VASP Workshop: Day 1

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VASP Workshop at CSC Helsinki 2009



- Projector Augmented Wave method
- 3 Hybrid functionals
- 4 New density functionals
- 5 Reaching the electronic groundstate
- 6 Hartree-Fock in PAW

A system of \boldsymbol{N} electrons

$$\hat{H}\Psi(\mathbf{r}_1,...,\mathbf{r}_N) = E\Psi(\mathbf{r}_1,...,\mathbf{r}_N)$$

$$\begin{pmatrix} -\frac{1}{2}\sum_i \Delta_i + \sum_i V(\mathbf{r}_i) + \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \end{pmatrix} \Psi(\mathbf{r}_1,...,\mathbf{r}_N) = E\Psi(\mathbf{r}_1,...,\mathbf{r}_N)$$

Many-body WF storage requirements are prohibitive

 $(\# grid points)^N$

Map onto "one-electron" theory

$$\Psi(\mathbf{r}_1,...,\mathbf{r}_N) \to \{\psi_1(\mathbf{r}),\psi_2(\mathbf{r}),...,\psi_N(\mathbf{r})\}$$

such as Hohenberg-Kohn-Sham density functional theory

Do not need $\Psi(\mathbf{r}_1,...,\mathbf{r}_N)$, just the density $\rho(\mathbf{r})$:

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

$$\Psi(\mathbf{r}_1,...,\mathbf{r}_N) = \prod_i^N \psi_i(\mathbf{r}_i) \qquad \rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2 \qquad E_H[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

One-electron Kohn-Sham equations

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

Hartree

Exchange-Correlation

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$$V_H[\rho](\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \qquad \qquad E_{\rm xc}[\rho] = ??? \qquad V_{\rm xc}[\rho](\mathbf{r}) = ???$$

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

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 **k**. All electronic states can be indexed by this quantum number

$|\Psi_{\mathbf{k}}\rangle$

• In a one-electron theory, one can introduce a second index, corresponding to the one-electron band **n**,

$|\psi_{n\mathbf{k}}\rangle$

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

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

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

• k is usually constrained to lie within the first Brillouin zone in reciprocal space.

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 $\mathbf{b}_1 = \frac{2\pi}{\Omega} \mathbf{a}_2 \times \mathbf{a}_3 \quad \mathbf{b}_2 = \frac{2\pi}{\Omega} \mathbf{a}_3 \times \mathbf{a}_1 \quad \mathbf{b}_3 = \frac{2\pi}{\Omega} \mathbf{a}_1 \times \mathbf{a}_2$

 $\Omega = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 \qquad \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$

• 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

$$\rho(\mathbf{r}) = \frac{1}{\Omega_{\rm BZ}} \sum_{n} \int_{\rm BZ} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k}$$

- f_{nk} are the occupation numbers, i.e., the number of electrons that occupy state nk.
- Exploiting the fact that the wave functions at k-points that are close together will be almost identical, one may approximate the integration over k by a weighted sum over a discrete set of points

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

where the weights $w_{\mathbf{k}}$ sum up to one.

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The intractable task of determining $\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$ (for $N \sim 10^{23}$) has been reduced to calculating $\psi_{n\mathbf{k}}(\mathbf{r})$ at a discrete set of points $\{\mathbf{k}\}$ in the first BZ, for a number of bands that is of the order of the number of electrons *per unit cell*.

Monkhorst-Pack meshes

Idea: equally spaced mesh in Brillouin-zone.

Construction-rule:

$$\mathbf{k}_{prs} = u_p \mathbf{b}_1 + u_r \mathbf{b}_2 + u_s \mathbf{b}_3$$

$$u_r = \frac{2r - q_r - 1}{2q_r}r = 1, 2, \dots, q_r$$

 \mathbf{b}_i reciprocal lattice-vectors q_r determines number of

k-points in r-direction

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Example

- quadratic 2-dimensional lattice
- $q_1 = q_2 = 4 \Rightarrow 16$ k-points
- only 3 inequivalent k-points (\Rightarrow IBZ)

•
$$4 \times \mathbf{k}_1 = (\frac{1}{8}, \frac{1}{8}) \Rightarrow \omega_1 = \frac{1}{4}$$

• $4 \times \mathbf{k}_2 = (\frac{3}{8}, \frac{3}{8}) \Rightarrow \omega_2 = \frac{1}{4}$
• $8 \times \mathbf{k}_3 = (\frac{3}{8}, \frac{1}{8}) \Rightarrow \omega_3 = \frac{1}{2}$



 $\frac{1}{\Omega_{\rm BZ}} \int\limits_{BZ} F(\mathbf{k}) d\mathbf{k} \Rightarrow \frac{1}{4} F(\mathbf{k}_1) + \frac{1}{4} F(\mathbf{k}_2) + \frac{1}{2} F(\mathbf{k}_3)$

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 $\Gamma \iff \Gamma$ belongs to mesh).
- centered around Γ . (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

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The total energy

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

• The kinetic energy

$$T_{s}[\{\psi_{n\mathbf{k}}[\rho]\}] = \sum_{n} \sum_{\mathbf{k}} w_{\mathbf{k}} f_{n\mathbf{k}} \langle \psi_{n\mathbf{k}}| - \frac{1}{2} \Delta |\psi_{n\mathbf{k}}\rangle$$

• The Hartree energy

$$E_{\rm H}[\rho, \{\mathbf{R}, Z\}] = \frac{1}{2} \iint \frac{\rho_{eZ}(\mathbf{r})\rho_{eZ}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$

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

• The electronic charge density

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

• The Kohn-Sham equations

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

• 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 $u_{n\mathbf{k}}$ of the wavefunctions

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}$$

with $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}).$

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

$$\begin{split} u_{n\mathbf{k}}(\mathbf{r}) &= \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \quad \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}} \\ \rho(\mathbf{r}) &= \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} \qquad V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} \end{split}$$

 $\bullet\,$ In practice only those plane waves $|{\bf G}+{\bf k}|$ are included for which

$$\frac{1}{2}|\mathbf{G} + \mathbf{k}|^2 < E_{\text{cutoff}}$$

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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 $\mathbf{H}|\psi\rangle$ can be efficiently evaluated using FFT's.

