

Introduction

Recently, there has been renewed interest in using the Hartree-Fock approximation as a component of electronic structure calculations.[1, 2]. In this poster, we first examine how to represent the core electrons' effects within the Frozen-core Hartree Fock scheme. And based on that, we develop a projected augmented wave (PAW)[3, 4] formulation of Hartree-Fock theory. We investigate how the PAW formalism, developed for Kohn-Sham theory[5] can be modified to work with the integral-differential equations of Hartree-Fock theory, and how core electrons should be treated. In this paper, the examination focuses on the treatment of spherical atoms; application of the Hartree-Fock PAW formalism to non-spherical, spin polarize, and/or multi-component systems can be obtained with a straightforward extension of the basic equations. These investigations also provide useful insights into our Optimized Effective Potential(OEP)-PAW methods that we have been working on.

All-electron Hartree-Fock equations

The Hartree-Fock integral-differential equations can be derived as a total energy minimization problem with orthogonalization constraints. The object function can be given by :

$$F_{tot} = E_{tot} - \sum_{qp} N_p \lambda_{qp} (\langle \Psi_p^{HF} | \Psi_q^{HF} \rangle - \delta_{qp}) \quad (1)$$

Where N_p is the occupation number in orbital p , λ_{qp} denotes a Lagrange multiplier, E_{tot} is the total energy, which can be written as the sum of kinetic energy E_K , nuclear energy E_N , Hartree energy E_H and Exchange energy E_X .

$$E_{tot} = E_K + E_N + E_H + E_X \quad (2)$$

here E_x is the Fock exchange energy :

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

By taking functional derivative of the E_{tot} with respect to the orbital :

$$\frac{\partial F_{tot}}{\partial \Psi_p^{HF*}} = 0 \quad (4)$$

We obtain the Hartree-Fock integral-differential equations

$$H^{HF} \Psi_p^{HF}(r) + X_p(r) - \sum_{q, N_q > 0} \lambda_{qp} \Psi_q^{HF}(r) = 0 \quad (5)$$

Which must be solved self-consistently, here the Hartree-Fock Hamiltonian takes the form

$$H^{HF}(r) = K + V_N(r) + V_H(r) \quad (6)$$

And the exchange kernel is given by :

