Implementation of the Optimized Effective Potential Method within Projector Augmented Wave Scheme

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Motivation and Outline

Motivation

1. The optimized effective potential (OEP) or exact exchange (EXX) formalism is a method which can improve the accuracy of DFT because its ability to avoid self-interaction contributions and more generally treat orbital-dependent functionals.
2. The Projector Augmented Wave (PAW) formalism is an efficient pseudopotential-like scheme, which allows for an accurate treatment of the multipole moments in the Hartree and Exchange interactions , making it a natural choice for implementing OEP.

Outline of Talk

1. Explain a OEP Gradient Search Algorithm(R. A. Hyman et al, PRB 62, 15521 (2000)) .
2. Explain a Frozen Core +OEP Gradient Search Algorithm that we developed , with focus on :

Decoupling of valence and core orbital contributions

3. In the end , explain our PAW + OEP Gradient Search algorithm. Show some early results.

Main equations

Starting With Kohn-Sham equation:

$$\{-\frac{\hbar^2}{2m}\nabla^2 + v_s(\mathbf{r})\}\phi_n(\mathbf{r}) = \varepsilon_n\phi_n(\mathbf{r})$$

where

$$V_s(r) = V_N(r) + V_H(r) + V_{xc}(r)$$

and the local exchange potential is defined as :

$$V_{xc}(r) = \frac{\partial E_{xc}[\{\phi_n\}]}{\partial n(r)}.$$

The total energy is given by:

$$E_{tot}[n] = E_T[n] + E_N[n] + E_H[n] + E_{xc}[\{\phi_n(\mathbf{r})\}].$$

For the exchange-correlation energy E_{xc}, we use the **exact exchange functional**, and at this moment, we set $E_c = 0$

Exact Exchange Functional(EXX)

$$E_x[\{\phi_n(\mathbf{r})\}] = -\frac{e^2}{2}\sum_{nm}\Theta_n\Theta_m\delta_{\sigma_m\sigma_n}\int d^3r\int d^3r'\,\frac{\phi_n^*(\mathbf{r})\phi_m^*(\mathbf{r}')\phi_n(\mathbf{r}')\phi_m(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

Because the exact exchange energy is orbital dependent ,determining local potential $V_x(r) = \frac{\partial E_X[\{\varphi_k\}]}{\partial n(r)}$ involves solving integral equations. Alternatively , $V_x(r)$ can be solved by minimizing the energy with constraints, suggested by Hyman , Stiles and Zangwill (PRB 62, 15521 (2000)) and Kümmel Perdew (PRL 90, 043004 (2003))

Gradient Search Algorithm

All Electron And Frozen Core

Hyman suggested that the OEP object function F to be minimized can be constructed from the total energy and constraint relations.

All Electron OEP Object Function

$$F^{AE} = E_{tot}[\{\phi_n\}] - \sum_n \lambda_n(\langle\phi_n \mid \phi_n\rangle - 1) - \sum_n \langle g_n \mid H_{ks} - \varepsilon_n \mid \phi_n\rangle$$

1. λ_n **Lagrangian multiplier** $\leftarrow$ **Normalization Constraint**
2. $g_n(r)$ **Lagrangian multiplier function(Auxiliary Function)** $\leftarrow$ **KS equation Constraint**
3. $g_n(r), \lambda_n, \phi_n(r), \epsilon_n, v_x(r)$ **independent variables(functions)**

For the Frozen Core treatment, only **valence orbitals** $\phi_v(r)$ are treated variationally , and orbitals associated with core states $\phi_c(r)$ are " **frozen** " at their reference configuration.

Frozen Core OEP Object Function

$$F^{FC} = E_{tot}[\{\phi_v\}] - \sum_v \lambda_v(\langle\phi_v \mid \phi_v\rangle - 1) - \sum_v \langle g_v \mid H_{ks} - \varepsilon_v \mid \phi_v\rangle$$

Gradient Search Algorithm :All Electron And Frozen Core

AE Gradient Search

AE KS Equation Constraint

$$\frac{\partial F}{\partial g_n^*(r)} = 0 \rightarrow (\varepsilon_n - H_{KS})\phi_n = 0$$

All Electron Shift Function

$$s(r) = \frac{\partial F}{\partial V_X} = -\sum_n (g_n^*(r)\phi_n(r) + c.c) \rightarrow UpdateV_X$$

All Electron Auxiliary Function

$$(H_{KS} - \varepsilon_n)g_n(r) = \frac{\partial E_X}{\partial \phi_n^*(r)} - V_X\phi_n(r) - U_n\phi_n(r)$$

Orthogonalization Constraints

$$\frac{\partial F}{\partial \varepsilon_n} = 0 \rightarrow \langle g_n \mid \phi_n \rangle = 0$$

FC Gradient Search

FC KS Equation Constraint

$$\frac{\partial F}{\partial g_v^*(r)} = 0 \rightarrow (\varepsilon_v - H_{KS})\phi_v = 0$$

Frozen core Shift Function

$$s(r) = \frac{\partial F}{\partial V_X^{vale}} = -\sum_v (g_v^*(r)\phi_v(r) + c.c)$$

