

Introduction to Density Functional Theory and the LAPW method

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Centre for the Computational Science at Interdisciplinary Centre for Mathematical and Computational Modelling, Warsaw, Poland



The program package WIEN2k allows to perform electronic structure calculations of solids using density functional theory (DFT).
First Polish workshop and the 22-nd workshop in the history of the WIEN2k code: "WIEN2k and SPECTROSCOPY: HANDS-ON WORKSHOP" which was held at Institute of Physics PAS, Warsaw, Poland in Fall 2014.



Group of X-ray Spectroscopy and Microanalysis, Laboratory of X-ray and Electron Microscopy Research, Institute of Physics, PAS:
Dr. Iraida Demchenko, Mr. Yevgen Syryanny, Dr. Pawel Rejmak



Outline

- **Introduction into DFT**
 - What is *ab-initio* approach? What do we solve?
 - DFT foundations
 - Exchange-correlation functionals
 - Three basis methods to solve Kohn-Sham equations
 - Augmented plane waves method
- **Some practical aspects of calculations**
- **Examples of applications of DFT**
- **Core level spectroscopy (XPS, XAS, EELS)**
- **Conclusion**



What is an *Ab-Initio* approach?

Ab-initio approach is the approach which is utilised to describe/model experimentally observed physical properties of a particular material starting **only** from:

- crystal structure, or
- chemical composition (this is an absolute goal!)

Wide applicability to various quantum systems:

- single atom,
- molecule,
- solid state matter

To be useful, numerical modelling (i.e. performing numerical experiments successfully) requires faster computers and bigger resources.

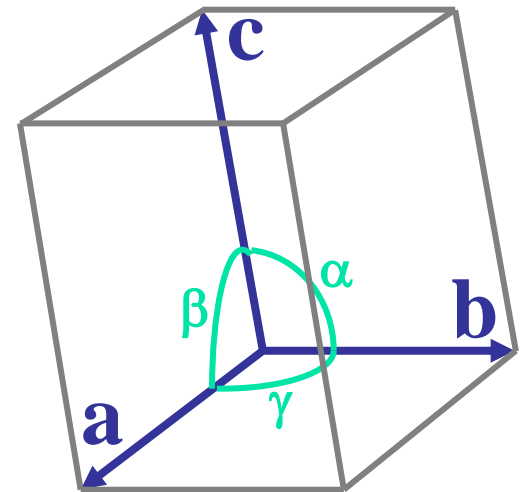
Solid State – Reminder

Crystal structure

- Unit cell (a volume in space that fills space entirely when translated by all lattice vectors)
- Atomic basis (Wyckoff positions)
- Space group
- Reciprocal lattice (Brillouin zone)

When solving Schrödinger equation quantum mechanics states that:

- Potential has lattice periodicity
- Electron density as well
- But wave function does not have
- Periodic boundary conditions are employed
- Bloch functions and Bloch theorem





What do We Solve?

The fundamental equation governing a non-relativistic quantum system is time-dependent Schrödinger equation:

$$i\hbar \frac{d\Psi(\{\vec{r}_i\}; t)}{dt} = \hat{H} \Psi(\{\vec{r}_i\}; t)$$

where \hat{H} Hamiltonian operator
 $\Psi(\{\vec{r}_i\}; t)$ many-body wavefunction

If Hamiltonian is time *independent*, the equation becomes time-independent Schrödinger equation:

$$\Psi(\{\vec{r}_i\}; t) = \Psi(\{\vec{r}_i\}) \exp(-i E \hbar / t)$$

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$



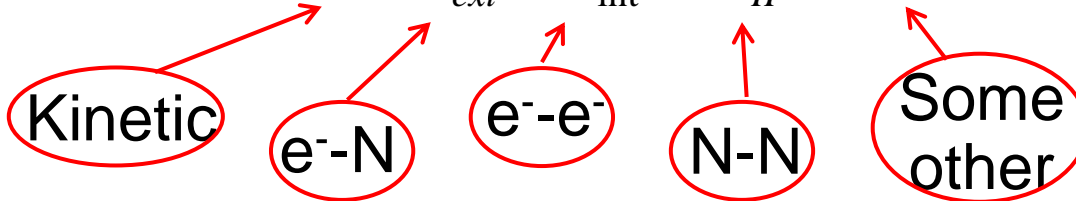
What do We Solve?

We solve time-independent Schrödinger equation for many-body electron system to find eigenstates and eigenvectors:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

where $\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{int} + E_{II} + etc.$

Hamiltonian operator



What do We Solve?

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{int} + E_{II} + etc.$$

Diagram illustrating the components of the Hamiltonian \hat{H} :

- \hat{T} (Kinetic)
- \hat{V}_{ext} (e^- -N)
- \hat{V}_{int} (e^- - e^-)
- E_{II} (N-N)
- $etc.$ (Some other)

$$\hat{T} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \frac{\hbar^2}{2} \sum_I \frac{\nabla_I^2}{M_I}$$

The second term is crossed out with a red line and a red '0' below it, indicating it is ignored in the Born-Oppenheimer approximation.

The Born-Oppenheimer approximation is to ignore the kinetic energy of the nuclei, i.e. $M_I \rightarrow \infty$

$$\hat{V}_{ext} = -\sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|}$$

$$\hat{V}_{int} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$E_{II} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|}$$



What do We Solve?

We solve time-independent Schrödinger equation for many-body electron system to find eigenstates and eigenvectors:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$|\Psi\rangle \equiv |\Psi(\vec{r}_1, \dots, \vec{r}_N)\rangle$ Many-body wavefunction
for the electrons

\vec{r}_i Spatial and spin electron coordinate

Many-body wavefunction for the electrons is a function of the number of electrons in a system

Too many variables, therefore, Schrödinger equation as is cannot be solved for complex systems!!!

DFT foundations – I

(1/2 of) 1998 Nobel Prize in Chemistry to
Prof. Walter Kohn
for fundamental work in density functional theory



Prof. Walter Kohn





DFT foundations – II

Hohenberg-Kohn 1st theorem and its corollary (1964):

- The total energy of a many-body system is a unique functional of electron density.
- Such functional is independent of external potential but is *unknown*.
- All properties of the system (*ground* and *excited*) are completely determined given only the ground state density.



DFT foundations – III

Hohenberg-Kohn 2nd theorem and its corollary (1964):

- The universal functional for the energy can be defined in terms of electron density.
- The exact ground state energy of the system is the global minimum value of this functional.
- The density that minimizes the functional is the exact ground state density.
- The functional *alone* is sufficient to determine the exact ground energy and density.



DFT foundations – IV

Kohn-Sham (based on Hohenberg-Kohn theorems for an *exact theory of many-body systems*) proposed a new approach to the many-body interacting electron system via ***ansatz*** (1965):

- Auxiliary independent-particle system is formulated instead but with interacting density;
- Density (electron density) is the main variable now;
- This newly formulated system will have the same total energy of the ground state;
- All many-body effects will be counted through additional functional: exchange-correlation functional, which becomes an extremely important factor now

DFT foundations – V

Kohn-Sham **ansatz** changes the many-body interacting electron system into an auxiliary independent-particle system which is described by Kohn-Sham (Schrödinger-like) equation:

$$\hat{H}_{KS} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

where \hat{H}_{KS} is the effective Hamiltonian, constructed out of the following functional:

$$E_{KS} = T + V + E_{ext} = T_S + E_C + E_H + E_X + E_{ext} = T_S + E_H + E_{XC} + E_{ext}$$

independent

Hartree

Exchange-
Correlation
not known
unfortunately

N-N
and other

DFT foundations – VI

Kohn-Sham **ansatz** changes the many-body interacting electron system into an auxiliary independent-particle system which is described by Kohn-Sham (Schrödinger-like) equation:

$$\hat{H}_{KS} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

where \hat{H}_{KS} is the effective Hamiltonian, constructed out of the following functional:

$$E_{KS} = T_S[n] + \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' + E_{XC}[n] + \int V_{ext} n d\vec{r}$$

Kinetic

Hartree

Exchange-
Correlation
not known
unfortunately

N-N
and other

DFT foundations – VII

N-body Schrödinger Equation:

$$\left(-\frac{1}{2} \nabla^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,I} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \right) \Psi(\{\vec{r}_i\}) = E \Psi(\{\vec{r}_i\})$$

$$n^{exact}(\vec{r}) = \int \dots \int \Psi^*(\{\vec{r}_i\}) \Psi(\{\vec{r}_i\}) d\vec{r}_2 d\vec{r}_3 \dots$$

Kohn-Sham Equations:

$$\left(-\frac{1}{2} \nabla_i^2 + \frac{1}{2} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' - \sum_I \int \frac{Z_I n(\vec{r}')}{|\vec{r}' - \vec{R}_I|} d\vec{r}' + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} + V_{xc}[n(\vec{r})] \right) \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

$$n^{DFT}(\vec{r}) = \sum_i \psi_i^*(\vec{r}) \psi_i(\vec{r})$$

$$n^{exact}(\vec{r}) = n^{DFT}(\vec{r})$$

These are quasi-particles, or Kohn-Sham eigenstates

Exchange-Correlation Functionals – I

Kohn-Sham Equations:

$$\left(-\frac{1}{2} \nabla_i^2 + \frac{1}{2} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' - \sum_I \int \frac{Z_I n(\vec{r}')}{|\vec{r}' - \vec{R}_I|} d\vec{r}' + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} + V_{xc}[n(\vec{r})] \right) \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$
$$n^{DFT}(\vec{r}) = \sum_i \psi_i^*(\vec{r}) \psi_i(\vec{r})$$

Within DFT we can write the **exact** exchange-correlation interaction as

$$E_{xc}[n] = \frac{1}{2} \iint n(\vec{r}) \frac{n_{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

which is simply the Coulomb interaction between an electron at \vec{r} and the value of its XC hole $n_{xc}(\vec{r}, \vec{r}')$ at \vec{r}' . Unfortunately, $n_{xc}(\vec{r}, \vec{r}')$ is unknown and, therefore:

Exact exchange-correlation functional is unknown !!!



Exchange-Correlation Functionals – II

All functionals are approximations:

- Reports of 'Failures of DFT' is actually a report of a failure of the XC functional;

No functional (so far) is accurate(?) for all properties of interest:

- No matter what functional is 'invented' someone will always find a case where it fails

Any functional can be applied to any electronic structure problem:

- In this sense it is *ab initio* but we use experience and intuition to decide which one to use

Exchange-Correlation Functionals – III

Citation: [AIP Conf. Proc. 577](#), 1 (2001);
doi: 10.1063/1.1390175

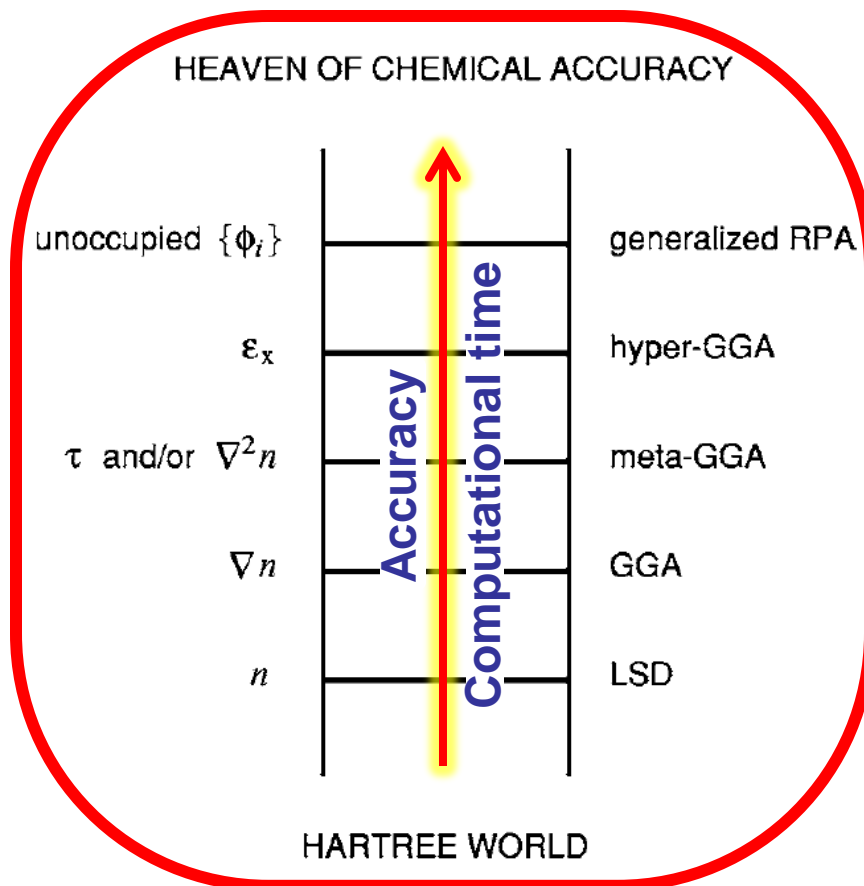
[Perdew and Schmidt](#)

