## Introduction to Density Functional Theory

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# Synopsis

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- Pormalism :
  - Elementary quantum mechanics
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    - Overational principle
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    - Wave function methods: Hartree-Fock method
    - Ø Modern DFT : Kohn-Sham
    - S Exchange correlation functionals (LDA, GGA ....)
- Third generation DFT
- Example

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# Motivation

Walter Kohn was awarded with the Nobel Prize in Chemistry in 1998 for his development of the DFT.



# Motivation

The following figure shows the number of publications where the phrase DFT appears in the title or abstract (taken from the ISI Web of Science).



# Motivation

#### Where can DFT be applied:

- DFT is presently the most successful (and also the most promising) approach to compute the electronic structure of matter.
- Its applicability ranges from atoms, molecules and solids to nuclei and quantum and classical fluids.
- Chemistry: DFT predicts a great variety of molecular properties: molecular structures, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths, etc
- The original DFT has been generalized to deal with many different situations: spin polarized systems, multicomponent systems, systems at finite temperatures, superconductors, time-dependent phenomena, Bosons, molecular dynamics ......

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# Elementary quantum mechanics

#### Schrödinger equation

$$\hat{H}\Phi_i(\mathbf{x}_1, \mathbf{x}_2...\mathbf{x}_N, \mathbf{R}_1, \mathbf{R}_2...\mathbf{R}_M) = E_i\Phi_i(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N, \mathbf{R}_1, \mathbf{R}_2...\mathbf{R}_M)$$
$$\mathbf{x} \equiv \{\mathbf{r}, \sigma\}$$

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## Schrödinger equation

### Kinetic energy

$$\hat{H} = -rac{1}{2}\sum_{i}^{N}
abla_{i}^{2}$$

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# Schrödinger equation

### Coloumb interaction

$$\hat{H} = -rac{1}{2}\sum_{i}^{N}
abla_{i}^{2} + \sum_{i}^{N}\sum_{j
eq i}^{N}rac{1}{\mathbf{r}_{ij}}$$



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# Schrödinger equation

### Nuclear electron interaction

$$\hat{H} = -rac{1}{2}\sum_{i}^{N}
abla_{i}^{2} + \sum_{i}^{N}\sum_{j
eq i}^{N}rac{1}{\mathbf{r}_{ij}} - \sum_{i}^{N}\sum_{A}^{M}rac{Z_{A}}{\mathbf{r}_{iA}}$$

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## Schrödinger equation

### Nuclear terms

$$\hat{H} = -\frac{1}{2} \sum_{i}^{N} \nabla_{i}^{2} + \sum_{i}^{N} \sum_{j \neq i}^{N} \frac{1}{\mathbf{r}_{ij}} - \sum_{i}^{N} \sum_{A}^{M} \frac{Z_{A}}{\mathbf{r}_{iA}}$$
$$-\frac{1}{2} \sum_{i}^{M} \frac{1}{M_{A}} \nabla_{A}^{2} + \sum_{A}^{M} \sum_{B \neq A}^{M} \frac{Z_{A}Z_{B}}{\mathbf{R}_{AB}}$$

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### Elementary quantum mechanics

#### Born-Oppenheimer approximation

Due to their masses the nuclei move much slower than the electrons. So we can consider the electrons as moving in the field of fixed nuclei.

$$\hat{H} = -\frac{1}{2} \sum_{i}^{N} \nabla_{i}^{2} + \sum_{i}^{N} \sum_{j \neq i}^{N} \frac{1}{\mathbf{r}_{ij}} - \sum_{i}^{N} \sum_{A}^{M} \frac{Z_{A}}{\mathbf{r}_{iA}} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee}$$
$$\hat{H} \Psi_{i}(\mathbf{x}_{1}, \mathbf{x}_{2} ... \mathbf{x}_{N}) = E_{i} \Psi_{i}(\mathbf{x}_{1}, \mathbf{x}_{2}, ... \mathbf{x}_{N})$$

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### Elementary quantum mechanics

#### Variational principle

The variational principle states that the energy computed from a guessed wave function  $\Psi$  is an upper bound to the true ground-state energy  $E_0$ . Full minimization of E with respect to all allowed N-electrons wave functions will give the true ground state.

$$E_0[\Psi_0] = \min_{\Psi} E[\Psi] = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} | \Psi 
angle$$

A (1) > A (2) > A

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## Elementary quantum mechanics

### Energy

$$E_0[\Psi] = \langle \Psi | \hat{H} | \Psi 
angle = \int \Psi^*(\mathbf{x}) \hat{H} \Psi(\mathbf{x}) d\mathbf{x}$$