Frozen core Auxiliary Function

$$(H_{ks} - \varepsilon_v)g_v(r) = \frac{\partial (E_X^{v-v})}{\partial \phi_v^*} - V_X^{vale}\phi_v(r) - U_v\phi_v(r)$$

Orthogonalization Constraints

$$\frac{\partial F}{\partial \varepsilon_v} = 0 \rightarrow \langle g_v \mid \phi_v \rangle = 0$$

Gradient Search Algorithm

All Electron And Frozen Core

How to decouple the differential equation for the auxiliary function :

AE Auxiliary Function

$$(H_{KS} - \varepsilon_n) g_n(r) = \frac{\partial E_x}{\partial \phi_n^*(r)} - V_x \phi_n(r) - U_n \phi_n(r)$$

Energy and Orbitals

$$\phi_n(r) \rightarrow \phi_c(r), \phi_v(r)$$

$$E_x \rightarrow E_x^{c-c} + E_x^{v-c} + E_x^{v-v}$$

Derivatives

$$\frac{\partial E_x}{\partial \phi_n^*(r)} \rightarrow \frac{\partial E_x^{c-c}}{\partial \phi_c^*(r)}, \frac{\partial E_x^{c-v}}{\partial \phi_c^*(r)}, \frac{\partial E_x^{c-v}}{\partial \phi_v^*(r)}, \frac{\partial E_x^{v-v}}{\partial \phi_v^*(r)}$$

Auxiliary Function : Core and Valence

$$(H_{KS} - \varepsilon_n) g_n(r) \rightarrow \begin{cases} (H_{KS} - \varepsilon_c) g_c(r) \\ (H_{KS} - \varepsilon_v) g_v(r) \end{cases}$$

Exchange Potential Partitioning

$$V_x(r) = V_x^{core}(r) + V_x^{vale}(r)$$

Gradient Search Algorithm

All Electron And Frozen Core

How to decouple the differential equation for the auxiliary function :

AE Auxiliary Function

$$(H_{KS} - \varepsilon_n)g_n(r) = \frac{\partial E_x}{\partial \phi_n^*(r)} - V_x\phi_n(r) - U_n\phi_{\ n}(r)$$

Frozen core Auxiliary Function

$$(H_{ks} - \varepsilon_v)g_v(r) = \frac{\partial (E_x^{v-v})}{\partial \phi_v^*} - V_x^{vale}\phi_v(r) - U_v\phi_v(r)$$

Frozen core Shift Function

$$s(r) = \frac{\partial F}{\partial V_x^{vale}} = -\sum_v (g_v^*(r)\phi_v(r) + c.c) \rightarrow Update V_x^{vale}$$

AE results : Ground State Energy

Total ground-state energies for H through Ar (Ry)

Atom	Present Work	Previous Work[a]	SUHF[a]
H	-1.0000	-1.000	-1.000
He	-5.7234	-5.7234	-5.7234
Li	-14.8647	-14.8650	-14.8656
Be	-29.1449	-29.1448	-29.1460
B	-49.0555	-49.0566	-49.0586
C	-75.3162	-75.3778	-75.3800
N	-108.5890	-108.8068	-108.8092
O	-149.5352	-149.6242	-149.6326
F	-198.8155	-198.8184	-198.8216
Ne	-257.0908	-257.0908	-257.0940
Na	-323.7126	-323.7132	-323.7180
Mg	-399.2231	-399.2232	-399.2292
Al	-483.7464	-483.7466	-483.7536
Si	-577.6613	-577.7014	-577.7090
P	-681.2891	-681.4300	-681.4386
S	-794.9477	-795.0032	-795.01260
Cl	-918.9542	-918.9552	-918.96520
Ar	-1053.6244	-1053.6244	-1053.6350

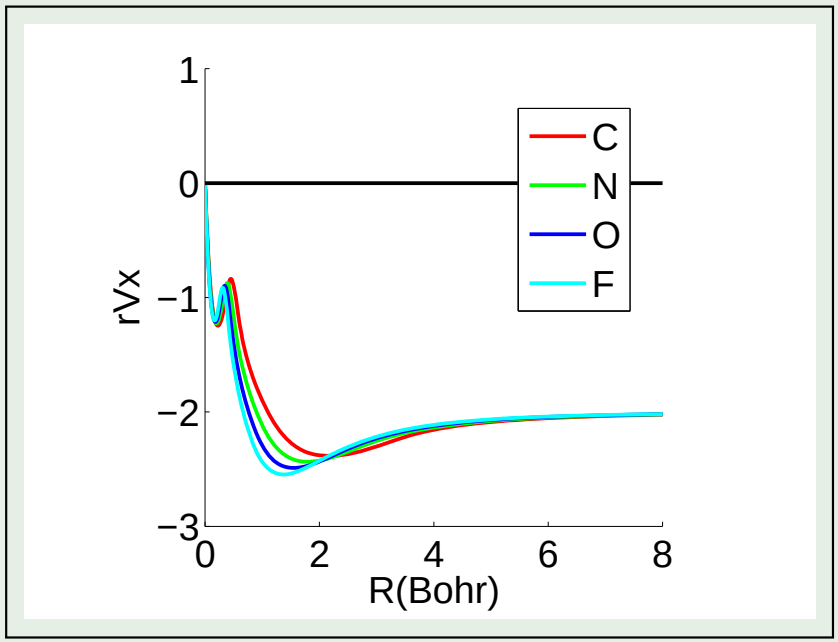
Total ground-state energies for K through Kr (Ry)

