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

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Outline

- Motivation : **W**hy
- Review Atom's All electron & Atompaw formalisms
- **Planewave** implementation of PAW Hartree-Fock and KLI
  1. Planewave PAW representation of $\widetilde{E}_x$, 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**.

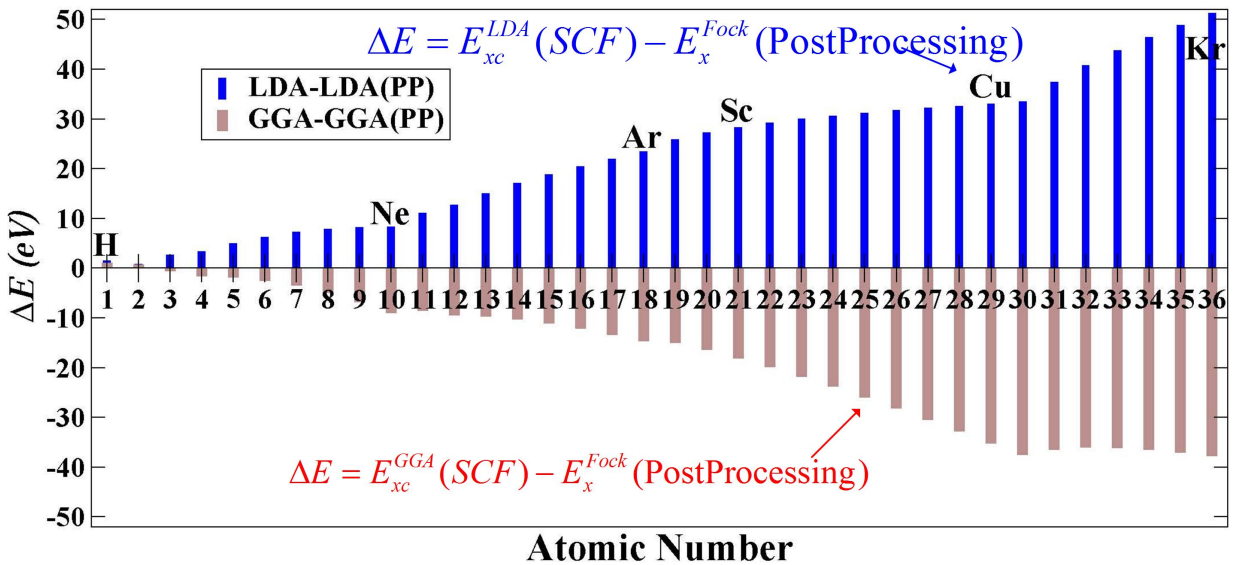
Motivation: Why orbital-dependent

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

$$E_x^{Fock} = -\frac{e^2}{2}\sum_{pq}\delta_{\sigma_p\sigma_q}\int d^3r\int d^3r'\,\frac{\Psi_p^{LDA*}(\mathbf{r})\Psi_q^{LDA}(\mathbf{r})\Psi_q^{*LDA}(\mathbf{r}')\Psi_p^{LDA}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

