ME 697R: Computational Methods for Nanoscale Energy Transport

Chapter 5: First Principles Method
Section 5.3: Density Functional Theory

Reading: Springborg, Chapter 15

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Nature of Interatomic Potential (Bonding)

- Overlap of Atomic Wavefunction

\[ \psi_1 = \frac{1}{a_0 \sqrt{\pi}} \exp\left(-\frac{(r-r_1)}{a_0}\right) \]
\[ \psi_2 = \frac{1}{a_0 \sqrt{\pi}} \exp\left(-\frac{(r-r_2)}{a_0}\right) \]

- For \( \text{H}_2 \), the interatomic potential is the ground state energy in quantum mechanics.

- For solid, the lattice energy is the ground state energy in quantum mechanics.

The overarching goal is to solve the Schrödinger equation and obtain the energy levels and the corresponding wavefunctions.

Only the hydrogen atom can be solved analytically. All other atoms, molecules, and solids need to be done using numerical methods.

Methods for solving the Schrödinger equation:
- Hartree-Fock
- Density functional theory
The Electronic Hamiltonian

- Example: He atom

\[
\begin{align*}
-T_e &= -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 \\
-U_{ee} &= \frac{e^2}{r_{12}} \\
-U_{ext} &= -\sum_i \frac{Ze^2}{r_i}
\end{align*}
\]

- The kinetic energy operator is the sum of the kinetic terms for all of the electrons. The external potential is the Coulomb attraction between nuclei and electrons.

Griffiths, Introduction to Quantum Mechanics, Section 5.2
The Total Hamiltonian

- Using these approximations we can write the total hamiltonian of an atom as

\[ H_{el} = T_e + V_{ext} + U_{ee} \]

- The first two terms alone comprise a set of \( N \) hydrogen atom calculations which can be solved exactly.

\[
T_e + V_{ext} = -\sum_i \left( \frac{\hbar^2}{2m} \nabla_i^2 + \frac{Ze^2}{r_i} \right) = \sum_i h_i
\]

- The total hamiltonian in this nomenclature is:

\[ H_{el} = \sum_i h_i + U_{ee} \]

- Note that the inclusion of the electron-electron repulsion term \( U_{ee} \) makes it impossible to solve the Schrödinger equation analytically.
Density Functional Theory: Introduction

- Density functional theory is an approach for the description of ground state properties of metals, semiconductors, and insulators.

- The main idea of DFT is to describe an interacting system of electrons via its density and not via its many-body wave function. The wave function $\psi$ of an $N$-electron system includes $3N$ variables, while the density, $\rho$ no matter how large the system is, has only three variables $x$, $y$, and $z$. Moving from $E[\psi]$ to $E[\rho]$ in computational chemistry significantly reduces the computational effort needed to understand electronic properties of atoms, molecules, and solids.

- Knowledge of the density is all that is necessary for a complete determination of all ground state properties.

- Formulation along this line provides the possibility of the linear scaling algorithm currently in fashion, whose computational complexity goes like $O(N\log N)$, essentially linear in $N$ when $N$ is very large.

- Electron correlation is included.
The Hohenberg-Kohn Theorems

- We add a term that accounts for electron exchange in terms of the density. The Hamiltonian in atomic units is:

\[
H = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} + \sum_{i=1}^{N} V_{\text{ext},i} + \sum_{i<j}^{N} \frac{1}{r_{i} - r_{j}} = T + V_{\text{ext}} + V_{\text{coul}} + V_{\text{xc}}
\]

- The major expense is the calculation of exchange. Instead of calculating using explicit exchange, DFT uses an additional function of the density \( V_{\text{xc}} \) where the \( x \) stands for exchange and the \( c \) stands for correlation. The central problem in DFT is that there is no unique prescription for how to find the exchange and correlation functionals.

- The first Hohenberg-Kohn theorem asserts that the density of any system determines all ground-state properties of the system, that is, \( E = E[\rho] \), where \( \rho \) is the ground-state density of the system.

- The second H-K theorem shows that there exists a variational principle for the above energy density functional \( E[\rho] \). Namely, if \( \rho' \) is not the ground state density of the above system, then \( E[\rho'] > E[\rho] \).
Consequences of the H-K Theorems

- Each local one-particle potential corresponds exactly to one ground state density. This permits us to express the potential as a function of the density \( V[\rho] \).

\[
\begin{align*}
H|\phi_{GS}\rangle &= E_{GS}|\phi_{GS}\rangle \\
V_{ext} &\rightarrow |\phi_{GS}\rangle \\
\rho_{GS}(r) &= \sum_{occ} |\phi_{GS}(r)|^2 \\
\rho_{GS}(x,y,z) &\Rightarrow V_{ext} \Rightarrow H \Rightarrow |\phi[\rho_{GS}]\rangle \Rightarrow O[\rho_{GS}] = \langle \phi[\rho_{GS}]|O|\phi[\rho_{GS}]\rangle
\end{align*}
\]

Ground state expectation values depend uniquely on \( \rho_{GS} \).
The Kohn-Sham Approach

- Treat the electrons as N fictitious non-interacting particles (electrons) moving in an effective potential.

\[ |\phi_i\rangle \equiv \text{independent particle wavefunction} \]

**density**: \( \rho_{KS} = \sum_{i=1}^{N} |\phi_i|^2 \)

**kinetic energy**: \( T_{KS} = -\frac{1}{2} \sum_{i=1}^{N} \langle \phi_i | \nabla^2 |\phi_i\rangle \)

- The Kohn-Sham assumption is that the K-S density \( \rho_{KS} \) is equal to the true density.