Atom	Present Work	Previous Work[a]	SUHF[a]
K	-1198.3175	-1198.3182	-1198.3298
Ca	-1353.5038	-1353.5038	-1353.5164
Sc	-1519.4522	-1519.4554	-1519.4718
Ti	-1696.7192	-1969.7604	-1696.8132
V	-1885.5846	-1885.7138	-1885.7712
Cr	-2086.3283	-2086.6914	-2086.7136
Mn	-2299.2269	-2299.7200	-2299.7396
Fe	-2524.5561	-2524.8760	-2524.9000
Co	-2762.5906	-2762.7636	-2762.8372
Ni	-3013.6049	3013.6680	-3013.6606
Cu	-3277.8730	-3277.9046	-3277.9284
Zn	-3555.6687	-3555.6688	-3555.6962
Ga	-3846.4969	-3846.4974	-3846.5224
Ge	-4150.6565	-4150.6966	-4150.7206
As	-4468.3206	-4468.4562	-4468.4798
Se	-4799.6628	-4799.7146	-4799.7382
Br	-5144.8590	-5144.8600	-5144.8836
Kr	-5504.0860	-5504.0860	-5504.1100

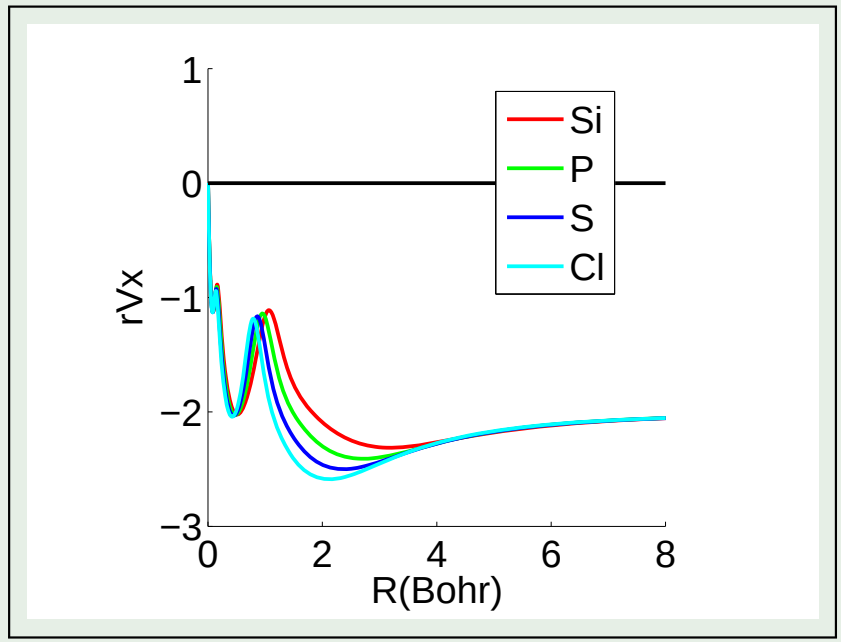
[a] Grabo, Kreibich, Kurth, & Gross, in Ansimov, ed. *Strong coulomb correlations in electronic structure calculations, (Gordon and Breach, 2000), pg. 203.*