“Jacob’s ladder of density functional approximations for the exchange-correlation energy”

Citation: [J. Chem. Phys. 123](#), 062201 (2005); doi: 10.1063/1.1904565

[Perdew et al.](#)

“Prescription for the design and selection of density functional approximations: More constraint satisfaction with fewer fits”



Types of functionals: Non-empirical

Local (Spin) Density Approximation L(S)DA:

- assuming that the charge density varies slowly

$$E_{XC}^{LSDA}[n] = \int n(\vec{r}) \varepsilon_{XC}(n) d\vec{r}$$

Generalized-Gradient Approximation GGA:

$$E_{XC}^{GGA}[n] = \int n(\vec{r}) \varepsilon_{XC}(n, |\nabla n|) d\vec{r}$$

Enhancement factor

$$\varepsilon_{XC}^{GGA}[n, |\nabla n|] = \varepsilon_{XC}^{LDA}[n] F_{XC}(r_s, s), \quad r_s \propto \frac{1}{n^{1/3}}, \quad s \propto \frac{|\nabla n|}{n^{4/3}}$$

meta-GGA:

$$E_{XC}^{m-GGA}[n] = \int n(\vec{r}) \varepsilon_{XC}(n, |\nabla n|, \nabla^2 n, \tau) d\vec{r}$$

Types of functionals: Non-empirical

- **L(S)DA** (PZ) is simplest but good approximation.
- **L(S)DA** and **GGA** (PW91, PBE, rPBE, WC, PBEsol, HTBS) are constructed based on exact conditions and, therefore, the reliability can usually be predicted
- For structural properties, **GGA** is (on average) more accurate than the **LDA**:
 - **LDA** still best for 5d-series (Pt, Au). PBE of **GGA** too large !
 - PBE of **GGA** best for 3d series (Fe, Ni, ..). **LDA** too small !
 - WC, PBEsol, HTBS of **GGA** best compromise for all elements
 - van der Waals: **LDA** overbinds, **GGA** underbind (sometimes non-bonding !)
- For cohesive properties, rPBE of **GGA** is much better than **LDA**
- For electronic structure, **LDA** and **GGA** produces very similar results, however, band gaps are underestimated by 50 % (therefore, use TB-mBJ correction)

strictly speaking empirical

Types of functionals: Non-empirical

- For systems with strongly correlated electrons (3d, 4f), often **LDA** and **GGA** give qualitatively wrong results:
 - metal instead of insulator,
 - too small magnetic moments or even non-magnetic instead of AFM cuprates,
 - no (too small) structural distortions,
 - orbital order,
- **meta-GGA** (TPSS, MGGA_MS2):
 - as good as best **GGA** for atomization energies (rPBE)
 - as good as best **GGA** for structural parameters (WC or PBEsol)
 - not so bad for van der Waals systems either
 - However, analytic form for **meta-GGA** is not possible due to kinetic energy density variable $\tau(r) = \frac{1}{2} \sum_i |\nabla \psi_i(r)|^2$, therefore, calculations are difficult
- Dateline for **LDA**, **GGA** and **meta-GGA** functionals:
 - PZ 1981, PW91 1992, PBE 1996, rPBE 1999, TPSS 2003, WC 2006, PBEsol 2008, revTPSS 2009, MGGA_MS2 2013

Types of functionals: Empirical

Hybrid (B3LYP, PBE0, HSE) with a few (?) empirical parameters

General strategy for construction of hybrids is to mix exact exchange (i.e. Hartree-Fock which is non-local) and (semi-)local-density energies:

$$E_x^{HF} = E_x^{exact} = -\frac{1}{2} \sum_{i,j} \int \frac{\phi_i^*(\vec{r}_1) \phi_j(\vec{r}_1) \phi_j^*(\vec{r}_2) \phi_i(\vec{r}_2)}{|\vec{r}_i - \vec{r}_j|} d\vec{r}_1 d\vec{r}_2$$

PBE0: $E_{xc}^{PBE0}[n] = E_{xc}^{PBE}[n] + \alpha(E_x^{HF}[\Phi] - E_x^{PBE}[n])$
with $\alpha=20-25-60\%$ for semiconductors and insulators
with α very small for metals

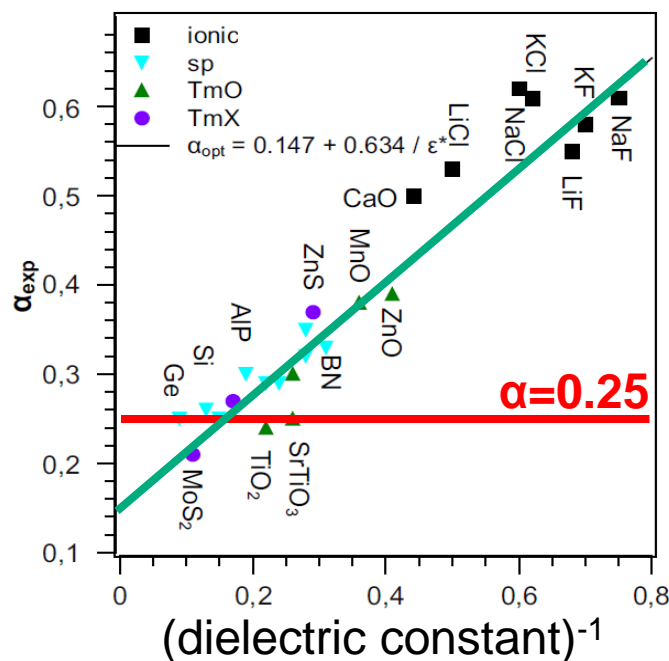
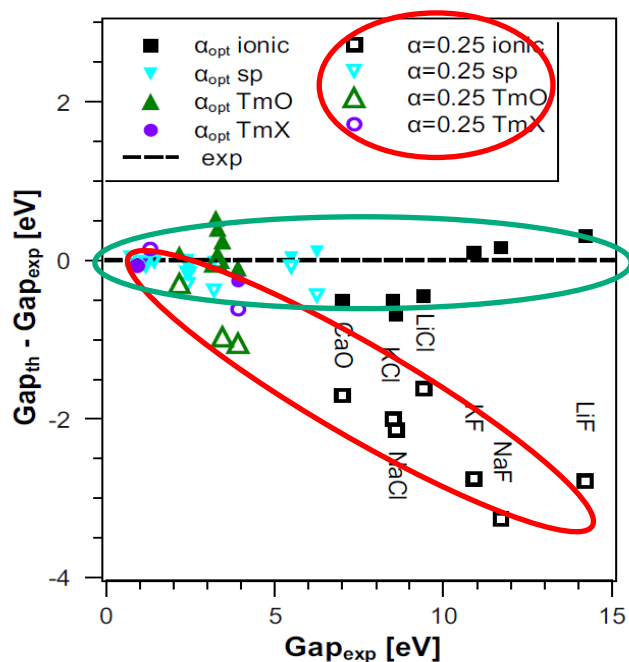
B3LYP: $E_{xc}^{B3LYP}[n] = (1-a)E_x^{LSDA} + aE_x^{HF} + bE_x^{B88} + cE_c^{LYP} + (1-c)E_c^{VWN}$
with a , b , and c being adjustable parameters

Exchange-Correlation Functionals – VIII

Types of functionals: Empirical

YS-PBE0 is PBE0 with extra screening parameter λ :

- YS-PBE0 reduces to PBE0 when $\lambda \rightarrow 0$
- YS-PBE0 reduces to PBE when $\lambda \rightarrow \infty$
- YS-PBE0 is similar to HSE06 when $\lambda = \frac{3}{2}\mu$



Types of functionals: Orbital dependent (LDA+U, EECE)

- Fixes a very specific problem that LDA/GGA can get wrong in highly correlated systems with localized 3d/4f orbitals:
 - LDA/GGA functionals tend to over-delocalize electrons;
 - Electrons see their own potential, self-interaction;
 - On-site Coulomb repulsion is not well accounted for;
 - In a lot of cases the correct structure will be predicted but **energy gap (if any) will be too small**;
- Main idea of DFT+U is to separate electrons into two subsystems:
 - localized *d*- or *f*-electrons for which the Coulomb interaction should be taken into account, and
 - delocalized *s*- and *p*-electrons which could be described by using an orbital-independent one-electron potential (i.e. LDA/GGA)

Types of functionals: Orbital dependent (LDA+U, EECE)

LDA+U functional:

$$E_{xc}^{\text{DFT+U}}[n] = E_{xc}^{\text{DFT}}[n] + E_{\text{Hub}}[\{n_{i\sigma}\}] - E_{\text{dc}}[\{n_{i\sigma}\}]$$

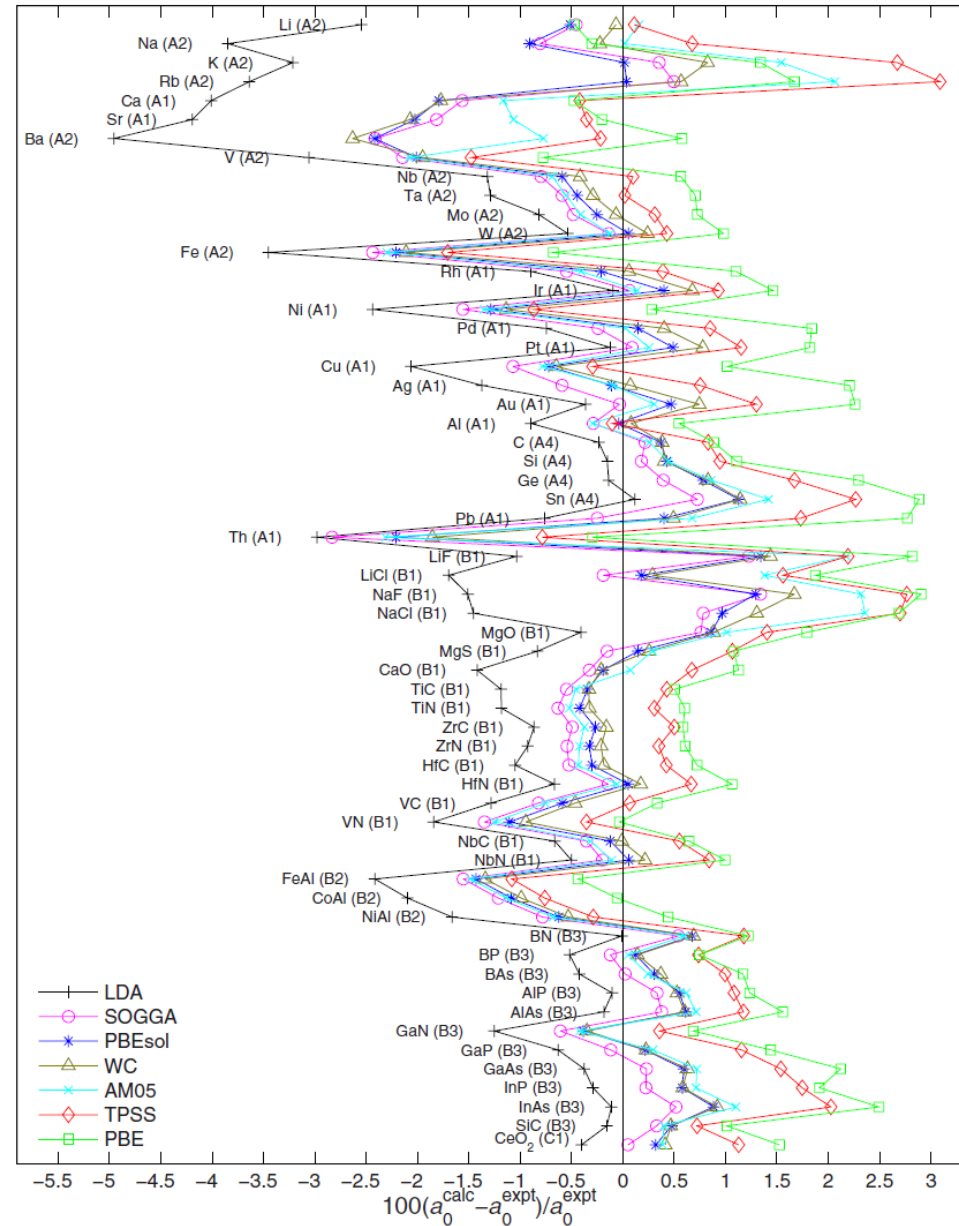
where $E_{\text{Hub}}[\{n_{i\sigma}\}] = \frac{1}{2}U \sum_{i \neq j} n_i n_j$ is mean-field Hubbard term

$E_{\text{dc}}[\{n_{i\sigma}\}] = -\frac{1}{2}UN(N-1)$ is to get rid of double-counting of some of the orbitals counted in DFT

- Addition of the Hubbard term leads to the following effect:
 - if the state is initially less than half occupied, the Hubbard potential is positive and tend to repulse electrons. On the other hand, if the occupation is more than half filled, the potential is attractive and encourage electrons to localized on this particular site

Exchange-Correlation Functionals – XI

Relative error in percent in the calculated lattice constants with respect to their experimental values



Citation: [Phys. Rev. B](#) **79**, 085104 (2009);
doi: 10.1103/PhysRevB.79.085104

Haas et al.

