

Basics of Density Functional Theory (DFT)

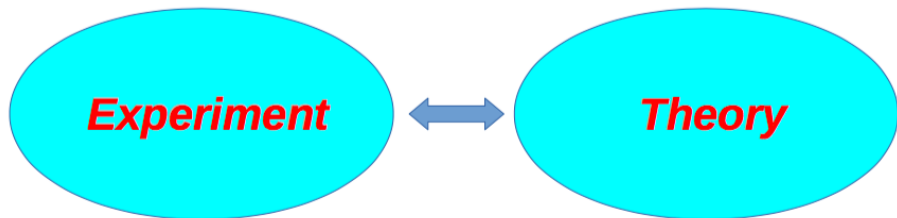
Ari Paavo SEITSONEN

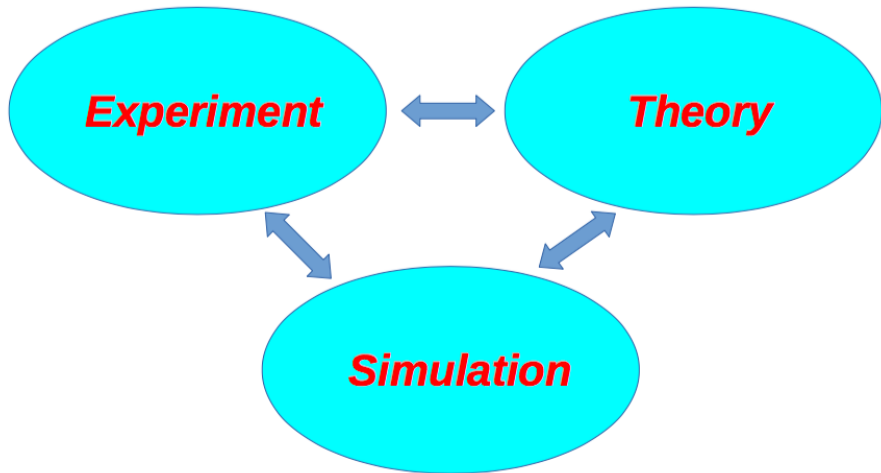
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École de Sidi-BelAbbès de Nanomateriaux // Octobre 8-12, 2016







Summary

- 1 Density functional theory
 - Motivation
 - Kohn-Sham method
 - Exchange-correlation functional
- 2 Bloch theorem / supercells
- 3 Localised basis sets
- 4 Plane wave basis set
- 5 Pseudo potentials

Motivation: Why use DFT?

- Explicit inclusion of electronic structure
 - ▶ Predictable accuracy (unlike fitted/empirical approaches)
 - ▶ Knowledge of the electron structure can be used for the analysis; many observables can be obtained directly
- Preferable scaling compared to many quantum chemistry methods

History of DFT — I

- There were already methods in the early 20th century
 - ▶ Thomas-Fermi-method
 - ▶ Hartree-Fock-method

History of DFT — II

Walter Kohn



History of DFT — III: Foundations

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†

École Normale Supérieure, Paris, France

AND

W. KOHN‡

École Normale Supérieure, Paris, France and Faculté des Sciences, Orsay, France

and

University of California at San Diego, La Jolla, California

(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \bar{n}(\mathbf{r})$, $\bar{n}/n_0 \ll 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \rightarrow \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

Hohenberg-Kohn theorems: Theorem I

- Given a potential, one obtains the wave functions via Schrödinger equation:

$$V(\mathbf{r}) \Rightarrow \psi_i(\mathbf{r})$$

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Thus

$$V(\mathbf{r}) \Rightarrow \psi_i(\mathbf{r}) \Rightarrow n(\mathbf{r})$$

Hohenberg-Kohn theorems: Theorem I

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The potential, and hence also the total energy, is a unique functional of the electron density $n(\mathbf{r})$

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Thus

$$V(\mathbf{r}) \Rightarrow \psi_i(\mathbf{r}) \Rightarrow n(\mathbf{r}) \Rightarrow V(\mathbf{r})$$

The electron density can be used to determine all properties of a system

Hohenberg-Kohn theorems: Theorem II

Theorem

The total energy is variational: In the ground state the total energy is minimised

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Thus

$$E[n] \geq E[n_{\text{GS}}]$$

History of DFT — IV: Foundations

PHYSICAL REVIEW

VOLUME 140, NUMBER 4A

15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM

University of California, San Diego, La Jolla, California

(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

History of DFT — V: The reward

... in 1998:



Kohn-Sham method: Total energy

Let us write the total energy as:

$$E_{\text{tot}}[n] = E_{\text{kin}}[n] + E_{\text{ext}}[n] + E_{\text{H}}[n] + E_{\text{xc}}[n]$$

- $E_{\text{kin}}[n]$ = *QM* kinetic energy of electrons
- $E_{\text{ext}}[n]$ = energy due to external potential (usually ions)
- $E_{\text{H}}[n]$ = classical Hartree repulsion ($e^- - e^-$)
- $E_{\text{xc}}[n]$ = exchange-correlation energy

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To solve the many-body Schrödinger equation as such is an unformidable task

Kohn-Sham method: Noninteracting electrons

To solve the many-body Schrödinger equation as such is an unformidable task

- Let us write the many-body wave function as a determinant of single-particle equations
- Then kinetic energy of electrons becomes

$$E_{\text{kin,s}} = \sum_i -\frac{1}{2} f_i \langle \psi_i(\mathbf{r}) | \nabla^2 | \psi_i(\mathbf{r}) \rangle$$

f_i = occupation of orbital i (with spin-degeneracy included)

Kohn-Sham method: External energy

- Energy due to external potential; usually $V_{\text{ext}} = \sum_I -\frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}$

$$E_{\text{ext}} = \int_{\mathbf{r}} n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$
$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

Kohn-Sham method: Hartree energy

- Classical electron-electron repulsion

$$\begin{aligned}
 E_{\text{H}} &= \frac{1}{2} \int_{\mathbf{r}} \int_{\mathbf{r}'} \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} \\
 &= \frac{1}{2} \int_{\mathbf{r}} n(\mathbf{r}) V_{\text{H}}(\mathbf{r}) d\mathbf{r}
 \end{aligned}$$

$$V_{\text{H}}(\mathbf{r}) = \int_{\mathbf{r}'} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

Kohn-Sham method: Exchange-correlation energy

- The remaining component: Many-body complications combined

⇒ Will be discussed later

Total energy expression

Kohn-Sham (total¹) energy:

$$\begin{aligned}
 E_{\text{KS}}[n] &= \sum_i -\frac{1}{2} f_i \langle \psi_i | \nabla^2 | \psi_i \rangle + \int_{\mathbf{r}} n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \\
 &+ \frac{1}{2} \int_{\mathbf{r}} \int_{\mathbf{r}'} \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + E_{\text{xc}}
 \end{aligned}$$

¹without ion-ion interaction

Kohn-Sham equations

Vary the Kohn-Sham energy E_{KS} with respect to $\psi_j^*(\mathbf{r}'')$: $\frac{\delta E_{\text{KS}}}{\delta \psi_j^*(\mathbf{r}'')}$

