Problem to solve:

Solution of the
- electronic
- time-independent
- non relativistic

Schrödinger equation for many electron systems:

\[ \mathcal{H}\Psi = \varepsilon\Psi \]

Chapter 3: How to represent \( \Psi \)

Chapter 4: Hartree-Fock (first approximate method to solve this equation)

4. The Hartree-Fock Method

Electronic Schrödinger equation for many electron system

\[
\begin{align*}
\hat{H}\Psi & = E\Psi \\
\frac{1}{2} \sum_i \nabla_i^2 + \sum_i \frac{Z_i}{|\mathbf{r}_i - \mathbf{r}|} + \sum_i \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi(\mathbf{r}, \mathbf{R}) = E_{\mathrm{el}}\Psi(\mathbf{r}, \mathbf{R})
\end{align*}
\]

Kinetic energy operator

Potential due to electron – nucleus attraction

nucleus-nucleus repulsion potential

electron – electron repulsion

This is a constant for a fixed set of nuclear coordinates

Simplest Ansatz for the many-electron wavefunction \( \Psi \):

1 single Slater determinant

\[
\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \begin{vmatrix} \phi_1, \phi_2, \ldots, \phi_N \end{vmatrix}
\]

Hartree (1927) – Fock (1930) Approximation
Why is that an approximation?

- We describe the many-electron wavefunction as an (antisymmetrized) product of one-electron wavefunctions.
- This is only exact when the probability distributions of the single electrons are independent of each other.
- In reality, the probability distributions of the single electrons are not independent of each other, i.e., the wavefunction of electron 1 depends on the instantaneous position of electron 2 etc. We say ‘the motion of the electrons is correlated’.

**Notabene:**
- By approximating the many electron wavefunction with a single determinant, we neglect electron correlation, i.e., the Hartree-Fock Method does not take account of electron correlation effects.
- The solution of the Hartree-Fock method is the Slater determinant that results in the lowest Hartree-Fock energy, i.e., this is the best 1 determinantal wavefunction that exists (within a given basis set).
**Shorthand Notations**

- **one electron operator** $\hat{h}$ (all the terms of the Hamiltonian that depend on 1 electron only)
  \[ \hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_{l} \frac{Z_l}{|\mathbf{r}_i - \mathbf{r}_l|} \]

- **two electron operator** $\hat{v}(i,j)$ (the term of the Hamiltonian that depends on 2 electrons)
  \[ \hat{v}(i,j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \]

- **electronic Hamiltonian in shorthand form**
  \[ \hat{H}_{el} = \sum_i \hat{h}(i) + \sum_{i<j} \hat{v}(i,j) + V_{NN} \]

- **one electron integrals**
  \[ \langle \varphi_i \hat{h} \varphi_j \rangle = \int dx_1 \psi_i^*(x_1) \hat{h}(x_1) \psi_j(x_1) \]

- **two electron integrals** (Chemist’s notation)
  \[ \left[ \varphi_i \varphi_j | \varphi_k \varphi_l \right] = \langle ij|kl \rangle = \int dx_1 dx_2 \psi_i^*(x_1) \psi_j(x_1) \psi_k(x_2) \psi_l(x_2) \]

**How do we find the Hartree-Fock solution ($E_{HF}$ and $\Psi_{HF}$) of the Schrödinger Equation?**

- As always when we want to determine the expectation value of a quantum operator we multiply to the left with the conjugate complex of the wavefunction and integrate over all space:
  \[ \langle \Psi_{HF} | \hat{H}_{el} | \Psi_{HF} \rangle = E_{HF} \] for an orthonormal $\Psi_{HF}$

- this formula tells us how to calculate the total Hartree-Fock energy $E_{HF}$ once we know the wavefunction $\Psi_{HF}$. But how do we find $\Psi_{HF}$?

- for this we can use the variational theorem that tells us that the correct wavefunction among all possible Slater determinants is the one for which $E_{HF}$ is minimal

-That means that in order to find the Hartree-Fock wavefunction we have to minimize the energy expression $E_{HF}$ with respect to changes in the one electron orbitals $\phi_i \rightarrow \phi_i + \delta \phi_i$ from which we construct the Slater determinant $\Psi$. The set of one electron orbitals $\phi_i$ for which we obtain the lowest energy are the Hartree-Fock orbitals, i.e. the solutions to the Hartree-Fock equations.
Hartree-Fock Energy Expression

Let’s look at this in detail…we first start with the Hartree-Fock energy expression $E_{HF}$:

$$E_{el} = \langle \Psi | \hat{H}_{el} | \Psi \rangle$$

$$\Psi = 1 / \sqrt{n} | \varphi_1 \varphi_2 \cdots \varphi_n \rangle$$

Let’s look at this in the case of a 2 electron system:

$$E_{HF} = \langle \Psi | \hat{H}_{el} | \Psi \rangle = 1 / \sqrt{2} | \varphi_1 \varphi_2 \rangle = 1 / \sqrt{2} [\varphi_1 (r_1) \varphi_2 (r_2) - \varphi_1 (r_2) \varphi_2 (r_1)]$$

…etc..this example is solved explicitly in Appendix 3 of the script!

