Introduction to Density Functional Theory

21 February 2011; V172
Predictive modeling and simulations must address all time and space scales.

Continuum Equations, Rate Equations and Finite Element Modeling

Electronic Structure Theory

Time

Electronic Dynamics

Ab initio Kinetic Monte Carlo

Ab initio Molecular

Density-functional theory

Space

The diagram illustrates the progression from electronic structure theory to kinetic Monte Carlo, showing the scales of time and space and the transition between different modeling approaches.
A computation that in 1972 took 1 full year to complete can today be done in ~ 4 seconds!
Vision

Ab initio Computational Based Design

Computational Approach: Advantages

- Detailed control of artificial materials systems
- Fundamental understanding of microscopic mechanisms
- Can be done without any adjustable empirical parameters
- Results directly compared with experiments
- Extreme conditions
- Low cost
Ab initio simulation vs. empirical potentials

**Empirical potentials**
- Computationally inexpensive - can handle large systems.
- Have to be fit for every new problem.

**Ab initio simulation**
- Computationally very expensive - only small systems, and the level of quantum mechanical calculation is limited.
- Very adaptable to new problems. Offers the promise of highly accurate results.
The calculation is really a “computer experiment”, as we can make intricate changes in the “experimental conditions” and measure our “observables” in arbitrarily minute details. It can make materials-specific predictions and also provide first-principles parameters for otherwise emprical models.
Growth of publications in computational materials science

![Bar chart showing the growth of publications in computational materials science from 1992 to 2006. The number of publications per year increases significantly from 1992 to 2006. The chart indicates a steady rise in publications, with a sharp increase after 2000.](image-url)
Methods Landscape (quantum calculations)

\[
\{-\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{r_i - r_j} + \sum_{i,I} \frac{Z}{r_i - R_I}\} \Psi(r_1,..r_N) = E\Psi(r_1,..r_N)
\]

Many Body Schrödinger Equation

Accuracy

- Many Body methods
  - GW
  - SX-LDA
  - HF
  - DFT LDA

Empirical Pseudopotential

Tight Binding

Number of atoms

10^1 \quad 10^2 \quad 10^3 \quad 10^4 \quad 10^5 \quad 10^6
Goal: Describe properties of matter from theoretical methods firmly rooted in fundamental equations
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**Quantum Mechanics:** Schrödinger equation (assuming no relativistic)

\[
i\hbar \frac{\partial \Psi \left( \{ \vec{x}_i \}, \{ \vec{R}_\alpha \}; t \right)}{\partial t} = \hat{H} \Psi \left( \{ \vec{x}_i \}, \{ \vec{R}_\alpha \}; t \right)
\]

Coordinates of electron \( i \) \( \vec{x}_i \) comprise

\[
\begin{align*}
\text{Space coordinates} & \quad \vec{r}_i \\
\text{Spin coordinates} & \quad \sigma_i
\end{align*}
\]

**Electromagnetism:** Coulomb’s law

\[
\hat{H} = \hat{T} + \hat{V}_{\text{Coulomb}}
\]

For a pair of charged particles

\[
\hat{V}_{\text{Coulomb}} = \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|}
\]
A macroscopic solid contains a huge number of atoms

Au atomic weight: 196.966569 \approx 200

Number of moles in 1 kg of Au \approx \frac{1000 \text{ gr}}{200 \text{ gr/mol}} = 5 \text{ mol} \approx 3 \times 10^{24} \text{ atoms of gold}
A closer look to the hamiltonian: A difficult interacting many-body system.

\[ \hat{H} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} + \frac{1}{2} \sum_{i\neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_\alpha -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} \]

Kinetic energy operator for the electrons
Potential acting on the electrons due to the nuclei
Electron-electron interaction
Kinetic energy operator for the nuclei
Nucleus-nucleus interaction
Many Particle problem in Solids

Many particle Hamiltonian

\[
\hat{H} = \frac{1}{2} \sum_I M_I \nabla_{R_I}^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|} + \frac{1}{2} \sum_i \nabla_{r_i}^2 + \frac{1}{2} \sum_{ij} \frac{1}{|r_i - r_j|} - \sum_{i,I} \frac{Z_I}{|r_i - R_I|}
\]

Many particle wave function: \( \Psi (\{R_I\}, \{r_i\}) \)

