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

Summer Semester 2013

Lecture

Modeling of Nanostructures and Materials

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Modeling of Nanostructures and Materials

SS 2013

Jacek A. Majewski

- Lecture for ☺ With the basis knowledge of **Quantum Mechanics**
- **Lecture --- 45 h**
- **Practical exercises – 45 h**
- Exam, elements of the note:
  - Test from lecture material,
  - Work during excercises
  - Project
- **Aim of the lecture: make familiar with modern modeling tools (ability to perform calculations with standard tools)**

Modeling of Nanostructures and Materials

SS 2013

Scope of the lecture

***Ab initio* Methods:**

- Density Functional Theory,
- Local Density Approximation (LDA),
- Hartree-Fock method,
- Kohn-Sham Method,
- Concept of Pseudopotential,
- Survey of available numerical codes.

Modeling of Nanostructures and Materials

SZ 2013

Scope of the Lecture (cnt.)

Semiempirical Methods for electronic structure calculations:

- Tight-Binding Method
- Pseudopotential Method

Principles of Molecular Dynamics:

- *Ab initio* molecular dynamics (Car-Parrinello method)
- Empirical methods and coarse-graining
- Valence-force field models

Monte Carlo Methods:

- Stochastic and Markov processes, ergodicity,
- Algorithms for Monte Carlo simulations

Modeling of Nanostructures and Materials

Jacek A. Majewski

Lecture 1 – *21 February 2013*

Introduction to

Computational Science,

(Computer Simulations, Computer Modeling),

Computational Materials Science

Modeling of Nanostructures

Why should we bother with it?

Computational Science

- a relatively new discipline
- involves using computers to study *scientific problems*
- complements the areas of theory and experimentation in traditional scientific investigation
- seeks to gain understanding of science principally through the use and analysis of mathematical models on (high performance) computers
- emerged as a powerful and indispensable method of analyzing a variety of problems in research, product and process development, and manufacturing.

→ Computational Simulations

Changing the way we do Science ?

Computational Simulations

- *Computer simulations* provide both qualitative and quantitative insights into many phenomena that are too complex to be dealt with by analytical methods or too expensive or dangerous to study by experiments.
- Many experiments and investigations that have traditionally been performed in a laboratory, a wind tunnel, or the field are being augmented or replaced by computer simulations.
- Some studies, such as nuclear repository integrity and global climate change, involve time scales that preclude the use of realistic physical experiments.

Computational Simulations

The availability of

- high performance computers,
- graphic workstations,
- and high speed networks,

coupled with major advances in algorithms and software, has brought about a revolution in the way scientific and engineering investigations are carried out.

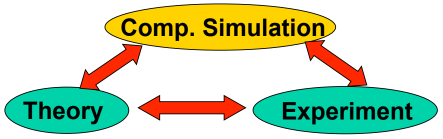
Computational Science vs. Computer Science

- **These two things should not be confused !**
- ***Computational science*** **focuses on a scientific or engineering problem and draws from computer science and mathematics to gain an improved understanding of the problem.**
- ***Computer science*** **focuses on the computer itself.**
- **However,**

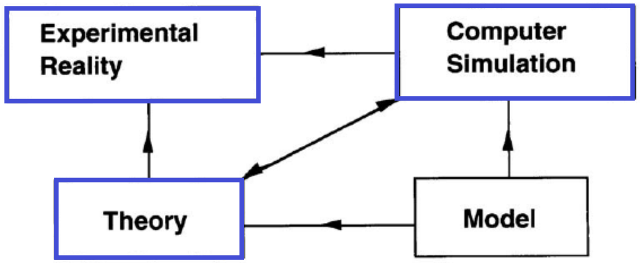
  Even though the areas are quite distinct,
  many of the topics typically considered to be in the
  domain of computer science are of much value
  in computational science.

