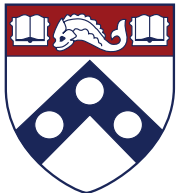


Pseudopotentials for hybrid density functionals and SCAN

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University of Pennsylvania

Why do we need pseudopotentials?



Valence electrons

- Dominate bonding
- Smooth exponential decay

Core electrons

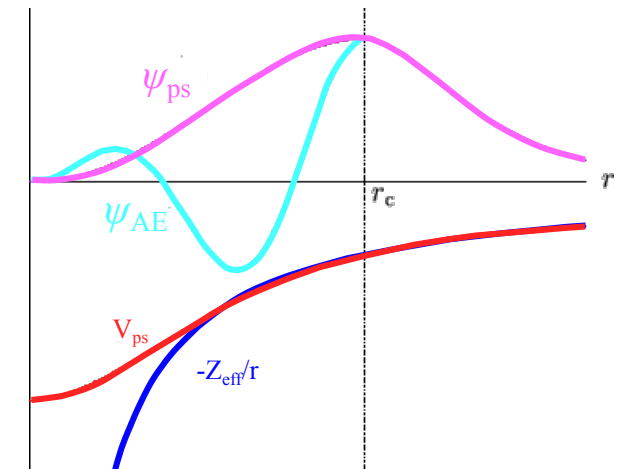
- Insensitive to chemical environment
- Oscillation near nucleus

Frozen-core approximation

- Combine core electron and nucleus to effective core (pseudo ion)
- Explicitly keep valence electrons ($N > n$)

• Pseudopotential

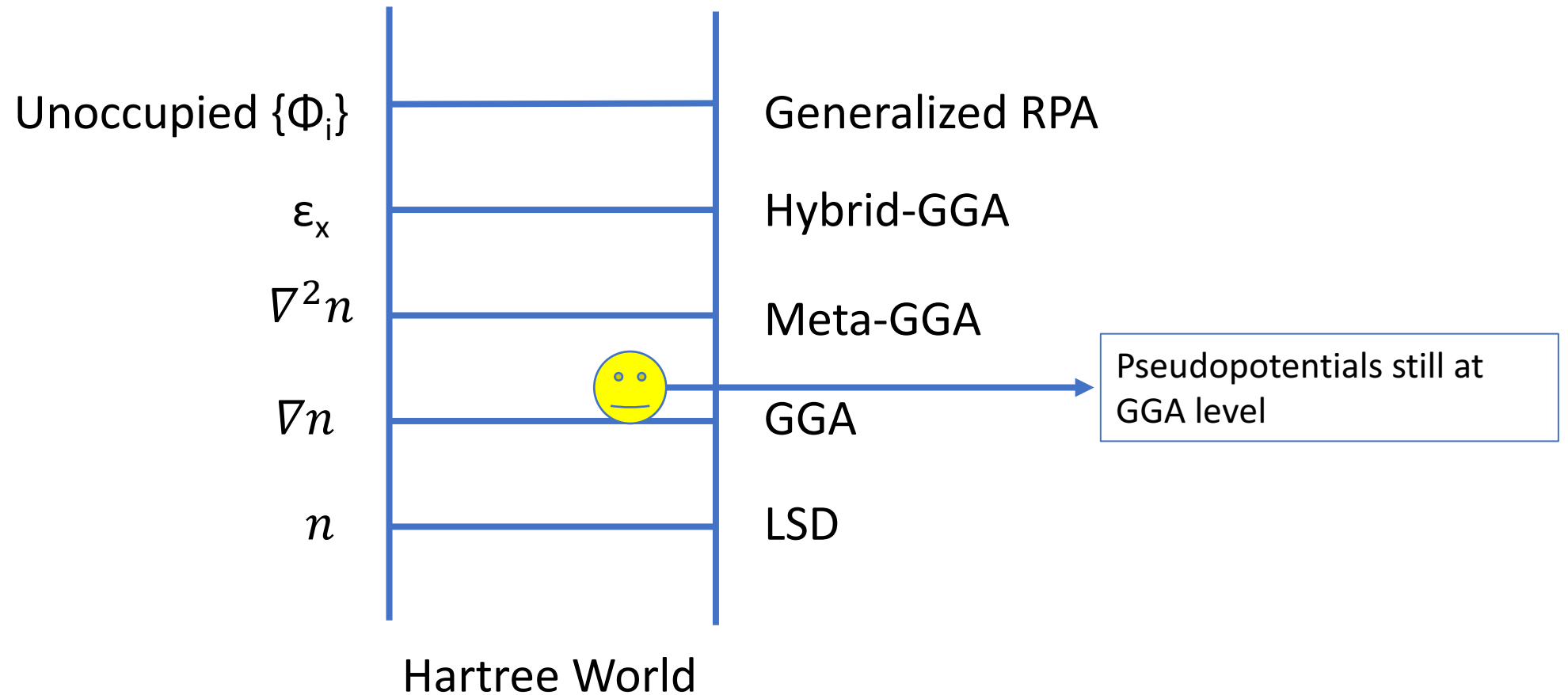
- Replace core region with a finite shallow potential
- Reduce the computational cost
- Preserve the accuracy