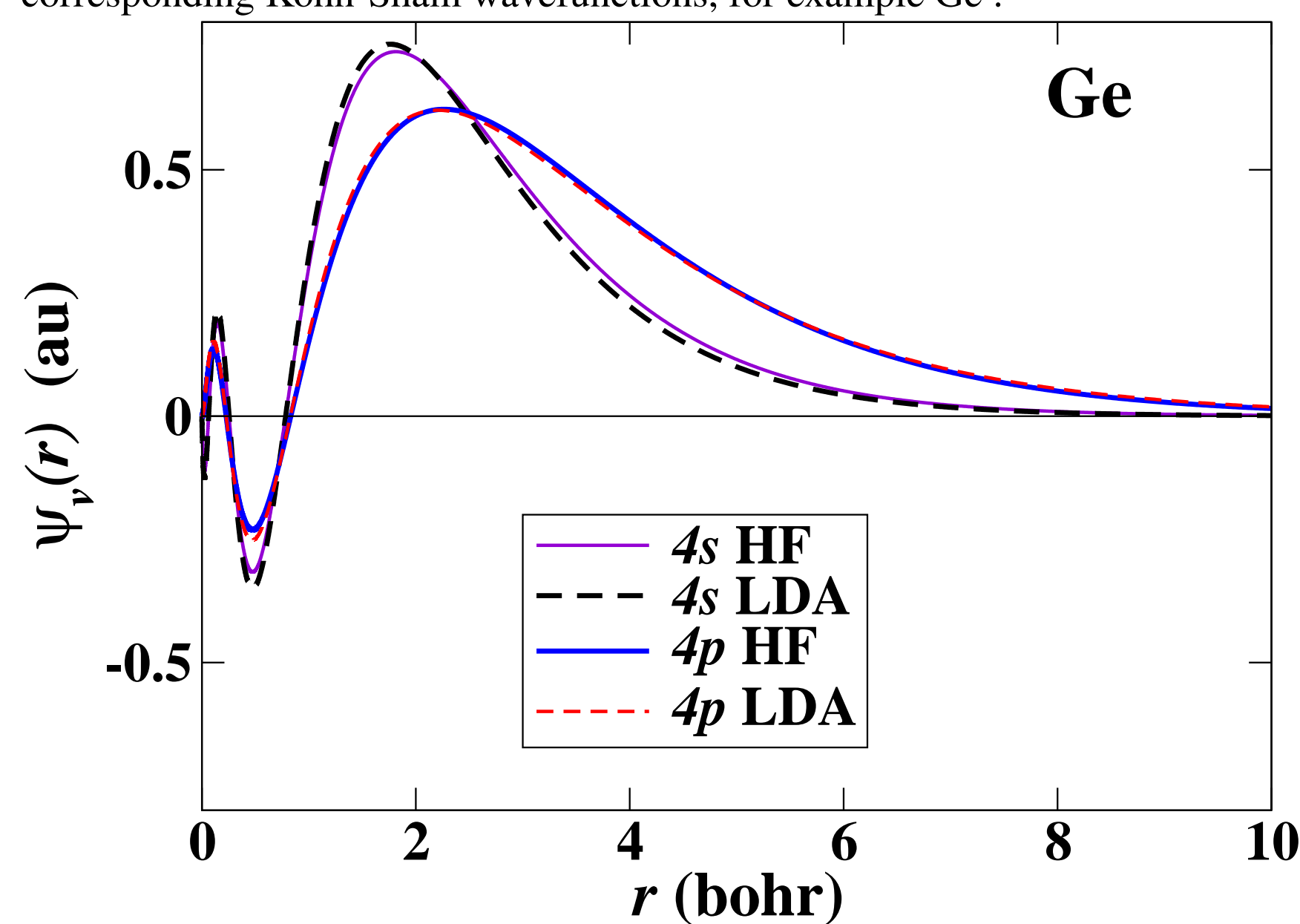
$$X_p(r) = \frac{1}{N_p} \frac{\partial E_x}{\partial \Psi_p^*} = - \sum_q \sum_{L=|l_p-l_q|}^{l_p+l_q} \frac{1}{N_p} \Theta_{pq}^L W_{qp}^L(r) \Psi_q^{HF}(r) \quad (7)$$

where :

$$W_{qp}^L(r) = e^2 \int_{r >}^{r'} \int_{r <}^{r'} \frac{r'^L}{r'^L - 1} \Psi_q^{HF*}(r') \Psi_p^{HF}(r') \quad (8)$$

and Θ_{pq}^L [6] is the weight factor for the moment L for spherically averaged atom.

The shapes of the Hartree-Fock wavefunctions are, in general, similar to the shapes of the corresponding Kohn-Sham wavefunctions, for example Ge :



AE HF iteration algorithm

In practice, rather than directly solving the integral-differential equations, we use iterative techniques [7]. Starting with an initial guess for the radial components $\{\psi_p^{HF(0)}(r)\}$, we solve a set of inhomogeneous differential equations iteratively to obtain updated $\psi_p^{HF(1)}(r)$.

$$(H^{HF(0)}(r) - \varepsilon_p^{(0)}) \psi_p^{HF(1)}(r) = R_p^{(0)} \quad (9)$$

Here the left hand side is obtained from previous iteration :

$$R_p^{(0)} = -X_p^{(0)}(r) + \sum_q \lambda_{qp}^{(0)} \psi_p^{HF(0)}(r) - \varepsilon_p^{(0)} \psi_p^{HF(0)}(r) \quad (10)$$

The parameters $\varepsilon_p^{(0)} \approx \lambda_{qp}^{(0)}$ are introduced to further stabilize the solution. [8]

