore to indicate the term should be confined inside of the augmentation region computationally. For configurations without unbound states, this constraint is not necessary due to exactly cancelation between two one centered terms outside of \( r^a_C \). The PAW method is designed so that the one-center all-electron and pseudo terms exactly cancel outside the augmentation region. In practice, numerical noise can cause small errors in the cancelation.

The electron density, following PAW formalism, is given by:

\[ \rho(r) = \tilde{\rho}(r) + \sum_a (\rho^a(r) - \tilde{\rho}^a(r)), \]  

(6.3)

where the radial part of the pseudo density \( \tilde{\rho}(r) \) can be expressed as:

\[ \tilde{\rho}(r) = \sum_v N_v |\tilde{\Psi}_v(r)|^2 + \sum_c N_c |\tilde{\Psi}_c(r)|^2. \]  

(6.4)
One center density terms can be handled as following:

\[
\rho^a(r) = \sum_{qij}\langle \tilde{\Psi}_q | P^a_i \phi^a_j(r) + \rho_c^a(r) = \sum_{ij} W_{ij}^a \phi^a_i(r) \phi^a_j(r) + \sum_{ca} N_c | \Psi^a_c(r) |^2. \quad (6.5)
\]

\[
\tilde{\rho}^a(r) = \sum_{qij}\langle \tilde{\Psi}_q | P^a_i \tilde{\phi}^a_j(r) + \tilde{\rho}_c^a(r) = \sum_{ij} W_{ij}^a \tilde{\phi}^a_i(r) \tilde{\phi}^a_j(r) + \tilde{\rho}_c^a(r). \quad (6.6)
\]

For the inner core states, we demand that:

\[
\tilde{\Psi}_c(r) = 0. \quad (6.7)
\]

For semi-core states, our scheme does not give its explicit projectors (and it is not necessary), we only need to enforce:

\[
\langle \tilde{\Psi}_c | P_c \rangle = 1, \quad (6.8)
\]

and

\[
\langle \tilde{\Psi}_c | P_{\text{others}} \rangle = 0. \quad (6.9)
\]

The moment function corresponding to (4.17) can be defined as:

\[
\tilde{M}_{qq'}^L = \sum_{aij} \langle \tilde{\Psi}_q | P^a_i \rangle \langle P^a_j | \tilde{\Psi}_{q'} \rangle \tilde{m}^a_{ij} L(r). \quad (6.10)
\]

Here the notation double underscore indicates that the quantity, by construction vanishes outside of \( r_c^a \). Here \( q \) and \( q' \) can be either core state or valence states, which is the major difference between current Atompaw KLI implementation and previous PAW formalism, for example (4.17). When \( q = q', L = 0 \), sum of (6.10) would yield the compensation charge:

\[
\sum_q N_q \tilde{M}_{qq}^0 = \tilde{n}(r), \quad (6.11)
\]

here

\[
\tilde{m}_{ij}^{aL}(r) = m_{ij}^{aL} \frac{r^2 s^L_L(r)}{\int du u^{L+2} s^L_L(u)} = m_{ij}^{aL} \tilde{q}^a_{ij}(r). \quad (6.12)
\]

Intuitively, the PAW interaction (both Hartree and Exchange) function can be directly written as:

\[
\begin{align*}
\tilde{W}_{qq'}^L(r) &= e^2 \int dr' \frac{r^L}{r'_{L+1}} \tilde{\psi}_q(r') \tilde{\psi}_{q'}(r') + M_{qq'}^L(r') \quad (6.13)
\end{align*}
\]
However, it is necessary to ensure that $\tilde{W}_{qq}^{L}(r)$ and $\tilde{W}_{qq}^{aL}(r)$ are overlapping inside of the augmentation region, in order to have the exchange kernel $\tilde{X}_q(r)$ and $\tilde{X}_v^a(r)$, together with the derived functions $\tilde{V}_x(r)$ and $\tilde{V}_z^a(r)$ to overlap inside of $r^a_c$, which is an intrinsic characteristic of PAW formalism. As a result, a simple procedure can be applied: Define the difference of $\tilde{W}_{qq}^{L}(r)$ and $\tilde{W}_{qq}^{aL}(r)$:

$$\Delta = \tilde{W}_{qq}^{L}(r) - \tilde{W}_{qq}^{aL}(r), \quad (6.14)$$

and then update both $\tilde{W}_{qq}^{L}(r)$ and $\tilde{W}_{qq}^{aL}(r)$:

$$\begin{cases} 
\tilde{W}_{qq}^{aL}(r) & \leftarrow \tilde{W}_{qq}^{aL}(r) + \Delta \\
W_{qq}^{aL}(r) & \leftarrow W_{qq}^{aL}(r) + \Delta 
\end{cases}. \quad (6.15)$$

A better and more generic modification by using the boundary values of $\tilde{W}_{qq}^{L}(r)$ and $\tilde{W}_{qq}^{aL}(r)$ will be presented in the future publication. Furthermore, the exchange integral functions take the form:

$$\begin{cases} 
\tilde{X}_q(r) = - \sum_{q'} \sum_{L = |q - q'|} \frac{1}{N_q} \Theta_{qq}^L \tilde{W}_{qq}^L(r) \tilde{\Psi}_q^a(r) \\
X_v^a(r) = - \sum_{q = v} \sum_{L = |v - L|} \frac{1}{N_v} \Theta_{qv}^L W_{qv}^{aL}(r) \sum_{ia} \left| \tilde{\Psi}_q^a \right| P_i^a \phi_i^a(r) - \sum_c \sum_{L = |c - L|} \frac{1}{N_v} \Theta_{vc}^L \tilde{W}_{cv}^L(r) \Psi_c(r) \\
\tilde{X}_v^a(r) = - \sum_{q} \sum_{L = |v - L|} \frac{1}{N_v} \Theta_{qv}^L \tilde{W}_{qv}^L(r) \sum_{ia} \left| \tilde{\Psi}_q^a \right| P_i^a \tilde{\phi}_i^a(r) - \sum_c \sum_{L = |c - L|} \frac{1}{N_v} \Theta_{vc}^L \tilde{W}_{cv}^L(r) \tilde{\Psi}_c(r) 
\end{cases}. \quad (6.16)$$

And its PAW representation is:

$$X_q(r) = \tilde{X}_q(r) + \sum_{ai} \left( X_v^a(r) - \tilde{X}_v^a(r) \right). \quad (6.17)$$
6.2 Unscreening Procedure

The unscreening procedure is similar to the procedure to obtain $\tilde{V}_x(r)$, $V^a_x(r)$ and $\tilde{V}^a_x(r)$, which will be explained in detail in the subsequent section. The difference is that here $\tilde{V}_{xq}$ and $\tilde{U}_{xq}$ are already known values from all-electron reference configuration calculations, therefore is no need to solve the linear equations. The three terms on left hand side of the following equations can be obtained easily:

\[
\begin{align*}
\tilde{V}_x &= \sum_q N_q \tilde{X}_q \tilde{\Psi}_q \frac{\tilde{\rho}_q}{\rho} + \sum_q (\tilde{V}_{xq} - \tilde{U}_{xq}) \frac{N_q \tilde{\Psi}_q^2}{\rho} \\
V^a_x &= \sum_q N_q X^a_q \Psi^a_q \frac{\rho^2}{\rho^a} + \sum_c (\tilde{V}_{xq} - \tilde{U}_{xq}) \frac{N_q \Psi^a_q^2}{\rho^a} \\
\tilde{V}^a_x &= \sum_q N_q \tilde{X}_q \tilde{\Psi}_q \frac{\rho^2}{\rho^a} + \sum_q (\tilde{V}_{xq} - \tilde{U}_{xq}) \frac{N_q \tilde{\Psi}_q^2}{\rho^a}
\end{align*}
\]

Therefore $\tilde{V}_{loc}(r)$ can be obtained as following:

\[
\tilde{V}_{loc} = V^{PS} - \int \frac{\tilde{\rho}(r') + \hat{\rho}(r')}{|r - r'|} - \tilde{V}_x(r) = V^{PS} - \tilde{V}_{val} - \tilde{V}_{core} - \hat{\rho} - \tilde{V}_x
\]

where:

\[
\tilde{\rho}(r) = \tilde{\rho}_{val}(r) + \tilde{\rho}_{core}(r)
\]

And:

\[
\hat{\rho}(r) = (-Z^a + Q^a_{core} - \tilde{Q}^a_{core} + \sum W^a_{ij} n^a_{lmnlm} g_{00}^a)
\]
6.3 Solving $\tilde{V}_x$, $V^a_x$ and $\tilde{V}^a_x$ self consistently

The working formula for solving Atompaw KLI exchange potential can be written as:

$$
\begin{align*}
\tilde{V}_x &= \sum_q N_q \frac{\tilde{X}_q \tilde{\Psi}_q}{\tilde{\rho}} + \sum_q (\tilde{V}_{xq} - \tilde{U}_{xq}) \frac{N_q \tilde{\Psi}_q^2}{\tilde{\rho}} \\
V^a_x &= \sum_q N_q \frac{X^a_q \Psi^a_q}{\rho^a} + \sum_c (\tilde{V}_{xq} - \tilde{U}_{xq}) \frac{N_q \Psi^a_q}{\rho^a} \\
\tilde{V}^a_x &= \sum_q N_q \frac{\tilde{X}^a_q \tilde{\Psi}^a_q}{\tilde{\rho}^a} + \sum_q (\tilde{V}_{xq} - \tilde{U}_{xq}) \frac{N_q \tilde{\Psi}^a_q}{\tilde{\rho}^a} \\
\tilde{V}_{xL} + \tilde{V}^a_{xL} - \tilde{V}^a_{xL} &= \tilde{U}_{xL}
\end{align*}
$$

(6.22)

Since the both sides contain the unknown exchange potential, we multiply by wavefunction squared on each side, and integrate over the designated range to yield:

$$
\begin{align*}
\tilde{V}_{xp} &= \sum_q N_q \int \frac{\tilde{X}_q \tilde{\Psi}_q^2}{\tilde{\rho}} dr + \sum_q (\tilde{V}_{xq} + \tilde{V}_{xp} - \tilde{V}_{xq} - \tilde{U}_{xq}) \int \frac{N_q \tilde{\Psi}_q^2}{\tilde{\rho}} dr \\
\tilde{V}^a_{xp} &= \sum_q N_q \int \frac{X^a_q \Psi^a_q \Psi^2_p}{\rho^a} dr + \sum_q (\tilde{V}_{xq} + \tilde{V}^a_{xq} - \tilde{V}_{xq} - \tilde{U}_{xq}) \int \frac{N_q \Psi^a_q \Psi^2_p}{\rho^a} dr \\
\tilde{V}^a_{xp} &= \sum_q N_q \int \frac{\tilde{X}^a_q \tilde{\Psi}^a_q \tilde{\Psi}^2_p}{\tilde{\rho}^a} dr + \sum_q (\tilde{V}_{xq} + \tilde{V}^a_{xq} - \tilde{V}^a_{xq} - \tilde{U}_{xq}) \int \frac{N_q \tilde{\Psi}^a_q \tilde{\Psi}^2_p}{\tilde{\rho}^a} dr
\end{align*}
$$

(6.23)

we further define:

$$
\begin{align*}
\tilde{\Gamma}_{pq} &= \int N_q \frac{\tilde{\Psi}_q^2 \tilde{\Psi}_p^2}{\tilde{\rho}} dr \\
\Gamma^a_{pq} &= \int \frac{N_q \Psi^a_q \Psi^2_p}{\rho^a} dr \\
\tilde{\Gamma}^a_{pq} &= \int \frac{N_q \tilde{\Psi}^a_q \tilde{\Psi}^2_p}{\tilde{\rho}^a} dr
\end{align*}
$$

(6.24)

and

$$
\begin{align*}
\tilde{\Xi}_p &= \sum_q N_q \int \frac{\tilde{X}_q \tilde{\Psi}_q \tilde{\Psi}^2_p}{\tilde{\rho}} dr \\
\Xi^a_p &= \sum_q N_q \int \frac{X^a_q \Psi^a_q \Psi^2_p}{\rho^a} dr \\
\tilde{\Xi}^a_p &= \sum_q N_q \int \frac{\tilde{X}^a_q \tilde{\Psi}^a_q \tilde{\Psi}^2_p}{\tilde{\rho}^a} dr
\end{align*}
$$

(6.25)
Notice that the only variable needed in order to get $\overline{V}_{xq}^\alpha$, $\overline{V}_{xq}^a$, $\overline{V}_{xq}$ is the sum of the three on the RHS, therefore, rather than solving three set of equations separately, we added all three equations together to become:

\[
\nabla_{xp} = (\Xi_p + \Xi_p^a - \Xi_p^a) + \sum_q (\nabla_{xq} - U_{xq})(M_{pq} + M_{pq}^a - M_{pq}^a).
\]

(6.26)

Or

\[
\nabla_{xp} = \Xi_p + \sum_q (\nabla_{xq} - U_{xq})M_{pq}.
\]

(6.27)

Then regroup the terms so that the unknowns are all on the LHS:

\[
\sum_q (\delta_{pq} - M_{pq})\nabla_{xq} = \Xi_p - \sum_q U_{xq}M_{pq}.
\]

(6.28)

Again here we are forcing the outermost orbital to have: $\nabla_{xL} = U_{xL}$. And we avoid the rank deficiency by replacing the row corresponding to the outermost one with its exact value:

\[
\begin{bmatrix}
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
\nabla_{xL}
\end{bmatrix}
= \begin{bmatrix}
U_{xL}
\end{bmatrix}.
\]

(6.29)

We include several solved pseudo exchange potential $\tilde{V}_\alpha(r)$ plots as following:
Figure 6.1: Comparison of all-electron $V_x(r)$ and pseudo $\tilde{V}_x(r)$ local exchange potential for C in ground state.
Figure 6.2: Comparison of all-electron $V_x(r)$ and pseudo $\tilde{V}_x(r)$ local exchange potential for P in ground state.
Figure 6.3: Comparison of all-electron $V_x(r)$ and pseudo $\tilde{V}_x(r)$ local exchange potential for Fe in ground state.
7 Conclusion

In this thesis, we primarily investigate and implement various schemes of orbital dependent exchange functional as an ingredient of electronic structure calculations. In section (2.2), section (2.5) and section (2.7) we reviewed formalism of all-electron Hartree-Fock, Optimized Effective Potential method and KLI approximation, and present our own implementation of HF, OEP and KLI in section (2.3), section (2.6) and section (2.8). The results are presented in Appendix (B.1)(B.2). In terms of frozen-core calculations, we developed two different schemes in section (3.2.2); the Frozen-core potential approximation in section (3.2.1) and the Frozen-core orbital approximation section (3.2.2). Comparing the accuracy of the two schemes, we conclude that the frozen-core orbital approximation is more suitable for orbital dependent exchange functional based on the numerical evidence in section (3.2). This scheme provides us insights of how to accurately represent core effects in solids, and this scheme is applied to subsequent OEP and KLI numerical investigations.

Furthermore, based on all-electron and frozen-core calculations, we further incorporated these orbital dependent exchange functional scheme into the PAW formalism and incorporated them into the Atompaw code. We have derived the necessary equations the PAW-HF, PAW-OEP and PAW-KLI formalisms in chapters (4, 5, 6). For all three formalisms, we also presented bases, and projectors, and test results of various elements across the periodic table. These results for atoms are going to be used as basis for solid calculations which will appear in a future publication.
A Additional Expressions

A.1 Inhomogeneous equation for $g_p(r)$

This part gives derivation of equation (2.59). Starting from the derivative of object function with respect to the wavefunction (2.58):

$$\frac{\delta F}{\delta \psi_p^*(r)} = \frac{\delta E}{\delta \psi_p^*(r)} - \lambda_p \psi_p - (H_{KS} - \varepsilon_p) g_p(r).$$  \hfill (A.1)

$E_{tot}$ can be written as:

$$E_{tot} = \sum_p N_p (\langle \psi_p | T + V_N | \psi_p \rangle) + E_x + E_H,$$  \hfill (A.2)

take Hartree Energy’s derivative with respect to $\psi_p^*(r)$ would yield $V_H(r)\psi_p(r)$. Therefore:

$$\frac{\delta E}{\delta \psi_p^*(r)} = (T + V_N(r) + V_H(r))\psi_p(r) + \frac{\delta E_x}{\delta \psi_p^*(r)},$$  \hfill (A.3)

According to (2.33):

$$(T + V_N(r) + V_H(r))\psi_p(r) = (\varepsilon_p - V_x(r))\psi_p(r),$$  \hfill (A.4)

substitute the right hand side of (A.4) back into (2.58) we arrived at:

$$(H_{KS} - \varepsilon_p) g_p(r) = (\varepsilon_p - \lambda_p) \psi_p(r) - V_x(r) \psi_p(r) + \frac{\delta E_x}{\delta \psi_p^*(r)};$$  \hfill (A.5)

define $(\varepsilon_p - \lambda_p)$ to be $U_p$. To obtain $U_p$: multiply both sides by $\psi_p^*(r)$ and integrate over r:

$$U_p = -\langle \psi_p | V_x | \psi_p \rangle + \left< \psi_p \left| \frac{\delta E_x}{\delta \psi_p^*} \right. \right>, \hfill (A.6)$$

therefore, we end up with the differential equation (2.57) for auxiliary function:

$$(H_{KS} - \varepsilon_p) g_p(r) = \frac{\delta E_x}{\delta \psi_p^*(r)} - V_x(r) \psi_p - U_p \psi_p(r).$$  \hfill (A.7)
A.2 Some derivation of KLI approximation

This section gives a brief justification on why the second terms of (2.93) can be omitted under a mean field approximation.

According to (2.93), we need to prove:

\[ \sum_p N_p \psi_p(r)[-K_p + \varepsilon_p]g^*_p(r) = - \sum_p N_p \frac{d}{dr}(g^*_p(r) \frac{d}{dr} \psi_p(r)). \]  \hspace{1cm} (A.8)

First of all, it’s obvious that:

\[ \sum_p N_p \psi_p(r)[-K_p + \varepsilon_p]g^*_p(r) = \sum_p (-N_p \psi_p K_p g^*_p(r) + N_p \varepsilon_p \psi_p(r) g^*_p(r)). \]  \hspace{1cm} (A.9)

Given the Kohn-Sham equation (2.33), it’s also true that:

\[ [K_p \psi_p(r) + V_s(r) \psi_p(r)]g^*_p(r) = \varepsilon_p \psi_p(r) g^*_p(r). \]  \hspace{1cm} (A.10)

Therefore (A.9) becomes:

\[ \sum_p N_p \psi_p(r)[-K_p + \varepsilon_p]g^*_p(r) = \sum_p (-N_p \psi_p K_p g^*_p(r) + N_p g^*_p K_p \psi_p(r)) + \sum_p N_p V_s(r) \psi_p(r) g^*_p(r). \]  \hspace{1cm} (A.11)

According to the OEP Integral equation \( \sum_p N_p g^*_p(r) \psi_p(r) = 0 \) it’s easy to see that:

\[ \sum_p N_p V_s(r) \psi_p(r) g^*_p(r) = V_s(r) \sum_p N_p \psi_p(r) g^*_p(r) = 0. \]  \hspace{1cm} (A.12)

Consequently, (2.93) becomes

\[ \sum_p N_p \psi_p(r)[-K_p + \varepsilon_p]g^*_p(r) = \sum_p (-N_p \psi_p K_p g^*_p(r) + N_p g^*_p K_p \psi_p(r)). \]  \hspace{1cm} (A.13)

According to the OEP integral equation, it’s also true that:

\[ 0 = -K_p \sum_p N_p g^*_p(r) \psi_p(r) = - \sum_p N_p K_p g^*_p(r) \psi_p(r) \]

\[ = \sum_p [-\psi_p K_p g^*_p - g^*_p K_p \psi_p + \frac{\hbar^2}{m} \frac{dg^*_p}{dr} \frac{d\psi_p}{dr}]. \]  \hspace{1cm} (A.14)

Adding (A.13) and (A.14), we obtain:

\[ \sum_p (-N_p \psi_p K_p g^*_p + N_p g^*_p K_p \psi_p) + \sum_p N_p [\psi_p K_p g^*_p + g^*_p K_p \psi_p - \frac{\hbar^2}{m} \frac{dg^*_p}{dr} \frac{d\psi_p}{dr}] \]

\[ = - \sum_p 2N_p g^*_p K_p \psi_p - \frac{N_p \hbar^2}{m} \frac{dg^*_p}{dr} \frac{d\psi_p}{dr} \]

\[ = - \sum_p N_p \frac{\hbar^2}{m} \frac{d}{dr}(g^*_p \frac{d\psi_p}{dr}). \]  \hspace{1cm} (A.15)
And it is obviously that the space average of this terms equals zero, therefore provides the justification of neglecting this term as an approximation.
A.3 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 [38, 22, 20, 47]. 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. (4.10) takes the form

\[ \tilde{E}_{\text{valenx}} = \tilde{E}_K^v + \tilde{E}_N^v + \tilde{E}_H^v + \tilde{E}_H^{vv}. \]  

(A.16)

here the kinetic energy contribution is given by

\[ \tilde{E}_K^v = \sum_v N_v \left< \tilde{\Psi}_v \left| K \right| \tilde{\Psi}_v \right>. \]  