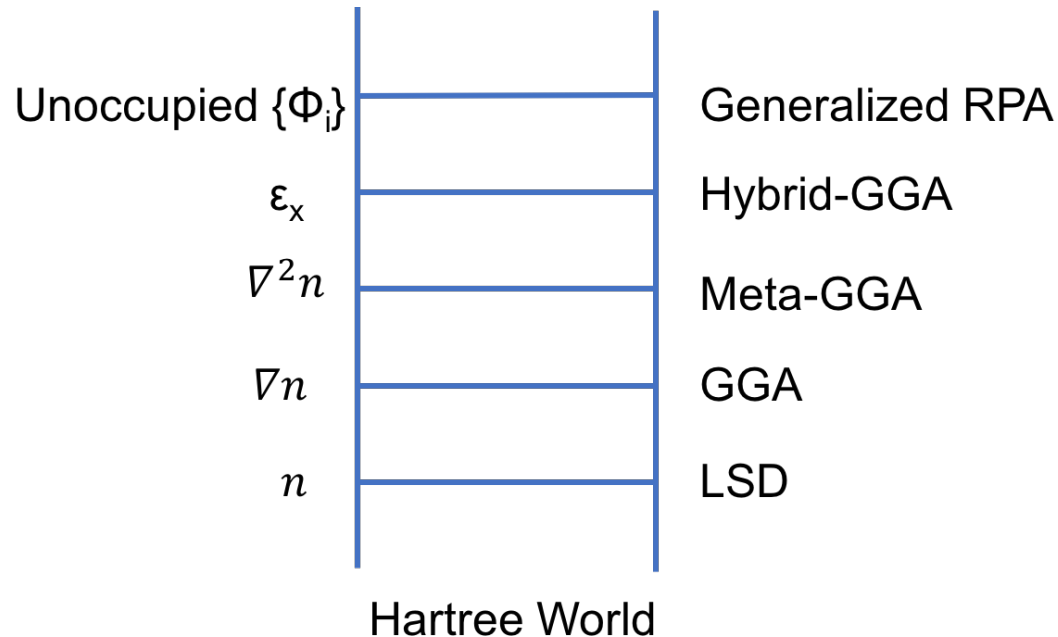
Pseudopotential developments

- Hamann-Schlüter-Chiang norm conserving pseudopotential (1979)
- Generalized norm conserving pseudopotential (1989)
- RRKJ optimized pseudopotential (1990)
- Troullier-Martine soft pseudopotential (1990)
- Ultrasoft pseudopotential (1990)
- Projector-augmented waves potentials (1994)
- Links to pseudopotential databases
 - <http://www.physics.rutgers.edu/~dhv/uspp/uspp-734.html>
 - <http://www.sas.upenn.edu/rappegroup/research/psp.html>
 - <http://www.physics.rutgers.edu/gbrv>

Density functional calculation vs. pseudopotential development



Hybrid density functional pseudopotentials



- The exchange-correlation functional must agree between pseudopotential and plane-wave calculation
- Non self-consistent PBE0 pseudopotential did not show improved accuracy
[Phys. Rev. B 80, 115201 (2009)]
- **First self-consistent construction of PBE0 pseudopotentials**

Hartree-Fock formalism

- The nonlocal Hamiltonian

$$\left(\hat{T} + \hat{V}_{\text{ion}} + \hat{V}_{\text{H}}[\{\psi_{n'l'}\}] + \hat{V}_{\text{x}}^{nl}[\{\psi_{n'l'}\}] \right) \psi_{nl}(\mathbf{r}) = \epsilon_{nl} \psi_{nl}(\mathbf{r})$$