Computational Sciences

- **Computational Physics**
- **Computational Astrophysics and Cosmology**
- **Computational Geophysics**
- **Computational Chemistry**
- **Computational Biology**
- **Computational Engineering**
- **Computational Materials Science**
- **Computational Nanoscience (Modeling of Nanostructures)**



Relationship between modeling, theory and experiment



Dr P. D. Bristowe, University of Cambridge,
Department of Materials Science and Metallurgy

The computer - the hallmark of the information age

- **Computational power has been compounding at an exponential rate for nearly 40 years,**
  - an achievement made possible by advances in silicon processing and fabrication at ever smaller length scales.
- **Breakthroughs in control and fabrication of magnetic media have driven disk capacity to likewise grow exponentially**.

Importance of Materials for Society

The computer is possibly the most visible example of a high tech product that depends critically upon advanced materials

There are many other similar examples that also profoundly affect our lives,

- **new lightweight alloys,**
- **polymers,**
- **composites, etc.**

→ *Materials Science*

Computational Materials Science

- From the Bronze Age to the silicon-driven Information Age, civilization has defined itself–and advanced itself–by mastering new materials.
- The ability to identify, improve and implement materials -- whether stone, iron, paper, steel or silicon – has profoundly shaped human societies.
- Today, thanks to increasingly powerful computers, the materials science community finds itself on the verge of another revolution.

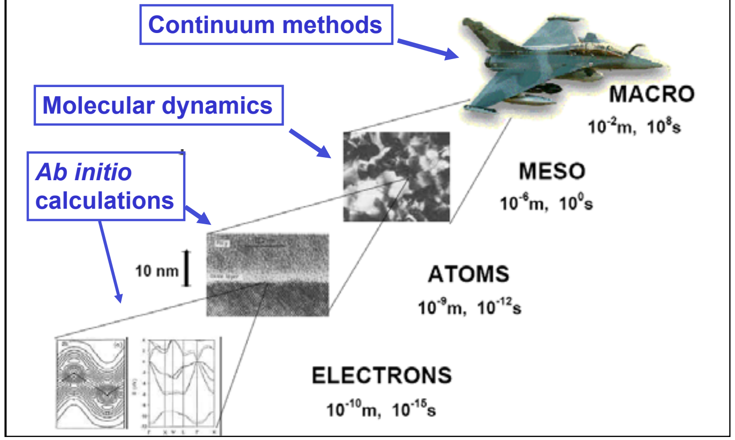
→ **extensive computational modeling will complement and sometimes even replace traditional methods of trial-and-error experimentation**.

→ **better understanding and design of new materials**

Computational Materials Science - Scales

- Scientists have a handle on the smallest length scale (relevant to materials), which cannot be seen with a microscope, and the largest length scale, which can be seen with the naked eye.
- In between is an intermediate length scale where there are particularly exciting new frontiers.
- The primary scientific challenge is to uncover the elusive connections in the hierarchy of time and length scales and to unravel the complexity of interactions that govern the properties and performance of materials.

