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

Xiao Xu, N. A. W. Holzwarth

Wake Forest University

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Outline

1. 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

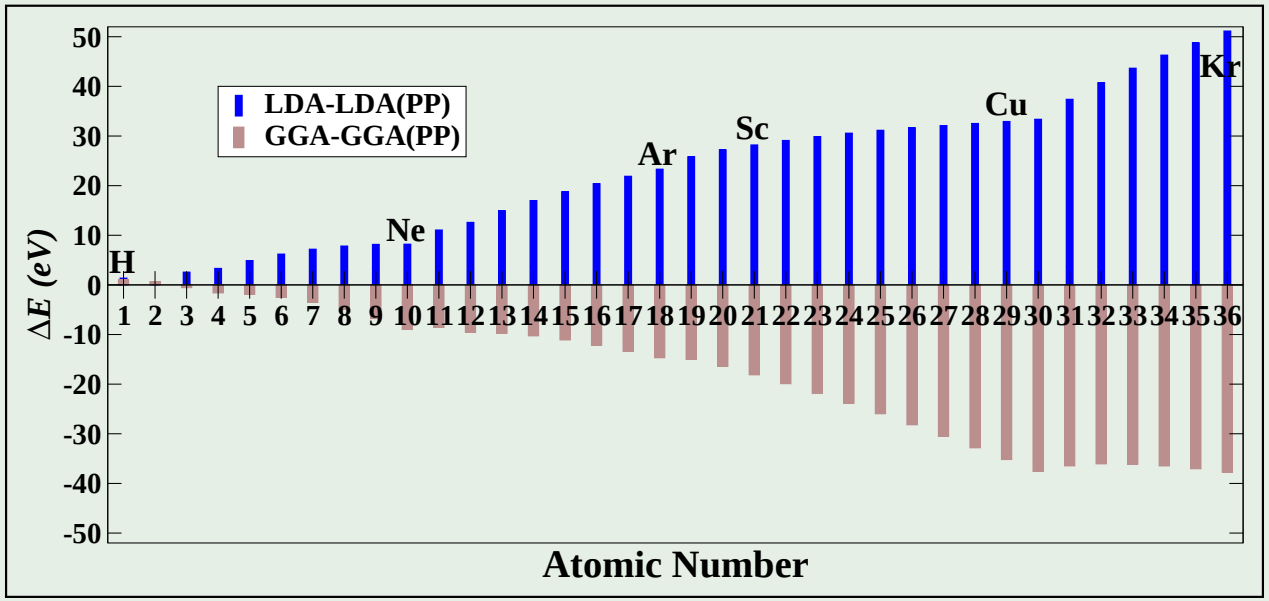
Motivation

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**

* J. B. Krieger, Y. Li and G. J. Iafrate: Phys. Rev. A 45 (1992) 101

Motivation: Magnitude of self-interaction error

$E_{xc}^{LDA/GGA}(SCF) - E_{x}^{Fock}(PP)$ Non-self-consistent post processing

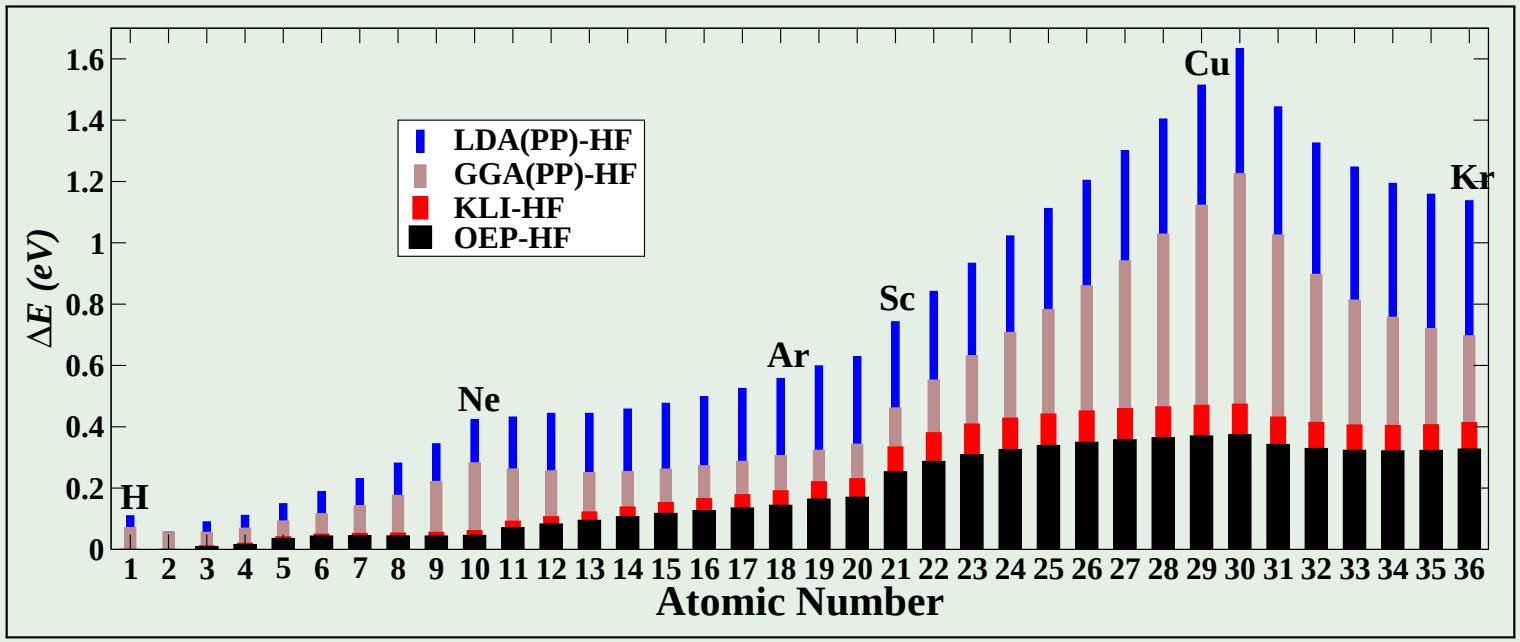


- The magnitude of self-interaction error is between 10ev-50ev.
- LDA overestimates xc energy, and GGA underestimates.

Post processing example: Harl,Schimka, and Kresse, PRB 81, 115126 (18pp) (2010).

Motivation: Non-self-consistent post processing VS Self consistent

