First Principles Calculation
Hands on Session (I)

Water molecule
Outline

• First-principles calculation
  • What to solve?
    • Schrödinger equation
    • Born-Oppenheimer approximation
    • Density Functional Theory and Kohn-Sham equation
  • What we get?
    • Molecule orbitals
  • How to solve it fast?
    • Basis set and pseudopotential

• H₂O molecule
  • Geometry relaxation / Self-consistent field (SCF) calculation
  • Wavefunctions
  • Dipole moment
Schrödinger equation

- Time-independent Schrödinger equation

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

- For systems of atoms:

\[ \left[ \hat{T}_n + \hat{T}_e + \hat{V}_{n-n} + \hat{V}_{n-e} + \hat{V}_{e-e} \right] \Phi(\{R\}, \{r\}) = E \Phi(\{R\}, \{r\}) \]

  - \( \hat{T}_i \): Kinetic term of nuclei(n) or electrons ε
  - \( \hat{V}_{i-j} \): Coulomb interaction between nucleus-nucleus (n-n), nucleus-electron (n-e) and electron-electron (e-e) in \( 1/r \) form
  - \( \Phi(\{R\}, \{r\}) \): wavefunction of both nuclei and electrons
  - \( \{R\} \): positions of nuclei, \( 3N_n \) variables
  - \( \{r\} \): positions of electrons, \( 3N_e \) variables

- Equation of \( 3N_n + 3N_e \) variables!
Born–Oppenheimer approximation

• Nuclei are much heavier than electrons ($m_p \approx 1836m_e$)
• Electron moves much faster than nuclei and always ‘feel’ interaction as nuclei are not moving
• Schrödinger equation of electrons at specific nuclei positions

$$\left[ \hat{T}_e + \hat{V}_{n-e} + \hat{V}_{e-e} \right] \Psi(\{r\}) = E \Psi(\{r\})$$

• $\Psi(\{r\})$: electron wavefunctions of $3N_e$ variables
• $\hat{V}_{n-e}$ and $\Psi(\{r\})$ depends parametrically on nuclei positions $\{R\}$
Density functional theory

• $3N_e$ variables, each in range $(-\infty, \infty)$; Still hard!

• Particle density $\rho$: number of particles per unit volume, only 3 variables (particle=electron in this problem)

• Hohenberg-Kohn theorem:
  • 1. The ground state energy of a many-particle system is a unique functional of the particle density: $E_0 = E[\rho_0]$
  • 2. Correct density minimize $E_0$

• The ground state can be solved by finding $\rho_0$
Kohn-Sham equation

• Ansatz: The ground state density can be represented by a Slater determinant of single-particle wavefunctions

\[ \Psi({\{r\}}) = \Psi(r_1, r_2, ..., r_n) = \begin{bmatrix} \psi_1(r_1) & \cdots & \psi_n(r_1) \\ \vdots & \ddots & \vdots \\ \psi_1(r_n) & \cdots & \psi_n(r_n) \end{bmatrix} \]

• Single-particle wavefunctions (Kohn-Sham orbitals) follows

\[ (\hat{T} + \hat{V}_{ext} + \hat{V}_{\text{Hartree}} + \hat{V}_{xc})\psi_i(r) = \varepsilon_i\psi_i(r) \]

  - \( \hat{T} \) : kinetic energy
  - \( \hat{V}_{ext} \) : external potential (from nuclei)
  - \( \hat{V}_{\text{Hartree}} \): classical Coulomb interaction between electrons
  - \( \hat{V}_{xc} \) : exchange-correlation functional (quantum effect of Coulomb interaction)

• Exact \( \hat{V}_{xc} \) to exact solution
Exchange-correlation functional

• Exact $\hat{V}_{xc}$ is unknown

• Approximation:
  • Local density approximation (LDA)
  • Generalized gradient approximation (GGA)
    • Perdew-Burke-Ernzerhof (PBE)
  • Hybrid: mix Hartree-Fock and LDA/GGA

• LDA/GGA: $\hat{V}_{xc}$ is solely functional of density $\rho$
• Hybrid: $\hat{V}_{xc}$ depends on $\rho$ and $\{\psi_i\}$
Self consistent field (SCF)

Finish! → Yes → $\rho_{j+1} = \rho_j$? → No → $\rho_j$ → $V_H, V_{xc}$ → $\psi_i, \varepsilon_i$ → External potential → Atomic Density
Wavefunctions : Molecule orbitals

- Molecule orbitals : linear combination of atomic orbitals (LCAO)
- \( \text{H}_2 : 1s \text{ AO} + 1s \text{ AO} \)
  - one bonding MO : density concentrates
  - one anti-bonding MO : nodal plane
Molecule orbitals

• $\sigma$ and $\pi$ bonds for two $p$ orbitals
Basis set and pseudo potential

• Electron density $\rho(r)$ and wavefunction $\psi(r)$ are functions of 3 spatial coordinates
• Represented with a basis set
  • Atomic orbitals
  • Planewaves
• Partial differential equation $\rightarrow$ Linear algebra

• Wavefunctions of atoms: O $[1s^2]2s^22p^4$
• Core electrons: approximately the same as those in individual atoms: O $[1s^2]$
• Pseudo potential:
  • A “pseudo” atom with only valence electrons
  • Less electrons and allows for less basis functions

• All electrons + $r^{-1}$ potential $\approx$ Valence electrons + pseudo potential
Example: $\text{H}_2\text{O}$ molecule

