Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

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Lecture

Modeling of Nanostructures and Materials

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Modeling of Nanostructures and Materials

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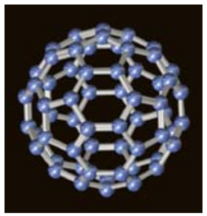
Lecture 2 – *February 28, 2013*

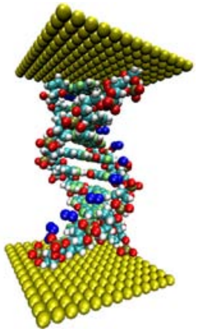
- **Density Functional Theory (DFT) – the key to the Computational Materials Science**
  The Basics
- **Kohn-Sham realization of the DFT**

Fundamental problem in materials science

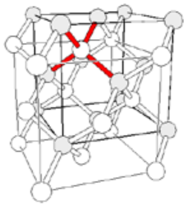
A fundamental problem in materials science is the prediction of condensed matter's electronic structure



C_{60} - molecule



DNA - molecule



Crystal - diamond

Materials Science: Examples of Schrödinger Equation?

- Materials are composed of nuclei $\{Z_\alpha, M_\alpha, \vec{R}_\alpha\}$ and electrons $\{\vec{r}_i\}$
  → the interactions are known

$$H = -\sum_\alpha \frac{\hbar^2 \nabla_\alpha^2}{2M_\alpha} - \sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \frac{1}{2}\sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|} + \frac{1}{2}\sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Kinetic energy of nuclei — Kinetic energy of electrons — Nucleus-Nucleus interaction — Electron-Nucleus interaction — Electron-Electron interaction

$$H\Psi = E\Psi$$

Ab-initio **(first principles) Method – ONLY Atomic Numbers $\{Z_i\}$ as input parameters**

Quantum Mechanics of Molecules and Crystals

Molecule or Crystal = a system of ***nuclei (Ions)*** and ***electrons***

Nuclei – mass M, coordinates X, and momenta P, $X \equiv \{\vec{R}_1, \vec{R}_2, \dots, \vec{R}_{N_{nucl}}\}$ (M, X, P)

Electrons – (m,x,p) $x \equiv \{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N\}$

$$H = \hat{T}_{el} + U(x,X) + \hat{T}_{Nucl}$$

Kinetic energy of electrons

$$\hat{T}_{el} = \sum_{i=1}^{N} \frac{1}{2m}\vec{p}_i^{\,2} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m}\vec{\nabla}_i^2$$

Kinetic energy of the nuclei

$$\hat{T}_{Nucl} = \sum_{a=1}^{N_{nucl}} \frac{1}{2m}\vec{P}_i^{\,2} = -\sum_{a=1}^{N_{nucl}} \frac{\hbar^2}{2M_a}\vec{\nabla}_a^2$$

Potential energy = The total Coulomb energy of nuclei and electrons

$$U(x,X) = \hat{V}_{en}(x,X) + \hat{V}_{ee}(x) + \hat{V}_{NN}(X)$$

Electron-nucleus

$$\hat{V}_{en}(x,X) = \sum_{ia} \frac{-Z_a e^2}{|\vec{r}_i - \vec{R}_a|}$$

Electron-Electron

$$\hat{V}_{ee}(x) = \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Nucleus-Nucleus

$$\hat{V}_{NN}(X) = \sum_{a<b} \frac{e^2}{|\vec{R}_a - \vec{R}_b|}$$

The Adiabatic Approximation (Born-Oppenheimer)

M. Born & J. R. Oppenheimer, Ann. Phys. 84, 457 (1927)

- It is natural to consider the full Hamiltonian of the system to be the sum of an ***ionic*** and an ***electronic*** part

$$\hat{H} = \hat{H}_N + \hat{H}_{el}$$

$$\hat{H}_N = \hat{T}_{Nucl} + \hat{V}_{NN}(X)$$

$$\hat{H}_{el} = \hat{T}_{el} + \hat{V}_{en}(x,X) + \hat{V}_{ee}(x)$$

The Adiabatic Approximation (Born-Oppenheimer)

- **The Schrödinger equation for the electrons in the presence of fixed ions**

$$\hat{H}_{el}\Psi_n(X,x) = E_n(X)\Psi_n(X,x)$$

Parametric dependence on ionic positions

- **The energy levels of the system of ions are determined by solving**

$$[\hat{H}_N + E(K',X)]\,\chi(Q,K',X) = \varepsilon(Q)\,\chi(Q,K',X)$$

The electronic energy contributes to the potential energy of the ion system. This implies that the potential energy depends on the state of the electrons.

