

A Projector Augmented Wave Formulation of the Optimized Effective Potential Formalism ^a

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- Motivation and overview
- OEP formalism
- “Frozen” core electrons
- PAW formalism
- Selected atomic examples
- Summary and conclusions

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Motivation

- **Why Optimized Effective Potential (OEP)?^a**
 - Orbital-dependent exchange-correlation functionals within the Kohn-Sham framework of density functional theory^b
 - *Self-interaction-free* treatment of electrons
- **Why Projector Augmented Wave (PAW)?^c**
 - Efficient pseudopotential-like scheme
 - Accurate evaluation of multipole moments in Coulomb and exchange interaction terms^d

^aReview articles: S. Kümmel and L. Kronik, *RMP* **80**, 3-60 (2008); T. Grabo *et al* in *Strong Coulomb correlations in electronic structure calculations*, V. Anisimov, ed. Gordon and Breach (2000), pg. 203-311.

^bW. Kohn and L. Sham, *PR* **140**, A1133-A1138 (1965)

^cP. Blöchl, *PRB* **50**, 17953-17979 (1994)

^dJ. Paier *et al*, *JCP* **122**, 234102 (2005)

Motivation (continued)

Self-interaction problem

Within Kohn-Sham theory, the total electronic energy is a functional of the electron density $\rho(\mathbf{r})$ having the form:

$$E_{tot}(\rho) = \underbrace{E_K(\rho)}_{\text{Kinetic}} + \underbrace{E_N(\rho)}_{\text{Nuclear}} + \underbrace{E_H(\rho)}_{\text{Hartree}} + \underbrace{E_x(\rho)}_{\text{Exchange}} + \underbrace{E_c(\rho)}_{\text{Correlation}} . \quad (1)$$

Here,

$$E_H(\rho) \equiv \frac{e^2}{2} \int \int d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2)$$

representing the Coulomb interaction between electrons, including the self-interaction.

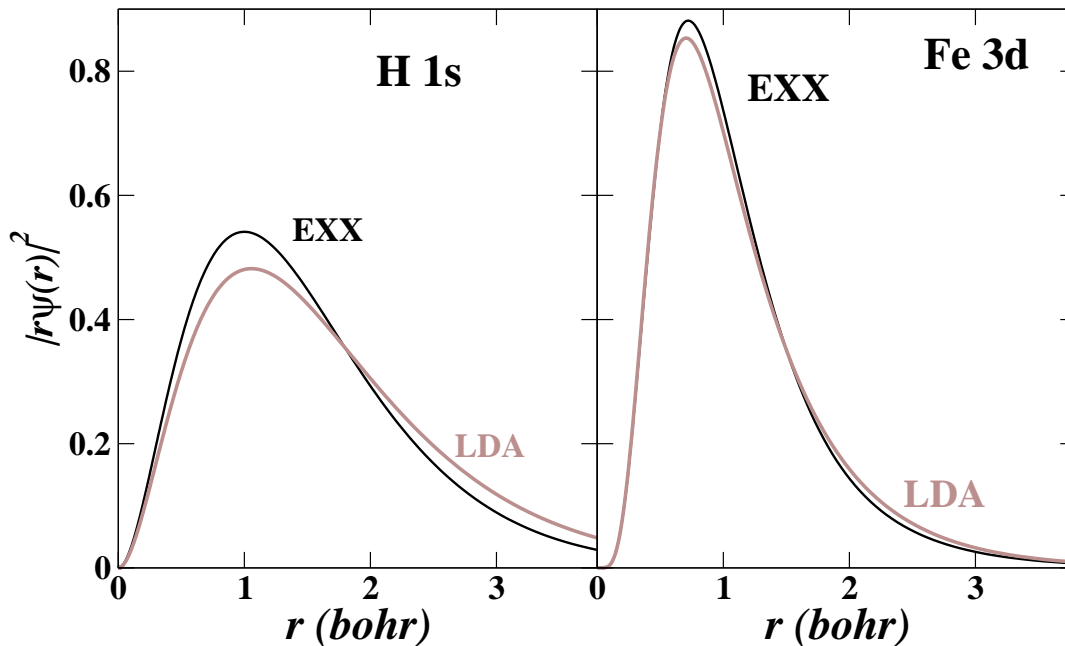
Only for E_x chosen to have the form of Fock exchange, can this self-interaction be completely removed from the formalism.

Motivation (continued)

Fock exchange form

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

where the summation over all occupied states includes the self-interaction correction for $p \equiv q$ and $\sigma_p \equiv \sigma_q$. For wavefunctions $\Psi_p(\mathbf{r})$ representing extended states, the self-interaction energy is not large. Two notable exceptions are:



For a H atom:

$$E_{tot}^{LDA} = -0.9 \text{ Ry}$$

$$E_{tot}^{EXX} = -1.0 \text{ Ry.}$$

For a Fe atom:

$$\epsilon_{4s}^{LDA} - \epsilon_{3d}^{LDA} = 0.2 \text{ Ry}$$

$$\epsilon_{4s}^{EXX} - \epsilon_{3d}^{EXX} = 0.3 \text{ Ry.}$$

Motivation (continued)

Some self-interaction correction schemes

- SIC-LSD – Perdew and Zunger, *PRB* **23**, 5048-5079 (1981)
- LDA+U – Anisimov *et al*, *PRB* **44**, 943-954 (1991); Cococcioni and Gironcoli, *PRB* **71**, 035105 (2005)

⇒ **Orbital-dependent density functionals:**

$E_x \approx$ **Fock exchange**

$E_c =$ **consistent correlation functional.**

Scope of present work (so far)

- Choose E_x to be Fock exchange (EXX). The corresponding Kohn-Sham local potential is $V_x(\mathbf{r})$.
- Choose $E_c \equiv 0$ for the moment (hoping that an appropriate functional will soon be developed) (OEP). The corresponding Kohn-Sham local potential $V_c(\mathbf{r})$ would then be added.
- Develop OEP-EXX for all electrons in spherical atoms
- **Adapt OEP-EXX formalism to the projector augmented wave (PAW) formalism in order to carry out calculations for extended systems.**
 - ⇒ **Formulate and test a frozen core approximation scheme.**
 - ⇒ **Apply the PAW formalism to valence electrons**

All-electron atomic OEP-EXX equations

The basic equations can be derived as a constrained minimization problem to determine Kohn-Sham radial orbitals $\{\psi_p(r)\}^a$ and to minimize the total energy of the system with the help of Lagrange multipliers:^b

$$F(\{\psi_p\}, V_x, \{g_p\}, \{\epsilon_p\}, \{\lambda_{qp}\}) = E_{tot}(\{\psi_p\}) - \sum_p (\langle g_p | H_{KS} - \epsilon_p | \psi_p \rangle + cc) - \sum_{pq} \lambda_{pq} (\langle \psi_p | \psi_q \rangle - \delta_{pq}). \quad (4)$$

The Kohn-Sham Hamiltonian H_{KS} is given by the kinetic energy operator and potential terms:

$$H_{KS} = \hat{K} + V_N(r) + V_H(r) + V_x(r), \quad (5)$$

where

$$V_N(r) \equiv \frac{\delta E_N}{\delta \rho(r)}, \quad V_H(r) \equiv \frac{\delta E_H}{\delta \rho(r)}, \quad (6)$$

and the local exchange potential $V_x(r)$ is to be determined.

^aThe index p stands for atomic shell quantum numbers $n_p l_p$ corresponding to shell occupancy N_p .

^bHyman, Stiles, and Zangwill, *PRB* **62**, 15521-15526 (2000)

All-electron atomic OEP-EXX equations (continued)

At self-consistency, the following equations must be satisfied simultaneously:

$$H_{KS} = \hat{K} + V_N + V_H + V_x \quad H_{KS}|\psi_p\rangle = \epsilon_p|\psi_p\rangle \quad \langle\psi_p|\psi_q\rangle = \delta_{pq} \quad (7)$$

$$(H_{KS} - \epsilon_p)|g_p\rangle = \frac{1}{N_p} \frac{\delta E_x}{\delta\psi_p^*(r)} - V_x(r)|\psi_p\rangle - \sum_q \lambda_{pq}|\psi_q\rangle, \quad (8)$$

where $\lambda_{pq} = \langle\psi_q|\frac{\delta E_x}{\delta\psi_p^*(r)}\rangle - \langle\psi_q|V_x|\psi_p\rangle$ and $\langle g_p|\psi_q\rangle = 0$.

