VASP Workshop: Day 1

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VASP Workshop at CSC Helsinki 2009
1. PBCs, k-points, plane waves, DFT
2. Projector Augmented Wave method
3. Hybrid functionals
4. New density functionals
5. Reaching the electronic groundstate
6. Hartree-Fock in PAW
A system of $N$ electrons

$$\hat{H}\Psi(r_1, ..., r_N) = E\Psi(r_1, ..., r_N)$$

$$\left(-\frac{1}{2}\sum_i \Delta_i + \sum_i V(r_i) + \sum_{i \neq j} \frac{1}{|r_i - r_j|}\right) \Psi(r_1, ..., r_N) = E\Psi(r_1, ..., r_N)$$

Many-body WF storage requirements are prohibitive

$$(\#\text{grid points})^N$$

Map onto “one-electron” theory

$$\Psi(r_1, ..., r_N) \rightarrow \{\psi_1(r), \psi_2(r), ..., \psi_N(r)\}$$

such as Hohenberg-Kohn-Sham density functional theory
Do not need $\Psi(r_1, \ldots, r_N)$, just the density $\rho(r)$:

$$E[\rho] = T_s[\{\psi_i[\rho]\}] + E_H[\rho] + E_{xc}[\rho] + E_Z[\rho] + U[Z]$$

$$\Psi(r_1, \ldots, r_N) = \prod_{i}^{N} \psi_i(r_i) \quad \rho(r) = \sum_{i}^{N} |\psi_i(r)|^2 \quad E_H[\rho] = \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} \, dr \, dr'$$

One-electron Kohn-Sham equations

$$\left(-\frac{1}{2} \Delta + V_Z(r) + V_H[\rho](r) + V_{xc}[\rho](r)\right) \psi_i(r) = \epsilon_i \psi_i(r)$$

Hartree

$$V_H[\rho](r) = \int \frac{\rho(r')}{|r-r'|} \, dr'$$

Exchange-Correlation

$$E_{xc}[\rho] = ??? \quad V_{xc}[\rho](r) = ???$$

Per definition: $E_{xc} = E - T_s - E_H - E_{ext}$

In practice: Exchange-Correlation functionals are modelled on the uniform electron gas (Monte Carlo calculations): e.g., local density approximation (LDA).
Translational invariance implies the existence of a good quantum number, usually called the Bloch wave vector $\mathbf{k}$. All electronic states can be indexed by this quantum number $|\Psi_k\rangle$.

In a one-electron theory, one can introduce a second index, corresponding to the one-electron band $n$, $|\psi_{nk}\rangle$.

The Bloch theorem states that the one-electron wavefunctions obey the equation:

$$\psi_{nk}(\mathbf{r} + \mathbf{R}) = \psi_{nk}(\mathbf{r}) e^{i\mathbf{k}\mathbf{R}}$$

where $\mathbf{R}$ is any translational vector leaving the Hamiltonian invariant.

$k$ is usually constrained to lie within the first Brillouin zone in reciprocal space.
\[ b_1 = \frac{2\pi}{\Omega} a_2 \times a_3 \quad b_2 = \frac{2\pi}{\Omega} a_3 \times a_1 \quad b_3 = \frac{2\pi}{\Omega} a_1 \times a_2 \]

\[ \Omega = a_1 \cdot a_2 \times a_3 \quad a_i \cdot b_j = 2\pi \delta_{ij} \]
The evaluation of many key quantities, e.g. charge density, density-of-states, and total energy) requires integration over the first BZ. The charge density $\rho(\mathbf{r})$, for instance, is given by

$$\rho(\mathbf{r}) = \frac{1}{\Omega_{\text{BZ}}} \sum_n \int_{\text{BZ}} f_{nk} |\psi_{nk}(\mathbf{r})|^2 d\mathbf{k}$$

where $f_{nk}$ are the occupation numbers, i.e., the number of electrons that occupy state $nk$.

Exploiting the fact that the wave functions at $\mathbf{k}$-points that are close together will be almost identical, one may approximate the integration over $\mathbf{k}$ by a weighted sum over a discrete set of points

$$\rho(\mathbf{r}) = \sum_n \sum_{\mathbf{k}} w_{\mathbf{k}} f_{nk} |\psi_{nk}(\mathbf{r})|^2 d\mathbf{k},$$

where the weights $w_{\mathbf{k}}$ sum up to one.
The intractable task of determining $\Psi(r_1, \ldots, r_N)$ (for $N \sim 10^{23}$) has been reduced to calculating $\psi_{nk}(r)$ at a discrete set of points \{k\} in the first BZ, for a number of bands that is of the order of the number of electrons \textit{per unit cell}.
Monkhorst-Pack meshes

**Idea:** equally spaced mesh in Brillouin-zone.

**Construction-rule:**

\[
k_{prs} = u_p b_1 + u_r b_2 + u_s b_3
\]

\[
u_r = \frac{2r - q_r - 1}{2q_r} r = 1, 2, \ldots, q_r
\]

\[b_i\] reciprocal lattice-vectors

\[q_r\] determines number of k-points in \(r\)-direction
Example

- quadratic 2-dimensional lattice
- \( q_1 = q_2 = 4 \Rightarrow 16 \) k-points
- only 3 inequivalent k-points (\( \Rightarrow \) IBZ)
  - \( 4 \times \mathbf{k}_1 = \left( \frac{1}{3}, \frac{1}{3} \right) \Rightarrow \omega_1 = \frac{1}{4} \)
  - \( 4 \times \mathbf{k}_2 = \left( \frac{1}{3}, \frac{2}{3} \right) \Rightarrow \omega_2 = \frac{1}{4} \)
  - \( 8 \times \mathbf{k}_3 = \left( \frac{1}{8}, \frac{1}{8} \right) \Rightarrow \omega_3 = \frac{1}{2} \)

\[
\frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} F(\mathbf{k}) d\mathbf{k} \Rightarrow \frac{1}{4} F(\mathbf{k}_1) + \frac{1}{4} F(\mathbf{k}_2) + \frac{1}{2} F(\mathbf{k}_3)
\]
Algorithm

Algorithm:

- calculate equally spaced-mesh
- shift the mesh if desired
- apply all symmetry operations of Bravais lattice to all k-points
- extract the irreducible k-points ($\equiv$ IBZ)
- calculate the proper weighting

Common meshes: Two choices for the center of the mesh

- centered on $\Gamma$ ($\Rightarrow \Gamma$ belongs to mesh).
- centered around $\Gamma$. (can break symmetry !!)
Example - hexagonal cell

- In certain cell geometries (e.g., hexagonal cells) even meshes break the symmetry.
- Symmetrization results in non-equally distributed k-points.
- Gamma point centered mesh preserves symmetry.
The total energy

\[ E[\rho, \{\mathbf{R}, Z\}] = T_s[\{\psi_{nk}[\rho]\}] + E_H[\rho, \{\mathbf{R}, Z\}] + E_{xc}[\rho] + U(\{\mathbf{R}, Z\}) \]

The kinetic energy

\[ T_s[\{\psi_{nk}[\rho]\}] = \sum_n \sum_k w_k f_{nk} \langle \psi_{nk} | -\frac{1}{2} \Delta | \psi_{nk} \rangle \]

The Hartree energy

\[ E_H[\rho, \{\mathbf{R}, Z\}] = \frac{1}{2} \int \int \frac{\rho_{eZ}(\mathbf{r})\rho_{eZ}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} \]

where \( \rho_{eZ}(\mathbf{r}) = \rho(\mathbf{r}) + \sum_i Z_i \delta(\mathbf{r} - \mathbf{R}_i) \)

The electronic charge density

\[ \rho(\mathbf{r}) = \sum_n \sum_k w_k f_{nk} |\psi_{nk}(\mathbf{r})|^2 d\mathbf{k}, \]

The Kohn-Sham equations

\[ \left( -\frac{1}{2} \Delta + V_H[\rho_{eZ}](\mathbf{r}) + V_{xc}[\rho](\mathbf{r}) \right) \psi_{nk}(\mathbf{r}) = \epsilon_{nk} \psi_{nk}(\mathbf{r}) \]

The Hartree potential

\[ V_H[\rho_{eZ}](\mathbf{r}) = \int \frac{\rho_{eZ}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \]
Introduce the cell periodic part $u_{nk}$ of the wavefunctions

$$\psi_{nk}(r) = u_{nk}(r)e^{ikr}$$

with $u_{nk}(r + R) = u_{nk}(r)$.