Evaluation of $\mathbf{H} |\psi_{n\mathbf{k}}\rangle$

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

using the convention

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

• Kinetic energy:

$$\langle \mathbf{G} + \mathbf{k} | -\frac{1}{2} \Delta | \psi_{n\mathbf{k}} \rangle = \frac{1}{2} |\mathbf{G} + \mathbf{k}|^2 C_{\mathbf{G}n\mathbf{k}}$$
 NNPLW

• Local potential:
$$V = V_{\rm H}[\rho] + V_{xc}[\rho] + V_{\rm ext}$$

) Exchange-correlation: easily obtained in real space $V_{\rm xc,r} = V_{\rm xc}[\rho_{\rm r}]$
) FFT to reciprocal space $\{V_{\rm xc,r}\} \rightarrow \{V_{\rm xc,G}\}$
) Hartree potential: Poisson equation in reciprocal space $V_{\rm H,G} = \frac{4\pi}{|G|^2}\rho_{\rm G}$
) add all contributions $V_{\rm G} = V_{\rm H,G} + V_{\rm xc,G} + V_{\rm ext,G}$
) FFT to real space $\{V_{\rm G}\} \rightarrow \{V_{\rm r}\}$
The action

The action

$$\langle \mathbf{G} + \mathbf{k} | V | \psi_{n\mathbf{k}} \rangle = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} V_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{Gr}} \qquad N_{\text{FFT}} \log N_{\text{FFT}}$$

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The action of the local potential





TAGS and links

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).

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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.



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$$|\psi_n\rangle = |\widetilde{\psi}_n\rangle + \sum_i (|\phi_i\rangle - |\widetilde{\phi}_i\rangle) \langle \widetilde{p}_i |\widetilde{\psi}_n\rangle$$

- $|\widetilde{\psi}_n\rangle$ is a pseudo wave function expanded in plane waves
- $|\phi_i
 angle$, $|\widetilde{\phi}_i
 angle$, and $|\widetilde{p}_i
 angle$ 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

$$|\phi_i\rangle \rightarrow |\widetilde{\phi}_i\rangle \qquad v_{\rm eff} \rightarrow \widetilde{v}_{\rm eff} \qquad \langle \widetilde{p}_i |\widetilde{\phi}_j\rangle = \delta_{ij}$$

• the pseudo partial waves $|\widetilde{\phi}_k
angle$ obey

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

• with the socalled PAW parameters:

$$\begin{split} Q_{ij} &= \langle \phi_i | \phi_j \rangle - \langle \phi_i | \phi_j \rangle \\ D_{ij} &= \langle \phi_i | -\frac{1}{2} \Delta + v_{\text{eff}} | \phi_j \rangle - \langle \widetilde{\phi}_i | -\frac{1}{2} \Delta + \widetilde{v}_{\text{eff}} | \widetilde{\phi}_j \rangle \end{split}$$

The all-electron and pseudo eigenvalue spectrum is identical, all-electron scattering properties are reproduced over a wide energy range.

1st s-channel: ϵ_1 Mn 4s "bound" state

2nd s-channel: ϵ_2 Mn s "non-bound" state



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Frozen core approximation:

$$\begin{aligned} v_{\text{eff}}[\rho_v] &= v_H[\rho_v] + v_H[\rho_{Zc}] + v_{xc}[\rho_v + \rho_c] \qquad \rho_v(\mathbf{r}) = \sum_i a_i |\phi_i(\mathbf{r})|^2 \\ \widetilde{v}_{\text{eff}}[\widetilde{\rho}_v] &= v_H[\widetilde{\rho}_v] + v_H[\widetilde{\rho}_{Zc}] + v_{xc}[\widetilde{\rho}_v + \widetilde{\rho}_c] \qquad \widetilde{\rho}_v(\mathbf{r}) = \sum_i a_i |\widetilde{\phi}_i(\mathbf{r})|^2 \end{aligned}$$



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 $|\widetilde{\psi}_n
angle$

 $|\widetilde{\psi}_n\rangle$

 $|\widetilde{\psi}_n
angle - \sum_i |\widetilde{\phi}_i
angle \langle \widetilde{p}_i|\widetilde{\psi}_n
angle$



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• Character of wavefunction: $c_{lm\epsilon} = \langle \tilde{p}_{lm\epsilon} | \tilde{\psi}_n \rangle$



- 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

$$E_{\rm kin} = \sum_{n} f_n \langle \psi_n | -\frac{1}{2} \Delta | \psi_n \rangle$$

• By inserting the transformation $(i = lm\epsilon)$

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

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

$$\underbrace{\sum_{\tilde{E}} f_n \langle \tilde{\psi}_n | -\frac{1}{2} \Delta | \tilde{\psi}_n \rangle}_{\tilde{E}} - \underbrace{\sum_{\text{site } (i,j)} \rho_{ij} \langle \tilde{\phi}_i | -\frac{1}{2} \Delta | \tilde{\phi}_j \rangle}_{\tilde{E}^1} + \underbrace{\sum_{\text{site } (i,j)} \rho_{ij} \langle \phi_i | -\frac{1}{2} \Delta | \phi_j \rangle}_{E^1}$$

• ρ_{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

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

 $\bullet~$ For instance the PS operator that corresponds to the density operator $|{\bf r}\rangle\langle{\bf r}|$ is given by

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

and the density

$$\begin{aligned} \langle \psi | \mathbf{r} \rangle \langle \mathbf{r} | \psi \rangle &= \langle \widetilde{\psi} | \mathbf{r} \rangle \langle \mathbf{r} | \widetilde{\psi} \rangle + \sum_{ij} \langle \widetilde{\psi} | \widetilde{p}_i \rangle \left(\langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle - \langle \widetilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \widetilde{\phi}_j \rangle \right) \langle \widetilde{p}_j | \widetilde{\psi} \rangle \\ &= \widetilde{\rho}(\mathbf{r}) - \widetilde{\rho}^1(\mathbf{r}) + \rho^1(\mathbf{r}) \end{aligned}$$

Non-local operators are more complicated

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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 ρ̂ is introduced (similar to FLAPW).



