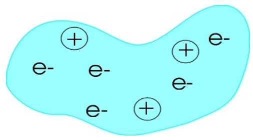
Problem to solve:

Solution of the

- electronic
- time-independent
- non relativistic



Schrödinger equation for many electron systems:

Chapter 3:
How to represent Ψ

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

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

$$H = -\frac{1}{2}\nabla^2 - \sum_{i=1}^{n}\sum_{I=1}^{N}\frac{Z_I}{r_{iI}} + \sum_{i}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}$$

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4. The Hartree-Fock Method

Electronic Schrödinger equation for many electron system

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

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

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

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

Hartree (1927) – Fock (1930) Approximation

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Douglas Rayner Hartree | **Vladimir Fock**

1897-1958

1898-1974

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4. The Hartree-Fock Method

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Hartree (1927) – Fock (1930) Approximation

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Quiz VIII: Hartree-Fock Approximation

1) Why is the description of the many-electron wavefunction as a single Slater determinant an approximation?

2) For which system would this Ansatz be exact?

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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

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

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

- two electron integrals (Chemist's notation)

bra-ket notation

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

- antisymmetrized two electron integrals

$$\langle ij \| kl \rangle = \langle ij|kl\rangle - \langle ij|lk\rangle$$

$$= \int dx_1 dx_2\, \phi_i^*(x_1)\phi_j^*(x_2)\frac{1}{r_{12}}\phi_k(x_1)\phi_l(x_2)$$
$$- \int dx_1 dx_2\, \phi_i^*(x_1)\phi_j^*(x_2)\frac{1}{r_{12}}\phi_l(x_1)\phi_k(x_2)$$
$$= [ik\|jl]$$

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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:

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

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.

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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?

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

$$\Psi = 1/\sqrt{n!} \, \| \phi_1\phi_2 \ldots \phi_n \|$$

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

=> Appendix C of the script!

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$$\Psi = 1/\sqrt{n!}\, | \phi_1 \phi_2 \ldots \phi_n |$$

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

$$E_{HF} = \langle \Psi | \hat{H}_{el} | \Psi \rangle \qquad \Psi = 1/\sqrt{2}\, |\phi_1\phi_2| = 1/\sqrt{2}\, [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)]$$

$$= \left(\frac{1}{\sqrt{2}}\right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 \left(\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)\right) H_{el} \left(\phi_1^*(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2) - \phi_1^*(\mathbf{r}_2)\phi_2^*(\mathbf{r}_1)\right)$$

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

In the general n electron case we obtain

$$E_{HF} = \sum_i \underbrace{\langle i|h|i\rangle}_{\text{One electron integrals}} + \frac{1}{2}\sum_{ij} \underbrace{\underbrace{[ii|jj]}_{\text{Coulomb integral } J} - \underbrace{[ij|ji]}_{\text{Exchange integral } K}}_{\text{two electron integrals}}$$

Restricted HF (n/2 orbitals)

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

Quiz IX: Hartree-Fock Energy Expression

1) What is the energy expression if you use a simple Hartree product instead of an antisymmetrized product?

2) How large is the self-interaction energy (i.e. the interaction of an electron with itself v(i,j) for i=j) in Hartree-Fock?

3) Can you motivate Hund's rule that for a given electronic configuration the term with the highest multiplicity has the lowest energy with the help of the Hartree-Fock energy expression?

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

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

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

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

Derivation in Appendix D of the script!

$\hat{f}(\mathbf{x}_1)$: Fock operator

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

One electron Fock operator

Coulomb operator

Exchange operator

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

Mean electrostatic field of all the other electrons

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

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)

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Hartree-Fock Roothaan Equations

- Hartree-Fock equations are a set of coupled integro-differential equations to determine the Hartree-Fock molecular one-electron orbitals ϕ_i

$$\boxed{\hat{f}_i(\vec{r}_1)\phi_i(\vec{r}_1) = \varepsilon_i\phi_i(\vec{r}_1)}$$

Unrestricted HF: i = 1…n

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

Restricted HF: i = 1…n/2

- If we represent the ϕ_i in a basis (of atomic-like orbitals χ), the HF equations transform into matrix equations that were first derived by Roothaan

$$\boxed{\phi_i(\vec{r}_1) = \sum_q c_{iq}\chi_q(\vec{r}_1)}$$

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Hartree-Fock Equations in Matrix Form: Roothaan Equations

Clemens C. J. Roothaan

1918-2019

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Derivation of the Roothaan Equations

(for closed-shell, restricted case)

$$\phi_i(\vec{r}_1) = \sum_q c_{iq}\chi_q(\vec{r}_1)$$

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

Multiply from left with χ^*_p and integrate over all space:

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

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

Fock matrix element

Overlap matrix element

$$\boxed{F_{pq} = \int d\vec{r}_1\chi_p^*(\vec{r}_1)\hat{f}_i(\vec{r}_1)\chi_q(\vec{r}_1) = \langle p|\hat{f}|q\rangle}$$

$$\boxed{S_{pq} = \int d\vec{r}_1\chi_p^*\chi_q(\vec{r}_1) = \langle p|q\rangle}$$

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Derivation of the Roothaan Equations (2)

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

Matrix equations:

$$FC = SCE$$

Transformation:

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

Yields eigenvalue problem:

$$\boxed{F'C' = C'E}$$

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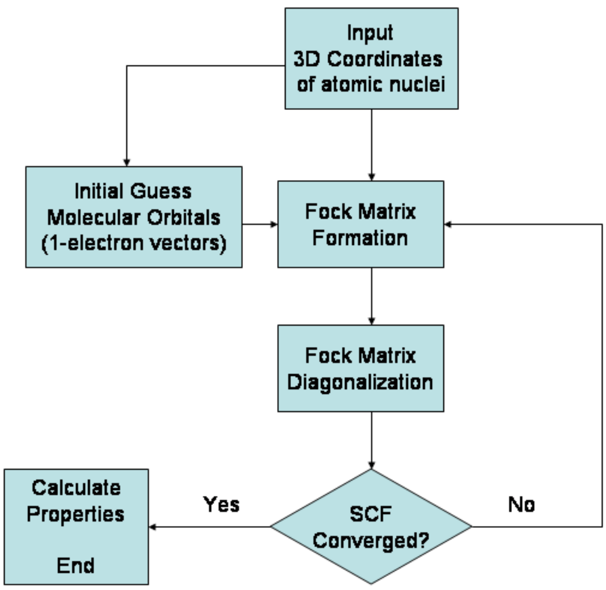
Self-Consistent Solutions of the Hartree-Fock Equations



(from wikipedia)

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Some Remarks:

- Solution of the HF eqs.
  $\rightarrow$ 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 $\rightarrow$ no electron correlation
- HF is variational (HF energy $>$ true energy)

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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

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Performance of Hartree-Fock

Relative good performance:

- structural properties:
  (bond distances ~0.05Å, bond angles ~ 5°, torsional angles ~ 10°
- enthalpies for isodesmic reactions:
  (error ~ 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 (~ 25-40 kcal/mol off), protonations (~ 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

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Performance

Wrong results

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

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