Quantum Mechanics: System of N electrons in an external potential

- Adiabatic approximation – interacting electrons move in the 'external' potential of nuclei (ions) at fixed positions $\{\vec{R}_1, \vec{R}_2, \dots\}$

$$\hat{T} = \sum_{i=1}^{N} -\frac{h^2}{2m}\nabla_i^2 \qquad \hat{H} = \hat{T} + \hat{V}_{en} + \hat{V}_{e-e} \qquad \hat{V}_{e-e} = \sum_{i<j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$\hat{V}_{en} = \sum_{ia}\frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{R}_a|} = \hat{V}_{ext} = \sum_i v_{ext}(\vec{r}_i) \qquad \left(E_{nn} = \sum_{a<b}\frac{Z_a Z_b e^2}{|\vec{R}_a - \vec{R}_b|}\right)$$

Schrödinger equation

$$H\Psi = E\Psi$$

$$\Psi(\{\vec{R}_\alpha\}, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \equiv \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

Many particle wave function $N \approx 10^{23}$

Ritz Variational Principle → Ground State Energy of the system

$$E_0 = \min_{\Psi \to N}\left\langle \Psi | \hat{H} | \Psi \right\rangle = \min_{\Psi \to N}\left\langle \Psi | \hat{T} + \hat{V}_{e-e} + \hat{V}_{ext} | \Psi \right\rangle$$

$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ Many-particle wavefunction

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \qquad E[\Psi] \geq E_0$$

Full minimization of the functional $E[\Psi]$ with respect to all allowed N-electron wave functions

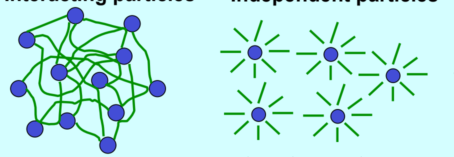
Quantum Mechanics:
System of N electrons in an external potential

Schrödinger equation
$$H\Psi = E\Psi$$

Exact analytical solutions are not known even for two electrons !

- **Approximations are needed !**
- **Concept of independent particles moving in an effective potential**

Interacting particles | **Independent particles**



$\Psi(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_{10^{23}})$ | $\varphi(\vec{x}_1)\varphi(\vec{x}_2)\ldots\varphi(\vec{x}_{10^{23}})$

Idea: consider electrons as independent particles moving in an effective potential

Hartree and Hartree-Fock Approximation

Ansatz for the wave-function

Hartree Method

$$\Phi_{Hartree}(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N)=\varphi_1(\vec{x}_1)\varphi_2(\vec{x}_2)\ldots\varphi_N(\vec{x}_N)$$

Hartree-Fock Method

$$\Phi_{H-F}(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\varphi_1(\vec{x}_1) & \varphi_2(\vec{x}_1) & \ldots & \varphi_N(\vec{x}_1)\\ \varphi_1(\vec{x}_2) & \varphi_2(\vec{x}_2) & \ldots & \varphi_N(\vec{x}_2)\\ \vdots & \vdots & & \vdots\\ \varphi_1(\vec{x}_N) & \varphi_2(\vec{x}_N) & \ldots & \varphi_N(\vec{x}_N)\end{vmatrix}$$

ψ_i - one-electron wavefunction of the *ith* level

Hartree-Fock Approximation

$$\Phi_{H-F} \Rightarrow E[\Phi_{H-F}]=\frac{<\Phi_{H-F}|\hat{H}|\Phi_{H-F}>}{<\Phi_{H-F}|\Phi_{H-F}>}$$

$$H=H_0+\frac{1}{2}\sum_{i,j}U(\vec{x}_i,\vec{x}_j)$$

$$H_0=\sum_i H_0(i)=\sum_i -\frac{1}{2}\nabla_i^2+V_{ext}(\vec{r}_i) \qquad U(\vec{x}_i,\vec{x}_j)=\frac{1}{|\vec{r}_i-\vec{r}_j|}$$

Variational Principle

$$\Rightarrow H_0\varphi_i(\vec{x}_i)+\left[\sum_{j=1}^{N}\int\varphi_j^*(\vec{x}_j)U(\vec{x}_i,\vec{x}_j)\varphi_j(\vec{x}_j)d\vec{x}_j\right]\varphi_i(\vec{x}_i)$$
$$-\left[\sum_{j=1}^{N}\int\varphi_j^*(\vec{x}_j)U(\vec{x}_i,\vec{x}_j)\varphi_i(\vec{x}_j)d\vec{x}_j\right]\varphi_j(\vec{x}_i)=\varepsilon_i\varphi_i(\vec{x}_i)$$

Spectrum of Electronic Hamiltonian: What *ab initio* methods do we have?