“Calculation of the lattice constant of solids with semilocal functionals”

All functionals are approximations:

- Reports of ‘Failures of DFT’ is actually a report of a failure of the XC functional;

No functional (so far) is accurate(?) for all properties of interest:

- No matter what functional is ‘invented’ someone will always find a case where it fails

Any functional can be applied to any electronic structure problem:

- In this sense it is *ab initio* but we use experience and intuition to decide which one to use

What do We Solve?

The universal functional for the energy can be defined in terms of electron density:

- the global minimum value being the exact ground state energy of the system, and
- with density being the exact ground state density.

Search for this minimum gives the Kohn-Sham equations:

Kohn-Sham Equations:

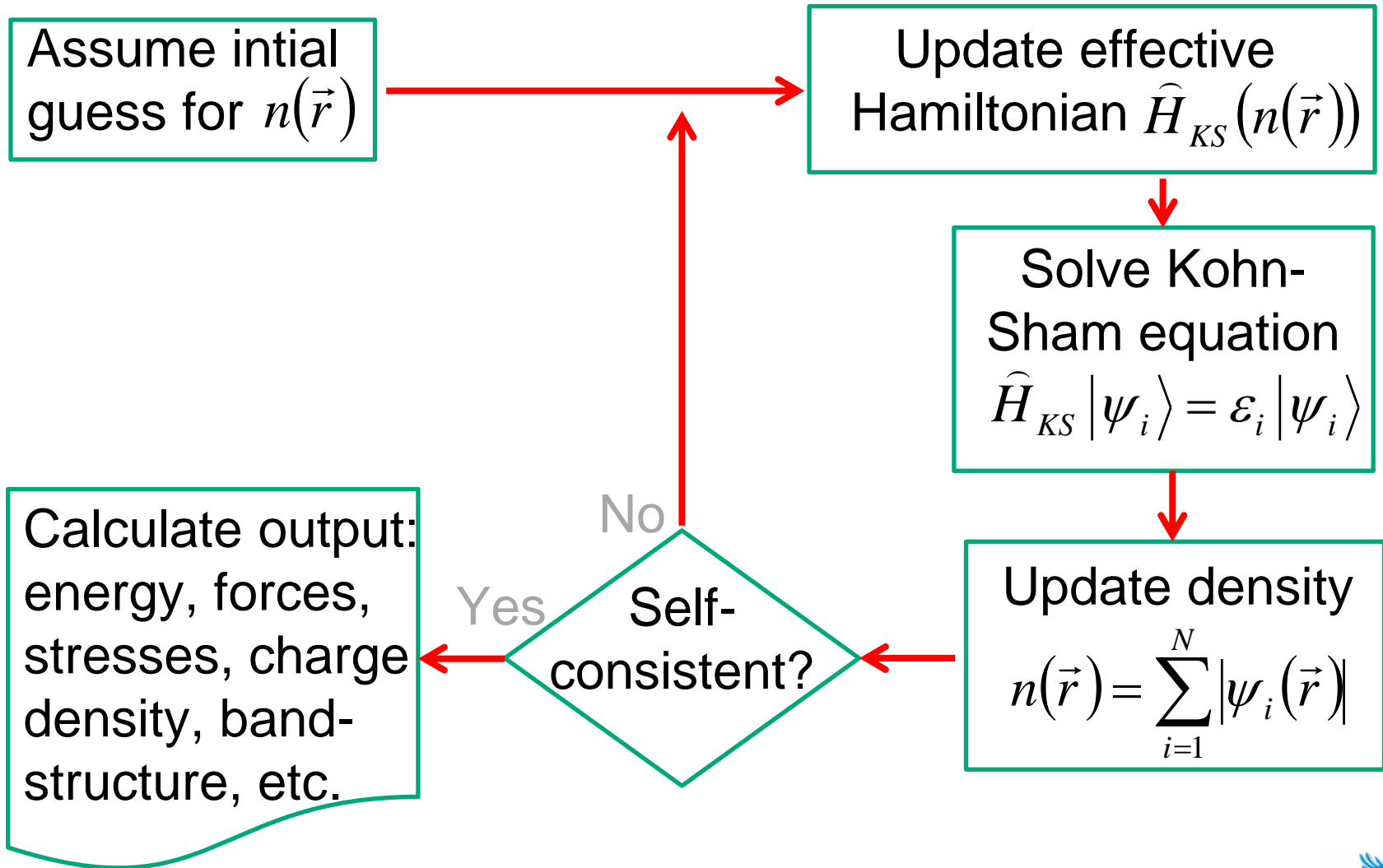
$$\left(-\frac{1}{2} \nabla_i^2 + \frac{1}{2} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' - \sum_I \int \frac{Z_I n(\vec{r}')}{|\vec{r}' - \vec{R}_I|} d\vec{r}' + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} + V_{xc}[n(\vec{r})] \right) \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

$$n^{DFT}(\vec{r}) = \sum_i \psi_i^*(\vec{r}) \psi_i(\vec{r})$$

Assuming that exchange-correlation functional is known (better say: set)!!!

These are quasi-particles, or Kohn-Sham eigenstates

Solving Kohn-Sham equations – I



Solving Kohn-Sham equations – II

Solve Kohn-Sham equation

$$\hat{H}_{KS} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

Special mathematical methods and tricks are used to make these calculations as fast as possible.

Linear combination of some “basis functions”:

$$\psi_k(\vec{r}) = \sum_{k_n} c_{k_n} \Phi_{k_n}(\vec{r})$$

This converts a problem into a set of linear equations which in matrix representation is called “generalized eigenvalue problem”:

$$\mathbf{H} \mathbf{C} = E \mathbf{S} \mathbf{C}$$

\mathbf{H}	\mathbf{S}	Hamilton and overlap matrices
	\mathbf{C}	eigenvectors
	E	eigenvalues



Three Basis Methods to Solve – II

Kohn-Sham (Schrödinger-like) equation:

$$\hat{H}_{KS} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

Plane waves:

$$\psi_i = \sum_{\vec{q}} c_{i,q} \exp(i\vec{q} \cdot \vec{r})$$

Pros: Perfect for periodic systems, simple to implement and to work with, complete basis set, Plane waves do not depend on the atomic positions

Cons: the number of plane waves needed is quite large, empty space is included in the calculation

Programs: Quantum Espresso sometimes also called PWSCF (GPL), Abinit (GPL), VASP (Commercial), ...

Three Basis Methods to Solve – III

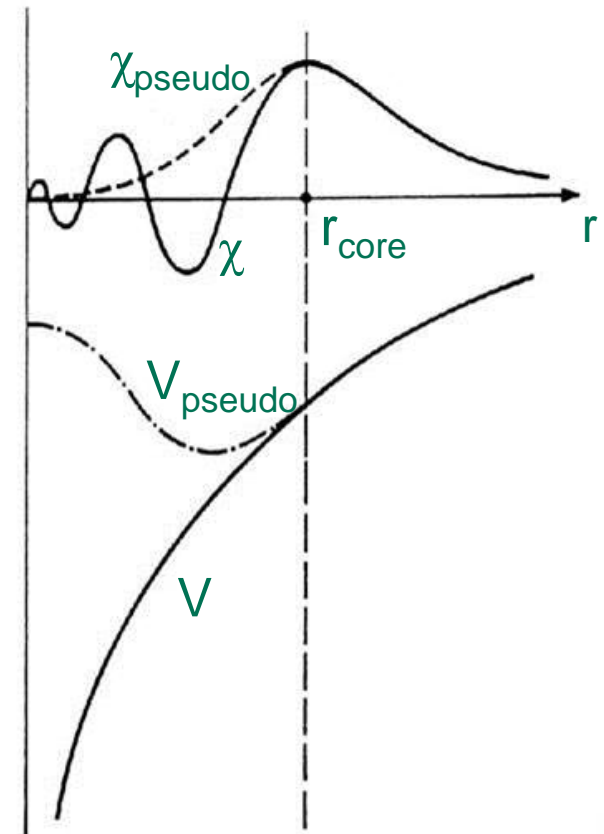
Kohn-Sham (Schrödinger-like) equation:

$$\hat{H}_{KS} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

Plane waves:

Pseudopotential approximation:

- Plane waves form a “complete” basis set,
- However, the number of plane waves, if all electrons are taken into account, would be very large
- Core-electron wave functions are localized, however,
- Valence-electron wave function are far from free-electron like near atomic cores and show oscillation behaviour due to the requirement to be orthogonal to core-electron wave functions



Three Basis Methods to Solve – IV

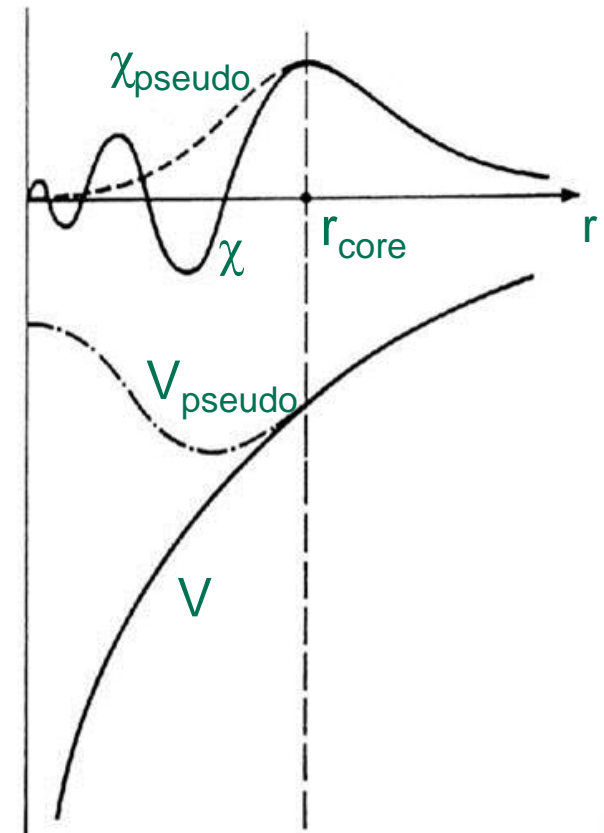
Kohn-Sham (Schrödinger-like) equation:

$$\hat{H}_{KS} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

Plane waves:

Pseudopotential approximation:

- To make plane wave basis set feasible, the exact pseudopotential is substituted by a much weaker (and physically dubious) pseudopotential allowing not to consider core electrons and, therefore, removing these oscillations
- This approximation works because only valence electrons participate in chemical bonding and core electrons are almost unaffected, and also
- The detail of valence wave functions near the atomic nuclei is unimportant





Three Basis Methods to Solve – V

Kohn-Sham (Schrödinger-like) equation:

$$\hat{H}_{KS} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

Plane waves:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{G}} \exp(i(\vec{k} + \vec{G}) \cdot \vec{r})$$

- Wave functions are represented as sum of plane waves, with summation over reciprocal lattice vectors
- Infinite number of plane waves is required theoretically, however, practically, the number of plane waves is truncated by the cut-off kinetic energy E_{cut}

$$|\vec{k} + \vec{G}|^2 \leq E_{\text{cut}}$$

- The quality of the plane wave basis set and, therefore, the results depend on E_{cut}



Three Basis Methods to Solve – VI

Kohn-Sham (Schrödinger-like) equation:

$$\hat{H}_{KS} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

Localized atomic(-like) orbitals:

$$\psi_i = \sum_{\alpha} c_{\alpha} \chi_{\alpha}(\vec{r})$$

Pros: appeal of atomic orbitals, speed of calculation (for Gaussian functions analytical calculations of integrals is performed), small basis sets, vacuum almost does not matter

Cons: Non-orthogonal, depend on atomic position

Programs Gaussian (Commercial), Turbomole (Commercial), SIESTA (Academic)...