AE results :Exchange potential of 1^{st} and 2^{nd} Row

Exchange potential of C N O F

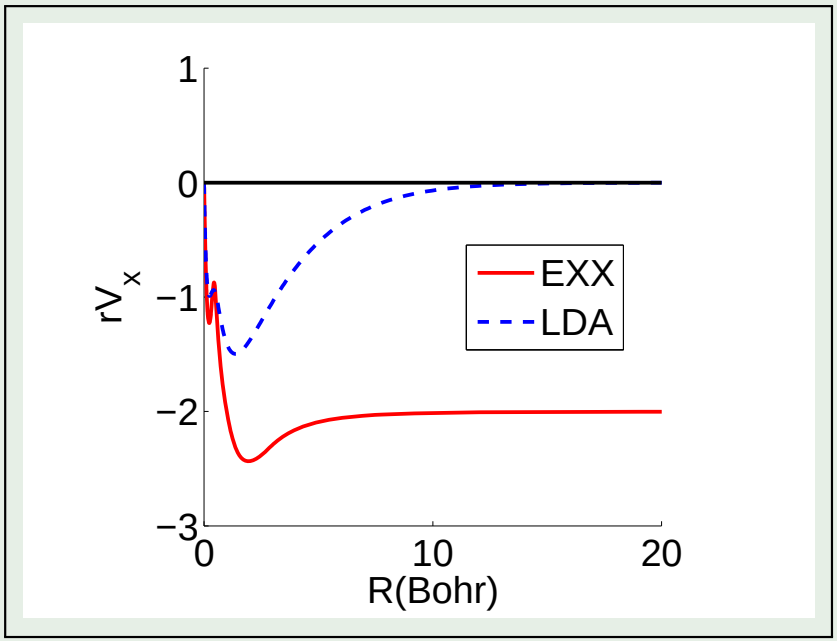


Exchange potential of Si P S Cl

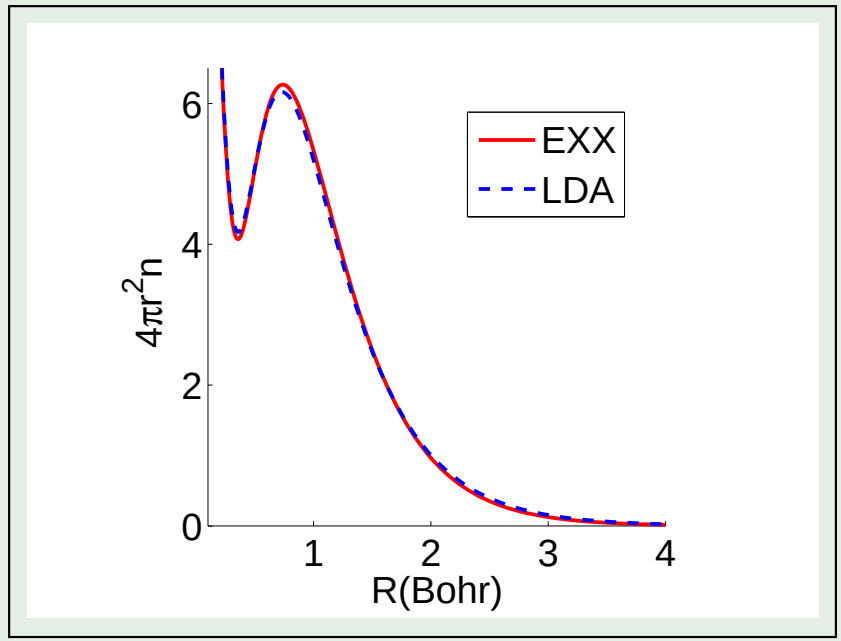


AE results :Comparing EXX and LDA of Fluorine

rV_x Fluorine EXX and LDA result

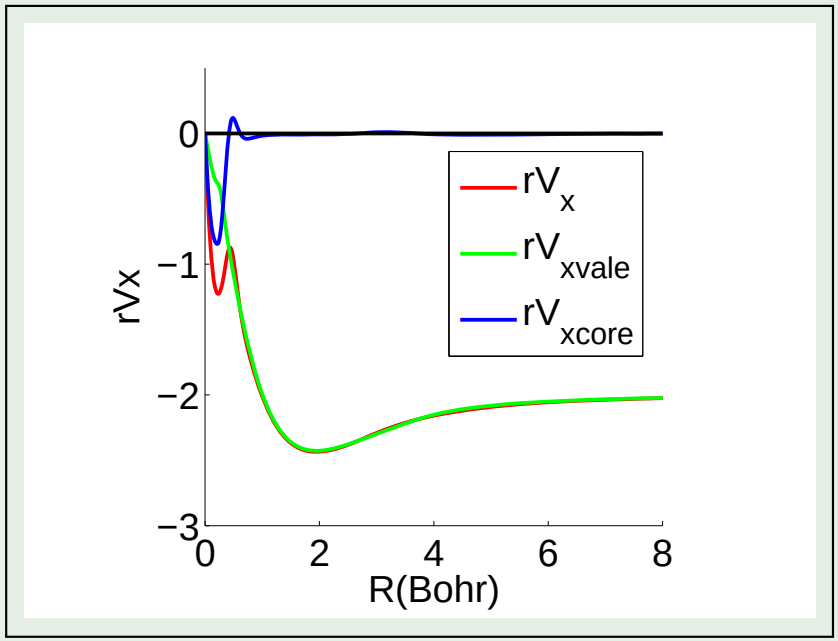


Density of Fluorine EXX and LDA result



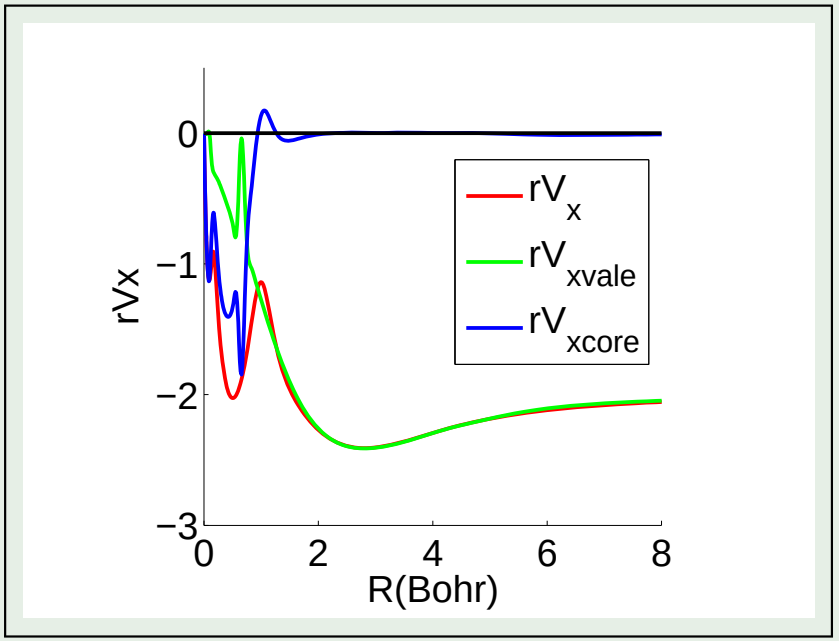
FC results :Partitioning of V_{xcore} and V_{xvale}