All cell periodic functions are now written as a sum of plane waves

$$u_{nk}(r) = \frac{1}{\Omega^{1/2}} \sum_G C_{Gnk}e^{iGr} \quad \psi_{nk}(r) = \frac{1}{\Omega^{1/2}} \sum_G C_{Gnk}e^{i(G+k)r}$$

$$\rho(r) = \sum_G \rho_G e^{iGr} \quad V(r) = \sum_G V_G e^{iGr}$$

In practice only those plane waves $|G + k|$ are included for which

$$\frac{1}{2}|G + k|^2 < E_{\text{cutoff}}$$
\[
x_1 = \frac{n_1}{N} \tau_1
\]

\[
C_{r n k} = \sum_{G} C_{G n k} e^{iG r} \quad \text{FFT} \quad C_{G n k} = \frac{1}{N_{\text{FFT}}} \sum_{r} C_{r n k} e^{-iG r}
\]
$$x_1 = \frac{n_1}{N} \quad \tau_1$$

$$g_1 = \frac{n_1 2\pi}{\tau_1}$$

$$C_{r_{nk}} = \sum_{G} C_{Gnk} e^{iG \mathbf{r}} \quad \text{FFT} \quad C_{Gnk} = \frac{1}{N_{FFT}} \sum_{\mathbf{r}} C_{r_{nk}} e^{-iG \mathbf{r}}$$
real space $\rightarrow$ FFT $\rightarrow$ reciprocal space

$$C_{r n k} = \sum_{G} C_{G n k} e^{i G r} \quad \text{FFT} \quad C_{G n k} = \frac{1}{N_{\text{FFT}}} \sum_{r} C_{r n k} e^{-i G r}$$

$$x_1 = n_1 / N \quad \tau_1$$

$$g_1 = n_1 \frac{2 \pi}{\tau_1}$$
\[ x_1 = n_1 / N \quad \tau_1 \]

\[ C_{rnk} = \sum_G C_{Gnk} e^{iGr} \quad \text{FFT} \quad C_{Gnk} = \frac{1}{N_{\text{FFT}}} \sum_r C_{rnk} e^{-iGr} \]

\[ g_1 = n_1 \frac{2\pi}{\tau_1} \]

Real space × Reciprocal space
\[ x_1 = \frac{n_1}{N} \tau_1 \]

\[ g_1 = n_1 \frac{2\pi}{\tau_1} \]

\[
C_{rnk} = \sum_{G} C_{Gnk} e^{iGr} \quad \xleftarrow{\text{FFT}} \quad C_{Gnk} = \frac{1}{N_{\text{FFT}}} \sum_{r} C_{rnk} e^{-iGr}
\]
Why use plane waves?

- **Historical reason:** Many elements exhibit a band-structure that can be interpreted in a free electron picture (metallic s and p elements). Pseudopotential theory was initially developed to cope with these elements (pseudopotential perturbation theory).

- **Practical reason:** The total energy expressions and the Hamiltonian $H$ are easy to implement.

- **Computational reason:** The action $H|\psi\rangle$ can be efficiently evaluated using FFT’s.
Evaluation of $H|\psi_{nk}\rangle$

$$\left(-\frac{1}{2}\Delta + V(r)\right)\psi_{nk}(r)$$

using the convention

$$\langle r|G + k\rangle = \frac{1}{\Omega^{1/2}}e^{i(G+k)r} \rightarrow \langle G + k|\psi_{nk}\rangle = C_{Gnk}$$

- Kinetic energy:

$$\langle G + k| - \frac{1}{2}\Delta|\psi_{nk}\rangle = \frac{1}{2}|G + k|^2C_{Gnk}$$

- Local potential: $V = V_H[\rho] + V_{xc}[\rho] + V_{\text{ext}}$
  - Exchange-correlation: easily obtained in real space $V_{xc,r} = V_{xc}[\rho_r]$
  - FFT to reciprocal space $\{V_{xc,r}\} \rightarrow \{V_{xc,G}\}$
  - Hartree potential: Poisson equation in reciprocal space $V_{H,G} = \frac{4\pi}{|G|^2}\rho_G$
  - add all contributions $V_G = V_{H,G} + V_{xc,G} + V_{\text{ext,G}}$
  - FFT to real space $\{V_G\} \rightarrow \{V_r\}$

The action

$$\langle G + k|V|\psi_{nk}\rangle = \frac{1}{N_{\text{FFT}}} \sum_r V_r C_{rnk} e^{-iGr}$$

$N_{\text{FFT}} \log N_{\text{FFT}}$
The action of the local potential

\[ \frac{4\pi \varepsilon^2}{G^2} \]

\[ \rho_G \rightarrow V_G \rightarrow \text{FFT} \rightarrow V_r \] \[ \times \] \[ \psi_r \]

\[ G_{\text{cut}} \rightarrow \text{add} \rightarrow \psi_G \rightarrow R_G \rightarrow \text{FFT} \rightarrow R_r \] (residual vector)
## Basic Details

**Sampling the BZ**

- **The KPOINTS file** The file that specifies the k-point sampling for a VASP run.
- **Sampling the Brillouin zone** A lecture from the VASP workshop in Vienna (2003).

## Defining the Structure

- **The POSCAR file** The file that specifies the configuration of the simulation cell.

## INCAR tags

- **PREC** = (N)ormal | (A)ccurate
  Sets the precision with which densities and potentials are represented (the amount of aliasing one allows, if any), and the plane wave basis set kinetic energy cutoff (when ENCUT is not set explicitly).

- **ENCUT** (or ENMAX) = [real]
  Plane wave basis set kinetic energy cutoff for WFs.

## DFT

- **Introduction to DFT, DFT in depth** Lectures from the VASP workshop in Vienna (2003).
The PAW method

The number of plane waves needed to describe

- tightly bound (spatially strongly localized) states
- the rapid oscillations (nodal features) of the wave functions near the nucleus

exceeds any practical limit, except maybe for Li and H.

The common solution:

- Introduce the frozen core approximation:
  Core electrons are pre-calculated in an atomic environment and kept frozen in the course of the remaining calculations.

- Use pseudopotentials instead of exact potentials:
  - Norm-conserving pseudopotentials
  - Ultra-soft pseudopotentials
  - The Projector-Augmented-Wave (PAW) method
**Basics**

Hybrids, NewDF, Optimization, HF-PAW

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### Al

- **3p**
- **3s**

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#### Effective Al Atom

- **2p**
- **1s**

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#### PAW Al Atom

- **3p**
- **3s**

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- **2p and 1s are nodeless !!!**
- **Nodal structure is retained**

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**Wave-Function**

- **s**: $E = -0.576$, $R_c = 1.9$
- **p**: $E = -0.205$, $R_c = 1.9$

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**Graph**

- Wave function vs. $R$ (a.u.)
- **Y-axis**: Wave function
- **X-axis**: $R$ (a.u.)

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**Diagram**

- **Exact potential (interstitial region)**
- **Pseudopotential**

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**Notation**

- **Al**
- **2p**
- **2s**
- **1s**
- **PAW**

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**Marsman**

VASP Workshop: Day 1
\[ |\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\psi}_n \rangle \]

- \( |\tilde{\psi}_n\rangle \) is a pseudo wave function expanded in plane waves
- \(|\phi_i\rangle\), \(|\tilde{\phi}_i\rangle\), and \(|\tilde{p}_i\rangle\) are atom centered localized functions
- The all-electron partial waves \(|\phi_i\rangle\) are obtained as solutions to the radial scalar relativistic Schrödinger equation for the spherical non-spinpolarized atom

\[ (-\frac{1}{2} \Delta + v_{\text{eff}}) |\phi_i\rangle = \epsilon_i |\phi_i\rangle \]

- A pseudization procedure yields

\[ |\phi_i\rangle \rightarrow |\tilde{\phi}_i\rangle \quad v_{\text{eff}} \rightarrow \tilde{v}_{\text{eff}} \quad \langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij} \]
the pseudo partial waves $|\tilde{\phi}_k\rangle$ obey

$$\left( -\frac{1}{2} \Delta + \tilde{v}_{\text{eff}} + \sum_{ij} |\tilde{p}_i\rangle D_{ij} \langle \tilde{p}_j| \right) |\tilde{\phi}_k\rangle = \epsilon_k \left( 1 + \sum_{ij} |\tilde{p}_i\rangle Q_{ij} \langle \tilde{p}_j| \right) |\tilde{\phi}_k\rangle$$

with the so-called PAW parameters:

$$Q_{ij} = \langle \phi_i | \phi_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle$$

$$D_{ij} = \langle \phi_i | -\frac{1}{2} \Delta + v_{\text{eff}} | \phi_j \rangle - \langle \tilde{\phi}_i | -\frac{1}{2} \Delta + \tilde{v}_{\text{eff}} | \tilde{\phi}_j \rangle$$

The all-electron and pseudo eigenvalue spectrum is identical, all-electron scattering properties are reproduced over a wide energy range.
1st s-channel: $\epsilon_1$
Mn $4s$ ”bound” state