Connection of atomistic and macroscopic scales



Continuum methods

Molecular dynamics

***Ab initio* calculations**

MACRO
10^{-2}m, 10^{8}s

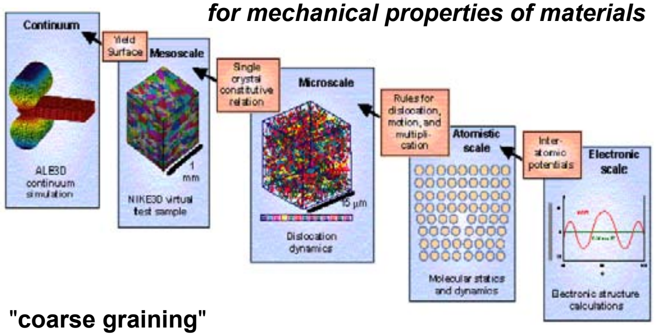
MESO
10^{-6}m, 10^{0}s

ATOMS
10^{-9}m, 10^{-12}s

ELECTRONS
10^{-10}m, 10^{-15}s

Computational Materials Science – Multi-scale Simulations

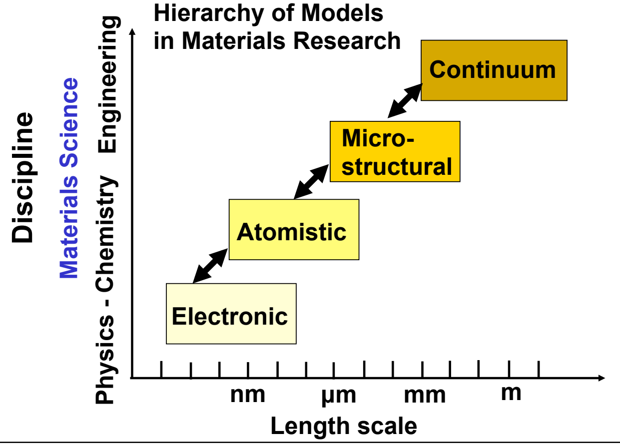
A schematic of the multi-scale challenge for mechanical properties of materials



"coarse graining"

the forces among the aggregated pieces can be accurately described by a new model with "renormalized" interactions.

Types of Physical Models Based on Length Scale



Hierarchy of Models
in Materials Research

Continuum

Micro-structural

Atomistic

Electronic

Discipline

Physics - Chemistry Engineering

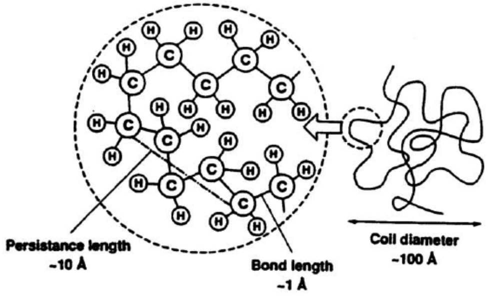
Materials Science

nm µm mm m

Length scale

Examples of Models Based on Length Scale (1)

Polymers



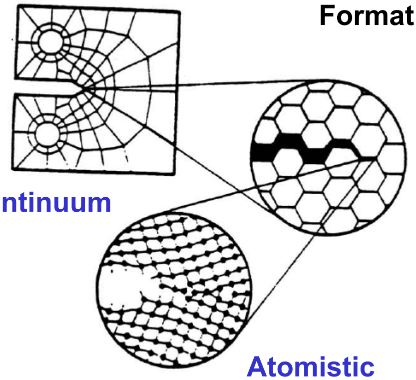
Microstructural

Atomistic

Electronic

Examples of Models Based on Length Scale (2)

Formation of cracks



Continuum

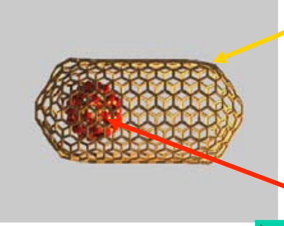
Microstructural

Atomistic

Examples of Computational Simulations

- Future nano-electronics
- Chemical reactions
- Computational biology

Simulation of a nanotube-based memory element

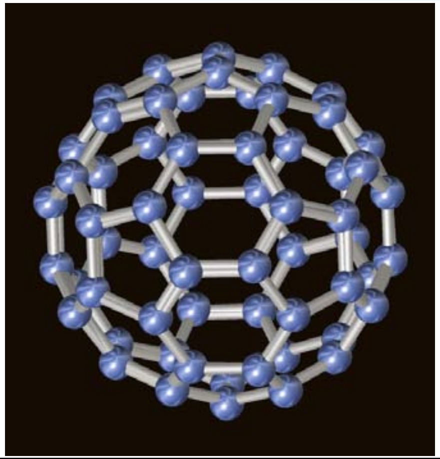


The outer capsule - short segment of (10,10) carbon nanotube with diameter 1.4 nm terminated at both ends by perfect fullerene caps.

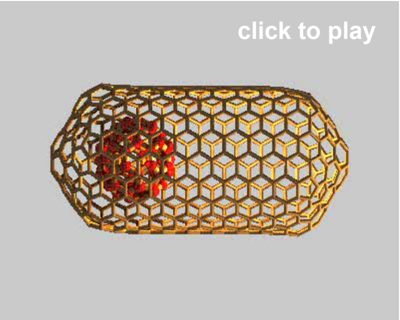
The capsule is large enough to hold a C_{60} buckyball molecule inside.