Three Basis Methods to Solve – VII

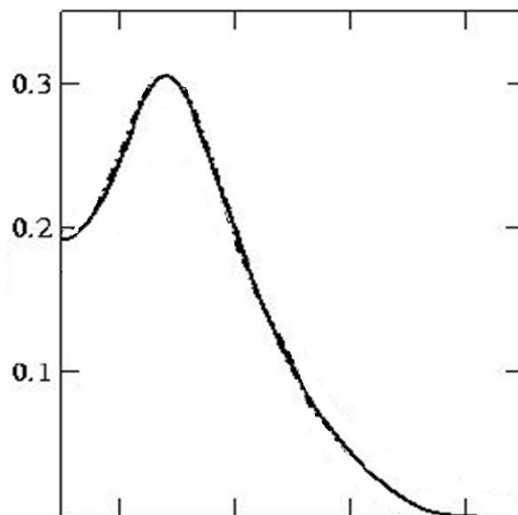
Kohn-Sham (Schrödinger-like) equation:

$$\hat{H}_{KS} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

Localized atomic(-like) orbitals:

$$\chi_\alpha(\vec{r}) \rightarrow \chi_{nlm}(\vec{r}) = \chi_{nl}(r) Y_{lm}(\hat{r})$$

Radial part

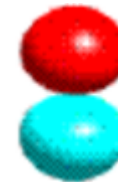


Spherical harmonics

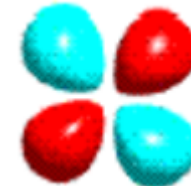
nlm values:



100



210



321

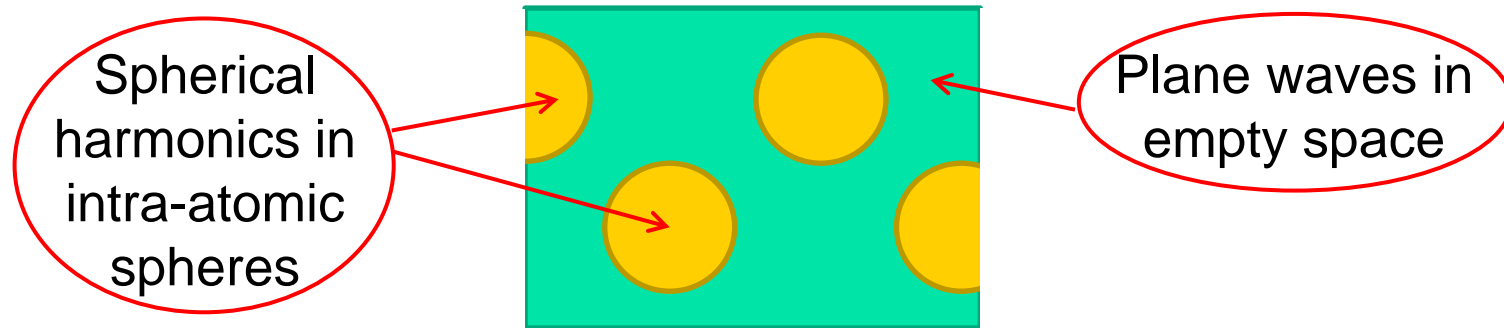
etc ...

Three Basis Methods to Solve – VIII

Kohn-Sham (Schrödinger-like) equation:

$$\hat{H}_{KS} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

Augmented plane wave (best of both worlds):



Cons: Require matching inside and outside functions

Programs: WIEN2k (Commercial), EXCITING (GPL), ...

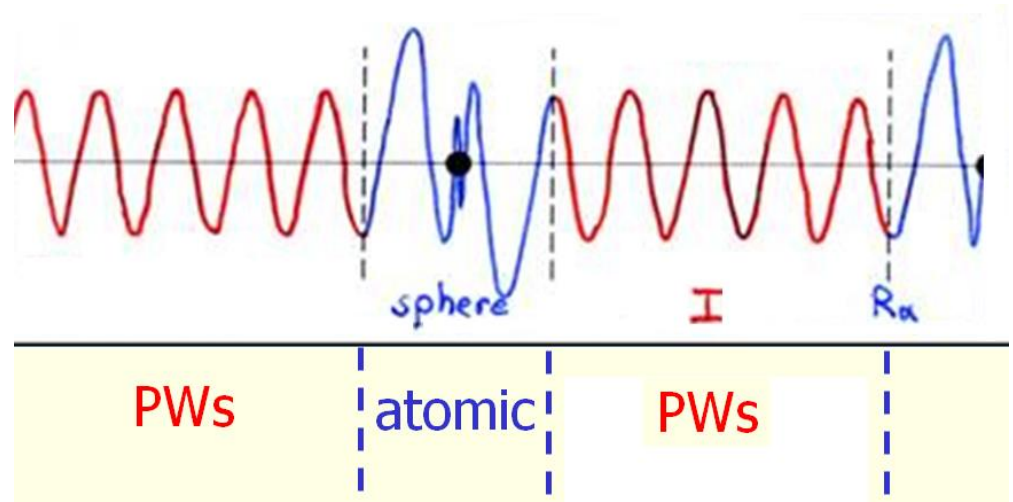
Augmented plane waves – I

PW: $e^{i(\vec{k} + \vec{K}) \cdot \vec{r}}$



Augmented plane waves

$$\sum_{\ell m} A_{\ell m}^K u_{\ell}(r', E) Y_{\ell m}(\hat{r}')$$



- $u_{\ell}(r, \varepsilon)$ are the numerical solutions of the radial Schrödinger equation in a given spherical potential for a particular energy ε
- $A_{\ell m}^K$ coefficients need to be found to match the PW
- However, these basis functions are energy dependent (which we need to find)
- This leads to a non-linear eigenvalue problem
- Numerical search for these energies is possible, however, it is computationally very demanding.

Augmented plane waves – II

Problem is linearized

Augmented plane waves

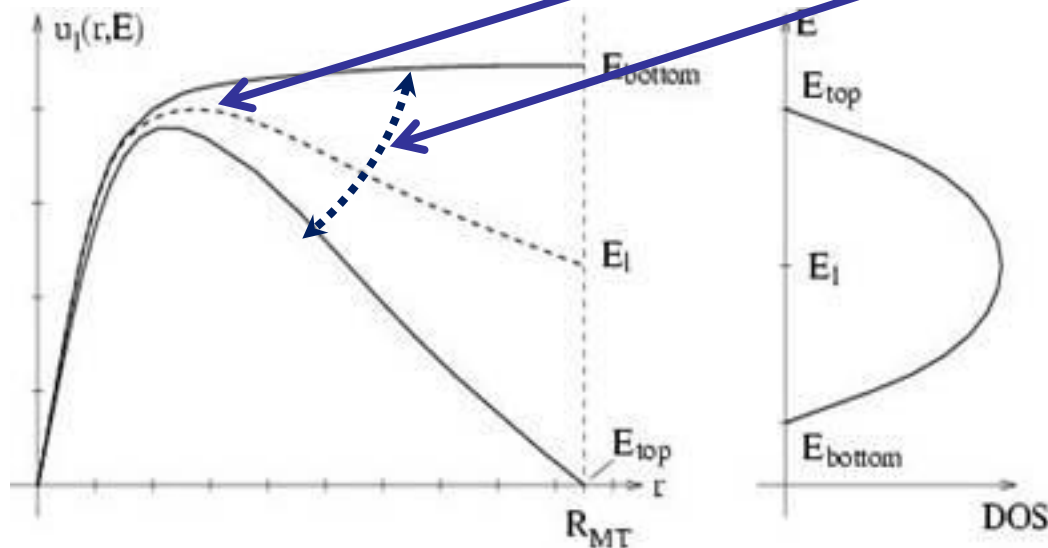
$$\sum_{\ell m} A_{\ell m}^K u_{\ell}(r', E) Y_{\ell m}(\hat{r}')$$

APW

Linearized Augmented plane waves

$$\sum_{\ell m} [A_{\ell m}^{k_n} u_{\ell}(r', E_l) + B_{\ell m}^{k_n} \dot{u}_{\ell}(r', E_l)] Y_{\ell m}(\hat{r}')$$

LAPW

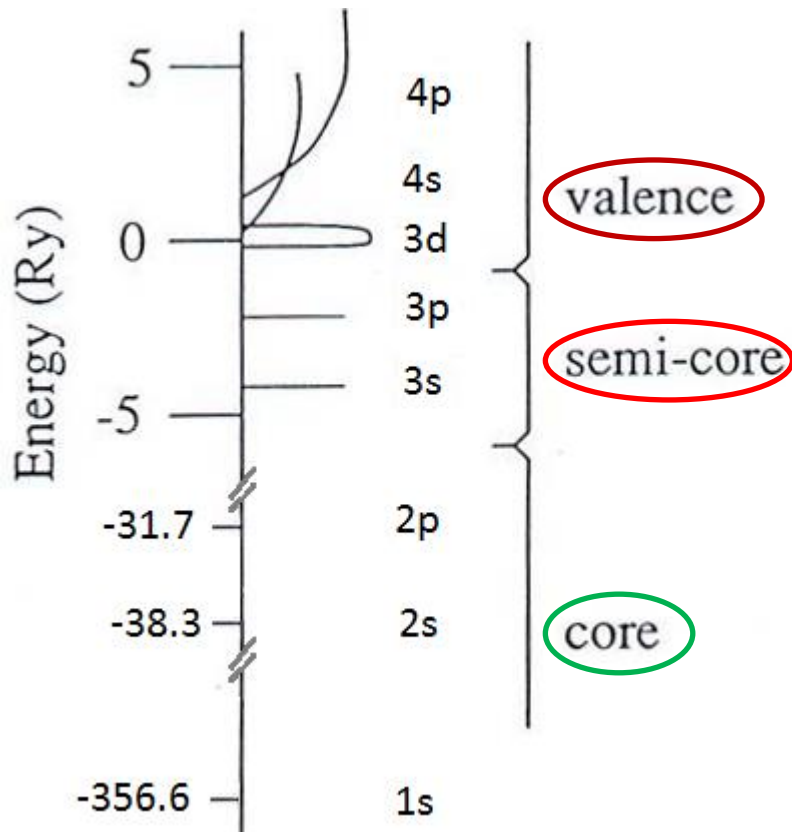


$u_l(R_{MT}, E_{\text{top}}) = 0$
antibonding state, i.e.
Top of the band

$d(u_l(r, E))/dr = 0$ at E_{bottom} and R_{MT}
bonding state, i.e.
Bottom of the band

Augmented plane waves – III

Example: Titanium



Valences states:

- High in energy
- Must use delocalized wavefunctions

Semi-core states:

- Medium energy
- Not completely confined inside the specified sphere, i.e. charge leakage

Core states:

- Very low in energy
- Fully confide inside the specified sphere

Augmented plane waves – IV

Summary of LAPW method

These basis functions are used to describe valence states.

$$\phi_{\vec{K}}^{\vec{k}}(\vec{r}) = \begin{cases} \exp[i(\vec{k} + \vec{K})\vec{r}] & \vec{r} \in I \\ \sum_{\ell m} \left[A_{\ell m}^{\alpha, \vec{k} + \vec{K}} u_{\ell}^{\alpha}(r', E_{1, \ell}^{\alpha}) + B_{\ell m}^{\alpha, \vec{k} + \vec{K}} \dot{u}_{\ell}^{\alpha}(r', E_{1, \ell}^{\alpha}) \right] Y_{\ell m}(\hat{r}') & \vec{r} \in S_{\alpha} \end{cases}$$

$$\phi_{\alpha, LO}^{lm}(\vec{r}) = \begin{cases} 0 & \vec{r} \notin S_{\alpha} \\ \left[A_{\ell m}^{\alpha, LO} u_{\ell}^{\alpha}(r', E_{1, \ell}^{\alpha}) + B_{\ell m}^{\alpha, LO} \dot{u}_{\ell}^{\alpha}(r', E_{1, \ell}^{\alpha}) + C_{\ell m}^{\alpha, LO} u_{\ell}^{\alpha}(r', E_{2, \ell}^{\alpha}) \right] Y_{\ell m}(\hat{r}') & \vec{r} \in S_{\alpha} \end{cases}$$

Additional basis functions are added for low-lying valence states which are called semi-core states.

Augmented plane waves – V

Summary of APW-lo method

These basis functions are used to describe valence states.

$$\phi_{\vec{K}}^{\vec{k}}(\vec{r}) = \begin{cases} \exp[i(\vec{k} + \vec{K})\vec{r}] & \vec{r} \in I \\ \sum_{\ell m} A_{\ell m}^{\alpha, \vec{k} + \vec{K}} u_{\ell}^{\alpha}(\vec{r}', E_{1, \ell}^{\alpha}) Y_{\ell m}(\hat{r}') & \vec{r} \in S_{\alpha} \end{cases}$$

$$\phi_{\alpha, lo}^{lm}(\vec{r}) = \begin{cases} 0 & \vec{r} \notin S_{\alpha} \\ \left[A_{\ell m}^{\alpha, lo} u_{\ell}^{\alpha}(\vec{r}', E_{1, \ell}^{\alpha}) + B_{\ell m}^{\alpha, lo} \dot{u}_{\ell}^{\alpha}(\vec{r}', E_{1, \ell}^{\alpha}) \right] Y_{\ell m}(\hat{r}') & \vec{r} \in S_{\alpha} \end{cases}$$

$$\phi_{\alpha, LO}^{lm}(\vec{r}) = \begin{cases} 0 & \vec{r} \notin S_{\alpha} \\ \left[A_{\ell m}^{\alpha, LO} u_{\ell}^{\alpha}(\vec{r}', E_{1, \ell}^{\alpha}) + B_{\ell m}^{\alpha, LO} \dot{u}_{\ell}^{\alpha}(\vec{r}', E_{1, \ell}^{\alpha}) + C_{\ell m}^{\alpha, LO} u_{\ell}^{\alpha}(\vec{r}', E_{2, \ell}^{\alpha}) \right] Y_{\ell m}(\hat{r}') & \vec{r} \in S_{\alpha} \end{cases}$$

Additional basis functions are added for low-lying valence states which are called semi-core states.