(A.17)

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

\[ \tilde{E}_N^v + \tilde{E}_H^{cv} = \int dr \tilde{V}_j^a(r) \tilde{n}_v(r), \]  

(A.18)

where

\[ \tilde{V}_j^a(r) \equiv \tilde{V}_{\text{loc}}^a(r) + \tilde{V}_{\text{core}}^a(r) + ( -Z^a + Q_{\text{core}}^a - \tilde{Q}_{\text{core}}^a ) \tilde{v}_0^a(r) \]  

(A.19)

and

\[ \tilde{n}_v(r) \equiv \sum_v N_v \left| \tilde{\psi}_v \right|^2. \]  

(A.20)

Here \( \tilde{V}_{\text{loc}}^a(r) \) 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

\[ \tilde{v}_0^a(r) \equiv e^2 \int dr' \frac{\tilde{n}_0^a(r')}{r} \text{ with } \tilde{n}_c^a(r) \equiv \sum_c N_c \left| \tilde{\psi}_c^a(r) \right|^2. \]  

(A.21)

The long range contribution of the nuclear and core electron charges is given by the last term of Eq. (A.19), where the compensation charge potential is defined in terms of the functional form defined in Eq. (4.12)

\[ \tilde{v}_0^c(r) \equiv e^2 \int dr' \frac{g_0^c(r')}{r}. \]  

(A.22)

with

\[ Q_{\text{core}}^a = \int dr n_c^a(r) \text{ and } \tilde{Q}_{\text{core}}^a = \int dr \tilde{n}_c^a(r). \]  

(A.23)
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. (4.19)

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

(A.24)

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

\[
(E_{\text{vale}}^0 - \tilde{E}_{\text{vale}}^0)_{nx} = \sum_{ij} \sum_v N_v \left( \tilde{\Psi}_v \mid \tilde{P}^a_i \right) \left( \tilde{P}^a_j \mid \tilde{\Psi}_v \right) \left( K^a_{ij} + [V^a_{ij}] + \frac{1}{2} [V_{H}^{\text{avv}}]_{ij} \right)
\]  

(A.25)

The kinetic energy contribution is

\[
K_{ij}^a \equiv \langle \Phi_i \mid K \mid \Phi_j \rangle - \langle \tilde{\Phi}_i \mid K \mid \tilde{\Phi}_j \rangle
\]  

(A.26)

The nuclear and core electron contribution is given by

\[
[V^a_{f}]_{ij} \equiv \langle \Phi_i \mid V^a_{f} \mid \Phi_j \rangle - \langle \tilde{\Phi}_i \mid \tilde{V}^a_{f} \mid \tilde{\Phi}_j \rangle
\]  

(A.27)

where

\[
V^a_{f}(r) \equiv -\frac{Z^a e^2}{r} + V^a_{H}(r).
\]  

(A.28)

The valence-valence Hartree interactions may be evaluated

\[
[V_{H}^{\text{avv}}]_{ij} \equiv \sum_{kl} \sum_{v'v} N_{v'} \left( \tilde{\Psi}_{v'} \mid \tilde{P}^a_k \right) \left( \tilde{P}^a_l \mid \tilde{\Psi}_{v'} \right) \left( R_{ijkl}^{0} - \tilde{R}_{ijkl}^{0} \right),
\]  

(A.29)

where the interaction integrals were defined in Eqs. (4.22) and (4.23).

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. (5.4)) and Hartree-Fock (Eq. (5.6)) Hamiltonian can be written in the form

\[
(D^a_{ij})_{nx} = [K^a_{ij}] + [V^a_{f}]_{ij} + [V_{H}^{\text{avv}}]_{ij} + [V^a_{0}]_{ij}
\]  

(A.31)

where the last term comes from the compensation charge contributions in Eq. (A.24):
A.4 Simplified expressions for core matrix elements.

When the core orbital is localized so that the corresponding pseudo-core orbital can be set to zero: \( \tilde{\psi}_c^a(r) \equiv 0 \), many of the expressions presented in Sect. 4.1 simplify. For example, the charge moment coefficient (4.15) takes the form

\[
m_{ic}^{aL} = \int dr r^L \phi_i^a(r) \psi_c^a(r)。
\] (A.33)

The pseudo-core-valence contributions to exchange energy can be written

\[
\tilde{R}_{iccv}^{L} = \sum_{aij} \langle \tilde{\psi}_v^HF_i | \tilde{p}_a \rangle \langle \tilde{p}_j | \tilde{\psi}_v^HF_j \rangle M_{iccj}^{aL}.
\] (A.34)

where

\[
M_{iccj}^{aL} \equiv e^2 \int \int drdr' r_r^L L+1 a^a_{ic}(r) a^a_{cj}(r')
\] (A.35)

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. (4.21) as defined by extending Eq. (4.23) to core states becomes

\[
\tilde{R}_{iccj}^{aL} = M_{iccj}^{aL},
\] (A.36)

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

\[
\tilde{E}_{cv}^x + \sum_a (E_{acv}^x - \tilde{E}_{x}^{acv}) = -\sum_{vc} \sum_{L=|l_v-l_c|\ldots|l_v+l_c|} \Theta_{vc}^L \sum_{aij} \langle \tilde{\psi}_v^HF_i | \tilde{p}_a \rangle \langle \tilde{p}_j | \tilde{\psi}_v^HF_j \rangle R_{icvj}^{aL},
\] (A.37)

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 \( \Theta_{vcq}^L \) defined in Eq. (2.15) will also be modified.

The self-consistent PAW-Hartree-Fock equations (4.24) can, in principle contain a contribution from localized core states if the Lagrange multiplier \( |\lambda_{cv}| > 0 \), since the extended overlap operator reduces to

\[
O_{HF}^{PAW} \tilde{\psi}_c^HF \rightarrow \sum_{ai} \tilde{p}_a \rangle O_a^{ic} \tilde{\psi}_c^H.
\] (A.38)

where \( O_a^{ic} \equiv m_{ic}^{a0} \). 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 \( O_a^{ic} = 0 \), otherwise \( O_a^{ic} \) may be non-zero.
While the pseudo-exchange kernel function $\tilde{X}_v(r)$ defined in Eq. (4.30) has no contributions from localized core states, the one-center matrix element for the pseudo-exchange kernel function $X^a_{iv}$ defined in Eq. (4.32) does have localized core state contributions. While the valence-valence terms of Eq. (4.32) 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,

$$X^a_{ivvc} = -\sum_c \sum_{L=\|l_v-l_c\|\cdots\|l_v+l_c\|} \frac{1}{N_v} \Theta_{vc} \sum_j \left\langle \tilde{P}_j^a \right| \tilde{\Psi}_{HF} \left| R_{iccj} \right\rangle R_{c_ic}$$. (A.39)

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. (4.26), 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. (4.26) is used also to calculate the denominator term $\left\langle \tilde{\Psi}_{c'}^H \left| O_{HF}^{PAW} \right| \tilde{\Psi}_c^H \right\rangle$. 

A.5 Atompaw KLI Energy Expression

In order to solve Atompaw KLI Schrödinger Equation, KLI PAW energy expression needs to be obtained first before the PAW Hamiltonian can be derived. In this section, details of working KLI PAW energy expression are provided:

A.5.1 Exchange Energy

The exchange energy between p and q orbital, here p and q can represent either core or valence orbitals.

\[ E_{pq}^x = \tilde{E}_{pq}^x + (E_{x}^{a,pq} - \tilde{E}_{x}^{a,pq}), \tag{A.40} \]

here:

\[ \tilde{E}_{pq}^x = - \sum_{pq} \sum_{L} \frac{1}{2} \Theta_{pq}^{L} \tilde{R}_{pq,pp}, \tag{A.41} \]

where

\[ \tilde{R}_{pq,pp}^{L} = e^2 \int \int dr dr' \frac{r_{pq}^{L}}{r_{pq}^{L} + 1} (\tilde{\Psi}_{q}(r)\tilde{\Psi}_{q}(r) + \tilde{\Psi}_{p}(r')\tilde{\Psi}_{q}(r') + \tilde{\Psi}_{p}(r'')), \tag{A.42} \]

and

\[ (E_{x}^{a,pq} - \tilde{E}_{x}^{a,pq}) = - \sum_{apq} \sum_{ijkl} \frac{1}{2} \Theta_{pq}^{L} \sum \langle \tilde{\Psi}_{p} | p_{i}^{a} \rangle \langle p_{i}^{a} | \tilde{\Psi}_{q} \rangle \langle \tilde{\Psi}_{p} | p_{j}^{a} \rangle \langle p_{j}^{a} | \tilde{\Psi}_{q} \rangle \left( R_{ijkl}^{aL} - \tilde{R}_{ijkl}^{aL} \right), \tag{A.43} \]

where

\[ R_{ijkl}^{aL} = e^2 \int \int dr dr' \frac{r_{pq}^{L}}{r_{pq}^{L} + 1} \phi_{i}^{a}(r)\phi_{j}^{a}(r)\phi_{k}^{a}(r')\phi_{l}^{a}(r''), \tag{A.44} \]

and

\[ \tilde{R}_{ijkl}^{aL} = e^2 \int \int dr dr' \frac{r_{pq}^{L}}{r_{pq}^{L} + 1} (\tilde{\phi}_{i}^{a}(r)\tilde{\phi}_{j}^{a}(r) + \tilde{\phi}_{i}^{a}(r')\tilde{\phi}_{j}^{a}(r'') + \tilde{\phi}_{i}^{a}(r')\tilde{\phi}_{j}^{a}(r'') + \tilde{\phi}_{i}^{a}(r')\tilde{\phi}_{j}^{a}(r'')). \tag{A.45} \]
A.5.2 Hartree Energy

Unlike the previous PAW formalism, the total Hartree Energy includes both core and valence electron interaction.

\[ E_H = \tilde{E}_H + (E_H^a - \tilde{E}_H^a), \quad (A.46) \]

where

\[ \tilde{E}_H = \frac{1}{2} \int \int \frac{\tilde{n}_v + \tilde{n}_c + \tilde{n})(\tilde{n}_v + \tilde{n}_c + \tilde{n})}{|r - r'|} dr dr' = \frac{1}{2} \int \int \frac{\tilde{n} + \tilde{n})(\tilde{n} + \tilde{n})}{|r - r'|} dr dr', \quad (A.47) \]

and \( \tilde{n} = \tilde{n}_v + \tilde{n}_c \),

\[ E_H^a = \frac{1}{2} \int \int \frac{(n_v^a + n_{v,\text{core}}^a)(n_v^a + n_{v,\text{core}}^a)}{|r - r'|} dr dr' = \frac{1}{2} \int \int \frac{n^a(r)n^a(r')}{|r - r'|} dr dr', \quad (A.48) \]

where \( n^a = n_v^a + n_{v,\text{core}}^a \).

\[ \tilde{E}_H^a = \frac{1}{2} \int \int \frac{\tilde{n}_v^a + \tilde{n}_{v,\text{core}}^a + \tilde{n})(\tilde{n}_v^a + \tilde{n}_{v,\text{core}}^a + \tilde{n})}{|r - r'|} dr dr' = \frac{1}{2} \int \int \frac{\tilde{n} + \tilde{n})(\tilde{n} + \tilde{n})}{|r - r'|} dr dr', \quad (A.49) \]

and \( \tilde{n}^a = \tilde{n}_v^a + \tilde{n}_{v,\text{core}}^a \)

Particularly, the compensation charge can be evaluated as:

\[ \tilde{n}(r) = \sum_{q,ij} N_q \langle \tilde{\Psi}_q | P_i \rangle \langle P_j | \tilde{\Psi}_q \rangle \tilde{m}_i^L(r) \quad (L = 0). \]

Together one center Hartree Energy can be written as

\[ \frac{1}{2} \int \int \frac{n^a(r)n^a(r')}{|r - r'|} dr dr' - \frac{1}{2} \int \int \frac{\tilde{n}^a + \tilde{n})(\tilde{n} + \tilde{n})}{|r - r'|} dr dr', \quad (A.50) \]

where

\[ \left\{ \begin{aligned} n^a &= \sum_q N_q \Psi_q^a \Psi_q^a \sum_{q,ij} N_q \langle \tilde{\Psi}_q | P_i \rangle \langle P_j | \tilde{\Psi}_q \rangle \phi^a_i \phi^a_j, \\ \tilde{n}^a &= \sum_q N_q \tilde{\Psi}_q^a \tilde{\Psi}_q^a = \sum_{q,ij} N_q \langle \tilde{\Psi}_q | P_i \rangle \langle P_j | \tilde{\Psi}_q \rangle \tilde{m}_i^L(r) \tilde{m}_j^L(r) \quad (L = 0). \end{aligned} \right\} \quad (A.51) \]

And therefore

\[ \frac{e^2}{2} \int \int \frac{n^a(r)n^a(r')}{|r - r'|} dr dr' - \frac{e^2}{2} \int \int \frac{\tilde{n}^a + \tilde{n})(\tilde{n} + \tilde{n})}{|r - r'|} dr dr', \quad (A.52) \]

\[ = \frac{e^2}{2} \sum_p \sum_{ij} N_p \langle \tilde{\Psi}_p | P_i \rangle \langle P_j | \tilde{\Psi}_p \rangle [V_H^a]_{ij}. \]
Here, Hartree matrix element \([V^a_H]_{ij}\) is defined as

\[
[V^a_H]_{ij} = \sum_{kl} \sum_q N_q \langle \tilde{\Psi}_q | P_k \rangle \langle P_l | \tilde{\Psi}_q \rangle (R^a_{ijkl} - \tilde{R}^a_{ijkl})
\]

This grouping is different from previous PAW formalism.

### A.5.3 Kinetic Energy

Total Kinetic Energy:

\[
E_K = E_{\tilde{K}} + E^a_K - \tilde{E}^a_K,
\]

where

\[
E_{\tilde{K}} = -\frac{\hbar^2}{2m} \sum_q N_q \langle \tilde{\Psi}_q | \nabla^2 | \tilde{\Psi}_q \rangle,
\]

and

\[
E^a_K - \tilde{E}^a_K = \sum_q \sum_{ij} N_q \langle \tilde{\Psi}_q | P_i \rangle \langle P_j | \tilde{\Psi}_q \rangle (\frac{-\hbar^2}{2m}) \int [\phi_i(d^2/dr^2 - \frac{l_i(l_i + 1)}{r^2})\phi_j - \bar{\phi}i(d^2/dr^2 - \frac{l_i(l_i + 1)}{r^2})\bar{\phi}j]dr.
\]

### A.5.4 Nuclear-Electron interaction energy and \(E_{V_{\text{loc}}}\)

Nuclear-Electron interaction energy:

\[
E_N = \tilde{E}_N + (E^a_N - \tilde{E}^a_N),
\]

where

\[
\tilde{E}_N = \int -Z\hat{V}_0(r)\tilde{n}(r) dr.
\]

Here \(\hat{V}_0(r) = e^2 \int dr' \frac{\tilde{g}_0(r)}{r'}\)

And

\[
E^a_N = \int -\frac{Ze^2}{r} n^a(r) dr.
\]

\[
\tilde{E}^a_N = \int -Z\hat{V}_0(r)\tilde{n}^a(r) dr.
\]

\(E_{v_{\text{loc}}}\) can be written as:

\[
E_{v_{\text{loc}}} = \tilde{E}_{v_{\text{loc}}} - \tilde{E}^a_{v_{\text{loc}}},
\]

where

\[
\tilde{E}_{v_{\text{loc}}} = \int V_{\text{loc}}(r)\tilde{n}(r) dr,
\]

\[
E_{v_{\text{loc}}} = \int V_{\text{loc}}(r)\tilde{n}(r) dr.
\]
\[ \tilde{E}_{\text{vloc}}^a = \int V_{\text{loc}}(r)\tilde{n}^a(r) dr. \] 

(A.62)

To sum up, the total PAW KLI energy expression can be written as:

\[ E_{\text{all}} = E_N + E_K + E_H + E_X + \tilde{E}_{\text{vloc}} - \tilde{E}_{\text{vloc}}^a \]
A.6 Atompaw KLI Hamiltonian

From section (A.5), we obtain the total Atompaw KLI energy expression:

\[ E_{\text{all}} = E_N + E_K + E_H + E_X + \tilde{E}_{\text{veloc}} - \tilde{E}_{\text{veloc}}^a. \]  

(A.63)

And the PAW Hamiltonian \( H^{PAW} \) comes from taking the derivative of total energy with respect to the pseudo-density:

\[ H^{PAW} = \frac{\partial E_{\text{all}}}{\partial \tilde{n}(r)} = \frac{\partial E_{\text{all}}}{\partial \tilde{n}(r)} \bigg| \tilde{n} + \int \frac{\partial E_{\text{all}}}{\partial \tilde{n}(r')} \frac{\partial \tilde{n}(r')}{\tilde{n}(r)} dr'. \]  

(A.64)

And according to the definition of exchange potential:

\[ V_x \equiv \frac{\partial E_{\text{x}}}{\partial n(r)}. \]  

(A.65)

Taking the derivatives

**The Derivative of \( E_N \)**

\[ E_N = \tilde{E}_N + (E_N^a - \tilde{E}_N^a) = - \int Z\tilde{V}_0(r)\tilde{n}(r) dr - \int \frac{Ze^2}{r}n^a(r) dr + \int Z\tilde{V}_0(r)\tilde{n}^a(r) dr \]

\[ \left\{ \begin{array}{l} \frac{\partial E_{\text{all}}}{\partial \tilde{n}(r')} = 0 \\ \frac{\partial E_N}{\partial \tilde{n}_{\text{elec}}(r)} \bigg| \tilde{n} = -Z\tilde{V}_0(r) - \sum_{ij} \langle P_i | P_j | \left[ \left\langle \phi_i^a \right| \frac{Ze^2}{r} \right\rangle \phi_j^a \rangle - \left\langle \phi_i^a \right| Z\tilde{V}_0(r) \left| \phi_j^a \right\rangle \end{array} \right\} \]

**The derivative of \( E_{\text{veloc}} \)**

\[ E_{\text{veloc}} = \tilde{E}_{\text{veloc}} - \tilde{E}_{\text{veloc}}^a = \int V_{\text{loc}}(r)\tilde{n}(r) dr - \int V_{\text{loc}}(r)\tilde{n}^a(r) dr \]

\[ \left\{ \begin{array}{l} \frac{\partial E_{\text{veloc}}}{\partial \tilde{n}(r')} = 0 \\ \frac{\partial E_{\text{veloc}}}{\partial \tilde{n}_{\text{elec}}(r)} \bigg| \tilde{n} = V_{\text{loc}}(r) - \sum_{ij} \langle P_i | P_j | \left\langle \tilde{n}^a \right| V_{\text{loc}}(r) \left| \tilde{n}^a \right\rangle \end{array} \right\} \]
The derivative of $E_K$

\[
E_K = \tilde{E}_K + E_K^a - \tilde{E}_K^a
\]

\[
\left\{ \begin{array}{l}
\frac{\partial E_K}{\partial \hat{n}(r')} = 0 \\
\frac{\partial E_K}{\partial \hat{n} \text{out}(r)}|_{\hat{n}} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{\hbar^2}{2m} \sum_{ij} |P_i\rangle \langle P_j| \left[ (\phi_i^a| V_x^a | \phi_j^a) - (\tilde{\phi}_i^a| \tilde{V}_x^a | \tilde{\phi}_j^a) \right] \\
\end{array} \right.
\]

The derivative of $E_x$

\[
E_x = \tilde{E}_x + E_x^a - \tilde{E}_x^a
\]

\[
\left\{ \begin{array}{l}
\frac{\partial E_x}{\partial \hat{n}(r')} = 0 \\
\frac{\partial E_x}{\partial \hat{n} \text{out}(r)}|_{\hat{n}} = \tilde{V}_x(r) + \sum_{ij} |P_i\rangle \langle P_j| \left[ V_x^a \right]_{ij} \\
\end{array} \right.
\]

The derivative of $E_H$

\[
E_H = \tilde{E}_H + (E_H^a - \tilde{E}_H^a)
\]

\[
\frac{\partial E_H}{\partial \hat{n}(r')} = \int \frac{(\tilde{n} + \hat{n})}{|r - r'|} dr' + \sum_{ij} |P_i\rangle \langle P_j| [V_H^a]_{ij} \\
= \tilde{V}_H + \sum_{ij} |P_i\rangle \langle P_j| [V_H^a]_{ij}
\]

where

\[
\int \frac{(\tilde{n} + \hat{n})}{|r - r'|} dr' = \sum_q N_q \tilde{W}_q^0
\]

and

\[
\int \frac{\partial E_H}{\partial \hat{n}(r')} \frac{\partial \hat{n}(r')}{\partial \hat{n}(r)} dr' = \int \frac{\partial \tilde{E}_H}{\partial \hat{n}(r')} \frac{\partial \hat{n}(r')}{\partial \hat{n}(r)} dr'
\]
Because:

\[ \hat{n}(r') = \sum_{q,i,j} N_q \langle \Psi_q | P_i \rangle \langle P_j | \Psi_q \rangle \hat{m}^0_{ij}(r') \]

\[ \frac{\partial \hat{n}(r')}{\hat{n}(r)} = \sum_{ij} |P_i \rangle \langle P_j | \hat{m}^0_{ij}(r') \]

\[ \frac{\partial E_H}{\partial \hat{n}(r')} = \int \frac{(\hat{n} + \tilde{n})}{|r' - r''|} dr'' \]

Therefore:

\[ \int \frac{\partial \tilde{E}_H}{\partial \tilde{n}(r')} \frac{\partial \hat{n}(r')}{\tilde{n}(r')} dr' = \sum_{ij} |P_i \rangle \langle P_j | m^0_{ij} \int \int dr' \hat{m}^0_{ij}(r') \frac{(\tilde{n} + \hat{n})}{|r' - r''|} dr'' \]

\[ = \sum_{ij} |P_i \rangle \langle P_j | m^0_{ij} \int \int dr' g_0(r') \frac{(\tilde{n} + \hat{n})}{|r' - r''|} dr'' \]

\[ = \sum_{ij} |P_i \rangle \langle P_j | m^0_{ij} \int \tilde{V}^a_0(\tilde{n} + \hat{n}) dr \text{ where } \tilde{n} = \sum_q N_q \tilde{M}^0_{qq} \]

(A.69)

To sum up:

\[ H^{PAW} = \tilde{H} + \sum_{ij} |P_i \rangle D_{ij} \langle P_j | \]

\[ \tilde{H} = -\frac{\hbar^2}{2m} \nabla^2 + \tilde{V}_{eff} \]

\[ = -\frac{\hbar^2}{2m} \nabla^2 - Z\tilde{V}_0(r) + \tilde{V}_H(r) + \tilde{V}_z(r) + V_{loc}(r) \]

\[ D_{ij} = K_{ij} + [V_f]_{ij} + [V^a_H]_{ij} + [V_z]_{ij} + [V_0]_{ij} \]

\[ [V_f]_{ij} = -\langle \phi_i^a \cdot \frac{Ze^2}{r} \phi_j^a \rangle - \langle \phi_i^a \nabla \tilde{V}_0(r) \rangle \phi_j^a - \langle \phi_i^a V_{loc}(r) \rangle \phi_j^a \]

\[ [V_0]_{ij} = m^0_{ij} \int \tilde{V}^a_0(\tilde{n} + \hat{n}) dr = m^0_{ij} \int \tilde{V}^a_0(\tilde{n} + \sum_q N_q \tilde{M}^0_{qq}) dr \text{ kernel is over the whole range} \]

(A.70)
A.7 Solving Atompaw KLI Schrodinger Equation Self Consistently

Previously Bl"ochl’s separable form of solving the the Schrodinger equation was first tested as PAW KLI Schr"odinger equation solver, and the solution in terms of wave-function is not always stable even for light elements, a relative robust direct method is applied here, by solving the PAWKLI Schr"odinger equation directly, and update the valence orbital only.

