COURSE 3

Note Title 3/25/2015

Hartree-Fock approximation

Objectives: E_e & E_{tot}

Ψ_e

How? 1. construct H_e

2. guess Ψ

3. use the Rayleigh-Ritz eq.:

$$\boxed{E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}}$$

Variational principle

$$\Psi_{trial} \longrightarrow E_{trial}$$

$$E_{trial} = \frac{\langle \Psi_{tr} | \hat{H} | \Psi_{tr} \rangle}{\langle \Psi_{tr} | \Psi_{tr} \rangle} \geq \underline{\underline{E_0}}$$

exact energy

$$E_0 = \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

Ψ_0 – exact w.f.

$\rightarrow$ minimize the energy

$E = E[\Psi]$ $\qquad$ $\Psi = \Psi(r_i; \{R_A\})$

– functional (of Ψ)

Hartree-Fock approximation

Note Title 10/19/2009

Electronic Hamiltonian:

$$\hat{H}_e = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}} =$$

$$= \sum_{i=1}^{N}\underbrace{\left(-\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{iA}}\right)}_{\hat{h}_i \text{ - one electron operator}} + \sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}}$$

$\hat{g}_{ij}$ – two electron operator

$\hat{h}_i$ – describes the motion of electron i in the field of all nuclei

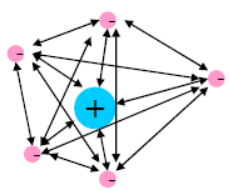
$\hat{g}_{ij}$ – describes the electron-electron repulsion

$$\Rightarrow \hat{H}_e = \sum_{i=1}^{N}\hat{h}_i + \sum_{i=1}^{N-1}\sum_{j>i}^{N} g_{ij}$$

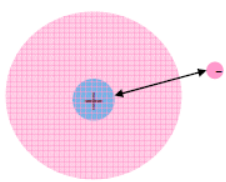
The Hartree idea (1928)

Introducing the coupling in an approximate way

The kth electron is treated as a point charge in the field of all of the other electrons. This procedure takes the many-electron problem and simplifies it to many one electron problems.



Many-electron system
All electron-electron repulsion is included explicitly.



One-electron system
with remaining electrons represented by an average charge density

one many-electron problem

$\Rightarrow$ many one-electron problems

Wavefunction: $\Psi = \Psi^{SD}$ χ-monod. orbitals

$$\Psi^{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \cdots & & & \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix}$$

← Slater determinant
- a drastic approx.
- replace the true wf. by a SD.

this form of Ψ → antisymmetry property (Pauli principle)
→ indistinguishability of electrons

On short:

$$\Psi^{SD} = \frac{1}{\sqrt{N!}} \left| \chi_1(1)\chi_2(2)\cdots\chi_N(N) \right\rangle$$

Why not a simpler wf.?

$$HP = \chi_1(1)\chi_2(2)\cdots\chi_N(N)$$

- Hartree product ⇒ Hartree approx.
- assign a particular wf. to a particular e^-
  ⇒ violates the indistinguishability principle.
- is not antisymmetric

since:

$$HP' = \chi_1(2)\chi_2(1)\cdots\chi_N(N) \neq -\chi_1(1)\chi_2(2)\cdots\chi_N(N)$$

6. Let us now consider a new function Φ which is a sum of two terms similar to Eq. (25.1):

$$\Phi = [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_i)\cdots\eta_j(r_j)\cdots] - [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_j)\cdots\eta_j(r_i)\cdots] \tag{25.4}$$

where in the second term we have just interchanged particles i and j. Equation (25.4) does satisfy permutation symmetry but only for particle i and j since:

$$\begin{aligned}\mathcal{P}_{i,j}\Phi &= \mathcal{P}_{i,j}\{[\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_i)\cdots\eta_j(r_j)\cdots] - [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_j)\cdots\eta_j(r_i)\cdots]\} \\ &= [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_j)\cdots\eta_j(r_i)\cdots] - [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_i)\cdots\eta_j(r_j)\cdots] \\ &= -\Phi \end{aligned} \tag{25.5}$$

However, Eq. (25.4) obeys permutation symmetry only for particles i and j and *no other set of particles*. (We can convince ourselves that this is true by interchanging particle 1 and particle 3 [redacted] and we would find that permutation symmetry is not obeyed. [redacted]

Ψ – is not observable

$|\Psi|^2$ – probability that e^- 1, 2, ..., N are found simultaneously in volume $dx_1 dx_2 \cdots dx_N$