- The buckyball carries a net charge if it contains an alkali atom in the hollow cage.
- **The C_{60} molecule can be shifted from one end to the other by applying an *electric field* between the ends of the capsule**

Fullerene (buckyball)



Simulation of a nanotube-based memory element



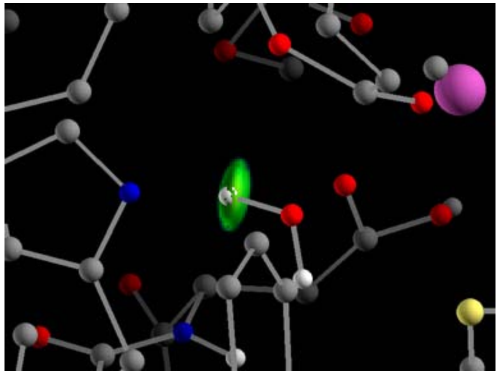
The **two energy minima** of this system, with the buckyball bonded to either end of the capsule, can be associated with **bit 0** and **bit 1**.

The simulation has been performed by Young-Kyun Kwon

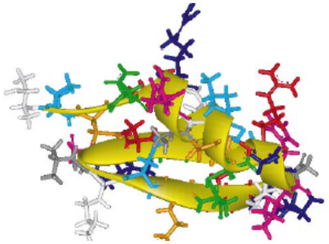
This structure has been patented as a non-volatile memory element and awarded U.S. Patent No. 6,473,351

Ab initio MD Simulations of Chemical Reaction

Dissociation of water molecule

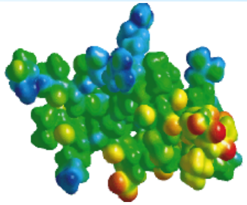


DFT as a new tool for computational biology



Structure of the 1PNH protein, a scorpion toxin (PO_5-NH_2)

- It consists of 31 amino acid Residues (ca. 500 atoms)
- Different colors are used to represent different amino acids



Electrostatic potential for electrons

- Zero value – green
- Repulsive regions – red and yellow
- Attractive regions - blue

Role of the protein charge state on the geometry – change of the charge state of the protein does not destabilize the local energy minima

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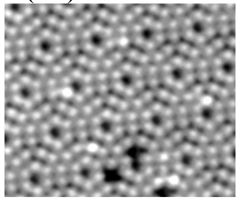
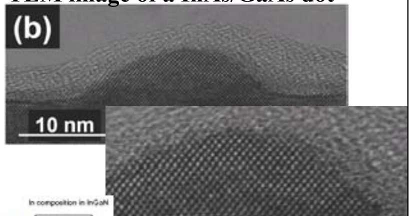
Modeling Nanostructures

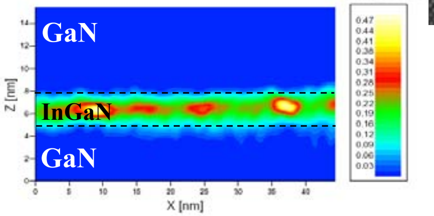
Examples of Nanostructures

Si(111)7×7 Surface



TEM image of a InAs/GaAs dot



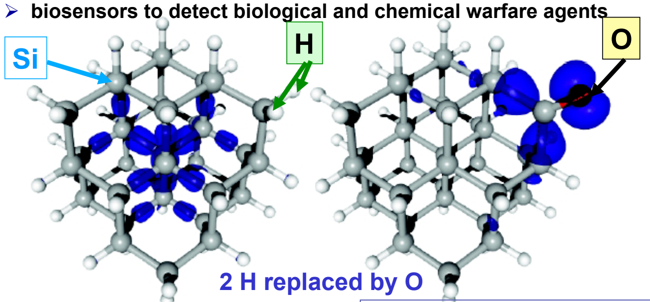


HRTEM image: segregation of Indium in GaN/InGaN Quantum Well

DFT for silicon nanostructures

Silicon nanoparticles (clusters, dots)

- **optoelectronic materials on silicon basis**
- **biosensors to detect biological and chemical warfare agents**



2 H replaced by O

- **71 Si atoms 'passivated' by hydrogens**
- **Electrons are in the center of the dot**

Dramatic change of the optical properties (wavelength) of the silicon nanostructure

G. Gali & F. Gygi, Lawrence Livermore National Laboratory

What about realistic nanostructures ?

