

# Lecture 6 - Density Functional Theory

## Lecture 6 - Density Functional Theory

Theoretical  
background

Local density  
approximation

Kohn-Sham  
formulation of  
DFT

- Theoretical background
- Hohenberg-Kohn theorems
- Local density approximation
- Kohn-Sham formulation of DFT
- Comparison of HF and DFT

# Density Functional Theory vs Quantum Theory

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- 1 quantum theory uses  $\Phi(\vec{r}_1, \dots, \vec{r}_N)$  as a basic quantity. Equations in multidimensional space. Usually difficult to solve.

$$H\Phi(\vec{r}_1, \dots, \vec{r}_N) = E\Phi(\vec{r}_1, \dots, \vec{r}_N)$$

- 2 Density Functional Theory uses  $\rho(\vec{r})$  as a basic quantity. Much simpler to treat provided  $E[\rho(\vec{r})]$  is known.

$$\min E[\rho(\vec{r})]$$

# Foundations of Density Functional Theory

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- Solid state physicists used to treating electrons as a continuous quantity.
- First models treating the electrons as a noninteracting gas.

## Basic principles:

- 1 existence of the functional.
- 2 variational principle.

# First Hohenberg-Kohn Theorem

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Year: 1964.

*The external potential  $v(\vec{r})$  is determined, within a trivial additive constant, by the electron density  $\rho(\vec{r})$ .*

Since  $\rho$  also determines the number of electrons,  $\rho$  determines the ground-state wave function  $\Phi$  and all other electronic properties.

# Second Hohenberg-Kohn Theorem

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Year: 1964.

*For a trial density  $\tilde{\rho}(\vec{r})$ , such that  $\tilde{\rho}(\vec{r}) \geq 0$  and  $\int \tilde{\rho}(\vec{r}) d\vec{r} = N$ ,*

$$E_0 \leq E[\tilde{\rho}]$$

*where  $E[\rho]$  is the energy functional.*

General conditions on the density

$$\rho(\vec{r}) \geq 0, \quad \int \rho(\vec{r}) d\vec{r} = N, \quad \int |\nabla \sqrt{\rho(\vec{r})}|^2 d\vec{r} < \infty \quad (1)$$

# Functionals: Introduction

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Usual partitioning of functionals:

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$$

$V_{ne}[\rho]$  is the external potential energy  $V = \int \rho(\vec{r})v(\vec{r})d\vec{r}$ .

In molecules:

$$V_{ne}[\rho(\vec{r})] = \int \rho(\vec{r}) \left( \sum_{A=1}^{N_A} \frac{Z_A}{|\vec{r} - \vec{R}_A|} \right) d\vec{r}$$

# Functionals: the Holy Grail

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- Difficult to find *The One*.
- The choice is crucial and determines the quality of the results.
- Thomas-Fermi – a historical one that set the DFT development back many years.
- Usually have an analytical formula with some coefficients fitted to match some properties. Should fulfill certain conditions.

$$E[\rho] = T[\rho] + J[\rho] + E_{\text{xc}}[\rho] + V_{\text{ext}}[\rho]$$

# Local density approximation – LDA

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$$E = E[\rho(\vec{r})] \quad (2)$$

Local Density approximation assumes that

$$E_{xc}^{\text{LDA}} = \int \rho(\vec{r}) \epsilon(\rho(\vec{r})) d\vec{r} \quad (3)$$

where  $\epsilon(x)\delta v$  is a energy contribution from a density  $x$ .

- Gradient dependence as a way of lifting the ultimate locality of such a functional.
- The LDA is applicable to systems with slowly-varying densities but cannot be formally justified for highly inhomogeneous systems such as atoms and molecules.

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# Kinetic Energy: Thomas Fermi Model

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Consider noninteracting uniform electron gas.

- Knowing that the electrons are fermions, figure out the minimal kinetic energy of such a gas in a certain volume, at fixed, constant density.

$$T_{\text{TF}}[\rho] = C_{\text{F}} \int \rho^{5/3} d\vec{r} \quad (4)$$

- Oversimplified model of not much real importance for quantitative predictions or molecular or solid-state physics.
- Inability to predict the existence of molecular bonds.