• Hartree energy becomes: $E_H = \tilde{E} - \tilde{E}^1 + E^1$

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

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

PAW energy functional

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

$$\begin{split} \tilde{E} &= \sum_{n} f_{n} \langle \tilde{\psi}_{n} | -\frac{1}{2} \Delta | \tilde{\psi}_{n} \rangle + E_{xc} [\tilde{\rho} + \hat{\rho} + \tilde{\rho}_{c}] + \\ &= E_{H} [\tilde{\rho} + \hat{\rho}] + \int v_{H} [\tilde{\rho}_{Zc}] \left(\tilde{\rho}(\mathbf{r}) + \hat{\rho}(\mathbf{r}) \right) d^{3}\mathbf{r} + U(\mathbf{R}, Z_{\text{ion}}) \\ \tilde{E}^{1} &= \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_{i} | -\frac{1}{2} \Delta | \tilde{\phi}_{j} \rangle + \overline{E_{xc}} [\tilde{\rho}^{1} + \hat{\rho} + \tilde{\rho}_{c}] + \\ &= \overline{E_{H}} [\tilde{\rho}^{1} + \hat{\rho}] + \int_{\Omega_{r}} v_{H} [\tilde{\rho}_{Zc}] \left(\tilde{\rho}^{1}(\mathbf{r}) + \hat{\rho}(\mathbf{r}) \right) d^{3}\mathbf{r} \right\} \\ E^{1} &= \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \phi_{i} | -\frac{1}{2} \Delta | \phi_{j} \rangle + \overline{E_{xc}} [\rho^{1} + \rho_{c}] + \\ &= \overline{E_{H}} [\rho^{1}] + \int_{\Omega_{r}} v_{H} [\rho_{Zc}] \rho^{1}(\mathbf{r}) d^{3}\mathbf{r} \right\} \end{split}$$

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• \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).

 $\begin{array}{ll} \widetilde{\rho} = \sum_n f_n \widetilde{\psi}_n \widetilde{\psi}_n^* & \qquad \mbox{pseudo charge density} \\ \widehat{\rho} & \qquad \mbox{compensation charge} \end{array}$

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

Kohn-Sham energy evaluated for basis sets $\{\widetilde{\phi}_i\}$ 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.

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• The pseudo wave functions $|\widetilde{\psi}_n\rangle$ (plane waves!) are the self-consistent solutions of

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

$$D_{ij} = \langle \phi_i | -\frac{1}{2}\Delta + v_{\text{eff}}^1 [\rho_v^1] | \phi_j \rangle - \langle \widetilde{\phi}_i | -\frac{1}{2}\Delta + \widetilde{v}_{\text{eff}}^1 [\widetilde{\rho}_v^1] | \widetilde{\phi}_j \rangle$$

$$\rho_v^1(\mathbf{r}) = \sum_{ij} \rho_{ij} \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle \qquad \widetilde{\rho}_v^1(\mathbf{r}) = \sum_{ij} \rho_{ij} \langle \widetilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \widetilde{\phi}_j \rangle$$

$$\rho_{ij} = \sum_{n} f_n \langle \widetilde{\psi}_n | \widetilde{p}_i \rangle \langle \widetilde{p}_j | \widetilde{\psi}_n \rangle$$

• 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!

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Accuracy

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



 $|\Delta E_{\rm AE}| < 1$ kcal/mol.

Accuracy

Relative PBE bond lengths of Cl₂, CIF, and HCl for various GTO basis sets specified with respect to plane-wave results:



aug-cc-pVXZ (X= D,T,Q,5) N.B.: aug-cc-pV5Z basis set for CI contains 200 functions!

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$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_{lm\epsilon} \left(|\phi_{lm\epsilon}\rangle - |\phi_{lm\epsilon}\rangle \right) \langle \tilde{p}_{lm\epsilon} |\tilde{\psi}_n\rangle$$

- $|\tilde{\psi}_n\rangle$ 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

$$\Psi(\mathbf{r}_{1},...,\mathbf{r}_{N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{1}(\mathbf{r}_{1}) & \psi_{1}(\mathbf{r}_{1}) & \cdots & \psi_{N}(\mathbf{r}_{1}) \\ \psi_{1}(\mathbf{r}_{2}) & \psi_{2}(\mathbf{r}_{2}) & \cdots & \psi_{N}(\mathbf{r}_{2}) \\ \vdots & \vdots & \vdots \\ \psi_{1}(\mathbf{r}_{N}) & \psi_{2}(\mathbf{r}_{N}) & \cdots & \psi_{N}(\mathbf{r}_{N}) \end{vmatrix}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \Big(\psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2) \psi_2(\mathbf{r}_1) \Big)$$

Pauli exclusion principle: $\Psi(\mathbf{r}_1, \mathbf{r}_2) = 0$ for $\psi_1 = \psi_2$

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

Orbital dependent:

compare to DFT: $V_{\rm xc}[n]({f r})\psi_i({f r})$ $V_X(\mathbf{r},\mathbf{r}') = -\sum_{j}^{N} rac{\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$

No electronic correlation!

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Hybrid functionals: PBE0, HSE03

PBE0:

$$E_{xc}^{\text{PBE0}} = \frac{1}{4}E_x^{\text{HF}} + \frac{3}{4}E_x^{\text{PBE}} + E_c^{\text{PBE}}$$

non-empirical: justified using the adiabatic connection formula. J. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. 105, 9982 (1996).

