Hartree-Fock Theory

Part I. Total and Orbital Energies

February 19, 2018

Schrödinger equation for a molecular system

- The Schrödinger equation is

$$\hat{H}\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$

- The Hamiltonian is

$$\hat{H} = \sum_i \left(-\frac{1}{2} \bigtriangledown_i^2 - \sum_A \frac{Z_A}{\left|\vec{r}_i - \vec{R}_A\right|} \right) + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

which includes

- kinetic energy, $-\frac{1}{2}\bigtriangledown_i^2$, of each electron
- nuclear attraction $-\sum_A \frac{Z_A}{\left|\vec{r}_i - \vec{R}_A\right|}$
- electron-electron repulsion, $\sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$

Hartree-Fock Energy for a Slater Determinant

- For N electrons in N orthonormal molecular orbitals, the Slater determinant is

$$\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \frac{1}{\sqrt{(N)!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix}$$

The energy of this Slater determinant is

$$E_{HF} = V_{NN} + \sum_{i=1}^{N} h_i + \sum_{i<j}^{N} [(ii|jj) - (ij|ij)]$$

where

$$\begin{aligned} h_i &= \int d\vec{r}\, \psi_i^*(\vec{r}) \left[-\frac{1}{2} \bigtriangledown^2 - \sum_A \frac{Z_A}{\left|\vec{r} - \vec{R}_A\right|} \right] \psi_i(\vec{r}) \\ (ii|jj) &= \iint d\vec{r}_1 d\vec{r}_2 \psi_i^*(\vec{r}_1)\psi_i^*(\vec{r}_1) \frac{1}{r_{12}} \psi_j(\vec{r}_2)\psi_j(\vec{r}_2) \\ (ij|ij) &= \iint d\vec{r}_1 d\vec{r}_2 \psi_i^*(\vec{r}_1)\psi_j^*(\vec{r}_1) \frac{1}{r_{12}} \psi_i(\vec{r}_2)\psi_j(\vec{r}_2) \end{aligned}$$

- Hartree-Fock energy (of a Slater determinant) is

$$\begin{aligned} E_{HF} &= V_{NN} + \sum_{i=1}^{N_e} h_i + \sum_{i<j}^{N_e} [(ii|jj) - (ij|ij)] \\ &= V_{NN} + \sum_{i=1}^{N_e} h_i + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1}^{N_e} [(ii|jj) - (ij|ij)] \end{aligned}$$

- For closed-shell molecules

$$\begin{aligned} E_{HF} &= V_{NN} + 2 \sum_{i=1}^{N_e/2} h_i + \sum_{i<j}^{N_e/2} [2(ii|jj) - (ij|ij)] \\ &= V_{NN} + \sum_{i=1}^{N_e/2} (h_i + \varepsilon_i) \end{aligned}$$

- We search for an optimal set of occupied molecule orbitals, $\psi_i(\vec{r})$, to minimize this energy. In practice, this is done through the **self-consistent field** (SCF) procedure.
- In DFT calculations, the $i = j$ term of Coulomb energy is no longer cancelled by its Hartree Fock exchange counterpart. This is called the **self-interaction error**.

- Notation for molecular orbitals
  - $i, j, \cdots$, **occupied** molecular orbitals
  - $a, b, \cdots$, **unoccupied (virtual)** molecular orbitals
  - $p, q, \cdots$, occupied or unoccupied molecular orbitals

- Orthonormality condition

$$\langle \psi_p | \psi_q \rangle = \int \psi_p^*(\vec{r}) \psi_q(\vec{r}) d\vec{r} = \delta_{pq}$$

