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 biophysics

"the ab initio line of computational sciences and engineering"

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

\[ \left( \hat{T} + \hat{T}^{\text{ext}} + \hat{V}^{\text{xc}} + \hat{V}^{\text{ion}} + \hat{V}^{\text{nuc}} \right) \Psi = E \Psi \]

With:

\[ T = \sum_{j=1}^{N} \frac{p_j^2}{2m_j} \]

\[ T^{\text{ion}} = \sum_{j=1}^{M} \frac{p_j^2}{2m_j} \]

\[ V^{\text{xc}} = \frac{1}{2} \sum_{k=1}^{N} \sum_{j=1}^{N} \frac{q^2}{|\mathbf{r}_k - \mathbf{r}_j|} \]

\[ V^{\text{nuc}} = \frac{1}{24\pi\epsilon_0} \sum_{j=1}^{M} \sum_{k=1}^{N} \frac{Z_j Z_k}{|\mathbf{r}_k - \mathbf{r}_j|} \]

\[ V^{\text{ion}} = \sum_{j=1}^{M} \sum_{k=1}^{N} \frac{1}{|\mathbf{r}_k - \mathbf{r}_j|} \]

Born Oppenheimer Approximation

\[ \Psi(\mathbf{r}_1, \ldots \mathbf{r}_N; \mathbf{R}_1, \ldots \mathbf{R}_M) = \sum_{\nu} \Lambda_{\nu}(\{ \mathbf{R}_1 \}) \Phi_{\nu}(\{ \mathbf{R}_1 \}) (\mathbf{r}_k) \]

Where \( \Phi_{\nu} \) are solutions of the “electronic Hamiltonian”:

\[ H_{\nu}^{\text{e}}(\mathbf{R}_1) \Phi_{\nu}(\{ \mathbf{R}_1 \}) (\mathbf{r}_k) = E_{\nu}(\{ \mathbf{R}_1 \}) \Phi_{\nu}(\{ \mathbf{R}_1 \}) (\mathbf{r}_k) \]

\[ H^{\text{e}} = \hat{T}^{\text{e}} + \hat{V}^{\text{xc}} + \hat{V}^{\text{ion}} \]

frequently (commonly) applied approximations:

- neglect non-adiabatic coupling (terms of order \( m/M_j \))
- keep only \( \Lambda_{\nu} \)

\( \Rightarrow \) electronic and nuclear degrees of freedom decouple
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.

Wave-Function Theories

Restrict the study to a selected subclass of functions $\Phi$ (Hartree and Hartree-Fock theory); or Quantum Monte Carlo.

The Hohenberg-Kohn Theorem

The set of non-degenerate ground state wave functions $\Phi$ of arbitrary $N$-particle Hamiltonians. The set of particle densities $n(r)$ belonging to non-degenerate ground states of the $N$-particle problem.

The dashed arrow is not possible
Density Functional Theory

The energy of the ground state of a many-electron system:

\[ E_0 (\{ \mathbf{R}_i \}) = \text{Min}_n \langle \Phi | H | \Phi \rangle \]

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, \( i.e., \)

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

This implies:

\[ E_0 (\{ \mathbf{R}_i \}) = \text{Min}_n \Phi[\Phi] \]

Comparison of Wave-Function and Density-Functional theory

\[ \langle \Phi | H | \Phi \rangle \quad \text{Schrödinger} \]

\[ E_0 \quad \Phi(\{ \mathbf{r}_i \}) \quad E_0 \]

\[ \Phi_0 \quad \Phi[n] \quad ~ 10^{23} \text{Variables} \]

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.
Kohn and Sham (1965):

\[ E_{\xi}[\rho] = T_{\xi}[\rho] + \int v(r)\rho(r)\,d^3r + E^{\text{Hartree}}[\rho] + E^{\text{xc}}[\rho] \]

with \[ E^{\text{Hartree}}[\rho] = \frac{\epsilon^2}{24\pi \hbar^2} \int \frac{\rho(r')\rho(r)}{|r-r'|}\,d^3r' \]

And \[ T_{\xi}[\rho] \] the functional of the kinetic energy of non-interacting electrons. \[ E^{\text{xc}}[\rho] \] contains all the unknowns.