Inorganics

3D (bulks) : **1-10** atoms in the unit cell

2D (quantum wells): **10-100** atoms in the unit cell

1D (quantum wires): **1 K-10 K** atoms in the unit cell

0D (quantum dots): **100K-1000 K** atoms in the unit cell

Organics

Nanotubes, DNA: **100-1000** atoms (or more)

Atomistic methods for modeling of nanostructures

- ***Ab initio* methods** (up to few hundred atoms)
- **Semiempirical methods** (up to 1M atoms)
  - Empirical Pseudopotential
  - **Tight-Binding Methods**

Tight-Binding methods

Tight-Binding Formalism

$$\varphi_n(\vec{r}) = \underbrace{\sum_{\alpha,i}}_{\text{index of orbital, index of atom}} c_n^{\alpha i}\chi_{\alpha i}(\vec{r})$$

index of orbital **index of atom**

$\{\chi_{\alpha i}\}$ **orthogonal set of functions**
➡ **NOT ATOMIC ORBITALS !**

$$\varepsilon_n =< \varphi_n | H | \varphi_n >= \sum_{i\alpha}\sum_{j\beta}(c_n^{\alpha i})^* c_n^{\beta j} < i\alpha | H | j\beta >$$

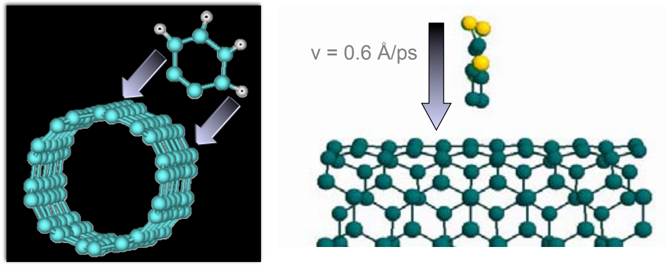
Tight –binding Hamiltonian

$$\boxed{H = \sum_{\alpha i}\varepsilon_{i\alpha} | i\alpha >< i\alpha | + \sum_{\alpha i,\beta j} t_{i\alpha,j\beta} | i\alpha >< j\beta |}$$

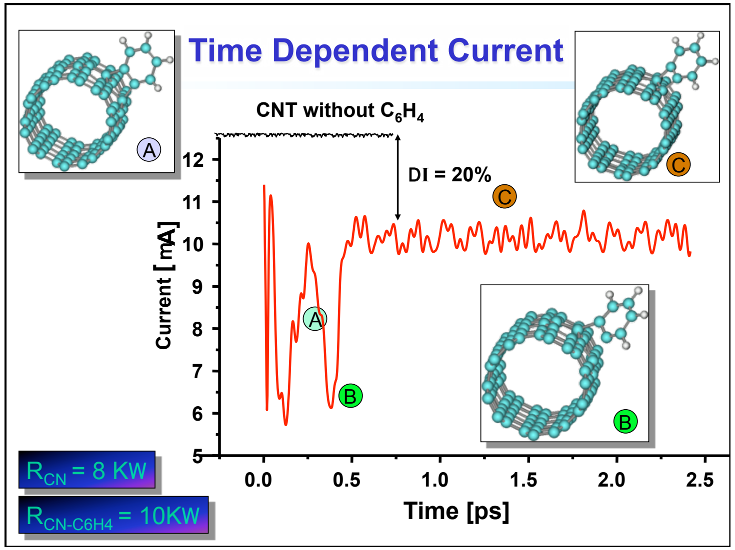
on-site **hoping TB-parameters**

Green's Function + Molecular dynamics Carbon Nanotubes

- **Molecular Dynamics** simulations of a reactive collision of a biased nanotube (V=100mV) and benzene
- **Current** flowing in the nanotube calculated at each MD step

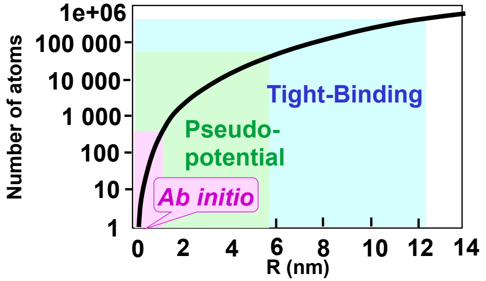


Time Dependent Current



Length scale for *ab initio* and tight-binding methods

- **Microscopic approaches can be applied to calculate properties of realistic nanostructures**



Number of atoms in a spherical Si nanocrystal as a function of its radius R.
Current limits of the main techniques for calculating electronic structure.
Nanostructures commonly studied experimentally
lie in the size range 2-15 nm.

