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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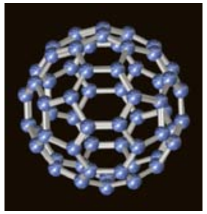
Lecture 2 – *March 3, 2014*

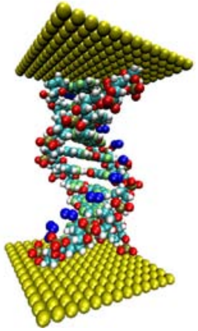
- **Density Functional Theory (DFT) – the key to the Computational Materials Science**
  The Basics
- **Kohn-Sham realization of the DFT**

Fundamental problem in materials science

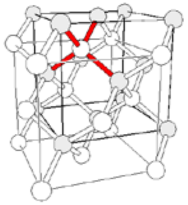
A fundamental problem in materials science is the prediction of condensed matter's electronic structure



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

$$\boxed{H\Psi = E\Psi}$$

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

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 $\{\vec{R}_1, \vec{R}_2, \ldots\}$

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

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

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

$$\Psi(\{\vec{R}_a\}, \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \equiv \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

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

Ritz Variational Principle → Ground State Energy of the system

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

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

$$E[\Psi] = \frac{<\Psi | \hat{H} | \Psi>}{<\Psi | \Psi>}$$

$$E[\Psi] \geq E_0$$

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

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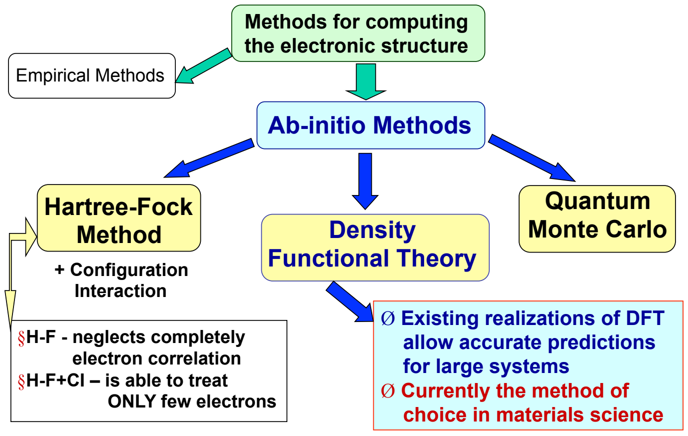
Spectrum of Electronic Hamiltonian:
What *ab initio* methods do we have?


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**

- **Existing realizations of DFT allow accurate predictions for large systems**
- **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**

$$\rho(\vec{r}) = \left\langle \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \middle| \sum_i \delta(\hat{\vec{r}}_i - \vec{r}) \middle| \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \right\rangle$$
$$= N \int d\vec{r}_2, \ldots, d\vec{r}_N \Psi^*(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N) \Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)$$

- 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 $F[\rho] \doteq \min_{\Psi_\rho \to \rho} \langle \Psi_\rho | \hat{T} + \hat{V}_{e-e} | \Psi_\rho \rangle$

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

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

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_{min}^{ρ} that minimizes $\langle \Psi_\rho | \hat{T} + \hat{V}_{e-e} | \Psi_\rho \rangle$

$$F[\rho] = \langle \Psi_{min}^{\rho} | \hat{T} + \hat{V}_{e-e} | \Psi_{min}^{\rho} \rangle \qquad F[\rho_0] = \langle \Psi_{min}^{\rho_0} | \hat{T} + \hat{V}_{e-e} | \Psi_{min}^{\rho_0} \rangle$$

Proof of Theorem I:

$$\int d\vec{r} v_{ext}(\vec{r})\rho(\vec{r}) + F[\rho] = \int d\vec{r} v_{ext}(\vec{r})\rho(\vec{r}) + \langle \Psi_{\min}^{\rho} | \hat{T} + \hat{V}_{e-e} | \Psi_{\min}^{\rho} \rangle =$$
$$= \langle \Psi_{\min}^{\rho} | \hat{V}_{ext} + \hat{T} + \hat{V}_{e-e} | \Psi_{\min}^{\rho} \rangle \geq E_0$$

Ritz variational principle

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

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

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

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

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

● $$= \min_{\rho\to N} E[\rho]$$

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

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 $F[\rho]$

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

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

Kinetic energy

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

Classical Coulomb energy

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

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

- 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)

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

and extensions

§ Thomas-Fermi-Dirac
§ Thomas-Fermi-Weizsacker

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

Very often these models give even qualitatively wrong results.