Methods for computing the electronic structure

Empirical Methods

Ab-initio Methods

- Hartree-Fock Method
  - + Configuration Interaction
- Density Functional Theory
- Quantum Monte Carlo

§ H-F - neglects completely electron correlation
§ H-F+CI – is able to treat ONLY few electrons

Ø Existing realizations of DFT allow accurate predictions for large systems
Ø Currently the method of choice in materials science

Density Functional Theory (DFT)

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

- **One particle density – Basic quantity of DFT**

$$\rho(\vec r)=\left\langle \Psi(\vec r_1,\vec r_2,\dots,\vec r_N)\,\Big|\sum_i \delta(\hat{\vec r}_i-\vec r)\Big|\,\Psi(\vec r_1,\vec r_2,\dots,\vec r_N)\right\rangle$$
$$= N\int d\vec r_2,\dots,d\vec r_N\,\Psi^*(\vec r,\vec r_2,\dots,\vec r_N)\Psi(\vec r,\vec r_2,\dots,\vec r_N)$$

- The DFT is based on two fundamental theorems for a functional of the one particle density.
- **One particle density determines the ground state energy of the system**
- Modern formulation – constrained-search method of Mel Levy

Mel Levy, Proc. Natl. Acad. Sci. USA, vol. 76, No. 12, p.606 (1979).

Density Functional Theory – constrained search formulation

Mel Levy, Proc. Natl. Acad. Sci. USA, vol. 76, No. 12, p.606 (1979).

Functional of the one particle density $F[\rho]\doteq\min_{\Psi_\rho\to\rho}\left\langle\Psi_\rho\,|\,\hat T+\hat V_{e-e}\,|\,\Psi_\rho\right\rangle$

The functional $F[\rho]$ searches all many particle functions Ψ that yield the input density $\rho(\vec r)$ and then delivers the minimum of $\left\langle\hat T+\hat V_{e-e}\right\rangle$

Theorem I $\int d\vec r v_{ext}(\vec r)\rho(\vec r)+F[\rho]\ge E_0$

Theorem II $\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)+F[\rho_0]=E_0$

ρ_0 - ground state density
E_0 - ground state energy

Let us define function Ψ^{ρ}_{min} that minimizes $\left\langle\Psi_\rho\,|\,\hat T+\hat V_{e-e}\,|\,\Psi_\rho\right\rangle$

$F[\rho]=\left\langle\Psi^{\rho}_{min}\,|\,\hat T+\hat V_{e-e}\,|\,\Psi^{\rho}_{min}\right\rangle$ $\quad F[\rho_0]=\left\langle\Psi^{\rho_0}_{min}\,|\,\hat T+\hat V_{e-e}\,|\,\Psi^{\rho_0}_{min}\right\rangle$

Proof of Theorem I:

$$\int d\vec r v_{ext}(\vec r)\rho(\vec r)+F[\rho]=\int d\vec r v_{ext}(\vec r)\rho(\vec r)+\left\langle\Psi^{\rho}_{\min}\,|\,\hat T+\hat V_{e-e}\,|\,\Psi^{\rho}_{\min}\right\rangle=$$
$$=\left\langle\Psi^{\rho}_{\min}\,|\,\hat V_{ext}+\hat T+\hat V_{e-e}\,|\,\Psi^{\rho}_{\min}\right\rangle\ge E_0$$

Ritz variational principle

Density Functional Theory – constrained search formulation

Proof of Theorem II: $E_0\le\left\langle\Psi^{\rho_0}_{min}\,|\,\hat V_{ext}+\hat T+\hat V_{e-e}\,|\,\Psi^{\rho_0}_{min}\right\rangle$

From variational principle

$$\left\langle\Psi_0\,|\,\hat V_{ext}+\hat T+\hat V_{e-e}\,|\,\Psi_0\right\rangle\le\left\langle\Psi^{\rho_0}_{min}\,|\,\hat V_{ext}+\hat T+\hat V_{e-e}\,|\,\Psi^{\rho_0}_{min}\right\rangle$$
$$\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)+\left\langle\Psi_0\,|\,\hat T+\hat V_{e-e}\,|\,\Psi_0\right\rangle\le\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)+\left\langle\Psi^{\rho_0}_{\min}\,|\,\hat T+\hat V_{e-e}\,|\,\Psi^{\rho_0}_{\min}\right\rangle$$

(A) $\left\langle\Psi_0\,|\,\hat T+\hat V_{e-e}\,|\,\Psi_0\right\rangle\le\left\langle\Psi^{\rho_0}_{min}\,|\,\hat T+\hat V_{e-e}\,|\,\Psi^{\rho_0}_{min}\right\rangle$

But, on the other hand, from the definition of $\Psi^{\rho_0}_{min}$

(B) $\left\langle\Psi_0\,|\,\hat T+\hat V_{e-e}\,|\,\Psi_0\right\rangle\ge\left\langle\Psi^{\rho_0}_{min}\,|\,\hat T+\hat V_{e-e}\,|\,\Psi^{\rho_0}_{min}\right\rangle$