Computational Materials Science –
The Era of Applied Quantum Mechanics

The properties of new and artificially structured materials can be predicted and explained
- *entirely by computations,*
- *using atomic numbers as the only input .*

Computational Materials Science:
A Scientific Revolution about to Materialize

- The materials science community is on the verge of a paradigm shift in the way it does science with the promise of building a sturdy bridge across the "valley of death" between basic science and technological impact.
- A useful construct for thinking about this potential paradigm is "**Pasteur's Quadrant**."

D. E. Stokes, *"Pasteur's Quadrant, Basic Science and Technological Innovation,,*
The Brookings Institution, Washington D.C., 1997

Recent technological developments cause increasing demands for materials with specific properties

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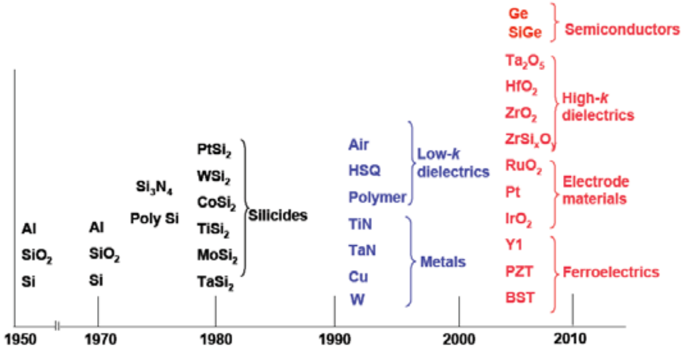
New Materials for Si- Technology

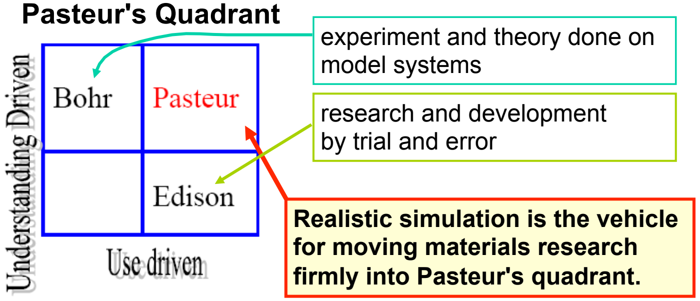


- **Moore's Law increasingly relies on material innovations !**

Computational Materials Science: A Scientific Revolution about to Materialize

- Due to the complexity of materials systems, progress has necessarily proceeded either within the Bohr quadrant or Edison's quadrant

Pasteur's Quadrant



experiment and theory done on model systems

research and development by trial and error

Realistic simulation is the vehicle for moving materials research firmly into Pasteur's quadrant.

Recent technological developments cause increasing demands for materials with specific properties

- **Experiments are without doubt the most important approach in studying materials**
- **However, Kohn and co-workers opened a new avenue to *study properties of materials from first-principles* with the formulation of *density functional theory (DFT)*.**

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

Density Functional Theory – the key to Computational Materials Science & Multiscale Modeling of Nanostructures

The Basics

Usage of Density Functional Theory (DFT)

- Using DFT many practical problems of materials science have been solved successfully.
- DFT is now employed not only by physicists, but also by chemists, geophysicists, biophysicists, metallurgist, and in other scientific fields.
- The computational implementations of DFT together with modern solid state theory allow it to obtain reliable results for ***thermodynamic, mechanical, electrical and magnetic properties*** of
    - metals,
    - semiconductors, or
    - insulators

  without any adjustable parameters fitted to the experiment.