Adiabatic motion of electrons

- Mass of nuclei and electrons: \( M_I/m_e \sim 1830 \) (hydrogen) \( 10000 \) (semiconductors)
  \( \Rightarrow \) fast motion of electrons compared to nuclei
- Ansatz for \( \Psi \) reflects that electrons adiabatically follow the nuclei

\[
\Psi (\{R_I\}, \{r_i\}) \approx \chi (\{R_I\}) \cdot \psi (\{r_i\}; \{R_I\})
\]
If the nuclear positions are fixed (ignore nuclear velocities), the wave function can be decoupled

\[ \hat{H} = \sum_i -\frac{\hbar^2}{2m_e} \nabla^2_i + \sum_{\alpha} -\frac{\hbar^2}{2M_\alpha} \nabla^2_{\alpha} + \frac{1}{2} \sum_{i \neq j} \left| \vec{r}_i - \vec{r}_j \right| - \sum_i \frac{Z_\alpha e^2}{\left| \vec{r}_i - \vec{R}_\alpha \right|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{\left| \vec{R}_\alpha - \vec{R}_\beta \right|} \]

**Electrons**

\[ \hat{H}^{el}_{\{\vec{R}_\alpha\}} = \sum_i -\frac{\hbar^2}{2m_e} \nabla^2_i + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\left| \vec{r}_i - \vec{r}_j \right|} + V^{ext}_{\{\vec{R}_\alpha\}} (\{\vec{r}_i\}) \]

\[ \hat{H}^{el}_{\{\vec{R}_\alpha\}} \Psi_{n_i(\vec{R}_\alpha)}^{el} (\{\vec{r}_i\}) = E_n^{el} \Psi_{n_i(\vec{R}_\alpha)}^{el} (\{\vec{r}_i\}) \]

**Nuclei**

\[ \hat{H} = \sum_{\alpha} -\frac{\hbar^2}{2M_\alpha} \nabla^2_{\alpha} + E_n^{el} (\{\vec{R}_\alpha\}) \]

Classical displacement

\[ \vec{F}_\alpha = -\frac{\partial E_0^{el} (\{\vec{R}_\mu\})}{\partial \vec{R}_\alpha} \]
The next problem... how to solve the electronic equation

\[
\hat{H}^{el}_{\{\vec{r}_i\}} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i\neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V^{ext}_{\{\vec{r}_i\}} (\{\vec{r}_i\})
\]

\[
\hat{H}^{el}_{\{\vec{r}_i\}} \Psi^{el}_{n,\{\vec{r}_i\}} (\{\vec{r}_i\}) = E^{el}_n \Psi^{el}_{n,\{\vec{r}_i\}} (\{\vec{r}_i\})
\]

Exact solution only for one electron systems \( \Rightarrow \) H, hydrogenoid atoms, \( \text{H}_2^+ \)

Main difficulty: very complicate electron-electron interactions.
Objective

- Understand the quasi-particle concept

Non-interacting many one-body problem

Interacting many-body problem
Solvation of Ion

Quasi particle: real particle dressed by other particles

Strongly interacting many particle system is transformed into a weakly interacting many quasi-particle system
Quasiparticle concept

Real particle

Quasi particle

Real horse

Quasi horse

R. D. Mattuck, a guide to Feynman Diagrams in the MB problem, Dover, 1976

A quasiparticle has an effective mass, selfenergy (energy and lifetime).
Hartree Method for many particle Solids

The Hartree idea (1928)

Introducing the coupling in an approximate way

The $k^{th}$ electron is treated as a point charge in the field of all of the other electrons. This procedure takes the many-electron problem and simplifies it to many one electron problems.

Many-electron system
All electron-electron repulsion is included explicitly.

One-electron system
with remaining electrons represented by an average charge density.
Hartree Hamiltonian

\[ h_i = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{r_{ik}} + V_i\{j\} \]

\[ V_i\{j\} = \sum_{j \neq i} \int \frac{\rho_j}{r_{ij}} \, d\mathbf{r} \]

\[ \rho_j = |\psi_j|^2 \]

\( V_i\{j\} \) = interaction potential with all of the other electrons occupying orbitals \( \{j\} \), can be defined as an effective potential \( V_{\text{eff}} \)

\( \rho_j = \) electron density associated with electron \( j \)

The problem: \( \psi_j \) appear in both the \( \rho_j \) term and in the 1-electron Schrödinger Eq

\[ h_i \psi_i = \varepsilon_i \psi_i \]

Containing \( \psi_j \) terms
SCF procedure

The Self Consistent Field Procedure

1. Guess the wavefunctions $\psi_i$ for all of the occupied MOs
2. Calculate the $V_{\text{eff}}$ for all the electrons
3. Construct the operators $h_i$
4. Solve the 1e− Schrödinger eq. for the new set of $\psi_i$
5. Repeat procedure with the new $\psi_i$ as the initial guess, until converged.

