Adaptation of Projector Augmented Wave Method to the treatment of orbital-dependent functionals

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Outline

- **Motivation : Why**
- **Review Atom’s All electron & Atompaw formalisms**
- **Planewave** implementation of PAW Hartree-Fock and KLI
  1. Planewave PAW representation of $\tilde{E}_x$, exchange kernel.
  2. Details: treatment the singularity, compensation charge.
  3. **PWPAW-Hartree-Fock & PWPAW-KLI** equations.
  4. Calculations results of periodic solids: C(Diamond) and LiF to demonstrate the formalism.
- **Conclusion**
Motivation

**Why? Orbital Dependent Functionals + PAW Method**

1. Because in our earlier investigations on cathode materials for Li ion batteries, we found that DFT with either LDA or GGA failed to explain the structural difference of certain materials, particularly those containing transition metals. **A likely source of this inaccuracy is described as the "Self-Interaction" error.**

2. **Orbital Dependent Functionals** (ex: exact exchange) can improve the accuracy of electronic structure calculations because their ability to avoid self-interaction.

3. **The Projector Augmented Wave (PAW)** method is an efficient pseudopotential-like scheme, which allows for an accurate treatment of the multipole moments in both the Hartree and Exchange interaction terms.

Therefore, it is a natural choice to implement **Orbital Dependent Functionals** within the **PAW framework**.
Motivation: Why orbital-dependent

The first intuitive way to correct self-interaction is to construct Fock exchange with obtained orbitals (after self-consistent calculation)

\[ E_x^{Fock} = -\frac{e^2}{2} \sum_{pq} \delta_{\sigma_p \sigma_q} \int d^3r \int d^3r' \frac{\Psi_{LDA}^* (r) \Psi_{LDA}^* (r') \psi_{LDA} (r') \psi_{LDA} (r)}{|r - r'|} \]

to replace its original xc functionals – **Post Processing**.

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

- The magnitude of difference is between 10ev-50ev, quite large!
- **Post processing example:** Harl, Schimka, and Kresse, PRB 81, 115126 (2010).
Further improvement: self-consistent calculation

(Post Processing - HF) VS (Self Consistent(Orbital Dependent) - HF)

As a first order approximation, KLI and OEP total energy are quite close.
Review: All Electron **Hartree-Fock** Theory

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

\[
E_x = -\frac{e^2}{2} \sum_{pq} \delta_{\sigma p \sigma q} \int d^3r \int d^3r' \frac{\psi_{p}^{HF\ast}(r)\psi_{q}^{HF}(r)\psi_{q}^{HF\ast}(r')\psi_{p}^{HF}(r')}{|r - r'|}
\]

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

\[
X_p(r) = \frac{\partial E_x}{\partial \psi_p^{HF\ast}(r)} = -e^2 \sum_q \delta_{\sigma p \sigma q} \psi_{q}^{HF}(r) \int d^3r' \frac{\psi_{q}^{HF\ast}(r')\psi_{p}^{HF}(r')}{|r - r'|}
\]

The general form of the integral-differential equations that need to be solved in the Hartree-Fock formalism has the form:

\[
H^{HF}\psi_{p}^{HF}(r) + X_p(r) - \sum_q \lambda_{pq} \psi_{q}^{HF}(r) = 0
\]
All Electron Kohn-Sham Theory with Exact Exchange

For Kohn-Sham theory, the Exact Exchange energy can be still represented as following:

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

The corresponding Kohn-Sham equation:

\[
\{-\frac{\hbar^2}{2m} \nabla^2 + V_s(r)\}\psi_p(r) = \varepsilon_p \psi_p(r)
\]
Review: PAW Method

PAW calculations requires the following Atom centered functions

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

Basic Idea of PAW

Atom or Solid
\[ \Psi(\mathbf{r}) = \tilde{\Psi}(\mathbf{r}) + \sum_{ai} (\phi^a_i(\mathbf{r}) - \tilde{\phi}^a_i(\mathbf{r})) \langle \tilde{P}^a_i | \tilde{\Psi} \rangle \]

Slow varying part
- One-Center
- One-Center pseudo
- All-electron

Quickly varying terms

PAW Diagram

Wave function \( \equiv \)
Slow varying term \( \rightarrow \)
Quickly varying but confined term “correction” \( \rightarrow \)
Kohn-Sham equation in PAW formalism

\[ H^{PAW} \tilde{\Psi}_p (r) = \varepsilon_p \tilde{O} \tilde{\Psi}_p (r) \]