HSE03:

$$E_{\mathrm{xc}}^{\mathrm{HSE03}} = \frac{1}{4} E_{\mathrm{x}}^{\mathrm{HF,SR}}(\mu) + \frac{3}{4} E_{\mathrm{x}}^{\mathrm{PBE,SR}}(\mu) + E_{\mathrm{x}}^{\mathrm{PBE,LR}}(\mu) + E_{\mathrm{c}}^{\mathrm{PBE}}$$

decomposed Coulomb kernel (Savin et. al.):

$$\frac{1}{r} = S_{\mu}(r) + L_{\mu}(r) = \frac{\operatorname{erfc}(\mu r)}{r} + \frac{\operatorname{erf}(\mu r)}{r}$$

semiempirical: μ is chosen to yield an optimal description of the atomization energies of the molecules in Pople's G2-1 test set.

J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003).

Hybrid functionals: B3LYP

$$\begin{array}{lll} E_{\rm X}^{\rm B3LYP} &=& 0.8 E_{\rm X}^{\rm LDA} + 0.2 E_{\rm X}^{\rm HF} + 0.72 \Delta E_{\rm X}^{\rm B88} \\ E_{\rm C}^{\rm B3LYP} &=& 0.19 E_{\rm C}^{\rm VWN3} + 0.81 E_{\rm C}^{\rm LYP} \end{array}$$

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.

A. D. Becke, J. Chem. Phys. 98, 5648 (1993).

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

Computational aspects

$$E_x^{\rm HF} \propto \sum_{\mathbf{k}n,\mathbf{q}m} \int \int d^3 \mathbf{r} d^3 \mathbf{r}' \psi^*_{\mathbf{k}n}(\mathbf{r}) \psi_{\mathbf{q}m}(\mathbf{r}) K(\mathbf{r},\mathbf{r}') \psi^*_{\mathbf{q}m}(\mathbf{r}') \psi_{\mathbf{k}n}(\mathbf{r}')$$

with

$$K(\mathbf{r}, \mathbf{r}') = rac{1}{|\mathbf{r} - \mathbf{r}'|}$$
 or $rac{\operatorname{erfc}(\mu |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}$

• FFT overlap density to reciprocal space $\rho({\bf G}) = {\rm FFT}\{\psi^*_{{\bf q}m}({\bf r}')\psi_{{\bf k}n}({\bf r}')\}$

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

evaluate

$$\int \psi_{\mathbf{k}n}^*(\mathbf{r})\psi_{\mathbf{q}m}(\mathbf{r})V(\mathbf{r})d^3\mathbf{r}$$

N.B.: for all combinations of ${\bf k},\,{\bf q},\,n,$ and m

$$E_x^{\rm HF} \propto \sum_{\mathbf{k}n,\mathbf{q}m} \int \int d^3 \mathbf{r} d^3 \mathbf{r}' \psi_{\mathbf{k}n}^*(\mathbf{r}) \psi_{\mathbf{q}m}(\mathbf{r}) K(\mathbf{r},\mathbf{r}') \psi_{\mathbf{q}m}^*(\mathbf{r}') \psi_{\mathbf{k}n}(\mathbf{r}')$$

Effort:

$$(N_{\rm bands} \times N_{\rm k})(N_{\rm bands} \times N_{\rm q}) \times N_{\rm FFT} \ln N_{\rm FFT}$$

• Bulk:
$$N_{
m bands} \propto N_{
m atoms}$$
, $N_{
m k} \propto 1/N_{
m atoms}$

$$\Rightarrow N_{\text{FFT}} \ln N_{\text{FFT}} \propto N_{\text{atoms}}$$

• Molecular systems: $N_{\rm k} = 1$

$$\Rightarrow N_{\mathsf{bands}} \times N_{\mathsf{bands}} \times N_{\mathsf{FFT}} \ln N_{\mathsf{FFT}} \propto N_{\mathsf{atoms}}^3$$

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Computational aspects: Downsampling

Convergence of $E_x^{\rm HF}$ w.r.t. the BZ sampling used to represent $V_x^{\rm HF}$



Example: AI (fcc) Short(er) range in real space \implies Reduced BZ sampling

Downsampling cont.



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 $k = 0 \qquad \Rightarrow$

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.

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The HSE Fock exchange energy

$$\begin{split} E_{\mathbf{x}}^{\mathrm{SR}}(\mu) &= -\frac{e^2}{2} \sum_{\mathbf{k}n,\mathbf{q}m} 2w_{\mathbf{k}} 2w_{\mathbf{q}} f_{\mathbf{k}n} f_{\mathbf{q}m} \\ &\times \iint d^3 \mathbf{r} d^3 \mathbf{r}' \frac{\mathrm{erfc}(\mu |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \phi_{\mathbf{k}n}^*(\mathbf{r}) \phi_{\mathbf{q}m}(\mathbf{r}) \phi_{\mathbf{q}m}^*(\mathbf{r}') \phi_{\mathbf{k}n}(\mathbf{r}'). \end{split}$$

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

$$V_{\mathbf{k}}^{\mathrm{SR}}\left(\mathbf{G},\mathbf{G}'\right) = \langle \mathbf{k} + \mathbf{G} | V_{x}^{\mathrm{SR}}[\mu] | \mathbf{k} + \mathbf{G}' \rangle = -\frac{4\pi e^{2}}{\Omega} \sum_{m\mathbf{q}} 2w_{\mathbf{q}} f_{\mathbf{q}m} \sum_{\mathbf{G}''} \frac{C_{\mathbf{q}m}^{*}(\mathbf{G}' - \mathbf{G}'')C_{\mathbf{q}m}(\mathbf{G} - \mathbf{G}'')}{|\mathbf{k} - \mathbf{q} + \mathbf{G}''|^{2}} \times \left(1 - e^{-|\mathbf{k} - \mathbf{q} + \mathbf{G}''|^{2}/4\mu^{2}}\right).$$

Full q-grid:

$$\{\mathbf{q}\} = \{\frac{m_1}{N_1}\mathbf{b}_1 + \frac{m_2}{N_2}\mathbf{b}_2 + \frac{m_3}{N_3}\mathbf{b}_3 | m_i = 0, ..., N_i - 1\}$$

Downsampled q-grid:

$$\{\mathbf{q}\}_{\mathbf{k}} = \{\mathbf{k} + \sum_{i=1}^{3} m_i \frac{C_i}{N_i} \mathbf{b}_i | m_i = 0, \dots, \frac{N_i}{C_i} - 1\}$$

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]

	Μ	IE	MAE		
	PAW	GTO	PAW	GTO	
PBE	+6.43	+6.85	8.57	8.79	
PBE0	-1.47	-1.04	3.65	3.42	
PBE	-0.42		0.46		
PBE0	-0.42		0.49		

- PAW calculations: Γ only, 10×11×12 Å³, 1000 eV cutoff
- GTO calculations: aug-cc-pV5Z basis set

J. Paier, R. Hirschl, M. Marsman, and G. Kresse, J. Chem. Phys. 122, 234102 (2005).

Solid state systems

Set of test systems

- Metals: Na, Mg, Li, Al, Cu, Rh, Pd, Ag
- 'Small' gap: Si, GaAs, BP, GaP, SiC, β -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

Solid state systems: PBE



- 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.

