

Computational Methods Applied to Materials Science:

Nanotechnology and Surface Phenomena

Introduction to DFT of Molecules & Solids

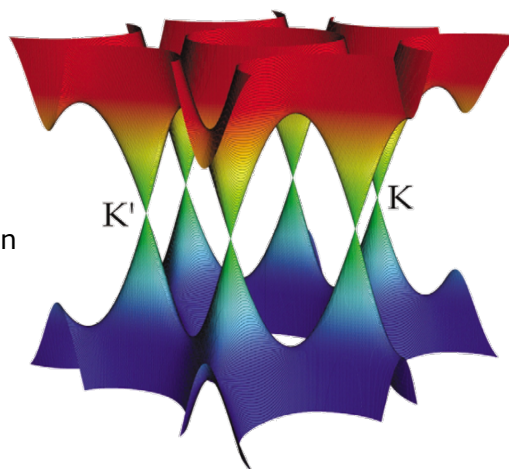


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Outline

- ▣ Intro
- ▣ Born-Oppenheimer approximation
- ▣ Hartree-Fock
- ▣ DFT
 - Theorems
 - Exchange & correlation
 - Functionals
- ▣ SCF
- ▣ Methods
- ▣ 0D, 1D, 2D and 3D systems



Introduction: Many Particles System

▣ Many Body System

$$\Psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

$$\hat{H}\Psi_0(\vec{r}) = \varepsilon_0\Psi_0(\vec{r})$$

$$\begin{aligned}\hat{H} = & -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{R}_i}^2}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} + \dots \\ & \dots + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}\end{aligned}$$

Intro: Second approximation

▣ Density Functional Theory (DFT)

$$\begin{aligned}\hat{H} = & -\frac{\hbar^2}{2} \sum_i \underbrace{\frac{\nabla_{\vec{R}_i}^2}{M_i}}_0 - \frac{\hbar^2}{2} \sum_i \underbrace{\frac{\nabla_{\vec{r}_i}^2}{m_e}}_{\hat{T}} - \underbrace{\frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|}}_{\hat{V}_{\text{ext}}} + \dots \\ & \dots + \underbrace{\frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\hat{V}} + \underbrace{\frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}}_{\text{constante}} \\ = & -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \text{cte.} \\ \hat{H} = & \hat{T} + \hat{V} + \hat{V}_{\text{ext}}\end{aligned}$$

Intro: First Approximation

▣ Adiabatic approximation Born-Oppenheimer

$$\begin{aligned}
 \hat{H} &= -\frac{\hbar^2}{2} \sum_i \underbrace{\frac{\nabla_{\vec{R}_i}^2}{M_i}}_0 - \underbrace{\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e}}_{\hat{T}} - \underbrace{\frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|}}_{\hat{V}_{ext}} + \dots \\
 &\quad \dots + \underbrace{\frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\hat{V}} + \underbrace{\frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}}_{\text{constante}} \\
 &= -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + cte.
 \end{aligned}$$

Intro: Hartree Fock Equation

▣ Central Equation

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + \hat{V}_{ext} + \Phi_i \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

▣ Non-interacting particles

$$\psi_i(\vec{r}_1, \dots, \vec{r}_N) = \psi_1(\vec{r}_1) \psi_2(\vec{r}_2) \dots \psi_N(\vec{r}_N)$$

▣ Fermionic behaviour?

■ Assymmetric Wave Function: Slater determinant

▣ Exact Exchange

▣ Correlation is neglected

$$\psi_i(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{r}_1) & \dots & \chi_N(\vec{r}_1) \\ \vdots & \ddots & \vdots \\ \chi_N(\vec{r}_1) & \dots & \chi_N(\vec{r}_N) \end{vmatrix}$$

Intro: DFT

□ What is a “functional”?

