

Solid State Theory: Band Structure Methods

Lilia Boeri

Wed., 11:15-12:45

HS P3 (PH02112)

<http://itp.tugraz.at/LV/boeri/ELE/>

	12/3 Intro	19/3 DFT1	26/3 DFT2	
2/4 DFT3	9/4 DFT4	16/4 BREAK	23/4 BREAK	30/4 BREAK
7/5 DFT5	14/5 P1	21/5 ADV1	28/5 ADV2	
4/6 P2	11/6 ADV3	25/6 P2		

Plan of the Lecture:

DFT1+2: Hohenberg-Kohn Theorem and Kohn and Sham equations.

DFT3+4: Solving K-S in practice; basis functions, augmented methods and psp theory.

DFT5: Practical problems in DFT (k space integration, convergence etc)

P1: EOS and band structure of silicon.

ADV1+2: Linear Response theory (mostly for phonons).

P2: Phonons of silicon

ADV3: Wannier Functions and TB approximation.

P3: Wannier Functions and BOM for silicon.

Introduction to Density Functional Theory(DFT 1-2):

- **Quantum-Mechanical Many-Electron Problem.**
- **Main Concepts of Kohn-Sham (Spin)-Density Functional Theory.**
- **Wavefunction Theory.**
- Density Functional Theory (Density is the Basic Variable).
- Uniform electron gas.

For this and the following 2 lectures I will be following “A primer in Density Functional Theory” (Springer), chapters 1 and 6. A free (pdf) copy can be downloaded at this address:

http://www.physics.udel.edu/~bnikolic/QTG/NOTES/DFT/BOOK=primer_dft.pdf

Quantum-Mechanical Many-Electron Problem

The material world of everyday experience is built up from electrons and a few (hundreds) kinds of nuclei. The interactions between them is electrostatic (Coulomb). In most cases, one assumes that the energy scales of electrons and nuclei are well separated in energy, so that the electrons maintain their fully quantum nature, while ions are treated semiclassically (**Born-Oppenheimer approximation**). The problem for the electrons is described by the following Hamiltonian:

$$\hat{H} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_i \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_I \sum_{J \neq I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

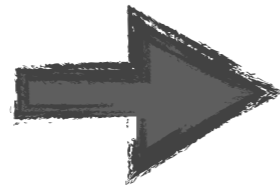
Finding the solutions (eigenvalues, eigenfunctions) of this quantum-mechanical many-electron problem is the main problem of solid state physics, and is still unsolved.

$$\hat{H} \Psi_k(\mathbf{r}_1 \sigma_1, \dots, \mathbf{r}_N \sigma_N) = E_K \Psi_k(\mathbf{r}_1 \sigma_1, \dots, \mathbf{r}_N \sigma_N)$$


Main Concepts of Density Functional Theory:


The quantum-mechanical many-electron problem can be greatly simplified if we are only interested in its ground-state properties.

$$\Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N)$$



$$n_0^\sigma(\mathbf{r}) = \sum_{\sigma_2 \dots \sigma_N} \int d^3r_2 \dots d^3r_N |\Psi_0(\mathbf{r}\sigma, \dots, \mathbf{r}_N\sigma_N)|^2$$

 **Hohenberg-Kohn Theorem:** The ground-state energy of a system of interacting electrons is a function of its ground-state density only. The complications induced by the electron-electron interaction are “dumped” into an effective exchange and correlation energy, whose exact form is unknown (but good approximation exists).

 **Kohn-Sham Equations:** It is possible to find the ground-state density of the interacting system solving self-consistently a system of single-particle equations for the **auxiliary (effective) Kohn-Sham quasi-particles**.

Main Concepts of Density Functional Theory:

In the (spin-)density functional method, we seek the ground-state total energy E and the spin densities for a collection of N electrons which interact with each other, and with a given external potential (typically a sum of nuclear potentials). The energy and densities can be found **by self-consistent (scf) solution of a set of equations.**

$$\left(-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + u([n]; \mathbf{r}) + v_{xc}^\sigma([n_\uparrow, n_\downarrow]; \mathbf{r}) \right) \psi_{\alpha\sigma}(\mathbf{r}) = \epsilon_{\alpha\sigma} \psi_{\alpha\sigma}(\mathbf{r})$$

Kinetic External Hartree Exchange-
Energy Potential Potential Correl. Potential

The Hartree and Exchange-Correlation energies are **functionals** of the (spin) **electron density**. The solutions of this set of one-particle equations are the auxiliary **Kohn-Sham** quasi-particles (Kohn, Sham, Phys. Rev. 1965).