Nitrogen



$$N : \underbrace{1s^2}_{core}\ \underbrace{2s^2 2p^3}_{valence}$$

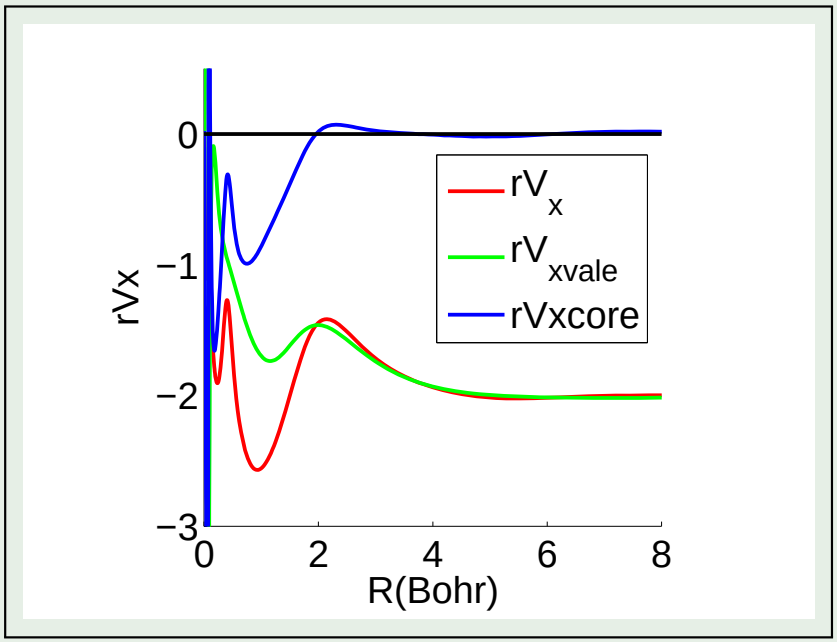
Phosphorus



$$P : \underbrace{1s^2 2s^2 2p^6}_{core}\ \underbrace{3s^2 3p^3}_{valence}$$

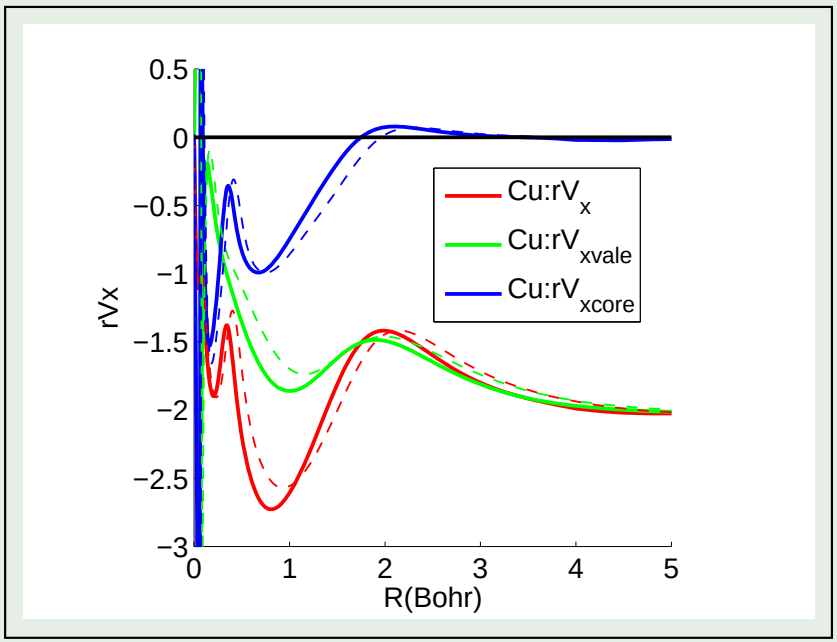
FC results :Partitioning of V_{xcore} and V_{xvale}