#### Wave function : example of two fermions

Pauli exclusion principle results in an antisymmetric wave function

$$\Psi(\mathbf{x}_1,\mathbf{x}_2) = \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2) - \phi_1(\mathbf{x}_2)\phi_2(\mathbf{x}_1)$$

This looks like a determinant

A (1) > A (2) > A

## Wave function method: Hartree-Fock

The ground state wave function is approximated by a Slater determinant:

$$\Psi_{HF}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \cdots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \cdots & \phi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \cdots & \phi_N(\mathbf{x}_N) \end{vmatrix}$$

The Hartree-Fock approximation is the method whereby the orthogonal orbitals  $\phi_i$  are found that minimize the energy. The variational principle is used.

$$E_{HF} = \min_{\phi_{HF}} E[\phi_{HF}]$$

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## Problems with wave function methods

#### I. Visualization and probing

The conventional wave function approaches use wave function as the central quantity, since it contains the full information of a system. However, is a very complicated quantity that cannot be probed experimentally and that depends on 3N variables, N being the number of electrons.

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## Problems with wave function methods

### II. Time consuming

The interactions are very difficult to calculate for a realistic system, in fact this is most time consuming part.

$$\hat{V}_{ee} = \sum_{i}^{N} \sum_{j 
eq i}^{N} rac{1}{\mathbf{r}_{ij}}$$



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## Problems with wave function methods

### III. Inefficient

One Slater determinant does a rather bad job for expanding the many-body wave function.

 $\Psi(x,y) \qquad \qquad \phi_1(x)\phi_2(y)$ 



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## Two Slater determinants



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# Eight Slater determinants



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# Density Functional Theory

### Experiments probe density

$$ho(\mathbf{r_1}) = \int \Psi^*(\mathbf{x_1},\mathbf{x_2},....\mathbf{x_N})\Psi(\mathbf{x_1},\mathbf{x_2},....\mathbf{x_N}) \mathrm{d}\mathbf{x_2}...\mathrm{d}\mathbf{x_N}$$

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## Hohenberg-Kohn theorems

#### I Hohenberg-Kohn theorem

$$\hat{H} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee}$$

This first theorem states that the  $\hat{V}_{Ne}$  is (to within a constant) a unique functional of density ( $\rho$ ); since, in turn this potential fixes  $\hat{H}$  we see that the full many particle ground state is a unique functional of density.

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## Hohenberg-Kohn theorems

#### II Hohenberg-Kohn theorem

The second H-K theorem states that the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density. This is nothing but the variational principle, but this time with density and not wave function

$$E_0[\rho_0] = \min_{\rho} E[\rho] = \min_{\rho} T[\rho] + E_{Ne}[\rho] + E_{ee}[\rho]$$

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# Modern DFT

### Energy as a functional of density

$$E[\rho] = T[\rho] + E_{Ne}[\rho] + E_{ee}[\rho]$$
$$E[\rho] = T[\rho] + E_{Ne}[\rho] + E_{H}[\rho] + E_{x}[\rho] + E_{c}[\rho]$$



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# Modern DFT: Kohn-Sham

The system is replaced by a fictitious non-interaction system with same density as the real system.

#### Kohn-Sham non-interacting system

$$E[\rho] = T[\rho] + E_{Ne}[\rho] + E_{H}[\rho] + E_{x}[\rho] + E_{c}[\rho]$$
$$T[\rho] = -\frac{1}{2} \langle \phi_{i} | \nabla^{2} | \phi_{i} \rangle$$
$$E_{Ne}[\rho] + E_{H}[\rho] = -Z \int \frac{\rho(\mathbf{r})}{r} d\mathbf{r} - \frac{1}{2} \int \frac{\rho(\mathbf{r}_{1})\rho(\mathbf{r}_{2})}{r_{12}} d\mathbf{r}_{1} d\mathbf{r}_{2}$$

#### Local Density Approximation

Based on the properties of uniform electron gas XC potential is approximated as:

$$E_{xc}[
ho] = -rac{3}{4\pi} (3\pi^2)^{1/3} \int 
ho^{4/3}(\mathbf{r}) d\mathbf{r}$$

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#### Kohn-Sham non-interacting system

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A (1) > A (2) > A

### Third generation DFT: Exact exchange

Treating exchange term exactly

$$E[\rho] = T[\rho] + E_{Ne}[\rho] + E_H[\rho] + E_x[\rho]$$

Using the Fock integral and its functional derivative the exchange term can be treated exactly . This method is called EXX or OEP.

S. Sharma, J. K. Dewhurst and C. Ambrosch-Draxl Phys. Rev. Lett. **95** 136402 (2005)

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# Phase transition in Ce using LDA



New physics captured with EXX



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