Density Functional Theory: Introduction and Applications

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October 5th, 2022
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Question: What do you need Density Functional Theory for?

1. Use DFT
2. Develop DFT
3. Mostly to understand other people’s work
4. My teaching
5. I am mostly just curious
Overview

- Motivation and Background
- Formulation and Implementation of Density Functional Theory
- Example Applications: Total Energy and Bulk Modulus, Electronic Band Structures
Computational cost depends on level of accuracy

Many different approaches/codes available (depends on goal)

Density Functional Theory: Microscopic scale
Today's standard model of materials:

• Materials consist of atoms

• Atoms consist of
  ◦ massive, point-like nuclei (protons + neutrons)
  ◦ surrounded by tightly bound core electrons
  ◦ held together in molecules, liquid, and solids by the bonds formed by valence electrons
Microscopic Scale: Quantum Mechanics

Today’s standard model of materials:

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Goal: Solve laws of quantum mechanics for actual materials

• Bonding and structure (structural properties)
• Electronic, magnetic, and optical properties of materials
• Chemistry and reactions
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- Chemistry and reactions

The general theory of quantum mechanics is now almost complete. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

P. A. M. Dirac, Proc. R. Soc. Lond. A 1929, pg. 123
Quantum Mechanics:

1. Write Down Hamilton Operator

\[ \hat{H} = \hat{T} + \hat{V} \]

2. Solve Schrödinger Equation to get \( E \) and \( \psi \)

\[ \hat{H} \psi (r) = \left( \hat{T} + \hat{V} \right) \psi (r) = E \psi (r) \]

3. Use this solution to compute observables

Probability of finding electron at position \( r \) in space

\[ n(r) = \sum \frac{\left| \langle \psi \rangle \right|^2}{\alpha} = \]

(c) https://www2.chemistry.illinois.edu/faculty/reusch/VirtTxtml/Images/hybrid1.gif
Microscopic Scale: Quantum Mechanics

Why is Quantum Mechanics/Solving Schrödinger Equation hard?

Example: Fe atom

- Fe has 26 electrons ⇒ wave function has $3 \times 26 = 78$ variables
- store wave function on a grid
- coarse grid of only 10 points along each direction
- to store wave function would require storage of $10^{78}$ numbers
- single precision 1 number = 4 Bytes
- compare to all data stored worldwide in 2020:
  
  $64$ zettabyte = $64 \times 10^{21}$ Bytes

(c) https://en.wikipedia.org/wiki/Iron#/media/File:Iron_electrolytic_and_1cm3_cube.jpg
Microscopic Scale: Quantum Mechanics

Many-electron Hamiltonian of a material

- Fix ions in their positions: Born-Oppenheimer Approximation
- Leads to Electronic Hamiltonian:

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + \sum_i \sum_{j \neq i} \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \sum_j \frac{Z_i e^2}{4\pi\varepsilon_0 |\mathbf{R}_i - \mathbf{r}_j|}$$

Solution requires approximations

- Historic approaches include Hartree Approximation, Hartree-Fock Approximation, …
- In general: Balance/tradeoff between accuracy and speed
- Density Functional Theory favorable on that spectrum and is very widespread nowadays
Overview

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- Formulation and Implementation of Density Functional Theory
- Example Applications: Total Energy and Bulk Modulus, Electronic Band Structures
Walter Kohn proved: Ground state energy of the electronic system can be written as functional of electron density (instead of wave function).

\[
\Psi(r_1, r_2, \ldots, r_n) \quad \text{Function of 3N variables}
\]

\[
n(r) \quad \text{Function of 3 variables}
\]
Density Functional Theory: Formulation and Implementation

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(c) https://www2.chemistry.msu.edu/faculty/reusch/VirtTextml/Images/hybrid1.gif

First Hohenberg-Kohn theorem

external potential is a unique functional of density

\[ V_{\text{ext}}(r) \]