The PAWKLI equation:
\[
\left(-\frac{1}{2}\nabla^2 + \tilde{V}_{\text{eff}} - \varepsilon_p\right) |\tilde{\Psi}_p\rangle + \sum_{i,j} \langle \tilde{P}_i | (D_{ij} - \varepsilon dO_{ij}) | \tilde{P}_j \rangle |\tilde{\Psi}_p\rangle = 0, \quad (A.71)
\]

where
\[
\tilde{V}_{\text{eff}}(r) = \tilde{V}_{\text{loc}}(r) + \tilde{V}_N(r) + \tilde{V}_{\text{V}}(r) + \tilde{V}_x(r). \quad (A.72)
\]

The updating scheme is to treat the RHS as knowns, which can be obtained from previous iteration:
\[
\left(-\frac{1}{2}\nabla^2 + \tilde{V}_{\text{eff}} - \varepsilon_p\right) |\tilde{\Psi}_p\rangle = \text{RHS} = -\sum_{i,j} \langle \tilde{P}_i | (D_{ij} - \varepsilon dO_{ij}) | \tilde{P}_j \rangle |\tilde{\Psi}_p\rangle. \quad (A.73)
\]

**The eigenvalue updating Scheme**

Here we only need to update the valence orbital’s eigen energy Given
\[
\varepsilon_p(\tilde{\Psi}_p) + \sum_{ij} \langle \tilde{\Psi}_p | \tilde{P}_i \rangle O_{ij} \langle \tilde{P}_j | \tilde{\Psi}_p \rangle = (-\frac{1}{2}\nabla^2 + \tilde{V}_{\text{eff}}) |\tilde{\Psi}_p\rangle + \sum_{i,j} \langle \tilde{\Psi}_p | \tilde{P}_i \rangle (D_{ij}) \langle \tilde{P}_j | \tilde{\Psi}_p \rangle. \quad (A.74)
\]

Consequently:
\[
\varepsilon_p = \frac{\langle \tilde{\Psi}_p | -\frac{1}{2}\nabla^2 + \tilde{V}_{\text{eff}} | \tilde{\Psi}_p \rangle + \sum_{i,j} \langle \tilde{\Psi}_p | \tilde{P}_i \rangle (D_{ij}) \langle \tilde{P}_j | \tilde{\Psi}_p \rangle}{\langle \tilde{\Psi}_p | \tilde{\Psi}_p \rangle + \sum_{i,j} \langle \tilde{\Psi}_p | \tilde{P}_i \rangle (O_{ij}) \langle \tilde{P}_j | \tilde{\Psi}_p \rangle}. \quad (A.75)
\]
B Numerical Results: All-electron, Frozen Core and Atompaw
### All-electron Hartree-Fock results for atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>NL</th>
<th>Occ</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>1s</td>
<td>2</td>
<td>-9.4503529962</td>
</tr>
<tr>
<td></td>
<td>2s</td>
<td>2</td>
<td>-0.6157090079</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Total Energy</strong> = -29.145920263504312</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Kinetic Energy</strong> = 29.223703381337305</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Ratio (P.E./K.E.)</strong> = -1.997338355210563</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Potential Energy</strong> = -58.369623644841617</td>
</tr>
<tr>
<td>B</td>
<td>1s</td>
<td>2</td>
<td>-15.3695514657</td>
</tr>
<tr>
<td></td>
<td>2s</td>
<td>2</td>
<td>-0.9839515486</td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>1</td>
<td>-0.6154203846</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Total Energy</strong> = -49.057964860682887</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Kinetic Energy</strong> = 49.185036589927776</td>
</tr>
<tr>
<td></td>
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<td><strong>Ratio (P.E./K.E.)</strong> = -1.997416455530890</td>
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<tr>
<td></td>
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<td></td>
<td><strong>Potential Energy</strong> = -98.24301450610663</td>
</tr>
<tr>
<td>C</td>
<td>1s</td>
<td>2</td>
<td>-22.6513740467</td>
</tr>
<tr>
<td></td>
<td>2s</td>
<td>2</td>
<td>-1.4183903253</td>
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<tr>
<td></td>
<td>2p</td>
<td>2</td>
<td>-0.8069546190</td>
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<td><strong>Total Energy</strong> = -75.31914784664023</td>
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<tr>
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<td></td>
<td><strong>Kinetic Energy</strong> = 75.525472467072362</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Ratio (P.E./K.E.)</strong> = -1.997268145253930</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Potential Energy</strong> = -150.844620313736390</td>
</tr>
</tbody>
</table>

Table B.1: Atom Beryllium (Be 2) to Atom Carbon (C 6) using grid point: 2001
<table>
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<tr>
<th>Element</th>
<th>NL</th>
<th>Occ</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>1s 2</td>
<td>-31.338436798</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2s 2</td>
<td>-1.9251127967</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2p 3</td>
<td>-1.012646489</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total Energy</td>
<td>-108.592105474232740</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kinetic Energy</td>
<td>108.809172697680110</td>
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<tr>
<td></td>
<td>Ratio(P.E./K.E.)</td>
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<tr>
<td></td>
<td>Potential Energy</td>
<td>-217.401278171912850</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>1s 2</td>
<td>-41.3458288069</td>
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</tr>
<tr>
<td></td>
<td>2s 2</td>
<td>-2.4994452207</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2p 4</td>
<td>-1.2299520564</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total Energy</td>
<td>-149.538234203997490</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kinetic Energy</td>
<td>149.755018681430100</td>
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</tr>
<tr>
<td></td>
<td>Ratio(P.E./K.E.)</td>
<td>-1.1998552405927084</td>
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<tr>
<td></td>
<td>Potential Energy</td>
<td>-299.293252885427590</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1s 2</td>
<td>-52.7560529558</td>
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</tr>
<tr>
<td></td>
<td>2s 2</td>
<td>-3.148290199</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2p 5</td>
<td>-1.4605487742</td>
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<tr>
<td></td>
<td>Total Energy</td>
<td>-198.81864934437590</td>
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</tr>
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<td></td>
<td>Kinetic Energy</td>
<td>198.91282308748580</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ratio(P.E./K.E.)</td>
<td>-1.1999232889477115</td>
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</tr>
<tr>
<td></td>
<td>Potential Energy</td>
<td>-397.78931653086170</td>
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</tr>
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Table B.2: Atom Nitrogen (N 7) to Atom Fluorine (F 9)
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<tbody>
<tr>
<td>Mg 12</td>
<td>1s 2  -98.0550007611</td>
<td>-399.229704287487490</td>
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<td>Al 13</td>
<td>1s 2  -116.9868898655</td>
<td>-483.753915981145040</td>
<td>483.888241011767490</td>
<td>-1.999722404646331</td>
<td>-967.642156992912530</td>
</tr>
<tr>
<td>Si 14</td>
<td>1s 2  -137.6206096995</td>
<td>-577.66976664536770</td>
<td>577.86880522778480</td>
<td>-1.99655451457073</td>
<td>-1155.538637168215200</td>
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Table B.3: Atom Magnesium (Mg 12) to Atom Silicon (Si 14)
### Table B.4: Atom Phosphorus (P 15) to Atom Chlorine (Cl 17)

<table>
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</tr>
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<td>P</td>
<td>1s 2</td>
<td>-159.9587584272</td>
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<td>3s 2</td>
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<tr>
<td></td>
<td>2p 6</td>
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<tr>
<td></td>
<td>3p 3</td>
<td>-0.6990337663</td>
<td></td>
</tr>
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</table>

**Total Energy** = -681.298339108637040

**Kinetic Energy** = 681.555438069286990

**Ratio (P.E./K.E.)** = -1.999622776158344

**Potential Energy** = -1362.853777177924000

---

<table>
<thead>
<tr>
<th>Element</th>
<th>NL</th>
<th>Occ</th>
<th>E</th>
</tr>
</thead>
<tbody>
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<td>S</td>
<td>1s 2</td>
<td>-184.0037223629</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2s 2</td>
<td>-18.0089010965</td>
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</tr>
<tr>
<td></td>
<td>3s 2</td>
<td>-1.7643806897</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2p 6</td>
<td>-13.3638139394</td>
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<tr>
<td></td>
<td>3p 4</td>
<td>-0.8512616387</td>
<td></td>
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</table>

**Total Energy** = -794.957878832838450

**Kinetic Energy** = 795.243963580120520

**Ratio (P.E./K.E.)** = -1.999640255367681

**Potential Energy** = -1590.201842412959000

---

<table>
<thead>
<tr>
<th>Element</th>
<th>NL</th>
<th>Occ</th>
<th>E</th>
</tr>
</thead>
<tbody>
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<td>Cl</td>
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<tr>
<td></td>
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<td>-21.2057341762</td>
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<td>3s 2</td>
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<td></td>
<td>2p 6</td>
<td>-16.138392804</td>
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<td></td>
<td>3p 5</td>
<td>-1.0121934460</td>
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</table>

**Total Energy** = -918.965154908413300

**Kinetic Energy** = 919.253207730997700

**Ratio (P.E./K.E.)** = -1.999686644745798

**Potential Energy** = -1838.21836239411000
<table>
<thead>
<tr>
<th>Element</th>
<th>Total Energy</th>
<th>Kinetic Energy</th>
<th>Ratio (P.E./K.E.)</th>
<th>Potential Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
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<td>-2707.0702316391175</td>
</tr>
<tr>
<td>Sc</td>
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<td>1519.5182414177971</td>
<td>-1.9999707467797100</td>
<td>-3038.9920320081833</td>
</tr>
<tr>
<td>Ti</td>
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<td>-3393.531786459252500</td>
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Table B.5: Atom Calcium (Ca 20) to Atom Germanium (Ge 32) I
<table>
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</tr>
<tr>
<td></td>
<td>3s 2</td>
<td>-6.3946816244</td>
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</tr>
<tr>
<td></td>
<td>4s 2</td>
<td>-0.4640693269</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2p 6</td>
<td>-40.0860248135</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3p 6</td>
<td>-4.0628516346</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3d 3</td>
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<td></td>
</tr>
<tr>
<td>Total Energy</td>
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<td>= 1885.656905569739600</td>
</tr>
<tr>
<td>Ratio(P.E./K.E.)</td>
<td>≈ -1.99975314002771</td>
<td>Potential Energy</td>
<td>= -3771.267261818332400</td>
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<table>
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<th>Occ</th>
<th>E</th>
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<tr>
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<td>3s 2</td>
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<td></td>
<td>4s 2</td>
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<td></td>
<td>2p 6</td>
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<td></td>
<td>3p 6</td>
<td>-4.534983889</td>
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</tr>
<tr>
<td></td>
<td>3d 4</td>
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</tr>
<tr>
<td>Total Energy</td>
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<td></td>
<td>3s 2</td>
<td>-7.6980902906</td>
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<td></td>
<td>4s 2</td>
<td>-0.5016723139</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2p 6</td>
<td>-49.7209339228</td>
<td></td>
</tr>
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<td></td>
<td>3p 6</td>
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<td>3d 5</td>
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<tr>
<td>Total Energy</td>
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</tr>
<tr>
<td>Ratio(P.E./K.E.)</td>
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<td>Potential Energy</td>
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Table B.6: Atom Calcium (Ca 20) to Atom Germanium (Ge 32) II
26 Fe

<table>
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<td>3s</td>
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<td>-8.3740658231</td>
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<tr>
<td>4s</td>
<td>2</td>
<td>-0.5191440333</td>
</tr>
<tr>
<td>2p</td>
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<td>-54.8809292773</td>
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<td>3p</td>
<td>6</td>
<td>-5.515397593</td>
</tr>
<tr>
<td>3d</td>
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<td>-1.2097204736</td>
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</tbody>
</table>

Total Energy = -2524.585975996628800
Kinetic Energy = 2524.634867335707000
Ratio(P. E./K. E.) = -1.99980634293018
Potential Energy = -5049.22084332335800

27 Co

<table>
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<tr>
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</thead>
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<tr>
<td>4s</td>
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<td>-0.5360250812</td>
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<td>2p</td>
<td>6</td>
<td>-60.2722608358</td>
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<tr>
<td>3d</td>
<td>7</td>
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</table>

Total Energy = -2762.621592977569400
Kinetic Energy = 2762.669978901396400
Ratio(P. E./K. E.) = -1.99982497031951
Potential Energy = -5525.291540878965900

28 Ni

<table>
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</thead>
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<td>2</td>
<td>-75.8492289553</td>
</tr>
<tr>
<td>3s</td>
<td>2</td>
<td>-9.7827791788</td>
</tr>
<tr>
<td>4s</td>
<td>2</td>
<td>-0.5525184864</td>
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<td>2p</td>
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<td>3p</td>
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<td>-6.5605828992</td>
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<tr>
<td>3d</td>
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</table>

Total Energy = -3013.636887463954300
Kinetic Energy = 3013.681129842485000
Ratio(P. E./K. E.) = -1.99985319489148
Potential Energy = -6027.318017306439300

Table B.7: Atom Calcium (Ca 20) to Atom Germanium (Ge 32) III
Table B.8: Atom Calcium (Ca 20) to Atom Germanium (Ge 32) IV
<table>
<thead>
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<th>E</th>
</tr>
</thead>
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</tr>
<tr>
<td>2s</td>
<td>2</td>
<td>-104. 3009518637</td>
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<td>3s</td>
<td>2</td>
<td>-14. 3900639606</td>
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<tr>
<td>4s</td>
<td>2</td>
<td>-1. 1173070665</td>
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<tr>
<td>2p</td>
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<td>-92. 4726371388</td>
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<td>3p</td>
<td>6</td>
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<tr>
<td>4p</td>
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</tr>
<tr>
<td>3d</td>
<td>10</td>
<td>-3. 2796394489</td>
</tr>
</tbody>
</table>

Total Energy = -4150. 688154219670700
Kinetic Energy = 4150. 844186042192600
Ratio(P. E./K. E.) = -1. 999962409617049
Potential Energy = -8301. 5388156046

Table B.9: Atom Calcium (Ca 20) to Atom Germanium (Ge 32) V
### B.2 All-electron OEP results for atoms

**Ground State Energy**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Present Work</th>
<th>Previous Work</th>
</tr>
</thead>
<tbody>
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<td>-1.0000</td>
</tr>
<tr>
<td>He</td>
<td>-5.7234</td>
<td>-5.7234</td>
</tr>
<tr>
<td>Li</td>
<td>-14.8647</td>
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</tr>
<tr>
<td>Be</td>
<td>-29.1449</td>
<td>-29.1448</td>
</tr>
<tr>
<td>B</td>
<td>-49.0555</td>
<td>-49.0566</td>
</tr>
<tr>
<td>C</td>
<td>-75.3162</td>
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</tr>
<tr>
<td>N</td>
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<tr>
<td>O</td>
<td>-149.5352</td>
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<tr>
<td>F</td>
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<tr>
<td>Ne</td>
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<td>-257.0908</td>
</tr>
<tr>
<td>Na</td>
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</tr>
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<td>Mg</td>
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<tr>
<td>Al</td>
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</tr>
<tr>
<td>Si</td>
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<td>P</td>
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<td>S</td>
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<tr>
<td>Cl</td>
<td>-918.9542</td>
<td>-918.9552</td>
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<tr>
<td>Ar</td>
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<td>-1053.6244</td>
</tr>
</tbody>
</table>

Table B.10: Total ground-state energies for H through Ar (Ry)

<table>
<thead>
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<th>Atom</th>
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<th>Previous Work</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>Ca</td>
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<tr>
<td>Sc</td>
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<td>Ti</td>
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<tr>
<td>V</td>
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<tr>
<td>Cr</td>
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</tr>
<tr>
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<td>Ni</td>
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<td>Cu</td>
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<tr>
<td>Ga</td>
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<tr>
<td>Ge</td>
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</tr>
<tr>
<td>As</td>
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<tr>
<td>Se</td>
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</tr>
<tr>
<td>Br</td>
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</tr>
<tr>
<td>Kr</td>
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<td>-5504.0860</td>
</tr>
</tbody>
</table>

Table B.11: Total ground-state energies for K through Kr (Ry)

Exact Exchange Potential

Table B.12: Exact Exchange Potential of Li Be B

Table B.13: Exact Exchange Potential of C N O F
Table B.14: Exact Exchange Potential of Na Mg Al

Table B.15: Exact Exchange Potential of Si P S Cl
C Design Pattern and UML of Implementation

UML

Unified Modeling Language is a standardized general-purpose modeling language. The Class Diagram of UML specifies the relationship and interactions between each classes. In this Appendix, we use Class Diagram to illustrate the design of the Atompaw MATLAB program.

Design Pattern

In software engineering, a design pattern is a general reusable solution to a commonly occurring problem in software design. The main advantage of using design pattern is to develop reusable code. In the process of developing a relatively large program, we want the existing module to be stand-alone and independent of changes being introduced later on. This requires to write program at more abstract level, so called programming to the interface and rely on run-time polymorphism to determine which function to use.

Programming to the interface can be simply illustrated using the following Strategy Diagram. Given two types of data and 2 different methods that need to be applied to the data, a simple design of the program would look like:

![Figure C.1: Simple Design](image)

Figure C.1: Simple Design
And the pseudo code could look like

```cpp
BigDataModule* dataA;
BigDataModule* dataB;

dataA->method1();
dataB->method2();
```

The disadvantage for this kind of design is that:

1. As the number of concrete date types and concrete methods grow, the module will get larger, and harder to maintain.
2. When the program wants to apply different methods on the data, all the code looks like `dataA. method1()` need to be changed. This would potentially causing the code impossible to maintain.

An alternative design further extracts the interrelationship between the classes (called Strategy Pattern), for example:

![Strategy Pattern Diagram](image)

Figure C.2: Strategy Pattern

And the pseudo code for applying different methods onto different data would be

```cpp
1 DataModule* dataptr = new dataA();
2 MethodModule* methodhandle = new method1();
3 dataptr->methodptrhandle();
```

Notice that in this way:

1. The module is expandable. For example: more types of methods can be applied to more types of data without affecting the existing code, as shown
in Fig (C.3). which is specially useful when trying out different algorithms.

2. In case the program wants to apply different methods onto the code, only line 1 and line 2 would need to be changed.

![Figure C.3: Strategy Pattern](image)

To sum up, there are generally two basics principles in the design pattern, which is also applied to the implementation of Hartree-Fock, OEP, and KLI approximation in PAW methods, which are:

- Program to the interface, not implementation
- Favor Composition over inheritance
Figure C.5: Design Pattern of Pot Class
Figure C.6: Design Pattern of SCF Class
Figure C.7: Design Pattern of Strategy Class
D Related Publication
Projector augmented wave formulation of Hartree-Fock calculations of electronic structure

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Department of Physics, Wake Forest University, Winston-Salem, North Carolina 27109, USA

(Received 19 February 2010; revised manuscript received 5 May 2010; published 4 June 2010)

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.

