DFT Computation of Materials Properties with WIEN2k

(introduction to Density Functional Theory)

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Motivation

- DFT is presently the most successful and the most popular method to compute the electronic structure of matter

- It works for atoms, molecules, solids, liquids and plasmas

e.g. DFT predicts molecular structures, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths, etc.

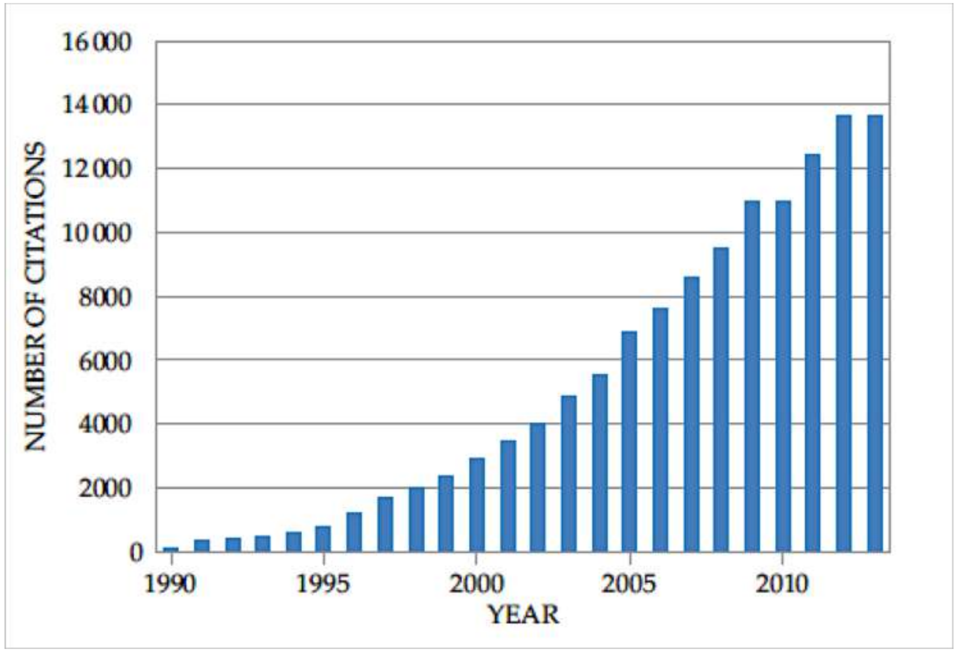
- DFT provides both the scientific justification and the basis for understanding the meaning behind the algorithms used in the computer codes

Motivation

The Density Functional Theory was introduced in two papers:

- Inhomogeneous Electron Gas, P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
- Self Consistent Equations Including Exchange and Correlation Effects, W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

Walter Kohn receiving Nobel Prize (1998)



The number of annual citations to one or both of the foundational of density functional theory (DFT). Both papers are among the most highly cited in the history of Physical Review (Data from the Web of Science.)

- The ultimate goal of most approaches in solid state physics and quantum chemistry is the solution of the time-independent, non-relativistic Schrödinger equation

$$\hat{H}\psi_i = E_i\psi_i \qquad\qquad \left(\hat{T} + \hat{V}\right)\psi_i = E_i\psi_i$$

- For the simple case we can solve the Schrödinger equation exactly to get the wave function of the system ψ_i

- Then we can determine the energy states of the system E_i

- In quantum mechanics, the physical state of an electron is described by a wave function. The quantum mechanical wave function contains, in principle, all the information about a given system.
- The wave function is a mathematical expression (not measurable).

- The wave function is a mathematical expression (not measurable)
- Born interpretation - the square modulus of the wavefunction, $|\psi_i|^2$, at any given point is proportional to the probability of finding the particle at that point. (The quantity $|\psi_i|^2$ is thus a probability density.)

electron density $$n(r) = \sum_i |\psi_i(r)|^2$$

The Schrödinger equation $\hat{H}\psi_i = E_i\psi_i$

Kinetic energy:

$$\hat{H} = -\overbrace{\sum_n \frac{\hat{\boldsymbol{p}}_n^2}{2M}}^{\text{ions}} - \overbrace{\sum_i \frac{\hat{\boldsymbol{p}}_i^2}{2m_e}}^{\text{electrons}} +$$

$$+\underbrace{\frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{n\neq m}\frac{Z_n Z_m e^2}{\left|\boldsymbol{R}_n-\boldsymbol{R}_m\right|}}_{\text{ions}} + \underbrace{\frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{i\neq j}\frac{e^2}{\left|\boldsymbol{r}_i-\boldsymbol{r}_j\right|}}_{\text{electrons}} - \underbrace{\frac{1}{4\pi\varepsilon_0}\sum_{i,n}\frac{Z_n e^2}{\left|\boldsymbol{r}_i-\boldsymbol{R}_n\right|}}_{\text{electrons - ions}}$$

Potential energy:

Elementary quantum mechanics

$$\hat{H} = \boxed{\hat{T}_R + \hat{V}_R} + \boxed{\hat{T}_r + \hat{V}_r} + \boxed{\hat{V}_{r,R}}$$

$$\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; t)$$

It is impossible to solve the Schrödinger equation for a N-body system

↓

we must use some approximations

DFT is a method of obtaining an approximate solution to the Schrödinger equation of a manybody system

Born-Oppenheimer approximation

Born-Oppenheimer approximation:

- motion of ions and electrons can be separated
- ions are fixed in space
  (ions are very massive in comparison to the electrons, nuclei move much slower than the electrons, the kinetic energy of the ions is much smaller than that of the electrons and their potential energy is merely a constant)

The ions kinetic energy is zero and their potential energy is constant.