Frozen-core atomic Hartree Fock equations

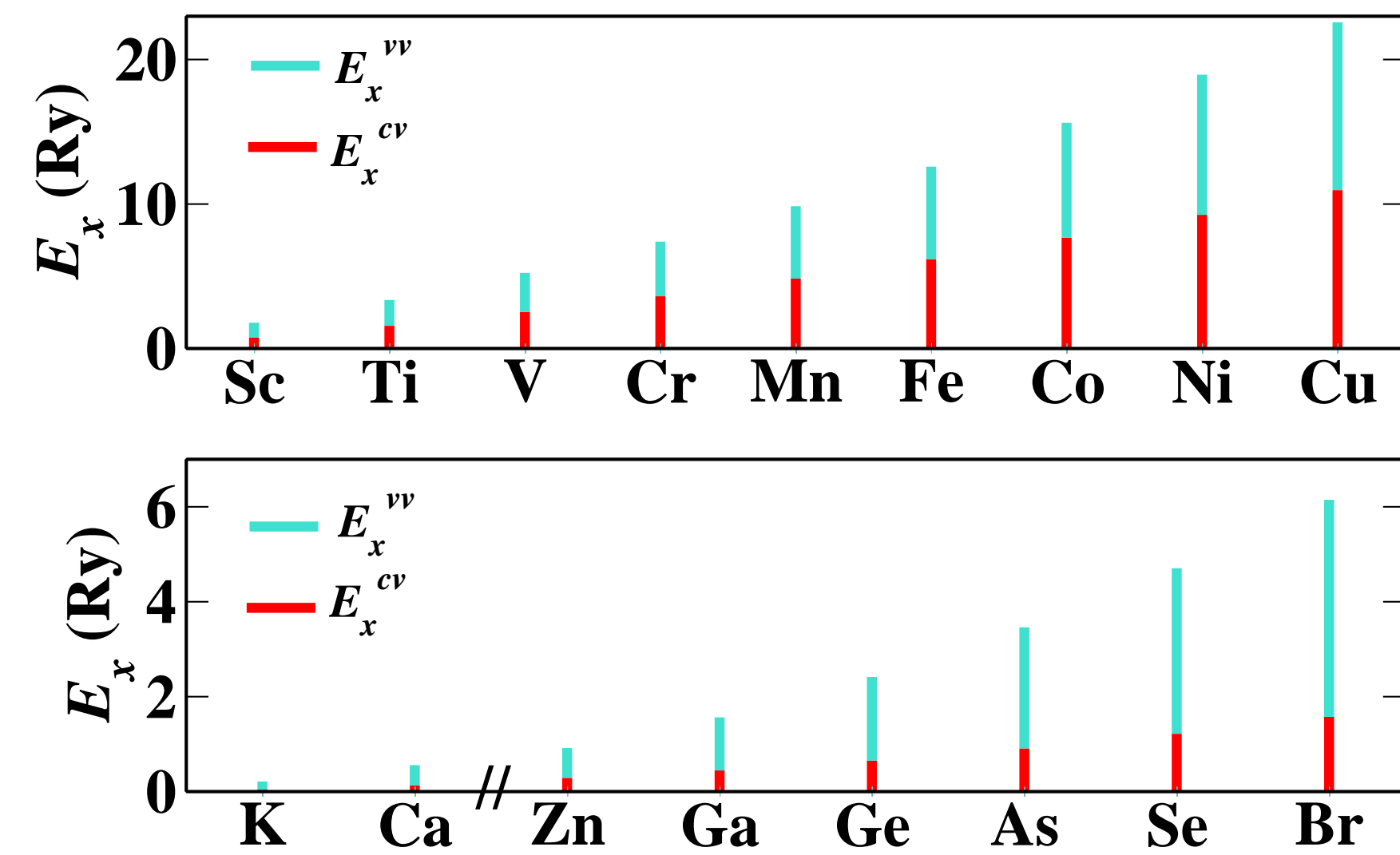
The frozen core wavefunction approximation within Hartree-Fock theory has also been well described in the literature [7]. In this case, the exchange energy can be divided into core-valence and valence-valence interactions :

$$E_x^{cv} = E_x^{cv} + E_x^{vv} \quad (11)$$

Here :

$$E_x^{cv} = - \sum_{vc} \sum_{L=|l_v-l_c|}^{l_v+l_c} \Theta_{vc}^L R_{vc,vc}^L(r) \quad \text{and} \quad E_x^{vv} = - \sum_{vv'} \sum_{L=|l_v-l_{v'}|}^{l_v+l_{v'}} \Theta_{vv'}^L R_{vv',vv'}^L(r) \quad (12)$$