DOI: 10.1103/PhysRevB.81.245105
PACS number(s): 31.15.xr, 71.15.Ap, 71.15.Dx

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) (Ref. 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 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

$$\Psi_p(r) = \Psi_{n_p q_p s_p t_p}(r) = \frac{\phi_p(r)}{r} Y_{l_p m_p}(\hat{r}),$$

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 $\phi_p(r)$ denotes the radial portion of the wave function. The number of electrons in a shell is given by $N_p = 2(2l_p+1)$. For simplicity, we consider only the averaged electronic configuration so that the electron density $\rho(r) = \rho(r)$ is spherically symmetric

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

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

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

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

$$E_H = \frac{\epsilon^2}{2} \int \int d^3r d^3r' \frac{\rho(r) \rho(r')}{|r-r'|}. \quad (4)$$

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

$$E_{xc} = \int d^3r \frac{\epsilon_{xc}(|\nabla \rho(r)|)}{\rho(r)}. \quad (5)$$

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
where the Kohn-Sham Hamiltonian takes the form
\[ H^{KS}(r) = K + V^{KS}(r). \]

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
\[ V^{KS}(r) = V_N(r) + V_H(r) + V_{xc}(r). \]

For a spherical atom the potential components take the form
\[ V_N(r) = \frac{Ze^2}{r}, \quad V_H(r) = \frac{\rho(r)}{r}, \quad V_{xc}(r) = \frac{\rho(r)}{|r - r'|}, \]

and the exchange-correlation potential is defined in terms of the functional derivative with respect to the electron density $\rho(r)$
\[ V_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)}. \]

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 $\Psi^{KS}_p(r)$ are eigenstates of the Kohn-Sham Hamiltonian (7). Since the Kohn-Sham Hamiltonian is Hermitian, the eigenstates $\Psi^{KS}_p(r)$ are unique up to normalization.

\[ \Theta^{L}_{pq} = \left\{ \begin{array}{ll}
\frac{1}{2}N_pN_q \begin{pmatrix} l_p & L & l_q \\ 0 & 0 & 0 \end{pmatrix}^2 & \text{for } p \neq q \\
\frac{1}{2}N_p(N_p-1)4l_pL + 4l_pL+2 \begin{pmatrix} l_p & L & l_q \\ 0 & 0 & 0 \end{pmatrix}^2 & \text{for } p = q \text{ and } L \neq 0 \\
N_p & \text{for } p = q \text{ and } L = 0.
\end{array} \right. \]

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

In order to find the Hartree-Fock orbitals $\{\phi^{HF}_p(r)\}$, 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
\[ F^{HF}(\{\phi^{HF}_p(r)\}, \{\lambda_{qp}\}) = E_{tot}(\{\phi^{HF}_p\}) - \sum_{qp} N_p\lambda_{qp}(\langle \phi^{HF}_p | \phi^{HF}_q \rangle - \delta_{qp}), \]

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

\[ H^{HF}(\phi^{HF}_p(r) + \chi_p(r)) = \sum_{q: N_q > 0} \lambda_{qp} \phi^{HF}_q(r) = 0. \]

The Hartree-Fock equations take the form
\[ H^{HF}(\phi^{HF}_p(r) + \chi_p(r)) = K + V_N(r) + V_H(r). \]
\[
X_p(r) = \frac{1}{N_p} \frac{\delta E_p}{\delta \phi_p} = - \sum_{q} \sum_{L=|p-q|}^{l_q+l_p} \frac{1}{N_p} \Theta^L \psi^w_p (r) \phi^w_q (r),
\]

(19)

where

\[
W_p^w (r) = e^2 \int d^3r' \frac{r}{r'} \psi^w_p (r') \psi^w_q (r').
\]

(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 \( \lambda_{qp} \) 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. Starting with an initial guess for the radial components \( \{ \phi^w_{qp}(r) \} \) the approximate form of the Hartree-Fock equations is a set of inhomogeneous differential equations for the updated radial components \( \{ \phi^{w'(1)}_{pq}(r) \} \) of the form

\[
[H^{HF(1)}(r) - \epsilon^{(0)} p] \phi^{w(1)}_p (r) = R^{(0)}_p,
\]

(21)

where

\[
R^{(0)}_p = - X_p (r) + \sum_{q} \lambda_{qp} \phi^w_q (r) - \epsilon^{(0)}_p \phi^w_p (r).
\]

(22)

Here the parameters \( \epsilon^{(0)}_p = \lambda^{(0)}_{pp} \) are introduced to further stabilize the solution. At convergence \( \{ \phi^{w(1)}_{pq}(r) \} = \{ \phi^{w(0)}_{pq}(r) \} \). The results obtained in this way are essentially identical to those obtained from the ATSP package developed by Fischer et al. That is, the values of \( \lambda_{qp} \) from the two programs agree within 10^{-4} Ry and graphs the radial wave functions \( \phi^w_p (r) \) 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

\[
\rho (r) = \rho_c (r) + \rho_v (r),
\]

(23)

where

\[
\rho_v (r) = \frac{n_v (r)}{4\pi r^2} \quad \text{with} \quad n_v (r) = \sum_{\nu} n_{\nu} |\psi_{\nu} (r)|^2.
\]

(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

\[
E_{val} = E^v_k + E^v_H + E^{val}_{xc} + E_{xc}.
\]

(25)

Here, the valence kinetic energy \( E^v_k \) and valence nuclear potential energy \( E^v_H \) 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

\[
E^v_H = e^2 \int \left[ \int d^3r d^3r' \frac{\rho_v (r) \rho_v (r')}{|r - r'|} \right] \rho_v (r) n_v (r)
\]

(26)

and a valence-valence interaction

\[
E^{val}_{xc} = \frac{e^2}{2} \int \left[ \int d^3r d^3r' \frac{\rho_v (r) \rho_v (r')}{|r - r'|} \right] \rho_v (r) n_v (r).
\]

(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. 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 \( \{ \psi_{\nu} (r) \} \) are determined from solving the Kohn-Sham Eq. (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 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. Since the exchange energy is formed from products of pairs of electron orbitals and can be divided into core-valence and valence-valence contributions

\[
E_{xc} \rightarrow E_x^{(val)} \quad \text{where} \quad E_x^{(val)} = E_x^v + E_x^{uv}.
\]

(28)

Here

\[
E_x^{uv} = - \sum_{\nu} \sum_{\nu' \in x} \Theta^\nu_{\nu'} R_{\nu'\nu} \Sigma_{\nu} \frac{1}{\xi_{\nu}} \psi_{\nu} \psi_{\nu'}
\]

and

\[
E_x^v = E_x^v \quad \text{where} \quad E_x^v = E_x^{uv} + E_x^{xc}.
\]
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 $E_{xv}^{Li}/E_{xv}^{F}=0.1$. 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 $E_{xv}^{Na}/E_{xv}^{Cl}=0.2$. 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 $E_{xv}^{K}/E_{xv}^{Ar}=0.3$. On the other hand, for the 4s3d materials in the fourth row of the periodic table, Sc-Cu calculated in the 4s3d2 state using the Ar configuration as core states, we find $E_{xv}^{Sc}/E_{xv}^{Ar}=1$. In addition to these trends in the $E_{xv}^{c}/E_{xv}^{v}$ 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 ($p=p$) while leaving the core orbitals $\psi_{q}^{HF}(r)$ fixed to the functions found for the reference state. It is important to require that the valence orbitals $\psi_{v}^{HF}(r)$ remain strictly orthogonal to each other as well as to the core orbitals

$$\langle \psi_{v}^{HF} | \psi_{q}^{HF} \rangle = 0$$

in order to avoid spurious contributions to the valence-core exchange energy $E_{xv}^{c}$ 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.\textsuperscript{1,2} In principle, pseudopotential formulations are based on corresponding full wave function frozen-core potential approximations. The frozen-core potential $V_{f}(r)$ 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 question is whether one can find a fixed potential $V_{c}^{HF}(r)$ which can accurately approximate the core-valence exchange interaction in the effective single-particle Hamiltonian

$$H_{HF}^{HF}(r) = K + V_{s}(r) + V_{p}^{HF}(r) + V_{c}^{HF}(r) + V_{v}^{HF}(r).$$

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

$$H_{HF}^{HF}(r) \psi_{q}^{HF}(r) + \lambda_{q}^{HF}(r) = \sum_{q'N_{q'}=0} \lambda_{q'}^{HF}(r),$$

where

$$\lambda_{q}^{HF}(r) = -\sum_{v} \sum_{L_{v}} \frac{1}{N_{v}} \Theta_{qv}^{L_{v}} W_{vL_{v}}^{HF}(r) \psi_{q}^{HF}(r).$$

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

$$E_{xv}^{c} \approx E_{xv}^{c} = \int dr V_{c}^{HF}(r) n_{v}(r).$$

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

$$V_{c}^{HF}(r) = \sum_{q} \lambda_{q}^{HF}(r) \psi_{q}^{HF}(r) \left| \frac{n_{v}(r)}{n_{ref}(r)} \right|,$$

where
\[ X_v^u(r) = - \sum_i^{\text{all elec}} \sum_{\ell \geq |l|} \sum_{\text{shell}} \frac{1}{N_v} \Theta_{\ell \text{tot}}^u(r) W_{\text{tot}}^\ell(r) \psi_i^\text{HF}(r). \]  

(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

\[ E_{\text{xc}}^u = \int dr \sum_v N_v X_v^u(r) \psi_i^\text{HF}(r), \]  

(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 excitation energy calculated in an all-electron treatment to be

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

(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 x 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 x 10^{-3} Ry or less for the Hartree-Fock frozen-core orbital approximation which is 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 (semiconductors) as valence states. By contrast, for results of 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 rows 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 of the frozen-core potential \( V_{\text{xc}}^u(r) \) 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 \( V_{\text{OEP}}^u(r) \) for use in the Kohn-Sham Hamiltonian consistent with the Fock exchange functional. However, in the OEP formulation, the \( V_{\text{OEP}}^u(r) \) 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 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\(^{4,5} \) 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.\(^{3,9,10,12,27,38}\) 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 \( \phi_i^a(r) \) for an all-electron basis function, \( \tilde{\Phi}_i^a(r) \) for the corresponding pseudoelectron basis function, and \( \hat{P}_i^a(r) \) 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 \( \{ \phi_i^a(r) \} \) 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

\[ \langle \hat{P}_i^a(\tilde{\Phi}_j^a) = \delta_{ij} \]  

(40)

and the radial pseudofunctions have the property

\[ \tilde{\phi}_i^a(r) = \phi_i^a(r) \quad \text{for} \quad r > r_c^a. \]  

(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 \( [\tilde{\Psi}_i^a(r)] \) corresponding to a valence state of the system and the corresponding fully nodal wave function \( [\Psi_i^a(r)] \) of that state which is given by\(^{7}\)
\( \Psi_a(r) = \Psi_a(r) + \sum_{ai} [\Phi_a^i(r - \mathbf{R}^a) - \Phi_a^i(r)](\tilde{P}_i^a\vert \Psi_a) \).

(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

\[
E_{\text{vale}} = \tilde{E}_{\text{vale}} + \sum_a \left( E_{\text{vale}}^{a} - \tilde{E}_{\text{vale}}^{a} \right) .
\]

(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 function of the valence pseudowave functions, the Kohn-Sham equations in the PAW formalism can be evaluated\(^7\) in terms of the functional derivative

\[
\frac{\delta E_{\text{vale}}}{\delta \tilde{\Psi}_v^a(r)} = \tilde{H}_{KS}^{PAW}(r)\tilde{\Psi}_v^a(r) = \varepsilon_v^a O^{PAW}\tilde{\Psi}_v^a(r).
\]

(44)

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

\[
\langle \tilde{\Psi}_v^a \vert O^{PAW} \tilde{\Psi}_v^{a'} \rangle = \delta_{v,a'}.
\]

(45)

Here the PAW Hamiltonian takes the form

\[
\tilde{H}_{KS}^{PAW}(r) = \tilde{H}_{KS}(r) + \sum_{aij} \langle \tilde{P}_i^a \vert D_{ij}^a \vert \tilde{P}_j^a \rangle
\]

(46)

and

\[
O^{PAW} = 1 + \sum_{aij} \langle \tilde{P}_i^a \vert O_{ij}^a \vert \tilde{P}_j^a \rangle.
\]

(47)

Here the Kohn-Sham pseudo-Hamiltonian has the form

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

(48)

The overlap matrix element is given by

\[
O_{ij}^a = \langle \Phi_a^i \vert \Phi_a^j \rangle - \langle \Phi_a^i \tilde{\Phi}_a^j \rangle.
\]

(49)

The general form of \( \tilde{H}_{KS}(r) \) 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

\[
(\tilde{H}_{KS}^{PAW} - \varepsilon_v^a)\tilde{\Psi}_v^a(r) = \sum_j \tilde{P}_j^a(r)\langle \tilde{\Phi}_v^j \vert \tilde{H}_{KS}^{PAW} - \varepsilon_v^a \vert \tilde{\Phi}_v^j \rangle .
\]

(50)

This relationship is consistent with the requirements that each pseudowave function basis function \( \tilde{\Phi}_v^j(r) \) 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

\[
D_{ij}^a \vert_{\text{ref}} = \langle \tilde{\Phi}_v^j \vert \tilde{H}_{KS}^{PAW} \vert \tilde{\Phi}_v^i \rangle - \langle \tilde{\Phi}_v^j \vert \tilde{H}_{KS}^{PAW} \vert \tilde{\Phi}_v^j \rangle \vert_{\text{ref}}.
\]

(51)

In practice, the projector functions \( \{ \tilde{P}_j^a(r) \} \) are determined by solving Eq. (50) from a knowledge of the reference pseudo-Hamiltonian \( \tilde{H}_{KS}(r) \), the basis functions \( \{ \tilde{\Phi}_v^j(r) \} \), and the eigenenergies \( \{ \varepsilon_v^a \} \), following a similar procedure developed by Vanderbilt.\(^40\)

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 pseudoorbitals \( \tilde{\Psi}_v^{HF}(r) \) 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 \( \{ \tilde{\Phi}_v^j(r) \} \) within the augmentation sphere.

Most of the core wave functions \( \Psi_v^{HF}(r) \) are contained within the augmentation sphere and for those we can define a trivial core pseudowave function \( \tilde{\Psi}_v^{HF} = 0 \). For some materials it is possible that at most one core orbital per l channel will have a nontrivial amplitude for \( r > r_{c}^\ast \). In such a case, it is convenient to define a continuous pseudocore orbital \( \tilde{\Psi}_v^c(r) \) with \( \tilde{\Psi}_v^c(r) = \psi_v^c(r) \) for \( r > r_{c}^\ast \), 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

\[
\tilde{\Psi}_v^c(r) = \begin{cases} r^{l+1} P_n(r) & \text{for } r \leq r_{c}^\ast \\
\left(\psi_v^c(r) - r^{l+1} P_n(r)\right) & \text{for } r > r_{c}^\ast, \end{cases}
\]

(52)

The \( n \)th order polynomial \( P_n(r) \) is chosen to ensure that \( \tilde{\Psi}_v^c(r) \) 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

\[
m_{ij}^{\delta L}(r) = \int dr \, u^{L+1} s_{L}(u)
\]

(53)

Here \( s_{L}(r) \) is a smooth shape function
or it could be similar smooth function such as one involving a spherical Bessel function $s_k(r) = j_k(x)$. More often we have chosen

$$ k(r) = \begin{cases} \sin(\pi r/r_c) \frac{1}{r} & \text{for } r < r_c \\ \frac{\pi}{r} & \text{for } r \geq r_c. \end{cases} $$  \hspace{1cm} (55) $$

The charge moment coefficient is given by

$$ m_{ij} = \int dr r^2 \left[ \delta_i(r) \delta_j(r) - \tilde{\delta}_i(r) \tilde{\delta}_j(r) \right]. $$  \hspace{1cm} (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\textsuperscript{11} 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\textsuperscript{13} so that they can be written in the PAW form (43)

$$ E_x^u = E_x + \sum_a (E_x^{au} - E_{a,x}^u), $$

$$ E_x^{ac} = \sum_a (E_x^{acu} - E_{a,c}^{ac}). $$  \hspace{1cm} (57) $$

The trick\textsuperscript{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 pseudocounterparts 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, $\psi^\alpha_v(r)\psi^\beta_v(r)$, we can define a compensation charge moment of order $L$

$$ \hat{M}_{uv}^{L}(r) = \sum_{a,b} (\tilde{\psi}_v^\alpha \tilde{\psi}_v^\beta)(\tilde{\psi}_v^\beta \tilde{\psi}_v^\alpha) m_{ab}^{L}(r). $$  \hspace{1cm} (58) $$

The significance of this moment is that, within the accuracy of the PAW transformation, the $L$th moment of $[\psi^\alpha_v(r)\psi^\beta_v(r)]$ is the same as the $L$th moment of $[\tilde{\psi}_v^\alpha(r)\tilde{\psi}_v^\beta(r) + \hat{M}_{uv}^{L}(r)]$. For the moment representing core-valence wave-function products, the moment coefficient $m_{uv}^{L}$ corresponding to valence-core contributions is defined by an expression similar to Eq. (56) with $\phi_i^c \rightarrow \tilde{\phi}_i^c$ and $\tilde{\phi}_i^c \rightarrow \tilde{\phi}_i^c$.

Because of orthogonality properties of core and valence states of the reference system and because $\tilde{\phi}_i^c = 0$ 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 pseudoelectron integrals take the form

$$ \tilde{E}_x^u = -\sum_{uv} \sum_{L \models v \mid u \mid} 2 \frac{1}{L} \left\{ \frac{1}{2} \langle \tilde{\psi}_v^\alpha | \tilde{\psi}_v^\beta \rangle \hat{R}_{uv}^L \tilde{R}_{uv}^L \right\}, $$

$$ \tilde{E}_x^c = -\sum_{uc} \sum_{L \models c \mid u \mid} \Theta_{uc}^L \hat{R}_{uc}^L, $$  \hspace{1cm} (59) $$

where

$$ \hat{R}_{uv}^L = e^2 \int dr dr' \sum_{L \models v \mid u \mid} \left[ \tilde{\psi}_v^\alpha(r) \tilde{\psi}_v^\beta(r) + \hat{M}_{uv}^{L}(r) \right] \times \left[ \tilde{\psi}_v^\beta(r') \tilde{\psi}_v^\alpha(r') \right]. $$  \hspace{1cm} (60) $$

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

$$ E_x^u - \tilde{E}_x^u = -\sum_{uv} \sum_{L \models v \mid u \mid} 2 \left\{ \frac{1}{2} \langle \tilde{\psi}_v^\alpha | \tilde{\psi}_v^\beta \rangle \hat{R}_{uv}^L \tilde{R}_{uv}^L \right\} \times (\tilde{\psi}_v^\alpha | \tilde{\psi}_v^\beta \rangle \hat{R}_{uv}^L \tilde{R}_{uv}^L), $$

$$ E_x^{ac} - \tilde{E}_x^{ac} = -\sum_{uc} \sum_{L \models c \mid u \mid} \Theta_{uc}^L \langle \tilde{\psi}_v^\alpha | \tilde{\psi}_v^\beta \rangle \times (\tilde{\psi}_v^\alpha | \tilde{\psi}_v^\beta \rangle \hat{R}_{uc}^L \tilde{R}_{uc}^L), $$  \hspace{1cm} (61) $$

Here

$$ R_{ij,kl} = e^2 \int dr dr' \sum_{L \models v \mid u \mid} \langle \tilde{\psi}_v^\alpha | \tilde{\psi}_v^\beta \rangle \hat{R}_{ij}^L \langle \tilde{\psi}_v^\beta | \tilde{\psi}_v^\alpha \rangle \times \hat{R}_{ij}^L, $$  \hspace{1cm} (62) $$

and

$$ R_{ij,kl}^{ac} = e^2 \int dr dr' \sum_{L \models c \mid u \mid} \langle \tilde{\psi}_v^\alpha | \tilde{\psi}_v^\beta \rangle \hat{R}_{ij}^L \langle \tilde{\psi}_v^\beta | \tilde{\psi}_v^\alpha \rangle \times \hat{R}_{ij}^L. $$  \hspace{1cm} (63) $$

These expressions for the valence electron contributions to

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the exchange energy are equivalent to results given by previous workers.\textsuperscript{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
\begin{equation}
\mathcal{H}_{\text{HF}}^{\text{PAW}}(\mathbf{r})\tilde{V}_v^{\text{HF}}(\mathbf{r}) + X_v^{\text{PAW}}(\mathbf{r}) = -\sum_q N_{V_q}\lambda_{qV}\tilde{V}_q^{\text{PAW}}(\mathbf{r}) = 0.
\end{equation}