J. Heyd and G. E. Scuseria, J. Chem. Phys. 121, 1187 (2004).
 J. Paier, et al., J. Chem. Phys. 124, 154709 (2006).

Solid state systems: PBE, PBE0, and HSE03

Lattice constants and bulk moduli

Solid		PBE	Н	ISE03	F	PBE0		Exp.
	a_0	B	a_0	B	a_0	B	a_0	B
С	3.574	431	3.550	466	3.549	467	3.567	443
Si	5.469	87.8	5.439	96.5	5.433	99.0	5.430	99.2
GaAs	5.752	59.9	5.696	69.5	5.672	72.9	5.648	75.6
MgO	4.258	149	4.212	168	4.211	169	4.207	165
Na	4.200	7.80	4.225	8.45	4.229	8.22	4.225	7.50
AI	4.040	76.6	4.025	81.1	4.012	86.0	4.032	79.4
Rh	3.830	254	3.786	285	3.785	291	3.798	269
				•••				
All systems:								
ME	0.039	-12.3	0.012	-2.6	0.007	-0.1		
MAE	0.045	12.4	0.024	8.6	0.022	7.9		
No metals:								
ME	0.048	-13.4	0.010	0.4	0.003	1.9		
MAE	0.048	13.4	0.022	5.7	0.019	5.4		
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Values given in Å and GPa, respectively.

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PBE, PBE0, HSE03, B3LYP: lattice constants



Relative error in the PBE, PBE0, HSE03, and B3LYP lattice constants with respect to experiment.

Solid state systems: band gaps



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Solid state systems: Atomization energies



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- Hybrid functionals overestimate the exchange splitting in *d*-elements: leads to an increased stability of the spin-polarized atom.
- B3LYP overestimates $E_{\rm xc}$ of localized electrons.
- B3LYP fails to describe 'free electron like' behaviour: LYP underestimates correlation energy in itinerant systems (does not attain HEG limit!).

J. Paier, M. Marsman, and G. Kresse, J. Chem. Phys. 127, 024103 (2007).

Heats of formation



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

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Transition metal monoxides: MnO





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C. Franchini, V. Bayer, R. Podloucky, J. Paier, and G. Kresse, Phys. Rev. B 72, 045132 (2005).

Transition metal monoxides cont.

		a_0 (Å)	M_s ($\mu_{ m B}$)	Δ (eV)
MnO	LDA	4.31	4.14	0.4
	HSE03	4.44	4.52	2.8
	exp.	4.45	4.58	3.9
FeO	LDA	4.17	3.26	-
	HSE03	4.33	3.63	2.2
	exp.	4.33	3.32/4.2	2.4
CoO	LDA	4.10	2.23	-
	HSE03	4.26	2.67	3.4
	exp.	4.25	3.35/4.0	2.5
N:O		4.00	1.00	0.4
NIO	LDA	4.06	1.06	0.4
	HSE03	4.18	1.65	4.2
	exp.	4.17	1.64	4.0

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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:

• 4 layers, $c(2 \times 4)$, $\Theta = 0.25$ ML, asymmetric setup, 10Å vacuum.



CO adsorption on d-metal surfaces cont. I

CO @		top	fcc	hcp	Δ
Cu(111)	PBE	0.709	0.874	0.862	-0.165
	PBE0	0.606	0.579	0.565	0.027
	HSE03	0.561	0.555	0.535	0.006
	exp.	0.46-0.52			
Rh(111)	PBE	1.870	1.906	1.969	-0.099
	PBE0	2.109	2.024	2.104	0.005
	HSE03	2.012	1.913	1.996	0.016
	exp.	1.43-1.65			
Pt(111)	PBE	1.659	1.816	1.750	-0.157
	PBE0	1.941	1.997	1.944	-0.056
	HSE03	1.793	1.862	1.808	-0.069
	exp.	1.43-1.71			

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CO adsorption on d-metal surfaces cont. II

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.

A. Stroppa, K. Termentzidis, J. Paier, G. Kresse, J. Hafner, Phys. Rev. B 76, 195440 (2007). A. Stroppa and G. Kresse. New Journal of Physics 10, 063020 (2008).

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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.

Conclusions cont.

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 funtionals 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 Specicifies 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.

 $\label{eq:pbergenergy} \begin{array}{l} \mbox{PBE0: LHFCALC} = .TRUE. \\ \mbox{HSE06:}^{\dagger} \mbox{ LHFCALC} = .TRUE. ; \\ \mbox{HSCREEN} = 0.2 \mbox{ (with PBE POTCAR, or GGA = PE)}. \\ \mbox{B3LYP: LHFCALC} = .TRUE. ; \\ \mbox{GGA} = B3 \mbox{ ; } \\ \mbox{AEXX} = 0.2 \mbox{ ; } \\ \mbox{AGGAX} = 0.72 \mbox{ ; } \\ \mbox{AGGAC} = 0.81 \mbox{ ; } \\ \mbox{ALDAC} = 0.19 \\ \mbox{Hartree-Fock: LHFCALC} = .TRUE. ; \\ \mbox{AEXX} = 1.0 \mbox{ ; } \\ \mbox{ALDAC} = 0.0 \mbox{ ; } \\ \mbox{AGGAC} = 0 \\ \mbox{AGGAC} = 0 \\ \end{array}$

[†]A. V. Krukau , O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. 125, 224106 (2006).