2nd s-channel: $\epsilon_2$
Mn $s$ ”non-bound” state

Frozen core approximation:

\[
v_{\text{eff}}[\rho_v] = v_H[\rho_v] + v_H[\rho Z_c] + v_{xc}[\rho_v + \rho_c] \quad \rho_v(r) = \sum_i a_i |\phi_i(r)|^2
\]

\[
\tilde{v}_{\text{eff}}[\tilde{\rho}_v] = v_H[\tilde{\rho}_v] + v_H[\tilde{\rho} Z_c] + v_{xc}[\tilde{\rho}_v + \tilde{\rho}_c] \quad \tilde{\rho}_v(r) = \sum_i a_i |\tilde{\phi}_i(r)|^2
\]
$|\tilde{\psi}_n\rangle$
$|\tilde{\psi}_n\rangle$

$|\tilde{\psi}_n\rangle - \sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\psi}_n\rangle$
\[ |\tilde{\psi}_n\rangle \]

\[ |\tilde{\psi}_n\rangle = -\sum_i |\phi_i\rangle \langle \tilde{p}_i |\tilde{\psi}_n\rangle \]

\[ |\tilde{\psi}_n\rangle = -\sum_i |\phi_i\rangle \langle \tilde{p}_i |\tilde{\psi}_n\rangle + \sum_i |\phi_i\rangle \langle \tilde{p}_i |\tilde{\psi}_n\rangle \]
Character of wavefunction: \( c_{lm\epsilon} = \langle \tilde{p}_{lm\epsilon} | \tilde{\psi}_n \rangle \)

\[
|\psi_n\rangle = |\tilde{\psi}_n\rangle - \sum |\tilde{\phi}_{lm\epsilon}\rangle c_{lm\epsilon} + \sum |\phi_{lm\epsilon}\rangle c_{lm\epsilon}
\]

- Same trick works for
  - Wavefunctions
  - Charge density
  - Kinetic energy
  - Exchange correlation energy
  - Hartree energy
The kinetic energy

- For instance, the kinetic energy is given by

\[ E_{\text{kin}} = \sum_n f_n \langle \psi_n | - \frac{1}{2} \Delta | \psi_n \rangle \]

- By inserting the transformation \((i = l m \epsilon)\)

\[ |\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\psi}_n \rangle \]

into \(E_{\text{kin}}\) one obtains: \(E_{\text{kin}} = \tilde{E} - \tilde{E}^1 + E^1\) (assuming completeness)

\[ \sum_n f_n \langle \tilde{\psi}_n | - \frac{1}{2} \Delta | \tilde{\psi}_n \rangle - \sum_{\text{site}} \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | - \frac{1}{2} \Delta | \tilde{\phi}_j \rangle + \sum_{\text{site}} \sum_{(i,j)} \rho_{ij} \langle \phi_i | - \frac{1}{2} \Delta | \phi_j \rangle \]

- \(\rho_{ij}\) is an on-site density matrix:

\[ \rho_{ij} = \sum_n f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle \]
For any (quasi) local operator $A$ there exists a PS operator

$$\tilde{A} = A + \sum_{ij} |\tilde{p}_i\rangle \left( \langle \phi_i | A | \phi_j \rangle - \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j |$$

so that

$$\langle \psi | A | \psi \rangle = \langle \tilde{\psi} | \tilde{A} | \tilde{\psi} \rangle$$

For instance the PS operator that corresponds to the density operator $|r\rangle\langle r|$ is given by

$$|r\rangle\langle r| + \sum_{ij} |\tilde{p}_i\rangle \left( \langle \phi_i | r | \phi_j \rangle - \langle \tilde{\phi}_i | r | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j |$$

and the density

$$\langle \psi | r \rangle \langle r | \psi \rangle = \langle \tilde{\psi} | r \rangle \langle r | \tilde{\psi} \rangle + \sum_{ij} \langle \tilde{\psi} | \tilde{p}_i \rangle \left( \langle \phi_i | r \rangle \langle r | \phi_j \rangle - \langle \tilde{\phi}_i | r \rangle \langle r | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j | \tilde{\psi} \rangle$$

$$= \tilde{\rho}(r) - \tilde{\rho}^1(r) + \rho^1(r)$$

Non-local operators are more complicated
The Hartree energy

- The pseudo-wavefunctions do not have the same norm as the AE wavefunctions inside the spheres.

- To deal with long range electrostatic interactions between spheres a soft compensation charge $\hat{\rho}$ is introduced (similar to FLAPW).

\[
E_H = \tilde{E} - \tilde{E}^1 + E^1
\]

\[
E_H[\tilde{\rho} + \hat{\rho}] - \sum_{\text{sites}} E_H[\tilde{\rho}^1 + \hat{\rho}^1] + \sum_{\text{sites}} E_H[\rho^1]
\]

$\tilde{\rho}^1$ one-center pseudo charge

$\hat{\rho}^1$ one-center compensation charge
PAW energy functional

Total energy becomes a sum of three terms: \( E = \tilde{E} + E^1 - \tilde{E}^1 \)

\[
\tilde{E} = \sum_n f_n \langle \tilde{\psi}_n | - \frac{1}{2} \Delta | \tilde{\psi}_n \rangle + E_{xc}[\tilde{\rho} + \hat{\rho} + \tilde{\rho}_c] + \\
E_H[\tilde{\rho} + \hat{\rho}] + \int v_H[\tilde{\rho} Z_c] (\tilde{\rho}(r) + \hat{\rho}(r)) \, d^3r + U(R, Z_{ion})
\]

\[
\tilde{E}^1 = \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | - \frac{1}{2} \Delta | \tilde{\phi}_j \rangle + E_{xc}[\tilde{\rho}^1 + \hat{\rho} + \tilde{\rho}_c] + \\
E_H[\tilde{\rho}^1 + \hat{\rho}] + \int_{\Omega_r} v_H[\tilde{\rho} Z_c] (\tilde{\rho}^1(r) + \hat{\rho}(r)) \, d^3r \right\}
\]

\[
E^1 = \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \phi_i | - \frac{1}{2} \Delta | \phi_j \rangle + E_{xc}[\rho^1 + \rho_c] + \\
E_H[\rho^1] + \int_{\Omega_r} v_H[\rho Z_c] \rho^1(r) \, d^3r \right\}
\]
\( \tilde{E} \) is evaluated on a regular grid

Kohn-Sham functional evaluated in a plane wave basis set with additional compensation charges to account for the incorrect norm of the pseudo-wavefunction (very similar to ultrasoft pseudopotentials).

\[
\tilde{\rho} = \sum_n f_n \tilde{\psi}_n \tilde{\psi}_n^* \quad \text{pseudo charge density}
\]

\( \hat{\rho} \quad \text{compensation charge} \)

\( E^1 \) and \( \tilde{E}^1 \) are evaluated on radial grids centered around each ion.

Kohn-Sham energy evaluated for basis sets \( \{\tilde{\phi}_i\} \) and \( \{\phi_i\} \)

these terms correct for the shape difference between the pseudo and AE wavefunctions.

No cross-terms between plane wave part and radial grids exist.
The pseudo wave functions $|\tilde{\psi}_n\rangle$ (plane waves!) are the self-consistent solutions of

$$
\left(-\frac{1}{2}\Delta + \tilde{V}_{\text{eff}} + \sum_{ij} |\tilde{p}_i\rangle (D_{ij} + \ldots) \langle \tilde{p}_j|\right) |\tilde{\psi}_n\rangle = \epsilon_n \left(1 + \sum_{ij} |\tilde{p}_i\rangle Q_{ij} \langle \tilde{p}_j|\right) |\tilde{\psi}_n\rangle
$$

$$
D_{ij} = \langle \phi_i | - \frac{1}{2} \Delta + v^1_{\text{eff}} [\rho^1_v] | \phi_j \rangle - \langle \phi_i | - \frac{1}{2} \Delta + \tilde{v}^1_{\text{eff}} [\tilde{\rho}^1_v] | \phi_j \rangle
$$

$$
\rho^1_v(r) = \sum_{ij} \rho_{ij} \langle \phi_i | r \rangle \langle r | \phi_j \rangle \quad \tilde{\rho}^1_v(r) = \sum_{ij} \rho_{ij} \langle \phi_i | r \rangle \langle r | \phi_j \rangle
$$

$$
\rho_{ij} = \sum_n f_n \langle \psi_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \psi_n \rangle
$$

If the partial waves form a complete basis within the PAW spheres, then the all-electron wave functions $|\psi_n\rangle$ are orthogonal to the core states!
Accuracy

Subset of G2-1 test set: Deviation PAW w.r.t. GTO, in [kcal/mol].

\[ |\Delta E_{AE}| < 1 \text{ kcal/mol.} \]
Accuracy

Relative PBE bond lengths of Cl$_2$, ClF, and HCl for various GTO basis sets specified with respect to plane-wave results:

$$\text{aug-cc-pVXZ (X= D,T,Q,5)}$$

N.B.: aug-cc-pV5Z basis set for Cl contains 200 functions!
$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_{lme} \left( |\phi_{lme}\rangle - |\phi_{lme}\rangle \right) \langle \tilde{p}_{lme} | \tilde{\psi}_n \rangle$$

- $|\tilde{\psi}_n\rangle$ is the variational quantity of the PAW method.