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



- 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.

Review: All Electron Hartree-Fock Theory

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

$$E_x = -\frac{e^2}{2}\sum_{pq}\delta_{\sigma_p\sigma_q}\int d^3r\int d^3r'\,\frac{\Psi_p^{HF*}(\mathbf{r})\Psi_q^{HF}(\mathbf{r})\Psi_q^{*HF}(\mathbf{r}')\Psi_p^{HF}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{1}$$

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

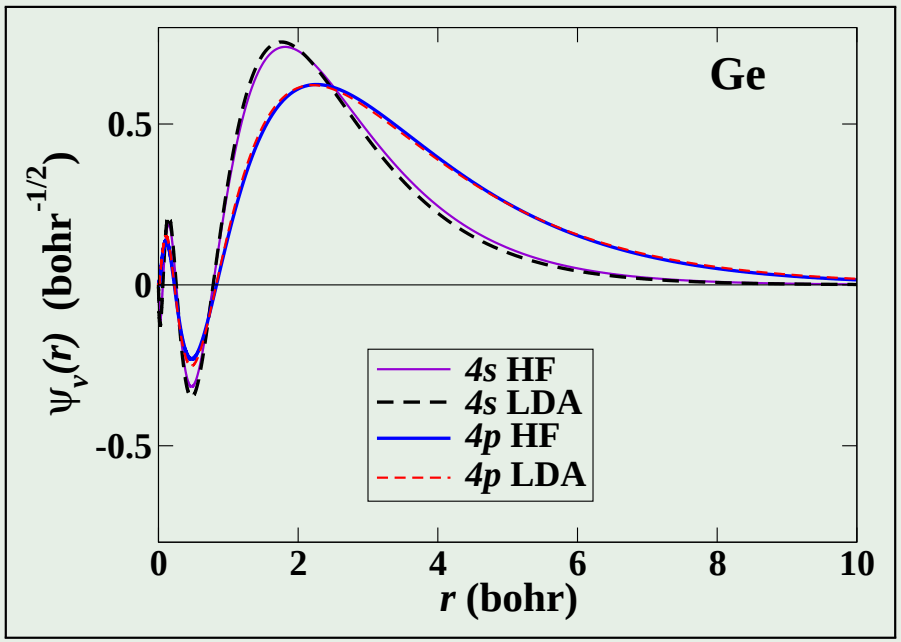
$$X_p(\mathbf{r}) = \frac{\partial E_x}{\partial\Psi_p^{HF*}(\mathbf{r})} = -e^2\sum_{q}\delta_{\sigma_p\sigma_q}\Psi_q^{HF}(\mathbf{r})\int d^3r'\,\frac{\Psi_q^{HF*}(\mathbf{r}')\Psi_p^{HF}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{2}$$