Born-Oppenheimer approximation

The Hamiltonian for electrons reduces to :

$$\hat{H}_e = -\sum_i \frac{\hat{\boldsymbol{p}}_i^2}{2m_e} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|} - \sum_{i,n}\frac{Z_n e^2}{|r_i - R_n|} = \underbrace{\boxed{\hat{T}_r + \hat{V}_r}}_{\text{electron}} + \underbrace{\boxed{\hat{V}_{r,R}}}_{\text{electrons - ions}}$$

The total energy is then the sum of electron energy and the constant nuclear repulsion.

Hohenberg, W. Kohn, L. J. Sham

$$\hat{H}_e = \hat{T}_r + \hat{V}_r + \boxed{\hat{V}_{r,R}}$$

electrons - ions

the only term that distinguishes
one material (e.g. alloy) from another

determines the wavefunction, which in turn determines the electron density *n*(*r*) and the total energy. The energy is thus a functional of $\hat{V}_{r,R}$

Kohn proposed a radical inversion of that thinking !

Is it possible that the total energy depends only on the electron density *n*(*r*)?

If it were true, knowledge of *n*(*r*) was sufficient to determine the external potential, the many-particle wavefunction, and all the ground-state properties

Hohenberg - Khon theorems

P. C. Hohenberg, W. Kohn, L. J. Sham, Adv. Quantum Chem. 21, 7 (1990)

1st theorem

For any electronic system in an external potential V_{ext}, this potential is determined uniquely, to within a constant, by the ground state density $n_0(r)$

- The Hamiltonian is thus fully determined → the many-body wave functions for all states are determined
- All properties of the system are completely determined only by the ground state density

Electron density

Electron density *n*(*r*) is a representation of the probability of finding an electron in a specific location (volume element).

- *n*(*r*) is a non-negative function of only the three spatial variables which vanishes at infinity and integrates to the total number of electrons:

$$n(\vec{r} \to \infty) = 0 \qquad \int n(\vec{r})\, d\vec{r} = N$$

- *n*(*r*) is an observable and can be measured experimentally, e.g. by X-ray diffraction

2nd theorem

Universal functional of the energy $E[n(r)]$ can be defined in terms of the density $n(r)$, which is valid for any external potential $V_{ext}(r)$

The universal functional contains the individual contributions of kinetic energy , classical Coulomb interaction , and

the non-classical exchange correlation energy $E_{xc}[n(r)]$

Electron correlation, refers to all the effects that are missed when the electrons are treated as independent.

Kohn-Sham energy functional

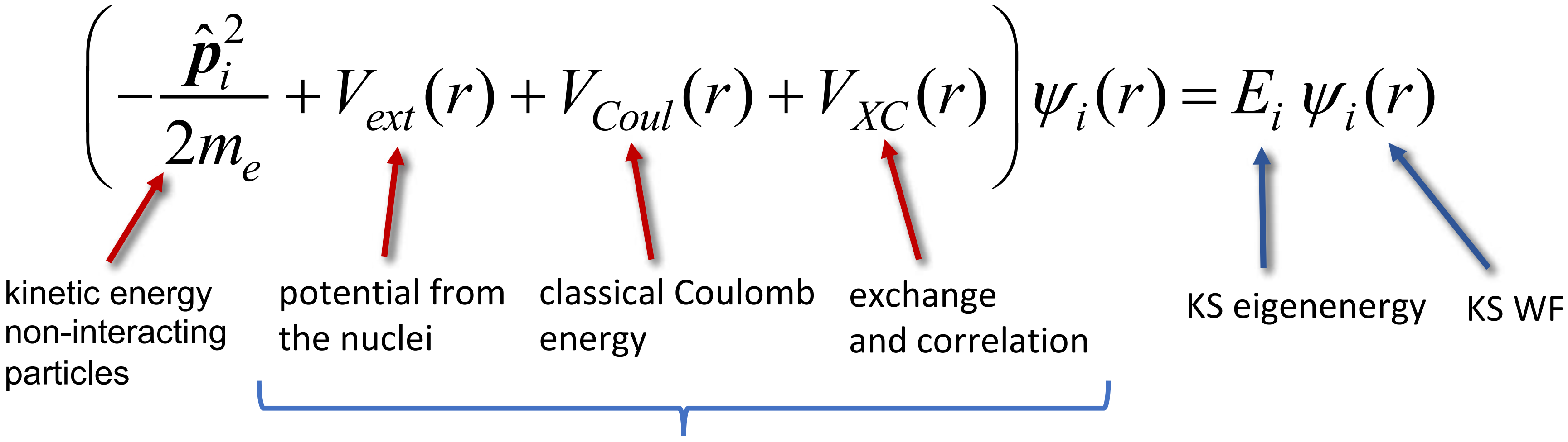
- An essential feature of the theory is the exchange correlation energy $E_{xc}[n(r)]$.
- It maps the electron density function $n(r)$ to the scalar energy E_{xc} associated with all exchange and correlation effects.
- An approximation to $E_{xc}[n(r)]$ is needed for practical work, and Kohn and Sham proposed useful approach.

Kohn-Sham energy functional

Replace the original many-body problem with an auxiliary non-interacting reference system with the same density as the real, interacting one!

The exchange and correlation energy E_{XC} contains everything that is unknown.