Hartree potential

$$\hat{V}_{\text{H}}[\{\psi_{n'l'}\}]|\psi_{nl}\rangle = \sum_{n'l'} \int d^3\mathbf{r}' \frac{|\psi_{n'l'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \psi_{nl}(\mathbf{r})$$

Hartree-Fock formalism

- The nonlocal Hamiltonian

$$\left(\hat{T} + \hat{V}_{\text{ion}} + \hat{V}_{\text{H}}[\{\psi_{n'l'}\}] + \hat{V}_{\text{x}}^{nl}[\{\psi_{n'l'}\}] \right) \psi_{nl}(\mathbf{r}) = \epsilon_{nl} \psi_{nl}(\mathbf{r})$$

Exchange potential operator

$$\hat{V}_{\text{x}}^{nl}[\{\psi_{n'l'}\}]|\psi_{nl}\rangle = \sum_{n'l'} \int d^3\mathbf{r}' \frac{\psi_{n'l'}^*(\mathbf{r}')\psi_{n'l'}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \psi_{nl}(\mathbf{r}')$$

Hartree-Fock formalism

- The nonlocal Hamiltonian

$$\left(\hat{T} + \hat{V}_{\text{ion}} + \hat{V}_{\text{H}}[\{\psi_{n'l'}\}] + \hat{V}_{\text{x}}^{nl}[\{\psi_{n'l'}\}] \right) \psi_{nl}(\mathbf{r}) = \epsilon_{nl} \psi_{nl}(\mathbf{r})$$

- Hartree and exchange potentials are orbital dependent
- Treated as spherical average over all orbital configurations via Slater integral

$$E_{\text{av}} = \frac{1}{N} \sum_{2S+1 L_J} E[\{\Psi\}_{2S+1 L_J}]$$

E.g., for C atom, valence configurations N=15 with 5 allowed term symbols:

$${}^3P_2(5), {}^3P_1(3), {}^3P_0(1), {}^1D_2(5), {}^1S_0(1)$$

$$E_{\text{av}} = \frac{1}{15} [5E\{\Psi\}_{{}^3P_2} + 3E\{\Psi\}_{{}^3P_1} + E\{\Psi\}_{{}^3P_0} + 5E\{\Psi\}_{{}^1D_2} + E\{\Psi\}_{{}^1S_0}]$$

Hartree-Fock formalism

- The nonlocal Hamiltonian

$$\left(\hat{T} + \hat{V}_{\text{ion}} + \hat{V}_{\text{H}}[\{\psi_{n'l'}\}] + \hat{V}_{\text{x}}^{nl}[\{\psi_{n'l'}\}] \right) \psi_{nl}(\mathbf{r}) = \epsilon_{nl} \psi_{nl}(\mathbf{r})$$

Slater integral is used to obtain the average energy of Hartree and exchange terms

$$E_{\text{av}} = I[\{\phi_{nl}(r)\}] + F[\{\phi_{nl}(r)\}] + G[\{\phi_{nl}(r)\}] \quad \text{[Slater integral J. C. Slater (1960)]}$$

$I[\{\phi_{nl}(r)\}]$, $F[\{\phi_{nl}(r)\}]$, $G[\{\phi_{nl}(r)\}]$ are Slater integrals containing radial wavefunctions with different n, l quantum numbers

Hybrid density functional formalism – PBE0 formalism

- Mix the HF exchange with PBE exchange

$$E_{xc}^{\text{PBE0}} = aE_x^{\text{HF}} + (1 - a)E_x^{\text{PBE}} + E_c^{\text{PBE}} \quad a = 0.25 \quad [\text{JCP } 105, 9982 (1996)]$$

- Combine HF formalism and Kohn-Sham equation

$$\left[\hat{T} + \hat{V}_{\text{ion}} + \hat{V}_{\text{H}}[\{\psi_{n'l'}\}] + \frac{1}{4}\hat{V}_x^{nl}[\{\psi_{n'l'}\}] + \frac{3}{4}\hat{V}_x^{\text{PBE}} + \hat{V}_c^{\text{PBE}} \right] \psi_{nl}(\mathbf{r}) = \epsilon_{nl}\psi_{nl}(\mathbf{r})$$

Invert the radial equation to obtain a screened pseudopotential

$$\hat{V}_{\text{scr}}^{nl}(r) = \epsilon_{nl}(r) - \frac{l(l+1)}{2r^2} + \frac{1}{2\phi_{\text{val}}(r)} \frac{d^2}{dr^2} [\phi_{\text{val}}(r)]$$