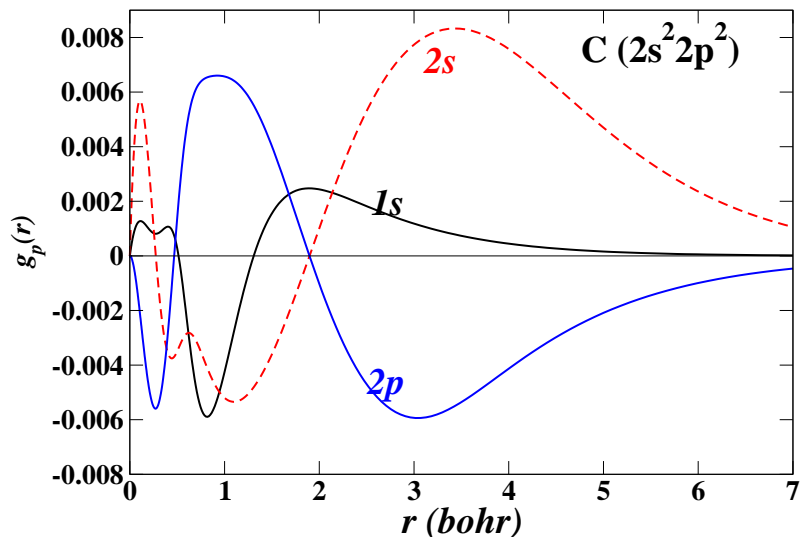
$$\sum_p N_p g_p(r) \psi_p(r) = 0. \quad (9)$$

In practice, the equations are solved iteratively yielding results consistent with the Green's function formulation of earlier work.^a

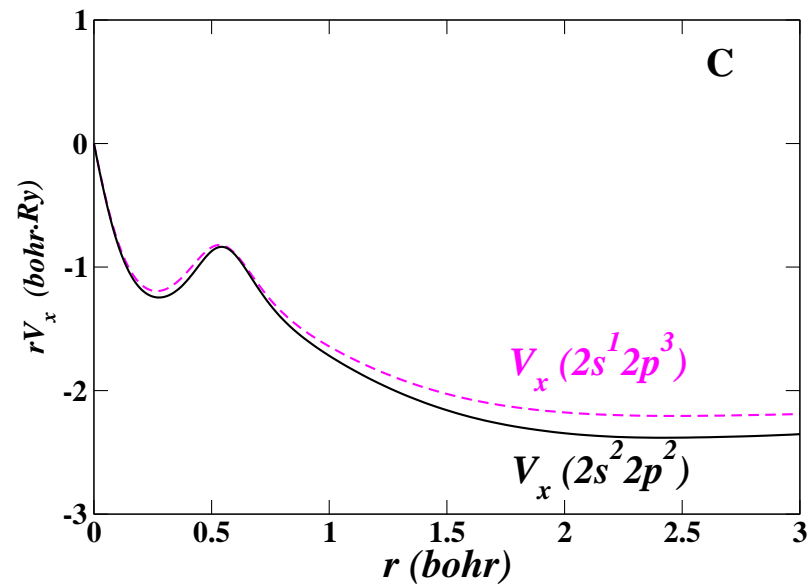
^aTalman and Shadwick, *PRA* **14** 36-40 (1976); Engel and Vosko, *PRA* **47** 2800-2811 (1993); T. Grabo *et al* in *Strong Coulomb correlations in electronic structure calculations*, V. Anisimov, ed. Gordon and Breach (2000), pg. 203-311.

All-electron atomic OEP-EXX results for carbon

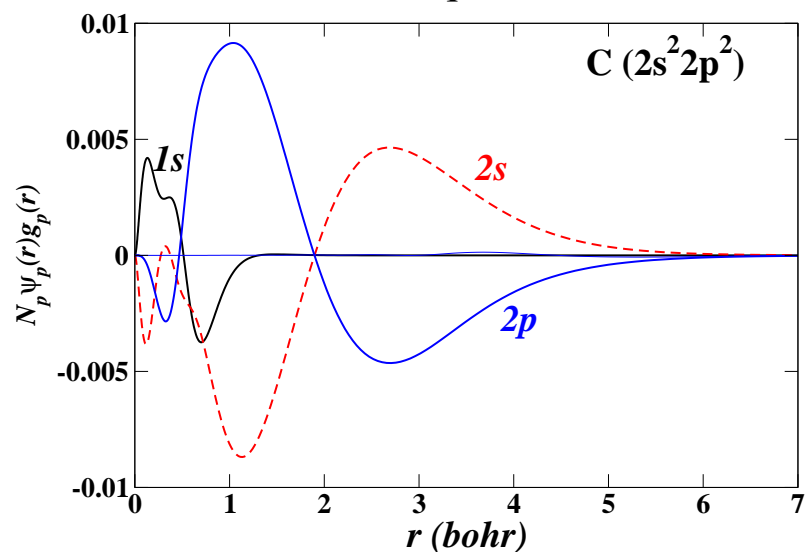
Auxiliary functions $g_p(r)$:



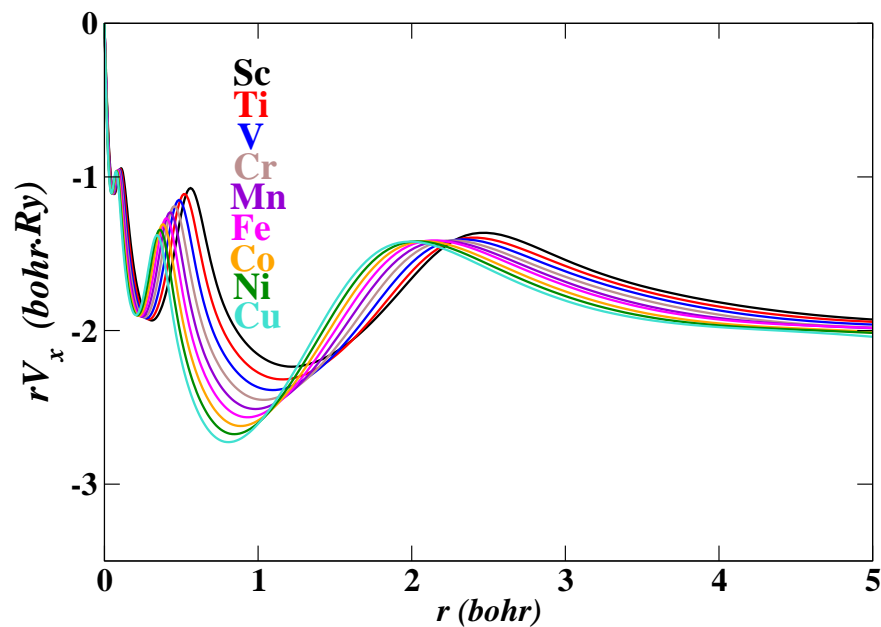
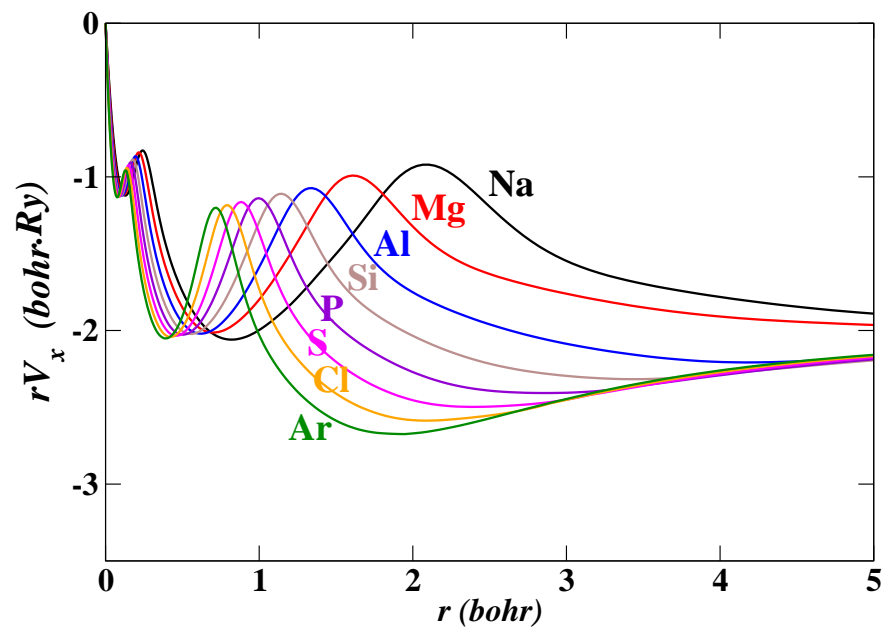
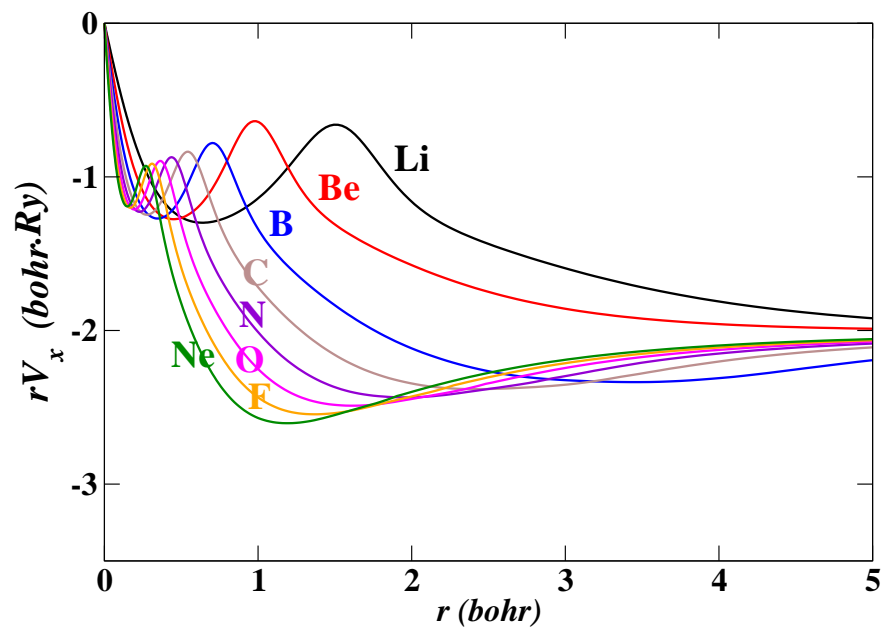
All-electron local exchange potential $V_x(r)$, for ground state ($2s^2 2p^2$) and for excited state ($2s^1 2p^3$).