Kohn-Sham equations



$$\left(-\frac{\hat{\boldsymbol{p}}_i^2}{2m_e}+V_{ext}(r)+V_{Coul}(r)+V_{XC}(r)\right)\psi_i(r)=E_i\,\psi_i(r)$$

kinetic energy non-interacting particles

potential from the nuclei

classical Coulomb energy

exchange and correlation

KS eigenenergy

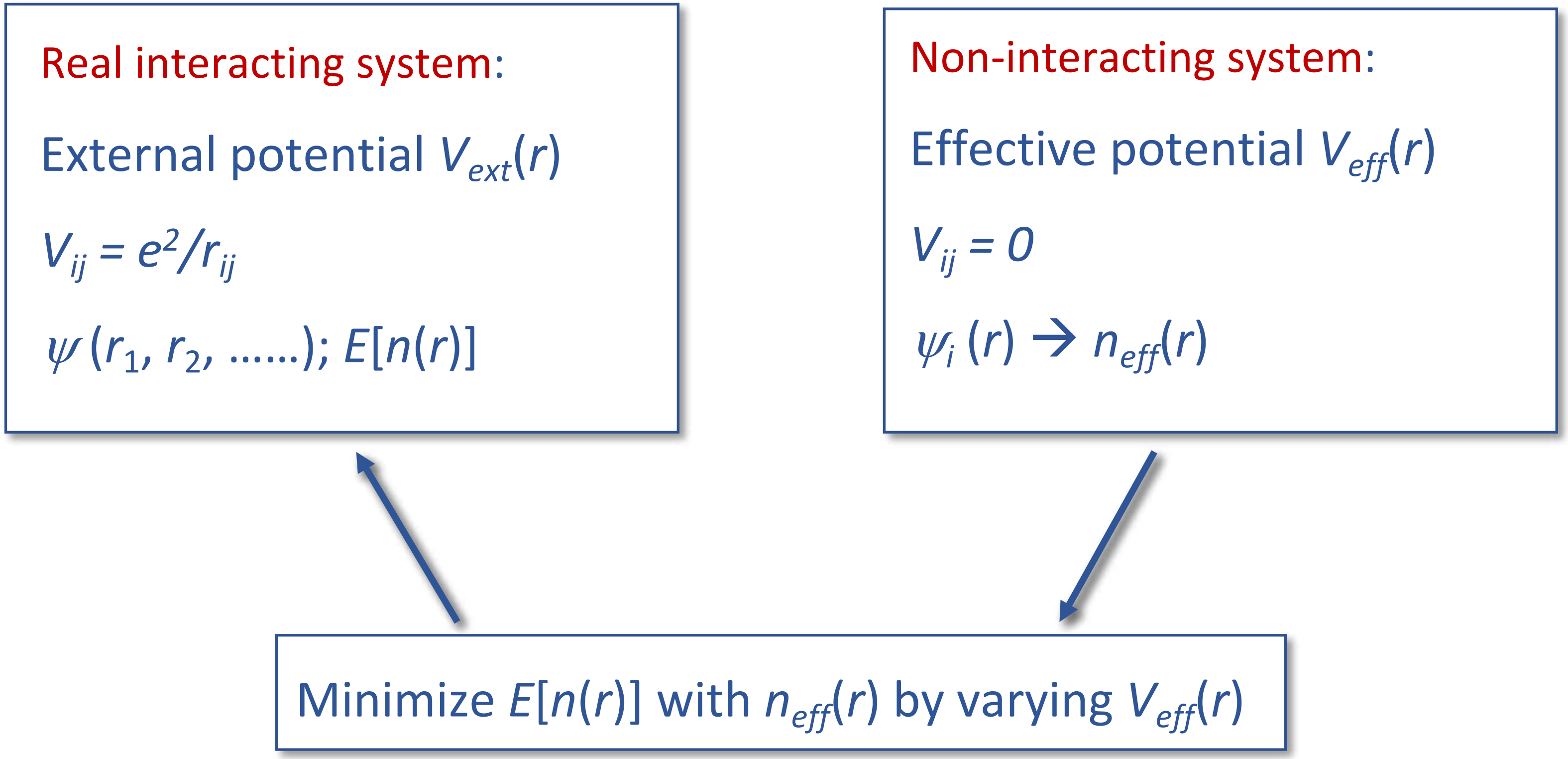
KS WF

effective potential $V_{eff}(\boldsymbol{r})$

$\psi_i(r)$ is the *i*-th single-electron wavefunction of a noninteracting electron system with the same density, *n*(*r*) as the interacting electron system of interest.

It is tempting to treat these states as proper electronic states;
but beware, this are fictitious states

Kohn-Sham formulation of DFT



Real interacting system:

External potential $V_{ext}(r)$

$V_{ij} = e^2/r_{ij}$

$\psi(r_1, r_2, \ldots\ldots); E[n(r)]$

Non-interacting system:

Effective potential $V_{eff}(r)$

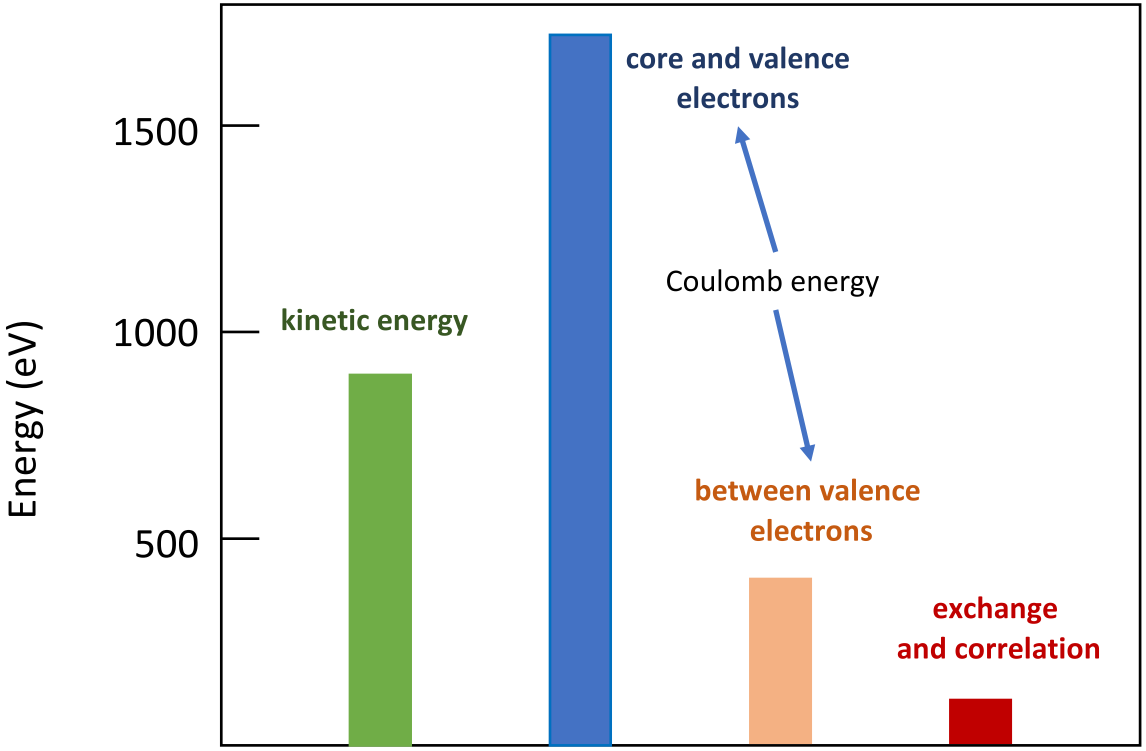
$V_{ij} = 0$

$\psi_i(r) \rightarrow n_{eff}(r)$

Minimize $E[n(r)]$ with $n_{eff}(r)$ by varying $V_{eff}(r)$

3N-dimensional problem is reduced to a 3-dimensional one

Kohn-Sham equations



Relative magnitudes of contributions to total valence energy of Mn atom

R. O. Jones, O. Gunnarsson, Reviews of Modern Physics, Vol. 61, No. 3, 1989

DFT in practice: LDA approximation

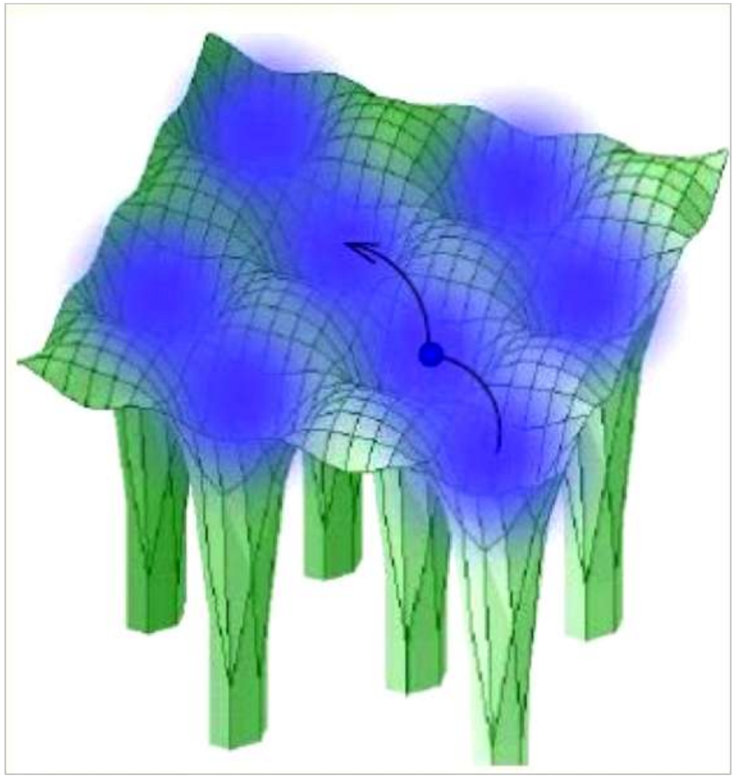
The functional derivative defines a local potential that takes account of both exchange and correlation.

$$V_{XC}(r) = \frac{\delta E_{XC}[n(r)]}{\delta n(r)}$$

Unfortunately, $E_{xc}[n(r)]$, is unknown.

So Kohn and Sham proposed a local density approximation (LDA) for $E_{xc}[n(r)]$, in which the exchange-correlation behavior of every tiny volume of an inhomogeneous system is taken to be the same as the behavior of a uniform electron gas with a density equal to the density of that volume.

DFT in practice: LDA approximation



time averaged
electron density

This is a system in which electrons move on a positive background charge distribution such that the total ensemble is neutral.

DFT in practice: LDA approximation

- LDA calculations yielded ground-state properties of solids to within 1–10% of their experimental value
- This accuracy that LDA delivers was insufficient for most applications in chemistry
- LDA also failed in systems, like heavy fermions, dominated by electron-electron interaction effects

DFT in practice: GGA approximation

In the 1980s new approximation for $E_{xc}[n(r)]$ - called generalized gradient approximation (GGA) were introduced.

It used not only the information about the density at a particular point but also information about the gradient of the charge density, in order to account for the non-homogeneity of the true electron density.

GGA outperformed the LDA when applied to atoms, solids, and surfaces.