In the general N electron case we obtain

$$E_{HF} = \sum_{ij} [i|H|i] + \frac{1}{2} \sum_{ij} [i|J|j] - \frac{1}{2} \sum_{ij} [i|K|i]$$

Restricted HF (N/2 orbitals)

Hartree-Fock Equations

How do we find the Hartree-Fock wavefunction? → minimize the Hartree-Fock energy expression with respect to variations in the one-electron orbitals $\varphi_i$ with the additional boundary condition that the orbitals have to remain orthonormal

Hartree-Fock Equations (1 Schrödinger equation for each 1 electron orbital $\varphi_i$)

$$f(x_i) \varphi_i (x_i) = \epsilon_i \varphi_i (x_i)$$

$f(x_i)$: Fock operator

$$f(x_i) = h(x_i) + \sum \tilde{J}_i (x_i) - K_i (x_i)$$

One electron Fock operator

Mean electrostatic field of all the other electrons

N.B. The Fock operator for electron i depends on all the other one-electron orbitals $\varphi_j$ → The Hartree-Fock equations have to be solved iteratively until self-consistency (self-consistent field SCF method)
Hartree-Fock Roothaan Equations

- set of coupled integro-differential eqs
- basis set expansion → matrix eqs

Hartree-Fock-Roothaan Eqs. (closed shell systems, singlets)

\[ \hat{f}_i(\vec{r}_i) = \varepsilon_i \phi_i(\vec{r}_i) \quad i = 1, 2, \ldots N/2 \]

\[ \hat{f}_i(\vec{r}_i) = \hat{h}_i(\vec{r}_i) + \sum_{j=1}^{n/2} 2\hat{J}_j(\vec{r}_i) - K_j(\vec{r}_i) \]

Expansion in basis set:

\[ \phi_i = \sum_q c_{iq} \chi_q \]

\[ \hat{f}_i(\vec{r}_i) \sum_q c_{iq} \chi_q = \varepsilon_i \sum_q c_{iq} \chi_q \]

\[ \int dV \chi_p^* \hat{f}_i(\vec{r}_i) \sum_q c_{iq} \chi_q = \varepsilon_i \int dV \chi_p^* \sum_q c_{iq} \chi_q \]

\[ \sum_q c_{iq} \int dV \chi_p^* \hat{f}_i(\vec{r}_i) \chi_q = \varepsilon_i \sum_q c_{iq} \int dV \chi_p^* \chi_q \]
\[ \sum_q c_i F_q = \epsilon_i \sum_q c_i S_{pq} \]

\[ FC = SCE \]

Transformation yields eigenvalue problem:

\[ F'C' = C'E \]

with

\[ \begin{align*}
F' &= S^{-1/2}FS^{-1/2} \\
C' &= S^{-1/2}C
\end{align*} \]

Matrix elements

Overlap matrix:

\[ S_{pq} = \int \chi_p^* \chi_q dV = \langle p|q \rangle \]

Fock matrix:

\[ F_{pq} = \int \chi_p^* \hat{\chi} \chi_q dV = \langle p|\hat{f}|q \rangle \]

Some Remarks:

- Solution of the HF eqs. gives "the best" 1 determinant wf, i.e. the Slater determinant with the lowest possible energy (for this basis)
- Motions of electrons with the same spin are correlated (Fermi hole)
- Exchange is exact
- Electrons with different spins move independently → no electron correlation
- HF is variational (HF energy > true energy)
Different Types of HF Methods

- **Restricted Hartree-Fock (RHF)**
  (Roothaan 1951, Hall 1951)
  closed-shell systems (spatial MO’s doubly occupied with one spin $\alpha$ and one spin $\beta$ electron) (non degenerate singlet ground state)

- **restricted open-shell Hartree-Fock (ROHF)**
  (Roothaan 1961)
  spatial MO’s are singly or doubly occupied

- **unrestricted Hartree-Fock (UHF)**
  (Pople-Nesbet 1954)
  different spatial MO’s for $\alpha$ and $\beta$ spins
  Wavefunctions no longer eigen functions of spin operator $S^2 \rightarrow$ occurrence of ‘spin contaminated’ states: Example: Li atom

  ROHF $|1_s^22_s\rangle$ doublet
  UHF $|1_s\alpha 1_s\beta 2s\alpha\rangle$ lower energy
  but not pure doublet

Performance of Hartree-Fock

Relative good performance:
- **structural properties:**
  (bond distances $\sim$0.05 Å, bond angles $\sim$ 5°, torsional angles $\sim$ 10°)
- **enthalpies for isodesmic reactions:**
  (error $\sim$ 2-4 kcal/mol)
- **barriers for internal rotations**

Relative bad performance:
- **whole PES**
- **vibrational frequencies:**
  systematically too high (10-12 %)
- **reaction energies:**
  homolytic bond breaking ($\sim$ 25-40 kcal/mol off), protonations ($\sim$ 10 kcal/mol off)
- **transition states**
- **excited states**
- **alkali metals** (e.g. Li$_2$, Na$_2$..)
  transition metal complexes (e.g. ferrocene)
- **systems with low lying excited states**
<table>
<thead>
<tr>
<th>Performance</th>
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<tbody>
<tr>
<td><strong>Wrong results</strong></td>
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<tr>
<td>• dissociation to open-shell fragments</td>
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<tr>
<td>• dispersion interactions:</td>
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<tr>
<td>e.g. $\text{Ar}_2$ not bound</td>
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<tr>
<td>• $F_2$</td>
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