FACULTY OF SCIENCES

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# PROGRAMMING PROJECT 3: RESTRICTED HARTREE-FOCK

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# WHY?

# WHY?

- Schrödinger Equation

$$\hat{\boldsymbol{H}}\Psi = E\Psi$$

- True Hamiltonian

$$\hat{\boldsymbol{H}} = \sum_{i}^{N} \hat{h}(i) + \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

# What do we need?

1. Slater Determinant

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\boldsymbol{x}_1) & \cdots & \chi_n(\boldsymbol{x}_1) \\ \cdots & \cdots & \cdots \\ \chi_1(\boldsymbol{x}_n) & \cdots & \chi_n(\boldsymbol{x}_n) \end{vmatrix}$$

2. spin-orbitals

$$\chi_i(\boldsymbol{x_j}) = \psi_i(\boldsymbol{r}_j)\gamma(\boldsymbol{\omega}_j)$$

- Expectation value

$$\langle \Psi | \, \hat{\boldsymbol{H}} \, | \Psi \rangle = \sum_{i}^{N} \langle \chi_i | \, \hat{h}(1) \, | \chi_i \rangle + \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} \left( \int \chi_i^*(1) \chi_i(1) \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \chi_j^*(2) \chi_j(2) d1 d2 - \int \chi_i^*(1) \chi_j(1) \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \chi_j^*(2) \chi_i(2) d1 d2 \right)$$

- Energy is stationary

$$E(\chi_i + \delta\chi_i) - E(\chi_i) = \delta E = 0$$

- Correct for non-orthonormality

$$L = E - \sum_{ij} \epsilon_{ij}(\langle\chi_i|\chi_j\rangle - \delta_{ij})$$

$$\delta L = \sum_i \langle\delta\chi_i|\,\hat{h}(1) + \sum_j (\hat{J}_j - \hat{K}_j)\,|\chi_i\rangle - \sum_{ij} \epsilon_{ij}\,\langle\delta\chi_i|\chi_j\rangle + CC = 0$$

# Some Helpfull Operators

- Coulomb operator

$$\langle \chi_i | \, \hat{J}_j \, | \chi_i \rangle = \int \chi_i^*(1) \chi_j^*(2) \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \chi_i(1) \chi_j(2) d1 d2$$

- exchange operator

$$\langle \chi_i | \, \hat{K}_j \, | \chi_i \rangle = \int \chi_i^*(1) \chi_j(1) \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \chi_j^*(2) \chi_i(2) d1 d2$$

- Condition

$$\left(\hat{h}(1) + \sum_j (\hat{J}_j - \hat{K}_j)\right) \chi_i = \sum_j \epsilon_{ij} \chi_j$$

- Hartree-Fock Equation

$$\hat{f}(1)\chi_i = \epsilon_i \chi_i$$

# Spin elimination

- No interaction with spin $\rightarrow$ remove it
- Example: $\alpha$-Spin

$$\langle\alpha|\,\hat{f}(1)\,|\psi_i(\boldsymbol{r}_1)\alpha\rangle = \epsilon_i\psi_i(\boldsymbol{r}_1)$$

- Exchange operator?

$$\hat{K}_j\,|\psi_i(1)\alpha(1)\rangle = \int \chi_j(1)\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}\chi_j^*(2)\psi_i(2)\alpha(2)d1d2$$

# Restricted Hartree Fock

- Only paired electrons (Pauli principle)
- In the same orbitals

$$\hat{f}(1) = \hat{h}(1) + 2\sum_{i}^{N/2} \hat{J}_i - \sum_{i}^{N/2} \hat{K}_i$$

# SOLVING EQUATIONS

- Begin iterations

$$\hat{\boldsymbol{H}}^{core}\boldsymbol{C} = \boldsymbol{SC}c$$

- Roothaan-Hall Equations

$$\boldsymbol{FC} = \boldsymbol{SC}\epsilon$$

# The Density Matrix

- Expansion in the basis

$$\hat{J}_i = \int \sum_{\sigma} C_{\sigma}^{*} \phi_{\sigma}^{*}(x_j) \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_j|} \sum_{\nu} C_{\nu} \phi_{\nu}(x_j) dx_j$$