- To say that F is a functional of the function $f(\tau)$ means that F is a number whose value depends on the form of the function $f(\tau)$.
- In other words: for every function f (defined on the same domain, given by τ) the functional $F[f]$ returns a unique number:

$$F: \mathcal{F} \mapsto \mathbb{R}: f \mapsto F[f]$$

- $\mathcal{F}$ is a space of functions, a functional is therefore a “function of functions”.
- Some examples of functionals are:
 - The integral of a function is a functional
 - The total energy of a quantum system is a functional of the density, as stated by the first theorem of Hohenberg and Kohn. The density is a function defined on $\mathbb{R}^3$.

$$F[f] = \int_{-\infty}^{\infty} f(t) e^{-t^2} dt$$

$$F[f] = f(0)$$

Intro:

P. Hohenberg & W. Kohn Theorem

First Theorem:

There is a one-to-one correspondence between the ground-state density $\rho(\vec{r})$ of a many-electron system (atom, molecule, solid) and the external potential V_{ext} . An immediate consequence is that the ground-state expectation value of any observable $\hat{O}$ is a unique functional of the exact ground-state electron density.

$$\langle \psi | \hat{O} | \psi \rangle = O[\rho]$$

P. Hohenberg y W. Kohn, Phys. Rev. 136 (1964) B864

Intro:

P. Hohenberg & W. Kohn Theorem

Second Theorem:

For $\hat{O}$ being the Hamiltonian $\hat{H}$, the ground-state total energy functional $H[\rho] \equiv E_{V_{ext}}[\rho]$ is of the form:

$$\begin{aligned} E_{V_{ext}}[\rho] &= \langle \psi | \hat{T} + \hat{V} | \psi \rangle + \langle \psi | \hat{V}_{ext} | \psi \rangle \\ &= F_{HK}[\rho] + \langle \psi | \hat{V}_{ext} | \psi \rangle \\ &= F_{HK}[\rho] + \int \rho(\vec{r}) V_{ext}(\vec{r}) d\vec{r} \end{aligned}$$

Where the Hohenberg-Kohn density functional $F_{HK}[\rho]$ is universal for any many-electron system. $E_{V_{ext}}[\rho]$ reaches its minimal value (equal to the ground-state total energy) for the ground-state density corresponding to V_{ext} .

P. Hohenberg y W. Kohn, Phys. Rev. 136 (1964) B864

Intro: Consequences

□ Invertibility: $\rho(\vec{r}) \leftrightarrow V_{ext}(\vec{r})$

□ Universality: $F_{HK}[\rho]$

$$\begin{aligned} \hat{\rho}(\vec{r}) &= \sum_{i=1}^N \delta(\vec{r}_i - \vec{r}) \\ \rho(\vec{r}) &= \langle \psi^*(\vec{r}_1, \dots, \vec{r}_N) | \hat{\rho}(\vec{r}) | \psi(\vec{r}_1, \dots, \vec{r}_N) \rangle \\ \rho(\vec{r}) &= \sum_{i=1}^N \int \psi^*(\vec{r}_1, \dots, \vec{r}_i = \vec{r}, \dots, \vec{r}_N) \psi(\vec{r}_1, \dots, \vec{r}_i = \vec{r}, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N \end{aligned}$$

□ Variational Principle: Rayleigh-Ritz

The Problem Remains the Same!

Intro: Kohn & Sham equations (DFT)

$$E[\rho] = T_0[\rho] + V_H[\rho] + V_{xc}[\rho] + V_{ext}[\rho]$$

$$\hat{H}_{KS} = \hat{T}_0 + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext}$$

$$\hat{H}_{KS} = \underbrace{-\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'}_{\text{Universal!}} + V_{xc} + V_{ext}$$

$$\hat{V}_{xc} = \frac{\delta V_{xc}[\rho]}{\delta \rho}$$

$$\rho(\vec{r}) = \sum_{i=1}^N \phi_i^*(\vec{r}) \cdot \phi_i(\vec{r})$$

W. Kohn y L. J. Sham, Phys. Rev. 140 (1965) A1133

Intro: Advantages and Disadvantages

Advantages:

Quasiparticle, single-electron, non-interacting wave functions can be used for describing the ground state of the system.