Hybrid functional all-electron solver

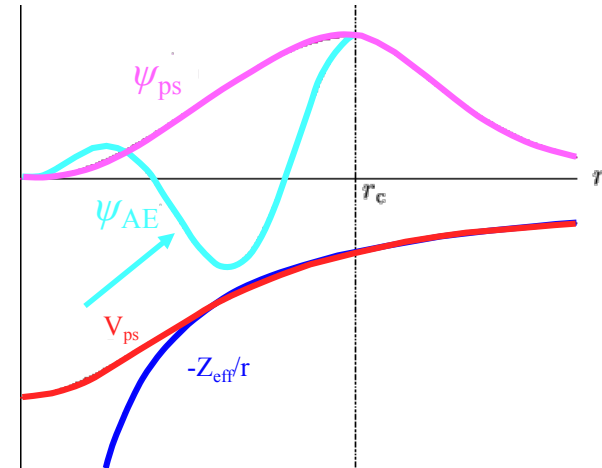
$$\text{Solve } \left[\hat{T} + \hat{V}_{\text{ion}} + \hat{V}_{\text{H}}[\{\psi_{n'l'}\}] + \frac{1}{4} \hat{V}_{\text{x}}^{\text{nl}}[\{\psi_{n'l'}\}] + \frac{3}{4} \hat{V}_{\text{x}}^{\text{PBE}} + \hat{V}_{\text{c}}^{\text{PBE}} \right] \psi_{nl}(\mathbf{r}) = \epsilon_{nl} \psi_{nl}(\mathbf{r}) \text{ iteratively}$$

Start with an initial guess for the wavefunctions ψ (e.g. hydrogenic wavefunctions)

Construct Hartree, exact-exchange potential, and DFT exchange-correlation potentials $V_{\text{H}}, V_{\text{X}}, V_{\text{XC}}$

Solve the modified HF differential equations to obtain updated wavefunctions ψ , and eigenvalues ϵ

Orthogonalize the wavefunctions ψ



Pseudopotential construction

$$\psi_l(r) = \begin{cases} \sum_i c_i j_l(q_i r) & r < r_c \\ \phi_l(r) & r \geq r_c \end{cases}$$

Use spherical Bessel functions to
construct Pseudowavefunctions

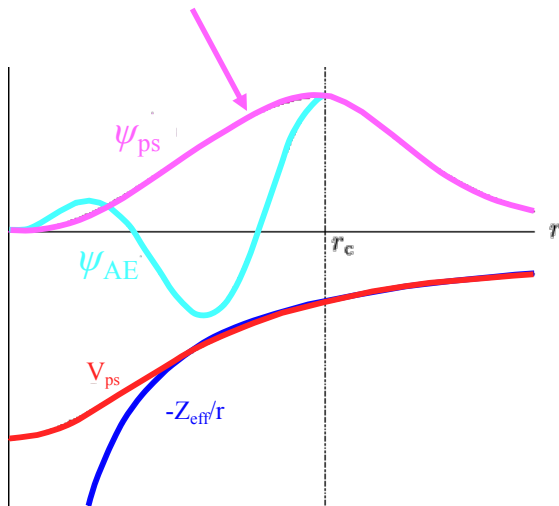
[Phys. Rev. B 44, 13175 (1990)]

Constructing the pseudowavefunctions using
the RRKJ method

Inverting the Schrödinger equation to obtain V_{PSP}

Design non-local transformation on V_{PSP}
[Phys. Rev. B 59, 1247 (1999)]

Descreening to obtain V_{ion}



Pseudopotential construction

$$\psi_l(r) = \begin{cases} \sum_i c_i j_l(q_i r) & r < r_c \\ \phi_l(r) & r \geq r_c \end{cases}$$

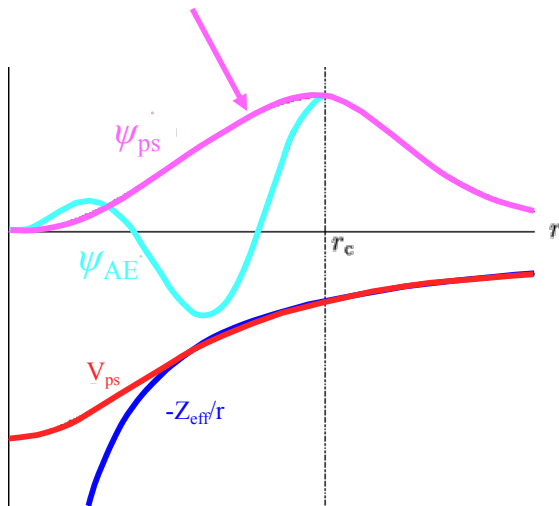
Use spherical Bessel functions to construct Pseudowavefunctions