- Density Matrix

$$D_{\sigma\nu} = 2 \sum_{j}^{N/2} C_{\sigma j}^{*} C_{\nu j}$$

# How?

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# How?

```
class Molecule:
    def __init__(self, geom_file):
        if "pubchem" in geom_file:
            self.id = psi4.geometry(geom_file)
        else:
            input = open(filename, 'r').readlines()
            data = ""
            for i, row in enumerate(input[1:]):
                Z, x, y, z = row.split()
                data += f"{int(float(Z))} {x} {y} {z}\n"
            ...
```

```
        ...
        data += "units bohr"
        self.id = psi4.geometry(data)
        self.id.update_geometry()
        self.wfn =  psi4.core.Wavefunction.build(self.id, psi4.core.
            ↪ get_global_option('basis'))
        self.basis = self.wfn.basisset()
        self.integrals = psi4.core.MintsHelper(self.basis)
        self.occupied = self.wfn.nalpha()
```

# NUCLEAR REPUSLTION ENERGY

```
def displayNucRep(self):
    return self.id.nuclear_repulsion_energy()
```

# One electron integrals

```
def one_electron_integrals(self):
    self.S = self.integrals.ao_overlap().np
    self.T = self.integrals.ao_kinetic().np
    self.V = self.integrals.ao_potential().np
    self.H_core = self.T + self.V
```

# TWO ELECTRON INTEGRALS

```
def ElectronRepulsion(self):
    self.tei = self.integrals.ao_eri().np
```

# The Initial (Guess) Matrix

```
def density_matrix(self, initial=False):
    # First time guess
    if initial:
        self.C = eigh(self.H_core, self.S)[1]

    # Return the density matrix
    self.D = 2 * np.einsum('ij,jk->ik', self.C[:, :self.occupied], self.C.
        ↪ T[:self.occupied, :], optimize=True)
```

# The Fock Matrix

```
def fock_matrix(self):
    # tei is a 4D numpy array where the indices are given according to the
        ↪ integral in step 2.3
    # The coulomb integral is the tei matrix, the exchange matrix is the
        ↪ tei matrix where the second and third
    # indices are swapped
    self.F =  self.H_core + np.einsum('ij,uvij->uv', self.D, self.tei -
        ↪ 1/2 * np.swapaxes(self.tei, 1, 2))
```

# THE SCF ENERGY

```
def electronic_energy(self):
    self.E_elec = 1/2*np.einsum('ij,ij', self.D, self.H_core + self.F)

def total_energy(self):
    self.E_tot = self.id.nuclear_repulsion_energy() + self.
        ↪ electronic_energy()
```

# THE SCF ENERGY

```
def SCF(self):
"""
Input:
    molecule: psi4.core.Molecule

Performs the restricted hartree fock iterations and print the
    ↪ progress on screen
"""

iteration = 0
iterations = [0]
energies = list()
```

```
        # Init
        self.one_electron_integrals()
        self.ElectronRepulsion()
        self.density_matrix(initial=True)
        self.fock_matrix()
        self.electronic_energy()
        self.total_energy()

        prev_D = self.D
        prev_E_elec = self.E_elec

        energies.append(prev_E_elec)
```

```
        # Convergence variables
        delta_E_elec = 1
        delta_D = 1

        # Print header
        print("{} {:>15} {:>15} {:>15}".format("i", "E(elec)" , "Delta(E)"
            ↪ , "RMS(D)"))
```

```
        # Repeat until the density and enery differences are in there
            ↪ thresholds or max iteration is reached
        while np.abs(delta_D) > 10**(-4) and iteration < 50:
            # Update
            self.C = eigh(self.F, self.S)[1]
            self.density_matrix()
            self.fock_matrix()
            self.electronic_energy()
```

```
            # Tets convergence
            delta_E_elec = self.E_elec - prev_E_elec
            delta_D = np.sqrt(np.einsum('ij->', np.square(self.D - prev_D)
                ↪ ))
```