Contributions to shift equation:



All-electron atomic OEP-EXX results for $V_x(r)$



Frozen core atomic OEP-EXX equations

In order to focus computational effort on the valence properties of materials, it is necessary to develop a frozen core approximation scheme. For each material (other than H and He), it is possible to partition the states into core and valence contributions:

$$p \rightarrow \begin{cases} v & \text{for valence shells (typically partially occupied)} \\ c & \text{for core shells} \end{cases} \quad (10)$$

In a similar way, we can partition, the electron wavefunctions

$$\psi_p(\mathbf{r}) \rightarrow \begin{cases} \psi_v(\mathbf{r}) & \text{for valence states} \\ \psi_c(\mathbf{r}) & \text{for core states} \end{cases} \quad (11)$$

and the auxiliary functions

$$g_p(\mathbf{r}) \rightarrow \begin{cases} g_v(\mathbf{r}) & \text{for valence states} \\ g_c(\mathbf{r}) & \text{for core states} \end{cases} \quad (12)$$

and the local exchange potential

$$V_x(\mathbf{r}) = V_x^{\text{core}}(\mathbf{r}) + V_x^{\text{vale}}(\mathbf{r}). \quad (13)$$

The challenge is to devise a scheme where the functional variation is allowed only for $\{\psi_v(\mathbf{r})\}$ and V_x^{vale} , consistent with the all-electron equations of the reference configuration.

Frozen core atomic OEP-EXX equations (continued)

Partitioning of the reference configuration to define V_x^{core}

All-electron auxiliary function equation:

$$(H_{KS} - \epsilon_v) |g_v\rangle = \frac{1}{N_v} \frac{\delta E_x}{\delta \psi_v^*(r)} - V_x(r) |\psi_v\rangle - \sum_q \lambda_{vq} |\psi_q\rangle \quad (14)$$

For the reference configuration, we assume a partitioning of the valence auxiliary function:

$$g_v(r) \equiv g_v^{\text{core}}(r) + g_v^{\text{vale}}(r) \quad (15)$$

satisfying the following two equations:

$$(H_{KS} - \epsilon_v) |g_v^{\text{vale}}\rangle = \frac{1}{N_v} \frac{\delta E_x^{vv}}{\delta \psi_v^*(r)} - V_x^{\text{vale}}(r) |\psi_v\rangle - \sum_q \lambda_{vq}^{\text{vale}} |\psi_q\rangle, \quad (16)$$

and

$$(H_{KS} - \epsilon_v) |g_v^{\text{core}}\rangle = \frac{1}{N_v} \frac{\delta E_x^{cv}}{\delta \psi_v^*(r)} - V_x^{\text{core}}(r) |\psi_v\rangle - \sum_q \lambda_{vq}^{\text{core}} |\psi_q\rangle. \quad (17)$$

The original shift equation becomes

$$\sum_p N_p g_p(r) \psi_p(r) = 0 \rightarrow \left\{ \begin{array}{l} \sum_v N_v g_v^{\text{vale}}(r) \psi_v(r) = 0 \\ \underbrace{\sum_c N_c g_c(r) \psi_c(r)}_{\text{Core shift}} + \sum_v N_v g_v^{\text{core}}(r) \psi_v(r) = 0 \end{array} \right. \quad (18)$$

Frozen core atomic OEP-EXX equations (continued)

Total valence energy in frozen core approximation

$$E_{tot}^{\text{vale}} = E_K(\rho_v) + E_N(\rho_v) + E_H^{cv}(\rho_v) + E_H^{vv}(\rho_v) + E_x^{cv}(\rho_v) + E_x^{vv}(\{\psi_v\}), \quad (19)$$

$$\text{where } E_x^{cv}(\rho_v) \approx \int d^3r V_x^{\text{core}}(r)\rho_v(r).$$

Once $V_x^{\text{core}}(r)$ has been determined for the reference configuration, the self-consistent equations to solve for excited valence configurations are:

$$H_{KS} = \hat{K} + V_N + V_H + V_x^{\text{core}} + V_x^{\text{vale}} \quad H_{KS}|\psi_v\rangle = \epsilon_v|\psi_v\rangle \quad (20)$$

$$(H_{KS} - \epsilon_v)|g_v^{\text{vale}}\rangle = \frac{1}{N_v} \frac{\delta E_x^{vv}}{\delta \psi_v^*(r)} - V_x^{\text{vale}}(r)|\psi_v\rangle - \sum_w \lambda_{vw}^{\text{vale}}|\psi_w\rangle, \quad (21)$$

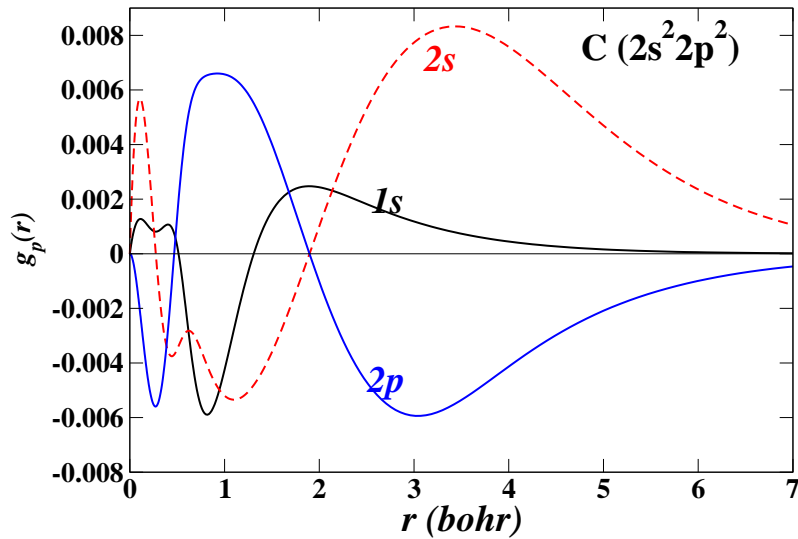
$$\text{where } \lambda_{vw}^{\text{vale}} = \langle \psi_w | \frac{\delta E_x^{vv}}{\delta \psi_v^*(r)} \rangle - \langle \psi_w | V_x^{\text{vale}} | \psi_v \rangle.$$

$$\sum_v N_v g_v^{\text{vale}}(r)\psi_v(r) = 0. \quad (22)$$

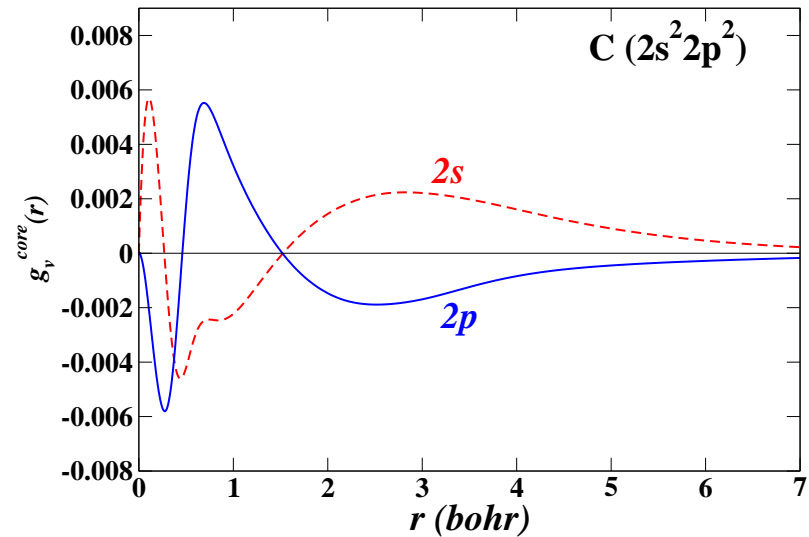
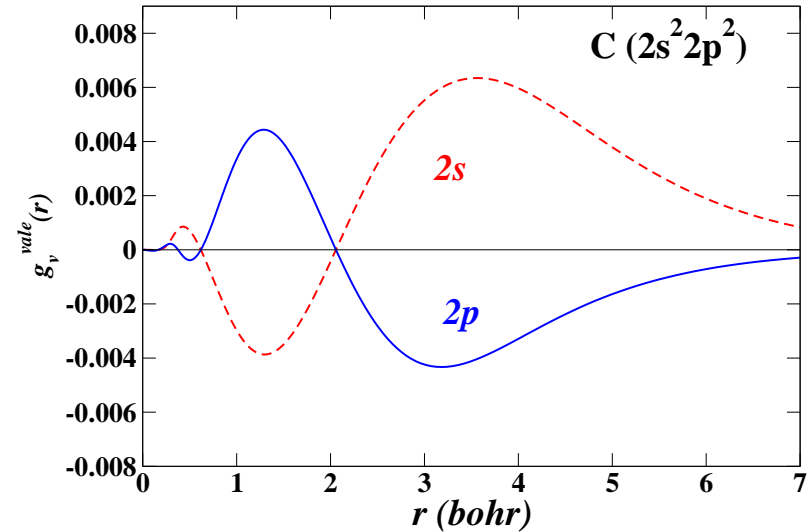
Here, $|\psi_v\rangle$, $|g_v^{\text{vale}}\rangle$, and V_x^{vale} are updated self-consistently through these equations.