Schrödinger equation

Integration of \(|\Psi_0|^2\) over N-1 electron coordinates

\[ \Psi_i(r_1, \ldots, r_N) \Rightarrow \Psi_0(r_1, \ldots, r_N) \]
Density Functional Theory: Formulation and Implementation

- Walter Kohn proved: Ground state energy of the electronic system can be written as functional of electron density (instead of wave function)

\[
E[n(r)] = E_{\text{kin}}[n(r)] + V_{\text{ext}}[n(r)] + V_{\text{ee}}[n(r)] \geq E_0
\]

First Hohenberg-Kohn theorem

external potential is a unique functional of density

Second Hohenberg-Kohn theorem

density that minimizes the total energy is the exact groundstate density
Question: Have we made an approximation yet?

1. Yes
2. No
3. I am not sure
Density Functional Theory: Formulation and Implementation

Find the solution in practice: Map to a non-interacting (Kohn-Sham) system

- Reason: We know the kinetic energy of non-interacting electrons

\[
n(r) = \sum_{k=1}^{N} n_k |\varphi_k(r)|^2 \quad \quad E_{\text{kin}}[n(r)] = -\frac{1}{2} \sum_{i=1}^{N} \int \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r})
\]

- Determine the Hamiltonian of that system, such that the ground-state electron density of interacting and non-interacting system are the same
- But: We replaced the interacting by the non-interacting kinetic energy
- And: We also replaced full electron-electron interaction by the Hartree potential
- Make up for the resulting error by introducing an exchange-correlation functional
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\[
\mathcal{H}_{\text{KS}} = -\frac{1}{2} \nabla^2 + V_H(r) + V_{xc}(r) + V_{\text{ext}}(r)
\]

\[
\varphi_i(r) = \epsilon_i \varphi_i(r)
\]
Question: Have we made an approximation yet?

1. Yes
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Density Functional Theory: Formulation and Implementation

Find the solution in practice: Map to a non-interacting (Kohn-Sham) system

\[
\begin{aligned}
\left[-\frac{1}{2} \nabla^2 + V_H(r) + V_{xc}(r) + V_{\text{ext}}(r)\right] \varphi_i(r) &= \epsilon_i \varphi_i(r) \\
\mathcal{H}_{KS} &= V_{xc} = \hat{T} - \hat{T}_S + \hat{U} - V_H
\end{aligned}
\]

- Kinetic energy of non-interacting electrons
- Hartree energy (classical electron-electron interaction)
- External potential (Coulomb potential of ions)
Find the solution in practice: Map to a non-interacting (Kohn-Sham) system

$$\mathcal{H}_{KS} = \left[-\frac{1}{2} \nabla^2 + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})\right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r})$$

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All quantum effects in exchange-correlation potential

- Exact form not known, but reliable approximations available
- Examples: Local-density approximation (take from free-electron gas of same density), generalized-gradient approximation, self-interaction correction, Hubbard $U$, hybrid functionals, exact exchange, Van der Waals, Machine-Learned Functionals, …
- Accuracy: depends on approximation used and material to be studied
Overview

- Motivation and Background
- Formulation and Implementation of Density Functional Theory
- Example Applications: Total Energy and Bulk Modulus, Electronic Band Structures
Predict atomic geometries and crystal structure, e.g. Si

Compression

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Crystal Structure</th>
<th>Point Group</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Si(I) diamond</td>
<td>D4h</td>
<td>4</td>
</tr>
<tr>
<td>13</td>
<td>Si(II) β–tin</td>
<td>D3d</td>
<td>6</td>
</tr>
<tr>
<td>16</td>
<td>Si(XI) Imma</td>
<td>D6d</td>
<td>6</td>
</tr>
<tr>
<td>36</td>
<td>Si(V) hexagonal</td>
<td>D6h</td>
<td>6</td>
</tr>
<tr>
<td>42</td>
<td>Si(VI) orthorhombic</td>
<td>C2/m</td>
<td>10</td>
</tr>
<tr>
<td>79</td>
<td>Si(X) fcc</td>
<td>Cm</td>
<td>12</td>
</tr>
</tbody>
</table>