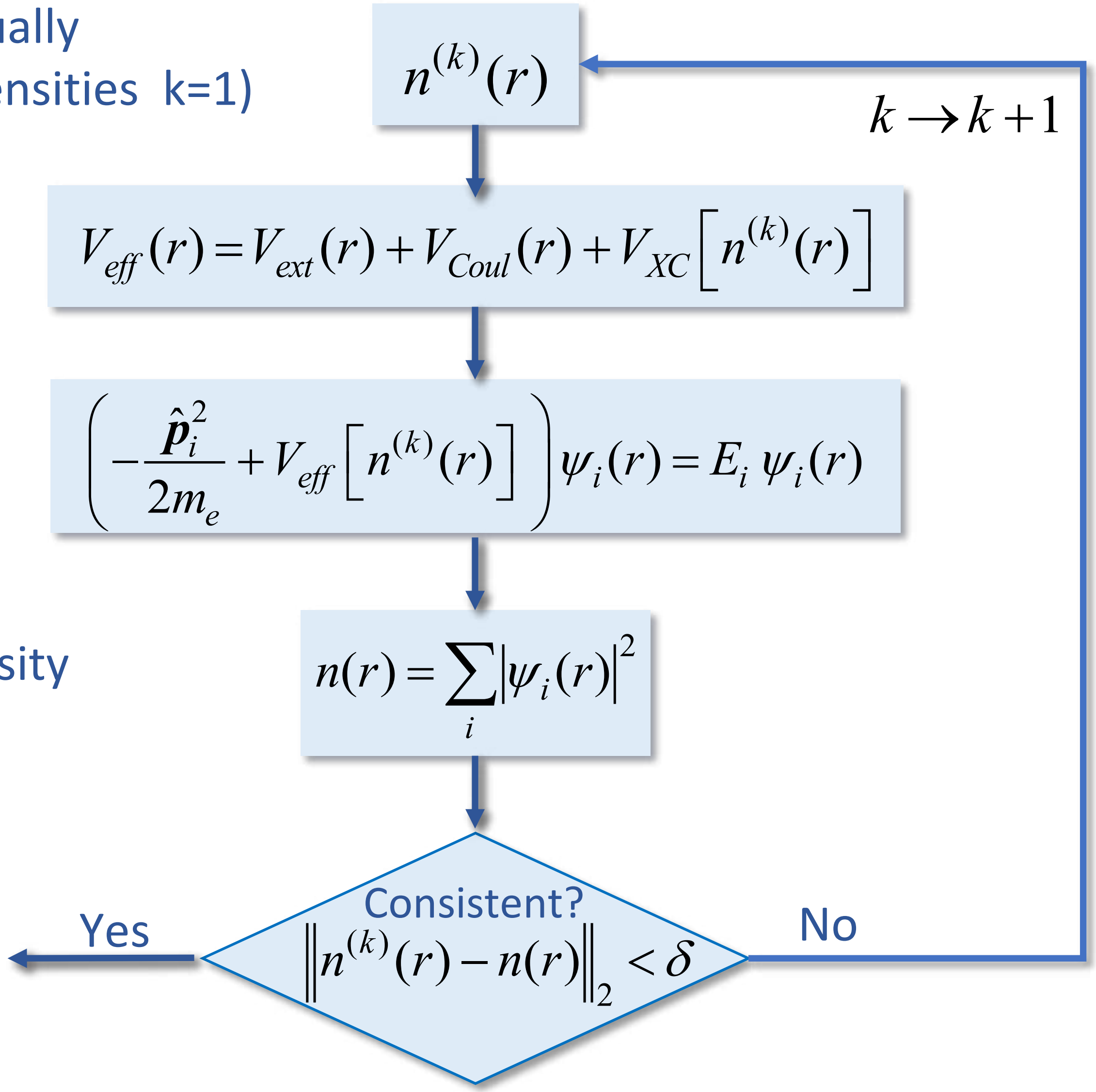
DFT in practice: The self-consistency problem

Both the Coulomb energy and the exchange-correlation energy depend on the density $n(r)$, which in turn depends on the ψ_i , which are the solution of the Schrödinger equation (that we search for!).

This means that we are dealing with a self-consistency problem: the solutions ψ_i determine the original equation (V_{eff}), and the equation cannot be written down and solved before its solution is known.

An iterative procedure is the solution.

DFT in practice: The self-consistency loop



Start with initial guess (usually superposition of atomic densities k=1)

$$n^{(k)}(r)$$

$k \rightarrow k+1$

Evaluate effective potential

$$V_{eff}(r) = V_{ext}(r) + V_{Coul}(r) + V_{XC}\left[n^{(k)}(r)\right]$$

Solve KS equations
(for given potential)

$$\left(-\frac{\hat{\boldsymbol{p}}_i^2}{2m_e} + V_{eff}\left[n^{(k)}(r)\right]\right)\psi_i(r) = E_i\,\psi_i(r)$$

Evaluate (construct) actual density

$$n(r) = \sum_i \left|\psi_i(r)\right|^2$$

Consistent?

$$\left\|n^{(k)}(r) - n(r)\right\|_2 < \delta$$

Yes

Compute energy,
forces, stresses …

No

DFT in practice

Commercial DFT software allow nonexperts with modest computational resources to perform calculations with great accuracy for many, if not all, systems of interest.

The program package WIEN2k allows to perform electronic structure calculations of solids using density functional theory (DFT).

Wien2k code

Wien2k code: developed during the last 35 years

- In the year 2000 (2k) the WIEN code (from Vienna) was called wien2k
- One of the most accurate DFT codes for solids based on the full-potential (linearized) augmented plane-wave ((L)APW) + local orbitals method
- All electron, relativistic, full-potential method