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
$\rho(\vec{r})$ $T[\rho]$

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

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

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

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

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

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

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

$$\begin{aligned}
E_0 &= \min_{\rho\to N} E[\rho] = \\
&= \min_{\rho\to N}\left\{T_S[\rho] + U[\rho] + E_{xc}[\rho] + \int d\vec{r}\,\upsilon_{ext}(\vec{r})\rho(\vec{r})\right\} \\
&= \min_{\rho\to N}\left\{[\underset{\Phi\to\rho}{Min}\langle \Phi | \hat{T} | \Phi \rangle] + U[\rho] + E_{xc}[\rho] + \int d\vec{r}\,\upsilon_{ext}(\vec{r})\rho(\vec{r})\right\} \\
&= \min_{\Phi\to N}\left\{T_S[\Phi] + U[\rho[\Phi]] + E_{xc}[\rho[\Phi]] + \int d\vec{r}\,\upsilon_{ext}(\vec{r})\rho[\Phi](\vec{r})\right\} \\
&= \min_{\{\varphi_i\}\to N}\left\{T_S[\{\varphi_i\}] + U[\rho[\{\varphi_i\}]] + E_{xc}[\rho[\{\varphi_i\}]] + \sum_{i=1}^{N}\int d\vec{r}\,\varphi_i^*(\vec{r})\upsilon_{ext}(\vec{r})\varphi_i(\vec{r})\right\}
\end{aligned}$$

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

The variational procedure leads to equations:

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

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

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

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

Kohn-Sham potential (local potential !)

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

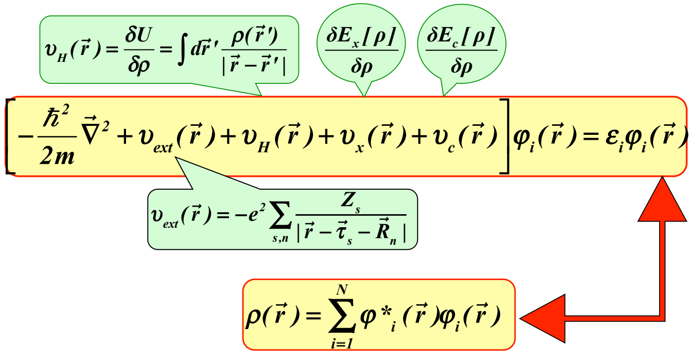
$\hat{H}_{KS} = -\dfrac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{KS}(\vec{r})$ **is hermitian** $\Rightarrow$ ε_{ij} **is also hermitian**

$(\varepsilon_{ij} = \langle \varphi_i | \hat{H}_{KS} | \varphi_j \rangle)$

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**



$$\upsilon_H(\vec r)=\frac{\delta U}{\delta\rho}=\int d\vec r\,'\frac{\rho(\vec r\,')}{|\vec r-\vec r\,'|}$$

$$\frac{\delta E_x[\rho]}{\delta\rho}$$

$$\frac{\delta E_c[\rho]}{\delta\rho}$$

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

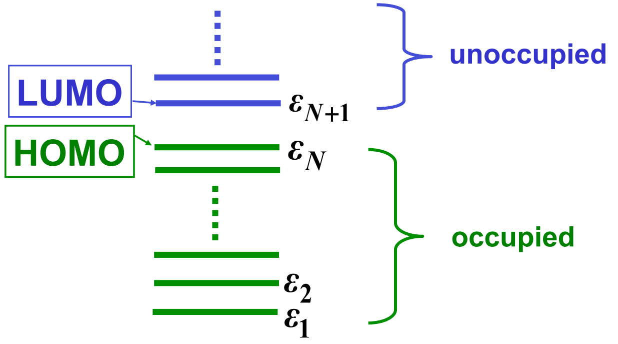
$$\upsilon_{ext}(\vec r)=-e^2\sum_{s,n}\frac{Z_s}{|\vec r-\vec\tau_s-\vec R_n|}$$