PAW Hamiltonian

\[ H^{PAW} = \tilde{H} + \sum_{a,ij} \left| \tilde{P}_i^a \right> D_{ij}^a \left< \tilde{P}_j^a \right| \]

PAW Overlap function

\[ \tilde{O} = 1 + \sum_{a,ij} \left| \tilde{P}_i^a \right> O_{ij}^a \left< \tilde{P}_j^a \right| \]

PAW Matrix element

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

\[ O_{ij}^a = \left< \phi_i^a \left| \phi_j^a \right> - \left< \tilde{\phi}_i^a \left| \tilde{\phi}_j^a \right> \right. \]
Atompaw Hartree Fock

First Step to combing PAW with Hartree-Fock ...

**Atompaw Hartree Fock equations**

\[
H_{\text{HF}}^{\text{PAW}} \Psi_v^{\text{HF}}(\mathbf{r}) + X_v^{\text{PAW}}(\mathbf{r}) - \sum_q \lambda_{qv} O_{\text{HF}}^{\text{PAW}} \Psi_q^{\text{HF}}(\mathbf{r}) = 0
\]

*Only valence*

\[
X_v^{\text{PAW}}(\mathbf{r}) = \tilde{X}_v + \sum_{ai} |\tilde{p}_i^a\rangle X_{iv}^a
\]

*All cores are confined*

**AE HF**

\[
H_{\text{HF}} \Psi_p^{\text{HF}}(\mathbf{r}) + X_p(\mathbf{r}) - \sum_q \lambda_{pq} \Psi_q^{\text{HF}}(\mathbf{r}) = 0
\]

Details:

2010 PRB Xiao Xu and N. A. W. Holzwarth: Phys. Rev. B 81 245105 (14pages)
Atompaw Hartree Fock

First Step to combing PAW with KLI...

**Atompaw KLI equations**

Local exchange potential can be divided into 3 parts

**Pseudo Term:**

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

**One-center AE:**

\[ V^a_x \rho^a = \sum_q N_q \Psi^a_q X^a_q + \sum_q (\bar{V}_{xq} - \bar{U}_{xq}) N_q |\Psi^a_q|^2 \]

**One-center Pseudo:**

\[ \tilde{V}^a_x \tilde{\rho}^a = \sum_q N_q \tilde{\Psi}^a_q \tilde{X}^a_q + \sum_q (\bar{V}_{xq} - \bar{U}_{xq}) N_q |\tilde{\Psi}^a_q|^2 \]

**AEKLI**

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

Details:

2011 *PRB* Xiao Xu and N. A. W. Holzwarth: Phys. Rev. B 84 155113 (16 pages)
Result: Atompaw KLI

Comparison of OEP and KLI AE $V_x(r)$ local exchange potential

- KLI is a very good approximation of OEP method
Result: Atompaw KLI

Comparison of KLI AE and pseudo $\tilde{V}_x(r)$ local exchange potential

From Atompaw Calculation

From AE Calculation

$Br$

$Cl$

$F$

$r (\text{bohr})$

$rV_x(r)$ (bohr Ry)

-2

-1

0

0
Plane wave expansion of wave function

\[
\Psi_p(r) \quad \rightarrow \quad \tilde{\Psi}_{nk}(r) = \sqrt{\frac{1}{V}} \sum_{G} A_{nk}(G) e^{i(k+G) \cdot r}
\]

Project Augmented Wave

Orbital Dependent Functionals \{ Hartree-Fock, KLI \} \quad \rightarrow \quad Periodic Solids

Wave function in Atom

Orbital label as index

Wave function in periodic solids

Band index n
Wavevector \( \mathbf{K} \)

Unit cell volume

Expansion coefficient

\[ |k + G|^2 \leq E_{cut} \]
Exchange energy & **Compensation charge** of Solids: HF & KLI

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

**Major Difference**

Smooth pair density between \( nk \) \( n'k' \)

\[ \tilde{\rho}_{nk,n'k'}(\mathbf{r}) \equiv \tilde{\Psi}_{nk}(\mathbf{r}) \tilde{\Psi}_{n'k'}(\mathbf{r}) + \hat{\rho}_{nk,n'k'}(\mathbf{r}) \]

**Compensation pair charge**

\[ \hat{\rho}_{nk,n'k'}(\mathbf{r}) = \sum_{aij} \left( P_i^a \left| \tilde{\Psi}_{nk} \right\rangle \left\langle \tilde{\Psi}_{n'k'} \right| P_j^a \right) \hat{\mu}_{ij}^a(\mathbf{r} - \mathbf{R}^a) \]