Convergence: usually $dE$ falls below a threshold

Important Note: The energy calculated using this approach needs a correction because of double counting of the electron-electron repulsion: $h_i$ includes repulsion between electron $i$ and electron $j$, but so does $h_j$.

Hartree Energy:

$$E = \sum_i \varepsilon_i - \frac{1}{2} \sum_{i \neq j} \int \int \frac{|\psi_i|^2 |\psi_j|^2}{r_{ij}} d\mathbf{r}_i d\mathbf{r}_j$$

The double-integral in this equation is called the Coulomb integral, abbreviated $J_{ij}$.
The Hartree approximation works well for atoms. However, the form of the wave function is not correct, and the method fails for molecules. In the 1930’s, Fock (and Slater) fixed this problem:

**Douglas Hartree**
Cambridge
1897-1958

**Vladimir A. Fock**
St. Petersburg
1898 -1974

**John Clark Slater**
Oak Park
1900-1976

**The Hartree-Fock method**

William Hartree (Father of Douglas Hartree) with a spiral and linear slide rule. Late 1930's

The Molecular Hamiltonian
The electrons are fermions, the solution must satisfy the Pauli exclusion principle.

A many electron wave function must be antisymmetric with respect to the interchange of the coordinate (both space and spin) of any two electrons.

\[ \Psi (\vec{x}_1, \ldots, \vec{x}_i, \ldots, \vec{x}_j, \ldots, \vec{x}_N) = -\Psi (\vec{x}_1, \ldots, \vec{x}_j, \ldots, \vec{x}_i, \ldots, \vec{x}_N) \]
Introduction of Exchange (Spin) : Hartree Fock Method

Electron, spin and antisymmetry

The electronic Hamiltonian depends only on the spatial coordinates.

\[ H_{elec} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \]

In the non-relativistic theory we specify the spin by introducing two spin functions \( \alpha(\omega) \) and \( \beta(\omega) \), corresponding respectively to spin up and spin down.

The spatial distribution of a single electron is determined by the spatial orbitals, \( \psi_i(\mathbf{r}) \).

From each spatial orbital, we can form two different spin orbitals by multiplying the spatial orbital by \( \alpha \) or \( \beta \) spin function,

\[ \chi(x) = \begin{cases} 
\psi(\mathbf{r})\alpha(\omega) & \text{or} \\
\psi(\mathbf{r})\beta(\omega) & \end{cases} \quad x = \{\mathbf{r}, \omega\} \]

The spin functions \( \alpha \) and \( \beta \) are orthonormal. If the spatial orbital are orthonormal, so are the spin orbitals.
Total Energy: Pauli Exclusion Principle

\[ E_H = \sum_{i=1}^{N} E_{ii} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} J_{ij} \]

\[ E_{HF} = \sum_{i=1}^{N} E_{ii} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=i}^{N} (J_{ij} - K_{ij}) \]

\[ J_{ij} = \int \int \varphi_i^*(r_i) \varphi_j^*(r_j) \nu_2(i, j) \varphi_i(r_i) \varphi_j(r_j) dr_i dr_j \]

\[ = \int \int \frac{\rho_i(r_i) \rho_j(r_j)}{|r_i - r_j|} dr_i dr_j \quad \text{where} \quad \rho_i(r_i) = \varphi_i^*(r_i) \varphi_i(r_i) \]

\[ K_{ij} = \int \int \varphi_i^*(r_i) \varphi_j^*(r_j) \nu_2(i, j) \varphi_i(r_i) \varphi_j(r_i) dr_i dr_j \]
### Failure of HF Method

#### Importance of Electron Correlation

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<td>$He_2$</td>
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</table>
Exchange and Correlation

For a system of two electrons with opposite spins

\[ \Psi(x_1, x_2) = |\chi_1(x_1)\chi_2(x_2)\rangle \]
\[ \chi_1(x_1) = \psi_1(r_1)\alpha(\omega_1) \]
\[ \chi_2(x_2) = \psi_2(r_2)\beta(\omega_2) \]

The probability of finding the electrons 1 & 2 in a small volume around the coordinates \( r_1 \) & \( r_2 \) is given by,

\[ P(r_1,r_2)dr_1 dr_2 = \int d\omega_1 d\omega_2 |\Psi|^2 dr_1 dr_2 = \frac{1}{2} \left[ |\Psi_1(r_1)|^2 |\Psi_2(r_2)|^2 + |\Psi_1(r_2)|^2 |\Psi_2(r_1)|^2 \right] dr_1 dr_2 \]

For the case when \( \psi_1 = \psi_2 \), we have \( P(r_1,r_2) = |\psi_1(r_1)|^2 |\psi_1(r_2)|^2 \).

