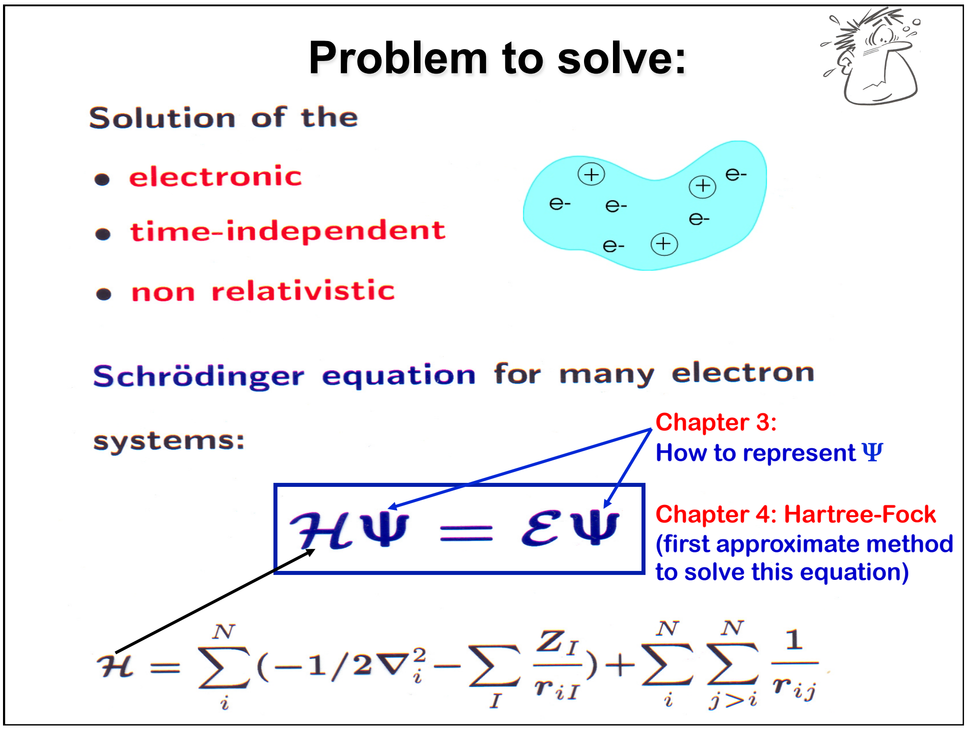


Problem to solve:

Solution of the

- electronic
- time-independent
- non relativistic

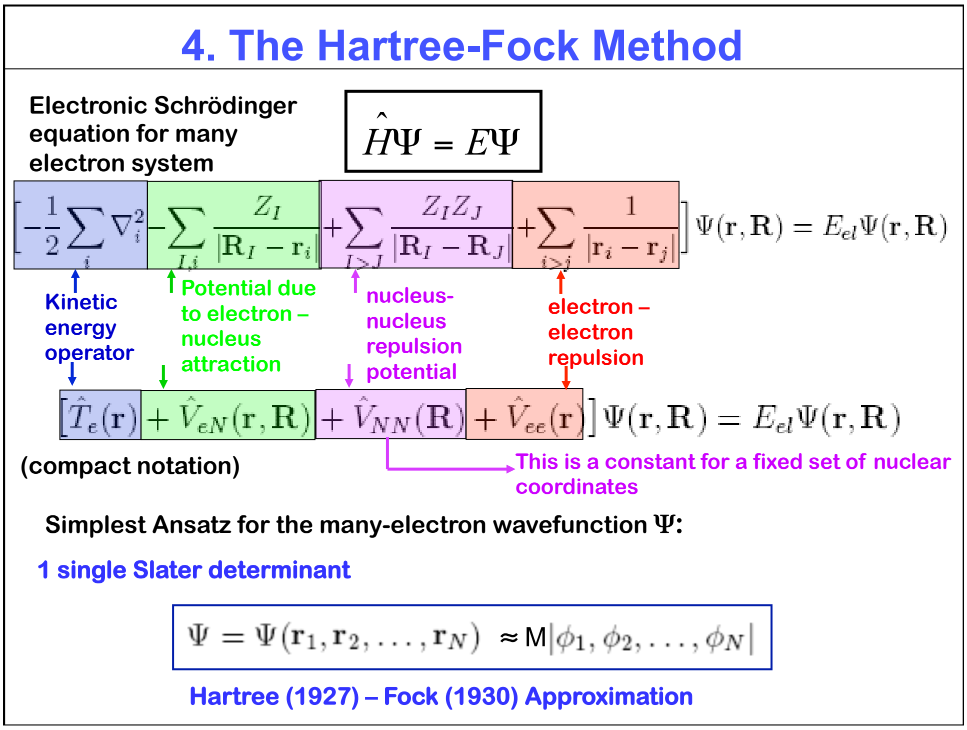
Schrödinger equation for many electron systems:

Chapter 3:
How to represent Ψ

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

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

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



4. The Hartree-Fock Method

Electronic Schrödinger equation for many electron system

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

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

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

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

Hartree (1927) – Fock (1930) Approximation

Vladimir Fock

Douglas Rayner Hartree

1897-1958

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 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)

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

- 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:

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

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.

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?