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

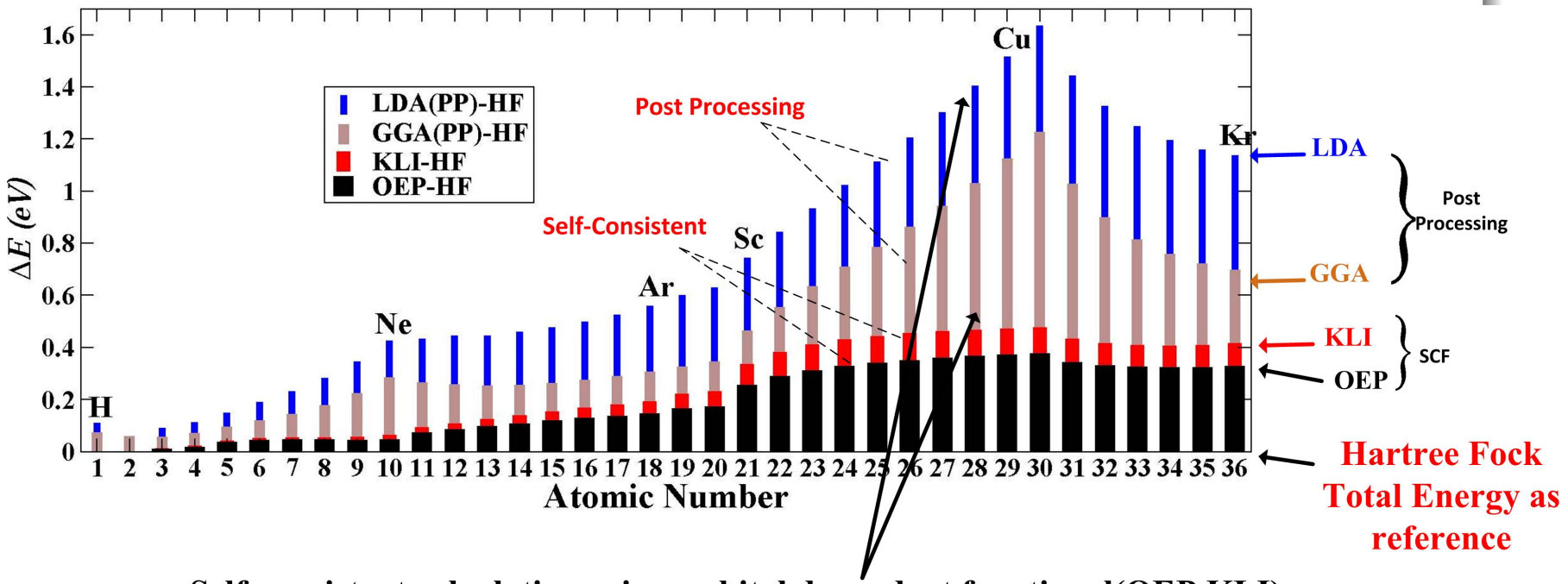
$\Delta E = E_{xc}^{LDA/GGA}(SCF) - E_x^{Fock}(PP)$



- 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 calcuation

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



- As a first order approximation , KLI and OEP total energy are quite close.

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

$$E_x = -\frac{e^2}{2}\sum_{pq}\delta_{\sigma_p\sigma_q}\int d^3r\int d^3r'\,\frac{\Psi_p^{HF*}(\mathbf{r})\Psi_q^{HF}(\mathbf{r})\Psi_q^{HF*}(\mathbf{r}')\Psi_p^{HF}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

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

$$X_p(\mathbf{r}) = \frac{\partial E_x}{\partial \Psi_p^{HF*}(\mathbf{r})} = -e^2\sum_q \delta_{\sigma_p\sigma_q}\Psi_q^{HF}(\mathbf{r})\int d^3r'\,\frac{\Psi_q^{HF*}(\mathbf{r})\Psi_p^{HF}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

The general form of the intregral-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:

$$E_x = -\frac{e^2}{2}\sum_{pq}\delta_{\sigma p\sigma q}\int d^3r\int d^3r'\,\frac{\Psi_p^{KS*}(\mathbf{r})\Psi_q^{KS}(\mathbf{r})\Psi_q^{KS*}(\mathbf{r}')\Psi_p^{KS}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

numerical expansive to combine with PAW

Local Exchange Potential

Orbital-dependent

$$V_x(r)=\frac{\partial E_x[\{\Psi_p^{KS}\}]}{\partial\rho(r)}$$

Differential Equations self-consistently

- **Optimized Effective Potential** method
- **Krieger-Li-Iafrate** approximation

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

Symbol	Meaning	Properties
AE basis function	$\phi_i^a(\mathbf{r})$	**AE** Kohn-Sham eigenstate
PS basis function	$\tilde{\phi}_i^a(\mathbf{r})$	Constructed; $\tilde{\phi}_i^a(\mathbf{r}) \equiv \phi_i^a(\mathbf{r})$ for $r \geq r_c^a$
Projector function	$\tilde{P}_i^a(\mathbf{r})$	$\tilde{P}_i^a(\mathbf{r}) \equiv 0$ for $r \geq r_c^a$ and $\langle \tilde{P}_i^a \vert \tilde{\phi}_j^a \rangle = \delta_{ij}$

Basic Idea of PAW

Atom or Solid

$$\Psi(\mathbf{r}) = \tilde{\Psi}(\mathbf{r}) + \underbrace{\sum_{ai} (\phi_i^a(r) - \tilde{\phi}_i^a(r)) \left\langle \tilde{P}_i^a \middle| \tilde{\Psi} \right\rangle}_{corrections}$$