DFT – Applied to real materials

- There are numerous applications of DFT in chemistry and physics (> 10 000 papers a year)
- The use of DFT based methods is still very new in the field of engineering
- The simulation of cracks in materials belongs to the most challenging problems in materials science.
- While the crack itself is a macroscopic property, the physical processes at the crack tip itself involve **the breaking of bonds governed by quantum mechanics**.

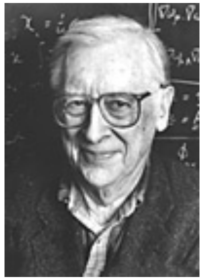
DFT – Nobel Prize in Chemistry, 1998

The big impact of DFT has been clearly high lightened by awarding the Nobel Prize in Chemistry in 1998 for the **development** and **application** of **DFT**.

Walter Kohn

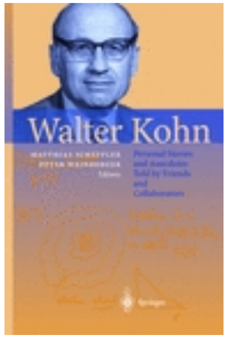
Born in 1923

John A. Pople



1925 - 2004

80th birthday of Walter Kohn



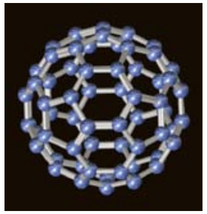
"Walter Kohn –
Personal Stories and Anecdotes
Told by Friends and Collaborators"

eds. Matthias Scheffler &
Peter Weinberger

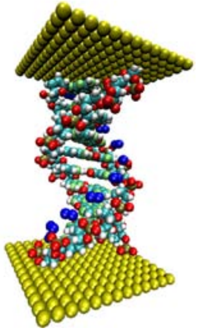
Springer Verlag

Fundamental problem in materials science

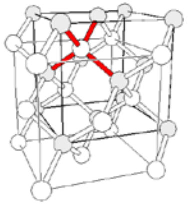
A fundamental problem in materials science is the prediction of condensed matter's electronic structure



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

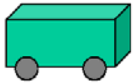
Electron-Electron interaction

$$H\Psi = E\Psi$$

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

Materials Science:
Why *ab-initio* approach is needed?

- **A model as simple as possible**



- **A model non-empirical and realistic**

- **Explanation and extrapolation of experimental results**
- **Physical insight**
- **Qualitative physics**

- **Reliable predictions of matter's properties**
- **Design of new materials**
- **Unexpected phenomena and unusual conditions (e.g., extreme pressures)**

Quantum Mechanics of Molecules and Crystals

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

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

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

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

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

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

Parametric dependence on ionic positions

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

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

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

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

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

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

Schrödinger equation

$$H\Psi = E\Psi$$

$$\text{�}(\{\vec{R}_{\text{�}}\}, \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \equiv \text{�}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

Many particle wave function

$$N \approx 10^{23}$$

Ritz Variational Principle → Ground State Energy of the system

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

$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ 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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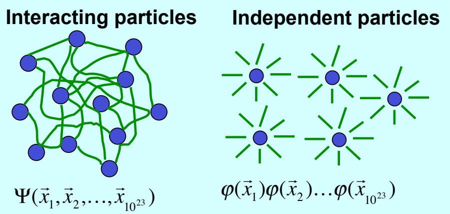
Quantum Mechanics:
System of N electrons in an external potential

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**



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

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

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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

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

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

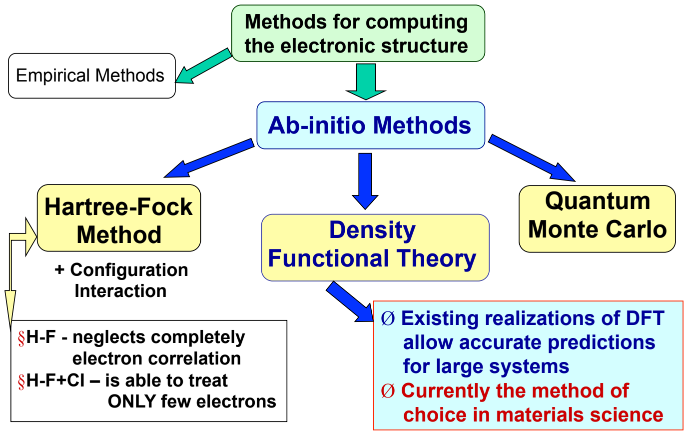
$$H_0 = \sum_i H_0(i) = \sum_i -\frac{1}{2}\nabla_i^2 + V_{ext}(\vec{r}_i) \qquad U(\vec{x}_i, \vec{x}_j) = \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Variational Principle