Frozen core atomic OEP-EXX results for carbon

All-electron auxiliary functions $g_v(r)$:

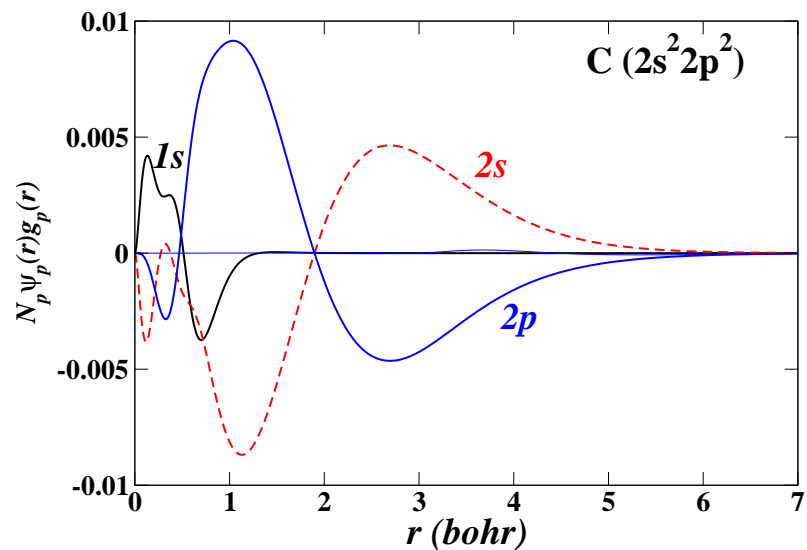


Frozen core functions $g_v^{vale}(r)$ and $g_v^{core}(r)$:

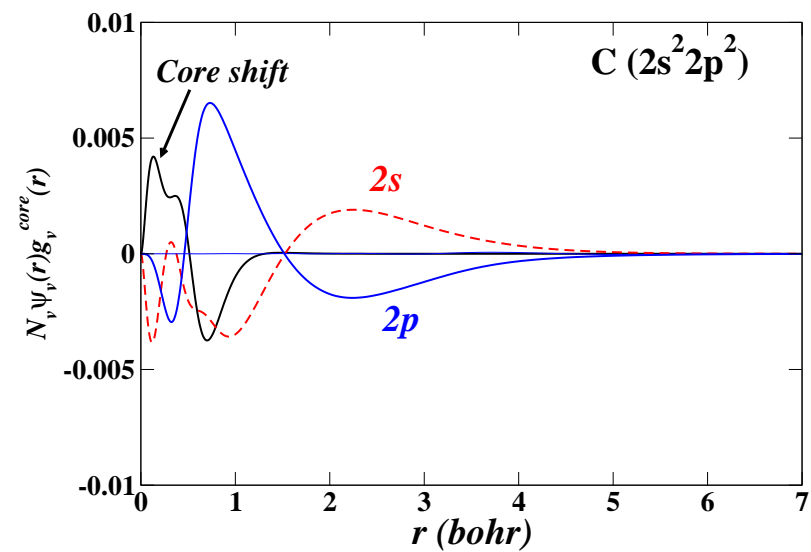
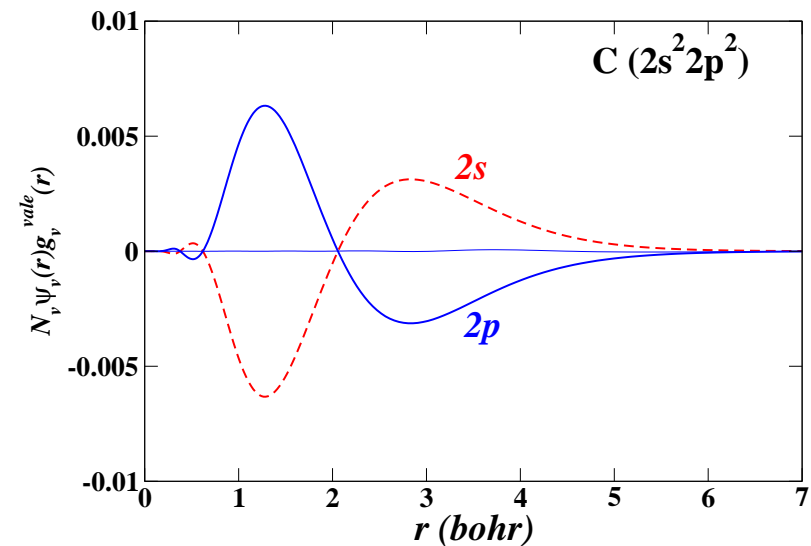


Frozen core atomic OEP-EXX results for carbon

All-electron shift components $N_p g_p(r) \psi_p(r)$

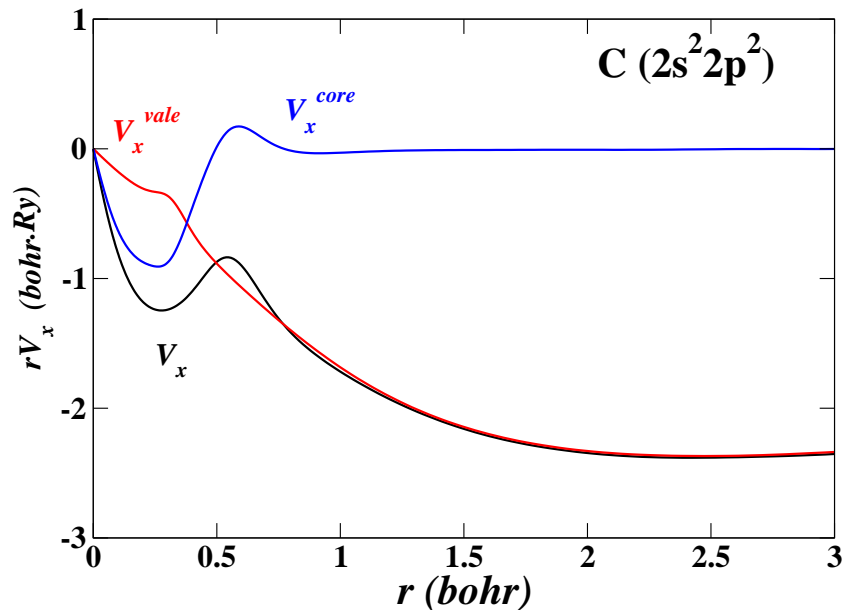


Frozen core shift components:

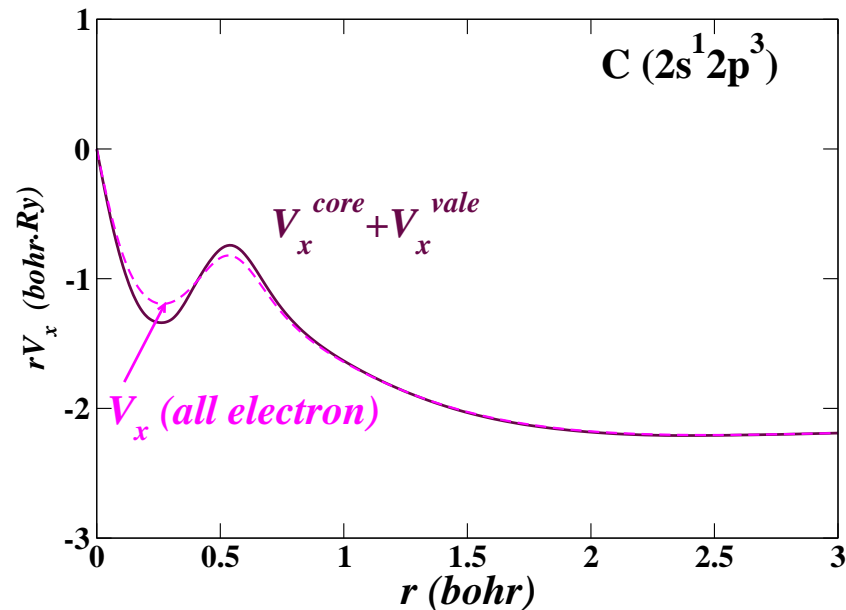


Frozen core atomic OEP-EXX results for carbon

Local exchange potential V_x for reference configuration ($[\text{He}]2s^22p^2$) and its decomposition into V_x^{vale} and V_x^{core} :

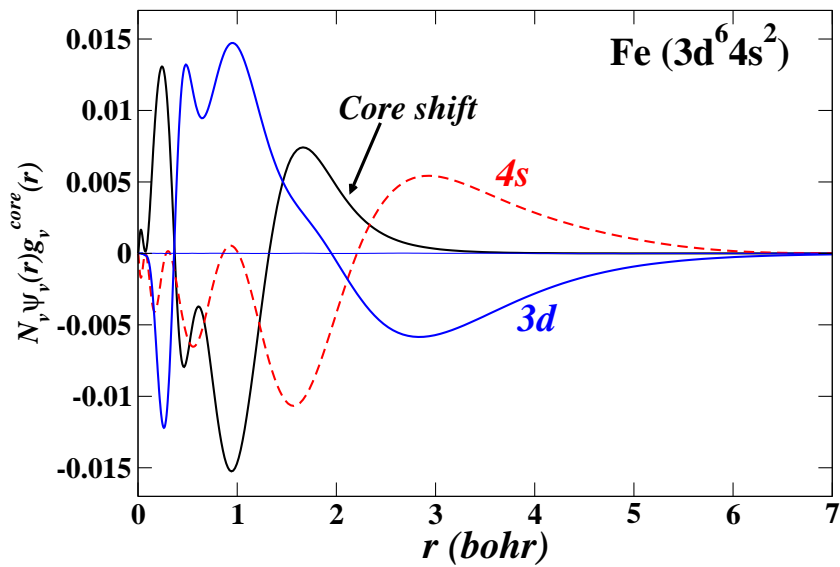
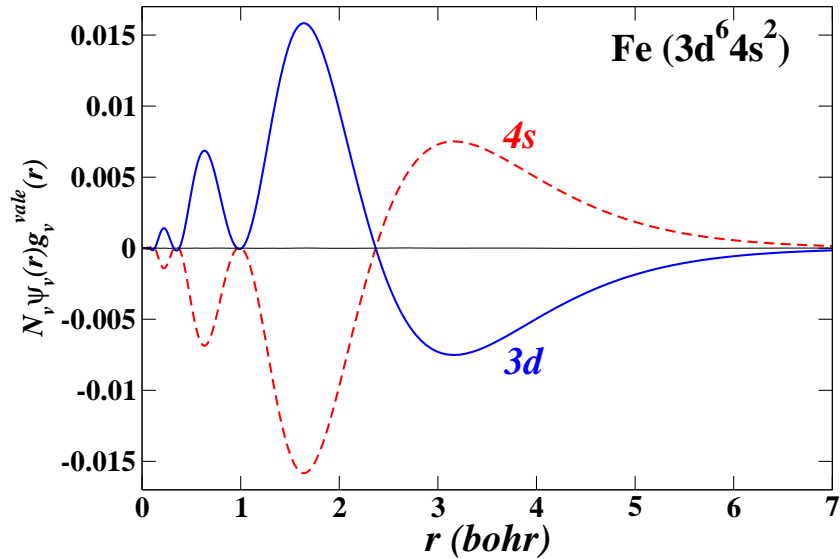