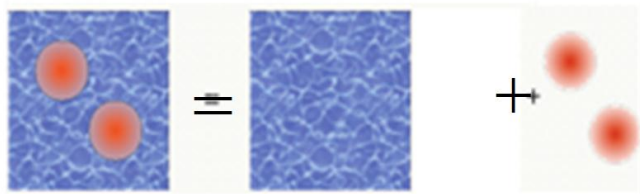
Slow varying part

One-Center All-electron

One-Center pseudo

Quickly varying terms

PAW Diagram



Wave function = **Slow varying term** + **Quickly varying but confined term "correction"**

Review of PAW Method

Kohn-Sham equation in PAW formalism

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

PAW Hamiltonian

$$H^{PAW} = \tilde{H} + \sum_{a,ij} \left|\tilde{P}_i^a\right\rangle D_{ij}^a \left\langle\tilde{P}_j^a\right|$$

PAW Overlap function

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

PAW Matrix element

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

$$O_{ij}^a = \left\langle\phi_i^a\middle|\phi_j^a\right\rangle - \left\langle\tilde{\phi}_i^a\middle|\tilde{\phi}_j^a\right\rangle$$

Atompaw Hartree Fock

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

Atompaw Hartree Fock equations

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

Only valence

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

All cores are confined

AE HF $H^{HF}\Psi_p^{HF}(\mathbf{r}) + X_p(\mathbf{r}) - \sum_q \lambda_{pq}\Psi_q^{HF}(\mathbf{r}) = 0$

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 equaions

Local exchange potential can be divided into 3 parts

Pseudo Term :

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

One-center AE:

$$V_x^a \rho^a = \sum_q N_q \Psi_q^a X_q^a + \sum_q (\overline{V}_{xq} - \overline{U}_{xq}) N_q \left|\Psi_q^a\right|^2$$

One-center Pseudo:

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

AEKLI

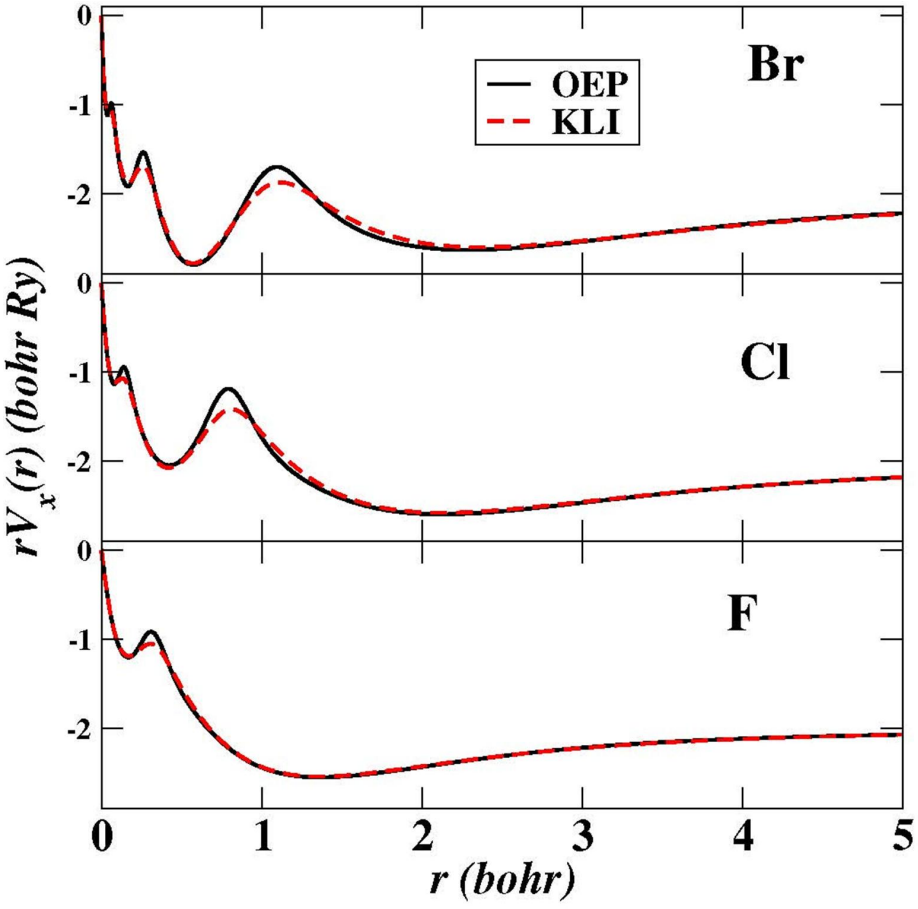
$$V_x(r)\rho(r) = \sum_q N_q \Psi_q(r) X_q(r) + \sum_q (\overline{V}_{xq} - \overline{U}_{xq}) N_q \left|\Psi_q(r)\right|^2$$