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⇒ Kohn-Sham equations

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\text{KS}}(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$$

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}$$

Kohn-Sham equations: Notes

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\text{KS}}(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad ; \quad n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

- Equation looking like Schrödinger equation
- The Kohn-Sham potential, however, depends on density
- The equations are coupled and highly non-linear
- \Rightarrow Self-consistent solution required
- ε_i and ψ_i are in principle only help variables (only $\varepsilon_{\text{HOMO}}$ has a meaning)
- The potential V_{KS} is local
- The scheme is in principle exact

Kohn-Sham equations: Self-consistency

- 1 Generate a starting density n^{init}
- 2 Generate the Kohn-Sham potential $\Rightarrow V_{\text{KS}}^{\text{init}}$
- 3 Solve the Kohn-Sham equations $\Rightarrow \psi_i^{\text{init}}$
- 4 New density n^1
- 5 Kohn-Sham potential V_{KS}^1
- 6 Kohn-Sham orbitals $\Rightarrow \psi_i^1$
- 7 Density n^2
- 8 ...

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... until self-consistency is achieved (to required precision)

Kohn-Sham equations: Self-consistency

- Usually the density coming out from the wave functions is mixed with the previous ones, in order to improve convergence
- In metals fractional occupations numbers are necessary
- The required accuracy in self-consistency depends on the observable and the expected

Kohn-Sham energy: Alternative expression

- Take the Kohn-Sham equation, multiply from the left with $f_i \psi_i^*$ and integrate:

$$-\frac{1}{2} f_i \int_{\mathbf{r}} \psi_i(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r} + f_i \int_{\mathbf{r}} V_{\text{KS}}(\mathbf{r}) |\psi_i(\mathbf{r})|^2 d\mathbf{r} = f_i \varepsilon_i$$

- Sum over i and substitute into the expression for Kohn-Sham energy:

$$E_{\text{KS}}[n] = \sum_i f_i \varepsilon_i - E_{\text{H}} + E_{\text{xc}} - \int_{\mathbf{r}} n(\mathbf{r}) V_{\text{xc}} d\mathbf{r}$$

Exchange-correlation functional

- The Kohn-Sham scheme is in principle *exact* — however, the exchange-correlation energy functional is not known explicitly
- Exchange *is* known exactly, however its evaluation is usually very time-consuming, and often the accuracy is not improved over simpler approximations (due to error-cancellations in the latter group)
- Many exact properties, like high/low-density limits, scaling rules *etc* are known
- Famous approximations:
 - ▶ Local density approximation, LDA
 - ▶ Generalised gradient approximations, GGA
 - ▶ Hybrid functionals
 - ▶ ...

Kohn-Sham method: Exchange-correlation energy

- The remaining component: Many-body complications combined

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Vary the Kohn-Sham energy E_{KS} with respect to $\psi_j^*(\mathbf{r}'')$: $\frac{\delta E_{\text{KS}}}{\delta \psi_j^*(\mathbf{r}'')}$

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Exchange-correlation functional: LDA

Local density approximation:

- Use the exchange-correlation energy functional for homogeneous electron gas at each point of space: $E_{xc} \simeq \int_{\mathbf{r}} n(\mathbf{r}) e_{xc}^{\text{heg}}[n(\mathbf{r})] d\mathbf{r}$
- Works surprisingly well even in inhomogeneous electron systems, thanks fulfillment of certain sum rules
 - ▶ Energy differences over-bound: Cohesion, dissociation, adsorption energies
 - ▶ Lattice constants somewhat (1-3 %) too small, bulk moduli too large
 - ▶ Asymptotic potential decays exponentially outside charge distribution, leads to too weak binding energies for the electrons, eg. ionisation potentials
 - ▶ Contains self-interaction in single-particle case

Exchange-correlation functional: GGA

Generalised gradient approximation:

- The gradient expansion of the exchange-correlation energy does not improve results; sometimes leads to divergencies
- Thus a more general approach is taken, and there is room for several forms of GGA: $E_{xc} \simeq \int_{\mathbf{r}} n(\mathbf{r}) e_{xc}[n(\mathbf{r}), |\nabla n(\mathbf{r})|^2] d\mathbf{r}$
- Works reasonably well, again fulfilling certain sum rules
 - ▶ Energy differences are improved
 - ▶ Lattice constants somewhat, 1-3 % too large, bulk moduli too small
 - ▶ Contains self-interaction in single-particle case
 - ▶ Again exponential asymptotic decay in potential
 - ▶ \Rightarrow Negative ions normally not bound
 - ▶ Usually the best compromise between speed and accuracy in large systems

Exchange-correlation functional: Hybrid functionals

Hybrid functionals

- Include partially the exact (Hartree-Fock) exchange:

$$E_{xc} \simeq \alpha E_{HF} + (1 - \alpha) E_x^{GGA} + E_c^{GGA}; \text{ again many variants}$$

- Works in general well
 - ▶ Energy differences are still improved
 - ▶ Vibrational properties slightly
 - ▶ Improved magnetic moments in some systems
 - ▶ Partial improvement in asymptotic form
 - ▶ Usually the best accuracy if the computation burden can be handled
 - ▶ Calculations for crystals appearing

Exchange-correlation functional: Observations

- The accuracy can not be systematically improved!
- van der Waals interactions still a problem (tailored approximations in sight)
- Most widely used parametrisations:
 - ▶ GGA
 - ★ Perdew-Burke-Ernzerhof, PBE (1996); among phycisists
 - ★ Beck-Lee-Yang-Parr, BLYP (early 1990's); among chemists
 - ▶ Hybrid functionals
 - ★ PBE0; among phycisists
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 - ★ DFT-D3; empirical (pair-)potential
 - ★ vdW-DF*; rVV10?

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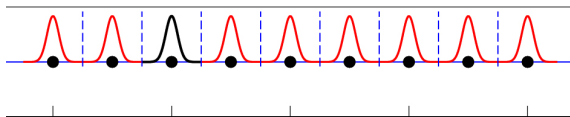
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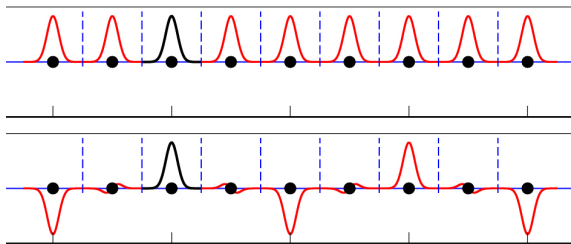
Periodic systems

- In realistic systems there are $\approx 10^{20}$ atoms in cubic millimetre — unformidable to treat by any numerical method
- At this scale the systems are often repeating (crystals)
- . . . or the observable is localised and the system can be made periodic
- Choices: Periodic boundary conditions or isolated (saturated) cluster

