

**Basics of density-functional theory and fast guide to actual calculations**

- I. From the many-particle problem to the Kohn-Sham functional
- II. From the total energy to materials science and bio-physics

**"the ab initio line of computational sciences and engineering"**

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**Modeling Materials and Bio-Molecular Properties and Functions: The Many-Body Schrödinger Equation**

$$(\hat{T}^e + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi$$

With:  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_M)$

$$\hat{T}^e = \sum_{k=1}^N \frac{\mathbf{p}_k^2}{2m} \quad \hat{T}^{ion} = \sum_{l=1}^M \frac{\mathbf{p}_l^2}{2M_l}$$

$$\hat{V}^{e-e} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{k \neq k'}^{N,N} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|}$$

$$\hat{V}^{ion-ion} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{l \neq l'}^{M,M} \frac{Z_l Z_{l'}}{|\mathbf{R}_l - \mathbf{R}_{l'}|}$$

$$\hat{V}^{e-ion}(\mathbf{r}_k, \mathbf{R}_l) = \sum_{k=1}^N \sum_{l=1}^M v_l^{ion}(|\mathbf{R}_l - \mathbf{r}_k|)$$

w3.rz-berlin.mpg.de/~michael/member/MaterialsScienceLectures/k3-2005.pdf

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**Born Oppenheimer Approximation**

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_M) = \sum_v \Lambda_v(\{\mathbf{R}_I\}) \Phi_{v, \{\mathbf{R}_I\}}(\mathbf{r}_k)$$

Where  $\Phi_v$  are solutions of the "electronic Hamiltonian":

$$H_{\{\mathbf{R}_I\}}^e \Phi_{v, \{\mathbf{R}_I\}}(\mathbf{r}_k) = E_{v, \{\mathbf{R}_I\}}^e \Phi_{v, \{\mathbf{R}_I\}}(\mathbf{r}_k)$$

$$H^e = T^e + V^{e-e} + V^{e-ion}$$

frequently (commonly) applied approximations:

- neglect non-adiabatic coupling (terms of order  $m/M_l$ )
- keep only  $\Lambda_0$

➡ electronic and nuclear degrees of freedom decouple

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## Some Limits of the Born-Oppenheimer Approximation

It does not account for correlated dynamics of ions and electrons. For example:

- polaron-induced superconductivity
- dynamical Jahn-Teller effect
- some phenomena of diffusion in solids
- non-adiabaticity in molecule-surface scattering
- etc.

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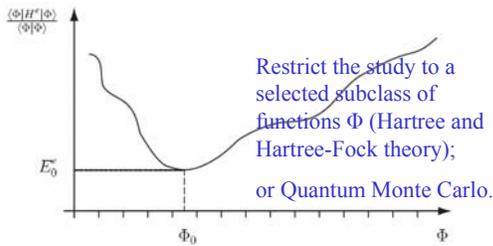
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## Wave-Function Theories

$$H^e = \sum_{k=1}^N -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_k}^2 + \sum_{k=1}^N v(\mathbf{r}_k) + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{k,k'=1 \\ k \neq k'}}^{N,N} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|}$$




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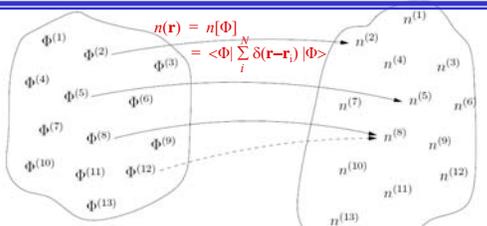
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## The Hohenberg-Kohn Theorem



The set of non-degenerate ground state wave functions  $\Phi$  of arbitrary  $N$ -particle Hamiltonians.

The set of particle densities  $n(\mathbf{r})$  belonging to non-degenerate ground states of the  $N$ -particle problem.