[(A) & (B) true] $\Rightarrow\left\langle\Psi_0\,|\,\hat T+\hat V_{e-e}\,|\,\Psi_0\right\rangle=\left\langle\Psi^{\rho_0}_{min}\,|\,\hat T+\hat V_{e-e}\,|\,\Psi^{\rho_0}_{min}\right\rangle$

$F[\rho_0]=\left\langle\Psi^{\rho_0}_{min}\,|\,\hat T+\hat V_{e-e}\,|\,\Psi^{\rho_0}_{min}\right\rangle$

$$\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)+\left\langle\Psi_0\,|\,\hat T+\hat V_{e-e}\,|\,\Psi_0\right\rangle=F[\rho_0]+\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)$$
$$\left\langle\Psi_0\,|\,\hat V_{ext}+\hat T+\hat V_{e-e}\,|\,\Psi_0\right\rangle=F[\rho_0]+\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)$$
$$E_0=F[\rho_0]+\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)$$

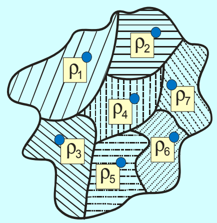
Density Functional Theory – Constrained Search Formulation Relation to Ritz Variational Principle

The ground-state energy minimization procedure of $E[\Psi]=\frac{<\Psi|\hat H|\Psi>}{<\Psi|\Psi>}$ can be divided into two steps

$$E_0[\Psi]=\min_{\Psi\to N}\left\langle\Psi\,|\,\hat T+\hat V_{e-e}+\hat V_{ext}\,|\,\Psi\right\rangle=\min_{\rho\to N}\left[\min_{\Psi\to\rho}\left\langle\Psi^\rho\,|\,\hat T+\hat V_{e-e}+\hat V_{ext}\,|\,\Psi^\rho\right\rangle\right]$$

- The inner minimization is constrained to all wave functions that give $\rho(\vec r)$,
- while the outer minimization releases this constrain by searching all $\rho(\vec r)$

Percus-Levy partition of the N-electron Hilbert space



- Each shaded area is the set of Ψ that integrate to a particular $\rho(\vec r)$.
- The minimization $\Psi\to\rho$ for a particular ρ is constrained to the shaded area associated with this ρ, and is realized by one point (denoted by ●) in this shaded area.
- The minimization $\rho\to N$ is over all such points.

Density Functional Theory – Constrained Search Formulation Relation to Ritz Variational Principle

■ $E_0[\rho] = \min_{\Psi \to N} \langle \Psi | \hat{T} + \hat{V}_{e-e} + \hat{V}_{ext} | \Psi \rangle =$

$= \min_{\rho \to N} \left[\min_{\Psi \to \rho} \langle \Psi^\rho | \hat{T} + \hat{V}_{e-e} + \hat{V}_{ext} | \Psi^\rho \rangle \right] =$

$= \min_{\rho \to N} \left[\min_{\Psi \to \rho} \langle \Psi^\rho | \hat{T} + \hat{V}_{e-e} | \Psi^\rho \rangle + \int d\vec{r} \upsilon_{ext}(\vec{r}) \rho(\vec{r}) \right] =$

$= \min_{\rho \to N} [F[\rho] + \int d\vec{r} \upsilon_{ext}(\vec{r}) \rho(\vec{r})] =$

● $= \min_{\rho \to N} E[\rho]$

$E[\rho] = F[\rho] + \int d\vec{r} \upsilon_{ext}(\vec{r}) \rho(\vec{r})$

In ■ 2^N wave functions of 3N variables

In ● O N E function of 3 variables !!!

Density Functional Theory

PROBLEM: exact functional $F[\rho]$ is unknown !

One needs a good approximation to $F[\rho]$

$F[\rho] = \min_{\Psi \to \rho} \langle \Psi_\rho | \hat{T} + \hat{V}_{e-e} | \Psi_\rho \rangle = \langle \Psi^\rho_{min} | \hat{T} + \hat{V}_{e-e} | \Psi^\rho_{min} \rangle$

$= T[\rho] + U[\rho] + \{ \langle \Psi^\rho_{min} | \hat{V}_{e-e} | \Psi^\rho_{min} \rangle - U[\rho] \}$

Kinetic energy

Classical Coulomb energy

$U[\rho] = \frac{1}{2} \iint d\vec{r}\, d\vec{r}\,' \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$

Exchange & Correlation $E_{xc}[\rho]$

$F[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho]$

● The functional $F[\rho]$ is universal in the sense that it is independent of the external potential (field) $\upsilon_{ext}(\vec{r})$.