These equations must be solved self-consistently with orthonormalization constraint
\begin{equation}
\langle \tilde{V}_v^{\text{HF}}|O_{\text{PAW}}^{\text{PAW}}|\tilde{V}_c^{\text{HF}} \rangle = \delta_{vc},
\end{equation}
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
\begin{equation}
\langle \tilde{V}_v^{\text{HF}}|O_{\text{PAW}}^{\text{PAW}}|\tilde{V}_c^{\text{HF}} \rangle = -\sum_{uv} \langle \tilde{V}_v^{\text{HF}}|\tilde{P}_{ij}^{\text{HF}}\rangle O_{uv},
\end{equation}

where \( O_{uv} = m_{uv} \). In general, these terms are very small if not identically zero. The single particle term of Eq. (65) takes the form
\begin{equation}
\mathcal{H}_{\text{HF}}^{\text{PAW}}(\mathbf{r}) = \mathcal{H}_{\text{HF}} + \sum_{ij} |\tilde{P}_{ij}^{\text{HF}}|D_{ij}^{\text{HF}}\langle \tilde{P}_{ij}^{\text{HF}} \rangle,
\end{equation}

where the pseudo Hamiltonian-type terms depend on the pseudopotentials due to the nuclear and Hartree interactions
\begin{equation}
\tilde{P}_{ij}^{\text{HF}}(\mathbf{r}) = \mathcal{K} + \tilde{V}_i(\mathbf{r}) + \tilde{V}_j(\mathbf{r}).
\end{equation}
The exchange function term takes the form
\begin{equation}
X_v^{\text{PAW}}(\mathbf{r}) = \tilde{X}_v(\mathbf{r}) + \sum_{ai} |\tilde{P}_{ai}^{\text{HF}}|X_{ai}^v,
\end{equation}

where the pseudoexchange kernel function takes the form
\begin{equation}
\tilde{X}_v(\mathbf{r}) = -\sum_{q} \sum_{L[l\|l\|\alpha\beta]} N_{V_q}\lambda_{qV}\tilde{W}_{q\alpha\beta}(\mathbf{r})\phi_q^{\text{HF}}(\mathbf{r}).
\end{equation}

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 \( \tilde{W}_{q\alpha\beta}(\mathbf{r}) \) is the pseudoanalog of Eq. (20)
\begin{equation}
\tilde{W}_{q\alpha\beta}(\mathbf{r}) = e^2 \int dr' |\tilde{P}_{q\alpha}(r')\tilde{P}_{\beta}^{\text{HF}}(r') + M_{q\alpha}(r')|.
\end{equation}
The one center matrix element for the pseudoexchange kernel function takes the form
\begin{equation}
X_{ai}^v = -\sum_{q} \sum_{L[l\|l\|\alpha\beta]} N_{V_q}\lambda_{qV}\tilde{W}_{q\alpha\beta}(\mathbf{r})\phi_q^{\text{HF}}(\mathbf{r}) = 0.
\end{equation}

where the relationship between the projector and basis functions is somewhat different from that of the Kohn-Sham formalism, taking the form
\begin{equation}
\mathcal{H}_{\text{HF}}^{\text{PAW}}(\mathbf{r})\tilde{V}_v^{\text{HF}}(\mathbf{r}) + \tilde{X}_v(\mathbf{r}) - \sum_{q\neq V} \lambda_{qV}\tilde{V}_q^{\text{PAW}}(\mathbf{r}) = \sum_{j} \tilde{P}_j^{\text{HF}}(\mathbf{r})\Lambda_{ji}^q.
\end{equation}

Here the matrix coefficients are given by
\begin{equation}
\Lambda_{ji}^q = \langle \tilde{P}_j^{\text{HF}}|\tilde{P}_i^{\text{HF}}\rangle + \langle \tilde{P}_j^{\text{HF}}|\tilde{X}_v(\mathbf{r}) - \sum_{q\neq V} \lambda_{qV}\tilde{V}_q^{\text{PAW}}(\mathbf{r}) = \sum_{j} \tilde{P}_j^{\text{HF}}(\mathbf{r})\Lambda_{ji}^q.
\end{equation}

where the differential \( \mathcal{H}_{\text{HF}}^{\text{PAW}}(\mathbf{r}) \) and integral \( \tilde{X}_v(\mathbf{r}) \) operators as well as the Lagrange multipliers \( \lambda_{qV} \) 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 \{\( \tilde{P}_i^{\text{HF}}(\mathbf{r}) \}\). Equation (75) is consistent with the requirement that the pseudowave function basis functions \( \tilde{P}_i^{\text{HF}}(\mathbf{r}) \) 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
\begin{equation}
\langle \tilde{P}_i^{\text{HF}}|\mathcal{H}_{\text{HF}}^{\text{PAW}}|\tilde{P}_j^{\text{HF}} \rangle|_{\text{ref}} = \langle \tilde{P}_i^{\text{HF}}|\mathcal{H}_{\text{HF}}^{\text{PAW}}|\tilde{P}_j^{\text{HF}} \rangle|_{\text{ref}} - \langle \tilde{P}_i^{\text{HF}}|\mathcal{H}_{\text{HF}}^{\text{PAW}}|\tilde{P}_j^{\text{HF}} \rangle|_{\text{ref}}
\end{equation}

and the two-particle terms satisfy the relationship\textsuperscript{45}
\begin{equation}
\langle \Phi_i^{\text{HF}}|X_v(\mathbf{r}) = \langle \Phi_i^{\text{HF}}|\tilde{X}_v(\mathbf{r}) \rangle = \langle \tilde{P}_i^{\text{HF}}|\tilde{X}_v(\mathbf{r}) \rangle.
\end{equation}

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 \{\( \tilde{g}_v^{\text{HF}(0)}(\mathbf{r}) \)}, the Lagrange multipliers \( \lambda_{qV}^{(0)} \) can be estimated by multiplying both sides of Eq. (65) by \( \tilde{g}_v^{\text{HF}(0)}(\mathbf{r}) \) and integrating over all space. The Lagrange multipliers \( \lambda_{qV}^{(0)} \) corresponding to the interaction between core states and valence states can be estimated from the form
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, $\tilde{\phi}_i(r) = 0$, so that the main contributions of the core orbitals are expressed in the atom centered radial Coulomb integrals $R_{\text{ic},ij}$ similar to the expression defined in Eq. (63). When $\tilde{\phi}_i(r) = 0$, 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 $R_{\text{ic},ij}$ integrals which contribute to the core-valence exchange energy $E_{\text{xc}}^\text{val}$ as defined in Eqs. (57) and (62). They also contribute to the pseudexchange kernel function $X_{\text{ic}}^\text{loc}$ 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 pseudowave 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.

In constructing the pseudobasis functions, for each atom we vary only the augmentation radius $r_c^\text{a}$ and construct the pseudobasis functions $\tilde{\phi}_i(r)$ from all-electron basis functions $\phi_i^\text{loc}(r)$ using the polynomial form introduced by Vanderbilt in the construction of the ultrasoft pseudopotential scheme. [This also is the scheme for constructing the nontrivial pseudocore functions $\psi_i(r)$ of Eq. (52).] The other adjustable function in this construction is the localized potential $\tilde{V}_{\text{loc}}^\text{val}(r)$ 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 $\tilde{V}_{\text{loc}}^\text{val}(r)$. A simple, but reasonable choice is

$$\tilde{V}_{\text{loc}}^\text{val}(r) = V_0 k(r)$$

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

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 ($|\tilde{\phi}_i| > 0$) and excluding ($|\tilde{\phi}_i| = 0$) pseudocore orbitals are compared. The augmentation radii ($r_c^\text{a}$) 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.

| Atom | Type | $|\tilde{\phi}_i|$ | $r_c^\text{a}$ | $V_0$ | $E_{\text{val}}(ns^2np^2)$ | $E_{\text{val}}(ns^4np^3)$ |
|------|------|-----------------|-----------|------|----------------|----------------|
| C    | FC   | >0              | 1.3       | 2.0  | -10.5990       | -9.9541       |
| C    | PAW  | >0              | 1.3       | 2.0  | -10.5990       | -9.9541       |
| Si   | FC   | =0              | 2.0       | 3.0  | -7.3147        | -6.8070       |
| Si   | PAW  | >0              | 2.0       | 3.0  | -7.3147        | -6.8066       |
| 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       |
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 is sensitive to the choices of $r^{p}_{c}$ 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 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 $r^{p}_{c}$. 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 $r > r^{p}_{c}$ 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 wave function amplitudes have become negligible so that the left-hand side of Eq. (75) and therefore $p^{0}_{c}(r)$, remains nonzero beyond $r = r^{p}_{c}$. 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 3$d$ 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 multiorbital 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 $4s^{2}3d^{6} \rightarrow 4s^{2}3d^{5}$. The augmentation radius was chosen to be $r^{p}_{c} = 2.0$ 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

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
$V_{0}$   & AE    & FC    & PAW ($|\tilde{\phi}_{i}| > 0$)  \\
\hline
-2       & 0.4991 & 0.5002 & x \\
-4       & 0.4904 & 0.6288 & \\
-6       & x      & 0.4992 & \\
\hline
\end{tabular}
\caption{Hartree-Fock ionization energies (in Ry units) for configuration averaged Fe[$E(4s^{2}3d^{6}) - E(4s^{2}3d^{5})$] 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 $V_{0}$ is specified in Ry. Results including ($|\tilde{\phi}_{i}| > 0$) and excluding ($|\tilde{\phi}_{i}| = 0$) the pseudocore wave functions are compared. “x” indicates that the calculation diverged.}
\end{table}

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

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 $|\tilde{\phi}_{i}| > 0$ and $V_{0} = -2$ Ry and label “II” refers to $|\tilde{\phi}_{i}| = 0$ and $V_{0} = -6$ Ry, affecting only the shapes of the projector functions.
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 $\tilde{\psi}_c(r)$. 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 $|\tilde{\psi}_c(r)| > 0$, 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 $|\tilde{\psi}_c(r)| = 0$, the effects of the extended core functions are incorporated into extended parts of the projector functions $\tilde{P}_c(r)$. 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 $r_c^*$ and the optimal form of the local potential $V_{loc}(r)$. 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 been 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.

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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. 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

$$ E_{\text{val}}^{\text{ex}} = F_N^{\text{ex}} + F^{\text{ex}}_V + F^{\text{ex}}_H. $$

(A1)

Here the kinetic energy contribution is given by

$$ F_N^{\text{ex}} = \sum_v N_v \langle \vec{V}_v | \vec{K} | \vec{V}_v \rangle. $$

(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

$$ E_{\text{val}}^{\text{ex}} + E_{\text{H}}^{\text{ex}} = \int dr \vec{V}_i^e(r) \vec{n}_v(r), $$

(A3)

where

$$ \vec{V}_i^e(r) = \vec{V}_i^e \text{loc}(r) + \vec{V}_i^{\text{core}}(r) + (-2z + \vec{Q}_i^{\text{core}} - \vec{Q}_i^{\text{core}}) \vec{q}_0^v(r), $$

(A4)

and

$$ \vec{n}_v(r) = \sum_v N_v | \vec{q}_0(r) |^2. $$

(A5)

Here $\vec{V}_i^e \text{loc}(r)$ is a localized potential defined in the range $0 \leq r \leq \rho_i^v$. The potential due to extended core states is given by

$$ \vec{q}_0^v(r) = e^2 \int dr' \vec{r}_{\text{core}}^v(r') \left[ \int_{r'} dr'' \frac{\vec{r}_{\text{core}}^v(r'')}{r''} \right] | \vec{r}_{\text{core}}^v(r')|^2 $$

(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)

$$ \vec{q}_0^v(r) = e^2 \int dr' \frac{\vec{q}_0^v(r')}{r'} $$

(A7)

with

$$ Q_{\text{core}}^e = \int dr n^e_v(r) \quad \text{and} \quad \vec{q}_0^v(r) = \int dr \vec{r}_{\text{core}}^v(r). $$

(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)

$$ F^{\text{ex}}_V = \frac{1}{2} \sum_{\alpha \beta} N_{\alpha v} N_{\beta v} \vec{H}_{\alpha \beta}^{\text{ex}}. $$

(A9)

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

$$ (E_{\text{val}}^{\text{ex}} - E_{\text{val}}^{\text{ex}}) \text{int}_{\alpha \beta} = \sum_{ij} N_{ij} \langle \vec{V}_i^{\text{ex}} | \vec{P}_j^e \rangle \langle \vec{P}_j | \vec{V}_i^e \rangle $$

$$ \times \left( \vec{K}_{ij}^e + [V_f^e]_{ij} + \frac{1}{2} [V^\text{int}_{\text{ex}}]_{ij} \right). $$

(A10)

The kinetic energy contribution is

$$ K_{ij}^e = \langle \phi_i | K | \phi_j \rangle - \langle \phi_i | K | \phi_j \rangle. $$

(A11)

The nuclear- and core-electron contribution is given by

$$ [V_f^e]_{ij} = \langle \phi_i | V_f^e | \phi_j \rangle - \langle \phi_i | V_f^e | \phi_j \rangle, $$

(A12)

where

$$ V_f^e(r) = - \frac{Z e^2}{r} + V_H^e(r). $$

(A13)

The valence-valence Hartree interactions may be evaluated

$$ [V^\text{int}_{\text{ex}}]_{ij} = \sum_{kl} \sum_{v'} N_{v'} \langle \vec{V}_i^{\text{ex}} | \vec{P}_k^0 \rangle \langle \vec{P}_l | \vec{V}_j^e \rangle (R_{ijkl}^0 - \vec{R}_{ijkl}^0), $$

(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

$$ \vec{V}_i^e(r) + \vec{V}_H^e(r) = \vec{V}_i^e(r) + \sum_{\alpha v} N_{\alpha v} \vec{W}_{\alpha v}^0(r), $$

(A15)

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

$$ D_{ij}^{\text{ex}} \text{int}_{\alpha \beta} = K_{ij}^e + [V_f^e]_{ij} + [V^\text{int}_{\text{ex}}]_{ij} + [V^\text{int}_{\text{ex}}]_{ij}, $$

(A16)

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

$$ [V^\text{int}_{\text{ex}}]_{ij} = m_{ij}^e \int dr \vec{q}_0^v(r) (\vec{r}_v(r) + \sum_{\alpha v} N_{\alpha v} \vec{M}_{\alpha v}^0(r)). $$

(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: \( \tilde{\rho}_c(r) = 0 \), many of the expressions presented in Sec. IV simplify. For example, the charge moment coefficient in Eq. (56) takes the form

\[
m_{i_c} = \int dr \ r^2 \tilde{\psi}_i^*(r) \tilde{\psi}_i(r),
\]

(B1)

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

\[
\tilde{R}_{vcxc}^L = \sum_{aij} \langle \tilde{\Psi}_v^{\text{HF}} | \tilde{P}_i | \tilde{\Psi}_v^{\text{HF}} \rangle M_{i_cj}^{\text{L}}
\]

(B2)

where

\[
M_{i_cj}^{\text{L}} = \tilde{c} \int dr \ r^2 \tilde{m}_i(r) \tilde{m}_j(r')
\]

(B3)

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

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

\[
\tilde{R}_{vcxc}^L = M_{i_cj}^{\text{L}}
\]

(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

\[
\tilde{E}_v^c + \sum_a \langle E_v^c \rangle - \tilde{E}_{vcxc} = - \sum_a \sum_{L} \Theta_{i_c}^L \sum_{aij} \langle \tilde{\Psi}_v^{\text{HF}} | \tilde{P}_i | \tilde{\Psi}_v^{\text{HF}} \rangle
\]

\[
\times \langle \tilde{\Psi}_v^{\text{HF}} | \tilde{P}_j | \tilde{\Psi}_v^{\text{HF}} \rangle M_{i_cj}^{\text{L}}
\]

(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 \( \Theta_{i_c}^L \) 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 \( \lambda_{i_c} > 0 \) since the extended overlap operator reduces to

\[
\tilde{C}_{\text{PAW}}^{L} = \sum_{i} \langle \tilde{P}_i | \tilde{\Psi}_v^{\text{HF}} \rangle R_{i_c}^{L}
\]

(B6)

where \( R_{i_c}^{L} = m_{i_c}^L \). If the PAW basis function \( | \tilde{\Psi}_v^{\text{HF}} \rangle \) corresponds to an occupied valence state, it is constructed to be orthogonal to the core orbitals so that \( \tilde{C}_{i_c} = 0 \), otherwise \( \tilde{C}_{i_c} \) may be nonzero.

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

\[
X_{i_c}^{L} \rightarrow - \sum_{c} \sum_{\tilde{L}\tilde{L}} \frac{1}{\Theta_{i_c}^{\tilde{L}}} \sum_j \langle \tilde{P}_j | \tilde{\Psi}_v^{\text{HF}} \rangle R_{i_c}^{L}.
\]

(B7)

One final point regarding pseudocore orbitals needs clarification. That is, when \( | \tilde{\rho}_c(r) | = 0 \), 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 \( \langle \tilde{\Psi}_v^{\text{HF}} | \tilde{\Psi}_v^{\text{HF}} \rangle \).
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21 C. F. Fischer, T. Brage, and P. Jönsson, Computational Atomic Structure (Institute of Physics, Berkshire, 1997). The associated computer code, the ATS package is available at http://ats.vase.vanderbilt.edu
25 In designing the update procedure for \( \phi^\text{HF}(r) \), it is important to discriminate against converging to an excited state solution.
32 X. Xu and N. A. W. Holzwarth (unpublished).
37 Note that the Kohn-Sham pseudopotential calculations using the so-called nonlinear core corrections developed by Louie et al. (Ref. 43) are analogous to a frozen-core density approximation rather than a frozen-core potential approximation in the sense of Eq. (35).
40 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 \( \phi^\text{HF}(r) \) by fixing \( \lambda_{pp} \) at the positive energy of choice.
42 While all calculations are performed in terms of the radial functions, the bra and ket operators are written in terms of the full three-dimensional functions defined in Eq. (1) in order to simplify the relationships involving the angular momenta \( l_x, l_y, \) etc.
45 In terms of the radial integrals, the notation is meant to imply \( \langle \Phi^\text{HF}_l | X_a | X_b \rangle \).
51 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.
Adaptation of the Projector Augmented Wave (PAW) formalism to the treatment of orbital-dependent exchange-correlation functionals

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This paper presents the formulation and numerical implementation of a self-consistent treatment of orbital-dependent exchange-correlation functionals within the Projector Augmented Wave (PAW) method of Blöchl [Phys. Rev. B 50 17953 (1994)] for electronic structure calculations. The methodology is illustrated with binding energy curves for C in the diamond structure and LiF in the rock salt structure, comparing results from the Hartree-Fock (HF) formalism and the Optimized Effective Potential (OEP) formalism in the so-called KLI approximation [Krieger, Li, and Iafrate, Phys. Rev. A 45, 101 (1992)] with those of the local density approximation (LDA). While the work here uses pure Fock exchange only, the formalism can be applied to orbital-dependent functionals more generally.

I. INTRODUCTION

In order to improve the physical representation of materials beyond that of conventional density functional theory, there has recently been renewed interest in the use of orbital-dependent exchange-correlation functionals including the use of hybrid functionals[3–11] and the use of a combination of exact-exchange and random-phase approximation (EXX/RPA)[12–18]. At the moment, some of these treatments are not self-consistently within the KLI scheme. The corresponding KLI energies are slightly larger, differing from the OEP energies by at most 0.1 eV for transition metals. Other approximate OEP methods have been developed, including the localized Hartree-Fock method,[22] the common energy denominator,[26] and the effective local potential[27] approximations. Bula and Levy[28] have recently shown these methods to be equivalent to calculating the optimized effect potential within the subspace of occupied orbitals \( \langle \psi_{\text{occ}}(r) \rangle \). We have evaluated \( \langle \psi_{\text{occ}}(r) \rangle \) for the spherical atoms in Fig. 1, and find the corresponding ground state energies to differ by at most 0.005 eV from those calculated within the KLI scheme.

By contrast, the results from self-consistent wavefunctions obtained using GGA[29] or LDA[30] functionals and a post-processing evaluation of the Fock exchange, have significantly larger energies. On the one hand, given that the Hartree-Fock wavefunctions[31] are very similar in shape to those of LDA and GGA, the large values of post processing energy differ-
ences shown in Fig. 1 is somewhat surprising. On the other hand, the Hartree-Fock post processing energies themselves are considerably different from the self-consistent groundstate LDA and GGA atomic energies as shown in Fig. 2. Interestingly, this plot shows that the GGA energy differences have the opposite sign from the LDA energy differences, presumably primarily due to the different correlation functional forms of GGA and LDA. The results of Figs. 1 and 2 suggest that post processing treatments may introduce unintended effects in the calculations.

These results for atoms provide a motivation for developing methods to efficiently calculate the orbital dependent terms self-consistently. In previous work, we showed how to formulate the Hartree-Fock theory within the projector augmented wave (PAW) formalism of Blöchl. In this paper we extend this analysis to the OEP theory. For reasons discussed in Sec. II C, it turns out that treating the full OEP equations within the PAW formalism is difficult. As a step toward that goal, the present work focuses on the KLI approximation. It is assumed here that the orbital dependent contribution is that of the full Fock exchange. Extension of this approach to other orbital dependent functionals, including hybrid functionals and random phase approximation treatments is expected to follow similar steps.