Since the electrons are not distinguished

$$\Rightarrow |\Psi(x_1, x_2, \ldots, x_i, x_j, \ldots, x_N)|^2 = |\Psi(x_1, x_2, \ldots, x_j, x_i, \ldots, x_N)|^2$$

χ_i – spin-orbitals (orthonormal)

$$\langle \chi_i | \chi_j \rangle = \delta_{ij} \qquad \chi_i = \phi_i \cdot \sigma_i$$

↳ spin coordinate – no classical analogy

Variational principle

$$E_{trial} = \langle \Psi_{tr} | \hat{H} | \Psi_{tr} \rangle \geq E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

Ψ_0 - exact wf.

E is a functional of Ψ: $E = E[\Psi]$

Electronic energy:

$$E_e = \frac{\langle \Psi | \hat{H}_e | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \text{if } \Psi \text{ is normalized}$$

$$= \langle \Psi | \hat{H}_e | \Psi \rangle$$

Ψ^{SD} = sum of permutations over the diagonal of the determinant

- sum of Hartree products (HP)

$$\Psi = A\left[\chi_1(1)\chi_2(2)\dots\chi_N(N)\right] = A\,\Pi$$

↳ differ due to the interchange of electrons between spin-orbitals

where: $\Pi = \chi_1(1)\dots\chi_N(N)$

A - antisymmetrizing operator

p = # of permutations, $\mathbb{P}$ - permutation operator

$$A = \frac{1}{\sqrt{N!}}\sum_{p=0}^{N-1}(-1)^p\,\mathbb{P} = \frac{1}{\sqrt{N!}}\left[\mathbb{1} - \sum_{ij}P_{ij} + \sum_{ijk}P_{ijk} - \dots\right]$$

Operator P permutes the coordinates of the electrons, not the suffixes of the spin orbitals.

P_{ij} permutes 2 electrons, P_{ijk} permutes 3 electrons and so on.

$\mathbb{1}$ – identity operator

P_{ij} – generates all the possible permutations of two electrons coordinates

P_{ijk} – generates all the possible permutations of three electrons coordinates

...

$p=0 \Rightarrow$ 0 permutations $\rightarrow \mathbb{1}$

$p=1 \Rightarrow$ 1 permutation $\rightarrow P_{ij}$ $\quad i\ j \Rightarrow j\ i$

$p=2 \Rightarrow$ 2 permutation $\rightarrow P_{ijk}$

$i\ j\ k \Rightarrow j\ i\ k \Rightarrow j\ k\ i$

Example: 3 electron system (Li atom)

$$\Psi = \frac{1}{\sqrt{6}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \chi_3(1) \\ \chi_1(2) & \chi_2(2) & \chi_3(2) \\ \chi_1(3) & \chi_2(3) & \chi_3(3) \end{vmatrix}$$

$$\Psi = A\left[\chi_1(1)\chi_2(2)\chi_3(3)\right] = \frac{1}{\sqrt{6}}\left[\mathbb{1} - \sum_{ij} P_{ij} + \sum_{ijk} P_{ijk}\right] \cdot$$

$$\cdot \left[\chi_1(1)\chi_2(2)\chi_3(3)\right] =$$

$$P=1 < \begin{matrix}12\\13\\23\end{matrix} \qquad P=2 < \begin{matrix}12 & 23 \rightarrow 213 \rightarrow 312\\ 13 & 32 \rightarrow 321 \rightarrow \begin{matrix}2&3&1\\ \downarrow&\downarrow&\downarrow\\ \chi_1&\chi_2&\chi_3\end{matrix}\end{matrix}$$

$$= \frac{1}{\sqrt{6}}\Big[\overbrace{\chi_1(1)\chi_2(2)\chi_3(3)}^{p=0} - \overbrace{\chi_1(2)\chi_2(1)\chi_3(3)}^{p=1\quad(1\ 2)} -$$

$$- \overbrace{\chi_1(3)\chi_2(2)\chi_3(1)}^{p=1\quad(1\,3)} - \overbrace{\chi_1(1)\chi_2(3)\chi_3(2)}^{p=1\quad(2\,3)} +$$

$$+ \underbrace{\chi_1(3)\chi_2(1)\chi_3(2)}_{p=2\quad(12+23)}\Big] \qquad + \underbrace{\chi_1(2)\chi_2(3)\chi_3(1)}_{p=2\quad(13+32)}\Big]$$