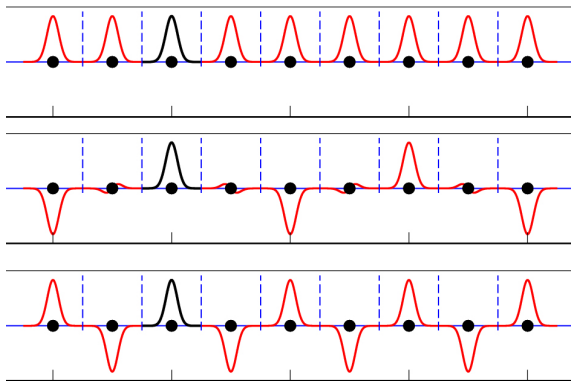
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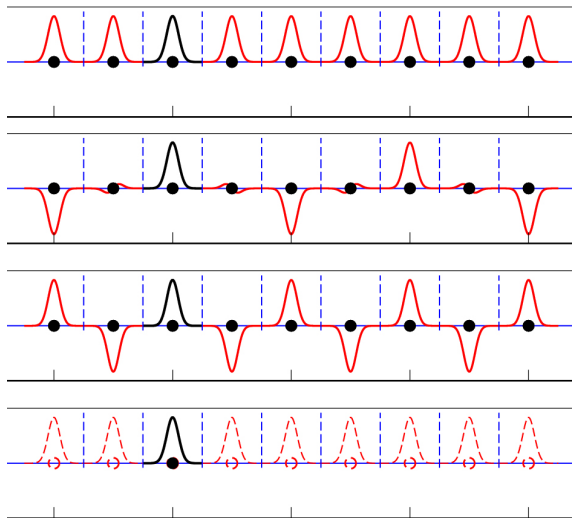
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Periodic systems

Is it possible to replace the summation over translations \mathbf{L} with a modulation?

Periodic systems

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Bloch's theorem

For a periodic potential $V(\mathbf{r} + \mathbf{L}) = V(\mathbf{r})$ the eigenfunctions can be written in the form

$$\psi_i(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{i\mathbf{k}}(\mathbf{r}) ,$$

$$u_{i\mathbf{k}}(\mathbf{r} + \mathbf{L}) = u_{i\mathbf{k}}(\mathbf{r})$$

Periodic systems: Reciprocal space

Reciprocal lattice vectors:

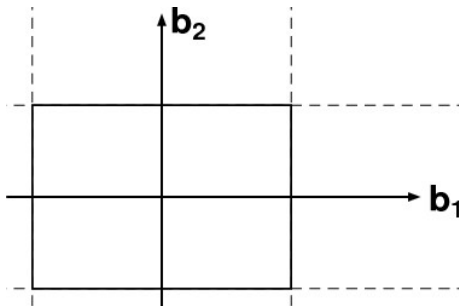
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$

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

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

Periodic systems: Brillouin zone

- First Brillouin zone: Part of space closer to the origin than to any integer multiple of the reciprocal lattice vectors,
 $\mathbf{K}' = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$



Integration over reciprocal space

- Thus the summation over infinite number of translations becomes an integral over the first Brillouin zone:

$$\sum_{\mathbf{L}}^{\infty} \Rightarrow \int_{\mathbf{k} \in 1.BZ} d\mathbf{k}$$

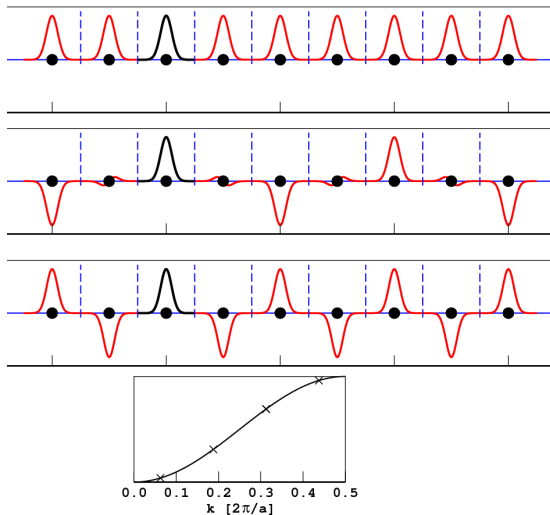
- In practise the integral is replaced by a weighted sum of discrete points:

$$\int_{\mathbf{k}} d\mathbf{k} \approx \sum_{\mathbf{k}} w_{\mathbf{k}}$$

- Thus eg.

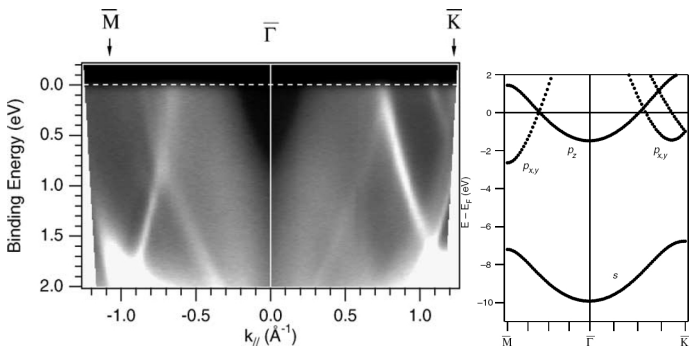
$$n(\mathbf{r}) = \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_i f_{i\mathbf{k}} |\psi_{i\mathbf{k}}(\mathbf{r})|^2$$

Periodic systems: Dispersion



Band structure: Example Pb/Cu(111)

Photoemission vs DFT calculations for a free-standing layer



Felix Baumberger, Anna Tamai, Matthias Muntwiler, Thomas Greber and Jürg Osterwalder;
 Surface Science **532-535** (2003) 82-86 doi:10.1016/S0039-6028(03)00129-8

Monkhorst-Pack algorithm

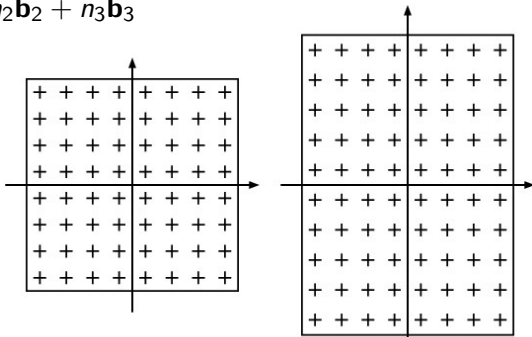
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Monkhorst-Pack algorithm

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$$n = \frac{2p - q - 1}{2q}, \quad p = 1 \dots q$$

$$\mathbf{k}_{ijk} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3$$



Symmetry operations

- If the atoms are related by symmetry operation S ($S\psi(\mathbf{r}) = \psi(S\mathbf{r})$) the integration over the whole 1st Brillouin zone can be reduced into the *irreducible Brillouin zone*, IBZ

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$$S\psi_{i\mathbf{k}}(\mathbf{r}) = \psi_{i\mathbf{k}}(S\mathbf{r}) = e^{i\mathbf{k}\cdot S\mathbf{r}} u_{i\mathbf{k}}(S\mathbf{r}) = e^{i\mathbf{k}'\cdot\mathbf{r}} u_{i\mathbf{k}'}(\mathbf{r}) , \mathbf{k}' = S^{-1}\mathbf{k}$$