Total local exchange potential $V_x^{\text{vale}} + V_x^{\text{core}}$ for excited configuration ($[\text{He}]2s^12p^3$), comparing frozen core and all-electron results:

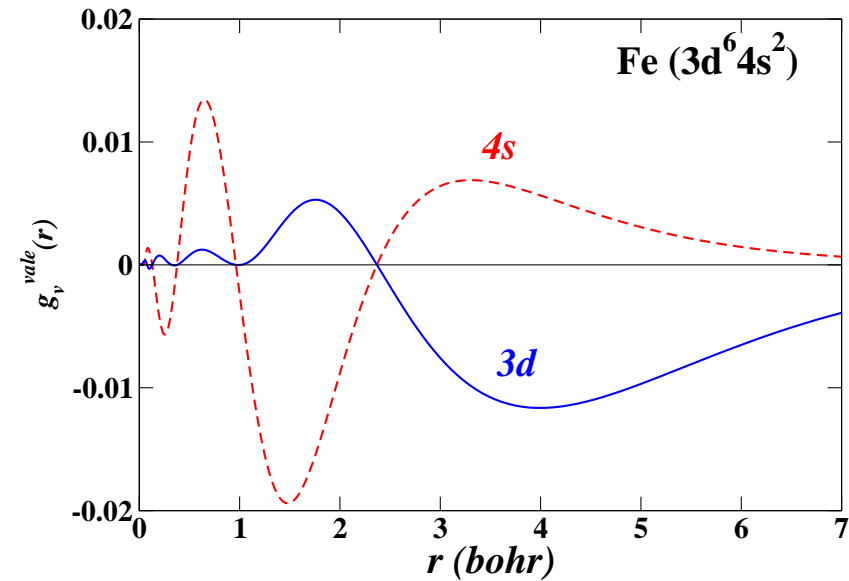


Frozen core atomic OEP-EXX results for iron

Frozen core shift components:

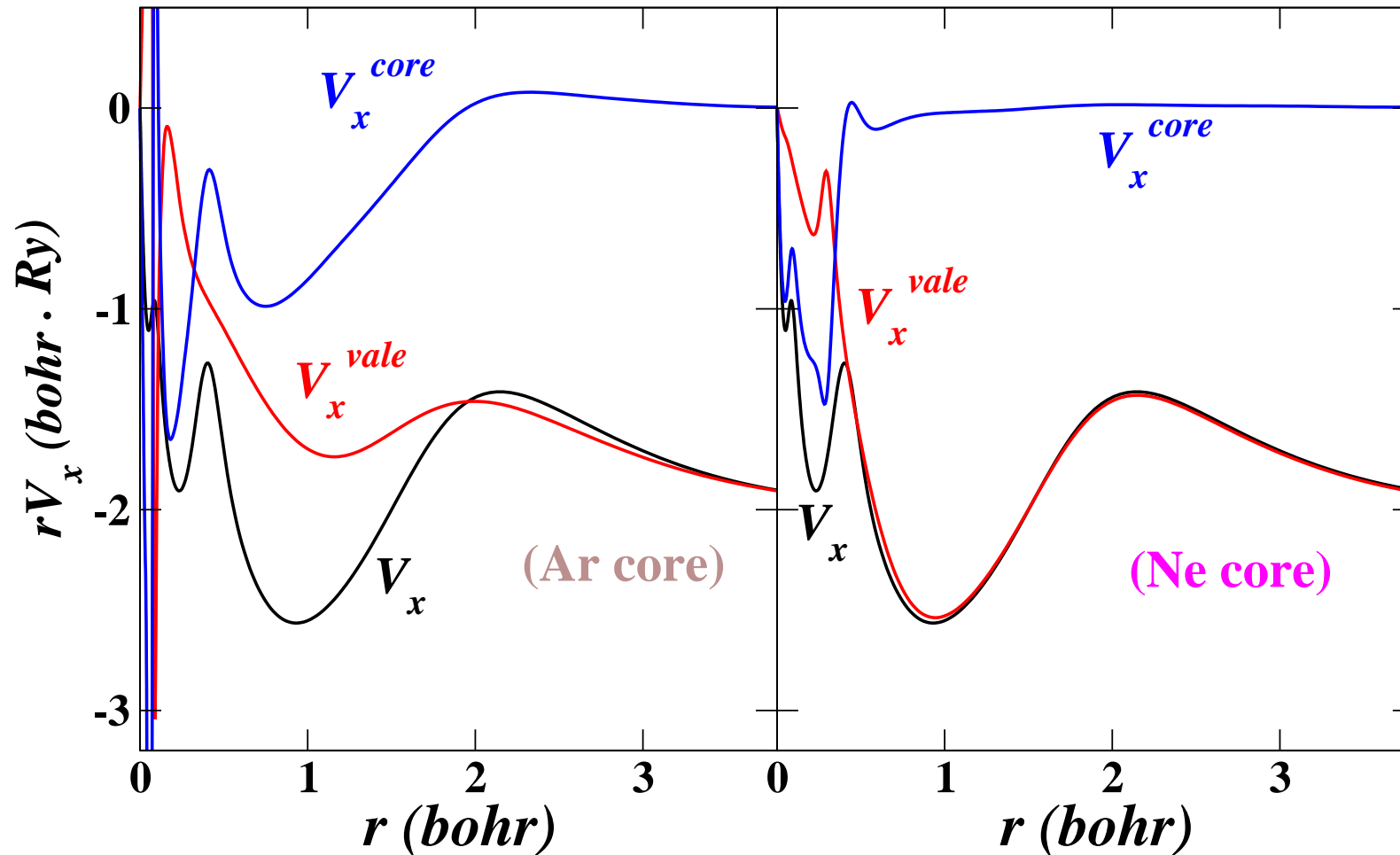


Valence auxiliary functions:



Frozen core atomic OEP-EXX results for iron

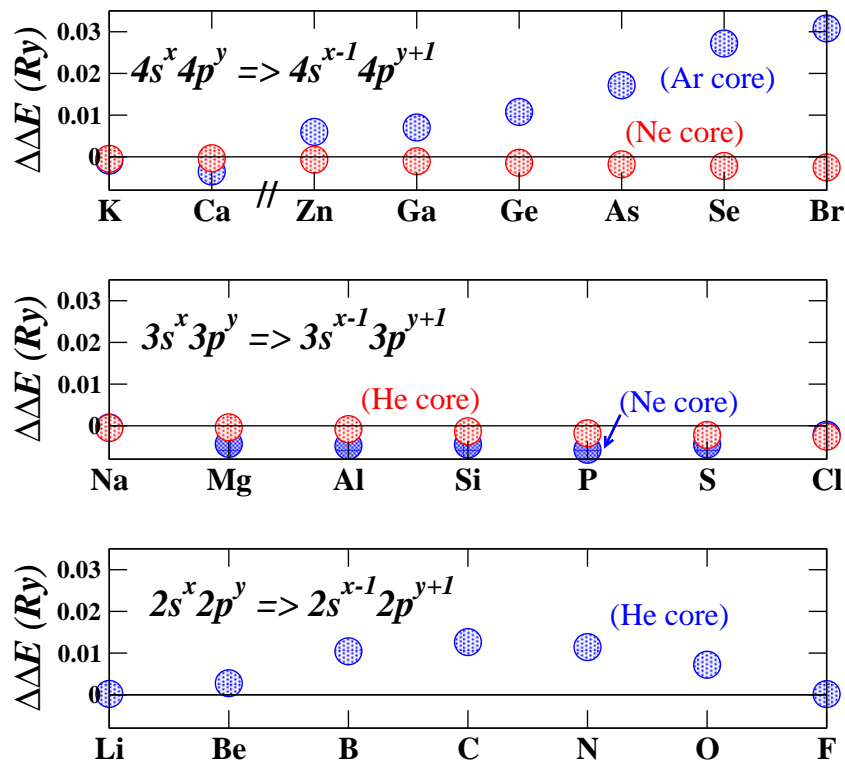
Comparing decomposition: $V_x = V_x^{\text{vale}} + V_x^{\text{core}}$ for two choices of core configuration



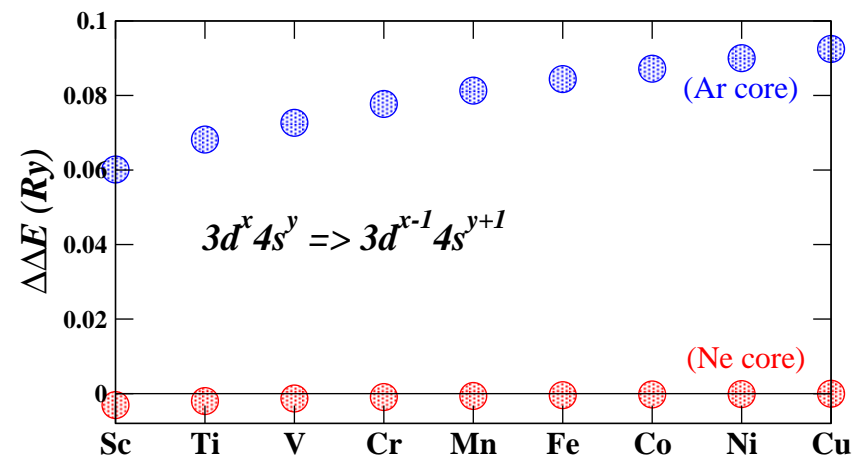
Summary of frozen core errors in excitation energies

$$\Delta\Delta E = \underbrace{E_{tot}^{vale}(\text{excited}) - E_{tot}^{vale}(\text{ground})}_{\text{Frozen core}} - \underbrace{E_{tot}(\text{excited}) - E_{tot}(\text{ground})}_{\text{All-electron}}$$