**The dashed arrow is not possible**

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## Density Functional Theory

The energy of the ground state of a many-electron system :  $E_0(\{\mathbf{R}_I\}) = \text{Min}_{\Phi} \langle \Phi | H^e | \Phi \rangle$

Hohenberg and Kohn (1964): The functional

$$n(\mathbf{r}) = n[\Phi] = \langle \Phi | \sum_i \delta(\mathbf{r}-\mathbf{r}_i) | \Phi \rangle$$

can be inverted, *i.e.*,

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Phi[n(\mathbf{r})] .$$

This implies:

$$E_0(\{\mathbf{R}_I\}) = \text{Min}_{n(\mathbf{r})} E_{\{\mathbf{R}_I\}}[n]$$

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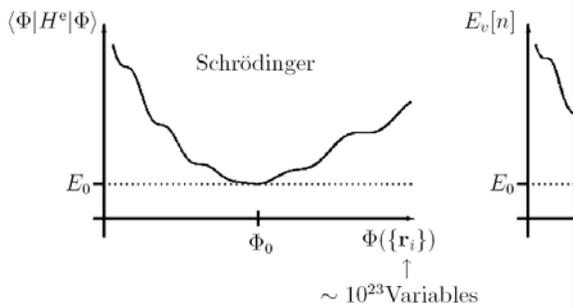
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## Comparison of Wave-Function and Density-Functional theory




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## Summary of Hohenberg-Kohn Density-Functional Theory (DFT) -- 1964

- There is a one-to-one correspondence between the ground-state wave function and the many-body Hamiltonian [or the nuclear potential,  $v^{\text{nuc}}(\mathbf{r})$ ].
- The many-body Hamiltonian determines everything.
- There is a one-to-one correspondence between the ground-state electron-density and the ground-state wave function.

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**Kohn and Sham (1965):**

$$E_v[n] = T_s[n] + \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E^{\text{Hartree}}[n] + E^{\text{xc}}[n]$$

with 
$$E^{\text{Hartree}}[n] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}d^3\mathbf{r}'$$

And  $T_s[n]$  the functional of the kinetic energy of **non-interacting** electrons.  $E^{\text{xc}}[n]$  contains all the unknowns.

At fixed electron number  $N$  the variational principle gives

$$\delta \left\{ E_v[n] - \mu \left( \int n(\mathbf{r})d^3\mathbf{r} - N \right) \right\} = 0$$

or 
$$\frac{\delta E_v[n]}{\delta n} = \mu = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v^{\text{eff}}(\mathbf{r})$$

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**Kohn and Sham (1965):**

$$v^{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})}$$

Because  $T_s[n]$  is the functional of non-interacting particles we effectively “restrict” the allowed densities to those that can be written as 
$$n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2$$

This implies:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v^{\text{eff}}(\mathbf{r}) \right\} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r})$$

$v^{\text{eff}}(\mathbf{r})$  depends on the density that we are seeking.

$$\begin{aligned} T_s[n] &= \sum_{k=1}^N \langle \varphi_k | -\frac{\hbar^2}{2m} \nabla^2 | \varphi_k \rangle, \\ &= \sum_{k=1}^N \epsilon_k - \int v^{\text{eff}}[n^{\text{in}}](\mathbf{r})n(\mathbf{r})d^3\mathbf{r}. \end{aligned}$$

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**The Kohn-Sham Ansatz**

-- Kohn-Sham (1965) – Replace the original many-body problem with an **independent electron problem that can be solved!**

-- Only the **ground state density** and the **ground state energy** are required to be the same as in the original many-body problem.

$$E_v[n] = T_s[n] + \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E^{\text{Hartree}}[n] + E^{\text{xc}}[n]$$

-- Maybe the exact  $E^{\text{xc}}[n]$  functional cannot be written as a closed mathematical expression. Maybe there is a detour similar to that taken for  $T_s[n]$ ? **The challenge is to find useful, approximate xc functionals.**