**Generalized moments**

\[ \hat{\mu}_{ij}^a(\mathbf{r} - \mathbf{R}^a) = \sum_{LM} \frac{G_{LM}^{ij} \tilde{m}_{ij}^a}{\sqrt{4\pi}} \frac{\hat{a}_L}{r^2} Y_{LM}(\hat{r}) \]

\[ \tilde{\rho}_{nk,n'k'}(\mathbf{G}) = \sum_{aij} \left( P_i^a \left| \tilde{\Psi}_{nk} \right\rangle \left\langle \tilde{\Psi}_{n'k'} \right| P_j^a \right) \tilde{\mu}_{ij}^a(\mathbf{k} - \mathbf{k}' + \mathbf{G}) \]

\[ \tilde{\mu}_{ij}^a(\mathbf{q}) = e^{-iq\mathbf{R}^a} \sum_{LM} G_{LM}^{ij} \frac{1}{\sqrt{4\pi}} (-i)^L \hat{Y}_{LM}(\hat{q}) \int_0^c \frac{d\mathbf{r}}{r^2} \frac{\hat{a}_L}{r} \hat{\mu}_{ij}^a(\mathbf{r}) \]

Removing Singularity

Plane Wave Representation

\[ \tilde{E}_x = -\frac{e^2 \pi}{V} \sum_{nk} \sum_{n'k'} f_{nk} f_{n'k'} \sum_G \left| \tilde{\rho}_{nk,n'k'}(G) \right|^2 \frac{1}{|k - k' + G|^2} \]

Looping through all band index and wave vector
Looping through all G points

\(|k - k' + G| \to 0\)

\{ Ivan Duehemin, Francois Gygi: Computer Physics Communications 181(5) \}
\{ Integral able singularity \}
\{ J. Spencer and A. Alavi, Phys. Rev. B 77, 193110 \}
\{ Adjusting real-space range of Coulomb kernel \}
Spencer and Alavi method in detail

\[ \tilde{E}_x = -\frac{e^2 \pi}{V} \sum_{nk} \sum_{n'k'} f_{nk} f_{n'k'} \left( \sum_G \left| \tilde{\rho}_{nk, n'k'}(G) \right|^2 \right) \left( \frac{1 - \cos(|k - k' + G| R_c)}{|k - k' + G|^2} \right) \]

When approaches to singular:

\[ \lim_{|k - k' + G| \to 0} \frac{1 - \cos(|k - k' + G| R_c)}{|k - k' + G|^2} = \frac{1}{2} R_c^2 \]

Cut-off radius:

\[ \frac{4\pi}{3} R_c^3 = N_k V \]

The number of k-points in the Brillouin zone

Details: numerical accuracy

**Plane Wave PAW Hartree-Fock Formalism**

\[ H_{	ext{HF}}^{\text{PAW}} \tilde{\Psi}_{nk}^{\text{HF}}(\mathbf{r}) + X_{nk}^{\text{PAW}}(\mathbf{r}) - \sum_{n',k'} \lambda_{n',k',nk} O_{\text{HF}}^{\text{PAW}} \tilde{\Psi}_{nk}^{\text{HF}}(\mathbf{r}) = 0 \]

\[ X_{nk}^{\text{PAW}}(\mathbf{r}) = \tilde{X}_{nk}^{\text{HF}} + \sum_{ai} \left| \tilde{P}_i^a \right\rangle X_{i,nk}^a \]

\[ X_{i,nk}^a = -\frac{1}{2} \sum_{ikl} \langle \tilde{P}_i^a | \tilde{\Psi}_{nk}^a \rangle V_{kj}^a V_{ijkl} \]

\[ -\frac{1}{2} \sum_{n'k'} f_{n'k'} \sum_j \langle \tilde{P}_j^a | \tilde{\Psi}_{n'k'}^a \rangle Z_{nk,n'k',ij}^a \]

\[ -\sum_j \langle \tilde{P}_j^a | \tilde{\Psi}_{nk}^a \rangle \delta_{i,j} \delta_{m,m_j} C_{ij}^a \]

**Generalized moments**

\[ Z_{nk,n'k',ij}^a = \sum_G \mu_{ij} (\mathbf{k} - \mathbf{k}' + \mathbf{G}) \tilde{W}_{nk,n'k'}(\mathbf{G}) \]
Plane Wave PAW Hartree-Fock Formalism