- Still we can use all the well known tools for determining the Wave Function.
- Variational Theorem

Disadvantages:

- The universal XC-functional is not known.

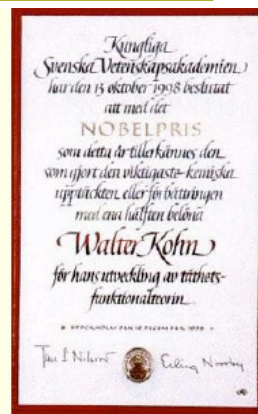
Physical Meaning?

- No
- Just the $\rho(\mathbf{r}) = \Phi(\mathbf{r})^* \Phi(\mathbf{r})$ can be interpreted in terms of density matrix

Intro: Nobel Prize Chemistry 1998



Walter Kohn



"Self-consistent Equations including Exchange and Correlation Effects"
W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

1923 - 2016

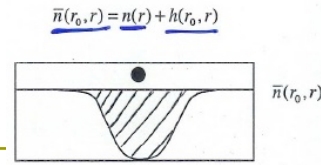
Intro: Exchange(x) & Correlation(c)

□ How to deal with... ?

- Exchange energy: indistinguishability of electrons (fermions)
- Correlation energy: coulombic interaction.
- The exchange-correlation hole describes the effect of the electronic repulsion. The electron positioned at r reduces the probability of finding another electron at position r' .
- Thus, the E_{xc} represents the interaction energy of the e^- with its xc-hole.

Intro: Exchange-Correlation

- The electronic density of the (N-1) e^- [$n_{N-1}(\mathbf{r})$] can be considered as: $n(\mathbf{r})$ density in the presence of a exchange-correlation hole
- The properties of the hole:
 - Locality.
 - Follows the Pauli Exclusion Principle.
 - The hole contains 1 electron.
 - It is negative.
- The exchange-hole affects e^- of the same spin (Pauli).
- The correlation-hole represents the Coulomb repulsion of e^- of different spins.
 - Short range interaction (poor charge redistribution).
 - It carries no charge.



$$h(r_0, r) \xrightarrow{|r-r_0| \rightarrow \infty} 0$$

$$h(r_0, r) \xrightarrow{|r-r_0| \rightarrow 0} -n(r_0)$$

$$\int d\mathbf{r} h(r_0, r) = -1$$

$$h(r_0, r) \leq 0$$

$$\int d\mathbf{r} h_c(r_0, r) = 0$$

Intro: Exchange-Correlation Functional

Local Density Approximation (LDA)

$$E_{xc}^{LDA} = \int \rho(\vec{r}) \epsilon_{xc}(\rho(\vec{r})) d\vec{r}$$

$$\text{LDA: } E_{xc}^{LDA} = \int f(\rho(\mathbf{r})) d^3r$$

$$\text{GGA: } E_{xc}^{GGA} = \int f(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|) d^3r$$

$$\text{MGGA: } E_{xc}^{MGGA} = \int f(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|, \nabla^2 \rho(\mathbf{r}), t(\mathbf{r})) d^3r$$

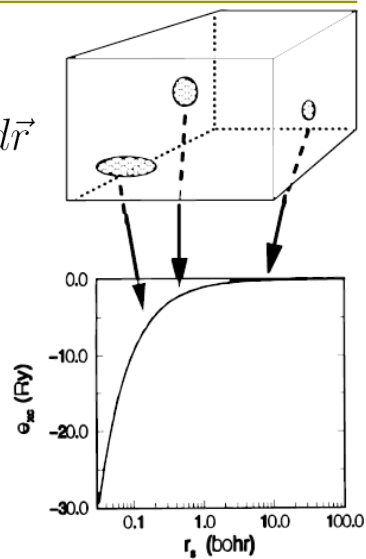
$$\text{LDA+U: } E_{xc}^{LDA+U} = E_{xc}^{LDA} + E_{ee} - E_{dc}$$