- The PAW method is often referred to as an all-electron method. Not in the sense that all electrons are treated explicitly, but in the sense that the valence electronic wave functions are kept orthogonal to the core states.
This general scheme applies to all operators.

Sometimes one may choose to include only parts of the PAW expressions.

lazy: only implement plane wave part (GW, ...)

efficient: physics of localized orbitals; only spheres (LDA+U, DMFT, ...,
Hartree-Fock/DFT hybrid functionals

Definition: Exchange correlation functionals that admix a certain amount of Fock exchange to (a part of) a local or semi-local density functional.

- Present a definite improvement over the (semi)-local density functional description of the properties of molecular systems.
- Some hybrid functionals yield an improved description of structural, electronic, and thermo-chemical properties of small/medium gap solid state systems.
Hartree-Fock Theory

Slater determinant

\[
\Psi(r_1, ..., r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(r_1) & \psi_1(r_1) & \cdots & \psi_N(r_1) \\
\psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_N(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(r_N) & \psi_2(r_N) & \cdots & \psi_N(r_N)
\end{vmatrix}
\]

\[
\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \left( \psi_1(r_1) \psi_2(r_2) - \psi_1(r_2) \psi_2(r_1) \right)
\]

Pauli exclusion principle: \( \Psi(r_1, r_2) = 0 \) for \( \psi_1 = \psi_2 \)

\[
\left(-\frac{1}{2} \Delta + V_Z(r) + V_H[n](r)\right) \psi_i(r) + \int V_X(r, r') \psi_i(r') dr' = \epsilon_i \psi_i(r)
\]

Orbital dependent:

\[
V_X(r, r') = -\sum_j^N \frac{\psi_j(r) \psi_j^*(r')}{|r - r'|}
\]

compare to DFT: \( V_{xc}[n](r) \psi_i(r) \)

No electronic correlation!
Hybrid functionals: PBE0, HSE03

PBE0:

\[
E^{\text{PBE0}}_{xc} = \frac{1}{4} E_x^{\text{HF}} + \frac{3}{4} E_x^{\text{PBE}} + E_c^{\text{PBE}}
\]

non-empirical: justified using the adiabatic connection formula.


HSE03:

\[
E^{\text{HSE03}}_{xc} = \frac{1}{4} E_x^{\text{HF,SR}}(\mu) + \frac{3}{4} E_x^{\text{PBE,SR}}(\mu) + E_x^{\text{PBE,LR}}(\mu) + E_c^{\text{PBE}}
\]

decomposed Coulomb kernel (Savin et. al.):

\[
1 = S_\mu(r) + L_\mu(r) = \frac{\text{erfc}(\mu r)}{r} + \frac{\text{erf}(\mu r)}{r}
\]

semiempirical: \(\mu\) is chosen to yield an optimal description of the atomization energies of the molecules in Pople’s G2-1 test set.

Hybrid functionals: B3LYP

\[ E_{X}^{\text{B3LYP}} = 0.8E_{X}^{\text{LDA}} + 0.2E_{X}^{\text{HF}} + 0.72\Delta E_{X}^{\text{B88}} \]

\[ E_{C}^{\text{B3LYP}} = 0.19E_{C}^{\text{VWN3}} + 0.81E_{C}^{\text{LYP}} \]

**Semiempirical:** coefficients chosen to reproduce experimental atomization energies, electron and proton affinities and ionization potentials of the molecules in Pople’s G2 test set and their atomic constituents.


M. J. Frisch et al., GAUSSIAN03 Rev. C.02, Gaussian Inc., Wallingford, CT 2004.
Computational aspects

\[ E_x^{HF} \propto \sum_{k_n, q_m} \int \int d^3r d^3r' \psi_{kn}^*(r) \psi_{qm}(r) K(r, r') \psi_{qm}^*(r') \psi_{kn}(r') \]

with

\[ K(r, r') = \frac{1}{|r - r'|} \text{ or } \frac{\text{erfc}(\mu |r - r'|)}{|r - r'|} \]

- FFT overlap density to reciprocal space
  \[ \rho(G) = \text{FFT}\{\psi_{qm}^*(r') \psi_{kn}(r')\} \]

- division by Laplace operator and FFT to real space
  \[ V(G) = \frac{4\pi e^2}{|G|^2} \rho(G), \text{ and } V(r) = \text{FFT}\{V(G)\} \]

- evaluate
  \[ \int \psi_{kn}^*(r) \psi_{qm}(r) V(r) d^3r \]

N.B.: for all combinations of \( k, q, n, \) and \( m \)
\[ E_x^{\text{HF}} \propto \sum_{kn,qm} \int \int d^3r d^3r' \psi^*_{kn}(r) \psi_{qm}(r) K(r, r') \psi^*_{qm}(r') \psi_{kn}(r') \]

Effort:

\[(N_{\text{bands}} \times N_k)(N_{\text{bands}} \times N_q) \times N_{\text{FFT}} \ln N_{\text{FFT}}\]

- **Bulk**: \(N_{\text{bands}} \propto N_{\text{atoms}},\) \(N_k \propto 1/N_{\text{atoms}}\)

  \[\Rightarrow N_{\text{FFT}} \ln N_{\text{FFT}} \propto N_{\text{atoms}}\]

- **Molecular systems**: \(N_k = 1\)

  \[\Rightarrow N_{\text{bands}} \times N_{\text{bands}} \times N_{\text{FFT}} \ln N_{\text{FFT}} \propto N_{\text{atoms}}^3\]
Convergence of $E_{x}^{HF}$ w.r.t. the BZ sampling used to represent $V_{x}^{HF}$

**Example: Al (fcc)**

Short(er) range in real space $\implies$ Reduced BZ sampling
Downsampling cont.

1 band
2 \( k \)-points

2 bands
1 \( k \)-point

unit cells \( \frac{1}{n} \) \( \Leftrightarrow \) \( k \)-points \( n \) \( \Leftrightarrow \frac{1}{1} \)
Assume a maximum interaction range $R = mL$, then a supercell of twice this size, i.e. $2m$ unit cells, correctly incorporates all interactions using only $k = 0 \implies$

This equivalent to the description one obtains using a single unit cell and an equidistant $2m$ sampling of the 1st BZ.

Ergo: reducing the range of the Fock exchange interaction in the HSE functional allows for the representation of the Fock potential on a courser grid of $k$-points.
The HSE Fock exchange energy

\[ E_x^{SR}(\mu) = -\frac{e^2}{2} \sum_{k_n,q_m} 2w_k 2w_q f_{kn} f_{qm} \]

\[ \times \int \int d^3r d^3r' \frac{\text{erfc}(\mu|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \phi_{kn}(\mathbf{r})\phi_{qm}(\mathbf{r})\phi_{qm}^{*}(\mathbf{r}')\phi_{kn}(\mathbf{r}'). \]

The representation of the corresponding short-range Fock potential in reciprocal space

\[ V_k^{SR} (\mathbf{G}, \mathbf{G}') = \langle \mathbf{k} + \mathbf{G} | V_x^{SR}[\mu] | \mathbf{k} + \mathbf{G}' \rangle = \]

\[ -\frac{4\pi e^2}{\Omega} \sum_{m\mathbf{q}} 2w_{\mathbf{q}} f_{\mathbf{qm}} \sum_{\mathbf{G}''} \frac{C_{\mathbf{qm}}(\mathbf{G}' - \mathbf{G}'')C_{\mathbf{qm}}(\mathbf{G} - \mathbf{G}'')}{|\mathbf{k} - \mathbf{q} + \mathbf{G}''|^2} \]

\[ \times \left( 1 - e^{-|\mathbf{k} - \mathbf{q} + \mathbf{G}''|^2/4\mu^2} \right). \]

Full \( \mathbf{q} \)-grid:

\[ \{ \mathbf{q} \} = \left\{ \frac{m_1}{N_1} \mathbf{b}_1 + \frac{m_2}{N_2} \mathbf{b}_2 + \frac{m_3}{N_3} \mathbf{b}_3 | m_i = 0, \ldots, N_i - 1 \right\} \]

Downsampled \( \mathbf{q} \)-grid:

\[ \{ \mathbf{q} \}_k = \{ \mathbf{k} + \sum_{i=1}^{3} m_i \frac{C_i}{N_i} \mathbf{b}_i | m_i = 0, \ldots, \frac{N_i}{C_i} - 1 \} \]
Atomization energies of small molecules

Subset of G2-1 test set: Deviation w.r.t. experiment, in [kcal/mol].