- Orbital energies

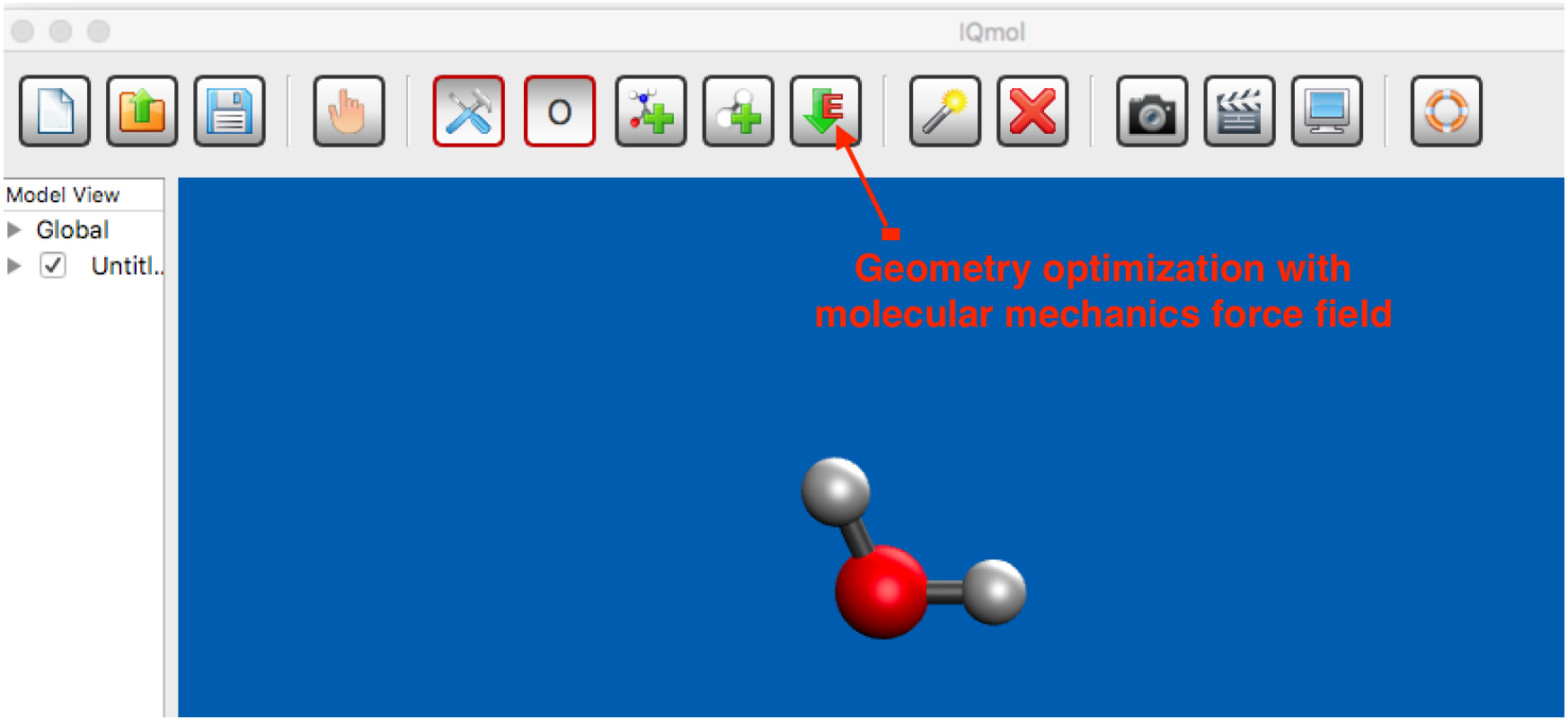
$$\varepsilon_p = h_{pp} + \sum_{i=1}^{N_e/2} [2(pp|ii) - (pi|pi)]$$