[Phys. Rev. B 44, 13175 (1990)]

Constructing the pseudowavefunctions using the RRKJ method

Inverting the Schrödinger equation to obtain V_{PSP}

Design non-local transformation on V_{PSP}
[Phys. Rev. B 59, 1247 (1999)]



$$V_{\text{ion}}^{\text{PS}} = V_l^{\text{PS}}(r) - Y[\{\phi_{\text{val}}\}](r) - \frac{1}{4} \frac{X[\{\phi_{\text{val}}\}](r)}{\phi_l(r)} - \frac{3}{4} V_{\text{x}}^{\text{PBE}}(r) - V_{\text{c}}^{\text{PBE}}(r)$$

Use of OPIUM

Only one input file: *.param

How to run? `./opium f f.log ae ps nl ke rpt upf plot vi`

```
[Atom]
F
3
100 2.00 -
200 2.00 -
210 5.00 -

[Pseudo]
2 1.14 1.63
opt

[Optinfo]
7.07 10
7.07 10

[Conigs]
2
#
200 2.00 -
210 5.20 -
#
200 2.00 -
210 5.40 -

[XC]
hy
```

Atomic reference configuration

Pseudopotential radial cut off

Pseudowave-function settings

Configurations for transferability test

Exchange-correlation method

Opium - pseudopotential generation project

Disclaimer: Opium is distributed under the [GNU General Public Licence](#). Like most open source software, it is not guaranteed to be bug free. Use at your own risk and please report any bugs to the Opium [mailing list](#).

Latest release
[Version 3.8](#) - April 4, 2014
View the [3.7 -> 3.8 Changelog](#)
View the [FULL Changelog](#)
Get the [Emacs highlighting mode here](#)

Scientific background / Features

The ab initio pseudopotential method is now a well established tool in condensed matter physics, computational chemistry and material science. At the present time there are a good number of codes available, both commercial and in the public domain, that perform electronic structure calculations of molecules and solids based on the pseudopotential scheme. The most important input information that these programs require are the pseudopotentials used in the calculation.

Features included in the current release of Opium:

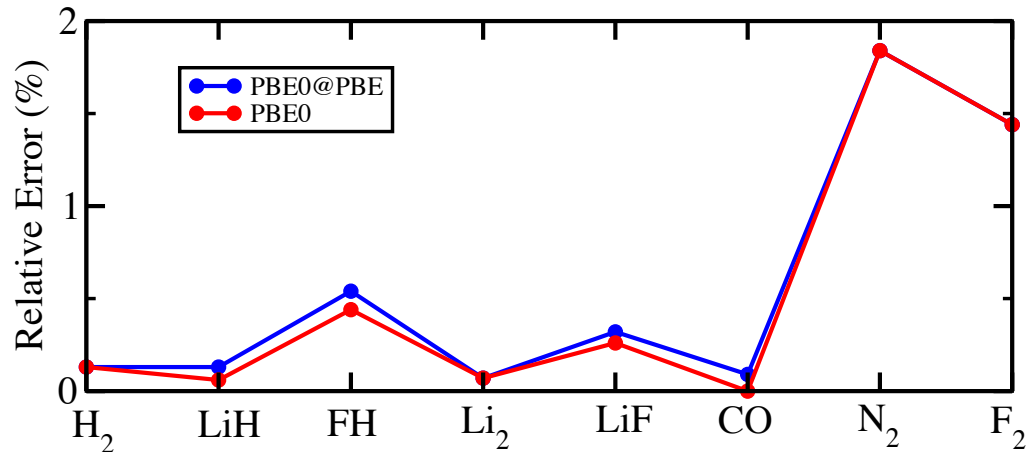
- Scalar-relativistic [1] and non-relativistic pseudopotential generation
- Ability to construct Optimized (RRKJ) [2] or Kerker [3] pseudopotentials
- Partial core correction of Louie, Froyen and Cohen [4]
- Can test and generate and test pseudopotentials that support semicore states
- Ghost state checking following the method suggested by Gonze, Stumpf, and Scheffler [5]
- Automatic plotting of wavefunctions, potentials, and density using [xmgrace](#)
- Implementation of the designed non-local potential approach of Ramer and Rappe [6].