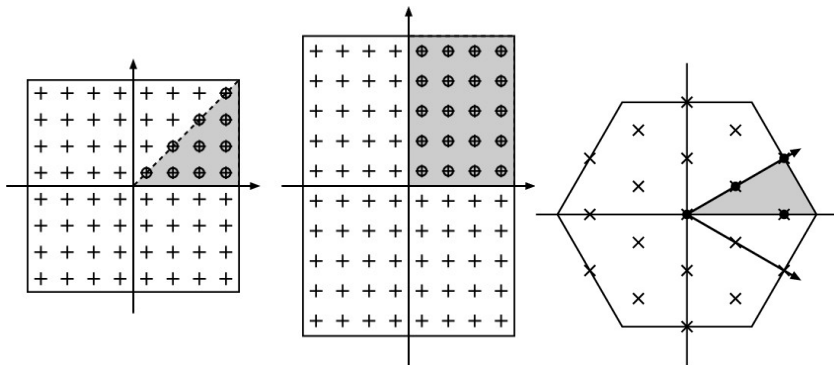
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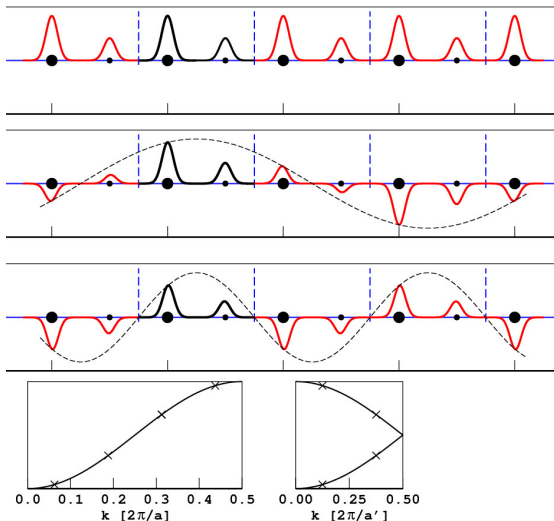
$$S\psi_{i\mathbf{k}}(\mathbf{r}) = \psi_{i\mathbf{k}}(S\mathbf{r}) = e^{i\mathbf{k}\cdot S\mathbf{r}} u_{i\mathbf{k}}(S\mathbf{r}) = e^{i\mathbf{k}'\cdot\mathbf{r}} u_{i\mathbf{k}'}(\mathbf{r}), \quad \mathbf{k}' = S^{-1}\mathbf{k}$$

$$\int_{\mathbf{k}} d\mathbf{k} \approx \sum_{\mathbf{k} \in \text{BZ}} w_{\mathbf{k}} = \sum_{\mathbf{k} \in \text{IBZ}} \sum_S w'_{S\mathbf{k}}$$

Irreducible Brillouin zone: Examples



Doubling the unit cell



Doubling the unit cell (super-cells)

- If one doubles the unit cell in one direction, it is enough to take only half of the k points in the corresponding direction in the reciprocal space

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- And has to be careful when comparing energies in cells with different size **unless** either equivalent sampling of k points is used **or** one is converged in the total energy in both cases

Summary

- 1 Density functional theory
- 2 Bloch theorem / supercells
- 3 Localised basis sets**
- 4 Plane wave basis set
- 5 Pseudo potentials

Implementation of Kohn-Sham equations: Discretisation

- Kohn-Sham orbitals expanded in a basis set: $\psi_{i\mathbf{k}} = \sum_{\alpha} c_{i\mathbf{k}\alpha} \chi_{\alpha}$
- Different choices of basis set:
 - ▶ Localised: Gaussian ($x^j y^k z^l e^{-(x/\sigma)^2}$), Slater ($x^j y^k z^l e^{-(x/\sigma)}$), wavelet, ...
 - ▶ Extended: Plane waves
 - ▶ Combination: FLAPW, GPW/GAPW, ...

Summary

- 1 Density functional theory
- 2 Bloch theorem / supercells
- 3 Localised basis sets
- 4 Plane wave basis set
 - Basics of plane wave basis set
 - Operators
 - Energy terms in plane wave basis set
- 5 Pseudo potentials

Kohn–Sham method

The ground state energy is obtained as the solution of a constrained minimisation of the Kohn-Sham energy:

$$\min_{\{\Phi\}} E_{KS}[\{\Phi_i(\mathbf{r})\}]$$

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$$\min_{\{\Phi\}} E_{\text{KS}}[\{\Phi_i(\mathbf{r})\}]$$

$$\int \Phi_i^*(\mathbf{r})\Phi_j(\mathbf{r})d\mathbf{r} = \delta_{ij}$$

Expansion using a basis set

- For practical purposes it is necessary to expand the Kohn-Sham orbitals using a set of basis functions
- Basis set $\{\varphi_\alpha(\mathbf{r})\}_{\alpha=1}^M$
- Usually a linear expansion

$$\psi_i(\mathbf{r}) = \sum_{\alpha=1}^M c_{\alpha i} \varphi_\alpha(\mathbf{r})$$

Plane waves

Philosophy

Assemblies of atoms are slight distortions to free electrons

$$\varphi_{\alpha}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}_{\alpha} \cdot \mathbf{r}}$$

$$(\dots = \cos(\mathbf{G}_{\alpha} \cdot \mathbf{r}) + i \sin(\mathbf{G}_{\alpha} \cdot \mathbf{r}))$$

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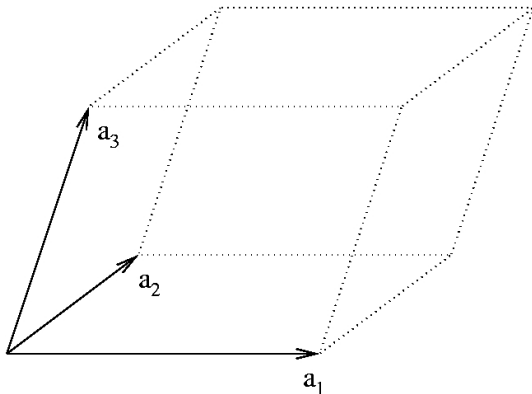
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- + independent of atomic positions
- + no BSSE
- ± naturally periodic
- many functions needed

Computational box



- Box matrix : $\mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$
- Box volume : $\Omega = \det \mathbf{h}$

Lattice vectors

- Direct lattice $\mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$
- Translations in direct lattice: $\mathbf{L} = i \cdot \mathbf{a}_1 + j \cdot \mathbf{a}_2 + k \cdot \mathbf{a}_3$

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- Translations in direct lattice: $\mathbf{L} = i \cdot \mathbf{a}_1 + j \cdot \mathbf{a}_2 + k \cdot \mathbf{a}_3$
- Reciprocal lattice $2\pi(\mathbf{h}^t)^{-1} = [\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3]$

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$

- Reciprocal lattice vectors : $\mathbf{G} = i \cdot \mathbf{b}_1 + j \cdot \mathbf{b}_2 + k \cdot \mathbf{b}_3$

Expansion of Kohn-Sham orbitals

Plane wave expansion

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

To be solved: Coefficients $c_{i\mathbf{k}}(\mathbf{G})$

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To be solved: Coefficients $c_{i\mathbf{k}}(\mathbf{G})$