- **Electron density**

$$\rho(\vec{r}) = \sum_{i=1}^{N_{occ}} (\psi_i(\vec{r}))^2$$

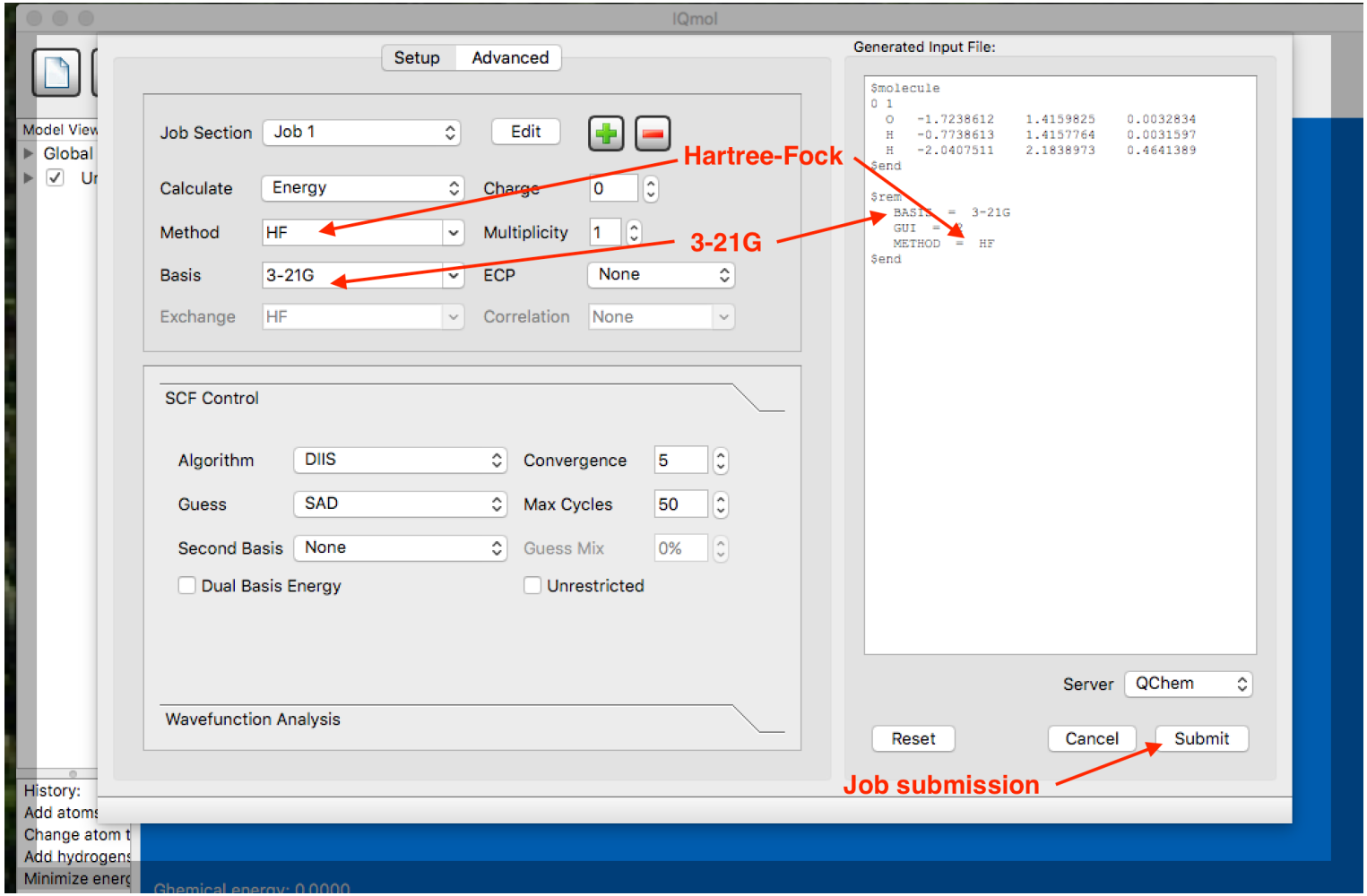
Case Study: Water Molecule

- Use IQmol to draw a water molecule
- Use molecular mechanics to optimize its geometry



