A Projector Augmented Wave Formulation of the Hartree-Fock and KLI Approximations

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Motivation of this work: **Why?** orbital dependent functionals + PAW

2 Review of All Electron Hartree-Fock Theory and KLI Approximation, present the implementation and results.

3 Explain: Implementation of frozen core **orbital** approximation.

4 Show: How to using Hartree-Fock and KLI within ATOMPAW framework.

5 Show: How to use KLI within plane wave PAW framework.

6 Conclusions
Motivation

1. Advantages: Orbital dependent functional can avoid self-interaction error by using functionals, like Fock exchange. PAW: treat multiple moments at higher accuracy.

2. In 2009 APS meeting, we reported our all electron OEP (Optimized Effective Potential) results, frozen core approximation scheme, as well as ATOMPAW+OEP. Later on, when implementing Plane wave PAW+OEP, we realize that OEP can not be well easily treated within the traditional PAW formalism because its inherent need to represent rapidly varying functions. Therefore, in this work, we take first order approximation of OEP, which is KLI* method, and combine it with PAW.

3. Continue: PAW + HF

**Motivation: Magnitude of self-interaction error**

\[ E_{xc}^{LDA/GGA}(SCF) - E_x^{Fock}(PP) \]

Non-self-consistent post processing

- The magnitude of self-interaction error is between 10ev-50ev.
- LDA overestimates xc energy, and GGA underestimates.

**Post processing** example: Harl, Schimka, and Kresse, PRB 81, 115126 (18pp) (2010).
Comparing total energy of LDA, GGA, OEP and KLI with Hartree-Fock (lowest reference) results.  
Conclusion: Self-consistent calculation with orbital dependent functional (OEP, KLI) can further increase the accuracy.  
As a first order approximation, KLI and OEP total energy are quite close.
Within Hartree-Fock theory, the Fock exchange energy is given by:

\[
E_x = -\frac{e^2}{2} \sum_{pq} \delta_{\sigma_p \sigma_q} \int d^3r \int d^3r' \frac{\psi_{p}^{\text{HF}*}(r)\psi_{q}^{\text{HF}}(r)\psi_{q}^{\text{HF}}(r')\psi_{p}^{\text{HF}}(r')}{|r - r'|} \tag{1}
\]

We define the derivatives of Fock exchange term with respect to the orbitals as the **Exchange Kernel Function** (non-local term):

\[
X_p(r) = \frac{\partial E_x}{\partial \psi_{p}^{\text{HF}*}(r)} = -e^2 \sum_{q} \delta_{\sigma_p \sigma_q} \psi_{q}^{\text{HF}}(r) \int d^3r' \frac{\psi_{q}^{\text{HF}*}(r')\psi_{p}^{\text{HF}}(r')}{|r - r'|} \tag{2}
\]

The Hartree-Fock equation, in terms of the radial part can be written as:

\[
H^{\text{HF}} \psi_{p}^{\text{HF}}(r) + X_p(r) - \sum_{q} \lambda_{pq} \psi_{q}^{\text{HF}}(r) = 0 \tag{3}
\]
Radial wavefunction for Ge, comparing Kohn-Sham (LDA) and Hartree-Fock (HF)

Review: All Electron KLI Theory

From Hartree-Fock $\rightarrow$ Kohn-Sham

$$H^{HF} \psi_p^{HF}(r) + X_p(r) \rightarrow H^{KS} \psi_p^{KS}(r)$$

Where

$$X_p(r) \rightarrow V_x(r) \psi_p^{KS}(r)$$

OEP $\rightarrow$ KLI Equation*

$$V_x(r) \rho(r) = \sum_q N_q \psi_q(r) X_q(r) + \sum_q (\bar{V}_{xq} - \bar{U}_{xq}) N_q \psi_q^2(r)$$

$$\Downarrow$$

$$A \bar{V}_x = B$$

Result of KLI Atom implementation

Comparing Exchange Potential between OEP and KLI

1. Comparison of OEP and KLI of $V_x(r)$ for Br, Cl and F in their ground states. (with different shell structure)

2. **Observation** Energy, exchange potential are quite close between KLI and OEP

3. Wavefunctions are almost identical.
Review: Frozen core approximation

After all-electron atom calculation, the next necessary step is to test frozen core calculations’s accuracy, which served as an indicator of accuracy in the future material calculations. The fundamental 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.

\[
\text{Fe : } 1s^1 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2
\]

\[
\text{Fe : } 1s^1 2s^2 2p^6 3s^2 3p^6 3d^7 4s^1
\]

\[
\text{Fe : } 1s^1 2s^2 2p^6 3s^2 3p^6 3d^7 4s^1
\]
Frozen Core Approximation: core-valence exchange energy

How to represent the core valence interaction (core effects)?