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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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PBEsol

PRL 100, 136406 (2008)

PHYSICAL REVIEW LETTERS

week ending 4 APRIL 2008

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

John P. Perdew,¹ Adrienn Ruzsinszky,¹ Gábor I. Csonka,² Oleg A. Vydrov,³ Gustavo E. Scuseria,³ Lucian A. Constantin,⁴ Xiaolan Zhou,¹ and Kieron Burke⁵

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

Lattice constants

CSONKA et al.

PHYSICAL REVIEW B 79, 155107 (2009)

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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 are form Ref. 14. The SOGGA GTO1 results are from Ref. 15.

	LDA	LDA	PBEsol	PBEsol	PBEsol	AM05	SOGGA	PBE	PBE	PBE	TPSS
	GTO2	VASP	GTO2	BAND	VASP	VASP	GTO1	GTO2	VASP	BAND	BAND
ME ^a (Å)	-0.047	-0.055	0.022	0.010	0.012	0.029	0.009	0.075	0.066	0.063	0.048
MAE ^b (Å)	0.050	0.050	0.030	0.023	0.023	0.036	0.024	0.076	0.069	0.067	0.052
MRE ^c (%)	-1.07	-1.29	0.45	0.19	0.24	0.58	0.19	1.62	1.42	1.35	0.99
MARE ^d (%)	1.10	1.15	0.67	0.52	0.52	0.80	0.50	1.65	1.48	1.45	1.10

TAGS and links

INCAR tags

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

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Electronic optimization

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

$$\label{eq:Gradient:} {\rm \ } F_n({\bf r}) = \left(-\frac{\hbar^2}{2m_e}\nabla^2 + V^{\rm eff}({\bf r},\{\psi_n({\bf r}')\}) - \epsilon_n\right)\psi_n({\bf r})$$

The Self Consistency Cycle (old fashioned)

Start with a trial density $\rho,$ set up the Schrödinger equation, and solve it to obtain wavefunctions $\psi_n({\bf r})$

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V^{\text{eff}}(\mathbf{r}, \{\rho(\mathbf{r}')\})\right)\psi_n(\mathbf{r}) = \epsilon_n\psi_n(\mathbf{r}) \qquad n = 1, ..., N_e/2$$

as a result one obtains a new charge density $\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2$ and a new Schrödinger equation \Rightarrow iteration

Direct mimization vs. SCC



G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).

Direct optimization (charge sloshing)

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

$$\begin{split} |g_n\rangle &= f_n \Big(1 - \sum_m |\psi_m\rangle \langle \psi_m| \Big) \hat{H} |\psi_n\rangle + \sum_m \frac{1}{2} \mathbf{H}_{nm} (f_n - f_m) |\psi_m\rangle \\ \text{where } \mathbf{H}_{nm} &= \langle \psi_m | \hat{H} | \psi_n \rangle. \\ \text{Consider two states} \\ \psi_n &= e^{i(\mathbf{k}_F - \delta \mathbf{k})\mathbf{r}} \quad \psi_m = e^{i(\mathbf{k}_F + \delta \mathbf{k})\mathbf{r}} \\ \psi'_n &= \psi_n + \Delta s \psi_m \quad \psi'_m = \psi_m - \Delta s \psi_n \\ \delta \rho(\mathbf{r}) &= 2\Delta s \operatorname{Re} e^{i2\delta \mathbf{k} \cdot \mathbf{r}} \quad \delta V_{\mathrm{H}}(\mathbf{r}) = \frac{2\Delta s 4\pi e^2}{|2\delta \mathbf{k}|^2} \operatorname{Re} e^{i2\delta \mathbf{k} \cdot \mathbf{r}} \end{split}$$

The smallest $|\delta \mathbf{k}| \propto 1/L$ where L is the largest dimension of the supercell. \Rightarrow the response of the potential $\delta V_{\rm H} \propto L^2 \Rightarrow$ 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

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

Self-consistency

$$\rho_0 \to \mathbf{H}_0 \to \rho' \to \rho_1 = f(\rho_0, \rho') \to \mathbf{H}_1 \to \dots$$

iterate until $\rho = \rho'$

BUT: we do not need $N_{\rm FFT}$ one-electron orbitals, at a cost of $\mathcal{O}(N_{\rm FFT}^3)$... we only need the N_b lowest eigenvectors of \mathbf{H}

 \Rightarrow Iterative diagonalization of H aimed at finding its N_b lowest eigenvectors ($N_b \approx N_{\rm el}/{\rm cell}$).

Blocked Davidson algorithm, RMM-DIIS, ...

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The Self-Consistency Cycle



Key ingredients: Subspace diagonalization and the Residual

• Rayleigh-Ritz: the diagonalization of the $N_b \times N_b$ subspace

$$\sum_{m} \bar{H}_{nm} B_{mk} = \sum_{m} \epsilon_k^{\text{app}} \bar{S}_{nm} B_{mk}$$

with

 $\bar{H}_{nm} = \langle \psi_n | \hat{H} | \psi_m \rangle$ and $\bar{S}_{nm} = \langle \psi_n | \hat{S} | \psi_m \rangle$

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

The residual vector:

$$|R(\psi_n)\rangle = (\hat{H} - \epsilon_{\rm app}\hat{S})|\psi_n\rangle, \quad \text{with } \epsilon_{\rm app} = \frac{\langle\psi_n|\hat{H}|\psi_n\rangle}{\langle\psi_n|\hat{S}|\psi_n\rangle}$$

(its norm is a measure of the error in the eigenvector).