Pseudo Exchange Kernel

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

\[ \tilde{w}_{nk,n'k'}(r) = e^2 \int dr' \frac{\tilde{\rho}_{nk,n'k'}(r)}{|r - r'|} \]

\[ = \sum_G \tilde{w}_{nk,n'k'}(G) e^{i(k-k'+G) \cdot r} \]

Plane wave representation

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

Spencer and Alavi Method

\[ \tilde{\rho}_{nk,n'k'}^*(G) \times \frac{1 - \cos(|k - k' + G| \cdot R_c)}{|k - k' + G|^2} \]
Plane Wave PAW KLI Formalism

\( \tilde{V}_x(r), V_x^a(r), \tilde{V}_x^a(r) \) need to be solved separately.

**Pseudo Term:**
\[
\tilde{V}_x(r) \tilde{\rho}(r) = \sum_{nk} f_{nk} \tilde{\Psi}_{nk}(r) \tilde{X}_{nk}(r) + \sum_{nk} (\overline{V}_{x,nk} - \overline{U}_{x,nk}) f_{nk} |\tilde{\Psi}_{nk}(r)|^2
\]

**One-center AE:**
\[
V_x^a(r) \rho^a(r) = [\gamma^{acc}(r) + \gamma^{acv}(r) + \gamma^{avv}(r)]
\]
\[
+ \sum_{nk} f_{nk} |\Psi_{nk}^a(r)|^2 (\overline{V}_{x,nk} - \overline{U}_{x,nk})
\]
\[
+ \sum_c N_c \frac{|\Psi_{c}^a(r)|^2}{4\pi r^2} (\overline{V}_{xc} - \overline{U}_{xc})
\]

**One-center Pseudo:**
\[
\tilde{V}_x^a(r) \tilde{\rho}^a(r) = [\tilde{\gamma}^{avv}(r)]
\]
\[
+ \sum_{nk} f_{nk} |\Psi_{nk}^a(r)|^2 (\overline{V}_{x,nk} - \overline{U}_{x,nk})
\]
PWPAW KLI Formalism

Pseudo exchange potential

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

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

Full PWPAW KLI equations: still a AX = B problem

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

\[
\sum_{c'} (\delta_{cc'} - N_{c'} \Gamma_{cc'}^{\text{PAW}}) \Delta_{c'} - \sum_{n'k'} f_{n'k'} \Gamma_{nk,c}^{\text{PAW}} \Delta_{n'k'} = \Xi_{c}^{\text{PAW}} - \bar{U}^x_{x,c'}
\]

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

\[
\bar{V}_{x,c} = \Delta_c + \bar{U}_{x,c}
\]
Calculation results of LiF & diamond

In order to test the formalism, we have calculated the self-consistent electronic structure of diamond and LiF.

### Comparison of lattice parameters

<table>
<thead>
<tr>
<th></th>
<th>Diamond</th>
<th>LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$B$</td>
</tr>
<tr>
<td>LDA (this work)</td>
<td>3.53</td>
<td>490</td>
</tr>
<tr>
<td>LDA (literature)</td>
<td>3.54</td>
<td>452</td>
</tr>
<tr>
<td>KLI (this work)</td>
<td>3.55</td>
<td>460</td>
</tr>
<tr>
<td>HF (this work)</td>
<td>3.56</td>
<td>490</td>
</tr>
<tr>
<td>HF (literature)</td>
<td>3.58</td>
<td>480</td>
</tr>
<tr>
<td>Experiment</td>
<td>3.57</td>
<td>443</td>
</tr>
</tbody>
</table>

Lattice constants $a$ are given in Å and bulk moduli $B$ are given in GPa.

- The present results are in general agreement with results in the literature using other computational methods.
PWPAW result: Diamond

**Binding energy curve** for C in the diamond structure

Hartree-Fock and KLI results for equilibrium lattice constants are closer to the experimental result.
PWPAW result: LiF

Binding energy curve for LiF in the rock salt structure
Conclusions

1. Provided **formalism** of **PAW** methods using **Fock Exchange** functional, but overall formalism is expected to work for **hybrid functional** too.

2. **Implementation** of Hartree-Fock and KLI Atompaw & **PWPAW**.

3. Details: **Planewave expansion** of $\tilde{E}_x$, $\tilde{X}_{nk}$, **singularity** etc.

4. **Calculations** results for LiF & C(diamond) to verify the formalism.

**Acknowledgments**

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Thank you!