To get an idea of the percentage of the core-valence and valence-valence contributions to the exchange energy, results are plotted below. The energy values are given in Ry units.



The self-consistent solution of the frozen core orbital approximation Hartree-Fock equations corresponds to solving only for the valence orbitals ($p \equiv v$) while leaving the core orbitals $\psi_c^{HF}(r)$ fixed at the reference state. It is important to require that the valence orbitals $\Psi_v^{HF}(r)$ remain orthogonal to each other as well as to the core orbitals : $\langle \Psi_v^{HF} | \Psi_c^{HF} \rangle = 0$

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

$$\Delta \Delta E = (E_{tot}^{excited} - E_{tot}^{ground})_{AE} - (E_{val}^{excited} - E_{val}^{ground}) \quad (13)$$

We find the frozen core wavefunction approximation in Hartree-Fock theory to have similar accuracy to that of the frozencore approximation in Kohn-Sham theory.

Another possible treatment on core effects is to eliminate the core wavefunctions and to represent their effects in terms of pseudopotential.[1, 2]. For the Hartree-Fock analogue, an intuitive question to ask is whether there existed such a fixed potential $V_x^{cv}(r)$ which can accurately approximate the core-valence exchange interaction.

$$H^{HF} = K + V_N(r) + V_H^v(r) + V_H^c(r) + V_x^{cv}(r) \quad (14)$$

Here the last term V_x^{cv} represents the core electrons' effects, and the Hamiltonian is different from (6)

The corresponding equations in the Hartree-Fock frozencore potential approximation take the form:

$$H^{HF}(r) \psi_v^{HF}(r) + X_v^{cv}(r) = \sum_{q, N_q > 0} \lambda_{vq} \psi_q^{HF}(r) \quad (15)$$

The corresponding valence-core exchange energy in comparison to (12) is then given by

$$E_x^{cv} = \int dr V_x^{cv}(r) n_c(r) \quad (16)$$

However, the results obtained by using the above choice of frozencore potential show the error in the valence energies of excited states to be larger by a factor of 5-10 than that of the frozencore orbital approximation. On the other hand, it is quite possible that the frozencore potential error can be reduced by improving the form[9] of the frozencore potential $V_x^{cv}(r)$.

PAW formulation of Hartree Theory

The Projector Augmented Wave (PAW) formalism was developed by Blöchl[3] and implemented by a number of authors.[3, 10, 11, 4]. A key idea of the PAW formalism is the transformation between a calculated pseudo-wavefunction ($\tilde{\Psi}_v(r)$) and the corresponding fully nodal wavefunction ($\Psi_v(r)$) of valence state :

$$\Psi_v(r) = \tilde{\Psi}_v(r) + \sum_{ai} (\Phi_i^a(r - R^a) - \tilde{\Phi}_i^a(r - R^a)) \langle \tilde{P}_i^a | \tilde{\Psi}_v \rangle \quad (17)$$

We denote these as $\Phi_i^a(r)$ for an all-electron basis function, $\tilde{\Phi}_i^a(r)$ for the corresponding pseudo-electron basis function, and $\tilde{P}_i^a(r)$ for the corresponding projector function. The projector functions satisfy the relationship $\langle \tilde{P}_i^a | \tilde{\Phi}_j^a \rangle = \delta_{ij}$. And the radial pseudo-functions have the property $\tilde{\phi}_i^a(r) = \phi_i^a(r)$ for $r > r_c^a$.