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

$$H^{HF}\psi_p^{HF}(r) + X_p(r) - \sum_q \lambda_{qp}\psi_q^{HF}(r) = 0 \tag{3}$$

Result of Hartree-Fock Atom Implementation

Radial wavefunction for Ge



Radial wavefunction for Ge, comparing Kohn-Sham(LDA) and Hartree-Fock(HF)

Xiao Xu and N. A. W. Holzwarth : Phys. Rev. B 81 245105 (14pp) (2010)

Review:All Electron KLI Theory

From Hartree-Fock $\rightarrow$ Kohn-Sham

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

Where

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

OEP $\rightarrow$ KLI Equation*

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

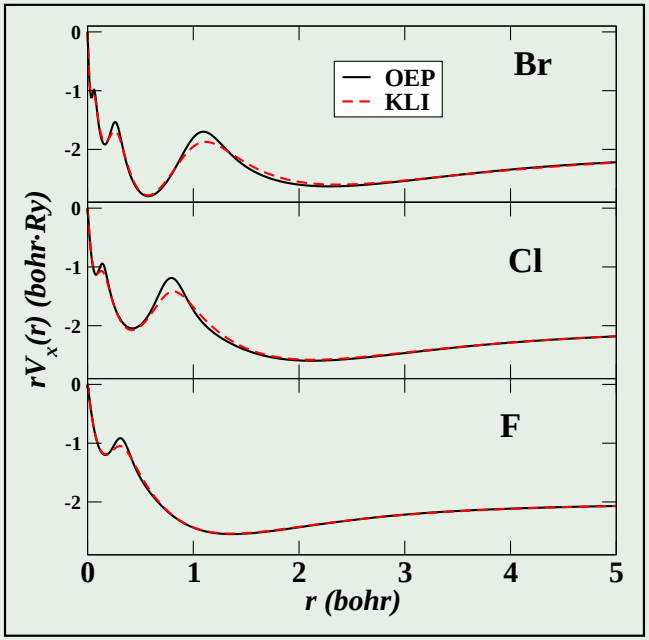
$$\Downarrow$$

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

* J. B. Krieger, Y. Li and G. J. Iafrate: Phys. Rev. A 45 (1992) 101 * J. B. Krieger, Y. Li and G. J. Iafrate: Phys. Rev. A 46 (1992) 5453

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 a 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.

1. $$Fe : \underbrace{1s^1 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2}_{All electron}$$

   $$Fe : \underbrace{1s^1 2s^2 2p^6 3s^2 3p^6}_{core} \underbrace{3d^7 4s^1}_{valence}$$

2. $$Fe : \underbrace{1s^1 2s^2 2p^6 3s^2 3p^6 3d^7 4s^1}_{All electron}$$

Frozen core Approximation : core-valence exchange energy

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

Frozen Core Potential Approximation

Core-Valence interaction

$$E_x^{cv} = \int V_x^{cv}(r)\rho_v(r)dr$$

$V_x^{cv}(r)$ is frozen.

