DFT for (almost) Beginners

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What is DFT good for?

- A tool to calculate properties of atoms and molecules
  - Structure
  - Energy, electronic structure (orbitals)
  - Reactivity (Gibbs Free Energies for reactions)
  - Spectroscopic properties: IR spectra, UV-Vis spectra,…

- How it is done?
  - Solving Kohn-Sham Equations (Related to Schrödinger Equation)

- Schrödinger Equation
  - Equation that describes Quantum Mechanical system
    - Classical Mechanics:
      - Motion of particles
      - Newton’s Equations of Motion F = ma
    - Electrodynamics:
      - Behavior of electromagnetic waves
      - Wave Equation, Maxwell’s Equations for electric and magnetic field
    - Quantum Mechanics:
      - Wave/particle duality (particles behave like waves)
      - Wave equation for particles called Schrödinger Equation: $\hat{H}\Psi = E\Psi$
      - $\hat{H}$ is called Hamiltonian operator
What is a Schrödinger Equation?

- **Schrödinger Equation**: \[ \hat{H} \Psi = E \Psi \]
  - Helps us to find energy of the system \( E \) and its wavefunction \( \Psi \)

- **Wavefunction** \( \Psi \)
  - Completely describes the state of the system
  - If I know \( \Psi \), I know EVERYTHING about the system (energy, orbitals, dipole moment, …)
  - It is an extremely complicated function
    - Depends on time and coordinates of all particles in the system
      - \( H^1 \): 1 electron + 1 nucleus
      - \( H^2 \): 1 electron + 1 nucleus  \( \) 13 particles total
      - \( O \): 8 electrons + 1 nucleus  \( \) 13 x 3 = 39 spatial coordinates

  \[
  \Psi(t, q_1, q_2, \ldots, q_{39})
  \]

  Wavefunction for \( H_2O \) is a function of 40 coordinates!
  (Note: not accounting for spin!)

  Chemists usually do not care about time:
  \[
  \Psi(q_1, q_2, \ldots, q_{39})
  \]

  Look for electronic wavefunction:
  \[
  \Psi(q_1, q_2, \ldots, q_{30})
  \]
What is a Schrödinger Equation?

- **Schrödinger Equation:** \( \hat{H} \Psi = E \Psi \)
  - Helps us to find energy of the system (\(E\)) and its wavefunction (\(\Psi\))

- **Hamiltonian:** \( \hat{H} \)
  - Total energy operator
  - Classical Mechanics: equations to calculate physically-observable properties
    - Kinetic Energy = \( \frac{1}{2} \) mass x (velocity)\(^2\)
    - Momentum = mass x velocity
  - Quantum Mechanics: There’s an Operator For That!
    - Operator is a prescription of what to do with a wavefunction (multiply by something, divide, take a derivative…)
    - Get a wavefunction \(\Psi\), apply a total energy operator to it \( \hat{H} \Psi \), out comes the energy: \( E \Psi \)!
    - \( \int \Psi^* \hat{H} \Psi = E \)
    - In general, property \(p\) (momentum, dipole moment, position) has an operator \(\hat{P}\) and to find its value, we calculate it using the wavefunction:
      \[ \int \Psi^* \hat{P} \Psi = p \]
What is a Schrödinger Equation?

- **Schrödinger Equation**: \( \hat{H} \Psi = E \Psi \)
- **Hamiltonian**: \( \hat{H} \)
  - Total energy operator
  - What is inside Hamiltonian?
  - Classical Mechanics:
    - Total Energy = Kinetic Energy of all particles + Potential Energy
  - Quantum Mechanics
    - Hamiltonian = Kinetic Energy operator for all particles + Potential Energy

Hamiltonian for Water Molecule:

\[
\hat{H} = \sum_{i=1}^{10} \frac{-\hbar}{2m_e} \nabla_i^2 + \sum_{i=1}^{3} \frac{-\hbar^2}{2M_N} \nabla_i^2 + \sum_{A=1}^{3} \sum_{B>A}^{3} \frac{Z_A Z_B e^2}{4\pi \varepsilon_0 R_{AB}} + \sum_{i=1}^{3} \sum_{j>i}^{10} \frac{Z_A^2 e^2}{4\pi \varepsilon_0 r_{ij}} + \sum_{i=1}^{10} \sum_{j>i}^{10} \frac{e^2}{4\pi \varepsilon_0 r_{ij}}
\]

- K.E. of electrons
- K.E. of nuclei
- P.E. of nuclear-nuclear repulsion
- P.E. of nuclear-electron attraction
- P.E. of electron-electron repulsion
QM Description of a System

• Describing quantum system is easy!

