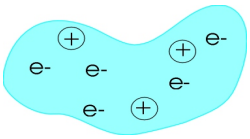
Problem to solve:

Solution of the

- electronic
- time-independent
- non relativistic



Schrödinger equation for many electron systems:

Chapter 3: How to represent Ψ

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

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

$$\mathcal{H} = \sum_i^N (-1/2\nabla_i^2 - \sum_I \frac{Z_I}{r_{iI}}) + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

4. The Hartree-Fock Method

Electronic Schrödinger equation for many electron system

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

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{I,i} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_{I>J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right] \Psi(\mathbf{r},\mathbf{R}) = E_{el}\Psi(\mathbf{r},\mathbf{R})$$

Kinetic energy operator

Potential due to electron – nucleus attraction

nucleus-nucleus repulsion potential

electron – electron repulsion

$$\left[\hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r},\mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})\right] \Psi(\mathbf{r},\mathbf{R}) = E_{el}\Psi(\mathbf{r},\mathbf{R})$$

(compact notation)

This is a constant for a fixed set of nuclear coordinates

Simplest Ansatz for the many-electron wavefunction Ψ:

1 single Slater determinant

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \approx |\phi_1, \phi_2, \ldots, \phi_N|$$

Hartree (1927) – Fock (1930) Approximation

Douglas Rayner Hartree

1897-1958

Vladimir Fock

1898-1974

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
- 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)

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$

- 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

$$\left\langle \varphi_i \middle| \hat{h} \middle| \varphi_j \right\rangle = \langle i|h|j\rangle = \int d\mathbf{x}_1 \phi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \phi_j(\mathbf{x}_1)$$

$\mathbf{x}_i = (\mathbf{r}_i, s_i)$ (combined coordinate for the position r_i and the spin s_i of electron i)

- two electron integrals (Chemist's notation)

$$\left[\varphi_i \varphi_j \middle| \varphi_k \varphi_l\right] = [ij|kl] = \int d\mathbf{x}_1 d\mathbf{x}_2 \phi_i^*(\mathbf{x}_1) \phi_j(\mathbf{x}_1) \frac{1}{r_{12}} \phi_k^*(\mathbf{x}_2) \phi_l(\mathbf{x}_2).$$

How do we find the Hartree-Fock solution (E_{HF} and Ψ_{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:

$$\left\langle \Psi_{HF} \middle| \hat{H}_{el} \middle| \Psi_{HF} \right\rangle = E_{HF} \left\langle \Psi_{HF} \middle| \Psi_{HF} \right\rangle$$

$$E_{HF} = \frac{\left\langle \Psi_{HF} \middle| \hat{H}_{el} \middle| \Psi_{HF} \right\rangle}{\left\langle \Psi_{HF} \middle| \Psi_{HF} \right\rangle}$$

$$E_{HF} = \left\langle \Psi_{HF} \middle| \hat{H}_{el} \middle| \Psi_{HF} \right\rangle = \int_V \Psi_{HF}^* \hat{H}_{el} \Psi_{HF} dV$$

For an orthonormal Ψ_{HF}

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

$$E_{\min} = \left\langle \Psi_{HF} \middle| \hat{H}_{el} \middle| \Psi_{HF} \right\rangle < \left\langle \Psi \middle| \hat{H}_{el} \middle| \Psi \right\rangle$$

-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 Ψ. The set of one electron orbitals ϕ_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}:

What kind of energy expression do we get if we use our 1 Slater determinant Ansatz for the wavefunction?

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

$$\Psi = 1/\sqrt{n} \, |\varphi_1 \varphi_2 \ldots \varphi_n|$$

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

$$\Psi = 1/\sqrt{2} \, |\varphi_1 \varphi_2| = 1/\sqrt{2} [\varphi_1(\boldsymbol{r}_1)\varphi_2(\boldsymbol{r}_2) - \varphi_1(\boldsymbol{r}_2)\varphi_2(\boldsymbol{r}_1)]$$

$$E_{HF} = \langle \Psi | \hat{H}_{el} | \Psi \rangle = \left(\frac{1}{\sqrt{2}}\right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 \, (\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)) \, \hat{H}_{el} \, (\phi_1^*(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2) - \phi_1^*(\mathbf{r}_2)\phi_2^*(\mathbf{r}_1))$$