Decompression

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Crystal Structure</th>
<th>Point Group</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Si(II) β–tin</td>
<td>C2h</td>
<td>980</td>
</tr>
<tr>
<td>2</td>
<td>Si(XII) R8</td>
<td>C2/c</td>
<td>320</td>
</tr>
<tr>
<td>&gt;800</td>
<td>Si(III) BC–8</td>
<td>C2/c</td>
<td></td>
</tr>
<tr>
<td>4400</td>
<td>Si(IV) hex., diamond</td>
<td>C2/c</td>
<td></td>
</tr>
</tbody>
</table>

Other examples include:

- Ab-initio molecular dynamics
- Vibrational properties
- Defect geometries and energetics
- …
Density Functional Theory: Applications

Quantum Espresso
• Integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale
• Core set of codes, plugins for more advanced tasks and third-party packages
• Contributed to by developers across the world
• Can be run on nanoHUB, including for teaching
• Uses plane wave expansion for Kohn-Sham states and pseudo-potentials for electron-ion interaction

Example I: Total-energy calculations and convergence
• Compute total energies for bulk fcc silicon, change either plane-wave cutoff and/or k-point grid

https://nanohub.org/tools/dftqe
Density Functional Theory: Applications

Quantum Espresso
- Uses plane wave expansion for Kohn-Sham states and pseudo-potentials for electron-ion interaction

Example I: Total-energy calculations and convergence

https://nanohub.org/tools/dftqe

(c) Wolfgang Goes, TU Vienna
Example II: Bulk modulus

- At constant temperature, bulk modulus relates change in volume with a change in pressure:

\[ B = -V \frac{dP}{dV} \]

- Decreasing the volume corresponds to positive external pressure on the material
- Pressure and energy are related via:

\[ P = -\frac{dE}{dV} \]

- This leads to the following expression for the bulk modulus:

\[ B = V \frac{d^2E}{dV^2} \]

- Produce an \( E(V) \) curve with nanoHUB by varying volume around \( 0.9V_0 < V < 1.1V_0 \), \( V_0 \) follows from the lattice parameter of Si (5.43 Angstrom)

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Example III: Electronic band structure

- Remember from free-electron gas (one-dimensional periodic lattice):

\[ E(k) = \hbar^2 \frac{k^2}{2m} = \hbar^2 \left( \frac{k_{\text{reduced}} + K}{2m} \right)^2 \]

(c) https://en.wikipedia.org/wiki/Empty_lattice_approximation
Density Functional Theory: Applications

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• in 2D or 3D path in k-space more complicated

• in a real material: electron-ion interaction

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Density Functional Theory: Applications

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- in a real material: electron-ion interaction

2D (square)  

BZ:  

3D (schematic)

(c) https://en.wikipedia.org/wiki/Empty_lattice_approximation

(c) http://lamp.tu-graz.ac.at/~hadley/ss1/empty/empty.php

Density Functional Theory: Applications

Example III: Electronic band structure

- Restart the DFT tool on nanoHUB
- Use 15 to 20 band structure points
- Pick high-symmetry k-points for your band structure path, e.g. (0.5, 0.5, 0.5); (0.0, 0.0, 0.0); (1.0, 0.0, 0.0)
- Compute the band structure and density of states

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Density Functional Theory: Applications

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- Compute the band structure and density of states

- Illustrate the corresponding Brillouin zone path (with the help of the Bilbao Crystallographic Server)
- Label direct and indirect band gaps
- Connect band structure and density of states
- Extract effective masses of electrons and holes
Summary

Literature on Density Functional Theory:
• “Density Functional Theory: An Approach to the Quantum Many-Body Problem”, Dreizler and Gross, Springer
• “Density Functional Theory: A Practical Introduction”, David Sholl, Wiley

Literature on Excited Electronic States:
• “Interacting Electrons: Theory and Computational Approaches”, Reining, Martin, Ceperley, Cambridge

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https://nanohub.org/groups/dft_users