Significant improvement of atomization energies
G2-1 test set (55 molecules): atomization energies

ME and MAE w.r.t. experiment, in [kcal/mol]

<table>
<thead>
<tr>
<th></th>
<th>ME</th>
<th>MAE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAW</td>
<td>GTO</td>
</tr>
<tr>
<td>PBE</td>
<td>+6.43</td>
<td>+6.85</td>
</tr>
<tr>
<td>PBE0</td>
<td>−1.47</td>
<td>−1.04</td>
</tr>
<tr>
<td>PBE</td>
<td>−0.42</td>
<td>...</td>
</tr>
<tr>
<td>PBE0</td>
<td>−0.42</td>
<td>...</td>
</tr>
</tbody>
</table>

- PAW calculations: Γ only, $10 \times 11 \times 12$ Å$^3$, 1000 eV cutoff
- GTO calculations: aug-cc-pV5Z basis set

Solid state systems

Set of test systems

- Metals: Na, Mg, Li, Al, Cu, Rh, Pd, Ag
- 'Small' gap: Si, GaAs, BP, GaP, SiC, $\beta$-GaN, C, BN, MgO
- 'Large' gap: NaCl, LiCl, NaF, LiF

- Lattice constants, bulk moduli
- Band gaps
- Atomization energies

- Transition metal monoxides
- Adsorption of CO on $d$-metal surfaces
Overall PAW-GTO agreement good:
MAE(PAW)=0.029 Å, MAE(GTO)=0.026 Å.

Sizeable discrepancies for Li, Al, C, Si, SiC, GaAs, Rh, and Ag. Probably due to basis set related inaccuracies in the GTO calculations.

# Solid state systems: PBE, PBE0, and HSE03

## Lattice constants and bulk moduli

<table>
<thead>
<tr>
<th>Solid</th>
<th>PBE</th>
<th>HSE03</th>
<th>PBE0</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_0$</td>
<td>$B$</td>
<td>$a_0$</td>
<td>$B$</td>
</tr>
<tr>
<td>C</td>
<td>3.574</td>
<td>431</td>
<td>3.550</td>
<td>466</td>
</tr>
<tr>
<td>Si</td>
<td>5.469</td>
<td>87.8</td>
<td>5.439</td>
<td>96.5</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.752</td>
<td>59.9</td>
<td>5.696</td>
<td>69.5</td>
</tr>
<tr>
<td>MgO</td>
<td>4.258</td>
<td>149</td>
<td>4.212</td>
<td>168</td>
</tr>
<tr>
<td>Al</td>
<td>4.040</td>
<td>76.6</td>
<td>4.025</td>
<td>81.1</td>
</tr>
<tr>
<td>Rh</td>
<td>3.830</td>
<td>254</td>
<td>3.786</td>
<td>285</td>
</tr>
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</table>

All systems:

<table>
<thead>
<tr>
<th></th>
<th>ME</th>
<th>MAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>0.039</td>
<td>−12.3</td>
</tr>
<tr>
<td>MAE</td>
<td>0.045</td>
<td>12.4</td>
</tr>
</tbody>
</table>

No metals:

<table>
<thead>
<tr>
<th></th>
<th>ME</th>
<th>MAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>0.048</td>
<td>−13.4</td>
</tr>
<tr>
<td>MAE</td>
<td>0.048</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Values given in Å and GPa, respectively.
Relative error in the PBE, PBE0, HSE03, and B3LYP lattice constants with respect to experiment.
Solid state systems: band gaps
Solid state systems: Atomization energies

![Graph showing atomization energies for various materials with different functionals.]

<table>
<thead>
<tr>
<th>Material</th>
<th>PBE</th>
<th>PBE0</th>
<th>HSE03</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>−0.045</td>
<td>−0.228</td>
<td>−0.184</td>
<td>−0.590</td>
</tr>
<tr>
<td>MAE</td>
<td>0.134</td>
<td>0.286</td>
<td>0.252</td>
<td>0.590</td>
</tr>
</tbody>
</table>

in eV/atom.
Hybrid functionals overestimate the exchange splitting in $d$-elements: leads to an increased stability of the spin-polarized atom.

B3LYP overestimates $E_{xc}$ of localized electrons.

B3LYP fails to describe 'free electron like' behaviour: LYP underestimates correlation energy in itinerant systems (does not attain HEG limit!).

Heats of formation

Figure 7. Relative error in the PBE, PBE0, HSE03, and B3LYP heats of formation with respect to experiment.
Transition metal monoxides: MnO

Comparison between PBE0 d-projected DOS (bottom) of both Mn sites together with the experimental (top) inverse photoemission data and the difference between on- and off-resonance photoemission spectra.

## Transition metal monoxides cont.

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ (Å)</th>
<th>$M_s$ ($\mu_B$)</th>
<th>$\Delta$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>LDA</td>
<td>4.31</td>
<td>4.14</td>
</tr>
<tr>
<td></td>
<td>HSE03</td>
<td>4.44</td>
<td>4.52</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>4.45</td>
<td>4.58</td>
</tr>
<tr>
<td>FeO</td>
<td>LDA</td>
<td>4.17</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>HSE03</td>
<td>4.33</td>
<td>3.63</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>4.33</td>
<td>3.32/4.2</td>
</tr>
<tr>
<td>CoO</td>
<td>LDA</td>
<td>4.10</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>HSE03</td>
<td>4.26</td>
<td>2.67</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>4.25</td>
<td>3.35/4.0</td>
</tr>
<tr>
<td>NiO</td>
<td>LDA</td>
<td>4.06</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>HSE03</td>
<td>4.18</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>4.17</td>
<td>1.64</td>
</tr>
</tbody>
</table>
CO adsorption on d-metal surfaces

- DFT predicts incorrectly that CO prefers the hollow site; P. Feibelman et al., J. Phys. Chem. B 105, 4018 (2001)

- unclear why, but the error is relatively large; best DFT/PBE calculations:
  - CO@Cu(111): $-170$ meV
  - CO@Rh(111): $-40$ meV
  - CO@Pt(111): $-100$ meV

- 4 layers, $c(2 \times 4)$, $\Theta = 0.25$ ML, asymmetric setup, 10Å vacuum.
## CO adsorption on d-metal surfaces cont. 1

<table>
<thead>
<tr>
<th>CO @</th>
<th>top</th>
<th>fcc</th>
<th>hcp</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>0.709</td>
<td>0.874</td>
<td>0.862</td>
<td>−0.165</td>
</tr>
<tr>
<td>PBE0</td>
<td>0.606</td>
<td>0.579</td>
<td>0.565</td>
<td>0.027</td>
</tr>
<tr>
<td>HSE03</td>
<td>0.561</td>
<td>0.555</td>
<td>0.535</td>
<td>0.006</td>
</tr>
<tr>
<td>exp.</td>
<td>0.46-0.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh(111)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>1.870</td>
<td>1.906</td>
<td>1.969</td>
<td>−0.099</td>
</tr>
<tr>
<td>PBE0</td>
<td>2.109</td>
<td>2.024</td>
<td>2.104</td>
<td>0.005</td>
</tr>
<tr>
<td>HSE03</td>
<td>2.012</td>
<td>1.913</td>
<td>1.996</td>
<td>0.016</td>
</tr>
<tr>
<td>exp.</td>
<td>1.43-1.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(111)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>1.659</td>
<td>1.816</td>
<td>1.750</td>
<td>−0.157</td>
</tr>
<tr>
<td>PBE0</td>
<td>1.941</td>
<td>1.997</td>
<td>1.944</td>
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</tr>
<tr>
<td>HSE03</td>
<td>1.793</td>
<td>1.862</td>
<td>1.808</td>
<td>−0.069</td>
</tr>
<tr>
<td>exp.</td>
<td>1.43-1.71</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Hybrid functionals reduce the tendency to stabilize adsorption at the hollow sites w.r.t. the top site.

Reduced CO $2\pi^*$ — metal-$d$ interaction

- Improved description of the CO LUMO ($2\pi^*$) w.r.t. the Fermi level (shifted upwards).
- Downshift of the metal $d$-band center of gravity in Cu(111).
- But: Overestimation of the metal $d$-bandwidth.

Conclusions

Implementation:

- Only small discrepancies between the PAW and GTO atomization energies for molecular systems at the PBE and hybrid functional level.

- For solid state systems the PAW and GTO results already differ at the PBE level; probably basis set related inaccuracies in the GTO calculations. PAW results validated through a comparison with FLAPW calculations.