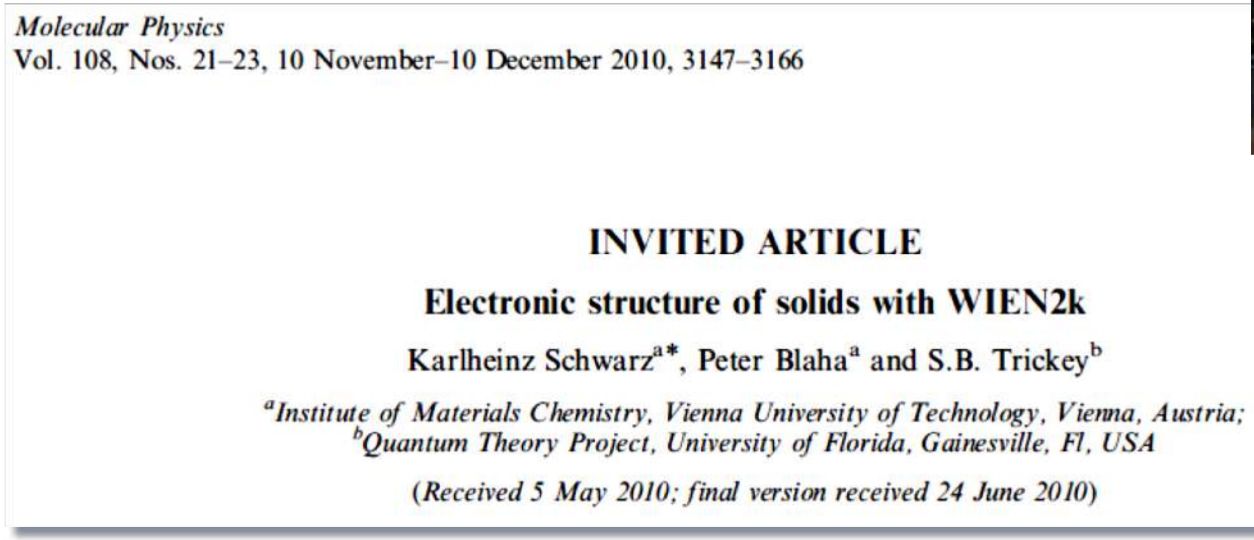
Applications:

- solids: insulators , covalently bonded systems, metals
- surfaces: catalysis
- electronic, magnetic, elastic , optical ,...properties
- many application in literature

Wien2k code

Wien2k is used worldwide by about 2600 groups

See www.wien2k.at



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Vol. 108, Nos. 21–23, 10 November–10 December 2010, 3147–3166

INVITED ARTICLE

Electronic structure of solids with WIEN2k

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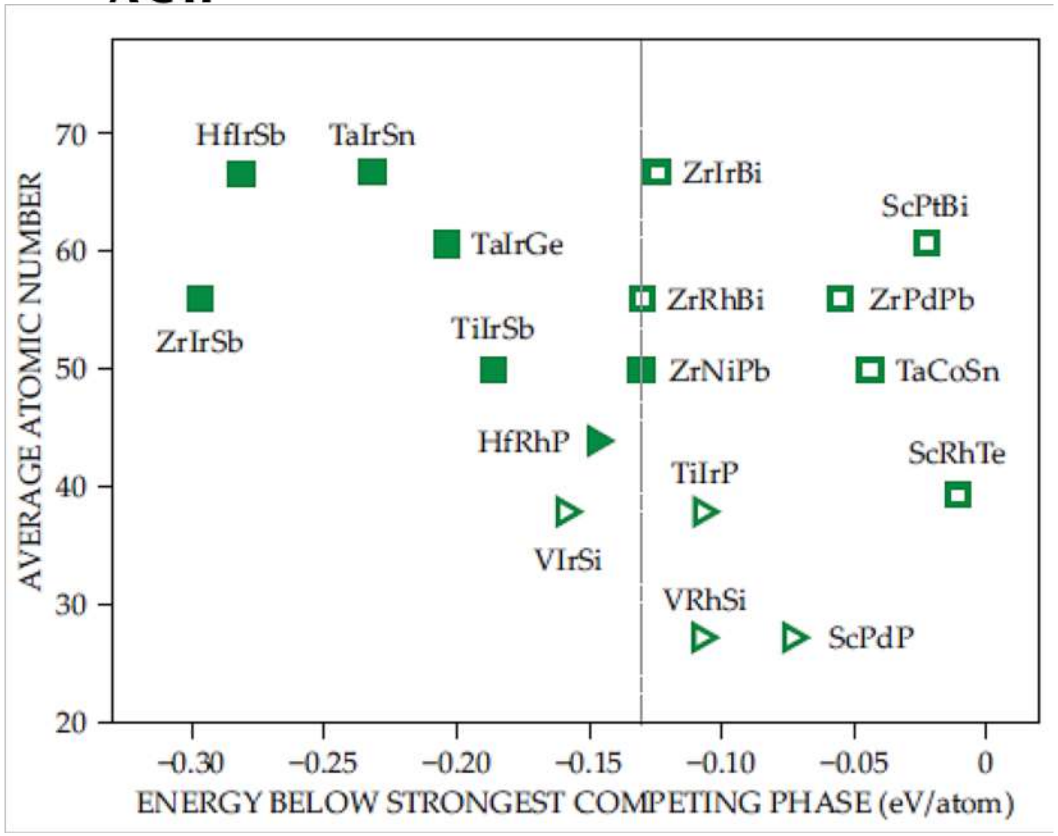
Structure prediction and phase stability



R. Gautier et al., Nat. Chem. 7, 308 (2015), „Prediction and accelerated laboratory discovery of previously unknown 18-electron ABX compounds”

Previously unknown ternary compounds were predicted by DFT to be thermodynamically stable and were later synthesized by experiment.