Details :

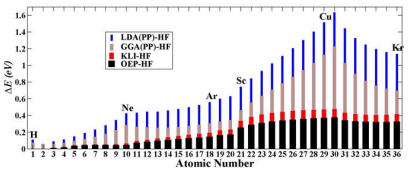
2011 PRB Xiao Xu and N. A. W. Holzwarth : Phys. Rev. B 84 155113 (16 pages)

Result:Atompaw KLI

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



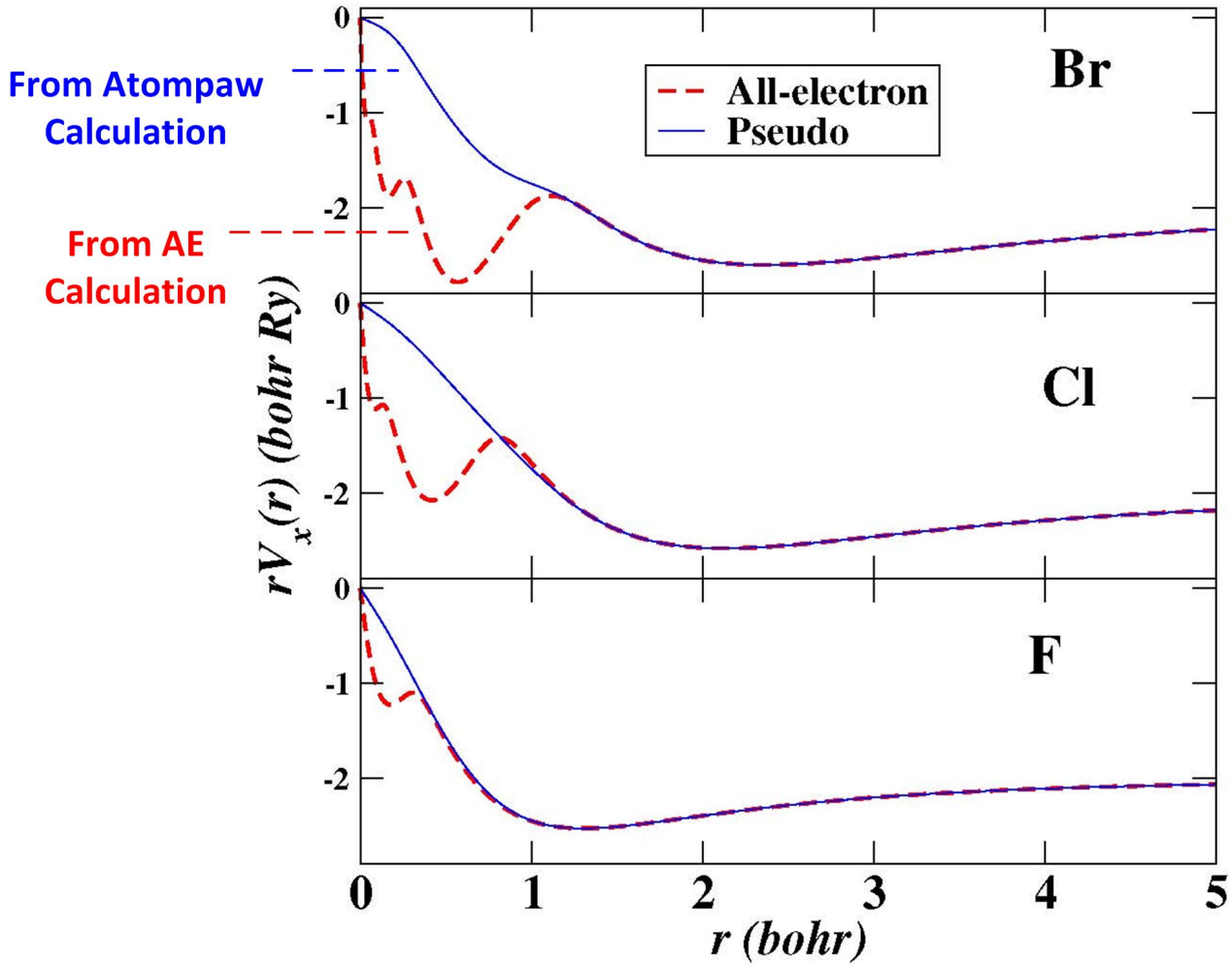
Total energy



- KLI is a very good approximation of OEP method

Result:Atompaw KLI

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



Plane wave expansion of wave function

Project Augmented Wave

Orbital Dependent Functionals { **Hartree-Fock**, **KLI** } ⟶ **Periodic Solids**

Wave function in Atom

Wave function In periodic solids

Unit cell volume

$$\Psi_p(\mathbf{r}) \dashrightarrow \tilde{\Psi}_{n\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{1}{V}} \sum_G A_{n\mathbf{k}}(G) e^{i(\mathbf{k}+G)\bullet\mathbf{r}}$$

Orbital label as index

Band index n
Wavevector **K**

Expansion coefficient

$$|\mathbf{k}+G|^2 \le E_{cut}$$

Exchange energy & **Compensation charge** of Solids : HF & KLI

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

NEW **Major Difference**

Smooth pair density between nk n'k'

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

NEW **Compensation pair charge**

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

Generalized moments

$$\hat{\mu}_{ij}^a (r - R^a) = \sum_{LM} \frac{G^{LM}_{l_j m_j l_i m_i}}{\sqrt{4\pi}} \frac{\hat{m}^{aL}_{ji}}{r^2} Y_{LM}(\hat{r})$$

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

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

$$\bar{\hat{\mu}}_{ij}^a (\mathbf{q}) = e^{-iqR^a} \sum_{LM} G^{LM}_{l_j m_j l_i m_i} \sqrt{4\pi}(-i)^L Y_{LM}(\hat{\mathbf{q}}) \int_o^{r_c^a} dr j_L(qr) \hat{}^{aL}_{ji}(r)$$

J.Paier, R.Hirschl.G.Kresse J.Chem.Phys. 122 563 (2006)