- Range decomposition of the Coulomb kernel in the HSE functional allows for a reduced Brillouin zone sampling in the representation of the Fock potential; the HSE results remain similar to the PBE0 results.
Solid state systems:

- The PBE0 and HSE hybrid functionals provide an improved description of the structural (lattice constants and bulk moduli) and electronic (band gap) properties of systems with a small/medium sized band gap.

- PBE0, HSE, and B3LYP atomization energies are in overall worse agreement with experiment than those obtained using the semi-local PBE density functional, in case of B3LYP even drastically so. This is mainly due to a worse description of metallic systems.

- CO adsorption on \(d\)-metal (111) surfaces: hybrid functionals reduce the tendency to stabilize adsorption at the hollow sites w.r.t. the top site.
TAGS and links

**INCAR tags**

**Hybrid functionals and Hartree-Fock** The VASP manual chapter on hybrid functionals and Hartree-Fock.

**LHFCALC** Switch on Hybrid and Hartree-Fock type calculations.

**HFSCREEN** Specifies the range separating parameter in HSE functionals.

**ENCUTFOCK** Specifies the FFT grids used in the HF routines.

**NKRED, NKREDX, NKREDY, NKREDZ, etc** Downsampling the k-point mesh in the representation of the Fock potential.

**GGA-tag** Override the type of density functional specified in the POTCAR.

**AEXX, AGGAX, AGGAC and ALDAC** The fractions of Fock-exchange, gradient corrections to the exchange and correlation, and the fraction of LDA correlation.

**PBE0**: LHFCALC = .TRUE.

**HSE06**:† LHFCALC = .TRUE. ; HFSCREEN = 0.2 (with PBE POTCAR, or GGA = PE).

**B3LYP**: LHFCALC = .TRUE. ; GGA = B3 ; AEXX = 0.2 ; AGGAX = 0.72 ; AGGAC = 0.81 ; ALDAC = 0.19

**Hartree-Fock**: LHFCALC = .TRUE. ; AEXX = 1.0 ; ALDAC = 0.0 ; AGGAC = 0

New density functionals: “new GGAs for solids”

AM05

PHYSICAL REVIEW B 72, 085108 (2005)

Functional designed to include surface effects in self-consistent density functional theory

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\textsuperscript{2}Computational Materials and Molecular Biology MS 1110, Sandia National Laboratories, Albuquerque, New Mexico 87185-1110, USA

PBEsol

PRL 100, 136406 (2008)

Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces

John P. Perdew,\textsuperscript{1} Adrienn Ruzsinszky,\textsuperscript{1} Gábor I. Csonka,\textsuperscript{2} Oleg A. Vydrov,\textsuperscript{3} Gustavo E. Scuseria,\textsuperscript{3} Lucian A. Constantin,\textsuperscript{4} Xiaolan Zhou,\textsuperscript{1} and Kieron Burke\textsuperscript{5}

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\textsuperscript{4}Donostia International Physics Center, E-20018, Donostia, Basque Country
\textsuperscript{5}Departments of Chemistry and of Physics, University of California, Irvine, Irvine, California 92697, USA

Better description of lattice constants and bulk moduli, and (jellium) surface energies.
CSONKA et al.

TABLE I. Statistical data for the equilibrium lattice constants (Å) of the 18 test solids of Ref. 38 at 0 K calculated from the SJEOS. The Murnaghan EOS yields identical results within the reported number of decimal places. Experimental low temperature (5–50 K) lattice constants are from Ref. 56 (Li), Ref. 57 (Na, K), Ref. 58 (Al, Cu, Rh, Pd, Ag), and Ref. 59 (NaCl). The rest are based on room temperature values from Ref. 60 (C, Si, SiC, Ge, GaAs, NaF, LiF, MgO) and Ref. 57 (LiCl), corrected to the T=0 limit using the thermal expansion from Ref. 58. An estimate of the zero-point anharmonic expansion has been subtracted out from the experimental values (cf. Table II). (The calculated values are precise to within 0.001 Å for the given basis sets, although GAUSSIAN GTO1 and GTO2 basis-set incompleteness limits the accuracy to 0.02 Å.) GTO1: the basis set used in Ref. 38. GTO2: For C, Si, SiC, Ge, GaAs, and MgO, the basis sets were taken from Ref. 41. For the rest of the solids, the GTO1 basis sets and effective core potentials from Ref. 38 were used. The best theoretical values are in boldface. The LDA, PBEsol, and PBE GTO2 results are from Ref. 14. The SOGGA GTO1 results are from Ref. 15.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>LDA</th>
<th>PBEsol</th>
<th>PBEsol</th>
<th>AM05</th>
<th>SOGGA</th>
<th>PBE</th>
<th>PBE</th>
<th>PBE</th>
<th>TPSS</th>
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<tbody>
<tr>
<td>GTO2 VASP</td>
<td>ME Å</td>
<td>MAE Å</td>
<td>MRE (%)</td>
<td>MARE (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>−0.047</td>
<td>−0.055</td>
<td>0.022</td>
<td>0.010</td>
<td>0.012</td>
<td>0.029</td>
<td>0.009</td>
<td>0.075</td>
<td>0.066</td>
<td>0.063</td>
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<tr>
<td></td>
<td>MAE Å</td>
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<td>0.036</td>
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<tr>
<td></td>
<td>MRE (%)</td>
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<td>0.58</td>
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<td>1.62</td>
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<td></td>
<td>MARE (%)</td>
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<td>1.15</td>
<td>0.67</td>
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<td>0.80</td>
<td>0.50</td>
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</tr>
</tbody>
</table>
TGAS and links

INCAR tags

GGA= AM | PS Select the AM05 or PBEsol GGA functional.
Electronic optimization

Direct minimization of the DFT functional (Car-Parrinello, modern)
Start with a set of wavefunctions \( \{\psi_n(r) | n = 1, \ldots, N_e/2 \} \) (random numbers) and minimize the value of the functional (iteration)

\[
F_n(r) = \left( -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(r, \{\psi_n(r')\}) - \epsilon_n \right) \psi_n(r)
\]

The Self Consistency Cycle (old fashioned)
Start with a trial density \( \rho \), set up the Schrödinger equation, and solve it to obtain wavefunctions \( \psi_n(r) \)

\[
\left( -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(r, \{\rho(r')\}) \right) \psi_n(r) = \epsilon_n \psi_n(r) \quad n = 1, \ldots, N_e/2
\]

as a result one obtains a new charge density \( \rho(r) = \sum_n |\psi_n(r)|^2 \) and a new Schrödinger equation ⇒ iteration
Direct minimization vs. SCC

Direct optimization (charge sloshing)

The derivative of the total energy w.r.t. the wave function $|\psi_n\rangle$ is

$$
|g_n\rangle = f_n \left(1 - \sum_m |\psi_m\rangle\langle\psi_m|\right) \hat{H} |\psi_n\rangle + \sum_m \frac{1}{2} H_{nm} (f_n - f_m) |\psi_m\rangle
$$

where $H_{nm} = \langle\psi_m|\hat{H}|\psi_n\rangle$.

Consider two states

$$
\psi_n = e^{i(k_F - \delta k)r} \quad \psi_m = e^{i(k_F + \delta k)r}
$$

$$
\psi'_n = \psi_n + \Delta s \psi_m \quad \psi'_m = \psi_m - \Delta s \psi_n
$$

$$
\delta\rho(r) = 2\Delta s \text{Re} e^{i2\delta k \cdot r} \quad \delta V_H(r) = \frac{2\Delta s \cdot 4\pi e^2}{|2\delta k|^2} \text{Re} e^{i2\delta k \cdot r}
$$

The smallest $|\delta k| \propto 1/L$ where $L$ is the largest dimension of the supercell.

$\Rightarrow$ the response of the potential $\delta V_H \propto L^2 \Rightarrow$ stable step size $\Delta s \propto 1/L^2$
A naively straightforward algorithm

Express the Hamiltonian in the plane wave basis set and diagonalize it

\[ H = \langle G | \hat{H}[\rho] | G' \rangle \rightarrow \text{diagonalize } H \rightarrow \{ \psi_i, \epsilon_i \} \quad i = 1, \ldots, N_{\text{FFT}} \]

Self-consistency

\[ \rho_0 \rightarrow H_0 \rightarrow \rho' \rightarrow \rho_1 = f(\rho_0, \rho') \rightarrow H_1 \rightarrow \ldots \]

iterate until \( \rho = \rho' \)

BUT: we do not need \( N_{\text{FFT}} \) one-electron orbitals, at a cost of \( O(N_{\text{FFT}}^3) \) ...

we only need the \( N_b \) lowest eigenvectors of \( H \)

\( \Rightarrow \) Iterative diagonalization of \( H \) aimed at finding its \( N_b \) lowest eigenvectors

\( (N_b \approx N_{\text{el}}/\text{cell}) \).

