

Overview of DFT Calculations for Nanoscience and Nanotechnology

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Jules Verne

A Trip to the Moon, 1865







Nanostructures:

- a. Contain a countable number of atoms
- b. Suites for atomic level detailed engineering
- c. Provide access to realms of quantum behavior that is not observed in larger (even 0.1 μm) structures
- d. Combine small size, complex organizational patterns, potential for very high packing densities, strong lateral interactions and high ratios of surface area to volume.

So....What are Nanoscience and Nanotechnology?

The ability to observe, measure, predict and construct — on the scale of atoms and molecules and exploit the novel properties found at that scale.





Percentage of Surface Atoms

Full-shell (Clusters	Total Number of Atoms	Surface Atoms (%)
1 Shell	88	13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35

in Chemistry, Wiley, 2001

Melting Point of Gold Particles



The melting point decreases dramatically as the particle size gets below 5 nm



- Nanostructures (< 30 nm) have become an exciting research field
 - New quantum phenomena occur at this length scale
 - New structure property relations are expected
 - Promising applications are expected in optics, electronics, thermoelectric, magnetic storage, NEMS (nano-electromechanical systems)
- Low-dimensional systems are realized by creating nanostructures that are quantum confined in one or more directions and <u>exhibit properties different from their 3D</u> counterparts



Some More Size-Dependent Properties



- For semiconductors such as ZnO, CdS, and Si, the bandgap changes with size
 - Bandgap is the energy needed to promote an electron from the valence band to the conduction band
 - When the bandgaps lie in the visible spectrum, changing bandgap with size means a change in color
- For magnetic materials such as Fe, Co, Ni, Fe₃O₄, etc., magnetic properties are size dependent
 - The 'coercive force' (or magnetic memory) needed to reverse an internal magnetic field within the particle is size dependent
 - The strength of a particle's internal magnetic field can be size dependent

Examples of Quantum Wires

CHARACTERISTICS of NANOWIRES

	BREAKJUNCTION	NANOTUBE	MOLECULAR WIRE	QUANTUM WIRE
Composition	Cu, Ag, Au	С	C,N,H,S	GaAs/AlGaAs
Geometry	ę	Tubular	Fixed by Q.M.	Planar (2-D)
Width	atomic	1-20 nanometers	~ 1 nm	100's of nanometers
Length	1 - 1000 nm	1 - 20 µ m	few nanometers	2 - 20 µ m
External Connections	Easy	Problematic	Challenging	Straightforward
				High Decelution
Fabrication	Contact Mechanics	Carbon Arc	Test Tube	Lithography

Quantum Confinement Produces New Materials Classes

- Group V element

Bi

- Semimetal in bulk form
- The conduction band (*L*-electron) overlaps with the valence band
 (*T*-hole) by 38 meV

- Bi nanowire
 - Semimetal-semiconductor transition at a wire diameter about 50 nm due to quantum confinement effects

Semimetal



Semiconductor

Semimetal-Semiconductor Transition We utilize novel properties in applications

Tunable Bandgap in Nanowires



M. S. Gudiksen et al., J. Phys. Chem B 106, 4036 (2002)

InP nanowire diameter ↓ energy ↑

With same material luminescence devices with different emission frequencies can be made

Various Nanostructures can occur in 1D

Each have different structure/properties Selectivity is therefore important



(a) Bi Nanowire

(b) Bi Nanotube



Dresselhaus Group (MIT)



Peidong Yang UC Berkeley





K. Miki ETL,Japan

Eigenstates of electrons

- For optical absortion, etc., one needs the spectrum of excited states
- For thermodynamics and chemistry the lowest states are most important
- In many problems the temperature is low compared to characteristic electronic energies and we need only the ground state
 - Phase transitions
 - Phonons, etc.

Fundamental laws for the properties of matter at low energies

Atomic scale (chemical bonds etc.)

Yes BUT Electrons and nuclei (simple Coulomb interactions)

 $=> Quantum Mechanics \quad \hat{H}\Psi(\{\vec{r}_i\}) = E\Psi(\{\vec{r}_i\})$

Schrödinger's Equation

Complete description

 Impossible to solve except for very simple systems such as neutral Hydrogen

Numerical methods and the fastest computers are not enough to solve Schrödinger's Equation for non-trivial systems

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$



Time-independent and nonrelativistic Schrödinger equation: system consists of *M* nuclei and *N* electrons



Many-particle problem Schroedinger's equation is exactly solvable for - Two particles (analytically) - Very few particles (numerically) The number of electrons and nuclei in a pebble is ~10²³

 $\hat{H}\Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N) = E\Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)$ => APPROXIMATIONS

Born-Oppenheimer

 $\underline{m_n} >>$

 \Rightarrow Nuclei are much

slower than electrons

 \mathcal{M}_{ρ}

electronic/nuclear decoupling

(1)