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

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

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

$$\Psi = 1/\sqrt{2}\,|\varphi_1\varphi_2| = 1/\sqrt{2}[\varphi_1(r_1)\varphi_2(r_2) - \varphi_1(r_2)\varphi_2(r_1)]$$

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

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

In the general N electron case we obtain

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

One electron integrals

two electron integrals

Coulomb integral J

Exchange integral K

Restricted HF (N/2 orbitals)

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

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

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

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

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

$f(x_1)$: Fock operator

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

One electron Fock operator

Coulomb operator

Exchange operator

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

Mean electrostatic field of all the other electrons

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

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:

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

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

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

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

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

$$\boldsymbol{FC} = \boldsymbol{SCE}$$

transformation yields eigenvalue problem:

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

with

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

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 $\mathcal{S}^2$ → 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 ~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

Performance

Wrong results

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

$$- \int \phi_p^*(1)[\sum_j \psi_j^*(2)\frac{1}{r_{12}}\psi_j(1)]\phi_q(2)dV$$

$$= h_{pq} - 2\sum_j \int \phi_p^*(1)\psi_j^*(2)\frac{1}{r_{12}}\psi_j(2)\phi_q(1)dV$$

$$- \sum_j \int \phi_p^*(1)\psi_j^*(2)\frac{1}{r_{12}}\psi_j(1)\phi_q(2)dV$$

$$\psi_j = \sum_r c_{ir}\phi_r$$

$$= h_{pq} + 2\sum_j\sum_r\sum_s c_{jr}^* c_{js}$$

$$x \int \phi_p^*(1)\phi_r^*(2)\frac{1}{r_{12}}\phi_s(2)\phi_q(1)dV$$

$$- \sum_j\sum_r\sum_s c_{jr}^* c_{js} \int \phi_p^*(1)\phi_r^*(2)\frac{1}{r_{12}}\phi_s(1)\phi_q(2)dV$$

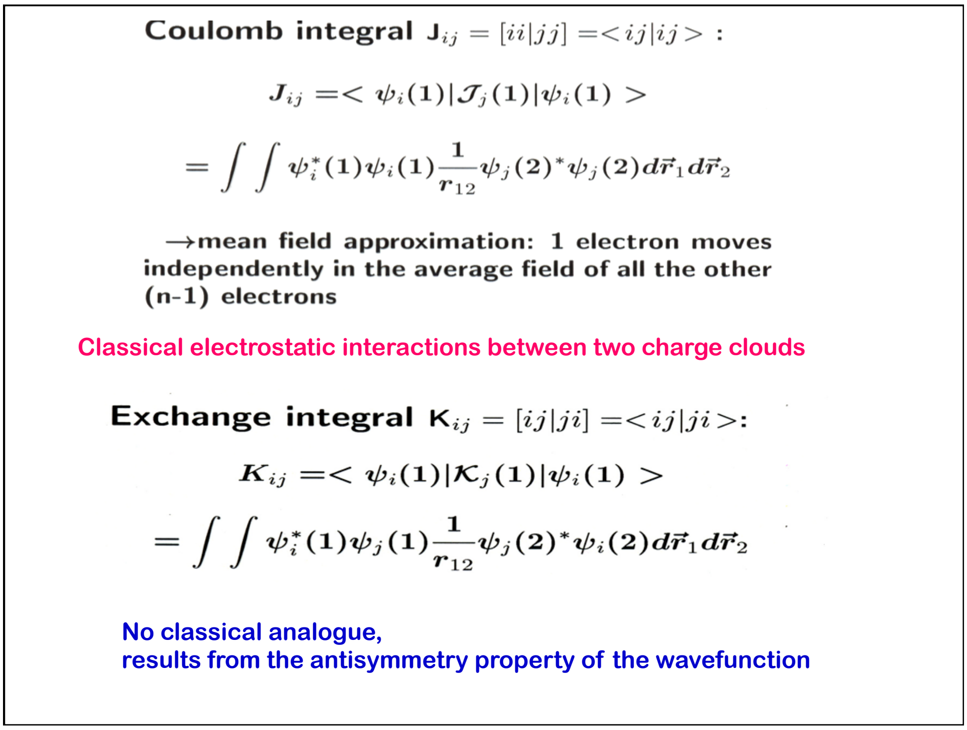
density matrix R = C^+C $R_{rs} = \sum_j c_{jr}^* c_{js}$
(j runs over occupied orbitals)

$$= h_{pq} + \sum_r\sum_s R_{rs}[2(pq|rs) - (ps|rq)]$$

	A=5	A ~ 16
1-el integrals: p_1=A/2(A+1)	15	120
2-el integrals: q_2=p_1/2(p_1+1)	55	1540

iterative scheme:
initial guess

$$\begin{tikzcd} F \arrow[r, "diag"] & C \arrow[r] & R \arrow[r, "converged?"] \arrow[ll, bend left] & stop \end{tikzcd}$$



Coulomb integral $\mathsf{J}_{ij} = [ii|jj] = <ij|ij>$:

$$J_{ij} = <\psi_i(1)|\mathcal{J}_j(1)|\psi_i(1)>$$

$$= \int\int \psi_i^*(1)\psi_i(1)\frac{1}{r_{12}}\psi_j(2)^*\psi_j(2)d\vec{r}_1 d\vec{r}_2$$

→mean field approximation: 1 electron moves independently in the average field of all the other (n-1) electrons

Classical electrostatic interactions between two charge clouds

Exchange integral $\mathsf{K}_{ij} = [ij|ji] = <ij|ji>$:

$$K_{ij} = <\psi_i(1)|\mathcal{K}_j(1)|\psi_i(1)>$$

$$= \int\int \psi_i^*(1)\psi_j(1)\frac{1}{r_{12}}\psi_j(2)^*\psi_i(2)d\vec{r}_1 d\vec{r}_2$$

No classical analogue,
results from the antisymmetry property of the wavefunction