Thomas-Fermi-Method (probably the oldest approximation to DFT)

$T^{T-F}[\rho] \cong \frac{3}{5}(3\pi^2)^{2/3} \frac{\hbar^2}{2m} \int d\vec{r} [\rho(\vec{r})]^{5/3}$ $\quad V^{T-F}_{ee}[\rho] \cong U[\rho]$

and extensions

§ Thomas-Fermi-Dirac

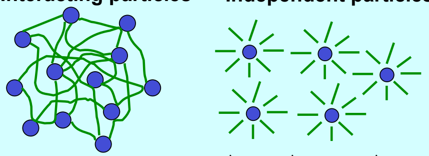
§ Thomas-Fermi-Weizsacker

PROBLEM: $T^{T-F}[\rho]$

Very often these models give even qualitatively wrong results.

Density Functional Theory (DFT) in Kohn-Sham realization

Interacting particles **Independent particles**



$\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_{10^{23}})$ $\quad \phi_1(\vec{x}_1)\phi_2(\vec{x}_2)\ldots\phi_3(\vec{x}_{10^{23}})$

Idea: consider electrons as independent particles moving in an effective potential

This reduction is rigorously possible !

DFT- The Kohn- Sham Method

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

W. Kohn & L. Sham (1965) invented an ingenious indirect approach to the kinetic- energy functional.

They turned density functional theory into a practical tool for rigorous calculations

The main idea:

System of interacting electrons with density $\rho(\vec{r})$ ⟷ **System of non-interacting electrons with the same density $\rho(\vec{r})$**

"Real" system $\rho(\vec{r})$ $\quad T[\rho]$

"Fictitious" or Kohn-Sham reference system $T_S[\rho]$ $\quad \rho_S(\vec{r}) = \rho(\vec{r})$

$$E[\rho] = \int d\vec{r} \upsilon_{ext}(\vec{r}) \rho(\vec{r}) + T_S[\rho] + U[\rho] + E_{xc}[\rho]$$

● $E_{xc}[\rho] = V_{ee}[\rho] - U[\rho] + T[\rho] - T_S[\rho]$

● *Exchange-correlation functional* contains now the difference between kinetic energy functional of interacting and non-interacting electrons.

The Kohn- Sham Method – Kinetic energy functional

How the $T_s[\rho]$ **looks like ?**

Hamiltonian of the non-interacting reference system

$$H_S = \sum_i^N -\frac{\hbar^2}{2m}\vec{\nabla}_i^2 + \sum_i^N \upsilon_S(\vec{r}_i)$$

$\upsilon_S(\vec{r})$ - local potential

For this system there will be an

exact determinantal ground-state wave function

$$\Phi = \frac{1}{\sqrt{N!}}\det[\phi_1, \phi_2, \ldots, \phi_N]$$

, where φ_i are the N lowest eigenstates of the one-electron Hamiltonian

$$\hat{h}_S\phi_i = \left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_S(\vec{r})\right]\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r})$$

The density

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

The Kohn- Sham Method – Kinetic energy functional

$T_S[\rho]$ - *can be defined by the constrained-search formula*

$$T_S[\rho] = \underset{\Phi\to\rho}{Min}\langle\Phi|\hat{T}|\Phi\rangle = \underset{\Phi\to\rho}{Min}\sum_{i=1}^N\left\langle\phi_i\left|-\frac{\hbar^2}{2m}\vec{\nabla}^2\right|\phi_i\right\rangle$$

The search is over all single-determinantal functions Φ that yield the given density ρ .

- The existence of the minimum has been proved by Lieb (1982).
- $T_S[\rho]$ is uniquely defined for any density.
- $T_S[\rho] \neq T[\rho]$

Crucial characteristics of the Kohn-Sham Method

Φ NOT Ψ

The Kohn-Sham Method: Variational Procedure

We cast the Hohenberg-Kohn variational problem in terms of the one-particle (Kohn-Sham) orbitals

$$E_0 = \min_{\rho\to N} E[\rho] =$$

$$= \min_{\rho\to N}\left\{T_S[\rho] + U[\rho] + E_{xc}[\rho] + \int d\vec{r}\,\upsilon_{ext}(\vec{r})\rho(\vec{r})\right\}$$

$$= \min_{\rho\to N}\left\{[\underset{\Phi\to\rho}{Min}\langle\Phi|\hat{T}|\Phi\rangle] + U[\rho] + E_{xc}[\rho] + \int d\vec{r}\,\upsilon_{ext}(\vec{r})\rho(\vec{r})\right\}$$

$$= \min_{\Phi\to N}\left\{T_S[\Phi] + U[\rho[\Phi]] + E_{xc}[\rho[\Phi]] + \int d\vec{r}\,\upsilon_{ext}(\vec{r})\rho[\Phi](\vec{r})\right\}$$

$$= \min_{\{\varphi_i\}\to N}\left\{T_S[\{\varphi_i\}] + U[\rho[\{\varphi_i\}]] + E_{xc}[\rho[\{\varphi_i\}]] + \sum_{i=1}^N\int d\vec{r}\,\varphi_i^*(\vec{r})\upsilon_{ext}(\vec{r})\varphi_i(\vec{r})\right\}$$

The dependence of the density ρ on the orbitals $\{\varphi_i\}$ is known

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

Variational search for the minimum of $E[\rho]$ can be equivalently performed in the space of the orbitals $\{\varphi_i\}$.