We decide to use the frozencore orbital approximation for our PAW implementation, and the self-consistent Hartree-Fock equations for the PAW formulation take the form:

$$H_{HF}^{PAW}(r) \tilde{\Psi}_v^{HF}(r) + X_v^{PAW}(r) - \sum_q \lambda_{vq} O_{HF}^{PAW} \tilde{\Psi}_q^{HF}(r) = 0 \quad (18)$$

Here :

$$H_{HF}^{PAW}(r) = \tilde{H}^{HF} + \sum_{aij} \langle \tilde{P}_i^a | D_{ij}^{HF} | \tilde{P}_j^a \rangle \quad (19)$$

And

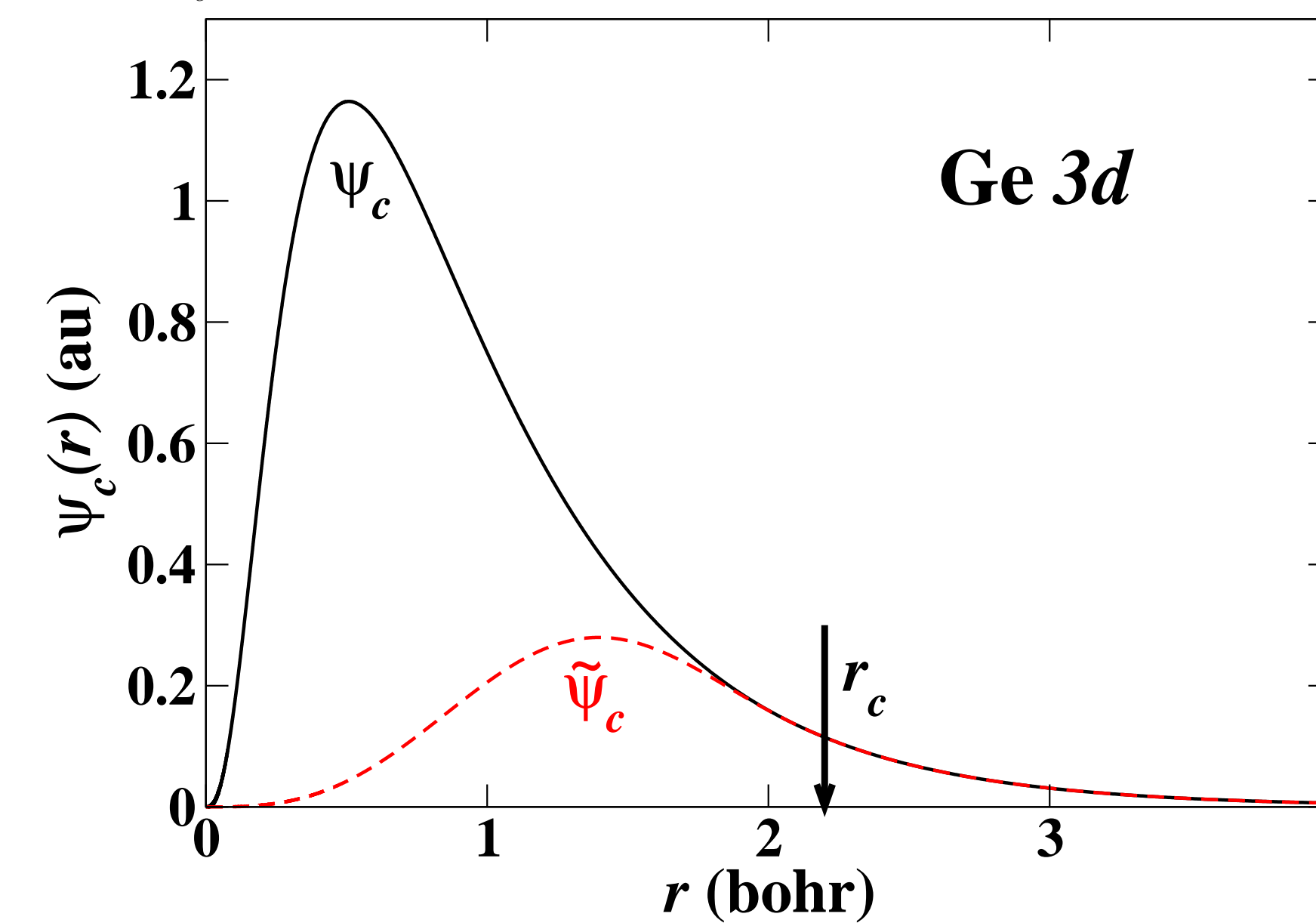
$$\tilde{H}^{HF} = K + \tilde{V}_N(r) + \tilde{V}_H(r) + \tilde{V}_{loc}(r) \quad (20)$$