Computational packages that are currently supported by Opium output formats

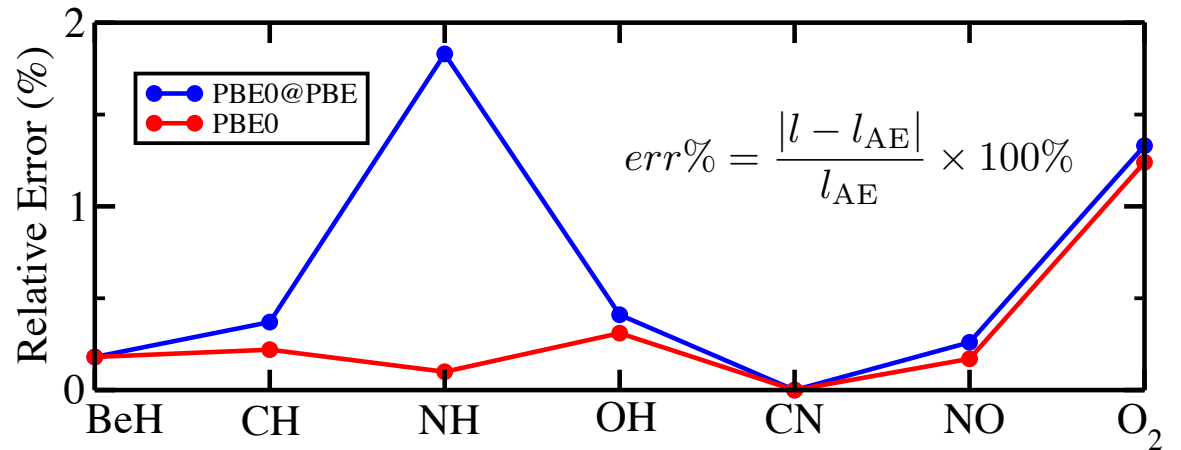
Format Package

- *.recpot [CASTEP](#)
- *.fhi [ABINIT](#) [JDFTx](#)
- *.ncpp [PWSCF](#)
- *.pwf [Bh](#)
- *.cpi [FHI98md](#)