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The blocked Davidson algorithm

- Take a subset of all bands $\{\psi_n | n = 1, .., N\} \Rightarrow \{\psi_k^1 | k = 1, .., n_1\}$
 - Extend this subset by adding the (preconditioned) residual vectors to the presently considered subspace

$$\{\psi_k^1/g_k^1 = \mathbf{K}(\mathbf{H} - \epsilon_{\mathrm{app}}\mathbf{S})\psi_k^1 | k = 1, .., n_1\}$$

- Raighley-Ritz optimization ("sub-space" rotation) in the 2n₁ dimensional subspace {ψ_k¹/g_k¹} to determine the n₁ lowest eigenvectors {ψ_k²|k = 1, ..., n₁}.
- Extend the subspace with the residuals from $\{\psi_k^2\}$ $\{\psi_k^1/g_k^1/g_k^2 = \mathbf{K}(\mathbf{H} \epsilon_{\mathrm{app}}\mathbf{S})\psi_k^2 | k = 1,..,n_1\}$

• Raighley-Ritz optimization
$$\Rightarrow \{\psi_k^3 | k = 1, .., n_1\}$$

- etc ...
- The optimized $\{\psi_k^m | k=1,..,n_1\}$ replace $\{\psi_n | n=1,..,n_1\}$
- Move on to subset $\{\psi_k^1|k=n_1+1,..,n_2\}$, ..., etc, ...

After treating all bands: Raighley-Ritz optimization of $\{\psi_n | n = 1, .., N\}$

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Charge density mixing (RMM-DIIS)

Minimization of the norm of residual vector

$$R[\rho_{\rm in}] = \rho_{\rm out}[\rho_{\rm in}] - \rho_{\rm in} \qquad |R[\rho_{\rm in}]| \Rightarrow \min$$

with $\rho_{\rm out}(\vec{r}) = \sum_{\rm occupied} w_k f_{nk} |\psi_{nk}(\vec{r})|^2$
DIIS algorithm is used for the optimization of the norm of the residual vector.

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

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

with the charge dielectric function ${\bf J}$

$$\mathbf{J} = \mathbf{1} - \chi \underbrace{\mathbf{U}}_{\frac{4\pi \mathbf{e}^2}{\mathbf{q}^2}}$$

leads to

$$R[\rho_{\rm in}] = \rho_{\rm out}[\rho_{\rm in}] - \rho_{\rm in} = \mathbf{J}(\rho_{\rm in} - \rho_{\rm sc})$$

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Divergence of the dielectric function

Eigenvalue spectrum of ${\bf J}$ determines convergence

$$\mathbf{J} = \mathbf{1} - \chi \underbrace{\mathbf{U}}_{\frac{4\pi\mathbf{e}^2}{\mathbf{q}^2}}$$

"Broader" eigenvalue spectrum \Rightarrow slower convergence

- For insulators and semi-conductors, the width of the eigenvalue spectrum is constant and system size independent (ε_∞)!
- For metals the eigenvalue spectrum diverges, its width is proportional to the square of the longest dimension of the cell:
 - Short wavelength limit $\mathbf{J} pprox \mathbf{1}$ (no screening)
 - Long wavelength limit $J\approx 1/q^2\propto L^2$ (metallic screening)

Complete screening in metals causes charge sloshing

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The dielectric matrix



$$\mathbf{J}^{-1} \approx \mathbf{G}_q^1 = \max(\frac{q^2 \mathrm{AMIX}}{q^2 + \mathrm{BMIX}}, \mathrm{AMIN})$$



• 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).

Return to direct optimization: Why?

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

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

with $\mathbf{H}_{nm} = \langle \psi_m | \hat{H} | \psi_n
angle$

• 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

$$\mathbf{U}_{nm} = \delta_{nm} - \Delta s \frac{\mathbf{H}_{nm}}{\mathbf{H}_{mm} - \mathbf{H}_{nn}}$$

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}.

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Optimal subspace rotation

- Define a Hamilton matrix $\bar{\mathbf{H}}_{kl} = \langle \psi_l | \bar{H}[\rho] | \psi_k \rangle$ where $\bar{H}[\rho] = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{eff}}[\rho] + \hat{V}_{\text{X}}^{\text{nl}}[\{\psi\}, \{f\}]$
- Determine the subspace rotation matrix ${\bf V}$ that diagonalizes $\bar{{\bf H}}_{kl}$
- Recompute the (partial) occupancies $\rightarrow \{f'\}$
- The transformed orbitals $\sum_l V_{nl} \psi_l$ and partial occupancies $\{f'\}$ define a new charge density ρ'
- mix ρ and ρ'
- ${\ensuremath{\, \bullet}}$ and iterate the above until a stable point is found $\rightarrow \rho_{\rm sc}$
- $\mathbf{H}_{nm}^{\mathrm{sc}} = \langle \psi_m | \bar{H}[\rho_{\mathrm{sc}}] | \psi_n \rangle$ defines the optimal subspace rotation

$$\mathbf{U}_{nm} = \delta_{nm} - \Delta s \frac{\mathbf{H}_{nm}^{\rm sc}}{\mathbf{H}_{mm}^{\rm sc} - \mathbf{H}_{nn}^{\rm sc}}$$

• N.B.: we do not update the orbital dependent part of the Hamiltonian $\hat{V}^{nl}_{\rm X}[\{\psi\},\{f\}]$

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The full mixed scheme

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

- construct the Hamiltonian, H, from the current wavefunctions and partial occupancies, and calculate $H|\psi\rangle$;
- inner loop: determine the self-consistent Hamiltonian, H^{sc}, defining the preconditioned direction for the subspace rotation U.
- 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 $\Delta E_{\rm thr}$ (usually 10^{-4} eV).

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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 (\bigcirc), diamonds (\diamondsuit), squares (\Box), and triangles (\triangle), respectively.

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TAGS and links

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 =AII | Damped) LDIAG = .TRUE. swithches 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).