At fixed electron number \( N \) the variational principle gives

\[ \delta \left\{ E_{\xi}[\rho] - \mu \left( \int \rho(r)\,d^3r - N \right) \right\} = 0 \]

or

\[ \frac{\delta E_{\xi}[\rho]}{\delta \rho(r)} = \mu = \frac{\delta T_{\xi}[\rho]}{\delta \rho(r)} + v^{\text{eff}}(r) \]

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Kohn and Sham (1965):

\[ v^{\text{eff}}(r) = v(r) + \frac{\epsilon^2}{8\pi \hbar^2} \int \frac{\rho(r')}{|r-r'|}\,d^3r' + \frac{\delta E^{\text{xc}}[\rho]}{\delta \rho(r)} \]

Because \[ T_{\xi}[\rho] \] is the functional of non-interacting particles we effectively “restrict” the allowed densities to those that can be written as \( \rho(r) = \sum |\psi_i(r)|^2 \)

This implies:

\[ \begin{cases} \frac{\hbar^2}{2m} \nabla^2 + v^{\text{eff}}(r) \psi_i(r) = r_i \psi_i(r) \end{cases} \]

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

\[ T_{\xi}[\rho] = \sum_{k=1}^{N} \langle \hat{\epsilon}_k \rangle - \frac{\hbar^2}{2m} \nabla^2 \psi_k \]

\[ = \sum_{k=1}^{N} \epsilon_k - \int v^{\text{xc}}[\rho]|(r)\rho(r)|\,d^3r \]

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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.

\[ E_{\xi}[\rho] = T_{\xi}[\rho] + \int v(r)\rho(r)\,d^3r + E^{\text{Hartree}}[\rho] + E^{\text{xc}}[\rho] \]

-- Maybe the exact \( E^{\text{xc}}[\rho] \) functional cannot be written as a closed mathematical expression. Maybe there is a detour similar to that taken for \( T_{\xi}[\rho] \)? The challenge is to find useful, approximate xc functionals.
Ts, $E_H$, and $E_x$ are all universal functionals in $n(r)$, i.e., they are independent of the special system studied. (general theory: see the work by Levy and Lieb)

$$E^{\text{ex}}[n] = \int \rho^{\text{ex}}[n(r)]d^3r$$

$$E^{\text{xc}}[n] = E^{\text{ex}}[n] - LDAG[n] + O(\nabla n)$$

Cepleys - Alder (1989)

Gell-Mann - Brueckner (1957)

more about xc functionals: later this week

**Most-Cited Papers in APS Journals**

11 papers published in APS journals since 1893 with >1000 citations in APS journals (~5 times as many references in all science journals)

From Physics Today, June, 2005

**The Total Energy**

From DFT

$$E_0 = \sum_{i<j} \frac{1}{2} \left[ \frac{\alpha_{ij}}{2\epsilon_0} + \frac{\alpha_{ij}^*}{2\epsilon_0^*} \right] + \frac{\alpha_{ij} - \alpha_{ij}^*}{2\epsilon_0} Z_i Z_j$$

+ quantum mechanical corrections for lattice vibrations

The total energy per atom without zero point vibrations as a function of the interatomic distance. The measured interatomic distance is the average over the positions of vibrating atoms.
Solving the Kohn-Sham Equations

- Structure, types of atoms
- Guess for input
- Solve KS Eqs.
- New density
- Self-consistent?
- Output:
  - Total energy, force, ...
  - Eigenvalues

The self-consistent field method
The Exchange-Correlation Hole

\[ E_{\text{xc}}(n) = \frac{1}{2} \int \frac{n(r') - n(xc(r,r'))}{|r - r'|} d^3r' \]

Comparison of Hartree, Hartree-Fock, and density-functional theories for jellium

For non-jellium systems and the LDA (or the GGA) the shape of \( n_{\text{xc}}(r,r') \) is incorrect. However, only its spherical average enters:

\[ E^{\text{avr}}[n] = \frac{1}{2} \int \frac{n(r') - n_{\text{xc}}(r,r')}{|r - r'|} d^3r' \]

The Exchange Hole in Ne Atom


Exchange-Correlation Hole in Silicon


The spherically averaged exchange-correlation hole in variational Monte Carlo (VMC) and DFT-LDA with (a) one electron fixed at the bond center, (b) one electron fixed at the tetrahedral interstitial site, and (c) plots (a) and (b) superimposed with the same scale.
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
Electron Density of Si

Electron density difference from sum of atoms

experiment DFT-LDA DFT-GGA


Ab initio melting curve of Fe as function of pressure

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

Bio-Physics: DFT vs Force Fields

both force fields predict the α-helix to be the most stable conformation
only AMBER reproduces all the helical minima

J. Ireta et al. more: later this week
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: \( n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2 \)

What about the individual \( \phi_i(r) \) 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 \( \phi(r) \) and \( \epsilon \) give an approximate description of quasi-particles, a (good) starting point for many-body calculations. -- more later this week.

What About the Kohn-Sham Eigenvalues?

The ionization energy is:

\[
I_k = E_k^{N-1} - E_k^N
\]

(Well defined for the highest occupied state. Otherwise, this only holds approximately.)

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.

Kohn-Sham Electron Bands

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

The measured (optical) band gap is something else:

\[
E_{gap} = E_{n-1}^N - E_{n+1}^N
\]

\[
A = E_{n-1}^N - E_{n+1}^N
\]

\[
I = E_{n-1}^N - E_{n+1}^N
\]

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

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