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

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

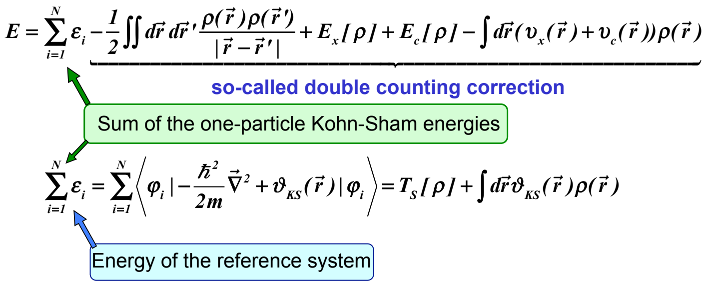
The Kohn- Sham Method –
‚Aufbau‘ principle

How to calculate one particle density?



The Kohn- Sham Method – The Total Energy

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



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

Sum of the one-particle Kohn-Sham energies

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

Energy of the reference system

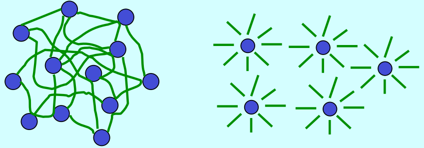
differs from the energy of ‘real’ system

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 $0\le f_i\le 1$
    $\rho(\vec r)=\sum_i f_i\varphi_i^*(\vec r)\varphi_i(\vec r)$ $\quad\boxed{\frac{\partial E}{\partial f_i}=\varepsilon_i}$ 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 $\upsilon_c(\vec r)$) 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: $\rho(\vec{r})$ $T[\rho]$

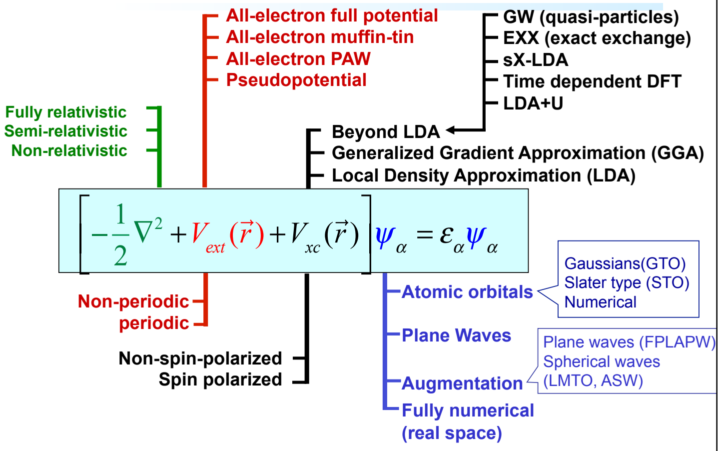
"Fictitious" or Kohn-Sham reference system: $T_S[\rho]$ $\rho_S(\vec{r})=\rho(\vec{r})$

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

unknown!!!

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

DFT: Implementations of the Kohn-Sham Method



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

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

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

Exchange energy per particle

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

- Dimensionless parameter characterizing density:

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

ρ in $(a_B)^{-3}$ ⇒

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

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

- **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)*

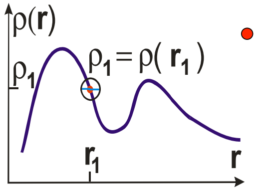
Correlation energy per particle

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

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

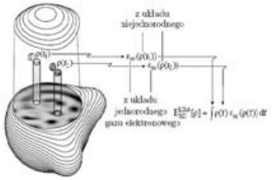
Local Density Approximation (LDA)

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**

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



$$\varepsilon_{xc}^{\text{hom}} = \varepsilon_{x}^{\text{hom}} + \varepsilon_{c}^{\text{hom}}$$

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.