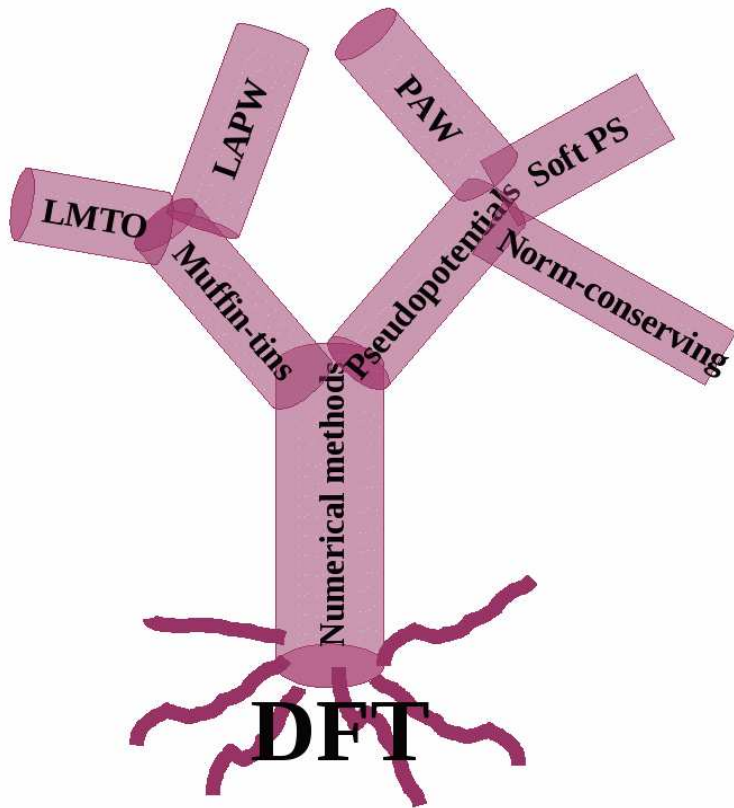
sp excitations :



sd excitations :



The projector augmented wave method (PAW)



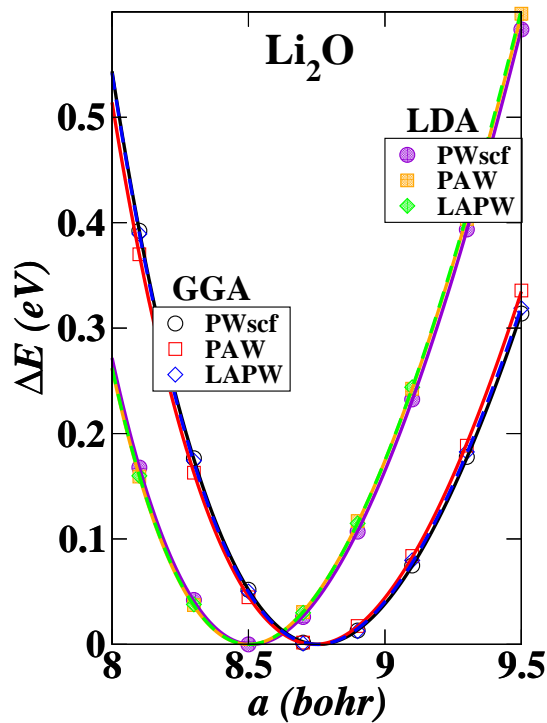
The PAW formalism was developed by P. Blöchl (*PRB* **50**, 17953–17979 (1994)), having similarities to the soft-pseudopotential formalism of D. Vanderbilt (*PRB* **41** 7892-7895 (1990)). One distinguishing feature of PAW, is the transformation between all-electron valence wavefunctions $\Psi_v(\mathbf{r})$ and $\tilde{\Psi}_v(\mathbf{r})$:

$$\Psi_v(\mathbf{r}) = \tilde{\Psi}_v(\mathbf{r}) + \sum_{ai} \left(\phi_i^a(\mathbf{r} - \mathbf{R}^a) - \tilde{\phi}_i^a(\mathbf{r} - \mathbf{R}^a) \right) \langle p_i^a | \tilde{\Psi}_v \rangle, \quad (23)$$

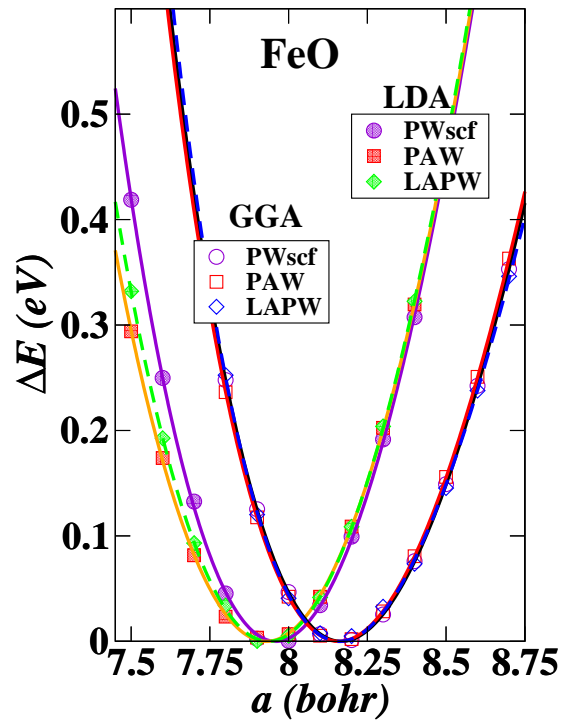
where ϕ_i^a , $\tilde{\phi}_i^a$, and p_i^a are atom-centered all-electron basis, pseudo-electron basis, and projector functions, respectively.

Computational work is performed on pseudofunctions $\tilde{\Psi}_v(\mathbf{r})$ after which all-electron functions $\Psi_v(\mathbf{r})$ can be retrieved from PAW transformation.

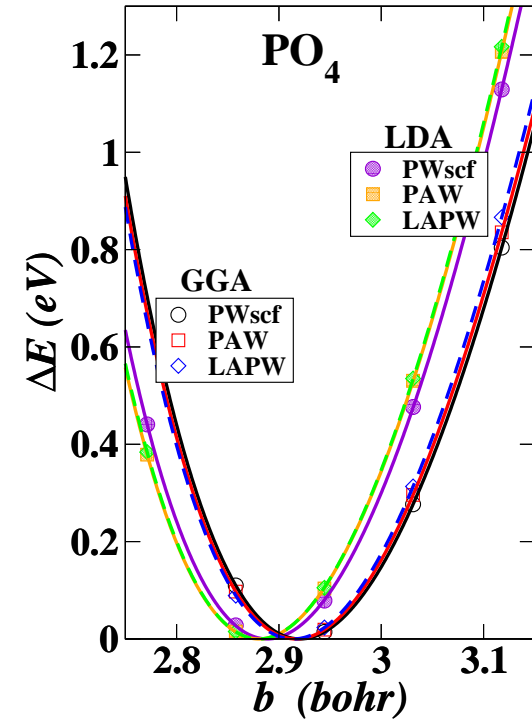
Comparison of results from different codes



Fluorite structure



NaCl structure



Tetrahedral molecule

With care, consistent numerical results can be achieved using different formalisms and codes.

PWscf

www.pwscf.org

soft-pseudopotentials

PAW

pwpaw.wfu.edu

Projector Augmented Wave

LAPW

www.wien2k.at

Linearized Augmented Plane Wave

The PAW method (continued)

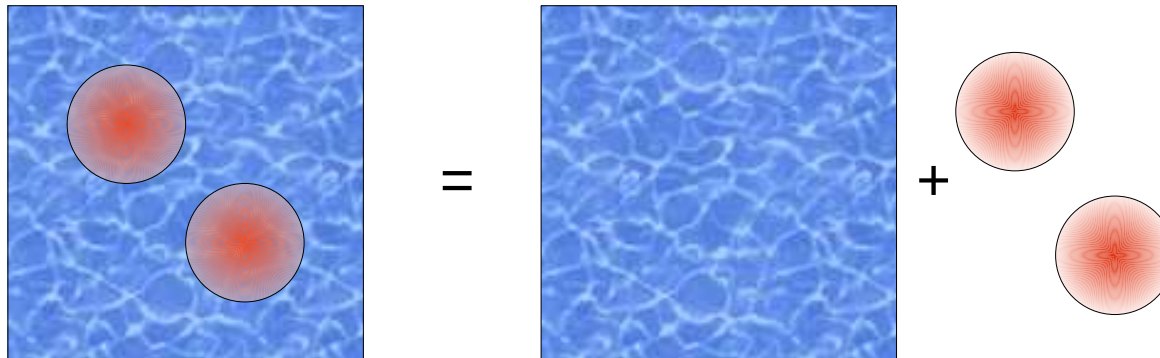
Importance of PAW transformation to Hartree and Fock integrals

Given the PAW transformation for a valence wavefunction:

$$\Psi_v(\mathbf{r}) = \tilde{\Psi}_v(\mathbf{r}) + \sum_{ai} \left(\phi_i^a(\mathbf{r} - \mathbf{R}^a) - \tilde{\phi}_i^a(\mathbf{r} - \mathbf{R}^a) \right) \langle p_i^a | \tilde{\psi}_v \rangle, \quad (24)$$

it is also possible to evaluate the valence electron energy of the system in the form:

$$E_{tot}^{vale} = \underbrace{\tilde{E}_{tot}}_{\text{pseudo energy}} + \sum_a \underbrace{\left(E_{tot}^a - \tilde{E}_{tot}^a \right)}_{\text{atom-centered corrections}}. \quad (25)$$



Hartree and Fock integrals (continued)