$$X_v^{PAW}(r) = \tilde{X}_v(r) + \sum_{ai} \langle \tilde{P}_i^a | X_{iv}^a \rangle \quad (21)$$

Here $\tilde{V}_{loc}(r)$ is a localized potential defined in the range $0 < r < r_c^a$. The effects of core electrons are incorporated in D_{ij}^{HF} and X_{iv}^a matrix element, and These equations must be solved self-consistently, with orthonormalization constraint:

$$\langle \tilde{\Psi}_v^{HF} | O^{PAW} | \tilde{\Psi}_q^{HF} \rangle = \delta_{vq} \quad (22)$$

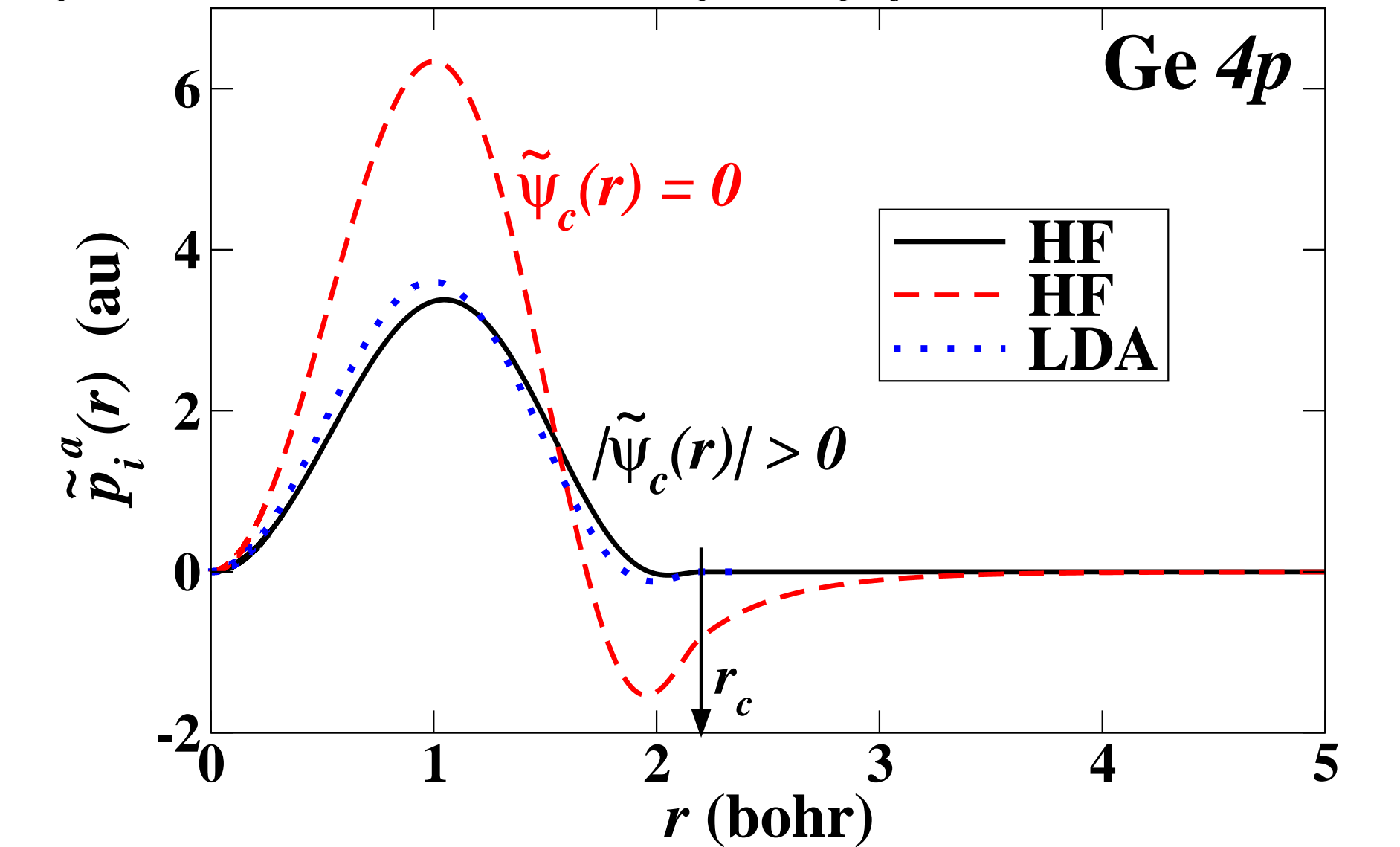
For the core wavefunctions $\Psi_c^{HF}(r)$, most of them are contained within the augmentation sphere and we can define a trivial core pseudowavefunction $\tilde{\Psi}_c^{HF}(r) \equiv 0$ for them. For some materials it is possible that the outer most core orbital will have a non-trivial amplitude for $r > r_c^a$. In such a case, we define a continuous pseudo-core orbital $\tilde{\psi}_c^a(r)$ with $\tilde{\psi}_c^a(r) \equiv \psi_c^a(r)$ for $r > r_c^a$.