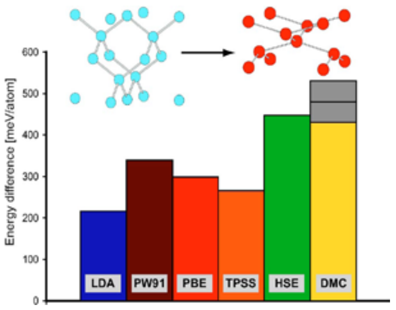
$$\upsilon_{xc} = \frac{\delta E_{xc}}{\delta\rho}$$

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 Functionals



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

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

Exact Exchange Method (EXX)

Exact Exchange for non-homogeneous systems + E_c in LDA or GGA

Main difficulty:

How to calculate the exchange potential $\upsilon_x(\vec{r}) = \dfrac{\delta E_x[\rho]}{\delta\rho(\vec{r})}$ ***?***

*M. Städele et al., Phys. Rev. B **59**, 10031 (1999).*

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

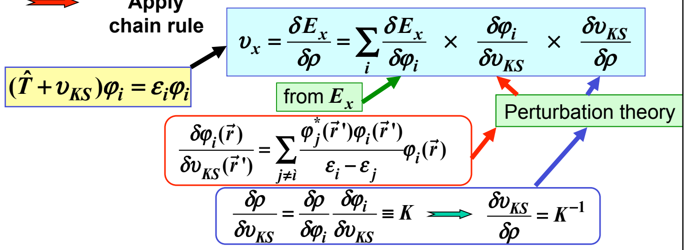
Problem: Explicit dependence of $E_x[\rho]$ (i.e., $\varphi_i[\rho]$) on ρ is unknown

Exact Exchange Method (EXX)

Solution: υ_x **is the first functional derivative of** E_x

→ **First order perturbation theory determines exactly** $\dfrac{\delta E_x}{\delta\rho}$

→ **Apply chain rule**



$$(\hat{T}+\upsilon_{KS})\varphi_i = \varepsilon_i\varphi_i$$

$$\upsilon_x = \frac{\delta E_x}{\delta\rho} = \sum_i \frac{\delta E_x}{\delta\varphi_i} \times \frac{\delta\varphi_i}{\delta\upsilon_{KS}} \times \frac{\delta\upsilon_{KS}}{\delta\rho}$$

from E_x

Perturbation theory

$$\frac{\delta\varphi_i(\vec{r})}{\delta\upsilon_{KS}(\vec{r}\,')} = \sum_{j\neq i}\frac{\varphi_j^*(\vec{r}\,')\varphi_i(\vec{r}\,')}{\varepsilon_i-\varepsilon_j}\varphi_i(\vec{r})$$

$$\frac{\delta\rho}{\delta\upsilon_{KS}} = \frac{\delta\rho}{\delta\varphi_i}\frac{\delta\varphi_i}{\delta\upsilon_{KS}} \equiv K \implies \frac{\delta\upsilon_{KS}}{\delta\rho} = K^{-1}$$

Exact Exchange Method (EXX) - CONCLUSSIONS

- Systematic improvement in comparison to LDA and GGA 🙂
- Numerically very costly in comparison to LDA and GGA 🙁
- Very good basis to search for better correlation energy functionals

  The work is going on ! (J. Perdew) 🙂

→ **New generation of the energy functionals**

Hybrid functionals

Hybrid functionals include a mixture of Hartree-Fock exchange with DFT exchange-correlation

EXAMPLE:

O3LYP: A three-parameter functional similar to B3LYP:

$\mathbf{E_{xc}}$ **=** $A{*}E_X^{LSD}+(1-A){*}E_X^{HF}+B{*}\Delta E_X^{OPTX}+C{*}\Delta E_C^{LYP}+(1-C)E_C^{VWN}$

lead very often to better accuracy with experiments

Extensions of the DFT

- **Relativistic DFT**

*A. K. Rajagopal and J. Callaway, Phys. Rev. B **7**, 1912 (1973)*

  - Kinetic energy operator (free Dirac field)

$$\hat{h} = c\vec{\alpha}\cdot\vec{p} + \beta mc^2$$

  - The ground-state energy is a functional of the ***four-vector current density*** $j_\mu(x)$