Electron Density

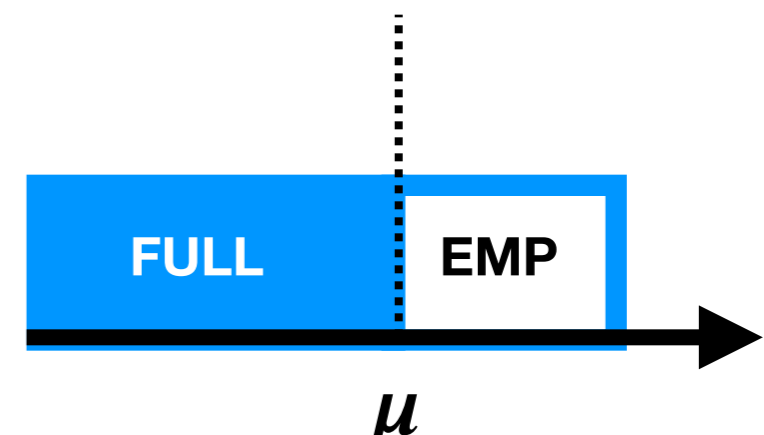
The **ground state electron density** is defined, in terms of the K-S quasi-particles, as:

$$n_{\sigma}(\mathbf{r}) = \sum_{\alpha} \theta(\mu - \varepsilon_{\alpha\sigma}) |\psi_{\alpha\sigma}(\mathbf{r})|^2$$

$$n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$$

μ is the **chemical potential**, defined by:

$$N = \int d^3r n(\mathbf{r})$$



Although the Kohn-Sham quasi-particles have no clear physical meaning, they are constructed in such a way that their ground state density is the same as that of the original, interacting

Main Concepts of K-S Density Functional Theory:

The **Hartree Potential** is a **functional** of the **K-S electron density**:

$$u([n]; \mathbf{r}) = \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$$



What is a **functional**? While a function is a rule which assigns a number $f(x)$ to a number x , a functional is a rule which assigns a number $F[f]$ to a function f .

EX:

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$$

The **Hartree Potential** represents the repulsive potential experienced by each K-S quasi-particle due to average effect of all other quasi-particles.

Main Concepts of Density Functional Theory:

The **Exchange and Correlation potential** is an unknown function, which contains all the (unknown) many-body effects, not included in the first two terms of the Kohn-Sham equations (effective kinetic energy term, Hartree potential). This is usually expressed as the **functional derivative** of an (unknown) **exchange and correlation energy**:

$$v_{xc}^{\sigma}([n_{\uparrow}, n_{\downarrow}]; \mathbf{r}) = \frac{\partial E_{xc}}{\partial n_{\sigma}(\mathbf{r})}$$

Hohenberg and Kohn Theorem (Phys. Rev. 1964) states that if the **exact form of the exchange and correlation energy** was known, it would be possible to calculate **the ground state energy exactly**, knowing only the ground-state electronic density. This is not possible but good approximations exist:

$$E_{xc}^{LSD} [n_{\uparrow}, n_{\downarrow}] = \int d^3r n(\mathbf{r}) e_{xc}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}))$$

**Local (Spin) Density
Approximation**

$$E_{xc}^{GGA} [n_{\uparrow}, n_{\downarrow}] = \int d^3r f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow})$$

**Generalized Gradient
Approximation**

What is a self-consistent solution?

The Schroedinger's equation for the Kohn-Sham quasi-particles depends on the **ground-state density**; on the other hand, the ground-state density is obtained summing over the occupied **K-S orbitals**.

$$\left(-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + u([n]; \mathbf{r}) + v_{xc}^\sigma([n_\uparrow, n_\downarrow]; \mathbf{r}) \right) \psi_{\alpha\sigma}(\mathbf{r}) = \epsilon_{\alpha\sigma} \psi_{\alpha\sigma}(\mathbf{r})$$

$$n_\sigma(\mathbf{r}) = \sum_{\alpha} \theta(\mu - \epsilon_{\alpha\sigma}) |\psi_{\alpha\sigma}(\mathbf{r})|^2$$

1. Start from a set of “guess functions”.
2. Calculate the corresponding charge density.
3. Compute the Hartree and xc potentials
4. Insert into the Schoedinger equations.