Given the basis function for the reference state, We use the following equation to obtain the projector within Hartree-Fock formalism :

$$\begin{aligned} \tilde{H}^{HF}(r) \tilde{\Phi}_i^a(r) + \tilde{X}_i^a(r) - \sum_{q, N_q} \lambda_{iq} \tilde{\Psi}_q^{HF}(r) \\ = \sum_j \tilde{P}_j^a(r) (\langle \tilde{\Phi}_j^a | \tilde{H}^{HF} | \tilde{\Phi}_i^a \rangle + \langle \tilde{\Phi}_j^a | \tilde{X}_i^a \rangle - \sum_{q, N_q > 0} \lambda_{iq} \langle \tilde{\Phi}_j^a | \tilde{\Psi}_q^{HF} \rangle) \end{aligned} \quad (23)$$

In practice, for some elements, we find that different treatments for upper core states give prominent visible difference. For example, the projectors of Ge :



The other adjustable function in this construction is the localized potential $\tilde{V}_{loc}^a(r)$ define in(20). A simple, but reasonable choice is:

$$\tilde{V}_{loc}^a(r) = \mathcal{V}_0 k(r) \quad (24)$$

where :

$$k(r) = \left[\frac{\sin(\pi r / r_c^a)}{(\pi r / r_c^a)} \right]^2 \quad (25)$$

For $r < r_c^a$, and zero elsewhere.

The following Table lists the Hartree-Fock valence energies of several atoms comparing the PAW energies with the corresponding frozen core results and also comparing the effects of including or excluding the pseudo-core orbitals, and the effects of \mathcal{V}_0 .

Atom	Type	$ \tilde{\psi}_c $	r_c^a	\mathcal{V}_0	$E_{val}(ns^2np^2)$	$E_{val}(ns^1np^2)$
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

Summary and Conclusion

In this paper, we first numerically compared the frozencore orbital and the frozencore potential approximations. For our choice of potential form, the frozencore orbital approximation gave results closer to the all-electron Hartree-Fock treatment. We then derived the equations and demonstrated examples of the PAW-HF formalism for atoms across the periodic table, and showed that with the proper choice of augmentation radii, local pseudopotentials, etc. atomic PAW calculations can achieve the same numerical accuracy as the frozencore orbital approximation within Hartree-Fock theory.

Acknowledgements

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