Derivation of the Kohn-Sham Equations

Performing variational search for the minimum of $E[\rho]$ one must actually constrain orbitals to be orthonormal $\int d\vec{r}\,\varphi_i^*(\vec{r})\varphi_j(\vec{r}) = \delta_{ij}$ (●)

Conservation of the number of particles

Let us define the constrained functional of the N orbitals

$$\Omega[\{\varphi_i\}] = E[\rho] - \sum_{i=1}^N\sum_{j=1}^N\varepsilon_{ij}\int d\vec{r}\,\varphi_i^*(\vec{r})\varphi_j(\vec{r})$$

where ε_{ij} are Lagrange multipliers for the constrain (●).

For $E[\rho]$ to be minimum, it is necessary that $\delta\Omega[\{\varphi_i\}] = 0$

$$\frac{\delta}{\delta\varphi_i^*(\vec{r})}\left\{E[\rho] - \sum_{i=1}^N\sum_{j=1}^N\varepsilon_{ij}\int d\vec{r}\,'\varphi_i^*(\vec{r}\,')\varphi_j(\vec{r}\,')\right\} = 0$$

Note: $\frac{\delta}{\delta\varphi_i^*(\vec{r})} = \frac{\delta\rho}{\delta\varphi_i^*(\vec{r})}\frac{\delta}{\delta\rho}$

The variational procedure leads to equations:

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_{xc}(\vec{r})\right]\varphi_i(\vec{r}) = \sum_{j=1}^N\varepsilon_{ij}\varphi_j(\vec{r})$$

$$\upsilon_H(\vec{r}) = \frac{\delta U}{\delta\rho} = \int d\vec{r}\,'\frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \qquad \upsilon_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho}$$

Derivation of the Kohn-Sham Equations

In Kohn-Sham method exchange-correlation functional can be split into separate exchange and correlation functional $E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$

$$E_x[\rho] = -\frac{1}{2}\sum_i \iint d\vec{r}d\vec{r}'\varphi_i^*(\vec{r})\left(\sum_j \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r}')}{|\vec{r}-\vec{r}'|}\right)\varphi_i(\vec{r}')$$

Exchange energy functional — Correlation energy functional — Exchange potential — Correlation potential

$$\upsilon_{xc}(\vec{r}) = \frac{\delta E_x[\rho]}{\delta\rho} + \frac{\delta E_c[\rho]}{\delta\rho} = \upsilon_x(\vec{r}) + \upsilon_c(\vec{r})$$

Kohn-Sham potential (local potential !)

$$\upsilon_{KS}(\vec{r}) = \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_x(\vec{r}) + \upsilon_c(\vec{r}) \quad (= \upsilon_S(\vec{r}))$$

$\hat{H}_{KS} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{KS}(\vec{r})$ **is hermitian** $\Rightarrow$ ε_{ij} **is also hermitian** $(\varepsilon_{ij} = \langle\varphi_i|\hat{H}_{KS}|\varphi_j\rangle)$

Unitary transformation of $\{\varphi_i\}$ diagonalizes ε_{ij}, but the density and $\hat{H}_{KS}$ remain invariant.

The Kohn- Sham Method – The Kohn-Sham Equations

- **Schrödinger-like equations with local potential**

$$\upsilon_H(\vec{r}) = \frac{\delta U}{\delta\rho} = \int d\vec{r}'\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} \qquad \frac{\delta E_x[\rho]}{\delta\rho} \qquad \frac{\delta E_c[\rho]}{\delta\rho}$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_x(\vec{r}) + \upsilon_c(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

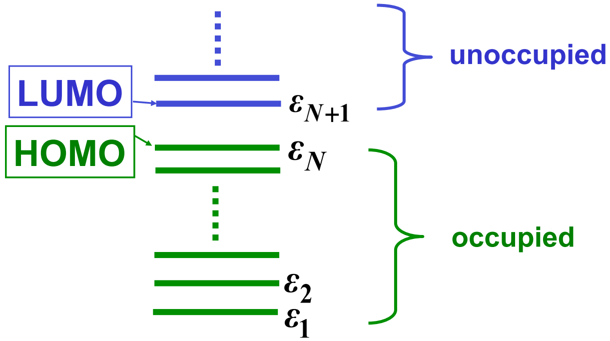
$$\upsilon_{ext}(\vec{r}) = -e^2\sum_{s,n}\frac{Z_s}{|\vec{r}-\vec{\tau}_s-\vec{R}_n|}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N}\varphi^*_i(\vec{r})\varphi_i(\vec{r})$$

- **These equation are nonlinear and must be solved iteratively (self-consistently)**

The Kohn- Sham Method – ‚Aufbau' principle

How to calculate one particle density?