Suggested by E.Sjostedt,
L.Nordstrom, D.J.Singh, 2000

Augmented plane waves – VI

FP-(L)APW-lo method

For basis functions one can use:

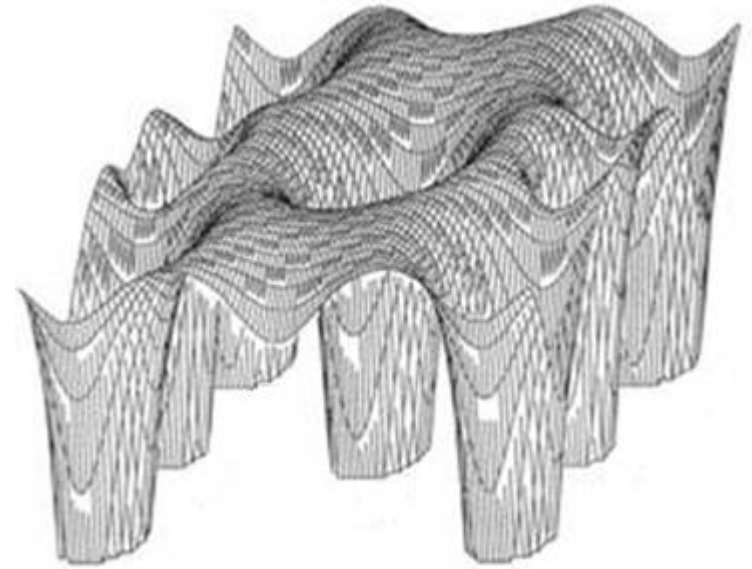
- LAPW (plus LO),
- APW-lo (plus LO),
- or mixed

For potential one can use:

- Muffin-tin approximation, or
- FP, i.e. Full Potential

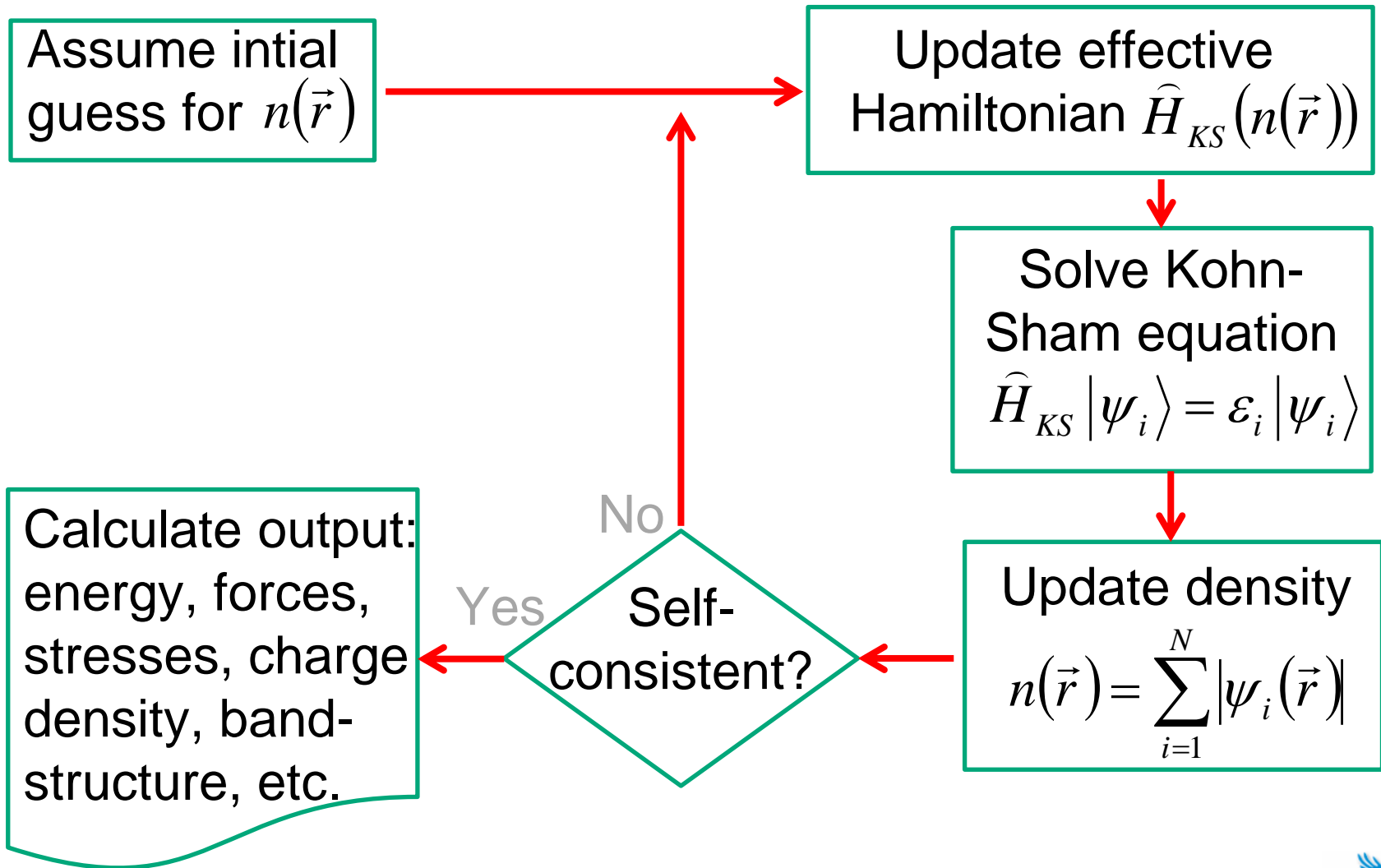
Practically, the numbers which control the accuracy of the solution are:

- The cut-off for the plane waves: RK_{\max}
- The cut-off for the angular functions L_{\max}



$$V(\vec{r}) = \begin{cases} \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r}) & \vec{r} \in S_{\alpha} \\ \sum_K V_K \exp[i\vec{K} \cdot \vec{r}] & \vec{r} \in I \end{cases}$$

Solving Kohn-Sham equations





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Some practical aspects of calculations – I

Brillouin zone integration (K-points)

One scheme to use:

- Many quantities require integration over BZ
- Computationally, the integrals are approximated by summation
- Point group symmetry is utilized fully
- Monkhorst-Pack grid **NxNxN** scheme constructs equally spaced points
- Good for SCF

$$n(\vec{r}) \approx \sum_n \sum_j w_j \left| \psi_n(\vec{k}_j, \vec{r}) \right|^2$$

Another scheme to use:

- Linear tetrahedron method
- Which divides BZ into tetrahedral
- Interpolation is performed
- Good for DOS

Some practical aspects of calculations – II

```
&control  
  calculation = 'scf',  
  prefix = 'Si_exc1',  
/  
&system  
  ibrav = 2,  
  celldm(1) = 10.26,  
  nat = 2,  
  ntyp = 1,  
  ecutwfc = 20  
/  
&electrons  
  mixing_beta = 0.7  
/  
ATOMIC_SPECIES  
Si 28.086 Si.pbe-rrkj.UPF  
ATOMIC_POSITIONS (alat)  
Si 0.0 0.0 0.0  
Si 0.25 0.25 0.25  
K_POINTS (automatic)  
6 6 6 1 1 1
```

Typical QE input file:

type of calculations and
where to find and store files

variables that specify the system
under study

variables that control the algorithms
used to reach the self-consistent
solution of KS equations for the
electrons

name, mass and pseudopotential
used for each atomic species
present in the system

type and coordinates of each atom
in the unit cell

coordinates and weights of the k-
points used for BZ integration



Some practical aspects of calculations – III

To run calculations:

```
prompt > espresso_dir/bin/pw.x < si.scf.in > si.scf.out
```

Output (from file si.scf.out)

```
.....  
End of self-consistent calculation  
.....  
!      total energy              =      -15.84452726 Ry  
.....  
convergence has been achieved in    6 iterations  
.....
```

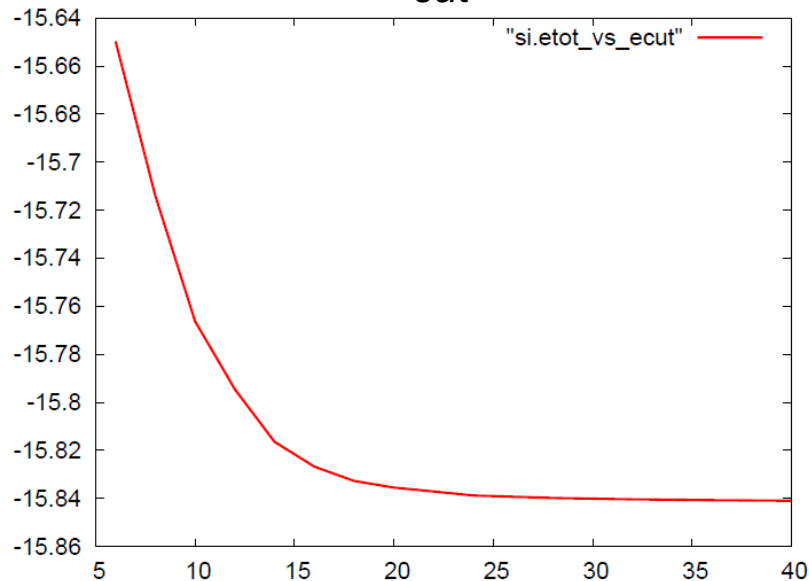
Is it all?

Unfortunately, no, even for scf calculations!!!

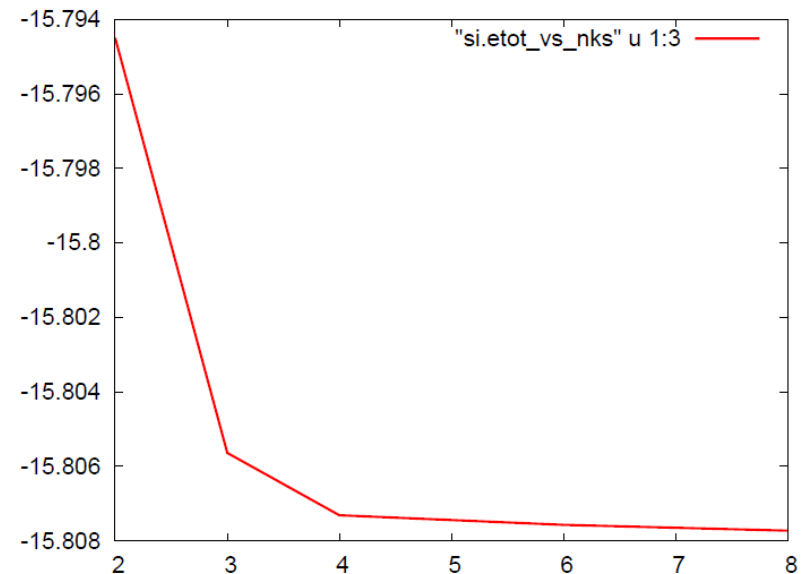
Some practical aspects of calculations – IV

As the solution is numerical, the convergence has to be checked for:

- E_{cut}



- number of k points



Keep in mind that the higher the parameters are set, the (**much!**) longer it takes to compute

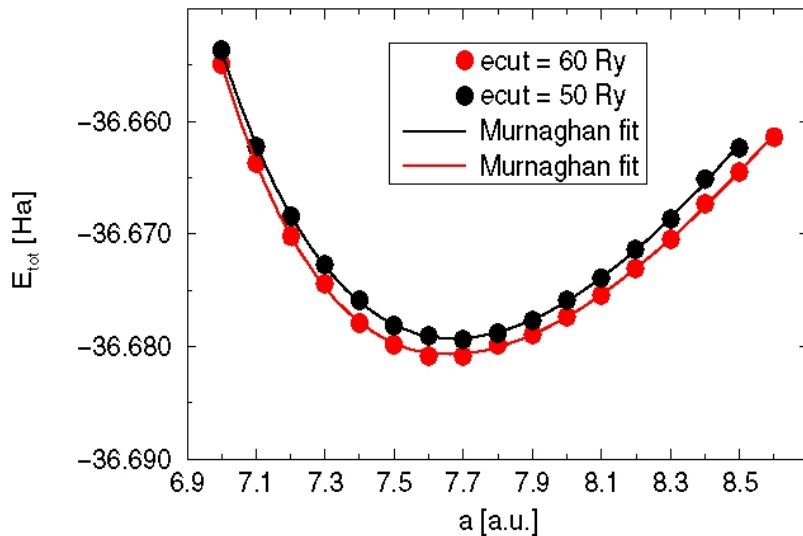
Some practical aspects of calculations – V

Strictly speaking the correct values are:

- electron density $n(\mathbf{r})$, and
- total energy E_{tot}

Total energy is a very useful quantity as it can be used to get structures, heats of formation, adsorption energies, diffusion barriers, activation energies, elastic moduli, vibrational frequencies,...