Blocked Davidson algorithm, RMM-DIIS, ...
The Self-Consistency Cycle

- trial-charge $\rho_{in}$ and trial-wavevectors $\psi_n$

  - set up Hamiltonian $H(\rho_{in})$

  - iterative refinements of wavefunctions \{\psi_n\}

  - new charge density $\rho_{out} = \sum_n f_n |\psi_n(r)|^2$

  - refinement of density $\rho_{in}, \rho_{out} \Rightarrow$ new $\rho_{in}$

  - no $\Delta E < \delta$

  - calculate forces, update ions

- two subproblems
  - optimization of \{\psi_n\} and $\rho_{in}$

- refinement of density:
  - DIIS algorithm
  - P. Pulay, Chem. Phys. Lett. 73, 393 (1980)

- refinement of wavefunctions:
  - DIIS or Davidson algorithm

Marsman VASP Workshop: Day 1
Key ingredients: Subspace diagonalization and the Residual

- Rayleigh-Ritz: the diagonalization of the $N_b \times N_b$ subspace
  $$\sum_m \tilde{H}_{nm} B_{mk} = \sum_m \epsilon_k^{\text{app}} \tilde{S}_{nm} B_{mk}$$

  with
  $$\tilde{H}_{nm} = \langle \psi_n | \hat{H} | \psi_m \rangle \quad \text{and} \quad \tilde{S}_{nm} = \langle \psi_n | \hat{S} | \psi_m \rangle$$

  The $N_b$ eigenvalues/eigenvectors $\epsilon_k^{\text{app}}$ and $|\tilde{\psi}_k\rangle = \sum_{m} B_{mk} |\psi_m\rangle$ are the best approximation to the exact $N_b$ lowest eigenvalues of $\hat{H}$ within the subspace spanned by the one-electron orbitals $\psi_m$.

- The residual vector:
  $$|R(\psi_n)\rangle = (\hat{H} - \epsilon^{\text{app}} \hat{S}) |\psi_n\rangle,$$
  with $\epsilon^{\text{app}} = \frac{\langle \psi_n | \hat{H} | \psi_n \rangle}{\langle \psi_n | \hat{S} | \psi_n \rangle}$

  (its norm is a measure of the error in the eigenvector).
The blocked Davidson algorithm

- Take a subset of all bands \( \{ \psi_n | n = 1, \ldots, N \} \Rightarrow \{ \psi_k^1 | k = 1, \ldots, n_1 \} \)

- Extend this subset by adding the (preconditioned) residual vectors to the presently considered subspace
  \[ \{ \psi_k^1 / g_k^1 = K(H - \epsilon_{\text{app}}S)\psi_k^1 | k = 1, \ldots, n_1 \} \]

- Raighley-Ritz optimization ("sub-space" rotation) in the \( 2n_1 \) dimensional subspace \( \{ \psi_k^1 / g_k^1 \} \) to determine the \( n_1 \) lowest eigenvectors \( \{ \psi_k^2 | k = 1, \ldots, n_1 \} \).

- Extend the subspace with the residuals from \( \{ \psi_k^2 \} \)
  \[ \{ \psi_k^1 / g_k^1 / g_k^2 = K(H - \epsilon_{\text{app}}S)\psi_k^2 | k = 1, \ldots, n_1 \} \]

- Raighley-Ritz optimization \( \Rightarrow \{ \psi_k^3 | k = 1, \ldots, n_1 \} \)

- etc ...

- The optimized \( \{ \psi_k^m | k = 1, \ldots, n_1 \} \) replace \( \{ \psi_n | n = 1, \ldots, n_1 \} \)

- Move on to subset \( \{ \psi_k^1 | k = n_1 + 1, \ldots, n_2 \} \), ..., etc, ...

After treating all bands: Raighley-Ritz optimization of \( \{ \psi_n | n = 1, \ldots, N \} \)
Minimization of the norm of residual vector

\[ R[\rho_{in}] = \rho_{out}[\rho_{in}] - \rho_{in} \quad |R[\rho_{in}]| \Rightarrow \text{min} \]

with \( \rho_{out}(\vec{r}) = \sum_{\text{occupied}} w_k f_{nk} |\psi_{nk}(\vec{r})|^2 \)

**DIIS algorithm** is used for the optimization of the norm of the residual vector.

Linearization of \( R[\rho_{in}] \) around \( \rho_{sc} \) (linear response theory)

\[ R[\rho] = -J(\rho - \rho_{sc}) \]

with the charge dielectric function \( J \)

\[ J = 1 - \chi \left( \frac{4\pi e^2}{q^2} \right) \]

leads to

\[ R[\rho_{in}] = \rho_{out}[\rho_{in}] - \rho_{in} = J(\rho_{in} - \rho_{sc}) \]
Divergence of the dielectric function

Eigenvalue spectrum of $J$ determines convergence

$$J = 1 - \chi \left( \frac{U}{\frac{4\pi e^2}{q^2}} \right)$$

“Broader” eigenvalue spectrum $\Rightarrow$ slower convergence

- For insulators and semi-conductors, the width of the eigenvalue spectrum is constant and system size independent ($\epsilon_\infty$)!

- For metals the eigenvalue spectrum diverges, its width is proportional to the square of the longest dimension of the cell:
  - Short wavelength limit $J \approx 1$ (no screening)
  - Long wavelength limit $J \approx 1/q^2 \propto L^2$ (metallic screening)

Complete screening in metals causes charge sloshing
The dielectric matrix

- Use a model dielectric function that is a good initial approximation for most systems

\[ \mathbf{J}^{-1} \approx \mathbf{G}_q^1 = \max\left(\frac{q^2_{\text{AMIX}}}{q^2 + q^2_{\text{BMIX}}}, \text{AMIN}\right) \]

- This is combined with a convergence accelerator.

  The initial guess for the dielectric matrix is improved using information accumulated in each electronic (mixing) step (DIIS).
Pure DFT functional depends only on the density

$$\left(-\frac{1}{2} \Delta + V_{\text{eff}}[\rho](\mathbf{r}) + V_{\text{ext}}(\mathbf{r})\right) \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r})$$

DFT-Hartree-Fock Hybrid functional depends explicitly on the wave functions

$$\left(-\frac{1}{2} \Delta + V_{\text{eff}}[\rho](\mathbf{r}) + V_{\text{ext}}(\mathbf{r})\right) \psi_n(\mathbf{r})+C \sum_{m}^{\text{occ}} \psi_m(\mathbf{r}) \int \frac{\psi^*_m(\mathbf{r}') \psi_n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \epsilon_n \psi_n(\mathbf{r})$$

so density-mixing will not work (reliably).

Unfortunately we know direct optimization schemes are prone to charge sloshing for metals and small-gap systems.
Mixed scheme

- The gradient of the wave functions is given by

\[ |g_n\rangle = f_n \left(1 - \sum_m |\psi_m\rangle\langle\psi_m|\right)\hat{H}|\psi_n\rangle + \sum_m \frac{1}{2} H_{nm}(f_n - f_m)|\psi_m\rangle \]

with \( H_{nm} = \langle\psi_m|\hat{H}|\psi_n\rangle \)

- A search direction towards the groundstate w.r.t. unitary transformations between the orbitals within the subspace spanned by wave functions can be found from perturbation theory

\[ U_{nm} = \delta_{nm} - \Delta_s \frac{H_{nm}}{H_{mm} - H_{nn}} \]

but this is exactly the term that is prone to charge sloshing!

**Solution:** Use density mixing to determine the optimal unitary transformation matrix \( U_{nm} \).
Optimal subspace rotation

- Define a Hamilton matrix $\bar{H}_{kl} = \langle \psi_l | \bar{H}[\rho] | \psi_k \rangle$
  where $\bar{H}[\rho] = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{eff}}[\rho] + \hat{V}^{\text{nl}}_{\chi}[\psi, \{ f \}]$
- Determine the subspace rotation matrix $V$ that diagonalizes $\bar{H}_{kl}$
- Recompute the (partial) occupancies $\rightarrow \{ f' \}$
- The transformed orbitals $\sum_l V_{nl} \psi_l$ and partial occupancies $\{ f' \}$ define a new charge density $\rho'$
- mix $\rho$ and $\rho'$
- and iterate the above until a stable point is found $\rightarrow \rho_{sc}$
- $H^{sc}_{nm} = \langle \psi_m | \bar{H}[\rho_{sc}] | \psi_n \rangle$ defines the optimal subspace rotation
- $U_{nm} = \delta_{nm} - \Delta s \frac{H^{sc}_{nm}}{H^{sc}_{mm} - H^{sc}_{nn}}$
- N.B.: we do not update the orbital dependent part of the Hamiltonian $\hat{V}^{\text{nl}}_{\chi}[\{ \psi \}, \{ f \}]$
The full mixed scheme

The iterative optimization of the wavefunctions cycles through the following steps:

1. construct the Hamiltonian, $H$, from the current wavefunctions and partial occupancies, and calculate $H|\psi\rangle$;

2. inner loop: determine the self-consistent Hamiltonian, $H^{sc}$, defining the preconditioned direction for the subspace rotation $U$.