Different routes:

- Direct optimisation of total energy
- Iterative diagonalisation/minimisation

Dependence on position

- Translation:

$$\phi(\mathbf{r}) \longrightarrow \phi(\mathbf{r} - \mathbf{R}_l)$$

$$\begin{aligned}\phi(\mathbf{r} - \mathbf{R}_l) &= \sum_{\mathbf{G}} \phi(\mathbf{G}) e^{i\mathbf{G} \cdot (\mathbf{r} - \mathbf{R}_l)} \\ &= \sum_{\mathbf{G}} \left(\phi(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} \right) e^{-i\mathbf{G} \cdot \mathbf{R}_l}\end{aligned}$$

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- Derivatives:

$$\frac{\partial \phi(\mathbf{r} - \mathbf{R}_l)}{\partial \mathbf{R}_{l,s}} = -i \sum_{\mathbf{G}} \mathbf{G}_s \left(\phi(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} \right) S_l(\mathbf{G})$$

Plane waves: Kinetic energy

- Kinetic energy operator in the plane wave basis:

$$-\frac{1}{2}\nabla^2\varphi_{\mathbf{G}}(\mathbf{r}) = -\frac{1}{2}(iG)^2\frac{1}{\sqrt{\Omega}}e^{i\mathbf{G}\cdot\mathbf{r}} = \frac{1}{2}G^2\varphi_{\mathbf{G}}(\mathbf{r})$$

- Thus the operator is diagonal in the plane wave basis set

$$E_{\text{kin}}(\mathbf{G}) = \frac{1}{2}G^2$$

Cutoff: Finite basis set

Choose all basis functions into the
basis set that fulfill

$$\frac{1}{2}G^2 \leq E_{\text{cut}}$$

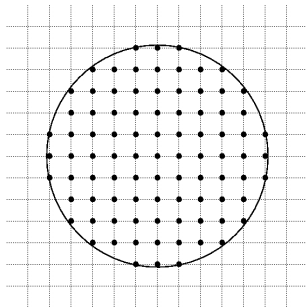
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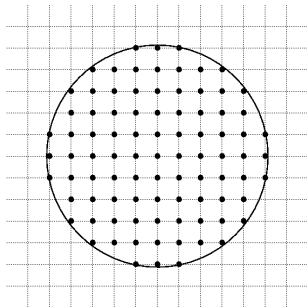


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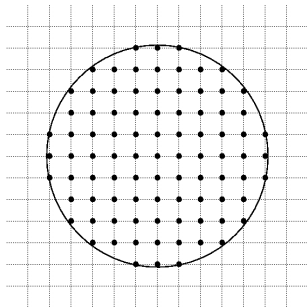
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 — and is **variational!**

Plane waves: Fast Fourier Transform

- The information contained in $\psi(\mathbf{G})$ and $\psi(\mathbf{r})$ are equivalent

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- Information can be handled always in the most appropriate space

Plane waves: Integrals

Parseval's theorem

$$\Omega \sum_{\mathbf{G}} A^*(\mathbf{G})B(\mathbf{G}) = \frac{\Omega}{N} \sum_i A^*(\mathbf{r}_i)B(\mathbf{r}_i)$$

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Proof.

$$\begin{aligned} I &= \int_{\Omega} A^*(\mathbf{r})B(\mathbf{r})d\mathbf{r} \\ &= \sum_{\mathbf{G}\mathbf{G}'} A^*(\mathbf{G})B(\mathbf{G}) \int \exp[-i\mathbf{G} \cdot \mathbf{r}] \exp[i\mathbf{G}' \cdot \mathbf{r}]d\mathbf{r} \\ &= \sum_{\mathbf{G}\mathbf{G}'} A^*(\mathbf{G})B(\mathbf{G}) \Omega \delta_{\mathbf{G}\mathbf{G}'} = \Omega \sum_{\mathbf{G}} A^*(\mathbf{G})B(\mathbf{G}) \quad \square \end{aligned}$$

Plane waves: Electron density

$$n(\mathbf{r}) = \sum_{ik} w_{\mathbf{k}} f_{ik} |\psi_{ik}(\mathbf{r})|^2 = \frac{1}{\Omega} \sum_{ik} w_{\mathbf{k}} f_{ik} \sum_{\mathbf{G}, \mathbf{G}'} c_{ik}^*(\mathbf{G}) c_{ik}(\mathbf{G}') e^{i(\mathbf{G}-\mathbf{G}') \cdot \mathbf{r}}$$

$$n(\mathbf{r}) = \sum_{\mathbf{G}=-2G_{\max}}^{2G_{\max}} n(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}$$

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$$n(\mathbf{r}) = \sum_{\mathbf{G}=-2G_{\max}}^{2G_{\max}} n(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

The electron density can be expanded *exactly* in a plane wave basis with a cut-off four times the basis set cutoff.

$$N_{\text{PW}}(4E_{\text{cut}}) = 8N_{\text{PW}}(E_{\text{cut}})$$

Plane waves: Operators

- The Kohn-Sham equations written in reciprocal space:

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\text{KS}}(\mathbf{G}, \mathbf{G}') \right\} \psi_{i\mathbf{k}}(\mathbf{G}) = \varepsilon_i \psi_{i\mathbf{k}}(\mathbf{G})$$

- However, it is better to do it like Car and Parrinello (1985) suggested: Always use the appropriate space (via FFT)
- There one needs to apply an operator on a wave function:

$$\sum_{\mathbf{G}'} \mathbf{O}(\mathbf{G}, \mathbf{G}') \psi(\mathbf{G}') = \sum_{\mathbf{G}'} c(\mathbf{G}') \langle \mathbf{G} | \mathcal{O} | \mathbf{G}' \rangle$$

- Matrix representation of operators in: $\mathbf{O}(\mathbf{G}, \mathbf{G}') = \langle \mathbf{G} | \mathcal{O} | \mathbf{G}' \rangle$
- Eg. **Kinetic energy operator**

$$\mathbf{T}_{\mathbf{G}, \mathbf{G}'} = \langle \mathbf{G} | -\frac{1}{2}\nabla^2 | \mathbf{G}' \rangle = \frac{1}{2} G^2 \delta_{\mathbf{G}, \mathbf{G}'}$$

Kohn–Sham energy

$$E_{\text{KS}} = E_{\text{kin}} + E_{\text{ES}} + E_{\text{pp}} + E_{\text{xc}}$$

E_{kin} Kinetic energy

E_{ES} Electrostatic energy (sum of electron-electron interaction + nuclear core-electron interaction + ion-ion interaction)