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

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

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**

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

$$= N\int d\vec{r}_2, \ldots, d\vec{r}_N \Psi^*(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)\Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)$$

- The DFT is based on two fundamental theorems for a functional of the one particle density.

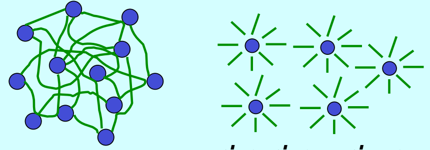
- **One particle density determines the ground state energy of the system**

- 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 (DFT) in Kohn-Sham realization

Interacting particles **Independent particles**



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

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

This reduction is rigorously possible !

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

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

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

Proof of Theorem I:

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

$$= \left\langle \Psi^{\rho}_{\min} | \hat{V}_{ext} + \hat{T} + \hat{V}_{e-e} | \Psi^{\rho}_{\min} \right\rangle \geq E_0$$

Ritz variational principle

🟩

Density Functional Theory – constrained search formulation

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

From variational principle

$$\left\langle \Psi_0 | \hat{V}_{ext} + \hat{T} + \hat{V}_{e-e} | \Psi_0 \right\rangle \leq \left\langle \Psi^{\rho_0}_{min} | \hat{V}_{ext} + \hat{T} + \hat{V}_{e-e} | \Psi^{\rho_0}_{min} \right\rangle$$

$$\int d\vec{r} \upsilon_{ext}(\vec{r})\rho_0(\vec{r}) + \left\langle \Psi_0 | \hat{T} + \hat{V}_{e-e} | \Psi_0 \right\rangle \leq \int d\vec{r} \upsilon_{ext}(\vec{r})\rho_0(\vec{r}) + \left\langle \Psi^{\rho_0}_{\min} | \hat{T} + \hat{V}_{e-e} | \Psi^{\rho_0}_{\min} \right\rangle$$

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

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

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

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

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

$$\int d\vec{r} \upsilon_{ext}(\vec{r})\rho_0(\vec{r}) + \left\langle \Psi_0 | \hat{T} + \hat{V}_{e-e} | \Psi_0 \right\rangle = F[\rho_0] + \int d\vec{r} \upsilon_{ext}(\vec{r})\rho_0(\vec{r})$$

$$\left\langle \Psi_0 | \hat{V}_{ext} + \hat{T} + \hat{V}_{e-e} | \Psi_0 \right\rangle = F[\rho_0] + \int d\vec{r} \upsilon_{ext}(\vec{r})\rho_0(\vec{r})$$

$$\boxed{E_0 = F[\rho_0] + \int d\vec{r} \upsilon_{ext}(\vec{r})\rho_0(\vec{r})}$$

🟩

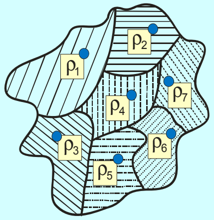
Density Functional Theory – Constrained Search Formulation
Relation to Ritz Variational Principle

The ground-state energy minimization procedure of $E[\Psi] = \dfrac{<\Psi | \hat{H} | \Psi>}{<\Psi | \Psi>}$ 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

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

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

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

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

🔴 $= \min_{\rho \to N} E[\rho]$

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

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 $F[\rho]$

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

$$=\underbrace{T[\rho]}_{\text{Kinetic energy}}+U[\rho]+\underbrace{\left\{\langle\Psi^\rho_{min}|\hat{V}_{e-e}|\Psi^\rho_{min}\rangle-U[\rho]\right\}}_{\text{Exchange \& Correlation } E_{xc}[\rho]}$$

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

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

The Kohn- Sham Method – Kinetic energy functional

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

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

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

Thank you!

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