PBE0 pseudopotential performance – bond lengths



Closed shell

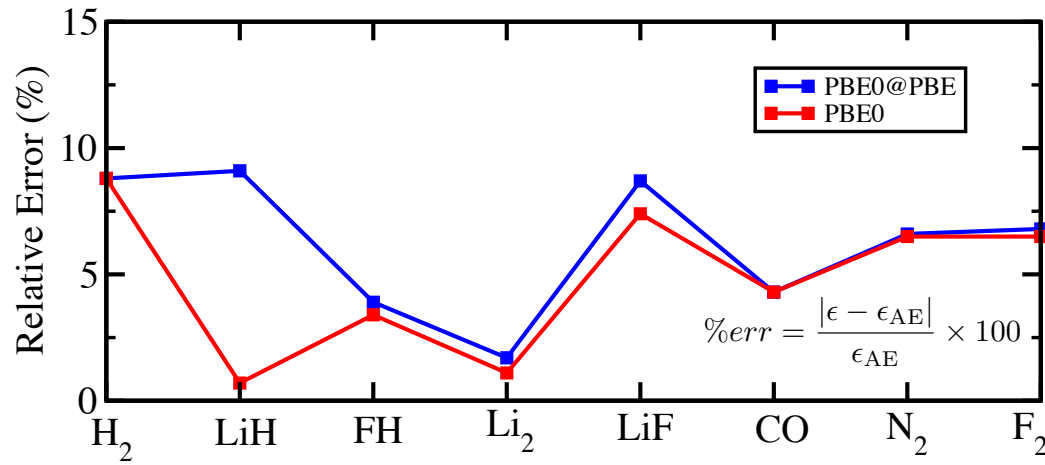


Open shell

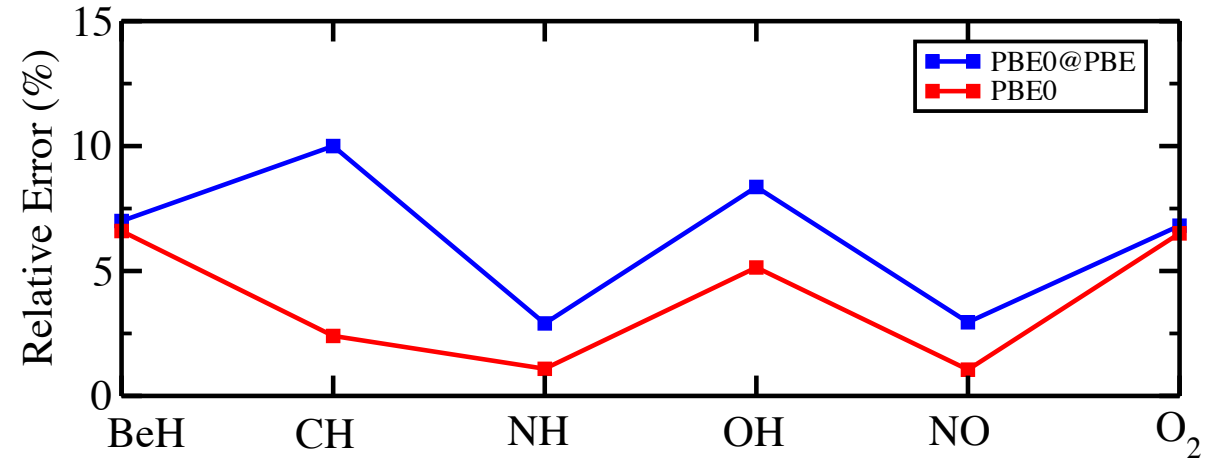
- Overall small (but systematic) improvements for bond lengths without further tuning the potential parameters
- Influence tends to be large in open-shell systems