The outline of the paper is as follows. In Sec. II, we present the KLI formalism for spherical atoms, briefly reviewing the all-electron formulas and discussing the frozen-orbital approximation. In Sec. II C we present the PAW formalism for spherical atoms and derive the relations for constructing basis functions and projectors for a KLI-PAW treatment. More details of this work are presented in the Ph. D. Thesis of Xiao Xu. In Sec. III we generalize the atomic formulations of both the Hartree-Fock and KLI theories to treat periodic solids. The methods are demonstrated in terms of binding energy curves for diamond and LiF in Sec. IV. Summary and conclusions are presented in Sec. V where we also compare the PAW-KLI approach with other previous treatments of the KLI equations within other pseudopotential approaches.

II. ELECTRONIC STRUCTURE OF SPHERICAL ATOMS
WITHIN THE KLI APPROXIMATION

A. All-electron formalism

For simplicity, we discuss the formalism for spin-unpolarized, spherically averaged atoms and use the same notation as in our previous work on developing a PAW formalism for Hartree-Fock theory. The total electron energy takes the same functional form as in Hartree-Fock theory, as a sum of kinetic energy \( E_K \), nuclear energy \( E_N \), electron-electron or Hartree energy \( E_H \), and exchange energy \( E_x \):

\[
E_{\text{tot}} = E_K + E_N + E_H + E_x.
\]

Here the exchange energy is written in terms of radial integrals defined by Condon and Shortley

\[
E_x = \sum_{pq} \sum_{L=|p-q|}^{l_p+l_q} \frac{1}{2} \Theta_{pq}^L R_{pq;gt}^L, \tag{2}
\]

where

\[
R_{pq;gt}^L \equiv e^2 \int dr dr' \frac{r_p^L(r)}{r'^2} \psi_p(r) \psi_q(r') \psi_{t}(r'). \tag{3}
\]

Here the Fock weight factor \( \Theta_{pq}^L \) for the moment \( L \) for the spherically averaged atom is derived by Ref. 37–39 and is given in Eq. (14) of Ref. 31. In contrast, to the Hartree-Fock theory, in the OEP approach, the one-electron orbitals \( \{ \psi_p(r) \} \) which appear in the energy expression are eigenstates of an effective Hamiltonian of the form

\[
\mathcal{H} = \mathcal{K} + \mathcal{V}_N(r) + \mathcal{V}_H(r) + \mathcal{V}_x(r) \quad \text{with} \quad \mathcal{H} \psi_p(r) = \epsilon_p \psi_p(r). \tag{4}
\]

Here the expressions for the nuclear and Hartree potentials are identical to those of Ref. 31. In the full OEP theory, the local potential \( V_x(r) \) can be determined iteratively in terms of orbital shift functions \( g_p(r) \) which are solutions to inhomogeneous differential equations of the form:

\[
(\mathcal{H} - \epsilon_p) g_p(r) = X_p(r) - V_x(r) \psi_p(r) - \left( \bar{U}_{x p} - \bar{U}_x \right) \psi_p(r). \tag{5}
\]

The converged local exchange potential \( V_x(r) \) is obtained when the combined shift function vanishes:

\[
\sum_p N_p g_p(r) \psi_p(r) = 0. \tag{6}
\]

Here

\[
\bar{U}_{x p} \equiv \langle \Psi_p | \bar{X}_x | \Psi_p \rangle \tag{7}
\]

and

\[
\bar{U}_x \equiv \langle \Psi_p | \bar{X}_x | \Psi_p \rangle. \tag{8}
\]

The exchange integral function \( X_p(r) \) is identical to that defined in Eq. (19) of Ref. 31 except that the orbitals \( \{ \psi_p(r) \} \) are the self-consistent OEP orbitals instead of the self-consistent Hartree-Fock orbitals. It takes the form:

\[
X_p(r) = -\sum_{q} \sum_{L=|p-q|}^{l_p+l_q} \frac{1}{N_p} \Theta_{pq}^L W_{qp}^L(r) \psi_q(r), \tag{9}
\]

where

\[
W_{qp}^L(r) \equiv e^2 \int dr' \frac{r_p^L(r')}{r'^2} \psi_q(r') \psi_p(r'). \tag{10}
\]

The Krieger, Li, and Iafrate (KLI) approximation to the OEP is based on the reasonable assumption that the orbital shift functions \( g_p(r) \) are numerically small so that the left had
side of Eq. (5) can be set to 0.43. Then a local exchange potential function $V_{x}^{\text{KLI}}(r)$ can be found which satisfies the following KLI equation:

$$V_{x}^{\text{KLI}}(r) n(r) = \sum_{p} N_{p} \psi_{p}(r) X_{p}^{\text{KLI}}(r)$$

$$+ \sum_{p} N_{p} |\psi_{p}(r)|^{2} \left( V_{x}^{\text{KLI}} - U_{x}^{\text{KLI}}(r) \right)$$

(11)

The radial density function is defined

$$n(r) \equiv \sum_{p} N_{p} |\psi_{p}(r)|^{2}.$$  

(12)

In order to solve Eq. (11) it is first necessary to determine the matrix elements $V_{x}^{\text{KLI}}$. The $p$ index references each of the $S$ atomic shells. The boundary conditions require that for the shell $p \equiv o$ corresponding to the outer most orbital $\psi_{o}(r)$, the exchange potential matrix element must satisfy $\psi_{o}^{2}(r)$.

$$V_{x}^{\text{KLI}}_{p o} \equiv U_{x}^{\text{KLI}}.$$  

(13)

For the $S - 1$ shell indices $p \neq o$, the following linear equations must be satisfied:\textsuperscript{20,24}

$$\sum_{q \neq o} \left[ \delta_{pq} - \Gamma_{pq} N_{q} \right] \Delta_{q} = \Xi_{p} - U_{x}^{\text{KLI}}.$$  

(14)

where

$$\Delta_{q} \equiv V_{x}^{\text{KLI}}_{x q} - U_{x}^{\text{KLI}}.$$  

(15)

Here

$$\Gamma_{pq} \equiv \int dr \frac{|\psi_{p}(r)|^{2} |\psi_{q}(r)|^{2}}{n(r)},$$  

(16)

and

$$\Xi_{p} \equiv \int dr \frac{|\psi_{p}(r)|^{2} \sum_{o} N_{p} \psi_{o}(r) X_{o}^{\text{KLI}}(r)}{n(r)}.$$  

(17)

Once the matrix elements $V_{x}^{\text{KLI}}_{x p}$ are determined from Eqs. (13, 14, and 15), the KLI exchange potential $V_{x}^{\text{KLI}}(r)$ can be determined from Eq. (11).

### B. Frozen core orbital approximation

The arguments favoring the frozen core orbital treatment over the frozen core potential treatment for the Hartree-Fock formalism were presented in our previous work\textsuperscript{31} and apply to the KLI formalism as well. The frozen orbital approximation within the KLI approach is almost a trivial extension of the all-electron treatment. The equations have the same form as given above, with the summation over shells $p$ including both valence states $\Psi_{v}(r)$ which are updated and core states $\Psi_{c}(r)$ which are “frozen” to the reference configuration form.\textsuperscript{44}

We note that in order that the KLI exchange potential (11) remain orbital independent and especially independent of core-valence orbital labels, it is essential for both valence and (frozen) core contributions be included in the evaluation of Eq. (11). As we will see, this will be true in the PAW formulation as well. On the other hand, it is often convenient to remove the constant contributions to the energy, and to define a valence electron energy from terms that involve valence electrons alone and terms that involve interactions between core and valence electrons:

$$E_{\text{val}} = E_{K} + E_{N} + E_{H} + E_{cv} + E_{cv} + E_{cv}.$$  

(18)

Numerical results for the frozen core orbital approximation of KLI are comparable to those of the frozen core orbital approximation of Hartree-Fock reported in our earlier work.\textsuperscript{31} For example, we considered ionization energies for spherically averaged 3$d$ atoms. The results are shown in Fig. 4 comparing the Hartree-Fock and KLI results with those obtained using the local density approximation (LDA).\textsuperscript{30} The Hartree-Fock and KLI ionization energies are very similar throughout the 3$d$ series, differing from each other by less than 0.08 eV. Not surprisingly, the LDA ionization energies differ from the HF ionization energies by roughly 2 eV. Using the core states defined by the configuration of Ar, the errors introduced by calculating the ionization energies within frozen core approximations are not visible on this scale. For the frozen core orbital approach within HF, KLI, and LDA formalisms, the average error in the ionization energies is 0.002 eV, 0.002 eV, and 0.001 eV respectively. We also calculated the ionization energies using the frozen core potential approach described in Ref.\textsuperscript{31} (labeled HFV) on the graph. In this frozen core potential approach, the average error in calculating the ionization energies is 0.05 eV, 25 times larger than that of the frozen core orbital approach. This motivates...
the adoption of a frozencore orbital treatment for our PAW formulation, which can be accomplished in a straightforward way.

![Graph](image)

FIG. 4. Plot of ionization energies for spherically averaged 3d atoms, assuming transitions $3d^5 \rightarrow 4s^2 \rightarrow 3d^1 \rightarrow 4s^1$, using the HF, KLI, and LDA exchange approximations. The results designated as HF were calculated using the frozencore potential approximation as described in the text.

C. PAW formalism for a spherical atom

1. Motivation for various approximations

In addition to the approximations associated with the PAW formalism itself, the treatment presented here uses two major approximations which need justification. We first consider reason for using the KLI approximation rather than directly solving the full OEP equations. The reason follows from the fact that the PAW formalism is designed to represent a valence electron wavefunction $\Psi_v(r)$ in the form

$$
\Psi_v(r) = \tilde{\Psi}_v(r) + \sum_{i \alpha} \left( \Phi_i^\alpha(r - R^a) - \tilde{\Phi}_i^\alpha(r - R^a) \right) \langle \tilde{P}_i^\alpha | \tilde{\Psi}_v \rangle,
$$

where $\alpha$ denotes an atomic site (which is trivial for a spherical atom) and $i$ denotes atom-centered functions which include $|\Phi_i^\alpha\rangle$, $|\tilde{\Phi}_i^\alpha\rangle$, and $|\tilde{P}_i^\alpha\rangle$ for the all-electron basis functions, pseudo basis functions, and projector functions respectively. Typically, the index $i$ represents a small number of states (one or two states per angular momentum channel) to represent the electron wavefunction in typical environments found in solids. In order to directly use the PAW formalism for the OEP treatment, it is necessary to use this form to also represent the orbital shift function $g_\alpha(r)$ defined in Eq. (5). Because of the oscillatory shape of these $g_\alpha(r)$ functions, it is necessary to significantly augment the one-center basis functions included in the general transformation of Eq. (19). The recent paper by Bulat and Levy\textsuperscript{38} clarified this point by showing that the full optimized effective potential function can be determined as a sum of contributions from the space of occupied orbitals to determine $\psi_{\alpha}^{occ}(r)$ and additional terms generated by all unoccupied states. While the use of additional basis functions in the PAW expansion is in principle possible, it is computationally expensive. Some details are presented in the Appendix (A). In fact, recent work by Harl and coworkers\textsuperscript{12} describes the use of these additional basis functions for a post-processing treatment the random phase approximation within the PAW formalism. In this case, the additional basis functions are physically motivated by the excited state contributions within the random phase formalism, while in the exchange-only OEP treatment they are needed only to fulfull the numerical requirements of the equations. On the other hand, it turns out that within the KLI approximation, the minimal basis PAW formalism works quite well. The KLI-PAW approach presented here can be also extended to the full occupied space approximation $\psi_{\alpha}^{occ}(r)$ with few changes to the formalism.

The second approximation in this work is made for simplicity. We have argued that the core states provide important contributions to the exchange interactions and in Ref. 31 we have shown how to treat extended core states with frozen-core pseudo-wavefunctions $\tilde{\psi}_c(r)$ and their fully nodal counterpart $\psi_c(r)$. While including these upper core wavefunctions in the calculation is straightforward, in order to simplify the presentation in the present work, we make the assumption that for all core wavefunctions $\tilde{\psi}_c(r) \equiv 0$. This can be made precise for any system, by treating upper core states as valence states (with additional computational cost), leaving the core designation to refer only to states whose orbitals are well-confined within the augmentation sphere. What this means is that the summations over all states in the pseudo-space includes only valence states. The core states then only enter the calculations through the one-center all-electron terms. The more general case of allowing for non-zero $\tilde{\psi}_c(r)$ for upper core wavefunctions can be derived by straightforward extension.

2. KLI-PAW formalism for atoms

The purpose of deriving the KLI-PAW equations of a spherical atom is to define the consistent basis and projector functions which satisfy the atomic KLI-PAW equations for the reference configuration and to provide the basis for extending the formalism to a more general system. The PAW representation of the radial electron density of a spherical atom takes the form\textsuperscript{31,32}

$$
\tilde{n}(r) = \tilde{\tilde{n}}(r) + \left( n^\alpha(r) - \tilde{n}^\alpha(r) \right),
$$

where $\tilde{\tilde{n}}(r)$ represents the radial pseudodensity defined over all space and the terms with superscript $\alpha$ represent the atomic density confined within the augmentation sphere. For materials, the single index $\alpha$ will be replaced by a summation of one-center contributions over all augmentation spheres.
The PAW transformation allows us to approximate the left hand side of the KLI equality – Eq. (11) – by the form
\[ V_x^{\text{KLI}}(r) \, n(r) = \tilde{V}_x^{\text{KLI}}(r) \, \bar{n}(r) + \left( V_x^{\text{aKLI}}(r) \, n^a(r) - \tilde{V}_x^{\text{aKLI}}(r) \, \bar{n}^a(r) \right). \]  

(21)

Here \( \tilde{V}_x^{\text{KLI}}(r) \) denotes the smooth pseudo exchange potential in the KLI approximation which is defined over all space while \( V_x^{\text{aKLI}}(r) \) and \( \tilde{V}_x^{\text{aKLI}}(r) \) denote the atom-centered all-electron and pseudo exchange functions, respectively which will appear in atom-centered matrix elements in the PAW formalism. In order to determine these three contributions to the exchange potential, we assume that each of them satisfies Eq. (11) in their respective spacial and functional domains.

The pseudo-space contribution takes the form written
\[ \tilde{V}_x^{\text{KLI}}(r) \, \bar{n}(r) = \sum N_v \bar{\psi}_v(r) \tilde{X}_v^{\text{KLI}}(r) + \sum_{a} N_a \left| \bar{\psi}_a(r) \right|^2 \left( \tilde{V}_x^{\text{KLI}} - \tilde{V}_x^{\text{aKLI}} \right). \]  

(22)

Within the augmentation region, the two types of one-center contributions can be written
\[ V_x^{\text{aKLI}}(r) \, n^a(r) = \sum_{p} N_p \psi_p^a(r) \tilde{X}_p^{\text{aKLI}}(r) + \sum_{p} N_p \left| \psi_p^a(r) \right|^2 \left( \tilde{V}_x^{\text{aKLI}} - \tilde{V}_x^{\text{aKLI}} \right), \]  

(23)

and
\[ \tilde{V}_x^{\text{aKLI}}(r) \, \bar{n}^a(r) = \sum N_v \bar{\psi}_v(r) \tilde{\tilde{X}}_v^{\text{aKLI}}(r) \]  

(24)

The \( \tilde{V}_x^{\text{KLI}}(r) \) and \( \tilde{V}_x^{\text{aKLI}}(r) \) matrix elements that appear in each of the three equations are determined from a sum of contributions in the form:
\[ \tilde{V}_x^{\text{KLI}} \, \bar{n}(r) = (\tilde{\Phi}_p^{\text{KLI}} | \tilde{V}_x^{\text{KLI}} | \tilde{\Phi}_p^{\text{KLI}}) + \left( (\tilde{\Phi}_p^{\text{KLI}} | \tilde{V}_x^{\text{aKLI}} | \tilde{\Phi}_p^{\text{KLI}}) - (\tilde{\Phi}_p^{\text{KLI}} | \tilde{V}_x^{\text{aKLI}} | \tilde{\Phi}_p^{\text{KLI}}) \right), \]  

(25)

and
\[ U_x^{\text{KLI}} = \bar{n} \left( \tilde{V}_x^{\text{KLI}} \right) + \left( \bar{n} \left( \tilde{V}_x^{\text{aKLI}} \right) - \bar{n} \left( \tilde{V}_x^{\text{aKLI}} \right) \right). \]  

(26)

In these expressions and in others in this section, the index \( p \) for core states is non-trivial only for the one-center all-electron terms.

In order to determine the unknown coefficients \( \tilde{V}_x^{\text{KLI}} \), a set of linear equations similar to Eq. (14) must be solved. These can be written in the form
\[ \sum_{q \neq a} [\delta_{pq} - \Gamma_{pq}^{\text{PAW}}] \Delta_q = \Xi_{pq}^{\text{PAW}} - U_{pq}^{\text{KLI}}. \]  

(27)

Once the unknown matrix elements \( \Delta_q \) have been determined, they can be they can be used in Eqs. (22, 23, and 24) to determine \( V_x^{\text{KLI}}(r) \), \( V_x^{\text{aKLI}}(r) \), and \( V_x^{\text{aKLI}}(r) \), respectively. In Eq. (27) the \( 1_{pq}^{\text{PAW}} \) matrix elements are given by
\[ \Gamma_{pq}^{\text{PAW}} = \int_0^\infty \int_0^{r_p^a} \left[ \frac{\psi_p^a(r)}{n^a(r)} \right]^2 \frac{\psi_q^a(r)}{n^a(r)} \, dr \, dr \]  

(28)

The exchange coefficients \( \Xi_{pq}^{\text{PAW}} \) are given by
\[ \Xi_{pq}^{\text{PAW}} = \int_0^\infty \int_0^{r_p^a} \frac{\psi_p^a(r)}{n^a(r)} \left[ \psi_q^a(r) \right]^2 \frac{\psi_q^a(r)}{n^a(r)} \, dr \, dr \]  

(29)

In Eqs. (28 and 29), the one center integrands are confined within the augmentation spheres \( r \leq r_p^a \) and contributions for \( p \) or \( q \) representing core states come only from the one-center all-electron terms.

In these expressions the pseudo exchange kernel is given by
\[ \tilde{\tilde{X}}_v^{\text{KLI}}(r) = -\sum_{v'} \sum_{L=|l_v^e|\ldots|l_{v'}^e|} \frac{1}{N_v} \tilde{\Theta}_{L}^{L} \tilde{W}_{L}^{L}(r) \tilde{\psi}_{v'}(r), \]  

(30)

with the interaction function evaluated according to
\[ \tilde{\tilde{W}}_{L}^{L}(r) = e^2 \int dr' \frac{r_p^a}{r} \frac{1}{L+1}  \left[ \tilde{\psi}_{v'}(r') \tilde{\psi}_{v}(r') + \tilde{M}_{L}^{L}(r') \right]. \]  

(31)

The summation over shells \( e \) and \( e' \) includes contributions from valence pseudo-wavefunctions \( \tilde{\psi}_{v}(r) \). The moment function \( \tilde{M}_{L}^{L}(r) \) is defined by Eq. (58) of Ref. 31.

For the one-center all-electron terms (23), the sum over \( p \) includes both valence and core contributions. The one-center all-electron orbitals for the valence and core states are given by
\[ \psi_v^a(r) = \sum_{p} \left( \tilde{P}_p^{L} | \tilde{\psi}_{v} \right) \phi_v^a(r) \]  

and \( \psi_v^a(r) \equiv \psi_v^a(r) \). (32)

The PAW functions are denoted by \( \phi_v^a(r) \), \( \phi_v^a(r) \), and \( \psi_v^a(r) \) for the radial projector, all-electron basis, and pseudo basis functions, respectively, while the capitalized forms (for example \( \tilde{P}_p^{L}(r) \)) denote the corresponding full 3-dimensional function. For the all-electron core contributions (\( p = c \), the all-electron frozen-core functions \( \psi_v^a(r) \) are used directly. These expressions for the atom-centered radial wavefunctions are
only valid in the augmentation region $0 \leq r \leq r_a^e$. Fortunately, in all the expressions in which they are used, it is only necessary to evaluate the radial functions in the augmentation regions. For evaluating the one-center all-electron exchange kernel $X_{p}^{\text{KLI}}(r)$ the following form for the interaction integrals can be used for $r \leq r_a^e$:

$$W_{qp}^{aL}(r) = \sum_{ij} \langle \widetilde{\Psi}_i | \widetilde{P}_i^{aL} | P_j^{aL} \widetilde{\Psi}_j \rangle u_{ij}^{aL}(r) + \left( \frac{r}{r_a^e} \right)^L \omega_{qp}^{aL},$$

where

$$u_{ij}^{aL}(r) \equiv e^2 \int_0^{r_a^e} dr' \frac{r_L^{aL}}{r_a^{L+1}} \phi_i^a(r') \phi_j^a(r'). \quad (34)$$

This expression is correct for both shell indices $q$ and $p$ corresponding to valence states. If one or both of them correspond to core states, the expressions are modified according to

$$\langle \widetilde{\Psi}_i | \widetilde{P}_i^{aL} | \widetilde{\Psi}_j \rangle \rightarrow \delta_{i,j},$$

and the replacement of $\phi_i$ with $\psi_i(r)$. The one-center pseudo orbitals for the valence states are given by

$$\bar{\psi}_i^a(r) = \sum_i \langle \bar{P}_i | \bar{\Psi}_i \rangle \bar{\phi}_i^a(r), \quad (36)$$

using the same notation as above. For evaluating the one-center pseudo exchange kernel $X_{v}^{\text{KLI}}(r)$, the following form for the interaction integral can be used for $r \leq r_a^e$:

$$\bar{W}_{vp}^{aL}(r) = \sum_{ij} \langle \bar{\Psi}_i | \bar{P}_i^{aL} | P_j^{aL} \bar{\Psi}_j \rangle \bar{w}_{ij}^{aL}(r) + \left( \frac{r}{r_a^e} \right)^L \bar{\omega}_{vp}^{aL},$$

where

$$\bar{w}_{ij}^{aL}(r) \equiv e^2 \int_0^{r_a^e} dr' \frac{r_L^{aL}}{r_a^{L+1}} \left[ \phi_i^a(r') \phi_j^a(r') + \bar{m}_{ij}^{aL}(r') \right], \quad (38)$$

where the augmentation moment $\bar{m}_{ij}^{aL}(r)$ has been defined in Eq. (53) of Ref. 31. For convenience we repeat the definition here:

$$\bar{m}_{ij}^{aL}(r) \equiv m_{ij}^{aL} g_i^a(r), \quad (39)$$

where the change moment coefficient $m_{ij}^{aL}$ is given in terms of the $i$ and $j$ basis functions

$$m_{ij}^{aL} \equiv \int_0^{r_a^e} dr \ r^L \left( \phi_i^a(r) \phi_j^a(r) - \phi_i^a(r) \bar{\phi}_j^a(r) \right), \quad (40)$$

and the augmentation shape function $g_i^a(r)$ is localized to the augmentation sphere, $0 \leq r \leq r_a^e$ and is normalized according to

$$\int_0^{r_a^e} dr \ r^L \ g_i^a(r) = 1. \quad (41)$$

In the interaction integrals for valence states in Eqs. (33 and 37) the same constants $\omega_{qp}^{aL}, \bar{\omega}_{vp}^{aL}$ appear. (The corresponding contributions vanish for localized core states.) In atomic calculations, the constants can be evaluated from the pseudopair-density outside the augmentation region:

$$\omega_{vp}^{aL} \equiv \left( \frac{r_a^e}{r} \right)^L \int_{r_a^e}^{\infty} dr' \frac{\bar{w}_{vp}(r')}{r'^{L+1}}. \quad (42)$$

In general, it is necessary to evaluate the constants $\omega_{vp}^{aL}$ within the augmentation region. This can be accomplished by matching the boundary values of of $W_{vp}^{aL}(r_a^e)$ and $\bar{W}_{vp}^{aL}(r_a^e)$ to that of $W_{vp}^{aL}(r_a^e)$, the full pseudo interaction integral given in Eq. (31).