E_{pp} Pseudo potential energy not included in E_{ES}

E_{xc} Exchange–correlation energy

Kinetic energy

$$\begin{aligned}
 E_{\text{kin}} &= \sum_{ik} w_{\mathbf{k}} f_{ik} \langle \psi_{ik} | -\frac{1}{2} \nabla^2 | \psi_{ik} \rangle \\
 &= \sum_{ik} w_{\mathbf{k}} f_{ik} \sum_{\mathbf{G}\mathbf{G}'} c_{ik}^*(\mathbf{G}) c_{ik}(\mathbf{G}') \langle \mathbf{k} + \mathbf{G} | -\frac{1}{2} \nabla^2 | \mathbf{k} + \mathbf{G}' \rangle \\
 &= \sum_{ik} w_{\mathbf{k}} f_{ik} \sum_{\mathbf{G}\mathbf{G}'} c_{ik}^*(\mathbf{G}) c_{ik}(\mathbf{G}') \Omega \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} \\
 &= \Omega \sum_{ik} w_{\mathbf{k}} f_{ik} \sum_{\mathbf{G}} \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 |c_{ik}(\mathbf{G})|^2
 \end{aligned}$$

Periodic Systems

- Hartree-like terms are most efficiently evaluated in reciprocal space *via* the

Poisson equation

$$\nabla^2 V_H(\mathbf{r}) = -4\pi n_{\text{tot}}(\mathbf{r})$$

$$V_H(\mathbf{G}) = 4\pi \frac{n(\mathbf{G})}{G^2}$$

- $V_H(\mathbf{G})$ is a local operator with same cutoff as n_{tot}

Electrostatic energy

$$E_{\text{ES}} = \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + \sum_l \int n(\mathbf{r}) V_{\text{core}}^l(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \sum_{l \neq j} \frac{Z_l Z_j}{|\mathbf{R}_l - \mathbf{r}_j|}$$

Electrostatic energy

$$E_{\text{ES}} = \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + \sum_I \int n(\mathbf{r}) V_{\text{core}}^I(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{r}_J|}$$

- The isolated terms do not converge; the sum only for neutral systems
- Gaussian charge distributions a'la Ewald summation:

$$n_c^I(\mathbf{r}) = -\frac{Z_I}{(R_c^I)^3} \pi^{-3/2} \exp\left[-\left(\frac{\mathbf{r} - \mathbf{R}_I}{R_c^I}\right)^2\right]$$

- Electrostatic potential due to n_c^I :

$$V_{\text{core}}^I(\mathbf{r}) = \int \frac{n_c^I(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = -\frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \text{erf}\left[\frac{|\mathbf{r} - \mathbf{R}_I|}{R_c^I}\right]$$

Electrostatic energy

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$$E_{\text{ES}} = 2\pi \Omega \sum_{\mathbf{G} \neq 0} \frac{|n_{\text{tot}}(\mathbf{G})|^2}{G^2} + E_{\text{ovrl}} - E_{\text{self}}$$

$$E_{\text{ovrl}} = \sum'_{I,J} \sum_{\mathbf{L}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{r}_J - \mathbf{L}|} \operatorname{erfc} \left[\frac{|\mathbf{R}_I - \mathbf{r}_J - \mathbf{L}|}{\sqrt{R_I^c{}^2 + R_J^c{}^2}} \right]$$

$$E_{\text{self}} = \sum_I \frac{1}{\sqrt{2\pi}} \frac{Z_I^2}{R_I^c}$$

- Sums expand over all atoms in the simulation cell, all direct lattice vectors \mathbf{L} ; the prime in the first sum indicates that $I < J$ is imposed for $\mathbf{L} = \mathbf{0}$.

Exchange-correlation energy

$$E_{xc} = \int_{\mathbf{r}} n(\mathbf{r}) \varepsilon_{xc}(\mathbf{r}) d\mathbf{r} = \Omega \sum_{\mathbf{G}} \varepsilon_{xc}(\mathbf{G}) n^*(\mathbf{G})$$

- $\varepsilon_{xc}(\mathbf{G})$ is not local in \mathbf{G} space; the calculation in real space requires very accurate integration scheme.
- If the function $\varepsilon_{xc}(\mathbf{r})$ requires the gradients of the density, they are calculated using reciprocal space, otherwise the calculation is done in real space (for LDA and GGA; hybrid functionals are more intensive)

Plane waves: Basic self-consistent cycle

$$\begin{array}{ccc}
 n(\mathbf{r}) & \xrightarrow{FFT} & n(\mathbf{G}) \\
 V_{xc}[n](\mathbf{r}) & & V_{ES}(\mathbf{G}) \\
 V_{KS}(\mathbf{r}) = V_{xc}[n](\mathbf{r}) + V_{ES}(\mathbf{r}) & \xleftarrow{FFT} & V_{ES}(\mathbf{G}) \\
 \psi_{i\mathbf{k}}(\mathbf{r}) & \xleftarrow{N_i \times FFT} & \psi_{i\mathbf{k}}(\mathbf{G}) \\
 V_{KS}(\mathbf{r})\psi_{i\mathbf{k}}(\mathbf{r}) & \xrightarrow{N_i \times FFT} & [V_{KS}\psi_{i\mathbf{k}}](\mathbf{G}) \\
 & & \text{update } \psi_{i\mathbf{k}}(\mathbf{G}) \\
 \psi'_{i\mathbf{k}}(\mathbf{r}) & \xleftarrow{N_i \times FFT} & \psi'_{i\mathbf{k}}(\mathbf{G}) \\
 n'(\mathbf{r}) = \sum_{i\mathbf{k}} w_{\mathbf{k}} f_{i\mathbf{k}} |\psi'_{i\mathbf{k}}(\mathbf{r})|^2 & &
 \end{array}$$

Plane waves: Calculation of forces

- With the plane wave basis set one can apply the

Hellmann-Feynman theorem

$$(\mathbf{F}_I =) - \frac{d}{d\mathbf{R}_I} \langle \Psi | H_{KS} | \Psi \rangle = - \langle \Psi | \frac{\partial}{\partial \mathbf{R}_I} H_{KS} | \Psi \rangle$$

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- All the terms where \mathbf{R}_I appear explicitly are in *reciprocal space*, and are thus very simple to evaluate:

$$\frac{\partial}{\partial \mathbf{R}_I} e^{-i\mathbf{G}\cdot\mathbf{R}_I} = -i\mathbf{G}e^{-i\mathbf{G}\cdot\mathbf{R}_I}$$

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- The energies must only be compared with the same E_{cut}

Summary

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 - Introduction to pseudo potentials
 - Generation of pseudo potentials
 - Usage of pseudo potentials

Why use pseudo potentials?

- **Reduction of basis set size**
effective speedup of calculation
- **Reduction of number of electrons**
reduces the number of degrees of freedom
For example in Pt: 10 instead of 78
- **Unnecessary** “Why bother? They are inert anyway...”
- **Inclusion of relativistic effects**
relativistic effects can be included ”partially” into effective potentials

Why pp? Estimate for number of plane waves

plane wave cutoff \leftrightarrow most localized function

1s Slater type function $\approx \exp[-Zr]$

Z: effective nuclear charge

$$\phi_{1s}(\mathbf{G}) \approx \frac{16\pi Z^{5/2}}{G^2 + Z^2}$$

	Cutoff	Plane waves
H	1	1
Li	4	8
C	9	27
Si	27	140
Ge	76	663

Pseudo potential

What is it?