Removing Singularity

Plane Wave Representation

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

Looping through all band index and wave vector

Looping through all G points

$$\left|k-k'+G\right| \to 0$$

- Ivan Duchemin, 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

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

$$\left|\tilde{\rho}_{nk,n'k'}(G)\right|^2 \times \frac{1-\cos(\left|k-k'+G\right| R_c)}{\left|k-k'+G\right|^2}$$

Cut-off radius:

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

The number of k-points in the Brillouin zone

When approaches to singular

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

Details : numerical accuracy

2011 PRB Xiao Xu and N. A. W. Holzwarth : Phys. Rev. B 84 155113 (4 pages)

Plane Wave PAW Hartree-Fock Formalism

PWPAW HF equation

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

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

$$X_{i,nk}^a=-\frac{1}{2}\sum_{ikl}\left\langle\tilde{P}_l^a\middle|\tilde{\Psi}_{nk}\right\rangle W_{kj}^a V_{ijkl}^a$$

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

$$-\sum_j\left\langle\tilde{P}_j^a\middle|\tilde{\Psi}_{nk}\right\rangle\delta_{l_il_j}\delta_{m_im_j}C_{ij}^a$$

Generalized moments

$$Z_{nk,n'k',ij}^a=\sum_G\hat{\overline{\mu}}_{ij}^{a*}(\mathbf{k}-\mathbf{k}'+\mathbf{G})\overline{\tilde{W}}_{nk,n'k'}(\mathbf{G})$$

Pseudo Exchange Kernel

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

$$\tilde{W}_{nk,n'k'}(\mathbf{r}) = e^2 \int d\mathbf{r}' \frac{\tilde{\rho}_{nk,n'k'}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

$$= \sum_G \tilde{W}_{nk,n'k'}(\mathbf{G}) e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{G})\bullet\mathbf{r}}$$