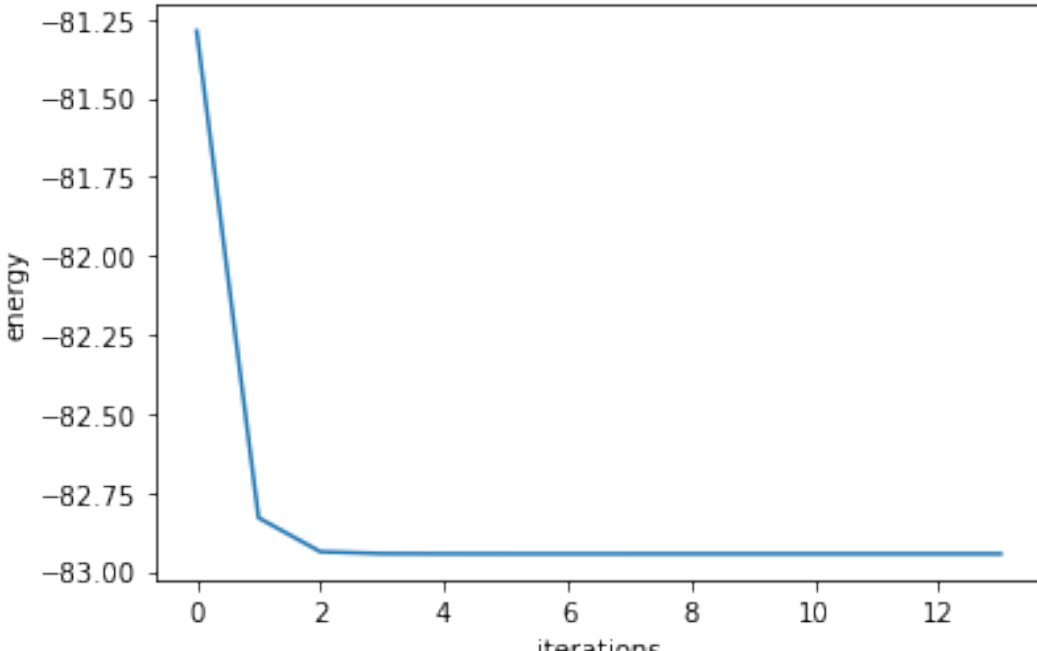
```
            # Print progress
            iteration += 1
            iterations.append(iteration)
            energies.append(self.E_elec)
            print("{} {:>15.10f} {:>15.10f} {:>15.10f}".format(iteration,
                ↪ E_elec , delta_E_elec, delta_D))

            prev_D = self.D
            prev_E_elec = self.E_elec
        print(self.total_energy)
```

```
        fig = plt.figure()
        ax = fig.add_subplot()
        ax.set_xlabel("iterations")
        ax.set_ylabel("energy")
        ax.plot(iterations, energies)
        plt.show()
```

# WATER

| i | E(elec) | Delta(E) | RMS(D) |
|---|---|---|---|
| 1 | −82.8304924416 | −1.5423289586 | 3.6533461690 |
| 2 | −82.9378550598 | −0.1073626183 | 0.9591407297 |
| 3 | −82.9438448043 | −0.0059897445 | 0.1736633778 |
| 4 | −82.9443390579 | −0.0004942536 | 0.0620522727 |
| 5 | −82.9444231232 | −0.0000840653 | 0.0215985664 |
| 6 | −82.9444414809 | −0.0000183577 | 0.0105096537 |
| 7 | −82.9444457095 | −0.0000042285 | 0.0048771593 |
| 8 | −82.9444466920 | −0.0000009825 | 0.0023545591 |
| 9 | −82.9444469206 | −0.0000002287 | 0.0011290864 |
| 10 | −82.9444469738 | −0.0000000532 | 0.0005444100 |
| 11 | −82.9444469862 | −0.0000000124 | 0.0002623606 |
| 12 | −82.9444469891 | −0.0000000029 | 0.0001265513 |
| 13 | −82.9444469898 | −0.0000000007 | 0.0000610451 |

−74.94207992798844


−81.25
−81.50
−81.75
−82.00
−82.25
−82.50
−82.75
−83.00
energy
0
2
4
6
8
10
12
iterations