Iron



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

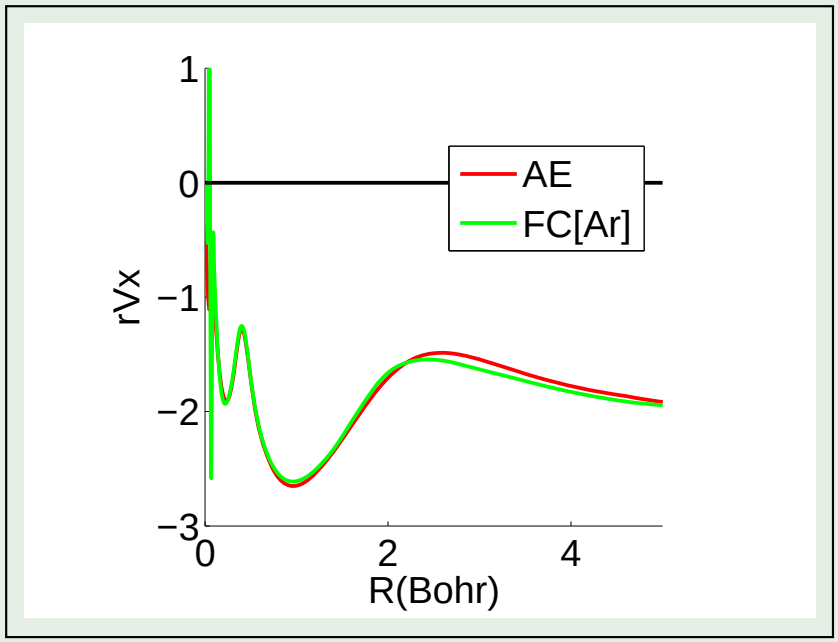
Copper



$$Cu : \underbrace{1s^1 2s^2 2p^6 3s^2 3p^6}_{core} \underbrace{3d^9 4s^2}_{valence}$$

FC results :Test of FC approximation

Fe : $3d^6 4s^2 \rightarrow 3d^7 4s^1$



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

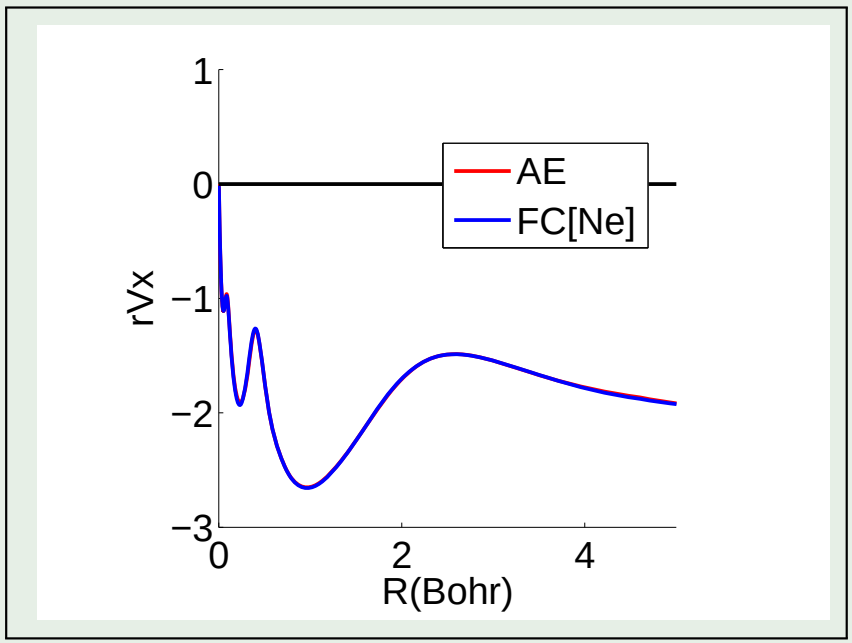
   $\underbrace{1s^1 2s^2 2p^6 3s^2 3p^6}_{core}\ \underbrace{3d^6 4s^2}_{valence}$

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

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

FC results :Test of FC approximation

Fe : $3s^2 3p^6 3d^6 4s^2 \rightarrow 3s^2 3p^6 3d^7 4s^1$



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

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

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

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

PAW Introduction

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 $r \geq r_c^a$
$p_i^a(\mathbf{r})$	Projector function	$p_i^a(\mathbf{r}) \equiv 0$ for $r \geq r_c^a$ and $\langle p_i^a \vert \widetilde{\phi}_j^a \rangle = \delta_{ij}$

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

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

a: site index
i: basis index

PAW Introduction

Kohn-Sham equations in PAW formalism

$$(H^{PAW} - \varepsilon_n O)\widetilde{\Psi}_n(r) = 0$$

Smooth Hamiltonian and Smooth Effective Potential

$$\widetilde{H} = -\frac{\hbar^2}{2m}\nabla^2 + \widetilde{V}$$

$$\widetilde{V}(r) = \widetilde{V}_{loc}(r) + \widetilde{V}_H(r) + \widetilde{V}_x^{vale}(r)$$

$\widetilde{V}_{loc}$ is unscreened local potential

PAW Hamiltonian

$$H^{PAW}(r) = \widetilde{H}(r) + \sum_{aij} \left|p_i^a\right\rangle D_{ij}^a \left\langle p_j^a\right|$$

PAW Matrix Elements

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

Contains All electron part , and corrections

PAW Overlap Function

$$O = 1 + \sum_{aij} \left|p_i^a\right\rangle O_{ij}^a \left\langle p_j^a\right|$$

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

PAW + OEP Formalism

All Electron OEP Object Function

$$F^{AE} = E_{tot}[\{\phi_n\}] - \sum_n \lambda_n(\langle \phi_n \mid \phi_n \rangle - 1) - \sum_n \langle g_n \mid H_{ks} - \varepsilon_n \mid \phi_n \rangle$$

Frozen Core OEP Object Function

$$F^{FC} = E_{tot}[\{\phi_v\}] - \sum_v \lambda_v(\langle \phi_v \mid \phi_v \rangle - 1) - \sum_v \langle g_v \mid H_{ks} - \varepsilon_v \mid \phi_v \rangle$$