The product of two wavefunctions $P_{vw}(\mathbf{r}) \equiv \Psi_v^*(\mathbf{r})\Psi_w(\mathbf{r})$ can be well-approximated with the form

$$P_{vw}(\mathbf{r}) = \tilde{P}_{vw}(\mathbf{r}) + \sum_a \left(P_{vw}^a(\mathbf{r} - \mathbf{R}^a) - \tilde{P}_{vw}^a(\mathbf{r} - \mathbf{R}^a) \right), \quad (26)$$

where

$$\tilde{P}_{vw}(\mathbf{r}) \equiv \tilde{\Psi}_v^*(\mathbf{r})\tilde{\Psi}_w(\mathbf{r}), \quad (27)$$

and

$$P_{vw}^a(\mathbf{r}) - \tilde{P}_{vw}^a(\mathbf{r}) \equiv \sum_{ij} \langle \tilde{\Psi}_v | p_i^a \rangle \langle p_j^a | \tilde{\Psi}_w \rangle \left(\phi_i^{a*}(\mathbf{r})\phi_j^a(\mathbf{r}) - \tilde{\phi}_i^{a*}(\mathbf{r})\tilde{\phi}_j^a(\mathbf{r}) \right). \quad (28)$$

Equivalently, we can write:

$$P_{vw}(\mathbf{r}) = \tilde{P}_{vw}(\mathbf{r}) + \hat{P}_{vw}(\mathbf{r}) + \sum_a \left(P_{vw}^a(\mathbf{r} - \mathbf{R}^a) - \tilde{P}_{vw}^a(\mathbf{r} - \mathbf{R}^a) - \hat{P}_{vw}^a(\mathbf{r} - \mathbf{R}^a) \right), \quad (29)$$

where the “compensation charge”

$$\hat{P}_{vw}(\mathbf{r}) \equiv \sum_a \hat{P}_{vw}^a(\mathbf{r} - \mathbf{R}^a) \quad (30)$$

is a smooth function localized within the atomic augmentation spheres such that:

$$\int d^3r' \frac{P_{vw}^a(\mathbf{r}') - \tilde{P}_{vw}^a(\mathbf{r}') - \hat{P}_{vw}^a(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \begin{cases} V_{vw}^a(\mathbf{r}) & \text{for } |\mathbf{r} - \mathbf{R}^a| \leq r_c^a \\ 0 & \text{otherwise} \end{cases}. \quad (31)$$

PAW atomic OEP-EXX equations

Based on the form of the frozen core constrained minimization problem:

$$F^{\text{vale}}(\{\Psi_v\}, V_x^{\text{vale}}, \{g_v^{\text{vale}}\}, \{\epsilon_v\}, \{\lambda_{vw}^{\text{vale}}\}) = E_{\text{tot}}^{\text{vale}}(\{\Psi_v\}) - \sum_v \left(\langle g_v^{\text{vale}} | H_{KS} - \epsilon_v | \Psi_v \rangle + cc \right) - \sum_{vw} \lambda_{vw} (\langle \Psi_v | \Psi_w \rangle - \delta_{vw}), \quad (32)$$

the PAW constrained minimization expression is given by:

$$\tilde{F}(\{\tilde{\Psi}_v\}, \tilde{V}_x^{\text{vale}}, \{[V_x^a]_{ij}\}, \{\tilde{g}_v\}, \{\epsilon_v\}, \{\lambda_{vw}\}) = E_{\text{tot}}^{\text{vale}}(\{\tilde{\Psi}_v\}) - \sum_v \left(\langle \tilde{g}_v | H^{\text{PAW}} - \epsilon_v O^{\text{PAW}} | \tilde{\Psi}_v \rangle + cc \right) - \sum_{vw} \lambda_{vw} \left(\langle \tilde{\Psi}_v | O^{\text{PAW}} | \tilde{\Psi}_w \rangle - \delta_{vw} \right). \quad (33)$$

The PAW Hamiltonian takes the form:

$$H^{\text{PAW}} = \tilde{H} + \sum_{aij} |p_i^a\rangle D_{ij}^a \langle p_j^a| \quad \text{and} \quad O^{\text{PAW}} = 1 + \sum_{aij} |p_i^a\rangle O_{ij}^a \langle p_j^a|, \quad (34)$$

where $O_{ij}^a \equiv \langle \phi_i^a | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{\phi}_j^a \rangle$. The smooth Hamiltonian takes the form:

$$\tilde{H} = \hat{K} + \tilde{V}(\mathbf{r}) \quad \text{where} \quad \tilde{V}(\mathbf{r}) = V_{\text{loc}}(\mathbf{r}) + \tilde{V}_H(\mathbf{r}) + \tilde{V}_x^{\text{vale}}(\mathbf{r}); \quad (35)$$

$V_{\text{loc}}(\mathbf{r})$ includes effects from the pseudized nuclear and core electron potentials. The atomic matrix elements D_{ij}^a include the valence local exchange potential contributions:

$$[V_x^a]_{ij} \equiv \langle \phi_i^a | V_x^{a,\text{vale}} | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{V}_x^{a,\text{vale}} | \tilde{\phi}_j^a \rangle. \quad (36)$$

Update equations for OEP-EXX in PAW formalism

Once basis and projector functions $|\phi_i^a\rangle$, $|\tilde{\phi}_i^a\rangle$, and $|p_i^a\rangle$ and local potential V_{loc}^a has been determined for each atom, the self-consistent PAW equations are:

$$H^{\text{PAW}} = \hat{K} + V_{loc} + \tilde{V}_H + \tilde{V}_x^{\text{vale}} + \sum_{aij} |p_i^a\rangle D_{ij}^a \langle p_j^a| \quad H^{\text{PAW}} |\tilde{\Psi}_v\rangle = \epsilon_v O^{\text{PAW}} |\tilde{\Psi}_v\rangle \quad (37)$$

$$\left(H^{\text{PAW}} - \epsilon_v O^{\text{PAW}} \right) |\tilde{g}_v\rangle = \frac{1}{N_v} \frac{\delta E_x^{vv}}{\delta \tilde{\Psi}_v^*(r)} - \tilde{V}_x^{\text{vale}}(r) |\tilde{\Psi}_v\rangle - \sum_{aij} |p_i^a\rangle [V_x^a]_{ij} \langle p_j^a | \tilde{\Psi}_v\rangle - \sum_w \lambda_{vw} O^{\text{PAW}} |\tilde{\Psi}_w\rangle, \quad (38)$$

$$\text{where } \lambda_{vw} = \langle \tilde{\Psi}_w | \frac{\delta E_x^{vv}}{\delta \tilde{\Psi}_v^*(r)} \rangle - \langle \tilde{\Psi}_w | \tilde{V}_x^{\text{vale}} | \tilde{\Psi}_v \rangle - \sum_{aij} \langle \tilde{\Psi}_w | p_i^a \rangle [V_x^a]_{ij} \langle p_j^a | \tilde{\Psi}_v \rangle.$$

$$\sum_v N_v \tilde{g}_v(r) \tilde{\Psi}_v(r) = 0. \quad (39)$$

$$\sum_v N_v \langle \tilde{g}_v | p_i^a \rangle \langle p_j^a | \tilde{\Psi}_v \rangle = 0. \quad (40)$$

Here, $|\tilde{\Psi}_v\rangle$, $|\tilde{g}_v\rangle$, $\tilde{V}_x^{\text{vale}}$, and $\{[V_x^a]_{ij}\}$ are updated self-consistently through these equations.

Recipes for constructing PAW atomic functions

$$\{|\phi_i^a\rangle\}, \{|\tilde{\phi}_i^a\rangle\}, \{|p_i^a\rangle\}, \text{ and } V_{loc}^a$$

⇒ There is considerable flexibility in choice of functions (within some constraints).

⇒ *atompaw* code is available from website <http://pwpaw.wfu.edu> (OEP part not yet included); interfaces with codes for solids – (*pwpaw*, *socorro* (from Sandia National Labs), and *abinit* (international code based in Belgium))

General recipe

Based on D. Vanderbilt's scheme for soft pseudopotentials (other possibilities were programmed by Marc Torrent in *atompaw* for *abinit*)

1. Generate all-electron basis set: $H_{KS}|\phi_i^a\rangle = \epsilon_i|\phi_i^a\rangle$ including valence states $|\psi_v\rangle$ and (optionally) some continuum states.
2. For every all-electron basis functions $|\phi_i^a\rangle$, construct corresponding pseudo basis function $|\tilde{\phi}_i^a\rangle$ such that $\tilde{\phi}_i^a(r) \equiv \phi_i^a(r)$ for $r > r_c^a$.
3. Construct projector functions $|p_i^a\rangle$ such that $\langle \tilde{\phi}_i^a | p_j^a \rangle = \delta_{ij}$.
 - (a) Construct local pseudopotential V^{PS} such that $V^{PS}(r) \equiv V(r)$ for $r > r_c^a$.
 - (b) Solve the following equations for $\{|p_i^a\rangle\}$:

$$\left(\hat{K} + V^{PS} - \epsilon_i\right) |\tilde{\phi}_i^a\rangle = \sum_j |p_j^a\rangle \langle \tilde{\phi}_j^a | \hat{K} + V^{PS} - \epsilon_i | \tilde{\phi}_i^a \rangle.$$

4. Unscreen local pseudopotential to find V_{loc}^a :

$$V_{loc}^a(r) = V^{PS}(r) - \tilde{V}_H(r) - \tilde{V}_x^{\text{vale}}(r)$$

Recipes for V_{loc}^a (continued)

In order to determine $\tilde{V}_x^{\text{vale}}(r)$ for unscreening the local pseudopotential, the following simplified OEP relations must be satisfied.