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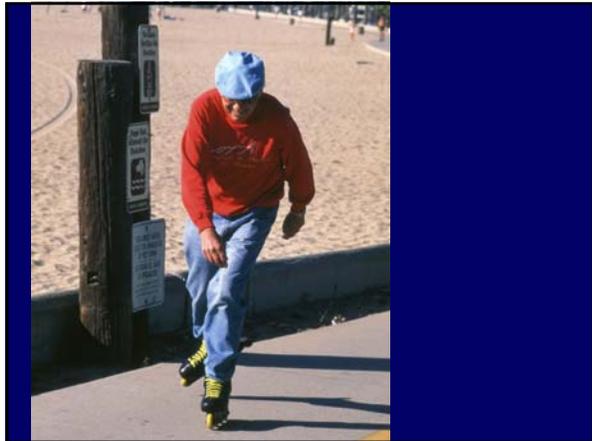
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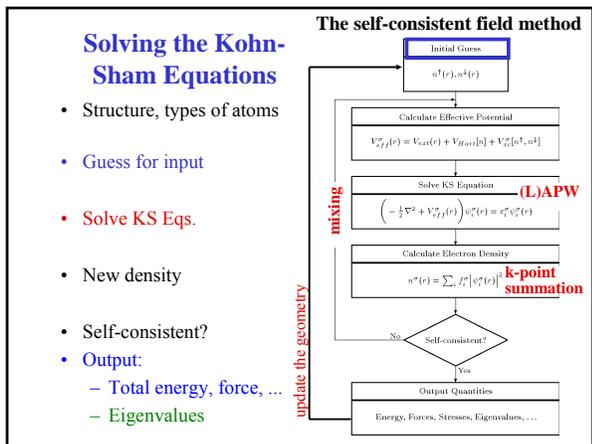
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## Quantum-Mechanics Based Technology Challenges for the Near Future

Create **new materials** and systems by design, e.g. quantum dots, quantum wires, nano-catalysis, etc.

For nanotechnology to become affordable, nano-structures will have to build themselves; normal manufacturing methods will be useless

⇒ **self-organization and assembly.**

Make progress in **understanding biological systems** starting from the fundamental equations of quantum mechanics.

**Bridging the time and length scales**

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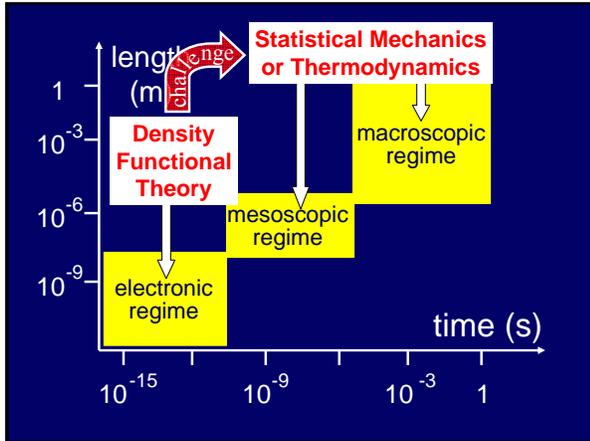
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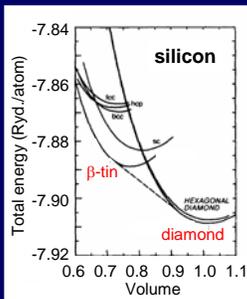
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## The first (convincing) DFT calculations: Stability of crystals and crystal phase transitions



*M. T. Yin and  
M. L. Cohen  
PRB 26 (1982)*

*see also:  
V.L. Moruzzi, J.F. Janak,  
and A. R. Williams  
Calculated Electronic  
Properties of Metals  
Pergamon Press (1978)*

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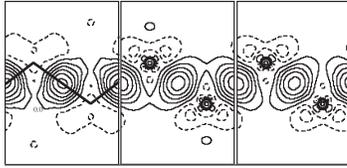
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## Electron Density of Si

Electron density *difference* from sum of atoms



experiment DFT-LDA DFT-GGA

*J. M. Zuo, P. Blaha, and K. Schwarz, J. Phys. Cond. Mat. 9, 7541 (1997)*

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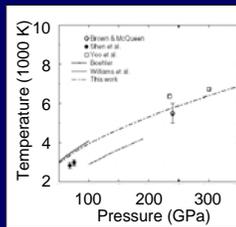
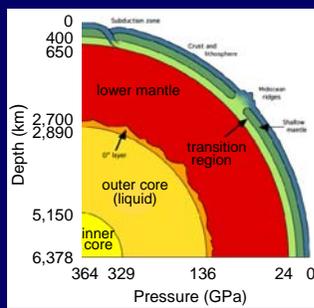
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## Ab initio melting curve of Fe as function of pressure