■	cubic	single phase
▶	noncubic	
□	cubic	multiphase
▷	noncubic	

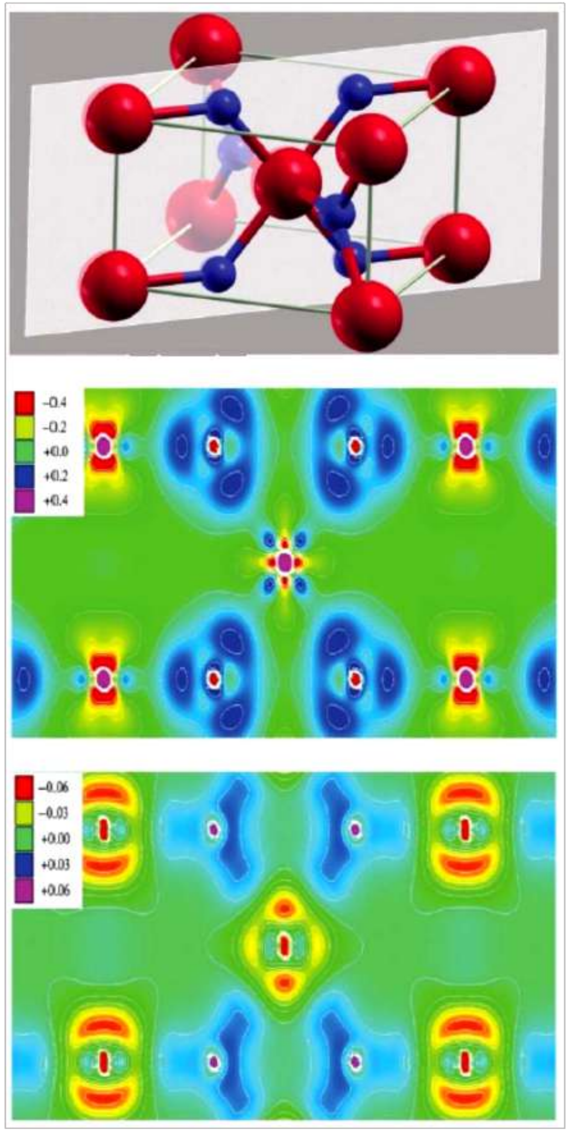
DFT calculations also predicted the correct optical properties for the compounds.

DFT: applications in solid state physics

TiO_2 in the rutile structure

TiO_2 atomic densities
for the valence bands.

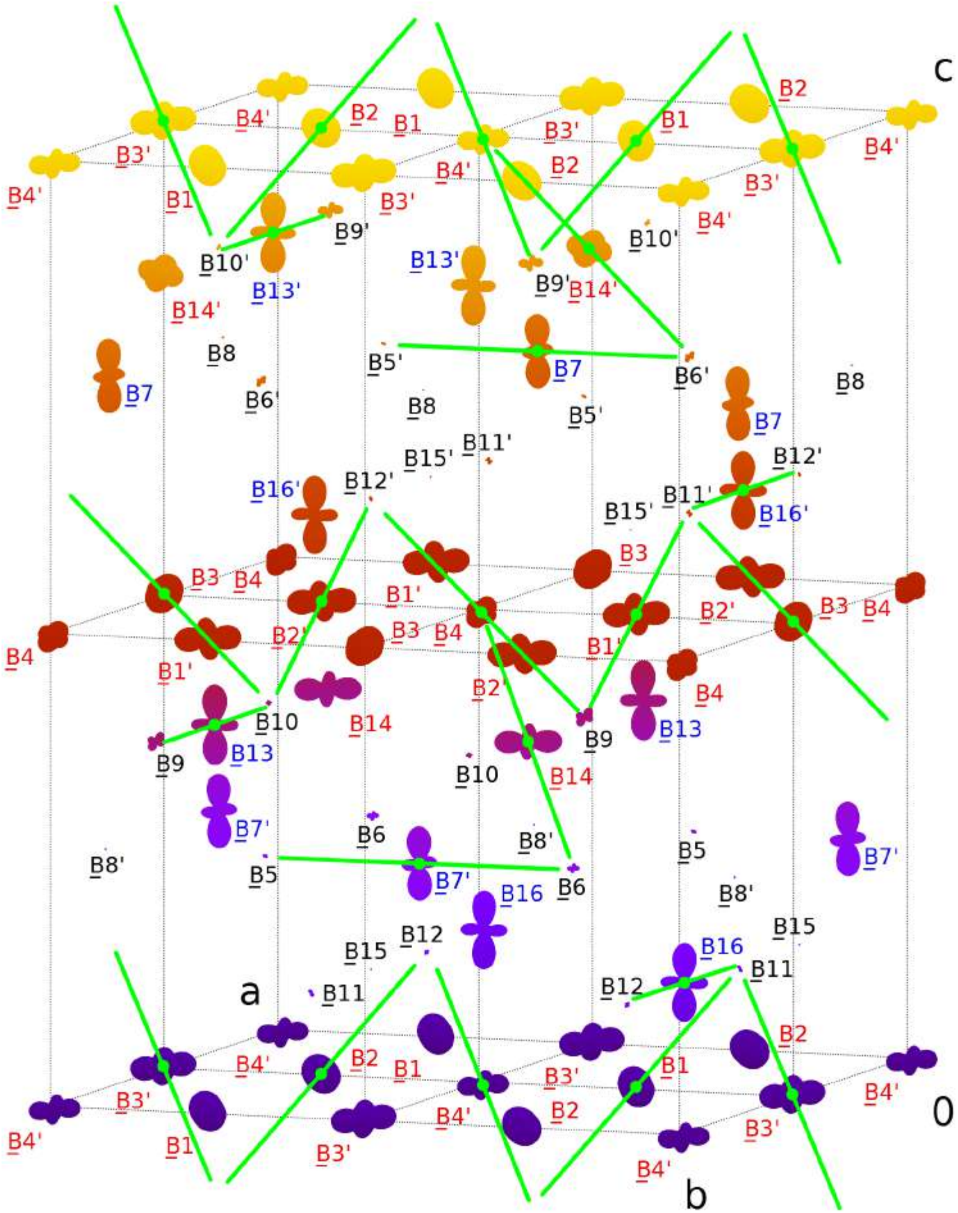
TiO_2 atomic densities
for the semi-core states.