The conclusion is that there is a finite probability of finding two electrons with opposite spins at the same point in space or there is no exchange correlation between two electrons with opposite spin.
Exchange-correlation (x-c) hole in silicon

- Calculated by Monte Carlo methods

Exchange

Correlation

Hole is reasonably well localized near the electron
Supports a local approximation

Hood et al
The Exchange-Correlation Hole in Si
Density Functional Theory (DFT)

Hohenberg & Kohn (1964):

Electron density \( \rho(r) = |\psi|^2(r) \) UNIQUELY determines the energy and ALL ground-state properties.

Don’t need the wavefunction at all !!!!!

There exists a universal functional \( E[\rho] \).

\[
E = E_{\text{kin}} + E_{\text{e-n}} + \frac{1}{2} \int \rho(r) \, dr \int \frac{\rho(r')}{|r - r'|} \, dr' + E_{\text{xc}}
\]

BUT: The functional is unknown:

Non-trivial: \( E_{\text{kin}} \) and \( E_{\text{xc}} \).
The Kohn-Sham ansatz replaces the many-body problem with an independent-particle problem

All the properties of the system are completely determined given only the ground state density $n_0(\vec{r})$

But no prescription to solve the difficult interacting many-body hamiltonian

$$\hat{H}_el^{el}_{\{\vec{R}_\alpha\}} \Psi^{el}_{n,\{\vec{R}_\alpha\}} (\{\vec{r}_i\}) = E^{el}_n \Psi^{el}_{n,\{\vec{R}_\alpha\}} (\{\vec{r}_i\})$$

Ground state density of the many-body interacting system = Density of an auxiliary non-interacting independent particle system

Kohn-Sham ansatz

(never proven in general)
One electron or independent particle model

We assume that each electron moves independently in a potential created by the nuclei and the rest of the electrons.

Actual calculations performed on the auxiliary independent-particle system

\[ \hat{H}_{aux}^\sigma = -\frac{1}{2} \nabla^2 + V_{eff}^\sigma (\vec{r}) \]
The Hohenberg-Kohn Theorem (1964)

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

The set of non-degenerate ground state wave functions \( \Phi \) of arbitrary \( N \)-electron Hamiltonians.

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

The dashed arrow is not possible
The independent-particle kinetic energy is given explicitly as a functional of the orbitals

\[ T_s = -\frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_\sigma} \langle \psi_i^\sigma | \nabla^2 | \psi_i^\sigma \rangle = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_\sigma} | \nabla \psi_i^\sigma |^2 \]

They rewrote the functional as

\[ E_{KS}[n] = T_s[n] + \int d\vec{r} \ V_{\text{ext}}(\vec{r}) \ n(\vec{r}) + E_{\text{Hartree}}[n] + E_{\text{xc}}[n] \]

Coulomb

Exchange-correlation

Equivalent to independent particles under the potential

\[ V_{KS}^\sigma (\vec{r}) = V_{\text{ext}} (\vec{r}) + V_{\text{Hartree}} (\vec{r}) + V_{\text{xc}}^\sigma (\vec{r}) \]
How to get an approximate XC functional?

Contains information on the *many-body* system of *interacting electrons*

The easiest way: Local Density Approximation – LDA

- Assume the functional is the same as a model problem – *the homogeneous electron gas*
- Separate the exchange and correlation contributions: $E_{xc} = E_x + E_c$
- $E_{xc}$ can be calculated as a function of the density only
LDA

model problem: the homogeneous electron gas

\[ E_{XC}^{LDA}[\rho] = \int \rho(r) \varepsilon_{XC}(\rho(r)) dr = \int \rho(r) \left( \varepsilon_X(\rho(r)) + \varepsilon_C(\rho(r)) \right) dr \]

probability of finding the particle at \( r \)

homogeneous electron gas exchange-correlation energy per particle (at the point \( r \))

The value of the xc energy depends only on the local density. The e- density (\( \rho \)) may vary as a function of \( r \), but \( \rho \) is single-valued, and the fluctuations in \( \rho \) away from \( r \) do not affect the value of \( E_{XC} \) at \( r \).
What is functional?

The ingredients (2):

A function (f) maps a set of numbers to another set of numbers

\[ Y = f(X) \]

A functional (F) is a function of a function

A function which maps a set of functions to a set of numbers

Ex. \( F[A(X), B(X), C(X), \ldots] \)

Example: \( F_{\text{xc}}[\rho(r), \nabla \rho(r)] \)
Density Functional Theory (DFT)

Solving the non-relativistic Schrödinger equation can be done by exploiting the Hohenberg-Kohn theorem which states that the total energy of electrons moving in an external potential (the positive charged atoms) is a unique functional of the electron density.

