Introduce to Density Functional Theory and its Computational Study of Materials’ Ferroelectric Property

By Xin Chen
Outline

- DFT History
- DFT Theory Background
- An example of using DFT
- Study of BaTiO$_3$’s Ferroelectric Property
- DFT and Quantum Computation
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Density Functional Theory

• A computational quantum mechanical modeling method used to solve the electronic structure of matter and materials, like some particular atoms, molecules and condensed phases.

Walter Kohn

Walter Kohn received Nobel Prize in Chemistry in 1998 for his development of the density-functional theory.
What is DFT?

• One electron problem
  i.e. Hydrogen atom Schrodinger Equation

\[
\begin{align*}
- \frac{\hbar^2}{2m_e} & \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2} \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right) \\
& \quad - \frac{e^2}{4\pi \varepsilon_0} \frac{1}{r} \right] \psi = E \psi
\end{align*}
\]

\[
E_n = - \frac{m_e e^4}{32 \pi^2 \varepsilon_0^2 \hbar^2} \frac{1}{n^2}
\]

Will we able to find exact solutions for a systems with thousands electrons, atoms, and molecules?

Nooooooope!!! 😞
What can we do?

→ Use approximation and tricks.

**BO**(Born-Oppenheimer) approximation is introduced.

→ The motion of atomic nuclei and electrons in a molecule can be separated.

\[ \Psi_{\text{total}} = \psi_{\text{electronic}} \otimes \psi_{\text{nuclear}} \]

→ Reducing degrees of freedom.
Hohenburg - Kohn Theorem

→ Electron density of any system determines all ground-state properties of the system. In this case the total ground state energy of a many-electron system is a functional of the density.

→ If we know the electron density functional, we know the total energy of our system.

We use DFT as a functional.

Then we shall calculate all other ground state properties.
XC (Exchange Correlation) Functional

→ An approximation that takes care of all the quantum mechanical information, like spins, attraction and repulsion between atoms.

Kohn-Sham Equations

→ KS equation is the one electron Schrödinger equation of a fictitious system of non-interacting particles that generate the same density as any given system of interacting particles.

→ Walter Kohn & Lu Jeu Sham

→ K-S Method is widely used in material science.
Kohn-Sham Equations

\[
\begin{bmatrix}
\frac{-\nabla^2}{2} + V(r) + V_H(r) + V_{xc}[n](r)
\end{bmatrix}
\phi_j(r) = \varepsilon_j \phi_j(r)
\]

→ XC potential is defined as

\[
V_{xc}[n](r) = \frac{\delta E_{xc}[n]}{\delta n(r)}
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\(V(r)\) is the external potential acting on the interacting system
\(V_H\) is the hydrogen potential.
\(\varepsilon_i\) is the orbital energy of the corresponding Kohn–Sham orbital \(\phi_i\)
\(n\) is the density for an \(N\)-particle system.

In any practical approximation of the theory, we have to use an approximation to \(V_{xc}\)
An Example of Using DFT

DFT Calculation Packages

➔ **VASP** (Vienna Ab initio Simulation Package)
➔ John Popel shared second half of the Nobel Chemistry Prize with Walter Kohn in 1998.
➔ Popel is known for his development of computational methods in quantum chemistry. He created the Ab initio quantum chemistry method was created.
➔ CASTEP, CPMD, ABINIT, and etc.
VASP

- A computer program for atomic scale modeling
- It was based on code written by Mike Payne, a scientist at MIT.
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- Besides DFT, it also computes an approximate solution to the many-body Schrodinger equation, like the Kohn-Stam equations, or within the Hartree-Fock(HF) approximation, solving the Roothaan equations.
Input Structures

- VESTA

- Database
  - CCDC (The Cambridge Crystallographic Data Centre)
  - ICSD (The database for inorganic crystal structures)
  - COD (Free structural databases such as Crystallography Open Database)

Rutile
What else we need for DFT calculations?

Cluster

Some famous clusters:
No. 1 Summit (IBM, Oak Ridge)
No. 2 Sunway TaihuLight (China)
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No. 5 ABCI (Japan)

Price: $25,000 - $250,000
Band Structures

Silicon, band gap 1.1eV
DOS (Density of States)

Density of states in Si0.25Ge0.75
My Summer Project at NYU Shanghai

• Studying the ferromagnetic properties of materials
• BaTiO$_3$, LiOsO$_3$, BiBaTi$_2$O$_6$, and etc.
Ferromagnetic Properties:

- Ferromagnetism is the property of a material to be strongly attracted to a magnetic field and to become a powerful magnet.

- In ferromagnetic materials, the magnetic lines of forces due to the applied magnetic field are strongly attracted towards the material.

- All ferromagnetic materials become paramagnetic above a temperature called Curie temperature.

- The study of ferromagnetic phase transitions, had an important impact on the development of statistical physics.
Phonon

• A phonon is not a real particle.
• A phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter, like solids and some liquids.
• Phonon mode describes a collective vibration amplitudes of atoms in a crystal lattice
BaTiO$_3$’s Phonon Mode

Atom Ba, Ti, and O are represented by shaded, solid, and empty circles.

- Fully relaxation of the lattice will give the phonon mode of BaTiO$_3$.

\[ \xi_z = [ \text{Ba}, \text{Ti}, O_{z1}, O_{z2}] = [0.35686, 0.71463, -0.16355, -0.55539] \]
BaTiO$_3$ Base Phonon Mode

\[
 f(u) = \kappa u^2 + \alpha u^4, \quad \kappa = -5.06590496 \text{ ev/Å}^2, \quad \alpha = 50.07341082 \text{ ev/Å}^4
\]
$BiBaTi_2O_6$
\[\xi = (-0.62, -0.50, -0.30, -0.30, -0.17, -0.17, -0.17, -0.17, -0.17)\]

fix volumn, \( f(u) = \kappa u^2, \kappa = 0.90 \text{ ev}/\text{Å}^2 \)
Density functional theory and quantum computation

Frank Gaitan\textsuperscript{1,2,3} and Franco Nori\textsuperscript{1,3,4}

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\textsuperscript{2}Department of Physics, Southern Illinois University, Carbondale, IL 62901-4401

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\textsuperscript{4}Physics Department, Center for Theoretical Physics, University of Michigan, Ann Arbor, MI 48109

(Dated: October 22, 2018)
• This paper shows that ground-state and time-dependent DFT can be applied to quantum computing systems by proving the Hohenberg-Kohn and Runge-Gross theorems for a fermionic representation of an N qubit system.

• Time-dependent DFT is used to determine the minimum energy gap $\Delta(N)$ arising when the quantum adiabatic evolution algorithm is used to solve instances of the NP-Complete problem MAXCUT.

• This paper raises the realistic prospect of evaluating the gap $\Delta(N)$ for systems with $N \sim 10^3$ qubits.
Acknowledgement

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- Ruihan Yang from NYU Shanghai
Questions ?
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