The Kohn- Sham Method – The Total Energy

$$E[\rho] = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\vec{r}\varphi_i^*(\vec{r})\vec{\nabla}^2\varphi_i(\vec{r}) + U[\rho] + E_x[\rho] + E_c[\rho] + \int d\vec{r}\upsilon_{ext}(\vec{r})\rho(\vec{r})$$

$$E = \sum_{i=1}^{N}\varepsilon_i - \frac{1}{2}\iint d\vec{r}\,d\vec{r}'\frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + E_x[\rho] + E_c[\rho] - \int d\vec{r}(\upsilon_x(\vec{r}) + \upsilon_c(\vec{r}))\rho(\vec{r})$$

so-called double counting correction

Sum of the one-particle Kohn-Sham energies

$$\sum_{i=1}^{N}\varepsilon_i = \sum_{i=1}^{N}\left\langle\varphi_i\left|-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \vartheta_{KS}(\vec{r})\right|\varphi_i\right\rangle = T_S[\rho] + \int d\vec{r}\vartheta_{KS}(\vec{r})\rho(\vec{r})$$

Energy of the reference system

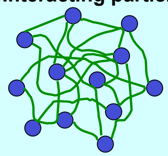
differs from the energy of ‘real’ system

The Kohn- Sham Method – Problems

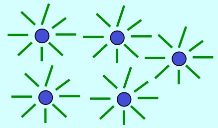
- **Physical meaning of the Kohn-Sham orbital energies ε_i ?**
  (Note, these energies were introduced as Lagrange multipliers)
  - Strictly speaking there is none ☹
  - The Kohn-Sham orbital energy of the highest occupied level is equal to the minus of the ionization energy, $\varepsilon_{max} = \mu = -I$ ☺
  - Extension to non-integer occupation numbers $0 \le f_i \le 1$
    $\rho(\vec{r}) = \sum_i f_i \varphi_i^*(\vec{r})\varphi_i(\vec{r})$ $\quad \frac{\partial E}{\partial f_i} = \varepsilon_i$ Janak theorem (1978) ☺
  - Kohn-Sham energies may be considered as the zero order approximation to the energies of quasi-particles in the many-particle theory. ☺
- **Correlation energy functional $E_c[\rho]$ (also $v_c(\vec{r})$) is *unknown* for *non-homogeneous* systems**
  - $E_c[\rho]$ - ***is known*** for ***homogeneous*** electron gas (constant density) ☺

Density Functional Theory (DFT) in Kohn-Sham realization

Interacting particles **Independent particles**



$\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_{10^{23}})$



$\phi_1(\vec{x}_1)\phi_2(\vec{x}_2)\ldots\phi_3(\vec{x}_{10^{23}})$

Idea: consider electrons as independent particles moving in an effective potential

This reduction is rigorously possible !

DFT- The Kohn- Sham Method

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

System of interacting electrons with density $\rho(\vec{r})$ ⟺ **System of non-interacting electrons with the same density $\rho(\vec{r})$**

"Real" system $\quad \rho(\vec{r}) \quad T[\rho]$

"Fictitious" or Kohn-Sham reference system $\quad T_S[\rho] \quad \rho_S(\vec{r}) = \rho(\vec{r})$

$$E[\rho] = \int d\vec{r}\, v_{ext}(\vec{r})\rho(\vec{r}) + T_S[\rho] + U[\rho] + E_x[\rho] + E_c[\rho]$$

unknown!!! (refers to $E_c[\rho]$)

- $\rho(\vec{r}) = \sum_{i=1}^{N} \varphi^*_i(\vec{r})\varphi_i(\vec{r})$
- $T_s[\rho] = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\vec{r}\,\varphi_i^*(\vec{r})\vec{\nabla}^2\varphi_i(\vec{r})$
- $E_x[\rho] = -\frac{1}{2}\sum_i \iint d\vec{r}\,d\vec{r}\,'\,\varphi_i^*(\vec{r})\left(\sum_j \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\right)\varphi_i(\vec{r}\,')$

DFT: Implementations of the Kohn-Sham Method

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + V_{xc}(\vec{r})\right]\psi_\alpha = \varepsilon_\alpha \psi_\alpha$$

- Fully relativistic / Semi-relativistic / Non-relativistic
- All-electron full potential / All-electron muffin-tin / All-electron PAW / Pseudopotential
- Local Density Approximation (LDA) / Generalized Gradient Approximation (GGA) / Beyond LDA
  - Beyond LDA: GW (quasi-particles) / EXX (exact exchange) / sX-LDA / Time dependent DFT / LDA+U
- Non-periodic / periodic
- Non-spin-polarized / Spin polarized
- Atomic orbitals (Gaussians(GTO), Slater type (STO), Numerical)
- Plane Waves
- Augmentation (Plane waves (FPLAPW), Spherical waves (LMTO, ASW))
- Fully numerical (real space)