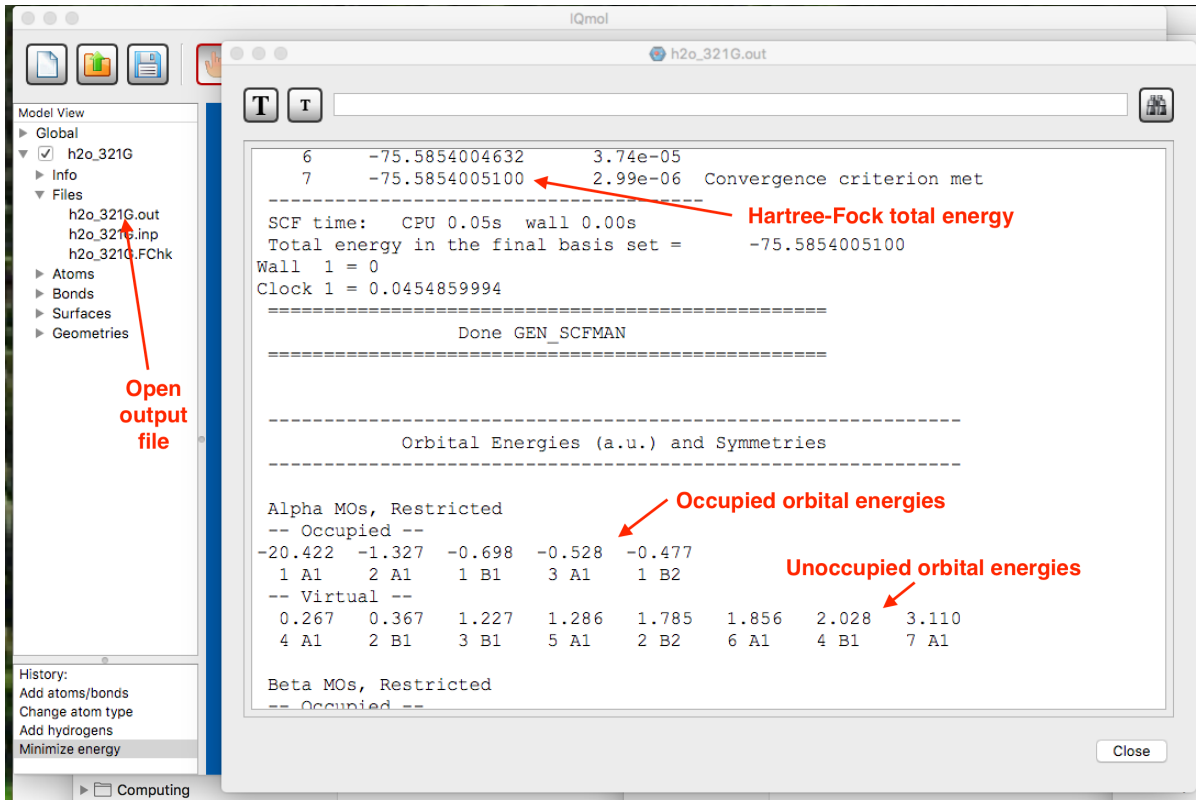
Case Study: Water Molecule

- Use IQmol to run Hartree-Fock/3-21G calculation



Case Study: Water Molecule

- In IQmol, open the output file to draw a water molecule
- Find Hartree-Fock total and orbital energies



- Go to schooner, and make a new folder
- Copy
  - /home/yihan/qm_tutorial/qchem_files/FCIDump
  - /home/yihan/qm_tutorial/qchem_files/read_fcidump.py

  to the new folder.
- Compute the Hatree-Fock total and orbital energies

```python
import numpy as np
from read_fcidump import *

integrals = ElectronIntegrals()
integrals.read_from_fcidump("FCIDUMP")
NOrb = integrals.NOrb
NEle = integrals.NEle
NOcc = NEle/2
NVir = NOrb - NOcc
print("NOrb=", NOrb, "NEle=", NEle, "NOcc=", NOcc, "NVir=", NVir)
ENuc = integrals.nuclear_repulsion_energy
print("ENuc=", ENuc)

E1 = 0.0
for i in range(0, NOcc):
        E1 += 2*integrals.one_e_integrals[i,i]

print("E1=", E1)

E2 = 0.0
for j in range(0, NOcc):
        for i in range(0, NOcc):
                E2 += 2.0 * integrals.two_e_integrals[i,i,j,j]
                E2 -= 1.0 * integrals.two_e_integrals[i,j,i,j]

print("E2=", E2)

ETot = ENuc + E1 + E2
print("ETot=", ETot)

orbital_energies = np.zeros(NOrb)
for p in range(0, NOrb):
        orbital_energies[p] = integrals.one_e_integrals[p,p]
        for i in range(0, NOcc):
                orbital_energies[p] += 2.0 * integrals.two_e_integrals[p, p, i, i]
                orbital_energies[p] -= 1.0 * integrals.two_e_integrals[p, i, p, i]

print("orbital_energies=", orbital_energies)

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