All-electron (AE) calculations are performed using FHI-aims

PBE0 pseudopotential performance – HOMO-LUMO gaps



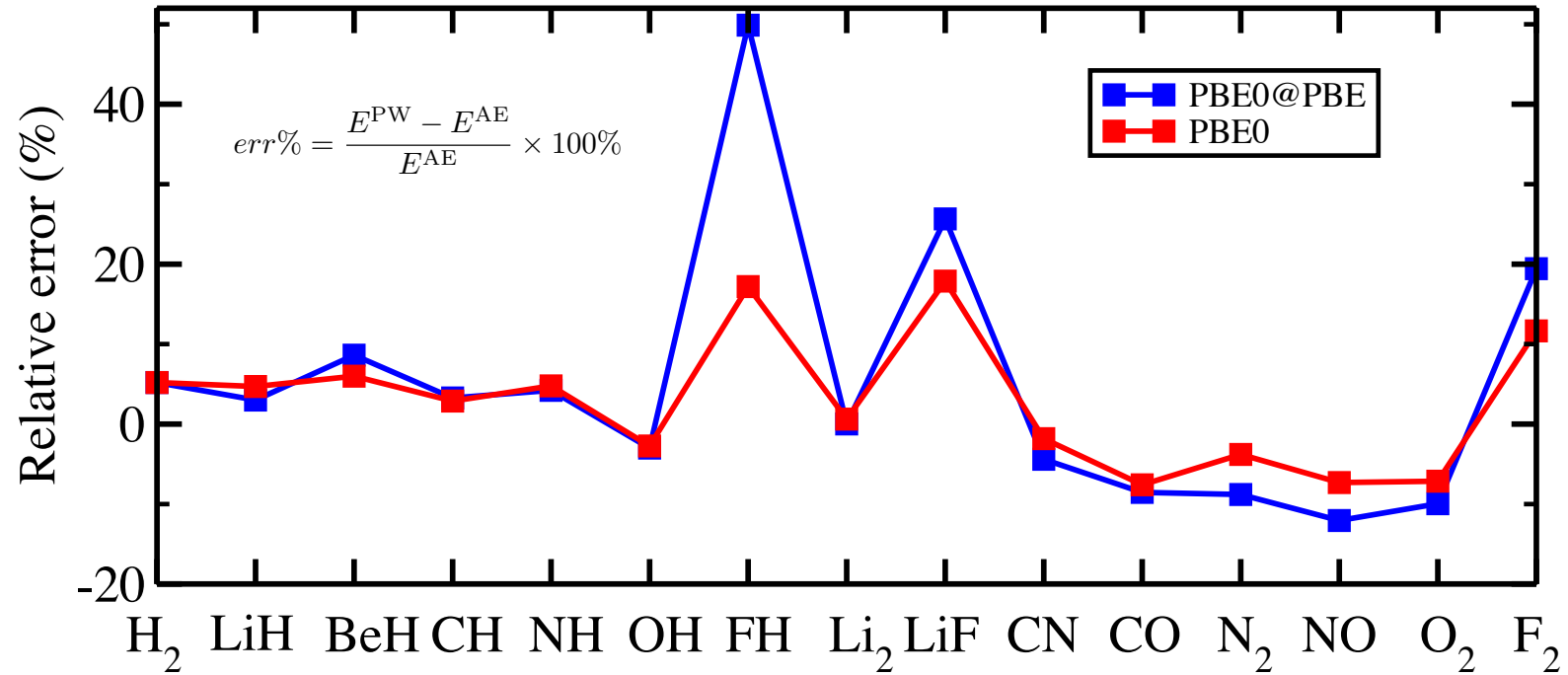
Closed shell



Open shell

- The error in HOMO-LUMO gaps is reduced using PBE0 pseudopotentials by 2% on average

PBE0 pseudopotential performance – bond formation energies



- Formation energies are improved by up to 4 % using PBE0 pseudopotentials

PBE0 pseudopotential performance - solids

Crystal	PBE-PBE0 (err%)	PBE0 (err%)	All Electron Calc.
Lattice constant (Å)			PBE0
Si	5.452 (0.073)	5.446 (-0.037)	5.448
GaN	4.539 (0.066)	4.537 (0.022)	4.536
Band Gap (eV)			
Si	1.79 (9.82)	1.78 (9.20)	1.63
GaN	3.58 (1.13)	3.56 (0.56)	3.54

- Lattice constants and band gaps are improved for solids

Implementation of SCAN

- SCAN (Strongly constrained and Appropriately Normed) density functional is a meta-GGA functional that obeys all currently known constraints
- Achieves remarkable accuracy for lattice constants of simple solids and weak interactions
- The computational time is similar to GGA
- Implemented in FHI-AIMS, VASP, (and pw.x)

Implementation of SCAN

Start with an initial guess for the wavefunctions ψ (e.g. hydrogenic wavefunctions)

Initialize the spin-dependent charge density by $\rho_i = \frac{1}{2} \int |\psi_i|^2$

Construct Hartree, and SCAN exchange-correlation potentials V_H, V_{XC}

Implement SCAN exchange-correlation

Solve spin-dependent Kohn-Sham equation to obtain updated wavefunctions ψ and eigenvalues ϵ

Develop a new solver to take care of the spin-polarization

Integrate the wavefunctions ψ to obtain charge density ρ

Apply to real systems

- Convergence test
- G2 dataset with bond length and HOMO-LUMO gaps
- Solids lattice constants, bulk moduli and band gaps
- Comparison between all electron and plane-wave calculations

First stage benchmarking – G2 data set bond lengths

	PBE	PBEPBE0	BPE0	AE-PBE	AE-PBE0	AE-SCAN
H ₂	0.753	0.747	0.747	0.75	0.746	0.741
LiH	1.6	1.597	1.596	1.603	1.595	1.59
BeH	1.348	1.343	1.351	1.355	1.348	1.348
CH	1.137	1.122	1.122	1.136	1.124	1.127
NH	1.07	1.056	1.036	1.05	1.037	1.045
OH	0.983	0.975	0.968	0.983	0.971	0.974
FH	0.928	0.913	0.914	0.93	0.918	0.917
Li ₂	2.719	2.725	2.725	2.728	2.723	2.726
LiF	1.578	1.567	1.566	1.574	1.562	1.563
CN	1.174	1.159	1.159	1.175	1.159	1.166
CO	1.135	1.123	1.122	1.136	1.122	1.125
N ₂	1.081	1.069	1.069	1.103	1.089	1.094
NO	1.132	1.142	1.142	1.157	1.139	1.151
O ₂	1.212	1.218	1.217	1.218	1.202	1.205
F ₂	1.42	1.382	1.382	1.413	1.376	1.386
MARE	1.088	0.611	0.607	0.871	0.452	

PBE0 pseudopotential plane-wave calculations still show smaller errors on bond lengths using SCAN all-electron data as a reference.

Conclusion

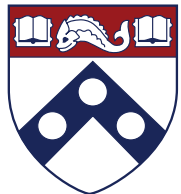
- First implementation of fully self-consistent PBE0 pseudopotentials
 - Open source OPIUM v4.0 will be published soon on sourceforge (<http://opium.sourceforge.net/>)
- Systematic improvement of accuracy for PBE0 calculations on molecules and solids
- Including relativity for spin-orbit coupling studies
- To implement SCAN functional in OPIUM

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