Thus the **ground state** of the quantum mechanical system of electrons in a solid can be found by minimising the total energy with respect to electron density $\rho$

$$E_{\text{Ground State}} = \min | E(\rho) |$$
Density Functional Theory (DFT) is a formally exact representation of the N electron Schrödinger Equation.

Schrödinger view

- Electron interaction
- External potential

DFT view

- Kohn-Sham particle (non-interacting)
- Effective potential

Formally equivalent

Hard problem to solve (scales like $N^5$)

“Easy” problem to solve (scales like $N^3$ or better)

Hohenberg and Kohn proved this (1964)

Nobel prize in Chemistry for Kohn in 1998
1998 Nobel Prize Laureates, Chemistry

Walter Kohn
University of California at Santa Barbara, USA

"for his development of the density-functional theory"

John A Pople
Northwestern University, Evanston, Illinois, USA

"for his development of computational methods in quantum chemistry"

Advent of Quantitative Theory and Modeling
DFT Summary

Hohenberg-Kohn theorem \( \rho_0(r) \rightarrow v_{\text{ext}}(r) \)

\[ E_v[\rho_0] \leq E_v[\rho] = F[\rho] + \int \rho(r)v_{\text{ext}}(r)dr \]

where \( F[\rho] = \langle \Phi[\rho]|T+U_{ee}|\Phi[\rho] \rangle \)

\[ E_0 = \min_{\rho \rightarrow N} E[\rho] \]

Search all (positive) densities that yield \( N \)

\[ F[\rho] = \min_{\Phi \rightarrow \rho} \{ \langle \Phi|T+U_{ee}|\Phi \rangle \} \]

Search all anti-symmetric wavefunctions that yield \( \rho \)
LDA

- If we have a system with non-uniform electron distribution where the density is slowly varying, one can divide the space into portions, where the density in each portion is almost constant.
- Each portion is a uniform electron gas.
- So if we assume that the exchange energy per particle in the uniform electron gas is \( \varepsilon_{xc}^{hom}(n) \) then:

\[
E_{xc}[n] = \int d\vec{r} n(\vec{r}) \varepsilon_{xc}^{hom}(n)
\]

- The corresponding exchange-correlation potential is:

\[
V_{xc}^{LDA} (\vec{r}) = \frac{\delta E_{xc}^{LDA} [n]}{\delta n} = \frac{d[n(\vec{r}) \varepsilon_{xc}^{hom}(n)]}{dn(\vec{r})}
\]
Exchange-Correlation Potential

- \( V_{xc} \equiv \frac{\delta E_{xc}}{\delta n} \) contains all the many-body information.
- Known [numerically, from Quantum Monte Carlo; various analytical approximations] for homogeneous electron gas.
- **Local Density Approximation**

\[
E_{xc}[n] = \int n(r) \ V_{xc}^{\text{HOM}}[n(r)] \ dr
\]

Surprisingly successful!
How can we specify $E_{XC}$?

At this point, we need to make approximations to get further. 

Example: local density approximation (LDA)

\[
E_{XC}[n(r)] = \int dr \, e_{XC}[n(r)] \, n(r)
\]

\[
\approx \int dr \, [e_{X}^{\text{hom}}(n(r)) + e_{C}^{\text{hom}}(n(r))] \, n(r)
\]

\[
e_{X}^{\text{hom}}(n) = -\frac{81}{64\pi} n^{1/3}(r)
\]

\[
e_{C}^{\text{hom}}(n) = \begin{cases} 
-0.1423(1 + 1.0529 \sqrt{r_s} + 0.3334r_s)^{-1} & \text{if } r_s \geq 1, \\
-0.0480 + 0.0311 \ln r_s - 0.0116r_s + 0.002 & r_s \ln r_s \\
\end{cases}
\]

$r_s := (4\pi n(r)/3)^{-1/3}$ Wigner-Seitz radius

[see, e.g. J. Perdew & A. Zunger, Phys. Rev. B 23 5048 (1981)]
The Kohn-Sham equations must be solved self-consistently.

The potential (input) depends on the density (output).