The PAW Object Function can be constructed in the same way, with similar constraints :

PAW OEP Object Function

$$F^{PAW} = E_{tot} - \sum_v \lambda_v(\left\langle \widetilde{\Psi}_v \mid O \mid \widetilde{\Psi}_v \right\rangle - 1) - \sum_v \left\langle \widetilde{g}_v \left| H^{PAW} - \varepsilon_v O \right| \widetilde{\Psi}_v \right\rangle$$

PAW Gradient Search Algorithm

Frozen Core And PAW

FC Gradient Search

Frozen core Shift Function

$$\frac{\partial F}{\partial V_x^{vale}} = -\sum_v (g_v^*(r)\phi_v(r) + c.c)$$

Frozen core Auxiliary Function

$$(H_{ks} - \varepsilon_v)g_v(r) = \frac{\partial(E_x^{v-v})}{\partial \phi_n^*} - V_x^{vale}(r)\phi(r) - U_v\phi_v(r)$$

PAW Gradient Search

PAW OEP Shift Function

$$S(r) = \frac{\partial F^{PAW}}{\partial \tilde{V}_x^{vale}} = -\sum_v (\tilde{g}_v^*(r)\tilde{\Psi}_v(r) + C.C)$$

$$[S]_{ij} = \frac{\partial F^{PAW}}{\partial [V_x^{vale}]_{ij}} = -\sum_v (\langle \tilde{g}_v \mid p_i \rangle \left\langle p_j \mid \tilde{\Psi}_v \right\rangle + C.C)$$

PAW Auxiliary Function

$$(H^{PAW} - E_v O)\tilde{g}_v = \frac{\partial E_x^{v-v}}{\partial \tilde{\Psi}_v^*} - \tilde{V}_x^{vale}\tilde{\Psi}_v - U_v O\tilde{\Psi}_v - \sum_{ij} |p_i\rangle [V_x^{vale}]_{ij} \left\langle p_j \mid \tilde{\Psi}_v \right\rangle$$

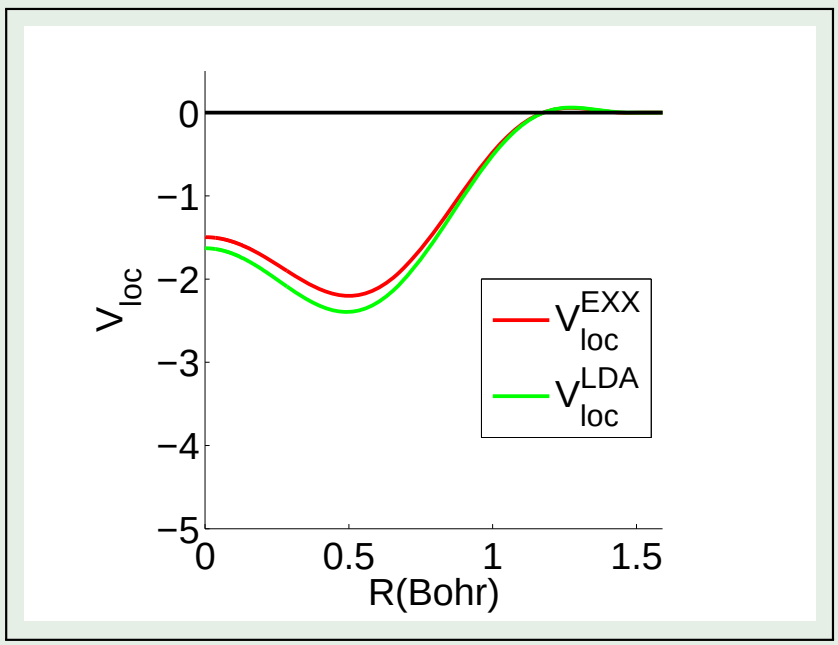
Construction of $\widetilde{V}_{loc}$

$\widetilde{V}_{loc}$ is a short range unscreened local potential related to the reference pseudopotential $V^{ps}(r)$ according to :