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

In the general N electron case we obtain

$$E_{HF} = \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{ij} [ii|jj] - [ij|ji]$$

One electron integrals — two electron integrals

Coulomb integral J — Exchange integral K

Restricted HF (N/2 orbitals)

$$E_{HF} = 2\sum_i^{N/2} \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{ij}^{N/2} 2J_{ij} - K_{ij}$$

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 ϕ_i with the additional boundary condition that the orbitals have to remain orthonormal

$$E_{HF} = 2\sum_i^{N/2} \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{ij}^{N/2} 2J_{ij} - K_{ij}$$

➡ Hartree-Fock Equations (1 Schrödinger equation for each 1 electron orbital ϕ_i)

$$f(\mathbf{x}_1)\phi_i(\mathbf{x}_1) = \epsilon_i \phi_i(\mathbf{x}_1)$$

$f(x_1)$: Fock operator

$$f(\mathbf{x}_1) = h(\mathbf{x}_1) + \sum_j \mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1)$$

One electron Fock operator

Coulomb operator

Exchange operator

$$\mathcal{J}_j(\mathbf{x}_1) = \int d\mathbf{x}_2 |\phi_j(\mathbf{x}_2)|^2 r_{12}^{-1}$$

Mean electrostatic field of all the other electrons

$$\mathcal{K}_j(\mathbf{x}_1)\phi_i(\mathbf{x}_1) = \left[\int d\mathbf{x}_2 \phi_j^*(\mathbf{x}_2) r_{12}^{-1} \phi_i(\mathbf{x}_2)\right] \phi_j(\mathbf{x}_1)$$

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

Clemens C. J. Roothaan

1918

Hartree-Fock Roothaan Equations

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

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

$$\hat{f}_i(\vec{r}_1) = \varepsilon_i \phi_i(\vec{r}_1) \qquad i = 1, 2, \ldots N/2$$

$$\hat{f}_i(\vec{r}_1) = \hat{h}_i(\hat{r}_1) + \sum_{j=1}^{n/2} 2\hat{J}_j(\vec{r}_1) - K_j(\vec{r}_1)$$

Expansion in basis set:

$$\phi_i = \sum_q c_{iq}\chi_q$$

$$\hat{f}_i(\vec{r}_1)\sum_q c_{iq}\chi_q = \varepsilon_i \sum_q c_{iq}\chi_q$$

$$\int dV \chi_p^* \hat{f}_i(\vec{r}_1)\sum_q c_{iq}\chi_q = \varepsilon_i \int dV \chi_p^* \sum_q c_{iq}\chi_q$$

$$\sum_q c_{iq} \int dV \chi_p^* \hat{f}_i(\vec{r}_1)\chi_q = \varepsilon_i \sum_q c_{iq} \int dV \chi_p^* \chi_q$$

$$\sum_q c_{iq} F_q = \varepsilon_i \sum_q c_{iq} S_{pq}$$

$$FC = SCE$$

transformation yields eigenvalue problem:

$$F'C' = C'E$$

with

$$F' = S^{-1/2} F S{-}1/2$$
$$C' = S^{-1/2} C$$

Matrix elements

overlap matrix:

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

Fock matrix:

$$F_{pq} = \int \chi_p^* \hat{f} \chi_q \, dV = \langle p | \hat{f} | q \rangle$$

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 α and one spin β electron) (non degenerate singlet ground state)

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

- **unrestricted Hartree-Fock (UHF)**
  (Pople-Nesbet 1954)
  different spatial MO's for α and β spins
  Wavefunctions no longer eigen functions of spin operator $\mathcal{S}^2 \rightarrow$ occurrence of 'spin contaminated' states: Example: Li atom

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

Performance of Hartree-Fock

Relative good performance:

- structural properties:
  (bond distances $\sim$0.05Å, 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

Performance

Wrong results

- dissociation to open-shell fragments
- dispersion interactions:
  e.g. Ar_2 not bound
- F_2