**Initial guess**

\[
n^\uparrow(\mathbf{r}) , n^\downarrow(\mathbf{r})
\]

**Calculate effective potential**

\[
V_{\text{eff}}^\sigma(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}[n] + V_{xc}[n^\uparrow, n^\downarrow]
\]

**Solve the KS equation**

\[
\left(-\frac{1}{2} \nabla^2 + V_{\text{eff}}^\sigma(\mathbf{r})\right) \psi_i^\sigma(\mathbf{r}) = \varepsilon_i^\sigma \psi_i^\sigma(\mathbf{r})
\]

**Compute electron density**

\[
n^\sigma(\mathbf{r}) = \sum_i f_i^\sigma |\psi_i^\sigma(\mathbf{r})|^2
\]

**Self-consistent?**

- No
- Yes

**Output quantities**

Energy, forces, stresses ...
Methods for the solution of Poisson’s equation

Poisson’s equation establishes the relation between a charge density $\rho$ and its resulting potential $V$

$$\nabla^2 V(r) = -4\pi \rho(r)$$

For non-periodic systems such as atoms and molecules, free boundary conditions where the potential vanishes at infinity are the appropriate ones. Formally the solution can then be written as

$$V(r) = \int \frac{\rho(r')}{|r - r'|} \, dr'$$

The numerical solution of Poissons equation is frequently based on the differential form rather than the integral form.
SOME NUMBERS

Binding energy of Fe: 2541.025 Ry
bcc-fcc energy difference in Fe: 0.013 Ry (austenite-ferrite in steels)

Binding of PZT (Navy SONAR): 46730.476 Ry
Ferroelectric instability in PZT: 0.006 Ry

Binding of Mn-ferrite (RADAR): 15987.192 Ry
Magnetic coupling of Mn-ferrite: 0.070 Ry

Small differences between very large energies are the keys to materials properties

⇒ We rely on careful choice of numerical methods and error cancellation in the differences.
Disadvantages of LDA

1. It is a good approximation for systems with slowly varying density.
2. It tends to overbind, which cause for example small lattice constants.
GGA

- $E_{xc}$ is calculated just as in the LDA method, but enhancement is introduced by multiplying $\varepsilon_{xc}^{\text{hom}}(n)$ with a factor $F_{xc}$ which takes into account the local variation of the density $n$.

\[
E_{xc}^{\text{GGA}}[n] = \int d\vec{r} \, \varepsilon_{xc}^{\text{hom}}[n] \, F_{xc}(r_s, s) \, n(\vec{r})
\]

where

\[
S = \frac{\left| \vec{\nabla} n \right|}{2 \left( \frac{3 \pi^2}{2} \right)^{1/3} n^{4/3}}
\]
Generalized Gradient Approximation (GGA)

General *semilocal* approximation to the exchange-correlation energy as a functional of the density and its gradient to fulfill a maximum number of exact relations.

\[
E_{xc}^{GGA}[n_\uparrow, n_\downarrow] = \int d\mathbf{r} \, f(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}), \nabla n_\uparrow(\mathbf{r}), \nabla n_\downarrow(\mathbf{r}))
\]

Exchange correlation potential:

\[
V_{xc}[n(\mathbf{r})] = \frac{\partial E_{xc}[n]}{\partial n(\mathbf{r})} - \nabla \cdot \frac{\partial E_{xc}[n]}{\partial (\nabla n(\mathbf{r}))}
\]

The gradient of the density is usually determined *numerically.*
GGA-PW91

Exchange energy:

\[ E_{\chi}^{\text{PW91}}[n] = - \int d\mathbf{r} n \frac{3k_F}{4\pi} \frac{1 + 0.1965s \sinh^{-1}(7.796s) + (0.274 - 0.151e^{-100s^2})s^2}{1 + 0.1964s \sinh^{-1}(7.796s) + 0.004s^4} \]

Correlation energy:

\[ E_{\text{c}}^{\text{PW91}}[n] = \int d\mathbf{r} n (\varepsilon_c(r_s, \zeta) + H(t, r_s, \zeta)) \]

with \( k_F = (3\pi^2 n)^{1/3} \), \( s = |\nabla n|/2k_F n \), \( t = |\nabla n|/2g k_s n \), \( g = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3})]/2 \)

and \( k_s = (4k_F/\pi)^{1/2} \).
Atomisation energies (in eV) of several molecules: theory vs experiment.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>LDA</th>
<th>GGA</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>3.64</td>
<td>4.90</td>
<td>4.55</td>
<td>4.73</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>6.72</td>
<td>11.58</td>
<td>10.15</td>
<td>10.06</td>
</tr>
<tr>
<td>HF</td>
<td>4.21</td>
<td>7.03</td>
<td>6.16</td>
<td>6.11</td>
</tr>
<tr>
<td>$O_2$</td>
<td>1.43</td>
<td>7.59</td>
<td>6.24</td>
<td>5.25</td>
</tr>
<tr>
<td>$F_2$</td>
<td>-1.60</td>
<td>3.34</td>
<td>2.30</td>
<td>1.69</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>14.22</td>
<td>20.03</td>
<td>18.21</td>
<td>18.17</td>
</tr>
</tbody>
</table>