 $\hat{H} = -\sum_{\mu} \frac{1}{2M_{\mu}} \nabla_{\mu}^{2} \left(-\sum_{i} \frac{1}{2} \nabla_{i}^{2} + \sum_{i,j>i} \frac{1}{r_{ij}} \left(\sum_{i,\mu} \frac{Z_{\mu}}{r_{i\mu}} + \sum_{\mu,\nu>\mu} \frac{Z_{\mu}Z_{\nu}}{R_{\mu\nu}} \right) \right)$ $\hat{H}_{\{\vec{R}_{\mu}\}}^{el} = -\sum_{i} \frac{1}{2} \nabla_{i}^{2} + \sum_{i, j > i} \frac{1}{r_{ii}} + V_{\{\vec{R}_{\mu}\}}^{ext}(\{\vec{r}_{i}\})$ electrons $\hat{H}_{\{\vec{R}_{\mu}\}}^{el}\Psi_{n,\{\vec{R}_{\mu}\}}^{el}(\{\vec{r}_{i}\}) = E_{n}^{el}(\{\vec{R}_{\mu}\})\Psi_{n,\{\vec{R}_{\mu}\}}^{el}(\{\vec{r}_{i}\})$ $-\frac{1}{\sqrt{2}} + E_{\mu}^{el}(\{\vec{R}_{\mu}\})$ nuclei $Classical => \quad \vec{F}_{v} = \frac{O}{\partial \vec{R}_{v}} E_{0}^{el}(\{\vec{R}_{\mu}\})$

The Ground State

- General idea: Can use minimization methods to get the lowest energy state
- Why is this difficult ?
- It is a Many-Body Problem
- Y_i (I₁, I₂, I₃, I₄, I₅, ...)
 How to minimize in such a large space?

Many-electron problem
Old and extremely hard problem!
Different approaches
Quantum Chemistry (Hartree-Fock, Cl...)

- Quantum Monte Carlo
- Perturbation theory (propagators)
- Density Functional Theory (DFT)
 Very efficient and general
 BUT implementations are approximate and hard to improve (no systematic improvement)
 (... actually running out of ideas ...)

Materials simulation

Applied Quantum Mechanics (other methods)



First-principles calculations

Fundamental laws of physics
 Set of "accepted" approximations
 to solve the corresponding equations on a computer
 No empirical input

PREDICTIVE POWER

1. $\Psi(\{\vec{r}_i\}) \rightarrow \rho(\vec{r}) \quad \begin{array}{c} particle \\ density \end{array}$

2. As if non–interacting electrons in an effective (self–consistent) potential



1998 Nobel Prize in Chemistry to Walter Kohn

- A prescription for replacing Schrödinger's Equation with similar, decoupled equations which we can solve with fast computers and clever algorithms
- Kohn-Sham Equations
- <u>Applied</u> Quantum Mechanics (other methods)
- An important long range for the field: protein folding



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 $H\Psi_{nk} = \varepsilon_{nk}\Psi_{nk},$ where $H = K + V_{ne}(r) + V_{ee}(r) + V_{xc}(r)$ and

$$K = -\frac{\hbar^2}{2m}\nabla^2,$$

$$V_{ne}(r) = -e^2 \sum_{a} \frac{Z_a}{|r - R_a|},$$

$$V_{ee}(r) = -e^2 \int \frac{\rho(r')}{|r-r'|} d^3r,$$

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho},$$

$$\rho(r) = \sum_{nk} f_{nk} |\Psi_{nk}(r)|^2,$$

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Hohenberg-Kohn Theorems and Kohn-Sham Approach

Wave function based methods

direct determination of the many particle wave function ψ by solving the Schrödinger equation

Density Functional Theory (DFT)

1964 Hohenberg & Kohn: Birth of DFT introducing the electron density ρ as a basic variable recall: $\rho(\vec{r}_1) = N \int ... \int |\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)|^2 ds_1 d\vec{x}_2 ... d\vec{x}_N$ central idea: express total energy as functional of ρ : $\mathbf{E} = \mathbf{E}[\rho]$

What's so great about DFT?