• Steps:

  1. Write down the Hamiltonian for the system. This is always possible for molecules.

\[
\hat{H} = \sum_{i=1}^{10} \frac{-\hbar}{2m_e} \nabla_i^2 + \sum_{i=1}^{3} \frac{-\hbar^2}{2M_N} \nabla_i^2 + \sum_{A=1}^{3} \sum_{B>A}^{3} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R_{AB}} - \sum_{A=1}^{3} \sum_{i=1}^{10} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \sum_{i=1}^{10} \sum_{j>i}^{10} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}
\]

  2. Find the wavefunction of the system by solving the Schrodinger Equation. This procedure will result in both energy and wavefunction of the system:

\[
\hat{H} \Psi = E \Psi
\]

• BUT
  – Hamiltonian is very complicated because of the many-body interactions in the potential energy term
  – Impossible to solve exactly for systems with 2 or more electrons
  – Wavefunction is a complicated multi-dimensional function
Meaning of the Wavefunction

• Schrödinger Equation:
  – Determine wavefunction $\Psi(q_1, q_2, \ldots, q_{39})$
  – Find all other properties using this wavefunction

• But wavefunction is not something we can measure in the lab or interpret physically

• Square of the wavefunction has a physical meaning
  \[
  \left| \Psi(q_1, q_2, \ldots, q_{30}) \right|^2 dq_1 dq_2 \ldots dq_{30} = \left| \Psi(x_1, x_2, \ldots, x_{10}) \right|^2 dx_1 dx_2 \ldots dx_{10}
  \]
  – Probability that electrons 1, 2, \ldots, 10 are found simultaneously in the volume elements associated with each electron: $dx_1, dx_2, \ldots, dx_{10}$

• Total probability of finding these 10 electrons anywhere in the space must be 1:
  \[
  \int_{\Omega} \left| \Psi(x_1, x_2, \ldots, x_{10}) \right|^2 dx_1 dx_2 \ldots dx_{10} = 1
  \]
Electron Density

- Square of the wavefunction defines probability density

\[ |\Psi(x_1, x_2, ..., x_{10})|^2 \, dx_1 \, dx_2 \ldots dx_{10} \]

\[ \int_{\Omega} |\Psi(x_1, x_2, ..., x_{10})|^2 \, dx_1 \, dx_2 \ldots dx_{10} = 1 \]

- It has a physical meaning, but it is still a function of many variables

- The goal is to find something similar to the wavefunction, but much simpler: Electron Density

  - Take probability density function
  - Sum all of the probabilities covering all space for electrons 2-10:

\[ \rho(x) = N \int \left| \Psi(x, x_2, ..., x_{10}) \right|^2 \, dx_2 \ldots dx_{10} \]

\[ N = 10 \) (number of electrons)\]
Electron Density

- The goal is to find something similar to the wavefunction, but much simpler: **Electron Density**
  - Take probability density function
  - Sum all of the probabilities covering all space for electrons 2-10:
    \[
    \rho(x) = 10 \int_{x_2, x_3, \ldots, x_{10}} |\Psi(x, x_2, \ldots, x_{10})|^2 \, dx_2 \ldots dx_{10}
    \]

- Electron density can be measured (X-ray diffraction)

\(\rho(x)\): How likely it is to find one electron within a particular volume element \(dx\) while all other electrons can be anywhere?
Electron Density vs. Wavefunction

Can we replace wavefunction by the electron density?

\[ \rho(x) \text{ vs. } \Psi(x_1, x_2, \ldots) \]

Schroedinger (1926): \( \Psi(x_1, x_2, \ldots) \)
- All I need to describe the system completely is the wavefunction

Hohenberg and Kohn (1964): \( \rho(x) \)
- Theorem 1: Electron density uniquely determines the properties of the system
  \[ E[\rho] = T[\rho] + E_{ee}[\rho] + E_{Ne}[\rho] \]
  - Kinetic Energy + Potential energy
- Theorem 2: Recipe for finding the true ground state density (it is the density that gives minimal energy)
Density Functional Theory