Extensions of the DFT – Spin-polarized systems

*U. Von Barth & L. Hedin, J. Phys. C **5**, 1629 (1972)*

- For example, systems with odd number of electrons

$$\rho_\uparrow \neq \rho_\downarrow \qquad \rho = \rho_\uparrow + \rho_\downarrow$$

- Energy functional of both spin densities $E_{xc}[\rho_\uparrow, \rho_\downarrow]$

Alternatively $E_{xc}[\rho, m]$ where $m = \rho_\uparrow - \rho_\uparrow$

Spin polarization (magnetization)

- Exchange-correlation potential $\upsilon_{xc\sigma} = \dfrac{\delta E_{xc}[\rho_\sigma, \rho_{-\sigma}]}{\delta\rho_\sigma}$

$$\sigma = (\uparrow, \downarrow)$$

- **Local Spin Density Approximation (LSDA)**

Important for magnetism !

Extensions of the DFT

- **Finite - Temperature** $(T \neq 0)$

*N. D. Mermin, Phys. Rev. **137**, A1441 (1965)*

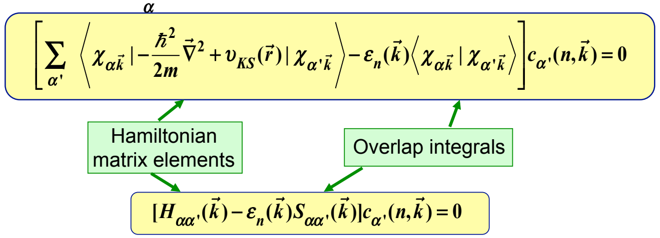
  - Grand canonical ensemble, $\Omega = -k_B T \ln Tr[e^{(\mu\hat{N}-\hat{H})/k_B T}]$
  - The grand potential of the a system at finite temperature is a functional of the density in the system at that temperature.

→ **Applications of DFT in statistical physics**

Solution of the Kohn-Sham Equations

- **Direct methods on a mesh in r-space**
- **Expansion of the Kohn-Sham orbitals in a basis** $\{\chi_{\alpha\vec{k}}(\vec{r})\}$

$$\varphi_{n\vec{k}}(\vec{r}) = \mathbb{N}\sum_{\alpha} c_\alpha(n,\vec{k})\chi_{\alpha\vec{k}}(\vec{r})$$



$$\left[\sum_{\alpha'} \left\langle \chi_{\alpha\vec{k}} \middle| -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{KS}(\vec{r}) \middle| \chi_{\alpha'\vec{k}} \right\rangle - \varepsilon_n(\vec{k})\left\langle \chi_{\alpha\vec{k}} \middle| \chi_{\alpha'\vec{k}} \right\rangle\right] c_{\alpha'}(n,\vec{k}) = 0$$

Hamiltonian matrix elements

Overlap integrals

$$[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k})S_{\alpha\alpha'}(\vec{k})]c_{\alpha'}(n,\vec{k}) = 0$$

Eigenvalueproblem $\det[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k})S_{\alpha\alpha'}(\vec{k})] = 0$

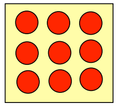
→ $\varepsilon_n(\vec{k})$ **Bandstructure**

Solution of the Kohn-Sham Equations – Survey of Methods involving basis

- **LCAO (Linear Combination of Atomic Orbitals)**
  All electron & pseudopotential
  Semiempirical Tight-Binding Method
- **Plane waves and pseudopotential**
  EMP – Empirical Pseudopotential Method
- **OPW (Orthogonalized Plane Waves)**
  All electron, plane waves orthogonalized to core states

Solution of the Kohn-Sham Equations – Survey of Methods

Multi-scattering Methods (All electron)