Frozen Core Orbital Approximation $\surd$

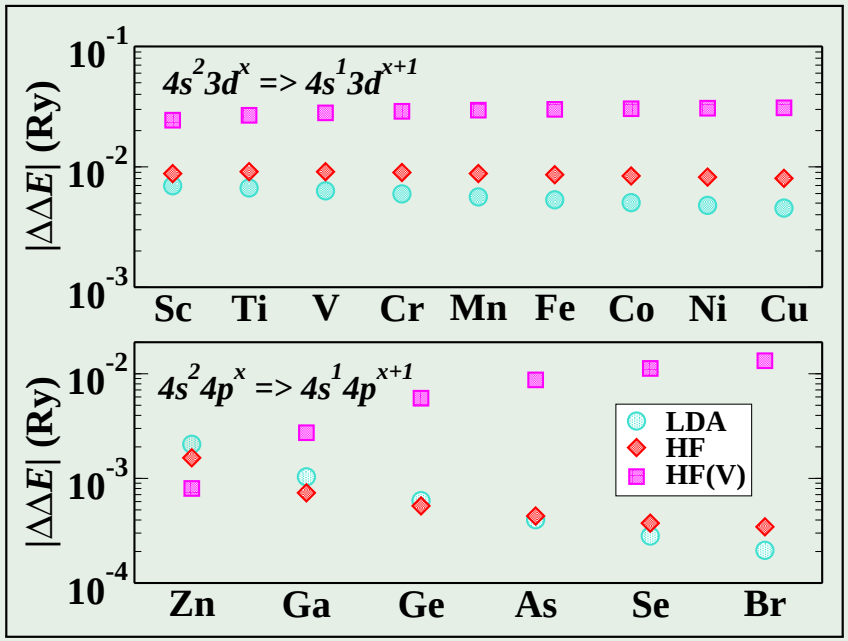
Core-Valence interaction

$$E_x^{vc} = -\frac{e^2}{2}\sum_{vc}\delta_{\sigma_v\sigma_c}\int\int d^3r d^3r' \frac{\Psi_v^*\Psi_c\Psi_v\Psi_c^*}{|\mathbf{r}-\mathbf{r}'|}$$

$\Psi_c(r)$ are frozen.

Result: Frozen core error

Frozen Core Error: Frozen Orbital $\surd$ VS Frozen Potential



$$\Delta\Delta E \equiv \left(E_{\text{tot}}^{\text{excited}} - E_{\text{tot}}^{\text{ground}}\right)\Big|_{\text{AE}} - \left(E_{\text{val}}^{\text{excited}} - E_{\text{val}}^{\text{ground}}\right)\Big|_{\text{FC}} \tag{4}$$

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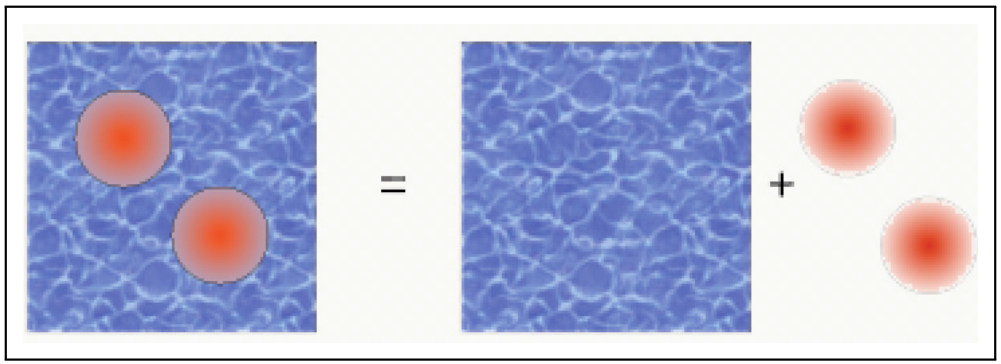
Review:PAW

Atom centered functions needed for PAW calculation

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

PAW transformation from PS$\widetilde{\Psi}_n(r)$ → AE$\Psi_n(r)$

$$\Psi_n(r) = \widetilde{\Psi}_n(r) + \sum_{ai} \underbrace{(\phi_i^a(r) - \widetilde{\phi}_i^a(r))}_{\textit{Corrections}} \left\langle p_i^a \,\middle|\, \widetilde{\Psi}_n \right\rangle$$



P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).

Review:PAW

Kohn-Sham equations in PAW formalism

$$H^{PAW} - \varepsilon_p O\tilde{\Psi}_p(r) = 0$$

PAW Hamiltonian

$$H^{PAW} = \tilde{H}(r) + \sum_{a,ij} \left|\tilde{P}_i^a\right\rangle \underbrace{D_{ij}^a}_{confined} \left\langle\tilde{P}_j^a\right|$$