- 3 atoms
- 10 electrons (H $1s^1$, O $1s^22s^22p^4$)
- 8 valence electrons (H $1s^1$, O $2s^22p^4$)
- Two H-O bonds
- Asymmetric $sp^3$ hybridization
- $C_{2v}$ point group symmetry

Practice in terminal

• Top left: Applications – System Tools – Terminal

• Type commands and press enter to run commands in terminal

• Run following commands one by one to start:
  • cp –r /home/chem263/h2o ./
  • cd h2o/input
H₂O in Quantum-Espresso

- Quantum-Espresso: an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials. [https://www.quantum-espresso.org/]

- Help of two programs used in this lesson: pw.x and pp.x
  - [https://www.quantum-espresso.org/Doc/INPUT_PW.html]
  - [https://www.quantum-espresso.org/Doc/INPUT_PP.html]

- Geometry relaxation of H₂O: (<2min)
  - Check input file: gedit relax.in
  - Run: pw.x < relax.in > relax.out
  - Check output file: gedit relax.out
Run a calculation

• ‘relax’ for a geometry relaxation
• set files/folder to read and write and what to write
• 15.12 Bohr (8Å) cubic cell
• 3 atoms and 2 types of atoms (H/O)
• basis set size of wavefunction
• Species: Pseudo potentials filename
• Position of 3 atoms
Parse outputs

- Check output file: `gedit relax.out` and find lines above
  - What is the difference between initial (in input) and final positions?

- Visualize the structure
  - `xcrysdent --pwo relax.out`
  - Click "OK"
  - Click "Continue" to open optimized coordinates

Final energy = -34.6670983123 Ry
Begin final coordinates

```
ATOMIC_POSITIONS (angstrom)
O        4.000000000   4.000000000   4.262145720
H        3.230906166   4.000000000   4.868927140
H        4.769093834   4.000000000   4.868927140

End final coordinates
```
Parse output

• View the structure
• Measure bond lengths, angles …
H₂O structure

• Question: why different?
  • Exchange-correlation functional
  • Basis set
  • Pseudo potential
  • Box size
  • Experimental error

Self-consistent field (SCF)

- Iteratively solve the Kohn-Sham equation to get wavefunctions
- We have done multiple SCF in geometry relaxation!

Use optimized geometry

More wavefunctions to plot
Correct the artificial cell size; here only used to show the dipole in output
Dipole moment

- Dipole moment
  \[ p = \left| \sum_i q(r_i - r_0) \right| \]
- Experiment: 1.8546 Debye
- Calculation: 1.8353 Debye

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<tr>
<th>reference position (x0):</th>
<th>7.55890453</th>
<th>7.55890453</th>
<th>8.34095072 bohr</th>
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<tbody>
<tr>
<td>Dipole moments (with respect to x0):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elect</td>
<td>-0.0000</td>
<td>-0.0000</td>
<td>0.7221 au (Ha),</td>
</tr>
<tr>
<td>Ionic</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000 au (Ha),</td>
</tr>
<tr>
<td>Total</td>
<td>-0.0000</td>
<td>-0.0000</td>
<td>0.7221 au (Ha),</td>
</tr>
</tbody>
</table>
Symmetry

- Point group \( C_{2v} \)
- Symmetry operation
  - \( E \)
  - \( C_2 \)
  - \( S_v \)
  - \( S_v' \)
- Question:
  - Identify the symmetry operation from structure?
Plot wavefunctions

- Parse the output files, only possible after SCF
  - `pp.x < wave1.in > wave1.out`
  - `pp.x < wave2.in > wave2.out`
  - ...
  - `pp.x < wave5.in > wave5.out`

- Wavefunctions are sorted in ascending order according to their eigenvalues

```
&INPUTPP
  prefix = "h2o"
  outdir = "./"
  filplot = "1.wave"
  plot_num = 7,
  kpoint(1) = 1,
  kpoint(2) = 1,
  kband(1) = 1,
  kband(2) = 1,
  lsign = .true.
/
&PLOT
  iflag = 3
  output_format = 5,
  fileout = "wave.1.xsf"
/
```
Plot wavefunctions

- `xcrysden --xsf wave.1.xsf`
- Menu - Tools - Data grid – OK
  - Turn on transparency
  - Tick “Render +/-” [except for wave.1.xsf]
  - Set a reasonable isovalue
  - Press “Submit” to update the display
Molecule orbitals

- 4 occupied orbitals for 8 electrons
- 1 unoccupied orbital shown

Questions
  - $\sigma$ or $\pi$ orbitals?
  - Number of nodal surfaces?
  - What the energy of each orbital means?
The five occupied and the lowest three unoccupied molecular orbitals of the isolated molecule $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)$

The two lowest energy orbitals $1a_1$(non-bonding) and $2a_1$(bonding) are contributed from the 1s and 2s (mostly) orbitals of the oxygen atom, respectively, and are consequentially approximately spherical.

The highest occupied molecular orbital (HOMO), $1b_1$, is predominantly $p_z^2$ in character with no contribution from the hydrogen 1s orbital and mainly contributes to the "lone pair" effects. The $2a_1$, $1b_2$ and $3a_1$ all contribute to the O-H bonds.

The two lowest unoccupied molecular orbitals $4a_1$ (LUMO) and $2b_2$ are O-H antibonding orbitals.