Muffin-tin form of the potential used to generate basis
Basis function – Numerically obtained wave function inside the muffin-tin sphere + augmented function outside

- **LAPW [FPLAPW] (Full Potential Linearized Augmented Plane Wave)**
  Plane waves outside muffin-tin spheres
  Considered to be the most accurate method
- **LMTO (Linearized Muffin-Tin Orbitals)**
  Hankel functions outside muffin-tin spheres
- **KKR (Kohn – Korringa – Rostoker)**
  Green's Function Method
  Very important for alloys (VCA, CPA)

Density Functional Calculations in Solids

Total energy of a solid: $E_{tot} = E_{el} + E_{ion-ion}$

$$E_{ion-ion} = \frac{e^2}{2}\sum_{nn'}\sum_{ss'}\frac{Z_s Z_{s'}}{|\vec{R}_n + \vec{\tau}_s - \vec{R}_{n'} - \vec{\tau}_{s'}|}$$

Lattice vectors $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ $\{\vec{a}_j\}$ - primitive translations
$\{\vec{\tau}_s\}$ - Basis vectors – positions of atoms in the unit cell

$$\boxed{E_{tot}(\{\varphi_i\},\{\vec{\tau}_s\},\{\vec{a}_j\}) = E_{el}(\{\varphi_i\},\{\vec{\tau}_s\},\{\vec{a}_j\}) + E_{ion-ion}(\{\vec{\tau}_s\},\{\vec{a}_j\})}$$

Density Functional Calculations in Solids

Equilibrium

- **Forces on all atoms disappear** $\vec{F}_s \equiv 0$

Force on atom s: $\vec{F}_s = -\frac{\partial E_{tot}}{\partial \vec{\tau}_s}$

➡ **Equilibrium positions of atoms in the unit cell** $\{\vec{\tau}_s^{eq}\}$

- **Crystal is stress free** $\sigma_{\alpha\beta} = 0$

Stress tensor: $\sigma_{\alpha\beta} = -\frac{\partial E_{tot}}{\partial u_{\alpha\beta}}$ $\alpha,\beta \in \{x,y,z\}$

$\vec{u}(\vec{r})$ -a vector field (deformation) that describes the displacement of every point in the solid

Before deformation: $\vec{r}$ After deformation: $\vec{r} + \vec{u}(\vec{r})$

Deformation tensor: $u_{\alpha\beta} = \frac{\partial u_\alpha}{\partial x_\beta}$

➡ **Shape of the unit cell, primitive translations** $\{\vec{a}_j^{eq}\}$

Hellmann-Feynman Theorem

$\vec{F}_s$ and $\sigma_{\alpha\beta}$ are usually calculated using Hellmann-Feynman Theorem

H. Hellmann, "Einführung in die Quantenchemie" (Denieke, Leipzig, 1937), p.285

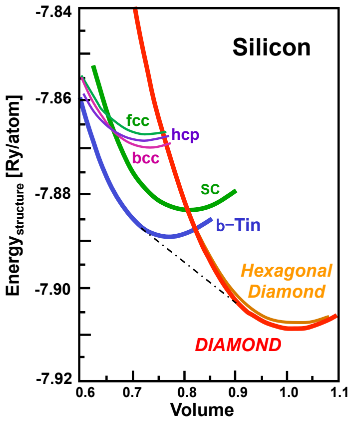
R. P. Feynman, Phys. Rev. 56, 340 (1939)

$$\frac{\partial E}{\partial \lambda} = \left\langle \psi(\lambda) \middle| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \middle| \psi(\lambda) \right\rangle$$

$\psi(\lambda)$ - Ground-state wavefunction of the Hamiltonian $\hat{H}(\lambda)$

Only these terms of the Hamiltonian contribute, which are explicitly dependent on the parameter λ .