$$\text{GGA+U: } E_{xc}^{GGA+U} = E_{xc}^{GGA} + E_{ee} - E_{dc}$$

$$\text{hybrid: } E_{xc}^{\text{hybrid}} = E_{xc}^{\text{DFT}} + \alpha (E_{xc}^{\text{HF}} - E_{xc}^{\text{DFT}})$$

where

$$E_{xc}^{\text{HF}} = -\frac{1}{2} \sum_{\sigma} \sum_{\mathbf{k}, \mathbf{k}'} w_{\mathbf{k}} w_{\mathbf{k}'} \iint \frac{\psi_{\mathbf{k}}^{\sigma*}(\mathbf{r}) \psi_{\mathbf{k}'}^{\sigma*}(\mathbf{r}') \psi_{\mathbf{k}}^{\sigma}(\mathbf{r}) \psi_{\mathbf{k}'}^{\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$



0 Introducción: Funcional Correlación-Intercambio

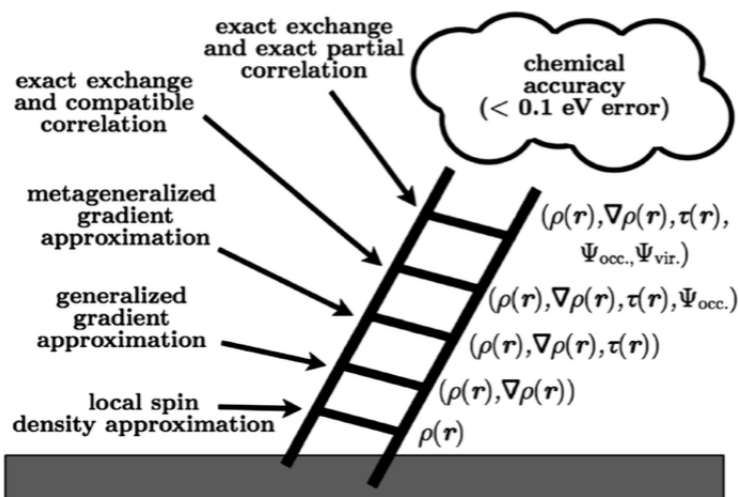


Figure 1.2 Jacob's ladder illustrating the hierarchy of exchange–correlation functionals.

Intro: Theory vs. Experiments

Lattice parameters (Å)

	Exp.	LDA	PBE	WC
Co	2.51	2.42	2.49	2.45
Ni	3.52	3.42	3.52	3.47
Cu	3.61	3.52	3.63	3.57
Ru	2.71	2.69	2.71	2.73
Rh	3.80	3.76	3.83	3.80
Pd	3.88	3.85	3.95	3.89
Ag	4.07	4.01	4.15	4.07
Ir	3.84	3.84	3.90	3.86
Pt	3.92	3.92	4.00	3.96
Au	4.08	4.07	4.18	4.11

3d elements:

- PBE superior, LDA much too small

4d elements:

LDA too small, PBE too large

- New functional Wu-Cohen (WC)

Z. Wu, R.E. Cohen, PRB 73, 235116 (2006)

5d elements:

- LDA superior, PBE too large

Intro: Solving the Wave Function

□ Hamiltonian:

$$\hat{H}_{KS} = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc} + V_{ext}$$

□ Basis Set Definition:

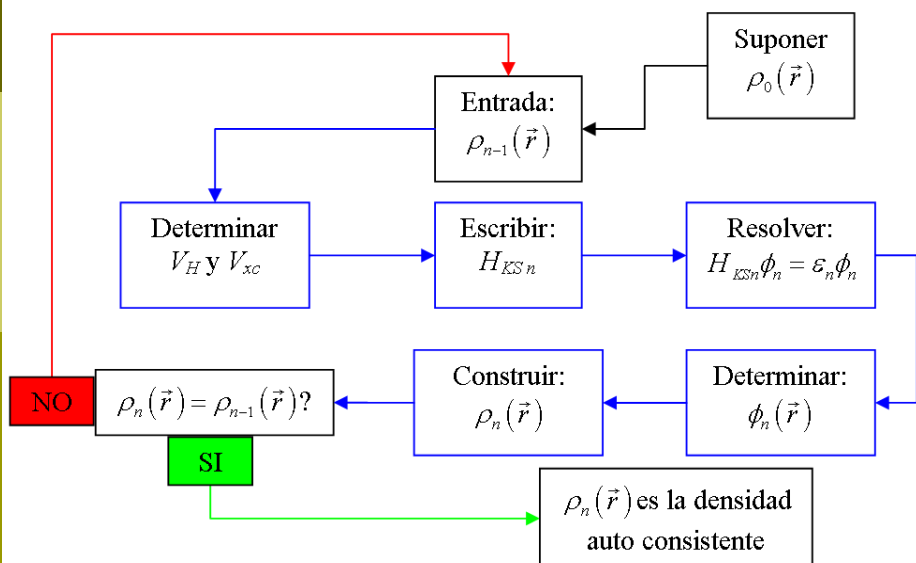
$$\phi_m = \sum_{p=1}^P c_p^m \phi_p^b$$

□ Secular Equation:

$$\begin{bmatrix} \dots & \dots & \dots \\ \vdots & \langle \phi_i^b | \hat{H}_{sp} | \phi_j^b \rangle - \epsilon_m \langle \phi_i^b | \phi_j^b \rangle & \vdots \\ \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} c_1^m \\ \vdots \\ c_P^m \end{bmatrix} = \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix}$$

Final $\rho_f(\mathbf{r})$ not necessarily equal to initial $\rho_i(\mathbf{r})$

Intro: Self Consistent Field (SCF)



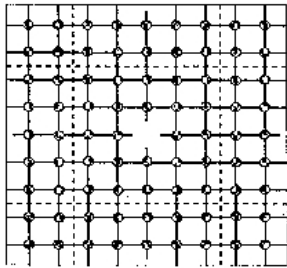
Intro: Basis Set and Codes

- ❑ Plane Waves with Pseudopotentials
 - Augmented Plane Waves
 - **Codes: VASP & Quantum Espresso**
- ❑ Partitioned Methods (augmented)
 - LMTO
 - ASW
 - LAPW
 - **Code: WIEN2k**
- ❑ Linear Combination of Atomic Orbitals
 - Localized Gaussian Basis Set.
 - **Codes: Gaussian & SIESTA**

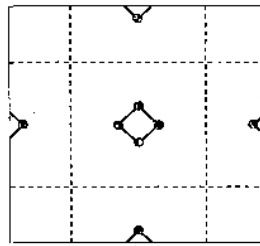
1. Structural Models

1 Models

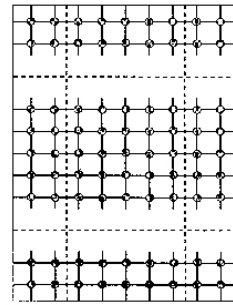
- PBC: Periodic Boundary Conditions
- Periodic Systems: Crystalline Samples
- Non-periodic Systems: *Supercells*



Defects



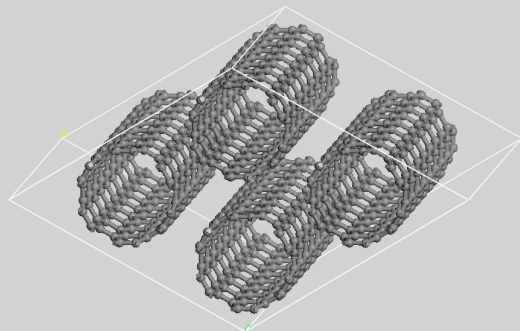
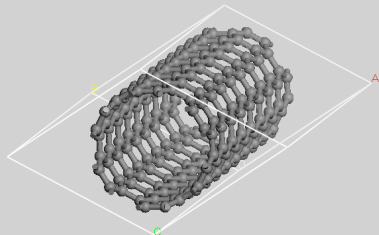
molecules



surfaces

1. Periodical Model

Carbon nanotubes (1D)



1. Periodic Model: Cluster and Surfaces

Surface (2D) and cluster (0D) of TiO_2