Frozen Core Potential Approximation

Core-Valence interaction

\[ E_{cv}^x = \int V_{cv}^x(r) \rho_v(r) dr \]

\( V_{cv}^x(r) \) is frozen.

Frozen Core Orbital Approximation

Core-Valence interaction

\[ E_{vc}^x = -\frac{e^2}{2} \sum_{vc} \delta_{\sigma_v \sigma_c} \int \int d^3 r d^3 r' \frac{\Psi_v^* \Psi_c \Psi_v \Psi_c^*}{|r - r'|} \]

\( \Psi_c(r) \) are frozen.
Result: Frozen core error

Frozen Core Error: Frozen Orbital $\sqrt{\text{VS Frozen Potential}}$

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

Motivation and Outline

Hatree-Fock Theory and KLI Approximation
Frozen core orbital approximation
Atompaw of HF and KLI
Planwave representation of HF and KLI
Conclusion

Review: PAW

Atom centered functions needed for PAW calculation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi^a_i(r)$</td>
<td>AE basis function</td>
<td>AE Kohn-Sham eigenstate</td>
</tr>
<tr>
<td>$\tilde{\phi}^a_i(r)$</td>
<td>PS basis function</td>
<td>Constructed; $\tilde{\phi}^a_i(r) \equiv \phi^a_i(r)$ for $r \geq r^a_c$</td>
</tr>
<tr>
<td>$\hat{P}^a_i(r)$</td>
<td>Projector function</td>
<td>$\hat{P}^a_i(r) \equiv 0$ for $r \geq r^a_c$ and $\langle \hat{P}^a_i</td>
</tr>
</tbody>
</table>

PAW transformation from $\tilde{\Psi}_n(r) \rightarrow$ AE $\Psi_n(r)$

$$\Psi_n(r) = \tilde{\Psi}_n(r) + \sum ai \left( \phi^a_i(r) - \tilde{\phi}^a_i(r) \right) \langle \hat{p}^a_i | \tilde{\Psi}_n \rangle$$

Corrections

Kohn-Sham equations in PAW formalism

\[ H_{\text{PAW}} - \varepsilon_p O \tilde{\Psi}_p(r) = 0 \]

PAW Hamiltonian

\[ H_{\text{PAW}} = \tilde{H}(r) + \sum_{a,ij} \tilde{P}_a \left| \tilde{P}_a^a \right\rangle \langle \tilde{P}_j^a | \]

PAW Matrix Elements

\[ D_{ij}^a = \langle \phi_i^a \left| H \right| \phi_j^a \rangle - \langle \tilde{\phi}_i^a \left| \tilde{H} \right| \tilde{\phi}_j^a \rangle \]

PAW Overlap Function

\[ O = 1 + \sum_{a,ij} \tilde{P}_a \left| \tilde{P}_a^a \right\rangle O_{ij}^a \langle \tilde{P}_j^a | \]

\[ O_{ij}^a = \langle \phi_i^a \left| \phi_j^a \rangle - \langle \tilde{\phi}_i^a \left| \tilde{\phi}_j^a \right\rangle \]
Hartree Fock equation $\implies$ PAW

\[ H_{HF}^{PAW}(\mathbf{r}) \tilde{\psi}_{HF}^{PAW}(\mathbf{r}) + X_{v}^{PAW}(\mathbf{r}) - \sum_{q} \lambda_{qv} O_{HF}^{PAW} \tilde{\psi}_{q}^{HF}(\mathbf{r}) = 0 \]

Hamiltonian like term $\implies$ pseudo + one center

\[ H_{HF}^{PAW}(\mathbf{r}) = \tilde{H}_{HF}^{HF} + \sum_{aij} \left| \tilde{P}_{i}^{a} \right\rangle D_{ij}^{a,\text{HF}} \left\langle \tilde{P}_{j}^{a} \right| \]

Exchange kernel $\implies$ pseudo + one center

\[ X_{v}^{PAW}(\mathbf{r}) = \tilde{X}_{v}(\mathbf{r}) + \sum_{ai} \left| \tilde{P}_{i}^{a} \right\rangle X_{iv}^{a} \]

Both $D_{ij}^{a,\text{HF}}$ and $X_{iv}^{a}$ contain the core-valence contributions.