- Normally, we need to describe solids by a wavefunction of all electrons
- Then, we need to find solutions for more than 10²³ electrons and combine them
- This is still an impossible task
- In Density Functional Theory (DFT) we only need to find the charge distribution throughout our system
- Then, we can describe single electrons moving in a crystal mean field of all ions and other electrons
- In this way, we can calculate solids of up to a few thousand atoms
- And that is all we need, usually

Overview

Hohenberg-Kohn Theorems (1964)

- First Theorem: Proof of Existence
- Second Theorem: Variational Principle
- Constrained-Search Approach by Levy (1979)

Kohn-Sham Approach (1965)

- Orbitals and Non-Interacting Reference System
- Kohn-Sham Equations
- Effective Potential and Exchange-Correlation Potential

Hohenberg - Kohn $\Psi(\{\vec{r}_i\}) \rightarrow \rho(\vec{r})$

For our many–electron problem $\hat{H} = T + V_{ee} + \sum_{i=1}^{n} V_{ext}(\vec{r}_i)$

1.
$$E[\rho(\vec{r})] \equiv \int d^{3}\vec{r} V_{ext}(\vec{r}) \rho(\vec{r}) + F[\rho(\vec{r})] \ge E_{GS}$$

(depends on nuclear positions) (universal functional)

2. $E[\rho_{GS}(\vec{r})] = E_{GS}$

PROBLEM: Functional unknown!

Kohn - Sham

Independent particles in an effective potential

They rewrote the functional as:

 $E[\rho] = T_0[\rho] + \int d^3 \vec{r} \,\rho(\vec{r}) [V_{ext}(\vec{r}) + \frac{1}{2} \Phi(\vec{r})] + E_{xc}[\rho]$

Kinetic energy for system with no e-e interactions

Hartree potential

Equivalent to independent particles under the potential

The rest: exchange correlation

 $V(\vec{r}) = V_{ext}(\vec{r}) + \Phi(\vec{r}) + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}$

PREDICTION of MATERIALS PROPERTIES FROM FIRST-PRINCIPLES CALCULATIONS



Kohn and Sham showed that it is possible to introduce an effective one-electron wavefunctions, $\{\psi_i (r)\}$, which give rise to a set of self-consistent single-electron equations:

$$\left[-\frac{1}{2}\nabla^{2} + V_{ion}(r) + V_{H}(r) + V_{XC}(r)\right]\Psi_{i}(r) = \varepsilon_{i}\Psi_{i}(r),$$

EXPAND

GaussiansNumerical atomic orbitalsPlanewaves





DFT (and other methods) iterate to <u>self-consistency</u>











Metallic Nanowires



An exotic morphology:

Is it DNA or an organic molecule or carbon nanotube?

Hard to believe, but, actually,

it is a metallic nanowire !!

Metallic Nanowires: experimental verification













1 nm 🛛

Gold nanowires: TEM images Y. Kondo and K. Takayanagi Science, 289, 606 (200).





Metallic Chains = Nanowires of the future technology?

Metal Chains :



TEM images of Formation of Gold chains: Ohnishi, Kondo and Takayanagi, Nature 395, 780-783 (1998).

Single atom Gold Chains :



TEM image of single row gold chain Nature 395, 780-783 (1998). Interatomic distances very large compared to the bulk bond lengths

Gold Chains :



Conductance as a function of distance between electrodes Yanson etal. Nature 395, 783-785 (1998).

Theoretical calculations couldn't predict the observed large interatomic distances!



So it is proposed either:

Zigzag chain structure rather than a linear chain Impurity atoms between the gold atoms



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Monoatomic Metal Chains :



NANOTUBES



Attachment of a single H atom on a nanotube is always exothermic. However, energy gain is less than dissociation of H_2 molecule.

> Can we tune the binding energy by radial deformation?

"Binding energy of single hydrogen (top) and aluminum (bottom) atom on zigzag (n,0) nanotubes as a function of tube radius."

NANOTUBES



a)Variation of the binding energy of a single H adsorbed on a (8,0) nanotube as a function of radial deformation. b)Variation of the binding energy of a single Al atom adsorbed on a (8,0) nanotube as a function of radial deformation.

The adsorption energy of foreign atoms on carbon nanotubes and associated properties can be modified by radial deformation. This tunable adsorption can have important Implications in metal coverage and can lead to a wide variety of applications...

TUNABLE ADSORPTION ON NANOTUBES

The remarkable and significant change of the binding energy with elliptical deformation can be understood in terms of the band structure of SWNTs.



Contour plot of the first conduction band of a (8,0) nanotube as a function of radial deformation. Deformation pushes the chemically most active electrons to the high curvature site of the tube, increasing the absorption energy at this site.

FUNCTIONALIZATION OF NANOTUBES

Different hydrogen decoration of nanotubes



Uniform exohydrogenation at half coverage

SQUARE CARBON NANOTUBE

Geometric and electronic properties as well as binding energies of H-SWNTs strongly depend on the pattern of hydrogenation (*decoration*)...

FUNCTIONALIZATION OF NANOTUBES

Very high density of states at Fermi level



Comparison of the electronic Density of states (DOS) of a bare (9,0) nanotube and its various hyrogenated isomers

Superconductivity ?

FUNCTIONALIZATION OF NANOTUBES

Metallic nanoring wrapping the nanotube



Induced B field at the center of the nanotube ~ 100 Gauss Total DOS (8x0) SWNT + Al Ring Al Ring Only