Plane wave representation

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

Spencer and Alavi Method

$$\tilde{\rho}^*_{nk,n'k'}(\mathbf{G}) \times \frac{1-\cos(|\mathbf{k}-\mathbf{k}'+\mathbf{G}|R_c)}{|\mathbf{k}-\mathbf{k}'+\mathbf{G}|^2}$$

Plane Wave PAW KLI Formalism

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

Pseudo Term :

$$\tilde{V}_x(\mathbf{r})\tilde{\rho}(\mathbf{r}) = \sum_{nk} f_{nk}\tilde{\Psi}_{nk}(\mathbf{r})\tilde{X}_{nk}(\mathbf{r}) + \sum_{nk}(\overline{V}_{x,nk} - \overline{U}_{x,nk}) f_{nk}\left|\tilde{\Psi}_{nk}(\mathbf{r})\right|^2$$

One-center AE:

$$V_x^a(r)\rho^a(r) = [\gamma^{acc}(r) + \gamma^{acv}(\mathbf{r}) + \gamma^{avv}(\mathbf{r}) + \sum_{nk} f_{nk}\left|\Psi_{nk}^a(\mathbf{r})\right|^2(\overline{V}_{x,nk} - \overline{U}_{x,nk}) + \sum_c N_c \frac{\left|\Psi_c^a(r)\right|^2}{4\pi r^2}(\overline{V}_{xc} - \overline{U}_{xc})]$$

One-center Pseudo :

$$\tilde{V}_x^a(r)\tilde{\rho}^a(r) = [\tilde{\gamma}^{avv}(\mathbf{r}) + \sum_{nk} f_{nk}\left|\Psi_{nk}^a(\mathbf{r})\right|^2(\overline{V}_{x,nk} - \overline{U}_{x,nk})]$$

Pseudo exchange potential

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

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

Full PWPAW KLI equations : still a $AX = B$ problem

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

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

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

$$\bar{V}_{x,c} = \Delta_c + \bar{U}_{x,c}$$

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

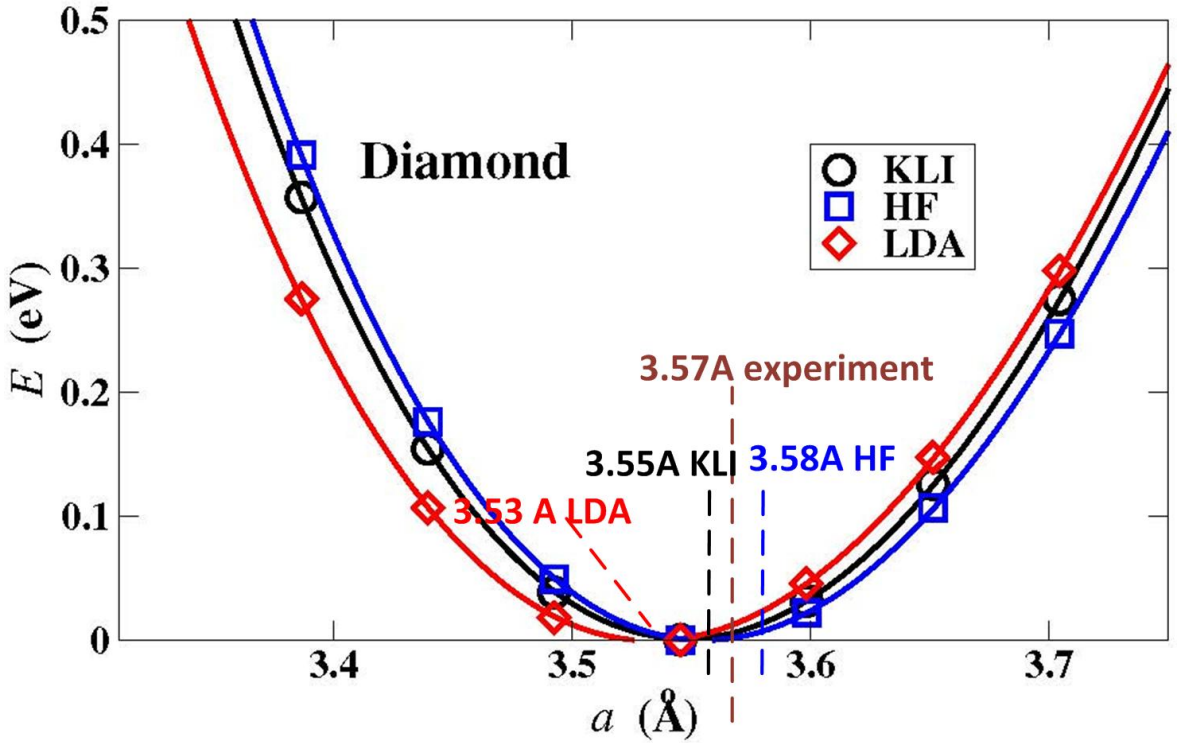
	Diamond		LiF	
	a	B	a	B
LDA (this work)	3.53	490	3.91	85
LDA (literature)	3.54	452	3.92	83
KLI (this work)	3.55	460	4.01	76
HF (this work)	3.56	490	3.97	79
HF (literature)	3.58	480	4.02	76
Experiment	3.57	443	4.03	67