In terms of the given representations of orbitals and of the interaction integrals, the one-center all-electron exchange kernel function can be written:

$$X_p^{\text{KLI}}(r) = -\sum_q \sum_{L=|l_i-l_q|} \frac{1}{N_p} \bar{\phi}_i^q W_{qp}^{aL}(r) \psi_q(r), \quad (43)$$

and the one-center pseudo exchange kernel function can be written:

$$\bar{X}_v^{\text{KLI}}(r) = -\sum_{v'} \sum_{L=|l_i-l_{v'}|} \frac{1}{N_v} \phi_i^v \bar{W}_{vp}^{aL}(r) \bar{\psi}_v(r). \quad (44)$$

The expressions for the exchange kernel functions given in Eqs. (31, 43) and 44 are consistent with the PAW exchange kernel function given in Ref. 31 for the Hartree-Fock formalism $X_{v}^{\text{PAW}}(r) = X_{v}^{\text{HF}}(r) + \sum_{a} \int \bar{P}_i^{aL} X_{v}^{aL}$, with the correspondence

$$\bar{X}_{v}^{\text{HF}}(r) \rightarrow \bar{X}_{v}^{\text{KLI}}(r) \quad (45)$$

and the approximate relation

$$X_i^{\text{aLHF}} \approx \langle \Phi_i^{aL} | X_i^{\text{aKLI}} \rangle - \langle \Phi_i^{aL} | \bar{X}_{v}^{\text{KLI}} \rangle. \quad (46)$$

These approximate relationships rely on the fact that within the augmentation spheres, $\psi_i(r) \approx \bar{\psi}_i^a(r)$, based on the PAW expansion given in Eq. (36) and approximate completeness relations\textsuperscript{12} for $0 \leq r \leq r_a^e$ such as:

$$\int \bar{P}_i^{aL} \langle \bar{\Psi}_i | \bar{\Psi}_j \rangle \approx \delta(r - r') \quad (47)$$

for the the pseudospaces functions.

The equations given above can be used to self-consistently solve the Kohn-Sham equations within the PAW-KLI approximation, given a PAW dataset of basis, projector, and pseudopotential functions. For the construction of a PAW dataset in the PAW-KLI approximation, it is necessary to evaluate these expressions for the reference configuration used to generate the basis and projector functions. In this case, Eqs. (22) and (24) are identical to each other, and Eq. (23) is identical to the all-electron result Eq. (11). By evaluating Eq. (22) or (24) to determine the pseudo exchange potential $V_{x}^{aL}(r)$, for
the given choice of basis and projector functions, it is possible to determine the unscreened local pseudopotential \( \tilde{V}_{\text{loc}}(r) \) from the chosen screened pseudopotential \( V^\text{PS}(r) \) according to
\[
\tilde{V}_{\text{loc}}(r) = V^\text{PS}(r) - Z^a \tilde{v}^a_0(r) - \tilde{V}^a_H(r) \bigg|_{\text{ref}} - \tilde{V}^a_2(r) \bigg|_{\text{ref}}.
\]
(48)

Here \( \tilde{v}^a_0(r) \) is defined as the Coulomb potential associated with the \( L = 0 \) augmentation shape function \( g^a_L(r) \) as given in Eq. (A7) of Ref. 31. The Hartree contribution can be evaluated as a sum of core and valence contributions in the form
\[
\tilde{V}^a_H(r) \equiv Q^a_{\text{core}} \tilde{v}^a_0(r) + \tilde{V}^a_H(r) \bigg|_{\text{ref}} \equiv \sum_v N_v \tilde{W}^a_v(r) \bigg|_{\text{ref}}.
\]
(49)

(The expression for \( \tilde{V}^a_H(r) \) differs from that of Ref. 31 because here we assume \( n^a_{\text{core}}(r) \equiv 0 \).) For evaluating both the reference Hartree potential and reference pseudoexchange kernel function
\[
\tilde{X}_v(r) \bigg|_{\text{ref}} = -\sum_{v'} \sum_{L=L_{v'=L}}^{L_{v'=L-1}} \frac{1}{N_v} \tilde{W}^L_{v'=v} \tilde{W}^L_v \bigg|_{\text{ref}} \tilde{\psi}_{v'}(r),
\]
(50)

the interaction function can be evaluated from
\[
\tilde{W}^L_{v'=v} \bigg|_{\text{ref}} = e^2 \int_0^{\infty} \mathrm{d}r' \frac{r^L_{v'=v}}{r^L_{v'=v} + 1} \left[ \tilde{\psi}_{v'}(r') \tilde{\psi}_v(r') + \tilde{\psi}_{v'}^*(r') \tilde{\psi}_v^*(r') \right],
\]
(51)

For the reference configuration, the shell labels \( v' \) and \( v \) correspond to valence basis functions so that the moment functions have the simplified form
\[
\tilde{M}^L_{v'=v} \bigg|_{\text{ref}} =
\]
\[
g_L(r) \int_0^r \mathrm{d}r' r'^L \left[ \tilde{\psi}_{v'}(r') \tilde{\psi}_v(r') - \tilde{\psi}_{v'}^*(r') \tilde{\psi}_v^*(r') \right].
\]
(52)

Figure 5 shows the pseudo versions of the KLI local exchange potentials given in Fig. 3. Figure 6 shows some examples of the unscreened local pseudopotential, \( \tilde{V}_{\text{loc}}(r) \), showing that for the same choices of construction parameters the shapes are quite similar to those of LDA. These results for F, Cl, and Br were generated using a variation of the atom-paw code, using the Vanderbilt scheme for generating the pseudo basis and projector functions.

III. PLANE WAVE REPRESENTATIONS OF PAW-HF AND PAW-KLI EQUATIONS

In order to develop the projector augmented wave approach for Hartree-Fock and KLI formalisms to treat periodic systems, it is necessary to extend the equations presented in Ref. 31 and in Sec. II C to consider multiple atomic sites \( a \) and additional angular dependence. A pseudo wavefunction for Bloch state of band \( n \) and wavevector \( k \), can be represented in a plane wave expansion of the form
\[
\tilde{\psi}_{nk}(r) = \sqrt{\frac{1}{V}} \sum_{G} A_{nk}(G) e^{i(k+G) \cdot r},
\]
(53)

where \( V \) denotes the unit cell volume, \( A_{nk}(G) \) is an expansion coefficient, and the summation over reciprocal lattice vectors \( G \) includes all terms for which \( |k + G|^2 \leq E_{\text{cut}} \), for an appropriate cutoff parameter \( E_{\text{cut}} \). For simplicity, we assume a spin unpolarized system with band weight and occupancy factors \( f_{nk} \).
A. Total energy expressions

The formulas for the total valence energy are the same in both the Hartree-Fock and KLI treatments. The energy differences are only due to differences in the wavefunctions used to evaluate the energies. Here we focus on the Fock exchange term only, since the other contributions are identical to those found earlier papers.\(^{32,50-52}\) The total valence exchange energy is a sum of smooth and one-center contributions of the form

\[
E_{x,\text{val}} = E_{x}^{\text{avv}} + \sum_{a} \left( E_{x}^{\text{avv}} + E_{x}^{\text{avc}} - E_{x}^{\text{avv}} \right).
\]  

(54)

The fact that the core-valence interactions enter only in the one-center all-electron term is a consequence of our assumption that only core states are treated as valence electrons so that only core states localized within the augmentation sphere are treated as frozen core states.

1. Smooth contributions to the Fock energy

For the purposes of evaluating the Fock energy and interaction terms, the smooth pair density function for band indices \(nk\) and \(n'k'\) can be written

\[
\tilde{\rho}_{nk,n'k'}(r) = \tilde{\Psi}_{nk}(r)\tilde{\Psi}_{n'k'}(r) + \tilde{\rho}_{nk,n'k'}(r),
\]  

(55)

where the second terms is the compensation pair charge.\(^{4,31}\) For a non-spherical system, the forms of these moments must be generalized from those presented in Eq. (58) of Ref. 31, in the form:\(^{53}\)

\[
\tilde{\rho}_{nk,n'k'}(r) = \sum_{ijkl} (P_{ijkl}^{a}) \tilde{\Psi}_{nk}(r)\tilde{\Psi}_{n'k'}(r)\tilde{\rho}_{ij}(r - R^{a}),
\]  

(56)

where the generalized moments are given by

\[
\tilde{\rho}_{ij}(r) = \sum_{LM} \overline{G}_{ij}^{LM} \sqrt{4\pi} \tilde{\rho}_{ij}^{a}(r) \tilde{\rho}_{ij}^{a}(r) Y_{LM}(\hat{r}).
\]  

(57)

Hier all of the terms are the same as defined in Ref. 31 except for the Gaunt coefficient\(^{54}\) which we take to be\(^{55}\)

\[
G_{ij}^{LM} \equiv 4\pi \int d\Omega Y_{ij}^{*}(\hat{r}) Y_{LM}(\hat{r}) Y_{LM}(\hat{r}).
\]  

(58)

By design, this pair density function has the property

\[
\lim_{N \to \infty} \frac{1}{N} \int_{N} d^{3}r \tilde{\rho}_{nk,n'k'}(r) = \delta_{nn'} (2\pi)^{3} \delta_{k - k'},
\]  

(59)

The Fourier transform of the smooth pair density function, is defined to be

\[
\tilde{\rho}_{nk,n'k'}(G) = \int d^{3}r \tilde{\rho}_{nk,n'k'}(r)e^{-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} e^{-i\mathbf{G} \cdot \mathbf{r}}.
\]  

(60)

The compensation pair charge contribution can be evaluated according to

\[
\tilde{\rho}_{nk,n'k'}(G) = \sum_{ijkl} (P_{ijkl}^{a}) \tilde{\Psi}_{nk}(G)\tilde{\Psi}_{n'k'}(G)\tilde{\rho}_{ij}(G - \mathbf{k} - \mathbf{k}' + \mathbf{G}),
\]  

(61)

where

\[
\tilde{\rho}_{ij}(q) = e^{-i\mathbf{q} \cdot \mathbf{r}} \sum_{LM} \overline{G}_{ij}^{LM} 4\pi (-i)^{L} Y_{LM}(\hat{q})
\]  

\[
\times \int_{0}^{\infty} dr L_{LM}(r) \tilde{\rho}_{ij}(r),
\]  

(62)

with \(j_{L}(x)\) denoting a spherical Bessel function.

In terms of smooth pair densities, the corresponding Fock energy can be written in the form

\[
\tilde{E}_{x} = -\frac{e^{2}}{4} \sum_{nn'k'k} f_{nk} f_{n'k'}
\]  

\[
\times \int d^{3}r d^{3}r' \tilde{\rho}_{nk,n'k'}(r)\tilde{\rho}_{n'k,n'k'}(r') \tilde{\rho}_{ij}(r - r')
\]  

\[
= -\frac{e^{2}}{V} \sum_{nn'k'k} f_{nk} f_{n'k'} \int_{0}^{\infty} dr \tilde{\rho}_{nk,n'k'}(G)^{2}
\]  

\[
\times \left( |k - k' + G|^{2} \right)^{2}.
\]  

(63)

The evaluation of this singular integral has been the subject of several investigations.\(^{56-59}\) In this work, we evaluated both the methods of Spencer and Alavi\(^{57}\) and of Duchemin and Gygi\(^{56}\) as described in more detail in the Brief Report.\(^{60}\)

Results given in Sec. IV were obtained using the method of Spencer and Alavi.\(^{57}\)

2. One-center contributions to the Fock energy

The combinations of angular contributions that appear in the one-center Coulombic contributions, can be expressed in terms of the 4-index matrix elements

\[
\gamma_{ijkl}^{a} \equiv \sum_{LM} \overline{G}_{ijkl}^{LM}(\mathbf{R}_{ijkl}^{a} - \mathbf{R}_{ijkl}^{a}) 2L + 1,
\]  

(64)

where the generalized Condon-Shortley radial interaction integrals \(R_{ijkl}^{a}\) and \(R_{ijkl}^{a}\) have been defined in Eqs. (63) and (64) of Ref. 31.

It is also convenient to define a weighted projector product

\[
W_{ij}^{a} \equiv \int \Psi_{nk}^{a}(P_{ij}^{a})^{*}\tilde{\Psi}_{nk}(G).
\]  

(65)

In evaluating both \(\gamma_{ijkl}^{a}\) and \(W_{ij}^{a}\) each basis index \(i, j, k, l\) stands for both the radial and angular quantum numbers \((n, l, m, l, \text{etc})\).

The one-center valence-valence contribution to the Fock energy can then be written

\[
E_{x}^{avv} - E_{x}^{avv} = -\frac{1}{4} \sum_{ijkl} W_{ij}^{a} W_{ij}^{a} \gamma_{ijkl}^{a}.
\]  

(66)
We note that in this formulation which follows Ref. 31 and is slightly different from that of our earlier work (Eqs. A26 and A31 of Ref. 50), the corresponding one-center Hartree energy contributions take the form
\[ E^H_{\text{exc}} - \tilde{E}^H_{\text{exc}} = \frac{1}{2} \sum_{ij} W^a_{ij} \bar{W}^a_{ij} \bar{Y}^a_{ij}, \quad (67) \]

The one-center valence-core contribution to the Fock energy depends only on the Condon-Shortley interaction integrals between valence all-electron basis functions and frozen-core orbitals and takes the form
\[ E^\text{exc}_{\text{val}} = \sum_{ij} \bar{W}^a_{ij} \delta_{l_i,l_j} \delta_{m_i,m_j} c^a_{ij}, \quad (68) \]

where
\[ c^a_{ij} = \sum_{c \in L} \frac{N_e}{2} \left[ l_i - l_j L \right] \left( 0 0 0 \right)^2 \rho^{aL}_{c \rightarrow c; ij}. \quad (69) \]

Here the sum over \( c \) is a sum over core shells with occupancies \( N_c = 2(2c + 1) \) for each atom \( a \).

### B. Fock exchange kernel for Hartree-Fock formalism

The generalization of Eqs. (70-74) of Ref. 31 for a Bloch state \( n_k \) can be written
\[ X^\text{PAW} = X^\text{HF} + \sum_{\alpha \beta} |\tilde{P}^\beta_{\alpha}| X^\alpha_{\text{val},n_k}. \quad (70) \]

The pseudo-exchange kernel takes the form
\[ \tilde{X}^\text{HF}_{n_k}(r) = -\frac{1}{2} \sum_{\alpha \beta} f_{\alpha \beta} \tilde{W}_{n_k \alpha}(r) \bar{W}_{n_k \beta}(r), \quad (71) \]

where the interaction function is defined by
\[ \tilde{W}_{n_k \alpha \beta}(r) \equiv e^2 \int d^3r' \tilde{\rho}_{n_k \alpha \beta} \frac{\Psi_{n_k \alpha}(r') \bar{\Psi}_{n_k \beta}(r)}{|r - r'|}, \quad (72) \]

The Fourier transform of the interaction kernel is given by
\[ \tilde{W}_{n_k \alpha \beta}(G) = \frac{4\pi e^2}{V} \tilde{\rho}_{n_k \alpha \beta} \frac{\Psi_{n_k \alpha}(G)}{|K - K'| + G^2}. \quad (73) \]

In order to treat its singular behavior in evaluating the pseudo-exchange kernel and related quantities, we used the method of Spencer and Alavi also used for evaluating the smooth contributions to the exchange energy.

The one-center matrix elements for the Hartree-Fock pseudo-exchange kernel function analogous to Eq. (73) in Ref. 31 (but simplified for treating only localized core orbitals) take the form
\[ X^\alpha_{\text{val},n_k} = -\frac{1}{2} \sum_{\alpha \beta} |\tilde{P}^\beta_{\alpha}| W^a_{\alpha \beta} \bar{W}^a_{\alpha \beta} \bar{Y}^a_{\alpha \beta}, \quad (74) \]

where
\[ Z^\alpha_{n_k \alpha \beta} \equiv \int d^3r \bar{\Psi}_{n_k \alpha}(r) \bar{\Psi}_{n_k \beta}(r), \quad (75) \]

### C. Fock exchange potential for KLI formalism

The smooth pseudoexchange kernel \( \tilde{X}^\text{KLI}_{n_k}(r) \) in the KLI approximation analogous to Eq. (31) takes the same form as the Hartree-Fock expression given in Eq. (71), evaluated using the appropriate KLI pseudo wavefunctions \( \Psi_{n_k}(r) \). The corresponding pseudo-space potential function \( \tilde{V}^\text{KLI}_{n_k}(r) \) can be determined from an expression analogous to Eq. (22) in Sec. II C 2:
\[ \tilde{V}^\text{KLI}_{n_k}(r) = \frac{1}{\rho(r)} \left( \sum_{n_k} f_{n_k} \bar{\Psi}_{n_k}(r) \bar{X}^\text{KLI}_{n_k}(r) \right) + \sum_{n_k} f_{n_k} |\bar{\Psi}_{n_k}(r)|^2 \left( \tilde{V}^\text{KLI}_{n_k} + \tilde{U}^\text{KLI}_{n_k} \right). \quad (76) \]

In this expression, the valence pseudo-density is given by
\[ \tilde{\rho}(r) \equiv \sum_{n_k} f_{n_k} |\bar{\Psi}_{n_k}(r)|^2. \quad (77) \]

Once the constant matrix elements \( \tilde{V}^\text{KLI}_{n_k} \) and \( \tilde{U}^\text{KLI}_{n_k} \) are known, this expression can be evaluated most conveniently using fast fourier transform (FFT) methods.