- Replacement of the all-electron, $-Z/r$ problem with a Hamiltonian containing an effective potential
- It should reproduce the necessary physical properties of the full problem at the reference state
- The potential should be transferable, *ie.* also be accurate in different environments

The construction consists of two steps of approximations

- Frozen core approximation
- Pseudisation

Frozen core approximation

- Core electrons are chemically inert
- Core/valence separation is sometimes not clear
- Core wavefunctions are from atomic reference calculation
- Core electrons of different atoms do not overlap

Remaining problems

- Valence wavefunctions must be orthogonal to core states
→ nodal structures → high plane wave cutoff
- Thus pseudo potential should produce node-less functions and include Pauli repulsion
- Pseudo potential replaces Hartree and XC potential due to the core electrons

Remaining problems

- Valence wavefunctions must be orthogonal to core states
→ nodal structures → high plane wave cutoff
- Thus pseudo potential should produce node-less functions and include Pauli repulsion
- Pseudo potential replaces Hartree and XC potential due to the core electrons
- XC functionals are not linear: approximation

$$E_{XC}(n_c + n_v) = E_{XC}(n_c) + E_{XC}(n_v)$$

This assumes that core and valence electrons do not overlap. This restriction can be overcome with the "non-linear core correction" (NLCC) discussed later

Atomic pseudo potentials: Basic idea

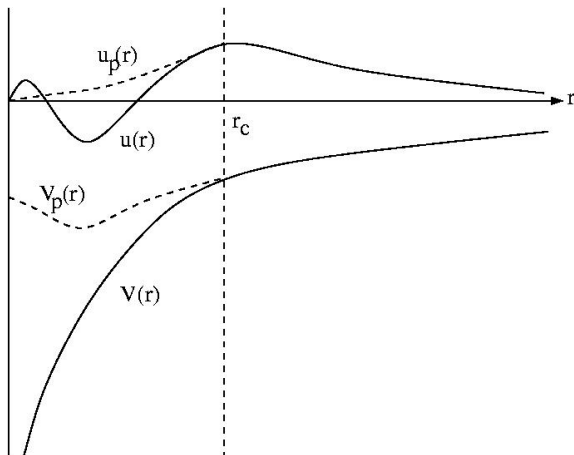
- 1 Create a pseudo potential for each atomic species separately, in a reference state (usually a neutral or slightly ionised atom)
- 2 Use these in the Kohn-Sham equations for the valence only

$$(T + V(\mathbf{r}, \mathbf{r}') + V_H(n_v) + V_{XC}(n_v)) \Phi_i^v(\mathbf{r}) = \epsilon_i \Phi_i^v(\mathbf{r})$$

Goal

Pseudo potential $V(\mathbf{r}, \mathbf{r}')$ has to be chosen such that the main properties of the all-electron atom are imitated as well as possible

Pseudisation of valence wave functions



Generation of pseudo potentials: General recipe

- ① Atomic all-electron calculation (reference state)
 $\Rightarrow \Phi_j^v(\mathbf{r})$ and ϵ_j .
- ② Pseudize $\Phi_j^v \Rightarrow \Phi_j^{\text{PS}}$
- ③ Calculate potential from

$$[T + V_I(\mathbf{r})] \Phi_j^{\text{PS}}(\mathbf{r}) = \epsilon_j \Phi_j^{\text{PS}}(\mathbf{r})$$

- ④ Calculate pseudo potential by unscreening of $V_I(\mathbf{r})$

V_I^{PS} is dependent on l ! Otherwise poor transferability

$$V_I^{\text{PS}}(\mathbf{r}) = V_I(\mathbf{r}) - V_{\text{H}}(n^{\text{PS}}) - V_{\text{XC}}(n^{\text{PS}})$$

Norm-conserving pseudo potentials

Hamann-Schlüter-Chiang-Recipe (HSC) conditions

DR Hamann, M Schlüter & C Chiang, Phys Rev Lett **43**, 1494 (1979)

- ① Real and pseudo valence eigenvalues agree for a chosen prototype atomic configuration: $\epsilon_I = \hat{\epsilon}_I$
- ② Real and pseudo atomic wave functions agree beyond a chosen core radius r_c : $\Psi_I(r) = \Phi_I(r)$ for $r \geq r_c$
- ③ Integral from 0 to R of the real and pseudo charge densities agree for $R \geq r_c$ (norm conservation): $\langle \Phi_I | \Phi_I \rangle_R = \langle \Psi_I | \Psi_I \rangle_R$ for $R \geq r_c$,
 $\langle \Phi | \Phi \rangle_R = \int_0^R r^2 |\phi(r)|^2 dr$
- ④ The logarithmic derivatives of the real and pseudo wave function and their first energy derivatives agree for $r \geq r_c$.

Points 3) and 4) are related via $-\frac{1}{2} \left[(r\Phi)^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln \Phi \right]_R = \int_0^R r^2 |\Phi|^2 dr$

Semi-local pseudo potential

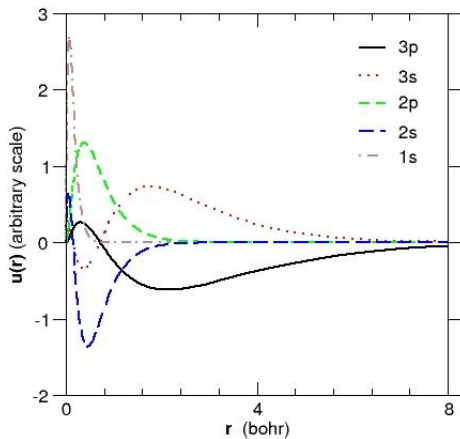
Final semi-local form

$$V^{\text{PS}}(\mathbf{r}, \mathbf{r}') = V_{\text{loc}}^{\text{PS}}(r) + \sum_{L=0}^{L_{\text{max}}} \Delta V_L^{\text{PS}}(r) |Y_L\rangle \langle Y_L|$$

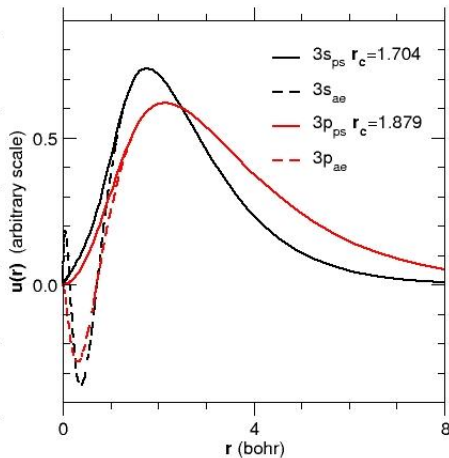
- Local pseudo potential $V_{\text{loc}}^{\text{PS}}$
- Non-local pseudo potential $\Delta V_L^{\text{PS}} = V_L^{\text{PS}} - V_{\text{loc}}^{\text{PS}}$
- Any L quantum number can have a non-local part

This form leads, however, to large computing requirements in plane wave basis sets