First (convincing) LDA Calculations: Stability of crystals and pressure induced phase transitions



*M. T. Yin & M. L. Cohen, Phys. Rev. B **26**, 5668 (1982)*

$$P_{transition} = \frac{E_{tot}^{(1)}(V_t^{(1)}) - E_{tot}^{(2)}(V_t^{(2)})}{V_t^{(2)} - V_t^{(1)}}$$

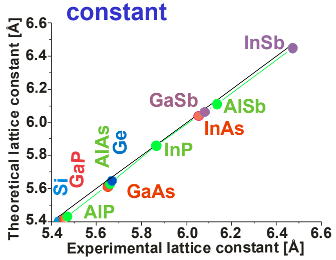
$$P = -\frac{\partial E}{\partial V}$$

Interesting prediction:
Under high hydrostatic pressure and in low temperature silicon becomes superconducting !

Later on confirmed experimentally

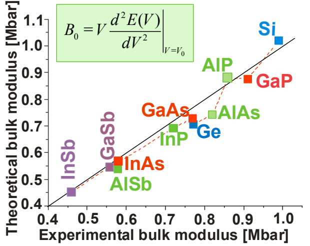
LDA calculations for semiconductors: lattice constants and bulk moduli

Equilibrium lattice constant



Averaged error: 0.46%
Min. error (InP): -0.1%
Max. error (AlP): -0.7%

Bulk modulus



$$B_0 = V \left.\frac{d^2E(V)}{dV^2}\right|_{V=V_0}$$

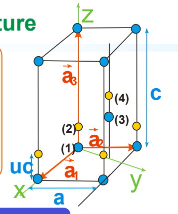
Averaged error: 4%
Min. error (InSb): -2.8%
Max. error (AlAs): -9.5%

Ground state properties of wurtzite nitride semiconductors

Wurtzite structure

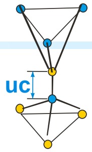
Lattice vectors

$\vec{a}_1 = a(1,0,0)$
$\vec{a}_3 = c(0,0,1)$
$\vec{a}_2 = a(-\frac{1}{2},\frac{\sqrt{3}}{2},0)$



Basis vectors

$\vec{d}_1 = (0,0,0)$
$\vec{d}_2 = (0,0,uc)$
$\vec{d}_3 = (0,\frac{a}{\sqrt{3}},c/2)$
$\vec{d}_3 = (0,\frac{a}{\sqrt{3}},c/2+uc)$



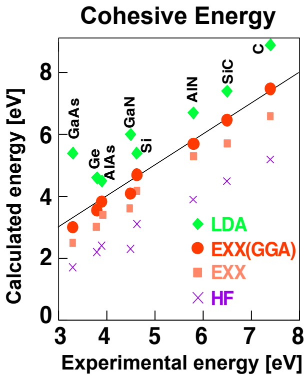
● Cation (Ga, Al, In)
● Anion (N)

	GaN			AlN			InN		
a [Å]	3.174	3.189	-0.47%	3.091	3.112	-0.67%	3.538	3.544	-0.17%
c [Å]	5.169	5.185	-0.31%	4.954	4.982	-0.56%	5.707	5.718	-0.19%
u	0.3768	0.377	-0.05%	0.3816	0.382	-0.10%	0.379		
c/a	1.6283	1.626	0.15%	1.6028	1.6009	0.12%	1.613		
B_0 [GPa]	196	195	0.5%	205	202	1.48%	146	139	5.0%
$E_{zb}-E_{wz}$ [meV/atom]	6			29			17		

🟩 Theory 🟦 Experiment 🟨 Relative error

Generally, LDA gives very good geometry of the unit cell

Cohesive energies in semiconductors Comparison of LDA, EXX, and HF Methods



Cohesive energy =
Energy of free (separated) atoms –
Energy of solid

Cohesive energy = -- Binding energy

LDA – **overestimates** (LDA world is smaller than the real one)