The one-center contributions to the exchange kernel can also be derived by extension of the atomic formalism. The one-center all-electron full density for atom \( a \) can be written in the form
\[ \rho^a(r) = \sum_{\alpha \beta} \bar{W}^a_{\alpha \beta} \bar{\Phi}_{\alpha \beta}^a(r) \Phi_{\alpha \beta}^a(r) + \sum_{\epsilon} \int \frac{|\bar{\psi}_{\epsilon}^a(r)|^2}{4\pi r^2}, \quad (78) \]

were the first term represents the valence states spanned by PAW basis functions indices \( i \) and \( j \), and the second term represents the localized core states with index \( c \) representing the core shells (with occupancy \( N_c = 2(2c + 1) \) ) for that atom. In order to evaluate the summations involving the all-electron exchange kernel, it is convenient to define the following functions. Analogous to the first term on the right hand side of Eq. (23) we define
\[ \sum_{\alpha} N_p |\bar{\psi}_{\epsilon}^a(r)|^2, \quad (79) \]
Representing pure core contributions, we define
\[ \Upsilon_{cc}^{\ell}(r) = -\sum_{cc'} \sum_{L} \Theta_{cc'}^{L} \phi_{cc'}^{\ell}(r) \psi_{c}(r) / r^2, \]
using the all-electron notation introduced in Sec. II A. Representing mixed core-valence contributions, we define
\[ \Upsilon_{cv}^{\ell}(r) = -\sum_{ijc} N_{c} \omega_{ijc} Y_{c}^{*}(\hat{r}) Y_{i} \left( \phi_{c}(r) \psi_{a}(r) / r^2 \right) \]
\[ \times \sum_{L} \left( \begin{array}{ccc} l_j & 0 & 0 \\ L & 0 & 0 \end{array} \right)^{L} \omega_{ijc}^{aL}(r). \]
In order to represent the pure valence contributions it is convenient to define the following one-center functions for the all-electron states:
\[ \Psi_{nk}^{a}(r) = \sum_{i} (\tilde{P}_{ni}^{a} | \Psi_{nk}(r). \]
and the pseudo states:
\[ \tilde{\Psi}_{nk}^{a}(r) = \sum_{i} (\tilde{P}_{ni}^{a} | \tilde{\Psi}_{nk}(r). \]
The one-center all-electron pure valence contributions can be written in the form
\[ \Upsilon_{vv}^{\ell}(r) = -\frac{1}{2} \sum_{ij,LM} \Phi_{ij}^{\ell}(r) \tilde{\Phi}_{ij}^{\ell}(r) Y_{LM} \tilde{\Phi}_{ij}^{\ell}(r). \]
The first term of this expression can be evaluated in terms of the interaction potentials (Eq. (34)) evaluated in the augmentation sphere
\[ \Delta \omega_{kl}^{aL}(r) \equiv \omega_{kl}^{aL}(r) - \left( \frac{r}{\alpha_{c}} \right)^{L} \omega_{kl}^{aL}(r_{c}) \]
with the expression
\[ \omega_{kl}^{aL}(r) = \sum_{kl} \omega_{kl}^{aL} \sqrt{4\pi(-1)^{M}} / 2L + 1 \left( \frac{m_{l} m_{l} m_{m}}{2L + 1} \right) G_{m_{l} m_{l} m_{m}}^{L-M} \Delta \omega_{kl}^{aL}(r). \]
The second term of Eq. (84) is related to the boundary value constant \( \omega_{b}^{aL} \), defined in Sec. II C 2 and can be expressed in the form
\[ B_{LM}^{a} \equiv \sum_{nk} f_{nk} B_{LM}^{a} \]
\[ \equiv \sum_{nk} f_{nk} \sum_{n'} W_{nk}^{a} \tilde{\Psi}_{nk}^{a} \langle \tilde{P}_{n'}^{a} | \tilde{\Phi}_{nk}^{a} \rangle J_{nk,n'k'}. \]
Here the \( J_{nk,n'k'}^{aL} \) is the angular component of the pseudo interaction integral defined Eq. (72) expanded about the atomic site \( a \) and evaluated at the augmentation radius \( r_{c}^{a} \).
In this expression, \( \Omega_{G} \equiv k - k' + G, R_{c}^{a} \) denotes the atomic position, and \( J_{G}(x) \) denotes the spherical Bessel function. Some details about the evaluation of the \( B_{LM}^{a} \) coefficients in terms of their singular values are presented in the appendix.
In terms of these functions, the one-center all-electron exchange potential function can be evaluated with the relation
\[ \tilde{V}_{x}^{aKLI}(r) = \frac{1}{\rho^{a}(r)} \left( \Upsilon_{vv}^{\ell}(r) + \Upsilon_{cv}^{\ell}(r) + \Upsilon_{vc}^{\ell}(r) \right) \]
\[ + \sum_{nk} f_{nk} \left| \Psi_{nk}^{a}(r) \right|^2 \left( \tilde{V}_{x}^{KLI} - U_{x}^{KLI} \right) \]
\[ + \sum_{c} N_{c} \left| \phi_{c}(r) \right|^2 \left( \tilde{V}_{x}^{KLI} - U_{x}^{KLI} \right). \]
The one-center pseudo density, by assumption includes only valence contributions and can be written in the form
\[ \tilde{\rho}^{a}(r) = \sum_{ij} \omega_{ij}^{a} \tilde{\Phi}_{ij}^{a}(r) \tilde{\Phi}_{ij}^{a}(r). \]
The one-center pseudo exchange function can be evaluated with an expression similar to that of 89:
\[ \tilde{V}_{x}^{aKLI}(r) = \frac{1}{\rho^{a}(r)} \left( \tilde{\Upsilon}_{vv}^{\ell}(r) \right) \]
\[ + \sum_{nk} f_{nk} \left| \tilde{\Psi}_{nk}^{a}(r) \right|^2 \left( \tilde{V}_{x}^{KLI} - U_{x}^{KLI} \right). \]
The function \( \tilde{\Upsilon}_{vv}^{\ell}(r) \) is evaluated using an expression similar to Eq. (84), replacing the all-electron basis functions \( \Phi_{ij}^{\ell}(r) \) with pseudo basis functions \( \tilde{\Phi}_{ij}^{a}(r) \) and the all-electron basis function kernel \( \tilde{w}_{kl}^{aL}(r) \) defined by Eq. (34) with the pseudo basis function kernel \( \tilde{w}_{kl}^{aL}(r) \) defined by Eq. (38). By construction, the basis function kernels are equal at the augmentation radii \( r_{c}^{a} \), \( \tilde{w}_{kl}^{aL}(r_{c}) = \tilde{w}_{kl}^{aL}(r_{c}) \), ensuring consistency of the equations.
In order to evaluate this expressions we need to determine the exchange integral matrix elements. Matrix elements corresponding to core shells, come only from the one-center terms:
\[ \tilde{U}_{x}^{aKLI} = -\sum_{c'_{L}} \frac{1}{N_{c_{L}}} \Theta_{ce}^{L} \Phi_{ce}^{L} \]
\[ - \sum_{ij \in L} \sum_{n} \omega_{ij}^{a} \delta_{i j}^{L} \delta_{m_{m} m_{m}} \left( \begin{array}{ccc} l_{c} & 0 & 0 \\ L & l_{c} & 0 \end{array} \right)^{2} R_{ce_{L}^{a}}^{L}. \]
In practice, each distinct core shell implies a particular site label \( a \) and core-core contributions (\( c \) and \( c' \)) are restricted to
the same site. Matrix elements corresponding to the valence 
bands can be evaluated using the expression
\[
U_{n,k}^{\text{KLI}} = \int d^3r \tilde{\psi}_n^*(r) \tilde{X}_{n,k}^{\text{KLI}}(r)
\]
\[
- \frac{1}{2} \sum_{a,ijkl} \langle \Psi_k | \hat{P}_i^a | \tilde{\Psi}_n \rangle \hat{F}^{aL}_{ijkl} U_{n,k}^{aL} \hat{F}^{aL}_{ijkl}
\]
\[
- \frac{1}{2} \sum_{a,ijLM} \frac{G_{ijLM}^{aL}}{4\pi} \left( \frac{r_c'}{r_c} \right)^2 E_{LM}^n \tilde{c}^a_{ij}
\]
(93)

In this expression, the coefficient \(U_{n,k}^{aL}\) is similar to the one-
center Coulomb coefficient \(V_{ij;kl}^{aL}\) defined in Eq. (64) and is 
given by
\[
U_{n,k}^{aL} \equiv \sum_{LM} G_{LM}^{aL} \sum_{ij} \frac{G_{ijLM}^{aL}}{2L+1} \left( \frac{r_c'}{r_c} \right)^2 \tilde{c}^a_{ij}
\]
(94)

As in the atomic formulation, in order to evaluate the three 
contributions to the exchange potential in Eqs. (76), (89), and 
(91), can be determined by first solving a set of linear equations 
for the potential matrix elements \(\tilde{V}_{n,k}^{\text{KLI}}\) and \(V_{n,k}^{\text{KLI}}\). For 
this purpose, we define
\[
\Xi_{n,k}^{\text{PAW}} \equiv \Xi_{n,k} + \sum_a \left( \Xi_{n,k} - \Xi_{n,k}^{a} \right)
\]
(96)

where
\[
\Xi_{n,k} \equiv \int d^3r \left| \tilde{\Psi}_n(r) \right|^2 \sum_{a,kl} f_{n,kl} \tilde{\Psi}_k^*(r) \tilde{X}_{n,k}^{\text{KLI}}(r)
\]
(97)

and the one-center contributions can be written
\[
\Xi_{n,k}^{a} - \Xi_{n,k} \equiv \sum_{ij} \langle \Psi_k | \hat{P}_i^a | \tilde{\Psi}_n \rangle \langle \Psi_n | \hat{P}_j^a | \tilde{\Psi}_k \rangle
\]
\[
\times \left( \int_{r \leq r_c} d^3r \tilde{\Phi}_i^*(r) \tilde{\Phi}_j^a(r) \tilde{\Phi}_k^a(r) \tilde{\Phi}_n^a(r) \tilde{\Phi}_j^a(r) \right)
\]
(98)

The corresponding core shell contribution can be written
\[
\Xi_{n,k}^{\text{PAW}} = \Xi_{n,k}^{a}
\]
(99)

where the notation implies that the core shell \(c\) corresponds to 
the particular atomic site \(a\). The term may be evaluated with 
the expression
\[
\Xi_{n,k}^{a} \equiv \int d^3r \left| \tilde{\psi}_n^a(r) \right|^2 \frac{\Gamma_{n,k}^{a}(r) + \Gamma_{n,k}^{a}(r) + \Gamma_{n,k}^{a}(r)}{\rho^a(r)}
\]
(100)

The coupling matrix elements between valence states can be 
written in the form
\[
\Gamma_{n,k}^{a,n,k'}^{a,c} = \Gamma_{n,k}^{a,n,k'} + \sum_a \left( \Gamma_{n,k}^{a,n,k'} - \Gamma_{n,k}^{a,n,k'}^{a} \right)
\]
(101)

Here, the pseudo space contribution is given by
\[
\Gamma_{n,k}^{a,n,k'}^{a} \equiv \int d^3r \left| \tilde{\psi}_n^a(r) \right|^2 \left| \tilde{\psi}_n^{a}(r) \right|^2 \frac{\rho^a(r)}{\rho^a(r)}
\]
(102)

which can be evaluated using FFT techniques. The one-center 
contributions can be evaluated from the expressions
\[
\Gamma_{n,k}^{a,n,k'}^{a} = \sum_{ijkl} \langle \Psi_k | \hat{P}_i^a | \tilde{\Psi}_n \rangle \langle \Psi_n | \hat{P}_j^a | \tilde{\Psi}_k \rangle \langle \Psi_n | \hat{P}_j^a | \tilde{\Psi}_n \rangle \langle \Psi_n | \hat{P}_j^a | \tilde{\Psi}_n \rangle
\]
\[
\times \left( \int_{r \leq r_c} d^3r \tilde{\Phi}_i^*(r) \tilde{\Phi}_j^a(r) \tilde{\Phi}_j^a(r) \tilde{\Phi}_n^a(r) \tilde{\Phi}_j^a(r) \right)
\]
(103)

The coupling matrix elements between valence and core shells 
and between core shells have only one-center contributions 
and depend only on the particular atomic site \(a\) associated 
with that core shell.
\[
\Gamma_{n,k,c}^{a} = \Gamma_{n,k,c}^{a,c} \quad \text{and} \quad \Gamma_{c,c'}^{a} = \Gamma_{c,c'}^{a,c}
\]
(104)

The one-center matrix elements are both Hermitian and can 
be evaluated from the expressions
\[
\Gamma_{n,k,c}^{a} = \sum_{ij} \langle \Psi_k | \hat{P}_i^a | \tilde{\Psi}_n \rangle \langle \Psi_n | \hat{P}_j^a | \tilde{\Psi}_k \rangle \int d^3r \tilde{\Phi}_i^*(r) \tilde{\Phi}_j^a(r) \tilde{\Phi}_j^a(r) \tilde{\Phi}_n^a(r) \tilde{\Phi}_j^a(r) \tilde{\Phi}_j^a(r)
\]
\[
\times \frac{\left| \tilde{\psi}_n^a(r) \right|^2}{4\pi^2} \frac{\left| \tilde{\psi}_n^a(r) \right|^2}{4\pi^2} \frac{1}{\rho^a(r)}
\]
(105)

and
\[
\Gamma_{c,c'}^{a} = \int d^3r \left| \tilde{\psi}_n^a(r) \right|^2 \frac{\left| \tilde{\psi}_n^a(r) \right|^2}{4\pi^2} \frac{1}{\rho^a(r)}.
\]
(106)

For evaluating the one-center integrals, it is most convenient 
to use a procedure found efficient in previous work.\(^5\) We use 
a generalized Gaussian quadrature method to sample the angular 
directions \(\vec{r}_o\) with weight factors \(w_o\) with \(\sum_o w_o = 4\pi\). 
For each direction, \(\vec{r}_o\), (usually 144 points are sufficient) 
the radial integrals \(0 \leq r \leq r_o\) are evaluated usual finite-
difference-based algorithms. For example
\[ \int d^3r \Phi_i^a(r)\Phi_j^b(r) \left| \psi_i^a(r) \right|^2 \rho^a(r) \]
\[ \approx \sum w_{i,n} Y^*_{i,n}(\hat{r}_a) Y_{j,m}(\hat{r}_a) \int_0^r dr \frac{\Phi_i^a(r)\Phi_j^b(r) \left| \psi_i^a(r) \right|^2}{4\pi r^2 \rho^a(r \hat{r}_a)}. \]

The linear equations that must be solved can then be put in the form
\[ \sum_{n'k'} \left( \delta_{nk,n'k'} - \Gamma_{nk,n'k'} \right) \Delta_{n'k'} = \sum_{c} \Gamma_{c,nc} \Delta_c = \sum_{c} \Gamma_{c,nc} \Delta_c - \sum_{c} \Gamma_{c,nc} \Delta_c - \sum_{c} \Gamma_{c,nc} \Delta_c = \sum_{c} \Gamma_{c,nc} \Delta_c - \sum_{c} \Gamma_{c,nc} \Delta_c. \]

In these expressions,
\[ \Delta_{nk} \equiv \bar{V}_{nk}^{\text{KLI}} - \bar{U}_{nk}^{\text{KLI}} \text{ and } \Delta_{c} \equiv \bar{V}_{c}^{\text{KLI}} - \bar{U}_{c}^{\text{KLI}}. \]

The dimension of the coupling matrix \( \Gamma_{\text{PAW}} \) is equal to the number of occupied bands \( n_k \) within the \( k \)-point sampling grid and the number of core shells \( c \) for all of the atoms of the unit cell. As in the atomic case, the coupling matrix is rank deficient, but the linear Eqs. (108) and (109) can be solved up to an arbitrary constant potential shift. In our case, the constant potential was fixed by setting \( \Delta_{n_0k_0} = \Xi_{n_0k_0}^{\text{PAW}} - \bar{U}_{n_0k_0}^{\text{KLI}} \), where the index \( n_0k_0 \) corresponds to the highest Kohn-Sham eigenvalue associated with an occupied state.

Once the potential matrix elements \( V_{c,nc}^{\text{KLI}} \) and \( V_{c,nc}^{\text{KLI}} \) are determined, the corresponding exchange potentials can be calculated. While \( V_{c,nc}^{\text{KLI}}(r) \) (Eq. (76)) contributes to the Kohn-Sham pseudopotential evaluated over all space, the one center contributions given in Eqs. (89) and (91) contribute to the one-center matrix elements of the Hamiltonian \( D_{ij}^{c} \) in the form
\[ [V_{ij}^{c}]_{ij} \equiv \langle \Phi_i^a | V_{c,nc}^{\text{KLI}} | \Phi_j^a \rangle - \langle \Phi_i^a | V_{c,nc}^{\text{KLI}} | \Phi_j^a \rangle. \]

With the determination of these exchange potentials, the calculations proceed in the same way as other Kohn-Sham PAW algorithms.

### IV. RESULTS FOR DIAMOND AND LIF

In order to test the formalism, we have calculated the self-consistent electronic structure of diamond and LiF. The PAW basis and projector functions were calculated using a modified version of the atomppaw code\(^6\) using the parameters listed in Table I. The same parameters were used to contract the Hartree-Fock, KLI, and LDA\(^8\) datasets. While the results are not extremely sensitive to the details of the PAW parameters, past experience has shown that the choice of parameters given in Table I are well-converged to the benchmark values.

The solid calculations for the [Hartree-Fock] and KLI calculations were performed using a modified version of the pw-paw code\(^6\). The LDA results were obtained using the abinit\(^6\) and quantum-espresso\(^6\) codes as well. The binding energy curves shown in Figs. 7 and 8 were fit to the Murnaghan equation of state\(^6\) in order to extract the equilibrium lattice constant \( a \) and bulk modulus \( B \). There are many results of these quantities in the literature; a few of these are listed for comparison in Table II.

### V. SUMMARY AND CONCLUSIONS

Comments about extended core treatment and voce. Comments about Kleinman-Bylander and Andrew Rappe.

Appendix A: An example of orbital shift functions

Figure 9 shows an example of the shell contributions to the combined shift function (Eq. (6)) for C in the spherically averaged \( 1s^22s^22p^2 \) configuration. While each curve represents a complicated function, the sum of the curves is zero at all radii as required at convergence by Eq. (6).
Figure 10 shows the shape of the individual orbital shift functions $g_p(r)$ for C which were determined from Eq. (5). While their magnitudes are small, their shapes are very complicated. From the forms of these functions it is evident that their accurate representation as a sum of atomic basis functions would require a large number of terms. In particular, the PAW transformation Eq. (19) would require that in the augmentation region, both the all-electron valence orbital function $\psi_v(r)$ and the corresponding all-electron valence orbital shift function $g_v(r)$ be well represented by a sum of all-electron basis functions $\{\phi_i(r)\}$ for $r \leq r^*_v$: 

$$
\psi_v(r) \approx \sum_i \phi_i(r) \langle \tilde{P}_i^v | \tilde{\Psi}_v \rangle \quad \text{and} \quad g_v(r) \approx \sum_i \phi_i(r) \langle \tilde{P}_i^v | \tilde{G}_v \rangle .
$$

(A1)

Without knowing the values of the expansion coefficients $\langle \tilde{P}_i^v | \tilde{G}_v \rangle$, the shape of the curves in Fig. 10 suggest that accurate representation of $g_v(r)$ requires many more terms than does accurate representation of $\psi_v(r)$.

**Appendix B: Some details of Hartree-Fock formalism**

In principle, the Hartree-Fock equations are not defined for unoccupied states. However, in order to generate a more complete basis set for the PAW formalism and to generate the local pseudopotential, it is convenient to use continuum states. For this purpose, we simplified a more rigorous treatment using Eq. (B1) and a method similar to that described by Al-Saidi and co-workers\cite{31} to generate a screened pseudopotential $V_{loc}^{\alpha PS}(r)$. By using Eq. (B1) and a method similar to that described by Al-Saidi and co-workers\cite{31} to generate a screened pseudopotential $V_{loc}^{\alpha PS}(r)$, we can then find $V_{loc}^{\alpha PS}(r)$ using a similar unscreening

\[(\mathcal{K} + V_N(r) + V_H(r) - \epsilon_p) \psi_p(r) + X_p(r) = 0, \quad (B1)\]
process described by Eq. (48).
In order to simplify the formulation, we relaxed the orthogonality constraints of the valence wavefunctions with respect to the core orbitals. We also assumed the core states to be confined within the augmentation region using the expressions given in Sec. III A 1, III A 2, and III B. In this case, matrix elements of the Hartree-Fock equations in the Bloch basis are diagonal in wavevector $k$ and Hermitian with respect to band indices. In order to use the same diagonalization procedures that are used for the Kohn-Sham formulations, it is convenient to regroup terms in the evaluation of matrix elements of the exchange interaction defined in Sec. III B:

\[
\langle \tilde{\Psi}_{n;k}^* | \tilde{X}_{nk}^{\text{PAW}} | \tilde{\Psi}_{n;k} \rangle = \langle \tilde{\Psi}_{n;k}^* | \tilde{X}_{nk}^{\text{PAW}} \rangle = \lambda_{\tilde{\Psi}_{n;k},k} + \sum_{\tilde{\Psi}_{n;k},l} \langle \tilde{\Psi}_{n;k}^* | \tilde{\Psi}_{n;l} \rangle \lambda_{\tilde{\Psi}_{n;l},k} \langle \tilde{\Psi}_{n;l}^* | \tilde{\Psi}_{n;k} \rangle.
\]

(B2)

Here

\[
\lambda_{\tilde{\Psi}_{n;k},k} \equiv -\frac{2\pi a^2}{V} \sum_{n'k'} f_{n'k'} \frac{\tilde{\rho}_{n'k',nkr}^{\text{G}} \tilde{\rho}_{nk'nkr}^{\text{G}}}{|k - k' + G|^2},
\]

(B3)

and

\[
\chi_{il}^2 = -\frac{1}{2} \sum_{jk} W_{ij}^{\alpha} Y_{ij;kl}^{\alpha} - \delta_{l,t} \delta_{n,m} C_{il}^{\alpha}.
\]

(B4)

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In this section, the basis function indices \((i, j, \ldots)\) are used both as a short hand notation for the radial function index and for the composite indices including the spherical harmonic values \(l, m_i\). Hopefully the interpretation of the expressions will be clear from their context.

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Note that the factor of \(\sqrt{4\pi}\) is included here for convenience, but is not present in the usual definition of Gaunt coefficients.

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