Iterate until the charge densities at step t and $(t+1)$ differ by less than a given threshold

DFT Total Energy

The ground-state energy is a functional of the ground-state density:

$$E = T_s [n_\uparrow, n_\downarrow] + \int d^3r n(\mathbf{r})v(\mathbf{r}) + U [n] + E_{xc} [n_\uparrow, n_\downarrow]$$

Kinetic Energy (of the K-S system), do not confuse with that of the interacting system!!!

$$T_s [n_\uparrow, n_\downarrow] = \sum_{\sigma} \sum_{\alpha} \theta(\mu - \varepsilon_{\sigma\alpha}) \langle \psi_{\alpha\sigma} | -\frac{1}{2} \nabla^2 | \psi_{\alpha\sigma} \rangle$$

Hartree Energy (electrostatic):

$$U [n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Exchange-Correlation Energy (unkwown):

$$v_{xc}^{\sigma} ([n_\uparrow, n_\downarrow]; \mathbf{r}) = \frac{\partial E_{xc}}{\partial n_{\sigma}(\mathbf{r})}$$

DFT Total Energy

DFT works because the x-c energy (the only approximate part) is a small fraction of the total energy of an atom, molecule or solid.

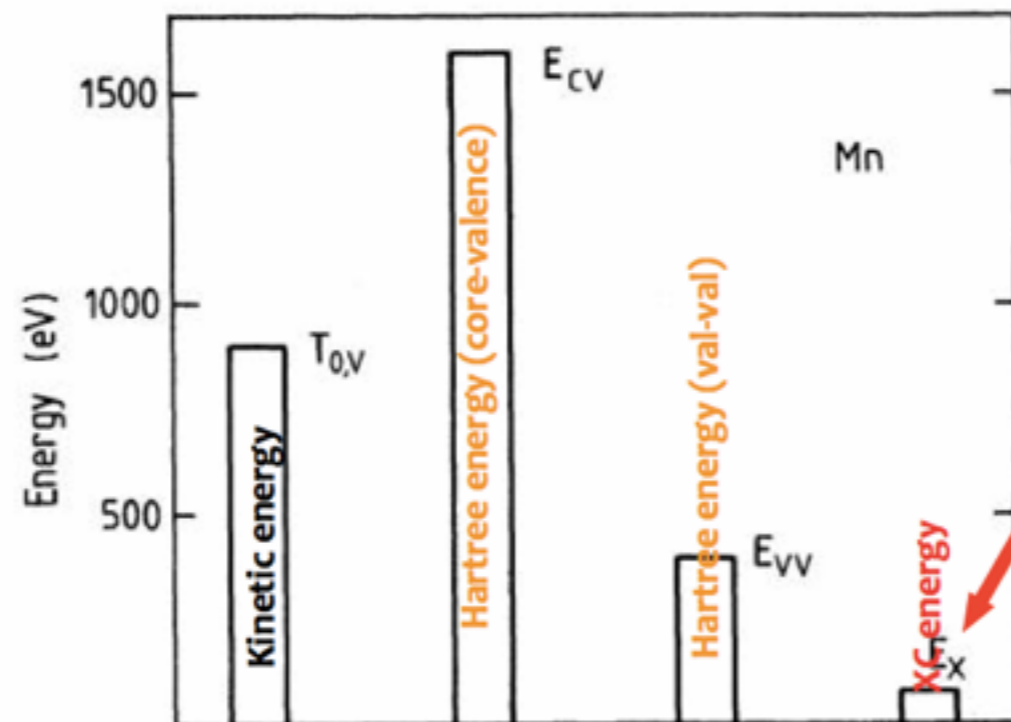



FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

However, this small energy is usually a large fraction ($> 90\%$) of the energy needed to break up a solid or molecule (binding energy) or to take one electron away from an atom (atomization energy).

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