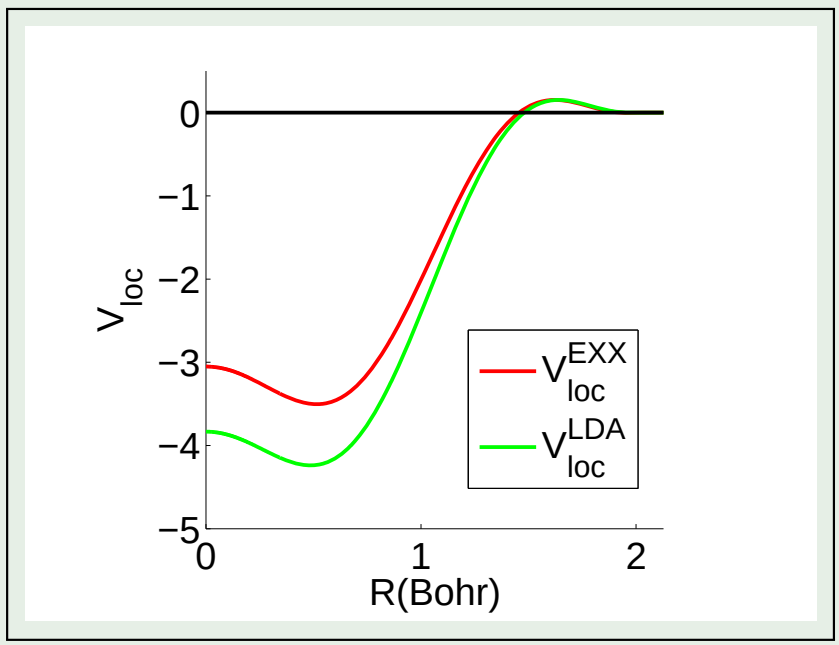
PAW Unscreen Procedure

$$\widetilde{V}_{loc}(r) = V^{PS}(r) - V_H[\widetilde{\rho}_v] - \widetilde{V}_x^{vale}(r)$$

$\widetilde{V}_{loc}$ of N

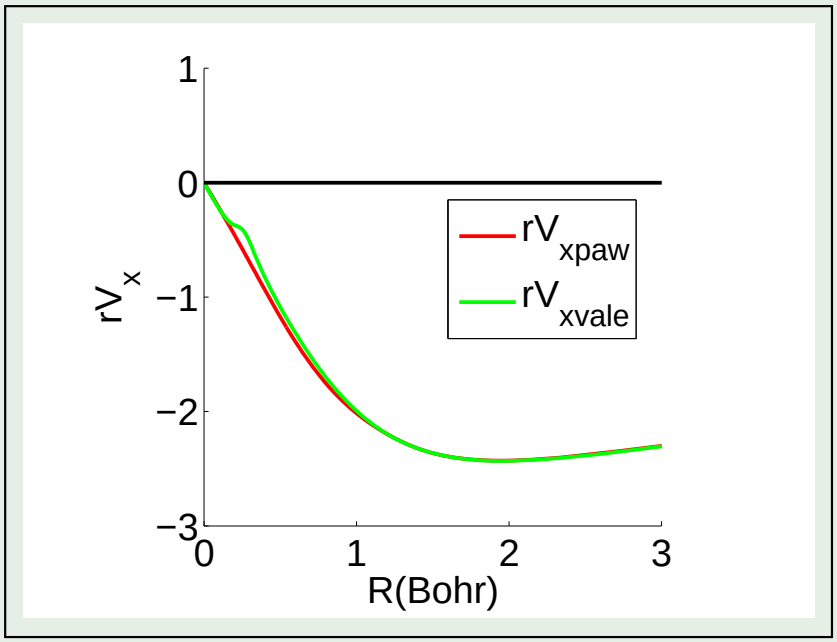


$\widetilde{V}_{loc}$ of P

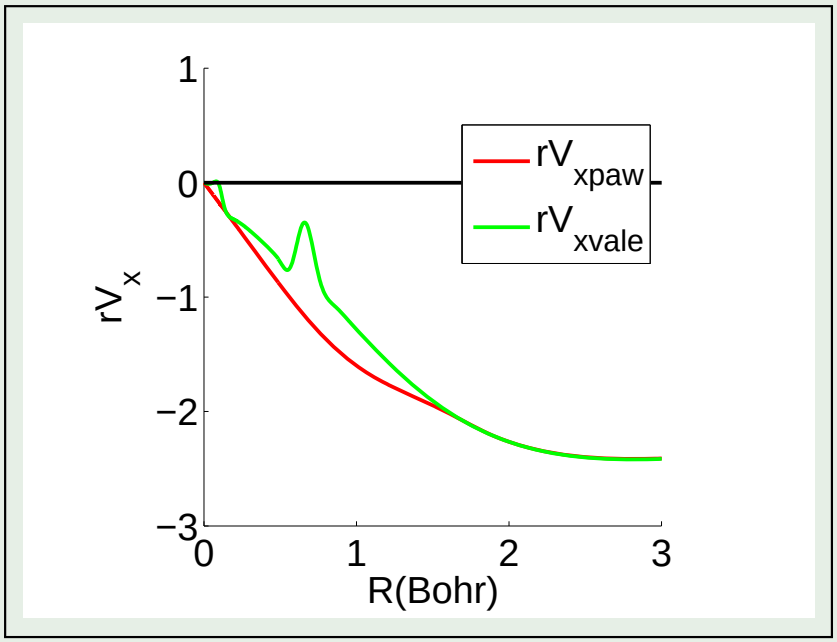


Atompaw OEP results:PAW pseudized exchange potential

$\widetilde{V}_x$ of N



$\widetilde{V}_x$ of P



Conclusion

- Implement a gradient search algorithm $\rightarrow$ All Electron + OEP code .
- Developed a Frozen core scheme ; decouple the equations for core and valence contributions.
- We examined some elements ,and showed that we can improve the FC accuracy by including more orbitals in the valence.
- Developed PAW + OEP scheme, constructed the

$$\widetilde{\phi}_n(r)\ ,\ p_i(r)\ ,D_{ij}\ ,\ \widetilde{V}_{loc}$$

- **Future work : PAW + OEP solid code**