Atompaw KLI

**AE KLI Equation**

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

\[ \Downarrow \]

**Atompaw KLI Equation**

\[ \tilde{V}_x \tilde{\rho} = \sum_q N_q \tilde{\psi}_q \tilde{X}_q + \sum_q (\tilde{V}_{xq} - \tilde{U}_{xq}) N_q \left| \tilde{\psi}_q \right|^2 \]

\[ V_x^a \rho^a = \sum_q N_q \psi_q^a X_q^a + \sum_q (\tilde{V}_{xq} - \tilde{U}_{xq}) N_q \left| \psi_q^a \right|^2 \]

\[ \tilde{V}_x^a \tilde{\rho}^a = \sum_q N_q \tilde{\psi}_q^a \tilde{X}_q^a + \sum_q (\tilde{V}_{xq} - \tilde{U}_{xq}) N_q \left| \tilde{\psi}_q^a \right|^2 \]

\[ \rho(r) \rightarrow \tilde{\rho}(r) + \sum_a (\rho^a(r) - \tilde{\rho}^a(r)) \]
**Motivation and Outline**

Hatree-Fock Theory and KLI Approximation
Frozen core orbital approximation
Aтомпaw of HF and KLI
Planewave representation of HF and KLI
Concluasion

**Result:** Atompaw KLI

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**All-electron \( V_x(r) \) and pseudo \( \tilde{V}_x(r) \)**

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**All-electron \( V_x(r) \) and pseudo \( \tilde{V}_x(r) \)**

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PAW + HF & KLI
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PWPAW + KLI

Pseudo Exchange Energy

\[ \tilde{E}_x = -\frac{e^2}{4} \sum_{nk, n' k'} f_{nk} f_{n' k'} \int \int d\mathbf{r} d\mathbf{r}' \frac{\tilde{\rho}_{nk, n' k'}(\mathbf{r}) \tilde{\rho}_{n' k'}^*(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \]

where:

\[ \tilde{\rho}_{nk, n' k'}(\mathbf{r}) = \tilde{\psi}_{nk}^*(\mathbf{r}) \tilde{\psi}_{n' k'}(\mathbf{r}) + \hat{\rho}_{n k n' k'}(\mathbf{r}) \leftarrow \text{compensation pair charge} \]

Plane wave representation of \( \tilde{E}_x \)

\[ \tilde{E}_x = -\frac{e^2 \pi}{V} \sum_{nk, n' k'} f_{nk} f_{n' k'} \sum_G \frac{|\tilde{\rho}_{nk, n' k'}(G)|^2}{|k - k' - G|} \]

Pseudo Exchange kernel

\[ \tilde{X}_{nk}(r) = -\frac{1}{2} \sum_{n'k'} f_{n'k'} \tilde{W}_{nk,n'k'}(r) \tilde{\Psi}_{n'k'}(r) \]

\[ \tilde{W}_{nk,n'k'}(r) = e^2 \int d^3 r' \frac{\tilde{\rho}_{nk,n'k'}(r')}{|r - r'|} = \sum_{G} \tilde{W}_{nk,n'k'}(G) e^{-i(k-k'-G) \cdot r} \]

Plane wave representation of \( \tilde{W}_{nk,n'k'} \)

\[ \tilde{W}_{nk,n'k'}(G) = \frac{4\pi e^2}{V} \frac{\rho^*_{nk,n'k'}(G)}{|k - k' - G|} \]

Plane wave PAWKLI equation

Pseudo \( \tilde{V}_x(r) = \frac{1}{\tilde{\rho}(r)} \left\{ \sum_{nk} f_{nk} \tilde{\psi}_{nk}(r) \tilde{X}_{nk}(r) + \sum_{nk} f_{nk} \left| \tilde{\psi}_{nk}(r) \right|^2 (\tilde{V}_{nk} - \bar{U}_{nk}) \right\} \)

One center \( V^a_x(r), \tilde{V}^a_x(r) \)......

Full PWPAW KLI equation

\[
\sum_{n'k'} (\delta_{nk,n'k'} - f_{n'k'} \Gamma^{PAW}_{nk,n'k'}) \Delta_{n'k'} - \sum_c N_c \Gamma^{PAW}_{nk,c} \Delta_c = \Xi^{PAW}_{nk} - \bar{U}_{x,n'k'}
\]

\[
\sum_{c'} (\delta_{cc'} - N_{c'} \Gamma^{PAW}_{cc'}) \Delta_{c'} - \sum_{n'k'} f_{n'k'} \Gamma^{PAW}_{nk,c} \Delta_{n'k'} = \Xi^{PAW}_c - \bar{U}^x_{x,c'}
\]

where

\[
\bar{V}_{x,nk} = \Delta_{nk} + \bar{U}_{x,n'k'}
\]

\[
\bar{V}_{x,c} = \Delta_c + \bar{U}_{x,c}
\]
Conclusion & Acknowledgments

1. Incorporated: Frozen core orbital approximation within PAWHF & PAWKLI.

2. Implementation + Result: Atompaw-Hartree-Fock* & Atompaw-KLI

3. Implementation : Plane wave PAW + KLI


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