- The most important quantity is the electron density – it tells us everything we need to know about the system

\[ \rho(x) = N \int_{x_2, x_3, \ldots, x_N} |\Psi(x, x_2, \ldots, x_N)|^2 \, dsdx_2 \ldots dx_N \]

- Energy of the system is given as a functional of the electron density:

\[ E[\rho] = T[\rho] + E_{ee}[\rho] + E_{Ne}[\rho] \]

  - Unfortunately nobody knows the exact form of the terms

\[ E[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho] \]

  Kinetic energy of non-interacting system  +  Electrostatic energy of Charge distribution  +  Everything we do not know
Kohn-Sham (KS) Equations: Finding the Density

- The true density for the system of interacting electrons may be identical with the density for a system of non-interacting electrons
  - Schrodinger equation is separable and a Slater determinant of orbitals of non-interacting electrons is an exact solution defining the exact density

\[
\Psi_{\text{elec}} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1 \alpha & \phi_1 \beta & \phi_2 \alpha & \ldots & \phi_n \beta \end{vmatrix} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1 & \varphi_2 & \varphi_3 & \ldots & \varphi_n \end{vmatrix}
\]

\[
\varphi = \phi(x, y, z) \omega, \quad \omega = \alpha, \beta
\]

**KS orbital** = orbital that describes an electron in a system with non-interacting electrons with the same density as the one we are looking for.
Kohn-Sham (KS) Equations: Finding the Density

$$\varphi = \phi(x, y, z) \omega, \quad \omega = \alpha, \beta$$

**spinorbital**  **spatial orbital**  **spin**

$$\rho = \sum_{i}^{n} N_i \phi_i^* \phi_i$$

$$E[\rho] = T[\rho] + E_{ee}[\rho] + E_{Ne}[\rho]$$

$$T[\rho] = T_{non}[\rho] + \Delta T[\rho]$$

$$E[\rho] = \sum_{i}^{n} \left\langle \phi_i | t(i) | \phi_i \right\rangle - \sum_{i,A} \left\langle \phi_i \left| \frac{Z_A}{r_i - R_A} \right| \phi_i \right\rangle + \sum_{i} \left\langle \phi_i \left| \frac{1}{2} \int \frac{\rho(r')}{r_i - r'} dr' \right| \phi_i \right\rangle + E_{XC}$$

$$E_{tot}[\rho] = E[\rho] + \sum_{A>B}^{\text{atoms}} \frac{Z_A Z_B}{|R_A - R_B|}$$
Kohn-Sham (KS) Equations: Finding the Density

• Use SCF (self-consistent field) approach similar to HF to find density
  – Minimize the energy $E[\rho]$ with respect to the forms of the orbitals for the noninteracting electrons

\[ h^{KS}_i \varphi_i = \varepsilon_i \varphi_i \]

\[ h^{KS}_i = -\frac{1}{2} \nabla_i^2 - \sum Z_A \frac{1}{|r_i - R_A|} + \int \frac{\rho(r')}{|r_i - r'|} dr' + V_{XC}[\rho] \]

\[ \varphi_i = \sum c_{ij} \chi_j \]

– Equations have to be solved iteratively since KS operator $h_i$ depends on the density (and orbitals)
– Very similar to solving Hartree-Fock equations

\[ V_{XC} \] is approximate
(if exact, we would know the exact $E$)
Periodic Systems

- Crystalline solids consist of a periodic array of atoms called the lattice
  - Semiconductors (Si, GaAs)
  - Conductors (Ni, Al, Cu, Au)
- This periodicity results in a periodic potential acting on electrons in this system

STM image of Ni (100) surface

\[ V(r) \sim 1/r \]

\[ V^{sp}(r + R) = V^{sp}(r) \]

https://archive.education.mrsec.wisc.edu/SlideShow/slides/nanoscale/Ni_atoms.html
Bloch Theorem

When the potential in the single-particle Hamiltonian has the translational periodicity of the lattice

\[ V^{sp}(\mathbf{r} + \mathbf{R}) = V^{sp}(\mathbf{r}) \]

The single-particle wavefunctions have the same symmetry, up to a phase factor:

\[ \psi_k(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_k(\mathbf{r}) \]

In other words, the single particle wavefunctions must have the following form

\[ \psi_k(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_k(\mathbf{r}) \]