*D. Alfe, M. J. Gillan, and G. D Price  
NATURE 401 (1999)*

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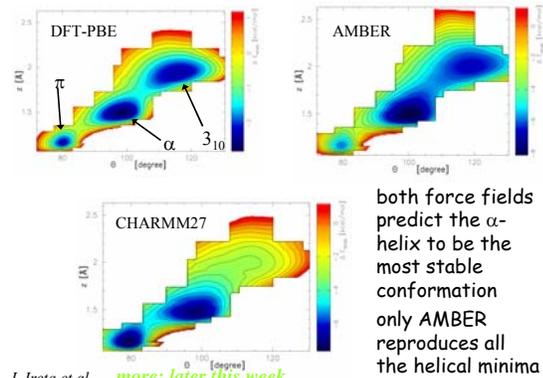
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## Bio-Physics: DFT vs Force Fields



*J. Ireta et al. more: later this week*

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### What About the Kohn-Sham Eigenvalues?

The **only** quantities that are supposed to be correct in the Kohn-Sham approach are **density, energy, forces, ...**

These are **integrated quantities**:  $n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2$

What about the individual  $\varphi_i(\mathbf{r})$  and  $\epsilon_i$ ?

In the real interacting many-electron system, energies to add and subtract electrons are well-defined **only** at the Fermi energy.

The Kohn-Sham  $\varphi_i(\mathbf{r})$  and  $\epsilon_i$  give an approximate description of quasi-particles, a **(good) starting point** for many-body calculations. -- *more later this week.*

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### What About the Kohn-Sham Eigenvalues?

The ionization energy is:  $I_k = E_k^{N-1} - E^N$   
 (Well defined for the highest occupied state. Otherwise, this only holds approximately.)  $= -\int_0^1 \frac{\partial E_v[n]}{\partial f_k} df_k$   
 $= -\int_0^1 \epsilon_k(f_k) df_k$

Here we assume that the positions of the atoms don't change upon ionization, or that they change with some delay (Franck-Condon principle). Using the mean-value theorem of integral algebra gives:  $I_k = -\epsilon_k(0.5)$

This is called the Slater-Janak "transition state". It can be viewed as **the DFT analog of Koopmans' theorem.**

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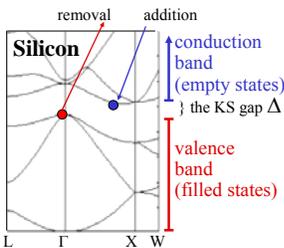
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### Kohn-Sham Electron Bands

Kohn-Sham band gap:  $\Delta = \epsilon_{\text{LB}} - \epsilon_{\text{VB}}$  of the  $N$ -particle system

**The measured (optical) band gap is something else:**



$$E_{\text{gap}} = I - A$$

$$A = E^N - E^{N+1}$$

$$I = E^{N-1} - E^N$$

$$E_{\text{gap}} = E^{N-1} + E^{N+1} - 2E^N$$

$$= \Delta + \Delta \epsilon^{\text{xc}}$$

Modern calculations of  $E_{\text{gap}}$  employ the ***GW*** approach, starting from KS energies and wave functions. *more comes later this week*

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## Summary

- *Interacting* electrons determine the **properties and function** of real materials and bio molecules.
- **Approximate xc functionals** have been very successful, but for highly correlated situations **there are problems**.

### Exciting arenas for theoretical work:

- Thermodynamic phase transitions, e.g. melting.
- Surfaces, interfaces, defects, nanostructures – in realistic environments, ... , e.g. catalysis
- modeling kinetics, e.g. for catalysis or crystal growth (self-assembly and self-organization)
- Molecules and clusters in solvents, electrochemistry, fuel cells, external fields, transport.
- Biological problems

### The challenges:

- Find practical ways to correct the xc approximation.
- Develop methods for bridging the length and time scales.

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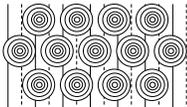
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## Three Basic Concepts for Modern Electronic Structure Calculations

### Plane waves

The simplicity and speed of Fast Fourier Transforms  
Requires smooth pseudopotentials



### Localized orbitals

The intuitive appeal of atomic-like states; good scaling with size.

### Augmented methods

“Best of both worlds” – also most demanding.  
Most general form: (L)APW

**Be aware of the limitations of present xc functionals.**  
**Use codes properly and carefully.**

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