Ag bulk – E_{tot} vs. a



Is NiO magnetic? NM, FM, AFM?

Solve three different problems:

- nonmagnetic,
- ferromagnetic, and
- antiferromagnetic

Compare E_{tot} for all three cases

The lowest E_{tot} is for AFM

Some practical aspects of calculations – VI

Supercell approach for modelling non-periodic systems

If the system is non-periodic, periodicity must be included via constructing 'supercell':

For molecule or cluster, add empty space from all sides.

For surface, add empty space from a required side and add more material from the opposite side.

For defect, add more material from all sides.

All that is needed to **reduce the interaction** between repeated images as much as possible!

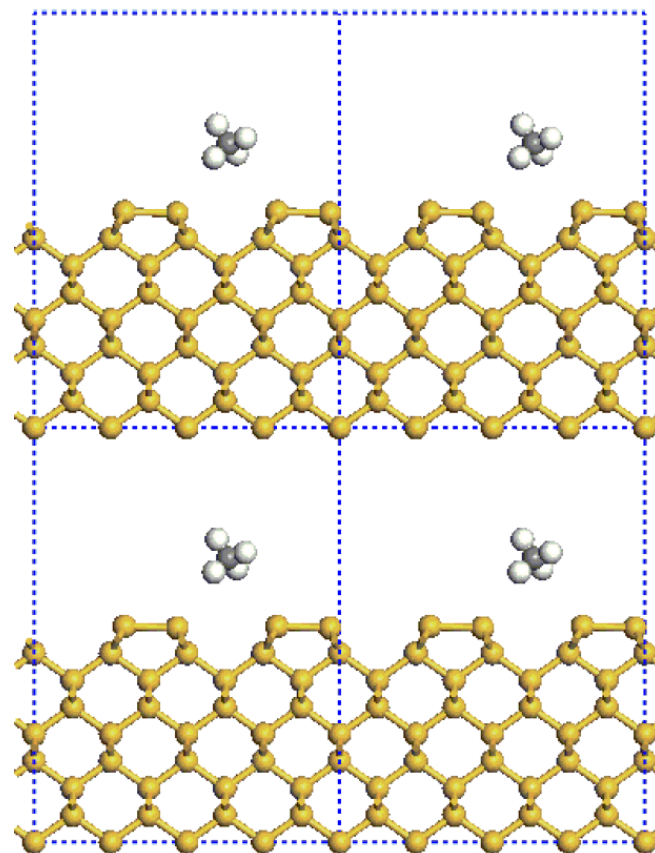


Figure taken from "DFT: Basic idea and Practical calculations" lecture by Dr. A. Phusittrakool (2007)

Some practical aspects of calculations – VII

Supercell approach for modelling non-periodic systems

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

One 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

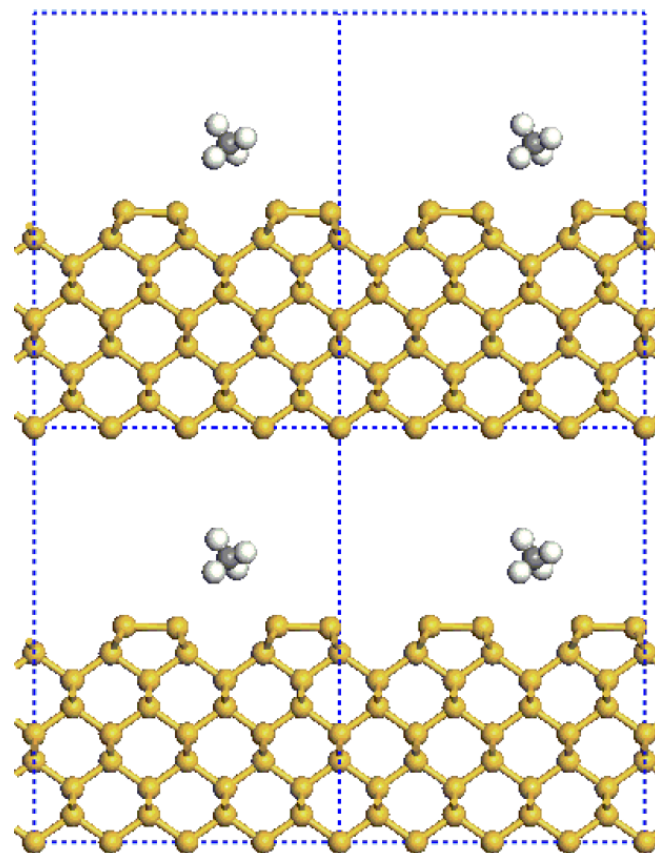


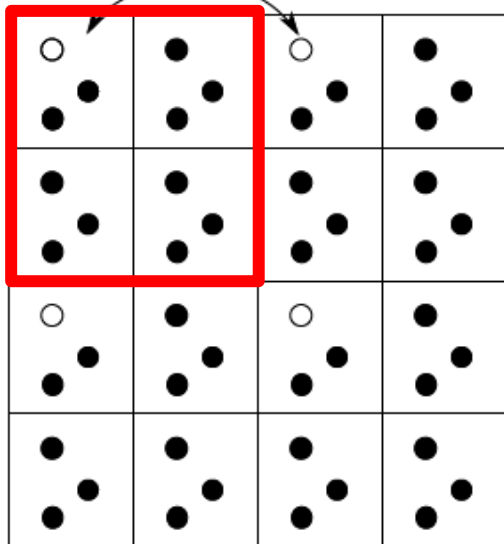
Figure taken from “DFT: Basic idea and Practical calculations” lecture by Dr. A. Phusittrakool (2007)

Some practical aspects of calculations – VIII

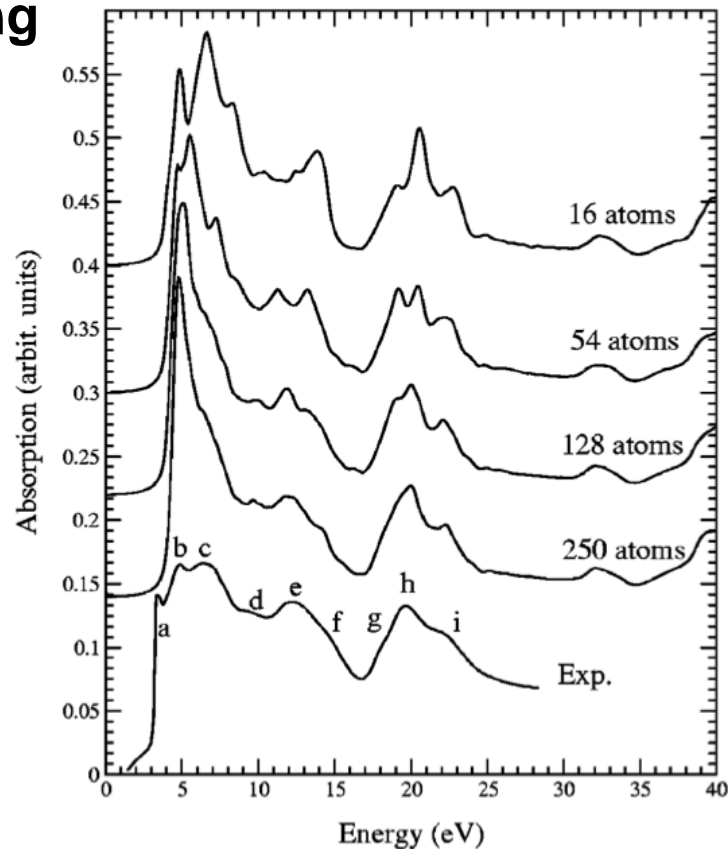
Defects (e.g. core-hole) handling

Calculated C K-edge x-ray absorption spectra in diamond (with core-hole) for different supercell sizes, compared with experimental data

weaker interaction



2x2 supercell with
one core hole by supercell



Figures taken from “XSpectra: A tool for X-ray absorption spectra (XAS) calculations” lecture by Dr. M. Calandra (2009) and M. Taillefumier et al. *PRB* **66** (2002) 195107.



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Examples of applications of DFT

Elemental Crystal Structure (using GGA)

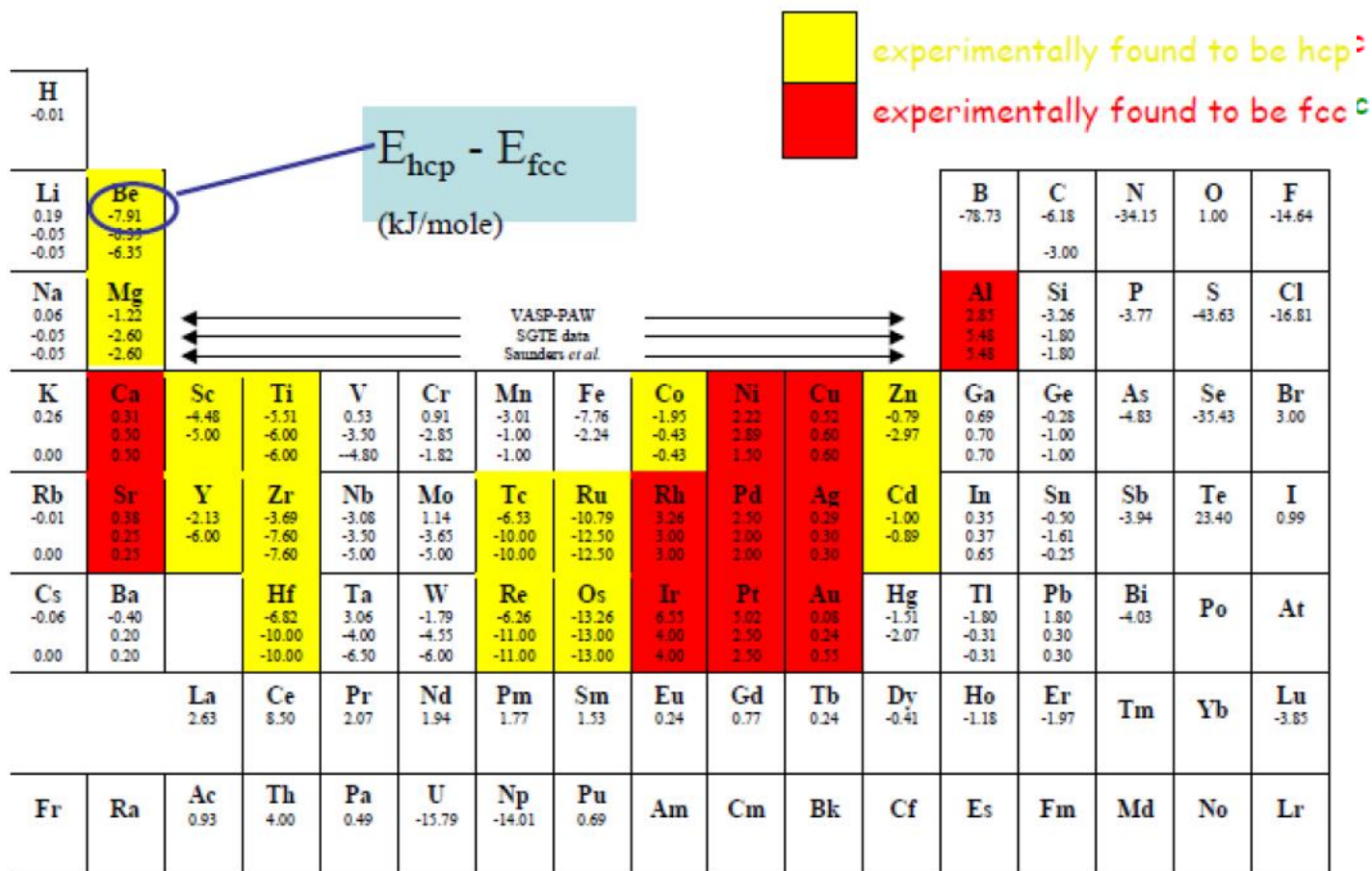


Figure taken from "LDA and the other approaches: Successes and Failures" lecture

Examples of applications of DFT

Charge and spin density for zb-CaAs:

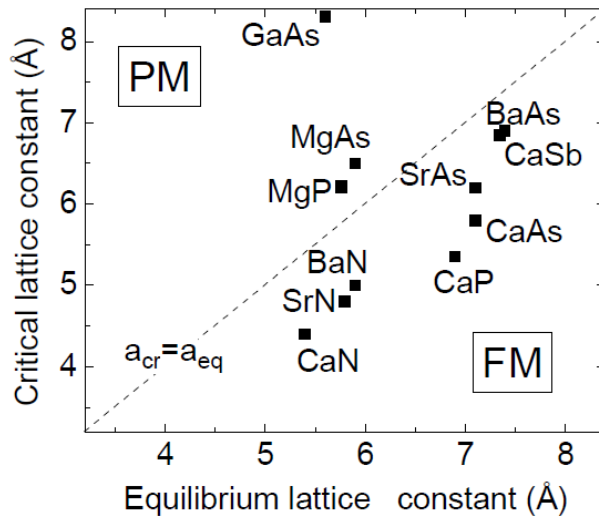
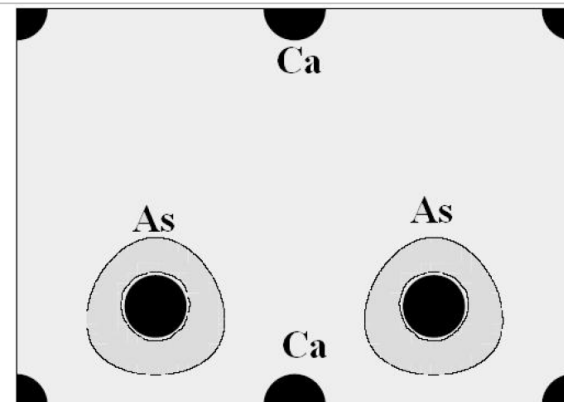
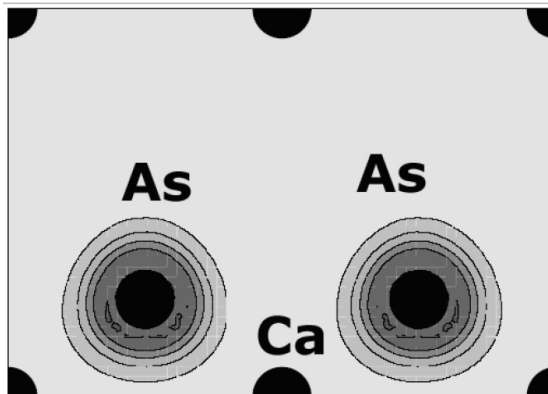


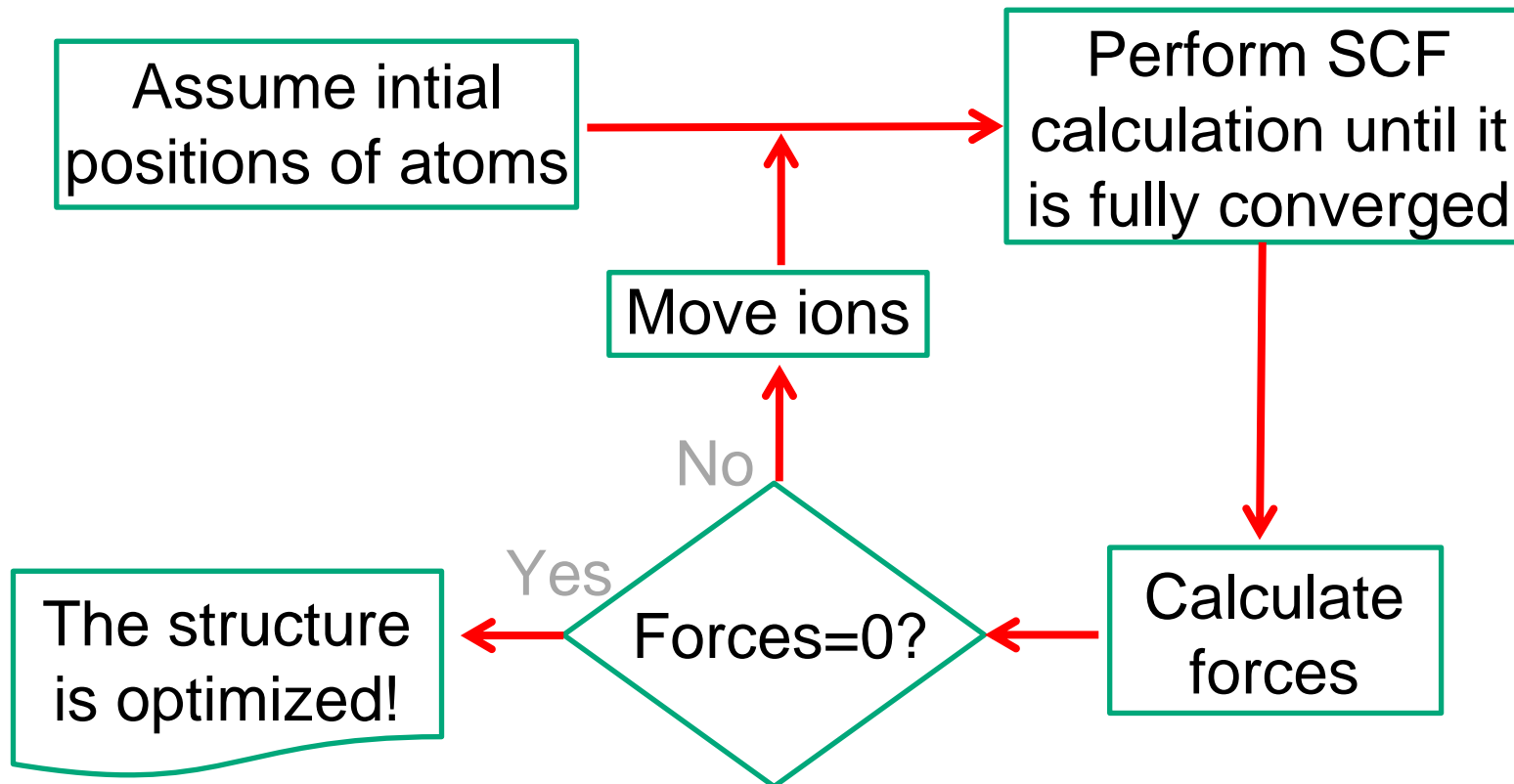
Figure taken from “Theory of magnetic properties based on atomic p-orbitals in perfect and defected solids” PhD thesis by Dr. O. Volnianska (2009)



Examples of applications of DFT

Ionic relaxation, i.e. structure optimization

The positions of atoms in the unit cell are not known (e.g. for surface relaxation).



Examples of applications of DFT

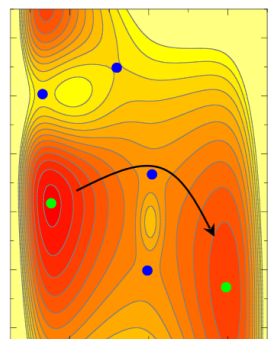
Nudged Elastic Band (NEB) method

will find a minimum energy pathway connecting two local minima and, therefore, can be used to calculate reaction pathways and energy barriers.

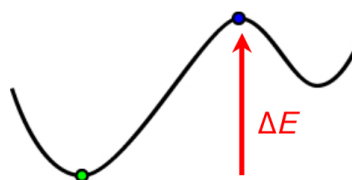
An example: diffusion of a single vacancy in 16-atom cell of Be

Starting structure with
vacancy in (0,0,0)

```
ATOMIC_POSITIONS crystal
Be 1/2 0.0 0.0
Be 0.0 1/2 0.0
Be 1/2 1/2 0.0
Be 0.0 0.0 1/2
Be 1/2 0.0 1/2
Be 0.0 1/2 1/2
Be 1/2 1/2 1/2
Be 1/6+0.0 1/3+0.0 1/4+0.0
Be 1/6+1/2 1/3+0.0 1/4+0.0
Be 1/6+0.0 1/3+1/2 1/4+0.0
Be 1/6+1/2 1/3+1/2 1/4+0.0
Be 1/6+0.0 1/3+0.0 1/4+1/2
Be 1/6+1/2 1/3+0.0 1/4+1/2
Be 1/6+0.0 1/3+1/2 1/4+1/2
Be 1/6+1/2 1/3+1/2 1/4+1/2
```



● Minima
● Saddle Point



Ending structure with
vacancy in (1/6,1/3,1/4)

```
ATOMIC_POSITIONS crystal
Be 1/2 0.0 0.0
Be 0.0 1/2 0.0
Be 1/2 1/2 0.0
Be 0.0 0.0 1/2
Be 1/2 0.0 1/2
Be 0.0 1/2 1/2
Be 1/2 1/2 1/2
Be 0.0 0.0 0.0
Be 1/6+1/2 1/3+0.0 1/4+0.0
Be 1/6+0.0 1/3+1/2 1/4+0.0
Be 1/6+1/2 1/3+1/2 1/4+0.0
Be 1/6+0.0 1/3+0.0 1/4+1/2
Be 1/6+1/2 1/3+0.0 1/4+1/2
Be 1/6+0.0 1/3+1/2 1/4+1/2
Be 1/6+1/2 1/3+1/2 1/4+1/2
```

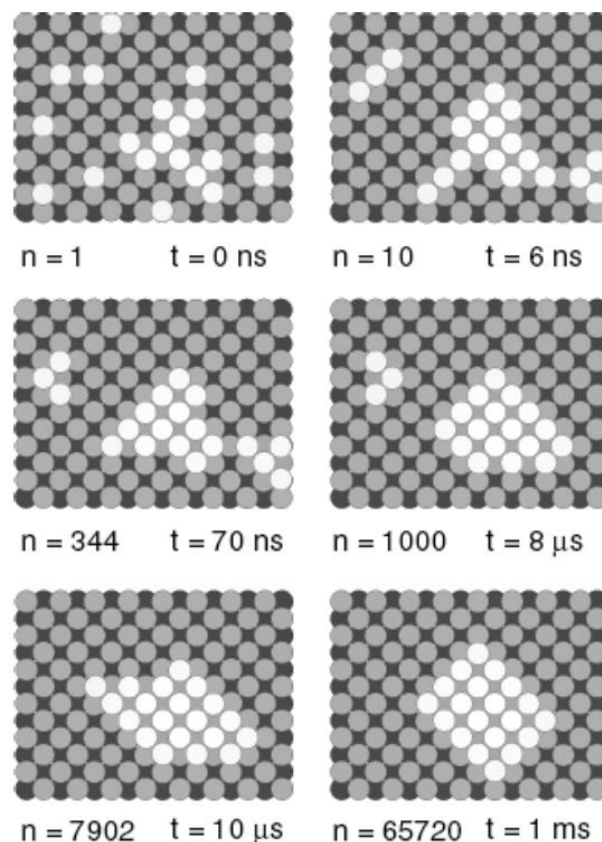
Figures taken from "Simulations of kinetic events
at the atomic scale" lecture by Dr. G. Henkelman

Examples of applications of DFT

Nudged Elastic Band (NEB) method

will find a minimum energy pathway connecting two local minima and, therefore, can be used to calculate reaction pathways and energy barriers.

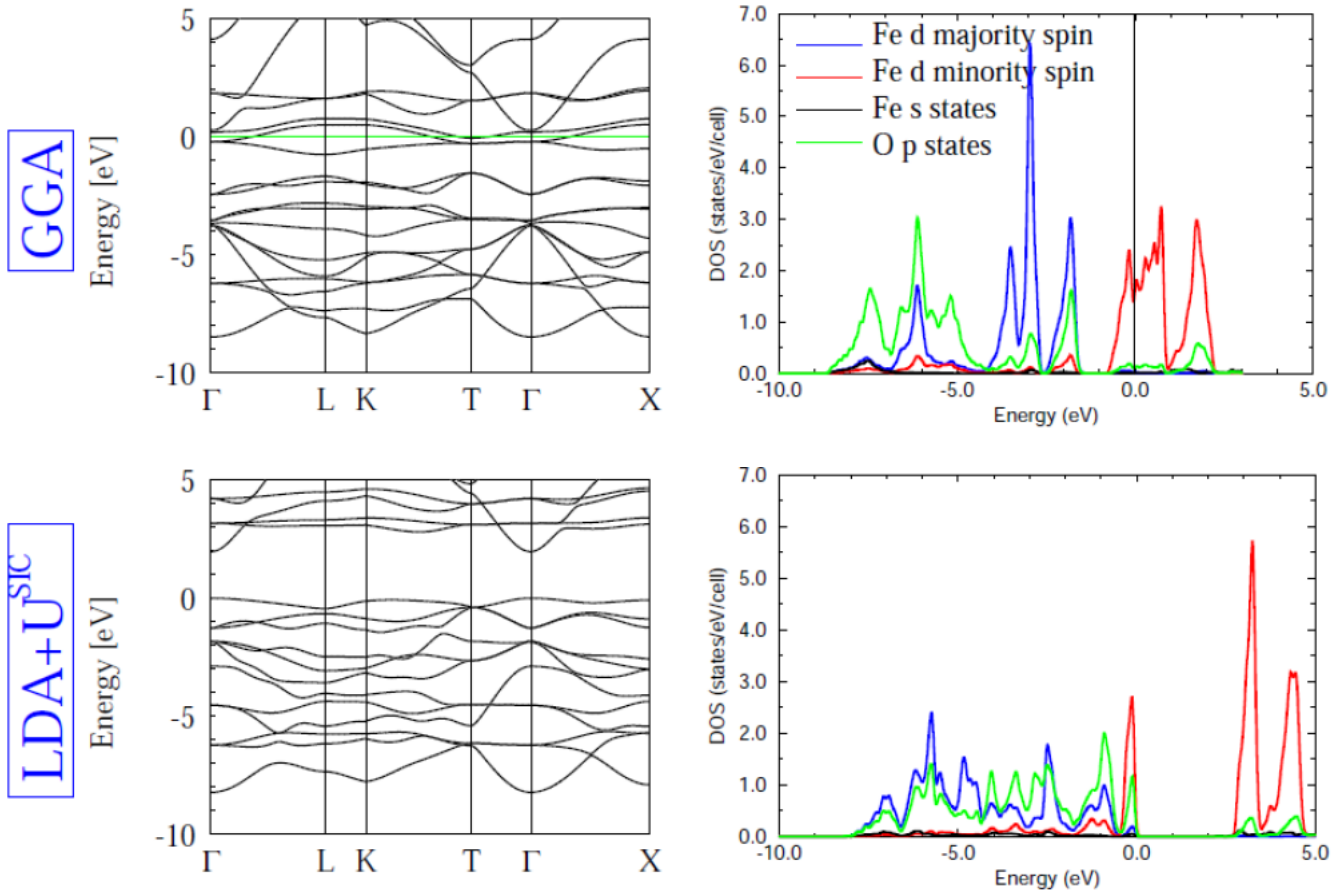
After ΔE is found
(from DFT), it can
be used in kinetic
Monte Carlo method
(~10k of atoms)
to study complex
events as a function
of time and
temperature.



