Exercise Session 4
IESM Fall 2024-2025

Yuri, Salomé, Sophia, Andrea, Qihao, Junwu

October 8, 2024

Course Reminders

- Monday 14.10: mock written exam during the lecture time
- Tuesday 15.10: mock exam solutions and Q&A session (we'll gather questions on the Moodle forum by Monday 18:00 14.10)
- **Monday 28.10:** written exam
- Tuesday 05.11: report for exercise 4 due by 09:00; session for exercise 5

Report Templates

- To assist in making easily uploadable/readable reports, Simon created Report Templates
- Google Doc or Overleaf (preferable) format
- Whenever you modify code, screenshot the cell/output using the Snipping Tool or use the code environment in latex as described in the hints at the top of the template

4. The hartree fock procedure in detail

So far you have run some Hartree Fock calculations using Psi4 and in the lectures we have seen the theoretical derivation of the scheme.

In this exercise, we will recapitulate the HF scheme by implementing it on our own using Psi4. That means we will go through the steps of the HF procedure but we will let Psi4 evaluate the integrals for us.

📥 Download introductory slides

`Report Template` `Google Docs`

`Report Template` `Overleaf`

✒️ Learning goals	📖 Chapter in script	💰 Resources

The Hartree-Fock procedure in detail (Reminder: you can download these slides from the Exercise page)

◎ **Learning goals**	▭ **Chapter in script**	▤ **Resources**
Build and diagonalize the Fock matrix	Chapter 4 - An introduction to Hartree Fock theory	Introduction to Hartree-Fock Molecular Orbital Theory by the Sherrill group: slides and videos (part 1, part 2)
Understand the steps in a HF SCF calculation	Appendix C	
Practice implicit summation in numpy		

Recap of HF Theory

HF method = approximate many-body wavefunction to a single Slater determinant

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \approx \Psi_{HF} \equiv \frac{1}{\sqrt{N}} \left| \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\ldots\phi_n(\mathbf{r}_n) \right|$$

$\rightarrow \Psi_{HF}$ inserted into time-independent Schrödinger equation to find eigenvalue, i.e. $E = \left\langle \Psi_{HF} \middle| \hat{H}_{el} \middle| \Psi_{HF} \right\rangle$. What is found is a **variational solution**, i.e. HF energy is always above true energy.

Recap of SCF Method

HF equations (will be derived in detail during Lectures)

$$E_{HF} = \sum_i \left\langle \phi_i \middle| \hat{h} \middle| \phi_i \right\rangle + \frac{1}{2} \sum_{i,j} \left([\phi_i \phi_i | \phi_j \phi_j] - [\phi_i \phi_j | \phi_j \phi_i] \right) \qquad \forall \phi_i$$

where $[\ldots | \ldots]$ integrals contain Coulomb and Exchange operators, whose action on orbital ϕ_i depends on all the other one-electron orbitals ϕ_j. Hence, HF equations have to be solved iteratively until self-consistency (**self consistent field SCF method**)

```
                        Total Energy        Delta E      RMS |[F,P]|

  @DF-UHF iter SAD:    -0.85212229561042   -8.52122e-01   0.00000e+00
  @DF-UHF iter   1:    -1.12493424123815   -2.72812e-01   1.62339e-02 DIIS
  @DF-UHF iter   2:    -1.12669596352817   -1.76172e-03   2.38980e-03 DIIS
  @DF-UHF iter   3:    -1.12673509439903   -3.91309e-05   3.36383e-06 DIIS
  @DF-UHF iter   4:    -1.12673509447661   -7.75795e-11   2.74379e-09 DIIS
  Energy and wave function converged.
```

Hartree-Fock Roothaan Equations

- HF equations area set of coupled integro-differential equations to determine the HF molecular one-electron orbitals
- If we represent the orbitals in a basis (of AO-like orbitals), the HF equations transform into matrix equations that were first derived by **Roothaan**

$$\Rightarrow \mathbb{F}\mathbb{C} = \mathbb{S}\mathbb{C}\mathbb{E}$$

- Note: as you will see today, this problem can be recast in an eigenvalue problem via a basis set transformation

$$\Rightarrow \mathbb{F}'\mathbb{C}' = \mathbb{C}'\mathbb{E}'$$

Building the Fock Matrix

The HF method recasts into a pseudo-eigenvalue problem

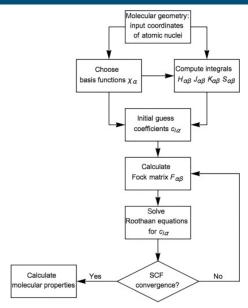$$\mathbb{F}\mathbb{C} = \mathbb{S}\mathbb{C}\mathbb{E}$$

where:

- $\mathbb{F} = \mathbb{H} + 2\mathbb{J} - \mathbb{K}$ is the **Fock matrix**
- $\mathbb{C}$ is the **wavefunction amplitude matrix**
- $\mathbb{S}$ is the **overlap matrix**
- and $\mathbb{E}$ is the **energy value matrix**

The issue? $\mathbb{F}$ relies on an orbital solution in order to iteratively solve (with **SCF method**) for the "best" molecular orbitals which make a single Slater determinant description of the system wavefunction. We will begin with a guess and iteratively improve on the guess.

$\mathbb{S}$, the overlap matrix, describes the inter-relationships of the basis set vectors. Other details about $\mathbb{S}$:

- The number of basis functions, n, defines the size and shape of $\mathbb{S}(n$x$n)$
- $\mathbb{S}$ is an idenity matrix in the case of orthonormal basis set functions
- By properly transforming the $\mathbb{S}$ matrix, we can ensure orthonormality

Implicit Einstein Summation

The einsum function in numpy allows for efficient matrix multiplication.

$$(AB)_{pq} = \sum_i A_{p,i} B_{i,q} \qquad \text{explicit summation}$$

$$(AB)_{pq} = A_{p,i} B_{i,q} \qquad \text{implicit summation}$$

`np.einsum('ij,jk->ijk', A, B)`

`np.einsum('ij,jk->ik', A, B)`

```
     j                    k                    k
   [[1, 1, 1],         [[0, 1, 0],         [[ 2,  3,  1],
i    [2, 2, 2],   x  j   [1, 1, 0],   =  i   [ 4,  6,  2],
     [5, 5, 5]]          [1, 1, 1]]           [10, 15,  5]]
```

```
              k
          [[0, 1, 0],
      j    [1, 1, 0],
           [1, 1, 1]],

          [[0, 2, 0],
   i  j    [2, 2, 0],
           [2, 2, 2]],

          [[0, 5, 0],
      j    [5, 5, 0],
           [5, 5, 5]]]
```