K. Schwarz, P. Blaha and S. B. Trickey, Molecular Physics, Vol. 108, 21–23, 2010, „Electronic structure of solids with WIEN2k”

DFT: applications in solid state physics

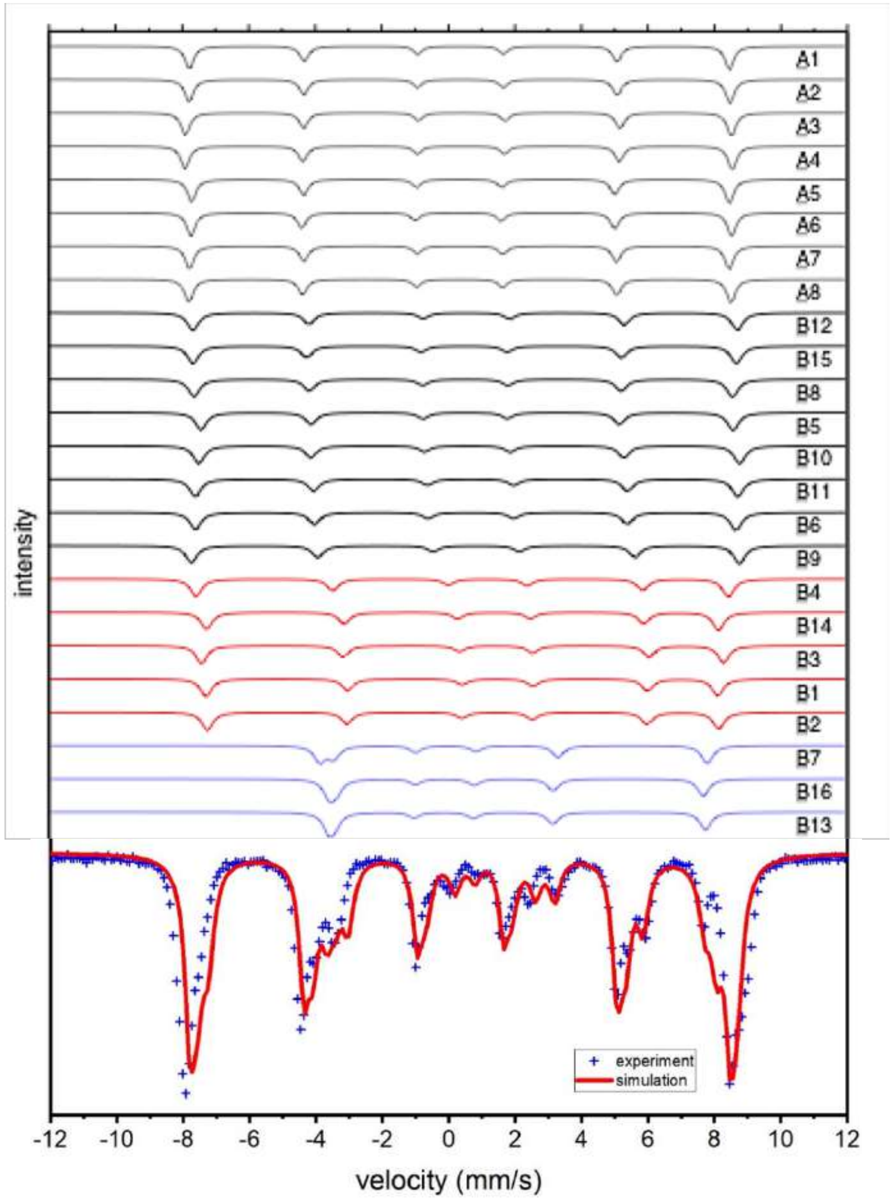
Visualization of the Electric Field Gradient tensors at Fe(B - octahedral) sites in the elementary cell



DFT: applications in solid state physics

Simulation of a zero-field ^{57}Fe Mössbauer spectrum;
comparison with experimental data

All features visible in experimental Mössbauer spectrum can be explained by the ab initio calculated electronic structure



Summary

1. Hohenberg-Kohn theorems
    - All properties determined by electron density
    - A functional can be defined the minimum of which yields the ground energy state

2. Kohn-Sham equations
    - Replace fully interacting system with set of fictitious effective single-particle problems
    - The exchange-correlation functional plays a key role
    - Can be solve iteratively

$$\begin{tikzcd}
V_{ext}(r) \arrow[d] & n_0(r) \arrow[l, "\text{H-K}"'] \arrow[rr] & & n_0(r) \arrow[rr, "\text{K-S}"] & & V_{KS}(r) \arrow[dl] \\
\psi_n(r_1, r_2, \dots,) \arrow[r] & \psi_0(r_1, r_2, \dots,) \arrow[u] & & & \psi_{i=1 \dots N}(r) \arrow[ul] &
\end{tikzcd}$$

Density functional theory (DFT)

3. … yields total energies, forces, and electronic structure, allows computing e.g.,
   - Structural relaxation and phase stability
   - Energy differences (input for thermodynamics, kinetics …)
   - Phonon dispersions (mechanical stability)
   - Property prediction and screening
   - Band structures

Density functional theory (DFT)

4. … provides a reasonable balance between computational efficiency and accuracy (scales N^3 or better, thousands of electrons, hundreds of atoms)

5. … has limitations e.g., with respect to
   - Band gaps and optical properties
   - Strongly correlated systems

Literature

- *Inhomogeneous Electron Gas*, P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)
- *Self Consistent Equations Including Exchange and Correlation Efects*, W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)
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Literature

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DFT Computation of Materials Properties
- introduction to Density Functional Theory