Solids: diamond

<table>
<thead>
<tr>
<th>Property</th>
<th>HF</th>
<th>LDA</th>
<th>GGA</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$, Å</td>
<td>3.58</td>
<td>3.53</td>
<td>3.57</td>
<td>3.567</td>
</tr>
<tr>
<td>$E_a$, eV</td>
<td>-5.2</td>
<td>-8.87</td>
<td>-7.72</td>
<td>-7.55</td>
</tr>
<tr>
<td>$K_0$, GPa</td>
<td>471</td>
<td>455</td>
<td>438</td>
<td>442</td>
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</table>
### Density Functional Theory

**Accuracy of the XC functionals in the structural and electronic properties**

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>-1% , -3%</td>
<td>+1%</td>
</tr>
<tr>
<td>( B )</td>
<td>+10% , +40%</td>
<td>-20% , +10%</td>
</tr>
<tr>
<td>( E_c )</td>
<td>+15%</td>
<td>-5%</td>
</tr>
<tr>
<td>( E_{\text{gap}} )</td>
<td>-50%</td>
<td>-50%</td>
</tr>
</tbody>
</table>

**LDA**: simplest approximation but accurate enough (structural properties, ...).

**GGA**: usually tends to overcompensate LDA results, but not always better.
In some cases, GGA is a must: DFT ground state of iron

Results obtained with Wien2k.
Courtesy of Karl H. Schwartz
FeF$_2$: GGA works surprisingly well

FeF$_2$: GGA splits $t_{2g}$ into $a_{1g}$ and $e_g$.  

Fe-EFG in FeF$_2$:
- LSDA: 6.2
- GGA: 16.8
- exp: 16.5

agree
Success and failure of “standard” DFT in solids

• Standard LDA (GGA) gives good description of structural and electronic properties of most solids (lattice parameters within 1-2%, at least qualitatively correct bandstructure, metal-insulator, magnetism,…)

• Problems: “localized” (correlated) electrons
  – late 3d transition metal oxides/halides
    • metals instead of insulators (FeO, FeF$_2$, cuprates, …)
    • nonmagnetic instead of anti-ferromagnetic (La$_2$CuO$_4$, YBa$_2$Cu$_3$O$_6$)
  – 4f, 5f electrons
    • all f-states pinned at the Fermi energy, “always” metallic
    • orbital moments much too small
  – “weakly” correlated metals
    • FeAl is ferromagnetic in theory, but nonmagnetic experimentally
    • 3d-band position, exchange splitting,…
Is LDA/GGA repairable?

Ab initio methods

- GGA: usually improvement, but often too small.
- Hartree-Fock: completely neglects correlation, very poor in solids
- Exact exchange: imbalance between exact X and approximate (no) C
- Hybrid-Functionals: mix of HF + LDA; good for insulators, poor for metals
- GW: gaps in semiconductors, but ground state? expensive!
- Quantum Monte-Carlo: very expensive

Not fully ab initio

- Self-interaction-correction: vanishes for Bloch states
- Orbital polarization: Hund’s 2\textsuperscript{nd} rule by atomic Slater-parameter
- LDA+U: strong Coulomb repulsion via external Hubbard U parameter
- DMFT: extension of LDA+U for weakly correlated systems
"Accurate" result:

Nonlocal correlation is needed for describing the asymptotic behavior.
How to improve GGA results?

<table>
<thead>
<tr>
<th>John Perdew Jacob Ladder*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEAVEN (chemical accuracy)</td>
</tr>
<tr>
<td>rung 5</td>
</tr>
<tr>
<td>+ explicit dependence on unoccupied orbitals</td>
</tr>
<tr>
<td>rung 4</td>
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<tr>
<td>+ explicit dependence on occupied orbitals</td>
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<tr>
<td>rung 3</td>
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<tr>
<td>+ explicit dependence on kinetic energy density</td>
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<tr>
<td>rung 2</td>
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<tr>
<td>+ explicit dependence on gradients of the density</td>
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<tr>
<td>rung 1</td>
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<tr>
<td>local density only</td>
</tr>
</tbody>
</table>

EARTH (Hartree theory)

*DFT conference Menton 2000

* Philippe Ratner
How to improve the exchange energy: **Hybrid Functionals**

**Idea:** HF exchange is exact. Therefore we could think to combine exact (HF) exchange with a GGA correlation functional (Lie & Clementi 1974)

\[ E_{XC} = E_{X}^{\text{exact}} + E_{C}^{KS} \]

**How does it work? Very bad!**
Mean average error 32 kcal/mole for the G2 ensemble (50 molecules) while a MAE of 5-7 kcal/mol is obtained with standard GGA