Figures taken from “Simulations of kinetic events at the atomic scale” lecture by Dr. G. Henkelman

Examples of applications of DFT

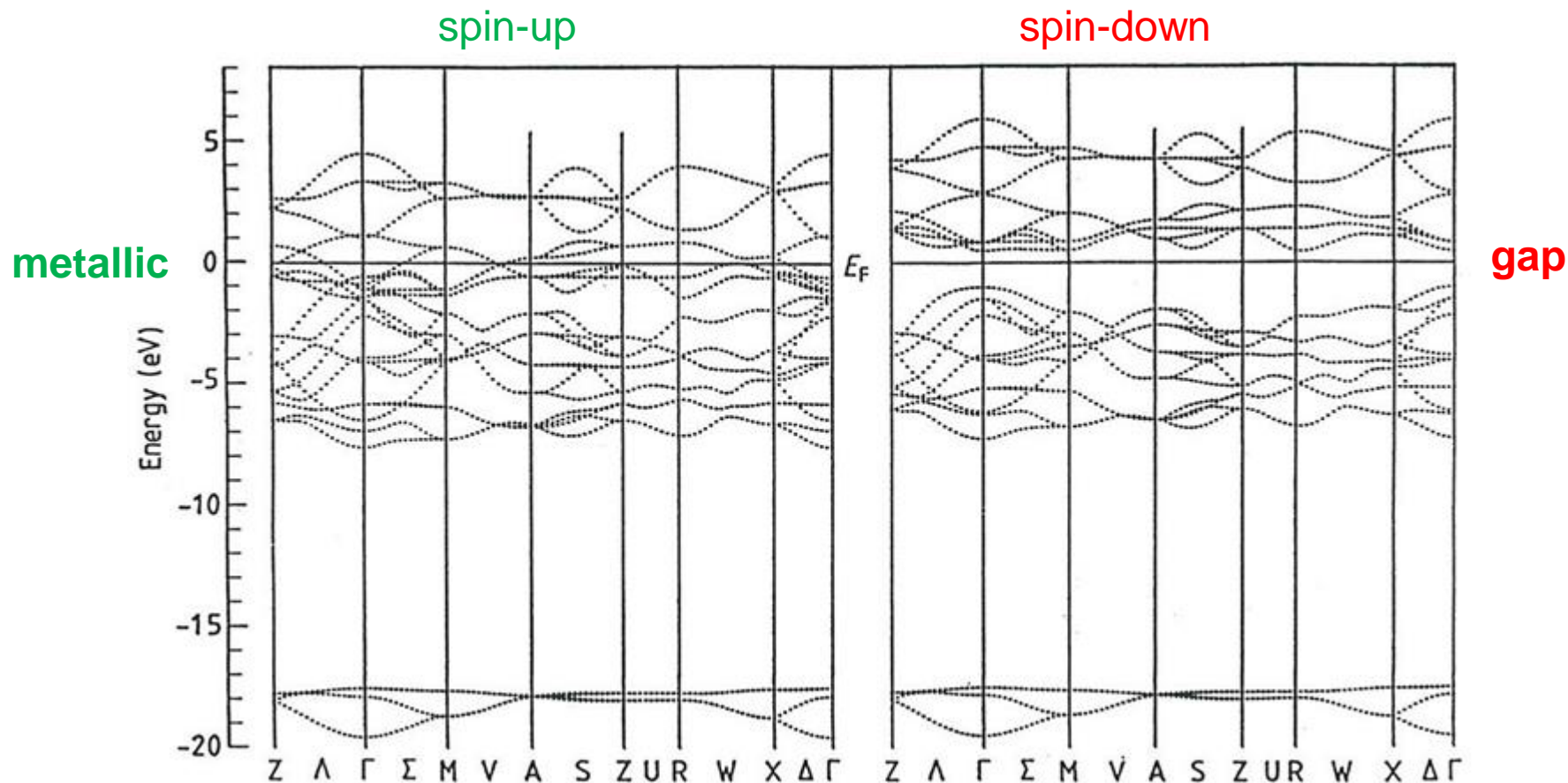
Electronic Structure of FeO



Figures taken from “LDA and the other approaches: Successes and Failures” lecture

Examples of applications of DFT

CrO₂ half-metallic ferromagnet





Examples of applications of DFT

Calculation of cohesive energy:

$$E_{A_x B_y}^{\text{cohes}} = E^{\text{crystal}} - xE_A^{\text{atom}} - yE_B^{\text{atom}}$$

E^{crystal} SCF energy of crystal calculations

E_A^{atom} SCF energy of calculations of atom A

E_B^{atom} SCF energy of calculations of atom B

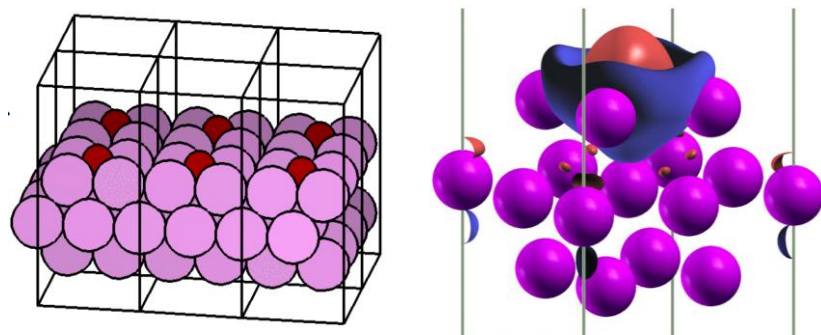
SCF calculations of atoms should be:

- performed in a supercell with one atom in a ~30 bohr FCC box
- The same RMT, RKmax as for crystal
- 1 k-point

Calculation is pretty much similar in case of defect formation energy, however, one need to calculate chemical potential as well of an element, i.e. extra calculations are required.

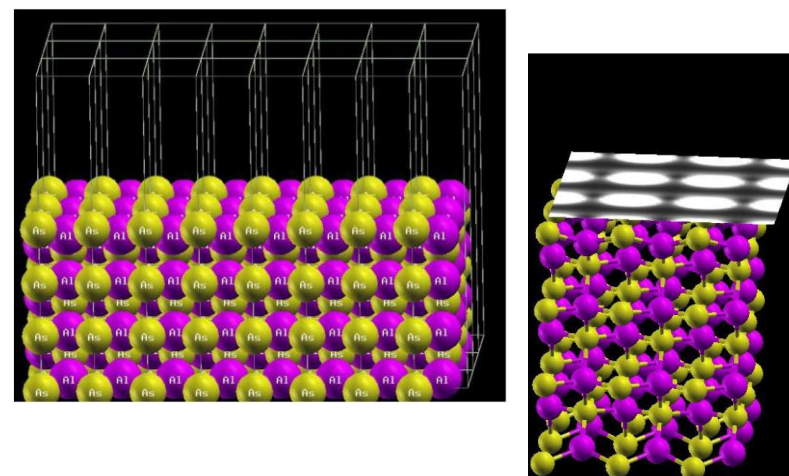
Examples of applications of DFT

Supercell approach for modelling non-periodic systems



Bonding charge density of an O atom on the Al (001) surface calculated by QE and visualized by XCrysDen

Figures taken from “Hands-on tutorial on the Quantum Espresso package” lecture (2008)



Simulation of the STM image of the AlAs (110) surface by QE and visualized by XCrysDen

Figures taken from “Hands-on tutorial on the Quantum Espresso package” lecture (2008)



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Core level spectroscopy – XPS

Estimation of core-level shift:

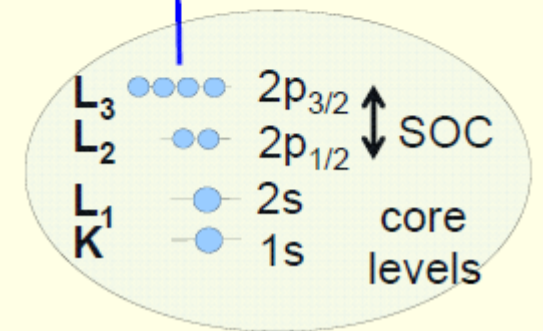
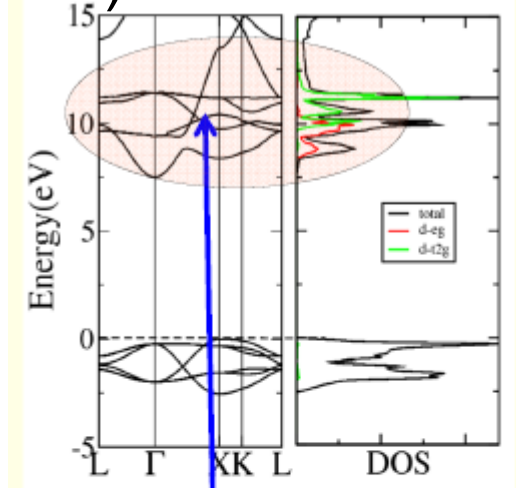
- i.e. estimation of ionization potential of core e^-
- Core-eigenvalues calculated during SCF are NOT a good approximation:
 - Fastest (qualitative agreement) but expect errors ~ 10 -50 eV
- Slater's "transition state" with half occupancy:
 - Fast (better agreement) but expect errors ~ 1 -3 eV
- Δ -SCF-calculation with and without core-hole: $E_{\text{tot}}(N) - E_{\text{tot}}(N-1)$:
 - Slow (good agreement) because supercell must be used, and
 - Two calculations has to be performed

C,N 1s	exp.(eV)	ϵ_i	Δ -SCF
TiC	281.5	264.7	281.9
Ti ₄ C ₄	281.5	263.3	281.1
TiN	397.0	377.5	397.1

Core level spectroscopy – XAS, EELS

WIEN2k has an option to calculate interaction of solid with:

- Light (XAS, more specifically XANES), or
- Electrons (EELS, more specifically ELNES)
- Core electrons are excited into a conduction band
- Transition is described by Fermi's "golden rule" between initial (core) and final (conduction-band) state and the e- or photon
- XAS is calculated via XSPEC or OPTIC
- EELS is calculated via TELNES3





Core level spectroscopy – XAS, EELS

- No core hole, i.e. ground state (or sudden approximation)
 - Usually not a good approximation (maybe in metals?)
- Z+1 approximation also not good (e.g. replacing C by N)
- In absorption spectroscopy, core-hole has a large effect on the spectrum **(make sure that supercell is used)**
 - Remove 1 core e^- on ONE atom in the supercell, add 1 e^- to conduction band
 - Remove 1 core e^- on ONE atom in the supercell, add 1 e^- as uniform background charge
 - Fractional core hole is possible



Core level spectroscopy – XAS, EELS

WARNING (or Reminder):

- DFT is a ground state theory!
- It should fail for the prediction of excited state properties
- However, for many systems it works pretty well
- Sometimes, adding a LO improves description of high-energy states



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Conclusion

- ✓ Density Functional Theory (DFT) is an excellent *computational* tool widely used in physics, chemistry and materials science
- ✓ DFT is an exact many-body theory in principle, but we do not have a practical exact functional
- ✓ Accurate for many simple and complicated systems, but ...
- ✓ ... Keep in mind limitations
- ✓ Many codes available (GPL, Academic, Commercial), tutorials, workshops, schools:

“WIEN2k and Spectroscopy: Hands-on Workshop”
was held on September 29 – October 2, 2014
at Institute of Physics PAS, Warsaw, Poland.