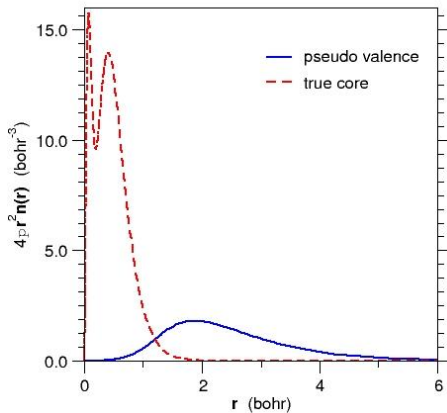
Silicon: Radial wave functions



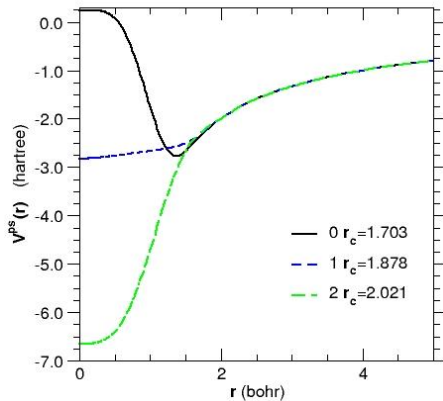
Silicon: Pseudo vs all-electron wave functions

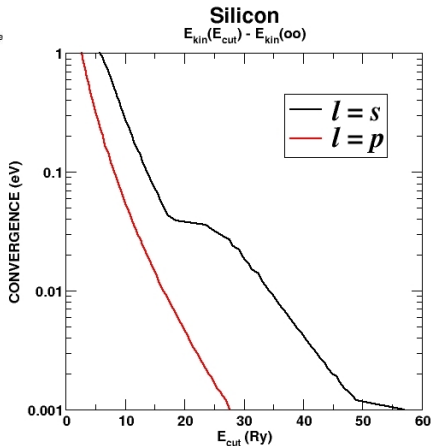
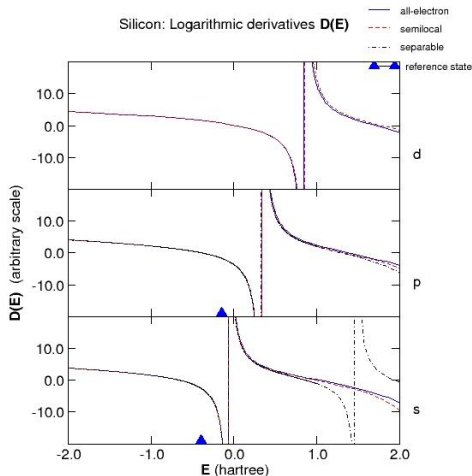


Silicon: Radial densities



Silicon: Ionic pseudo potentials





Kleinman–Bylander form

Write the pseudo potential terms as

Kleinman-Bylander operator

$$\hat{V}_{\text{PS,nl}}^{\text{KB}}(\mathbf{r}, \mathbf{r}') = \sum_L |\Delta V_L \phi_L\rangle \omega_L \langle \Delta V_L \phi_L|$$

$$\omega_L = \langle \phi_L | \Delta V_L | \phi_L \rangle$$

ϕ_L is the pseudo wave function

$$E_{\text{PS,nl}} = \sum_{\mathbf{ik}} w_{\mathbf{k}} f_{\mathbf{ik}} \sum_L \langle \psi_{\mathbf{ik}} | \Delta V_L \phi_L \rangle \omega_L \langle \Delta V_L \phi_L | \psi_{\mathbf{ik}} \rangle$$

Now the expression is *fully non-local* $\{f(\mathbf{r}') f(\mathbf{r})\}$ and thus computationally efficient also in plane wave basis set!

Ghost states

Problem: In Kleinman–Bylander form, the node-less wave function is no longer the solution with the lowest energy

Solution: Carefully tune the local part of the pseudo potential until the ghost states disappear

How to detect ghost states: Look for following properties

- Deviations of the logarithmic derivatives of the energy of the KB–pseudo potential from those of the respective semi-local pseudo potential or all–electron potential.
- Comparison of the atomic bound state spectra for the semi-local and KB–pseudo potentials.
- Ghost states below the valence states are identified by a rigorous criteria by Gonze *et al*

Ultra-soft pseudo potentials and PAW method

- Many elements require high cutoff for plane wave calculations
 - ▶ First row elements: O, F
 - ▶ Transition metals: Cu, Zn
 - ▶ f elements: Ce
- relax norm-conservation condition

$$\int n^{\text{PS}}(\mathbf{r})d\mathbf{r} + \int Q(\mathbf{r})d\mathbf{r} = 1$$

Ultra-soft pseudo potentials and PAW method

- Augmentation functions $Q(\mathbf{r})$ depend on environment.
- No full un-screening possible, $Q(\mathbf{r})$ has to be recalculated for each atom and atomic position.
- Complicated orthogonalisation and force calculations.
- Allows for larger r_c , reduces cutoff for all elements to about 30 Ry

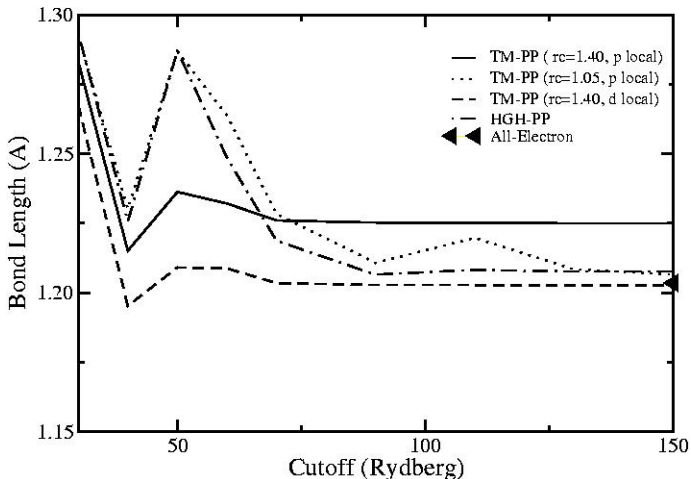
Non-linear core correction (NLCC)

- For many atoms (eg. alkali atoms, transition metals) core states overlap with valence states; thus linearisation of XC energy breaks down
- Possible cures
 - ▶ Add additional states to valence
 - ★ adds more electrons
 - ★ needs higher cutoff
 - ▶ Add core charge to valence charge in XC energy \Rightarrow non-linear core correction (NLCC)
S.G. Louie et al., Phys. Rev. B, **26** 1738 (1982)

Testing of pseudo potentials

- Calculation of other atomic valence configurations (occupations), comparison with all-electron results
- Calculation of transferability functions, logarithmic derivatives, hardness
- Calculation of small molecules, comparison with all electron calculations (geometry, harmonic frequencies, dipole moments)
- Calculation of other test systems
- Check of basis set convergence (cutoff requirements)

Convergence test for pseudo potentials in O₂



Pseudo potentials: Summary

- Pseudo potential are necessary when using plane wave basis sets in order to keep the number of the basis function manageable
- Pseudo potentials are generated at the reference state; transferability is the quantity describing the accuracy of the properties at other conditions
- The mostly used scheme in plane wave calculations is the Troullier-Martins pseudo potentials in the fully non-local, Kleinman-Bylander form
- Once created, a pseudo potential must be **tested, tested, tested!!!**