Actually combining a **percentage of HF exchange with a GGA exchange** works much better!!!
Hybrid functional: only for (correlated) electrons

- Only for certain atoms and electrons of a given angular momentum $\ell$

\[
E_{xc}^{\text{hybrid}} = E_{xc}^{\text{DFT}}[\rho^\sigma] + \alpha \left( E_x^{\text{HF}}[n_{m_im_j}^\sigma] - E_{xc}^{\text{DFT}}[\rho_\ell^\sigma] \right)
\]

\[
E_x^{\text{HF}}[n_{m_im_j}^\sigma] = -\frac{1}{2} \sum_{\sigma} \sum_{m_1,m_2,m_3,m_4} n_{m_1m_2}^\sigma n_{m_3m_4}^\sigma \langle m_1m_3 | v_{ee} | m_4m_2 \rangle
\]

\[
\langle m_1m_2 | v_{ee} | m_3m_4 \rangle = \sum_{k=0}^{2\ell} a_k F_k
\]

The Slater integrals $F_k$ are calculated according to P. Novák et al., phys.stat.sol (b) 245, 563 (2006)
Hybrid functionals (mixing of LDA with HF)

General principle:
Mixing a fraction of “exact change” with GGA semilocal exchange

- B3LYP (semi-empirical)

\[ E^{\text{B3LYP}}_{\text{XC}} = E_{\text{XC}}^{\text{LSDA}} + a_0 (E_{\text{X}}^{\text{exact}} - E_{\text{XC}}^{\text{LSDA}}) + a_X \Delta E_{\text{X}}^{\text{B88}} + a_C \Delta E_{\text{C}}^{\text{LYP}} \]

\[ a_0 = 0.20, \ a_X = 0.72, \ a_C = 0.81 \]

- PBE0 (non-empirical)

\[ E_{\text{XC}}^{\text{PBE0}} = 0.25 \times E_{\text{X}}^{\text{exact}} + 0.75 \times E_{\text{X}}^{\text{PBE}} + E_{\text{C}}^{\text{PBE}} \]

# Software supporting DFT

<table>
<thead>
<tr>
<th>Software supporting DFT</th>
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<th>Software supporting DFT</th>
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<td>ADF</td>
<td>JAGUAR</td>
<td>TURBOMOLE</td>
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<td>NOLCAS</td>
<td>VASP</td>
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<td>Ascalaph Quantum</td>
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<td>EXCITING</td>
<td>Parallel Quantum Solutions</td>
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<td>Fireball</td>
<td>Priroda</td>
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<tr>
<td>FLEUR</td>
<td>PWscf (Quantum-ESPRESSO)</td>
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<tr>
<td>FSaton, dozens of free and proprietary DFT programs</td>
<td>Q-Chem</td>
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<td>GAMESS (UK)</td>
<td>SIESTA</td>
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<td>GAMESS (US)</td>
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<tr>
<td>GPAW</td>
<td>S/FHI/nX</td>
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</tbody>
</table>

Density Functional Theory (DFT)

**VASP** (Vienna *ab initio* simulation package)
- plane-waves
- Pseudopotentials
- GGA exchange-correlation functional

**TB-LMTO-ASA** (Linear Muffin Tin Orbitals)
- local Basissets
- All-electron method
- COHP-Bond analysis

**Wien2k** - FP-LAPW
- All-electron method
Most of our calculations are based on the generalized gradient approximation (GGA) and all-electron PAW method

- State of art.
- Molar volumes: within 1-3% (LDA, GGA).
- Transition pressures: 10% underestimated (LDA), ± 5 GPa (GGA).
- Band gaps: ~30% underestimated (LDA, GGA), ±10% (GW).
- Unsatisfactory – for van der Waals crystals, systems with localised d- and f-electrons.
Lecture Summary

• Density functional theory is an exact reformulation of many-body quantum mechanics in terms of the probability density rather than the wave function.

• The ground-state energy can be obtained by minimization of the energy functional $E[n]$. All we know about the functional is that it exists, however, its form is unknown.

• Kohn-Sham reformulation in terms of single-particle orbitals helps in the development of approximations and is the form used in density functional calculations today.
Summary

• DFT has been the mainstay of electronic structure calculations more than 25 years.
• Because approximate functional provide a useful balance between accuracy and computational cost.
• This allowed much larger systems to be treated.
• DFT is a completely different way of approaching any interacting problem, by mapping it exactly to a much easier-to-solve non-interacting problem.
• Its methodology is applied into a large variety of systems as atoms, molecules, clusters and solids.
• Limitations of LDA/GGA were partly overcome by Hybrid functionals.
Books: Electronic Structure
Books: Electronic Structure