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

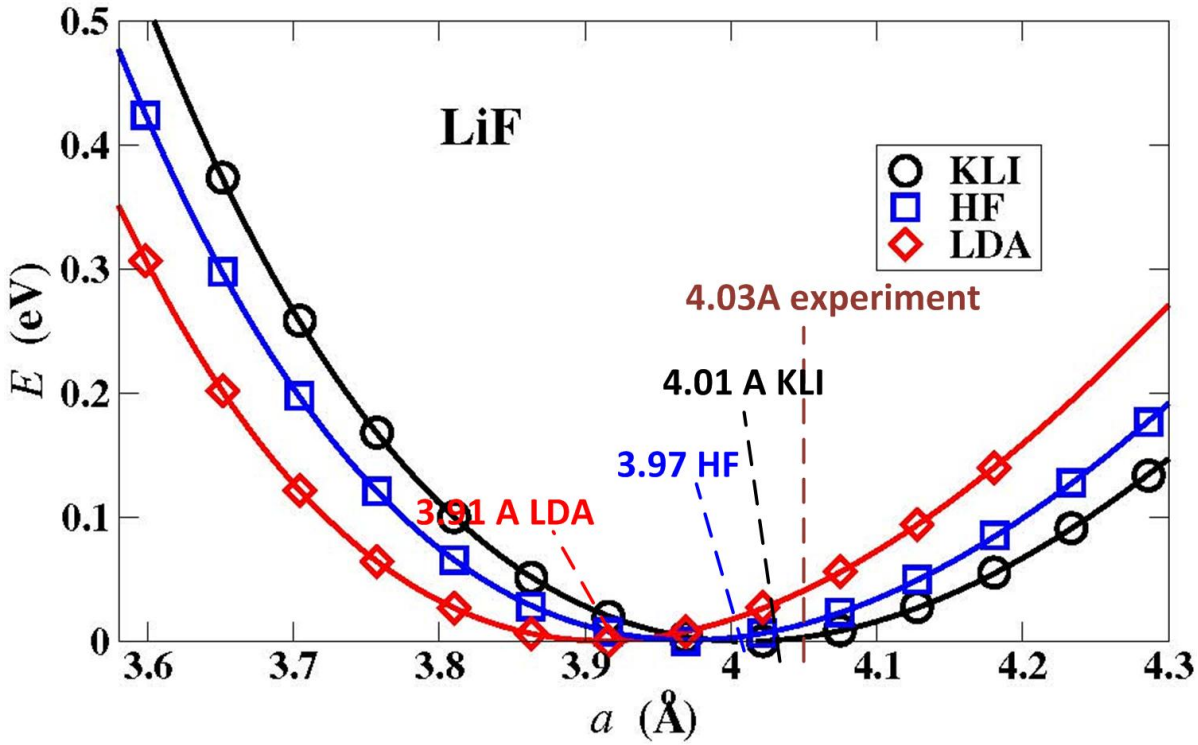
Binding energy curve for C in the diamond structure



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 over all formalism is expected to work for **hybrid functional** too.
2. **Implementation** of Hartree-Fock and KLI Atompaw & **PWPAW**.
3. Details : **Planewave expansion** of $\widetilde{E}_x$, $\widetilde{X}_{nk}$, **singularity** etc.
4. **Calculations** results for LiF & C(diamond) to verify the formalism.

Acknowledgments

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Thank you!