3. minimization along the preconditioned search direction, defined by $(1 - \sum_m |\psi_m\rangle\langle\psi_m|)\hat{H}|\psi_n\rangle$, $U$, and a gradient acting on the partial occupancies. For instance by means of a conjugate-gradient algorithm.

This loop is repeated until the change in the free energy from one iteration to the next drops below the required convergence threshold $\Delta E_{\text{thr}}$ (usually $10^{-4}$ eV).
It works: fcc Fe

The convergence behaviour of HSE03 calculations using the improved direct minimization procedure (solid lines) and a standard conjugate gradient algorithm (dotted lines). Calculations on single, double, four times, and eight times repeated cells are marked with circles (○), diamonds (♦), squares (□), and triangles (△), respectively.
## INCAR tags

**ALGO**  The INCAR tag that sets which algorithm is used for the electronic minimization.

**IALGO** and **LDIAG**  Same as above, but more to choose from (ALGO is the preferred tag). For the direct optimizers (ALGO = All | Damped) LDIAG = .TRUE. switches on the density mixer in the determination of the subspace rotation matrix.

**Mixing tags**  The VASP manual chapter on the settings for the density mixer.

**TIME**  Time step in the direct optimization method ALGO = Damped, and trial time step for the conjugate gradient direct optimizer ALGO = All.

**Electronic optimization**  Lecture from the VASP workshop in Vienna (2003).
Hartree-Fock within the PAW formalism

In principle we would want to follow the original scheme

- solve the non-spinpolarized spherical atom within the (scalar relativistic) Hartree-Fock approximation
- compute all-electron partial waves
- pseudize ... etc etc ...

Unfortunately this is already problematic in the second step, solving

\[ (-\frac{1}{2} \Delta + v_H + \hat{v}_X ) |\phi_i\rangle = \epsilon_i |\phi_i\rangle \]

with

\[ \langle r | \hat{v}_X | \phi_i \rangle \propto \sum_{\text{at.ref}} \phi_a(r) \int \frac{\phi^*_a(r') \phi_i(r')}{|r - r'|} dr' \]

\[ \Rightarrow \text{numerically unstable for unbound partial waves with } \epsilon < 0. \]
The HF-PAW method (cont.)

A pragmatic approximate solution:

- keep the partial waves and projector functions ($|\phi_i\rangle$, $|\tilde{\phi}_i\rangle$, and $|\tilde{p}_i\rangle$) obtained with DFT.

- orthogonalize the all-electron partial waves $|\phi_i\rangle$ with respect to the Hartree-Fock core states: $|\phi_i\rangle \rightarrow |\phi'_i\rangle$.

- compute the PAW parameters using $|\phi'_i\rangle$ and Hartree-Fock core states:

\[
D_{ij} = \langle \phi'_i | -\frac{1}{2} \Delta + v^1_H [\rho^1_v] + v^1_H [\rho^\text{HF} Z_c] + v^1_X [\{\rho_{ij}\}] + v^c_X [\{\phi^\text{HF}_c\}] | \phi'_j \rangle \\
- \langle \tilde{\phi}_i | -\frac{1}{2} \Delta + v^1_H [\tilde{\rho}^1_v] + v^1_H [\tilde{\rho} Z_c] + \tilde{v}^1_X [\{\rho_{ij}\}] | \tilde{\phi}_j \rangle
\]

and

\[
Q_{ij} = \langle \phi'_i | \phi'_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle
\]

The most important step is in this scheme: $v^1_H [\rho^\text{DFT} Z_c] \rightarrow v^1_H [\rho^\text{HF} Z_c]$. 
The HF-PAW method (cont.)

Bulk equilibrium volumes for GaAs and Si

<table>
<thead>
<tr>
<th>Valence electrons</th>
<th>GaAs: $\Omega_0$ ($\text{Å}^3$)</th>
<th>Si: $\Omega_0$ ($\text{Å}^3$)</th>
</tr>
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<tbody>
<tr>
<td>$4s^24p^1$</td>
<td>46.06</td>
<td>41.44</td>
</tr>
<tr>
<td>$3d^{10}4s^24p^1$</td>
<td>47.07</td>
<td>41.91</td>
</tr>
<tr>
<td>$3p^63d^{10}4s^24p^3$</td>
<td>47.74</td>
<td>41.93</td>
</tr>
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</table>

$3s$ and $3p$ levels in the spherical Si atom.

<table>
<thead>
<tr>
<th>$3s^23p^2$</th>
<th>$2s^22p^63s^23p^2$</th>
<th>HF ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAW</td>
<td>HF-PAW</td>
<td>PAW</td>
</tr>
<tr>
<td>$3p$</td>
<td>-2.761</td>
<td>-2.749</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>-13.205</td>
<td>-13.146</td>
</tr>
</tbody>
</table>

All energies in eV.
The HF-PAW method (cont.)

The remaining discrepancies are related to the fact that the one-center expansions of the wave functions inside the PAW spheres are not complete enough (particularly further away from the nucleus)

\[ \psi_n(r) \neq \sum_i \phi_i(r) \langle \tilde{p}_i | \tilde{\psi}_n \rangle \quad \tilde{\psi}_n(r) \neq \sum_i \tilde{\phi}_i(r) \langle \tilde{p}_i | \tilde{\psi}_n \rangle \]

This causes problems for at least two reasons:

1. The core-valence exchange interaction is computed between the Hartree-Fock core states \( \{ \phi_c^{\text{HF}} \} \) and the one-center expansion of \( \psi \) only.

2. The point where the Hartree potentials arising from the all-electron and pseudo ionic cores match moves into regions where the one-center expansions are not good. This is bound to happen to some degree since we adjust \( v_H^1[\rho^{\text{DFT}}_{Zc}] \rightarrow v_H^1[\rho^{\text{HF}}_{Zc}] \) and leave \( v_H^1[\tilde{\rho}_{Zc}] \) fixed.
The HF-PAW method (cont.)

\[ \left| \tilde{\psi}_n(r) \right|^2 \neq \sum_{ij} \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{\phi}_i | r \rangle \langle r | \tilde{p}_j \rangle \langle \tilde{\phi}_j | \tilde{\psi}_n \rangle \]

\[ \tilde{\rho} \neq \tilde{\rho}^1 \]
The HF-PAW method (cont.)

\[ |\tilde{\psi}_n(r)|^2 \neq \sum_{ij} \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{\phi}_i | r \rangle \langle r | \tilde{\phi}_j \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle \]
\[ \tilde{\rho} \neq \tilde{\rho}^1 \]

\[ \sum_{ij} \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \phi_i | r \rangle \langle r | \phi_j \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle \neq |\phi_{HF}^\text{ref}(r)|^2 \]
\[ \rho^1 \neq \rho_{HF}^1 \]
The HF-PAW method (cont.)

\[ |\tilde{\psi}_n (r)|^2 \neq \sum_{ij} \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \phi_i | \phi_j \rangle \langle r | \tilde{p}_j \rangle \langle \tilde{\psi}_n | \phi_n \rangle \]
\[ \tilde{\rho} \neq \tilde{\rho}^1 \]

\[ \sum_{ij} \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \phi_i | r \rangle \langle r | \phi_j \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle \neq |\phi_{HF}^\text{ref} (r)|^2 \]
\[ \rho^1 \neq \rho_{HF}^1 \]

\[ \tilde{\rho} - \tilde{\rho}^1 + \rho^1 \approx \rho_{HF}^1 \]
TAGS and links

INCAR tags

**LRHFATM = .TRUE.** Changes the DFT AE core charge density ($\rho^1$) to a Hartree-Fock one.
# Talks and examples

## Handson sessions
- Handson Session 1
- Handson Session 2
- Handson Session 3
- Handson Session 4

## Lectures
- SESSION 1: Introduction to Computational Materials Science
- SESSION 2: Introduction to DFT
- SESSION 3: Pseudopotentials I
- SESSION 4: Pseudopotentials II
- SESSION 5: Sampling the Brillouin zone
- SESSION 6: Ionic relaxation methods
- SESSION 7: Electronic relaxation methods
- SESSION 8: Computational Platforms
- SESSION 10: Accuracy and Validation of results
- SESSION 11: Pseudopotential Data Base
- SESSION 12: DFT in depth
- SESSION 13: Unpaired electrons in DFT
Some literature

Hybrid functionals in VASP


