DFT for (almost) Beginners

Elena Jakubikova
Chemistry Department
North Carolina State University
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
      - \( \text{H}^1 \): 1 electron + 1 nucleus
      - \( \text{H}^2 \): 1 electron + 1 nucleus
      - \( \text{O} \): 8 electrons + 1 nucleus
        - 13 particles total
        - 13 \times 3 = 39 spatial coordinates
      - Wavefunction for \( \text{H}_2\text{O} \) is a function of 40 coordinates!
        - (Note: not accounting for spin!)
  - Chemists usually do not care about time:
    - Look for electronic wavefunction: \( \Psi(q_1, q_2, ..., q_{39}) \)
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 = \( \frac{1}{2} \text{ mass} \times \text{ (velocity)}^2 \)
    - Momentum = mass \times \text{ 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: \( E \psi \mid \int \psi^* \hat{H} \psi = E \)
    - 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:

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

- 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
  $\left| \Psi(q_1, q_2, \ldots, q_{39}) \right|^2 dq_1 dq_2 \ldots dq_{30} = \left| \Psi(x_1, x_2, \ldots, x_{10}) \right|^2 dx_1 dx_2 \ldots dx_{10}$
  - Probability that electrons 1, 2, ..., 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
  \[ |\Psi(x_1, x_2, \ldots, x_{10})|^2 \, dx_1 \, dx_2 \ldots \, dx_{10} \]
  \[ \int_{\Omega} |\Psi(x_1, x_2, \ldots, x_{10})|^2 \, dx_1 \, dx_2 \ldots \, dx_{10} = 1 \]
  - It has a physical meaning, but 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:
    \[ \rho(x) = N \int_{x_2,x_3,\ldots,x_{10}} |\Psi(x, x_2, \ldots, x_{10})|^2 \, dx_2 \ldots \, dx_{10} \]
    \[ N = 10 \text{ (number of electrons)} \]
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:
    \[
    \rho(x) = 10 \int_{x_2, x_3, \ldots, x_{10}} \left| \Psi(x, x_2, \ldots, x_{10}) \right|^2 dx_2 \ldots dx_{10}
    \]
  - 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?

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

- Schrödinger (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

\[ \rho(x) = N \int_{x_2, x_3, \ldots, x_N} |\Psi(x_1, x_2, \ldots, x_N)|^2 \, dx_2 \ldots dx_N \]

- 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

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

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

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

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

\[ \rho = \sum_{i}^{n} N_i \varphi_i^* \varphi_i \]

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

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

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

\[ E_{\text{tot}}[\rho] = E[\rho] + \sum_{A>B} \frac{Z_A Z_B}{R_A - R_B} \]
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

$$h_{i}^{KS} \varphi_{i} = \varepsilon_{i} \varphi_{i}$$

$$h_{i}^{KS} = -\frac{1}{2} \nabla_{i}^{2} - \sum \frac{Z_{A}}{|r_{i} - R_{A}|} + \int \frac{\rho(r')}{|r_{i} - r'|} dr' + V_{XC}[\rho]$$

$$\varphi_{i} = \sum_{j} c_{ij} \chi_{j}$$

- 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

\[ V(r) \sim \frac{1}{r} \]

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

STM image of Ni (100) surface

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

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

Solutions to Schr. Eq. in a periodic potential look like a plane wave modulated by a periodic function with the same periodicity as the crystal.