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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

$$\langle r|\hat{v}_X|\phi_i
angle\propto\sum_a^{\mathrm{at.ref}}\phi_a(\mathbf{r})\intrac{\phi_a^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$

 \implies 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: $|\phi_i\rangle \rightarrow |\phi'_i\rangle$.
 - \bullet compute the PAW parameters using $|\phi_i'\rangle$ and Hartree-Fock core states:

$$D_{ij} = \langle \phi'_i | -\frac{1}{2}\Delta + v_H^1[\rho_v^1] + v_H^1[\rho_{Zc}^{\rm HF}] + v_X^1[\{\rho_{ij}\}] + v_X^{\rm c-v}[\{\phi_c^{\rm HF}\}] |\phi'_j\rangle - \langle \tilde{\phi}_i | -\frac{1}{2}\Delta + v_H^1[\tilde{\rho}_v^1] + v_H^1[\tilde{\rho}_{Zc}] + \tilde{v}_X^1[\{\rho_{ij}\}] |\tilde{\phi}_j\rangle$$

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

The most important step is in this scheme: $v_H^1[\rho_{Zc}^{\text{DFT}}] \rightarrow v_H^1[\rho_{Zc}^{\text{HF}}]$.

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The HF-PAW method (cont.)

			volumes			
Valence electrons		GaAs: Ω_0 (Å ³)		Valence electrons	Si: Ω ₀ (Å ³)	
04	A3	1700	111-1740	Si	PAW	HF-PAW
$4s^24p^1$ $3d^{10}4s^24p^1$ $2r^62d^{10}4r^2$	$4s^{2}4p^{3}$ $4s^{2}4p^{3}$ $4s^{1}$ $2s^{10}4s^{2}4s^{3}$	46.06 47.07	48.79 47.80	$\frac{3s^2 3p^2}{2s^2 2p^6 3s^2 3p^2}$	41.44 41.91	41.86 41.93

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

	$3s^2$	$^{2}3p^{2}$	$2s^22p^6$	HF ref.	
	PAW	HF-PAW	PAW	HF-PAW	
3s	-15.967	-15.918	-15.895	-15.908	-15.906
3p	-2.761	-2.756	-2.749	-2.756	-2.760
Δ	-13.205	-13.161	-13.146	-13.151	-13.147

All energies in eV.

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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)

$$\psi_n(\mathbf{r}) \neq \sum_i \phi_i(\mathbf{r}) \langle \widetilde{p}_i | \widetilde{\psi}_n \rangle \qquad \widetilde{\psi}_n(\mathbf{r}) \neq \sum_i \widetilde{\phi}_i(\mathbf{r}) \langle \widetilde{p}_i | \widetilde{\psi}_n \rangle$$

This causes problems for at least two reasons:

- 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 $v_H^1[\rho_{Zc}^{\text{DFT}}] \rightarrow v_H^1[\rho_{Zc}^{\text{HF}}]$ and leave $v_H^1[\tilde{\rho}_{Zc}]$ fixed.

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The HF-PAW method (cont.)

$$\begin{split} |\widetilde{\psi}_{n}(\mathbf{r})|^{2} \neq \sum_{ij} \langle \widetilde{\psi}_{n} | \widetilde{p}_{i} \rangle \langle \widetilde{\phi}_{i} | \mathbf{r} \rangle \langle \mathbf{r} | \widetilde{\phi}_{j} \rangle \langle \widetilde{p}_{j} | \widetilde{\psi}_{n} \rangle \\ \widetilde{\rho} \neq \widetilde{\rho}^{1} \end{split}$$



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The HF-PAW method (cont.)

$$\begin{split} |\widetilde{\psi}_{n}(\mathbf{r})|^{2} \neq \sum_{ij} \langle \widetilde{\psi}_{n} | \widetilde{p}_{i} \rangle \langle \widetilde{\phi}_{i} | \mathbf{r} \rangle \langle \mathbf{r} | \widetilde{\phi}_{j} \rangle \langle \widetilde{p}_{j} | \widetilde{\psi}_{n} \rangle & \begin{array}{c} 0.10 \\ 0.06 \\ 0.04 \\ 0.02 \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.01 \\ 0.10 \\ 0.00 \\$$

$$\begin{split} \sum_{ij} \langle \widetilde{\psi}_n | \widetilde{p}_i \rangle \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle \langle \widetilde{p}_j | \widetilde{\psi}_n \rangle \neq | \phi_{\rm HF}^{\rm ref}(\mathbf{r}) |^2 \\ \rho^1 \neq \rho_{\rm HF}^1 \end{split}$$

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The HF-PAW method (cont.)

$$\begin{split} |\widetilde{\psi}_n(\mathbf{r})|^2 \neq \sum_{ij} \langle \widetilde{\psi}_n | \widetilde{p}_i \rangle \langle \widetilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \widetilde{\phi}_j \rangle \langle \widetilde{p}_j | \widetilde{\psi}_n \rangle \\ \widetilde{\rho} \neq \widetilde{\rho}^1 \end{split}$$

$$\frac{\sum_{ij} \langle \widetilde{\psi}_n | \widetilde{p}_i \rangle \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle \langle \widetilde{p}_j | \widetilde{\psi}_n \rangle \neq |\phi_{\rm HF}^{\rm ref}(\mathbf{r})|^2}{\rho^1 \neq \rho_{\rm HF}^1}$$

$$\widetilde{\rho} - \widetilde{\rho}^1 + \rho^1 \approx \rho_{\rm HF}^1$$



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TAGS and links

INCAR tags

LRHFATM = .TRUE. Changes the DFT AE core charge density (ρ^1) to a Hartree-Fock one.



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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

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Some literature

Hybrid functionals in VASP

"The Perdew-Burke-Ernzerhof exchange-correlation functional applied to the G2-1 test set using a plane-wave basis set", J. Paier, R. Hirschl, M. Marsman, and G. Kresse, J. Chem. Phys. 122, 234102 (2005).

"Screened hybrid density functionals applied to solids", J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber, and J. G. Ángyán, J. Chem. Phys. 124, 154709 (2006); Erratum to the previous, J. Chem. Phys. 125, 249901 (2006).

"Why does the B3LYP hybrid functional fail for metals", J. Paier, M. Marsman, and G. Kresse, J. Chem. Phys. 127, 024103 (2007).

"Hybrid functionals applied to extended systems", M. Marsman, J. Paier, A. Stroppa, and G. Kresse, J. Phys.: Condens. Matter 20, 064201 (2008).

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