HF -- **underestimates**,

EXX – gives excellent cohesive energies in semiconductors

DFT – Calculation of the equation of state and elastic constants

- **Equation of state -** $E_{tot}(V)$ **or** $P(V)$

➡ $V_0 \quad B_0 \quad B_0'$

- **Elastic constants**

Energy of the strained system

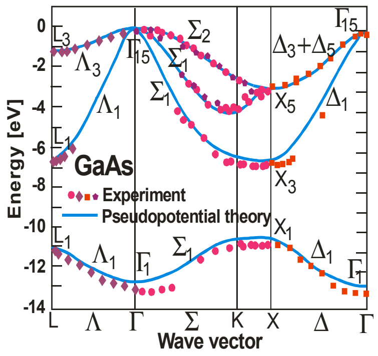
$$\boxed{\rho_0 E(\eta) = \frac{1}{2!}\sum_{i,j=1,6} c_{ij}\eta_i\eta_j + \frac{1}{3!}\sum_{i,j,k=1,6} c_{ijk}\eta_i\eta_j\eta_j + K}$$

Second order Elastic constants

Third order Elastic constants

LDA calculations in semiconductors

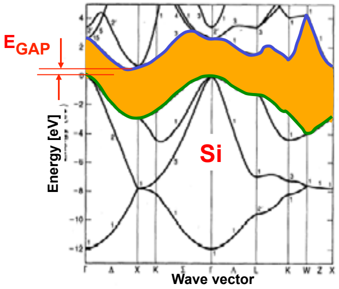
Valence bands for GaAs as determined from angle-resolved photoemission experiments and pseudopotential theory



- **LDA gives very good description of the occupied s-p valence bands (4s & 4p) in semiconductors**
- **Various methods of solving Kohn-Sham equations give very similar results**

LDA calculations in semiconductors – Energy gap

Band structure of diamond silicon



$E_{GAP} = E_{LUMO} - E_{HOMO}$

Too small by factor of 2

- For all semiconductors and insulators, LDA (GGA) give energy gaps that are 40%-70% of experimental gaps

Kohn-Sham gap

$$E^{KS}_{Gap} = \varepsilon^{KS}_{cbb} - \varepsilon^{KS}_{vbt}$$

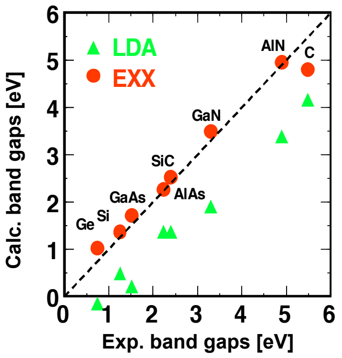
$$E^{KS}_{Gap} = \varepsilon^{KS}_{N+1}(N) - \varepsilon^{KS}_{N}(N)$$

- Relation of the Kohn-Sham gap to the ***quasi-particle energy*** (change of system energy caused by adding a particle) ?
- Is the Kohn-Sham gap generally wrong, for description of one particle excitations ?
- Does the error is caused by the approximation of the functionals ?

“**The band gap problem**”

Fundamental band gaps in semiconductors:
Local Density Approximation & Exact Exchange

Fundamental Band Gaps



- **EXX Method leads to Kohn-Sham gaps that agree very well with experiment**

➡ Large part of the error in the fundamental gaps is connected to the approximated functionals (LDA, GGA)

DFT (LDA, GGA, EXX) for weakly correlated systems

Accuracy of Common DFT implementations

- ☐ **Accuracy of geometries is better than 0.1 A**
- ☐ **Accuracy of calculated energies (relative) is usually better than 0.2 eV**
  Very often better than 0.01 eV

☹ Band Gap problem !

☹ Unsatisfactory accuracy of discussed approximations for highly correlated systems
(mostly involving 3d – electrons)

DFT - further developements required

May we reach so-called chemical accuracy within DFT?

- **Exact Exchange Kohn-Sham Method – a step in this direction**
  - ➢ **Systematic improvement of existing Kohn-Sham schemes**
  - ➢ **Computationally very demanding**
    - **Bulk systems up to now**
    - **Implementations for larger systems going on**
- **Crucial - Better correlation energy functionals**

DFT - further developements required

Density functional theory has revolutionized the way scientists approach the electronic structure of atoms, molecules,and solid materials in physics, chemistry, and materials science

We are not at the end of this way!

Thank you!

Thank you!

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