- Kohn-Sham energy partitioning:

\[ E[\rho] = T[\rho] + E_{ext}[\rho] + E_{Coul}[\rho] + E_{xc}[\rho] \]

- Electronic Kinetic energy
- Nuclei-electrons Coulombic energy
- electrons-electrons exchange and correlation energy
The Kohn-Sham Equation

Interacting electrons

Real electronic potential

Schroedinger’s Equation

\[
\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{Real}}\right] \Psi(r) = \varepsilon \Psi(r)
\]

Non-interacting particles

Effective electronic potential

Density Functional Theory (DFT)

Kohn-Sham’s Equation

\[
\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{KS}}\right] \phi_{nk}(r) = \varepsilon_{nk} \phi_{nk}(r)
\]

Iteratively solve for \( \phi_{nk}(r) \) and \( \varepsilon_{nk} \)
Local Density Approximation (LDA)

- While DFT in principle gives a good description of ground state properties, practical applications of DFT are based on approximations for the exchange-correlation potential. The exchange-correlation potential describes the effects of the Pauli exclusion principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons.

- A common approximation is the so-called local density approximation (LDA). It assumes that the exchange-correlation energy per electron at a point \( r \) in the electron gas is equal to the exchange-correlation energy per electron in a homogeneous electron gas that has the same density as the electron gas at point \( r \).

\[
E_{XC}[\rho(r)] = \int \varepsilon_{XC}(r) \rho(r) dr
\]

where \( \varepsilon_{XC} \) is the energy per particle (energy density).

\[
\varepsilon_{XC}(r) = \varepsilon_{XC}^{\text{hom}}[\rho(r)]
\]

- LDA assumes that the exchange-correlation energy functional is purely local. Not true in physics, but works well for many systems.
Generalized-Gradient Approximations (GGA)

- Consider the density gradient as well as density at each point \( r \)
  \[
  E_{XC}^{GGA} [\rho(r)] = \int \varepsilon_{XC}(\rho, |\nabla \rho|, \ldots) \rho(r) d^3r
  = \int \varepsilon_{XC}^{hom}(\rho) F_{XC}(\rho, |\nabla \rho|, \ldots) \rho(r) d^3r
  \]

- Typically, there are more rapidly varying density regions in atoms than in condensed matter, which lead to greater lowering of exchange energy in atoms than in molecules and solids. In this case, GGA usually works better.
In a periodic solid each electronic wave function can be written as the product of a cell-periodic part and a planewave part.

\[ \psi_i(\vec{r}) = f_i(\vec{r}) \exp[i\vec{k} \cdot \vec{r}] \]

Cell-periodic part can be expanded using a basis set consisting of a discrete set of plane waves for which wave vector \( \vec{s} \) are reciprocal lattice vectors of crystal.

\[ f_i(\vec{r}) = \sum_{\vec{G}} c_{i,\vec{G}} \exp(i\vec{G} \cdot \vec{r}) \]
Bloch’s Theorem

- Electronic wave function can be written as a sum of plane waves. $G$ is a reciprocal lattice vector.

- Change the problem of calculating an infinite number of electronic wave functions to one of calculating a finite number of electronic wave functions for each $k$-point.

$$\psi_i(\vec{r}) = \sum_{\vec{G}} c_{i,\vec{k}+\vec{G}} \exp[i(\vec{k} + \vec{G}) \cdot \vec{r}]$$

- This wavefunction depends on $k$. 
For solids, there are infinite number of 

k points. The density of allowed k 

points is proportional to the volume of 

the solid.

The wave functions at k points that are 

very close together will be almost 

identical.

Possible to represent the wave 

functions over a region of k space by 

the wave functions at a single k point.

The total energy will converge as the 

density of k point increases, and the 

error due to the k-point sampling 

approaches zero.

<table>
<thead>
<tr>
<th>k point grid</th>
<th>Number of sampled k points</th>
<th>Total energy (Hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 2 2</td>
<td>2</td>
<td>-8.866223E+00</td>
</tr>
<tr>
<td>4 4 4</td>
<td>10</td>
<td>-8.872490E+00</td>
</tr>
<tr>
<td>6 6 6</td>
<td>28</td>
<td>-8.872601E+00</td>
</tr>
<tr>
<td>8 8 8</td>
<td>60</td>
<td>-8.872605E+00</td>
</tr>
</tbody>
</table>
Coefficient of small kinetic energy are typically more important than those with large kinetic energy.

Plane-wave basis set can be truncated at a certain cutoff energy

A cutoff test is usually necessary before doing any calculations.
The Pseudopotential Concept

- Pseudopotential approximation is used to deal with electron-ion interaction.

\[
- \frac{\hbar^2}{2m} \nabla^2 + V_{ext}(\mathbf{r}) + V_{colu}(\mathbf{r}) + V_{XC}(\mathbf{r}) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})
\]

- Tightly bound core orbitals are rapid oscillating. Plane wave basis set is usually poorly suited to be used to expand wave functions, because a very large number of plane waves is needed.

- IDEA: group all the electrons around the nuclear core into an effective ionic core, where all the strong oscillations close to the nuclei are damped, and leave only the valence electrons that contribute to the bonding of the solid.
Real potential is replaced by a pseudopotential, so that the pseudo wave function outside the core region is the same as real wave function.

Pseudopotentials often determine the degree of success of the calculation. It has better transferability than classical interatomic potentials.