PAW Matrix Elements

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

PAW Overlap Function

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

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

Atompaw Hartree Fock

Hartree Fock equation $\Longrightarrow$ PAW

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

Hamiltonian like term $\rightarrow$ pesudo + one center

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

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

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Atompaw KLI

AE KLI Equation

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

$$\Downarrow$$

Atompaw KLI Equation

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

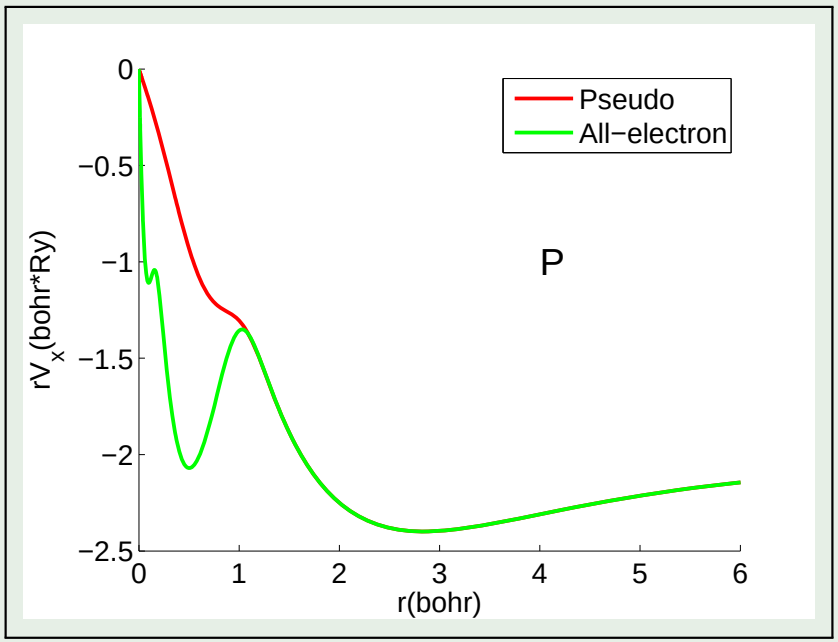
$$V_x^a \rho^a = \sum_q N_q \Psi_q^a X_q^a + \sum_q (\bar{V}_{xq} - \bar{U}_{xq}) N_q \left|\Psi_q^a\right|^2$$

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

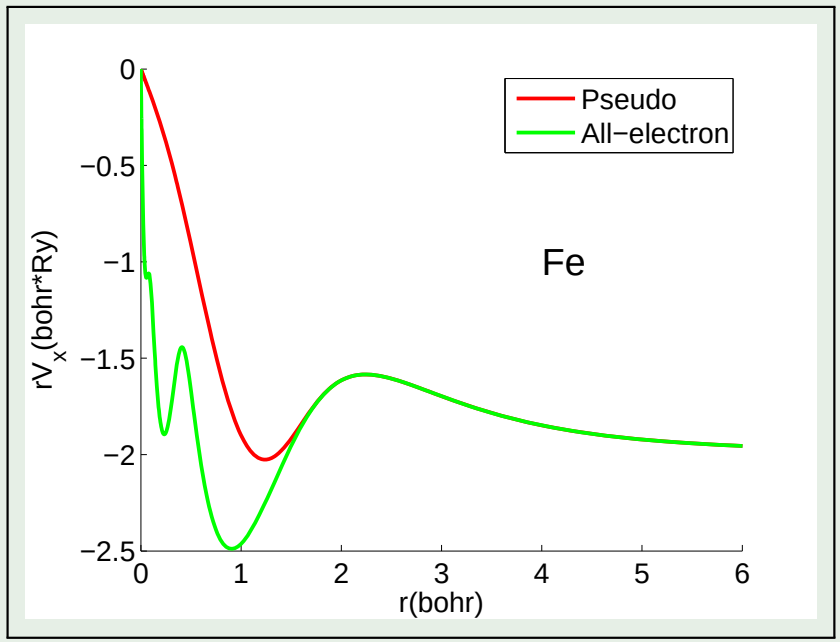
$$\rho(r) \to \tilde{\rho}(r) + \sum_a (\rho^a(r) - \tilde{\rho}^a(r))$$

Result:Atompaw KLI

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



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



PWPAW + KLI

Pseudo Exchange Energy

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

where:

$$\tilde{\rho}_{nk,n'k'}(\mathbf{r}) = \tilde{\Psi}^*_{nk}(\mathbf{r}) \tilde{\Psi}_{n'k'}(\mathbf{r}) + \widehat{\rho}_{nkn'k'}(\mathbf{r}) \leftarrow \textit{compensation pair charge}$$

Plane wave representation of $\tilde{E}_x$

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

Ivan Duchemin, Francois Gygi: Computer Physics Communications 181(5) (2010)

PWPAW + KLI

Pseudo Exchange kernel

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

$$\widetilde{W}_{nk,n'k'}(\mathbf{r}) = e^2\int d^3r'\,\frac{\tilde{\rho}_{nk,n'k'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \sum_G \tilde{W}_{nk,n'k'}(\mathbf{G})e^{-i(\mathbf{k}-\mathbf{k}'-\mathbf{G})\bullet r}$$

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

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

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Plane wave PAWKLI equation

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

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

Full PWPAW KLI 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

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

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

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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Acknowledgments

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