# $X_\alpha$ – Exchange only

Slater invoked the uniform-electron-gas model to produce the simplification, resulting in the  $X_\alpha$  method (Hartree-Fock-Slater)

$$\left[ -\frac{1}{2}\nabla^2 + v(\vec{r}) + \int \frac{\rho(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} d\vec{r}_1 + v_{x\alpha}(\vec{r}) \right] \psi_i = \epsilon_i \psi_i$$

with  $X_\alpha$  local potential

$$v_{x\alpha} = -\frac{3}{2}\alpha \left( \frac{3}{\pi} \rho(\vec{r}) \right)^{1/3}$$

where the parameter  $\alpha = 1$  in the original potential-based formulation but it is equivalent to Dirac exchange energy functional when  $\alpha = 2/3$ . Another value is  $\alpha = 3/4$ .

# Kohn-Sham Model

Problems finding the right functional + willingness to merge experience with at that time quality-leading quantum chemistry. Use a certain way of expanding the density

$$\rho(\vec{r}) = \sum_i^N |\psi_i(\vec{r})|^2 \quad (5)$$

$\psi_i(\vec{r})$  – Kohn-Sham orbitals.

Expand Kohn-Sham orbitals in a basis

$$\psi_i(\vec{r}) = \sum_p^K c_{pi} \phi_p(\vec{r}) \quad (6)$$

$$F_{pq} = \int \frac{\partial F}{\partial \rho} \Big|_{\rho=\rho(\vec{r})} \phi_p(\vec{r}) \phi_q(\vec{r}) d\vec{r} \quad (7)$$

Minimize gradient to get to the stationary point equivalent with solving generalized eigenproblem

# The Kohn-Sham Equations

Introduce a basis set – set of  $K$  known functions to represent one-electron functions.

$$\psi_i(\vec{r}) = \sum_{p=1}^K c_{pi} b_p(\vec{r}) \quad (9)$$

Choose a basis set and *solve for* set of coefficients  $c_{pi}$ .

- 1 equidistant grid either in real space or momentum space.
- 2 analytical solutions for hydrogen-like atoms – *Slater-type orbitals* with  $\propto \exp(-\alpha r)$
- 3 A variant of 2 where Gaussian functions  $\exp(-\alpha r^2)$  are used.

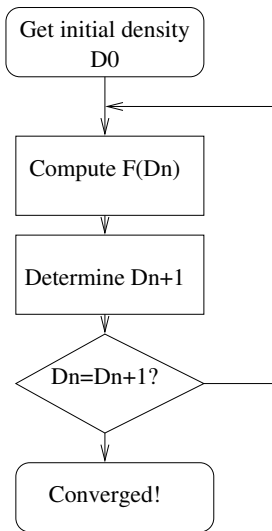
# Kohn-Sham Method: SCF Scheme

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- 1 Initial guess either from approximation to KS matrix  $F$  or from some chemical knowledge.
- 2 Construction of KS matrix from integrals.
- 3 Construction of new density from molecular orbitals (eigenvectors of KS matrix) or by direct optimization of density. Acceleration schemes that use history possible (DIIS).

# Kohn-Sham Method: Details

KS orbital coefficient matrix:

$$\psi_i(\vec{r}) = \sum_p c_{pi} b_p(\vec{r}).$$

KS matrix depends on density  $d_{\alpha\beta}$  (Factor 2 for closed-shell systems).

$$d_{pq} = \sum_{i=1}^{N/2} 2c_{pi}c_{qi}$$

$$f_{pq}(D) = h_{pq} + \sum_{rs} \underbrace{g_{pqrs}d_{rs}}_{\text{Coulomb term}} - \alpha \underbrace{\frac{1}{2}g_{prqs}d_{rs}}_{\text{exchange term}} + f_{xc}(D)$$

- $h_{pq}$  – one-electron part of the Hamiltonian
- Coulomb and exchange terms – a two electron contribution.

# Comparison of HF and DFT

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- Hartree-Fock: usually more time-consuming than DFT except for smallest systems. No correlation. Exact exchange with correct asymptotic behavior.
- DFT: Same speed or sometimes faster than Hartree-Fock.