$$\left(\hat{K} + V^{PS} - \epsilon_v\right) |\tilde{g}_v\rangle = \frac{1}{N_v} \frac{\delta E_x^{vv}}{\delta \tilde{\psi}_v^*(r)} - \tilde{V}_x^{\text{vale}}(r) |\tilde{\psi}_v\rangle + \sum_i |p_i^a\rangle [V_x^a]_{iv} - \sum_w \lambda_{vw} O^{\text{PAW}} |\tilde{\psi}_w\rangle, \quad (41)$$

$$\sum_v N_v \tilde{g}_v(r) \tilde{\psi}_v(r) = 0. \quad (42)$$

$$\langle \tilde{g}_v | p_i^a \rangle = 0 \quad \text{for all} \quad l_i = l_v. \quad (43)$$

$$\tilde{g}_v(r) \equiv g_v^{\text{vale}}(r) \quad \text{for} \quad r > r_c^a. \quad (44)$$

Most promising method:

- Assume

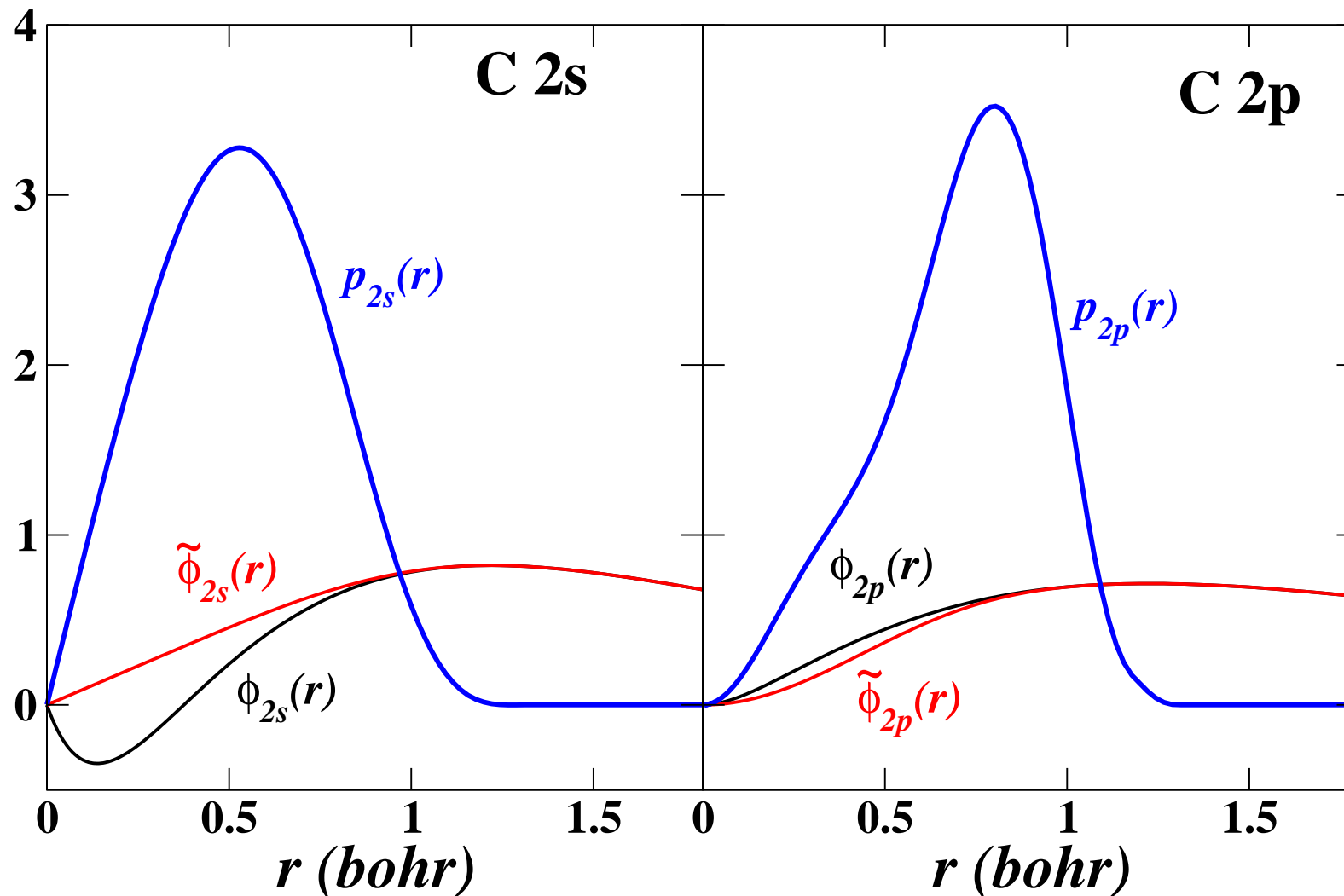
$$\tilde{g}_v(r) = \begin{cases} r^{l_v+1+s} \sum_{n=0}^M C_n r^n & r \leq r_c^a \\ g_v^{\text{vale}}(r) & r > r_c^a, \end{cases}$$

where coefficients $\{C_n\}$ are determined from matching conditions.

- Determine $\tilde{V}_x^{\text{vale}}(r)$ from $\tilde{g}_v(r)$ and other functions.

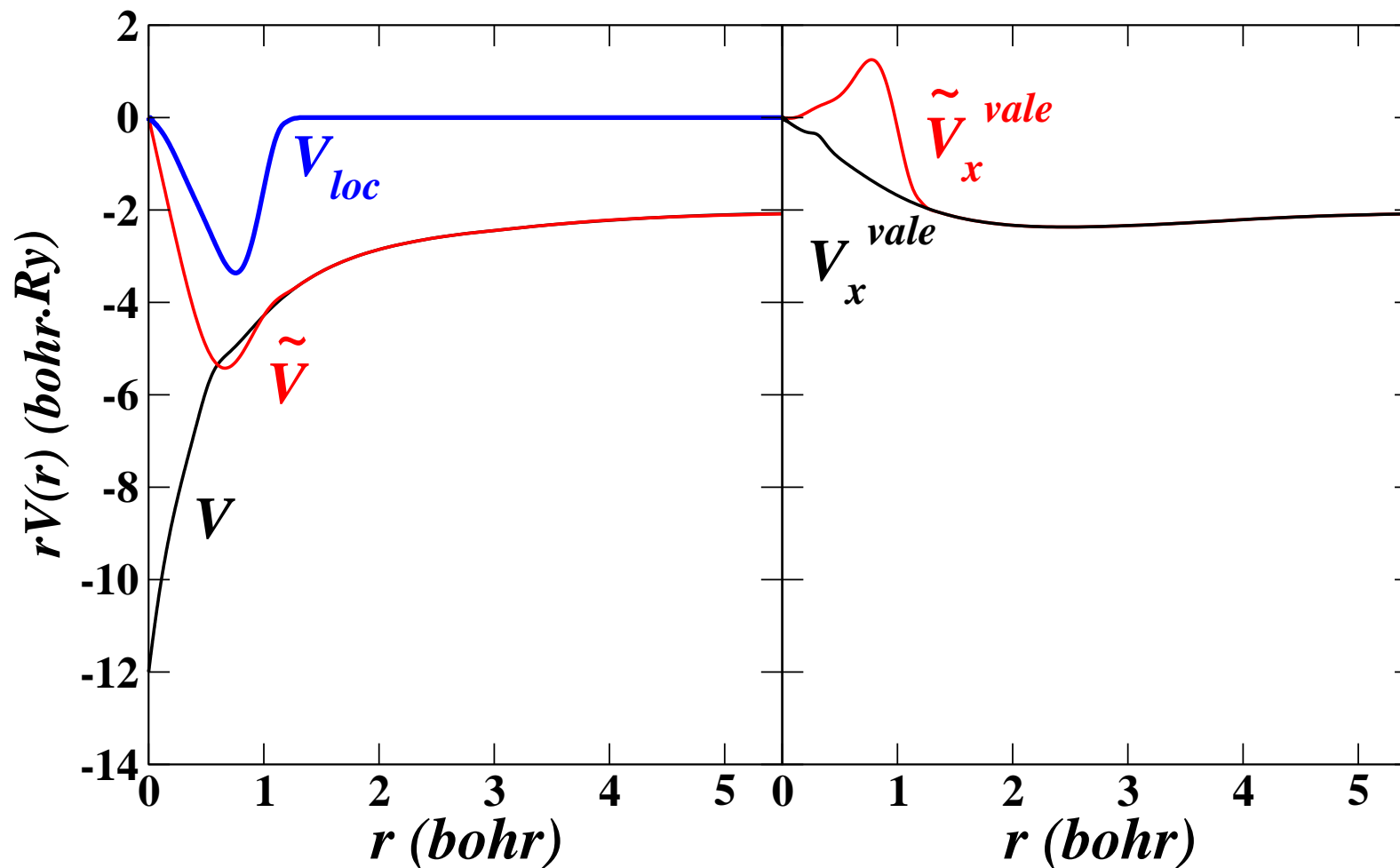
Example of basis and projector functions for carbon

Results for $r_c = 1.3$ bohr



Example of potential functions for carbon

Results for $r_c = 1.3$ bohr



Summary and Conclusions

- ⇒ Choosing E_x to have the form of Fock exchange has the advantage of removing electron self-interaction from the formalism. An orbital dependent correlation functional E_c can be added to the formalism in a straight-forward way.
- ⇒ It is possible to define a core electron contribution to the OEP, $V_x^{\text{core}}(r)$, which approximates the valence-core exchange contributions.
- ⇒ Tests of the frozen core approximation on atomic excitations show controllable errors. For increased accuracy, semi-core states can be included with the valence states.
- ⇒ The PAW formalism is able to treat the multipole moments of the Coulomb integrals of the Hartree and Fock functionals.
- ⇒ The PAW-OEP equations can be derived directly from the frozen core approximation. Full implementation including the calculation of $V_{loc}^a(r)$ looks promising.