Exchange and Correlation Energy of Homogeneous Electron Gas

- **Homogeneous electron gas** (free electron gas or "jellium")

Wave functions: $\psi(\vec{k},\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}}$ Constant electron density: $\rho = N/\Omega$

Exchange energy per unit volume

$$E_x = -\frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3} e^2 \rho^{4/3} = \varepsilon_x^{\text{hom}} \rho$$

- Dimensionless parameter characterizing density:

$$r_s = \frac{1}{a_B}\left(\frac{3}{4\pi\rho}\right)^{1/3} \qquad \rho \text{ in } (a_B)^{-3}$$

Exchange energy per particle

$$\varepsilon_x^{\text{hom}} = -\frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3} e^2 \rho^{1/3}$$

$$\varepsilon_x^{\text{hom}} = -\frac{3}{2}\left(\frac{9}{4\pi^2}\right)^{1/3} \frac{1}{r_s} \quad \text{in } [Ry]$$

$$\varepsilon_x^{\text{hom}}(r_s) = -0.91633/r_s \ [Ry]$$

- **Quantum Monte-Carlo simulations for homogeneous electron gas**

*D. M. Ceperly & B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980)*

Parametrization: *J. P. Perdew & A. Zunger, Phys. Rev. B **23**, 5048 (1981)*

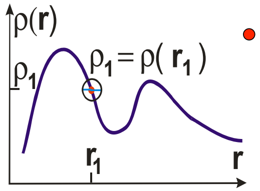
Correlation energy per particle

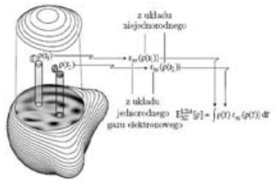
$$\varepsilon_c^{\text{hom}}(r_s) = \begin{cases} A\ln r_s + B + Cr_s \ln r_s + Dr_s & \text{for } r_s < 1 \\ \gamma/(1+\beta_1\sqrt{r_s} + \beta_2 r_s) & \text{for } r_s \geq 1 \end{cases} \quad [Ry]$$

$A, B, C, D, \gamma, \beta_1, \beta_2$ - fitted parameters

Local Density Approximation (LDA)

In atoms, molecules, and solids the electron density is not homogeneous





- **The main idea of the *Local Density Approximation*: the density is treated *locally* as constant**

$$E_{xc}^{LDA}[\rho] = \int d\vec{r}\, \rho(\vec{r})\, \varepsilon_{xc}^{\text{hom}}(\rho(\vec{r}))$$

$$\varepsilon_{xc}^{\text{hom}} = \varepsilon_x^{\text{hom}} + \varepsilon_c^{\text{hom}}$$

GGA - Gradient Corrections to LDA

Gradient Expansion Approximation

*D. C. Langreth & M. J. Mehl, Phys. Rev. B **28**, 1809 (1983)*

$$E_{xc}^{GEA}[\rho] = E_{xc}^{LDA}[\rho] + \int d\vec{r}\, \rho(\vec{r}) C_{xc}[\rho] \frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})^{4/3}}]$$

Generalized Gradient Approximation

*J. P. Perdew & Y. Wang, Phys. Rev. B **33**, 8800 (1986)*

$$E_{xc}^{GGA}[\rho] = \int d\vec{r}\, f_{xc}(\rho(\vec{r}), \nabla\rho(\vec{r}))$$

f_{xc} **-constructed to fulfill maximal number of "summation rules"**

Exchange-correlation potential can be calculated very easily, since explicit dependence of E_{xc} on the density ρ is known.

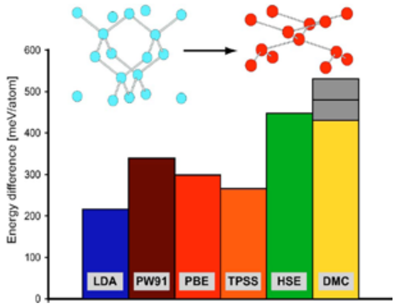
$$v_{xc} = \frac{\delta E_{xc}}{\delta\rho}$$

Examples of exchange functionals

- Becke 88: Becke's 1988 functional,
- Perdew-Wang 91
- Barone's Modified PW91
- Gill 96
- PBE: The 1996 functional of Perdew, Burke and Ernzerhof
- OPTX: Handy's OPTX modification of Becke's exchange functional
- TPSS: The exchange functional of Tao, Perdew, Staroverov, and Scuseri

and also many correlation functionals

Accuracy Benchmarks of the different DTF Functional



Difference in energy per atom
in the diamond phase and in the β-tin phase of Si.

Phys. Rev. B 74, 121102(R) (2006)

Thank you!

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