! Of course, the same result is obtained by developing the determinant using the rule of Sarrus

? Why the normalization factor of a Slater determinant is $1/\sqrt{N!}$?
Show this for a three electron system.
(see Leach p.47)

It can be shown that:

$$A\hat{H} = \hat{H}A \quad \text{– } A \text{ and } \hat{H} \text{ commute}$$

$$AA = \sqrt{N!}\,A \quad (A \text{ acting twice is } A \text{ acting once multiplied by } \sqrt{N!})$$

Electronic energy

$$E_e = \langle \Psi | \hat{H}_e \Psi \rangle = \langle A\Pi | \hat{H}_e | A\Pi \rangle = \langle \Pi | \hat{H}_e | \overbrace{AA}^{=\sqrt{N!}\,A} \Pi \rangle$$

$$= \sqrt{N!} \langle \Pi | \hat{H}_e | A\Pi \rangle$$

$$= \cancel{\sqrt{N!}} \langle \Pi | \hat{H}_e | \overbrace{\frac{1}{\cancel{\sqrt{N!}}} \sum_{p=0}^{N-1} (-1)^p P}^{A} \Pi \rangle$$

$$= \langle \Pi | \sum_{i=1}^{N} \hat{h}_i + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} g_{ij} | \sum_{p=0}^{N-1} (-1)^p P \Pi \rangle$$

where:

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}}$$

$$g_{ij} = \frac{1}{r_{ij}}$$

effect of the one-electron operator

$$\sum \hat{h}_i = \hat{h}_1 + \hat{h}_2 + \dots + \hat{h}_N$$

– depends on the coordinates of one e^- only

$$\langle \Pi | h_1 | [1 - \sum_{ij} P_{ij} + \sum_{ijk} P_{ijk} - \dots] \Pi \rangle$$

- only the identity operator gives non-zero matrix elements
- matrix elements involving any permutation operator (P_{ij}, P_{ijk}, ...) are zero.

Example

Conventions:

1) we will use label "1" wherever there is an integral involving the coordinates of a single electron, even if the actual electron is not the "electron 1".
2) we will use conventionally labels "1" and "2" when we will consider two electrons

Let's calculate some matrix elements:

acts only on the coordinates of electron 1

$$\langle \Pi | \hat{h}_1 | \Pi \rangle = \langle \chi_1(1)\chi_2(2)\cdots\chi_N(N) | \hat{h}_1 | \chi_1(1)\chi_2(2)\cdots\chi_N(N) \rangle$$

$$= \underbrace{\langle \chi_1(1) | \hat{h}_1 | \chi_1(1) \rangle}_{H_1\text{-core integral}} \underbrace{\langle \chi_2(2) | \chi_2(2) \rangle}_{=1} \cdots \underbrace{\langle \chi_N(N) | \chi_N(N) \rangle}_{=1}$$

$= H_1$

- kinetic energy of e^- "1" + its interaction energy with the nuclei

$$\langle \Pi | \hat{h}_1 | -P_{12} \Pi \rangle = \langle \chi_1(1)\chi_2(2)\cdots\chi_N(N) | \hat{h}_1 | -\chi_1(2)\chi_2(1)\cdots\chi_N(N) \rangle$$

$$= -\langle \chi_1(1) | \hat{h}_1 | \chi_2(1) \rangle \underbrace{\langle \chi_2(2) | \chi_1(2) \rangle}_{=0} \langle \chi_3(3) | \chi_3(3) \rangle \cdots = 0$$

Analogously

$$\langle \Pi | \hat{h}_2 | \Pi \rangle = H_2 \quad \text{and} \quad \langle \Pi | \hat{h}_2 | P_{12} \Pi \rangle = 0$$

- - -

In general:

$$\langle \Pi | \hat{h}_i | \Pi \rangle = H_i \; ; \; \langle \Pi | \hat{h}_i | P_{ij} \Pi \rangle = 0$$

$$\Rightarrow \boxed{\langle \Pi | \sum_{i=1}^{N} \hat{h}_i | \sum (-1)^P P \Pi \rangle = \sum_{i=1}^{N} H_i}$$

H_i - core one-electronic integral
- represents the sum of the kinetic energy of the electron in χ_i and the potential energy of attraction between electron i and the nuclei.

- effect of the $\underbrace{\text{two-electron operator}}_{\text{- depends on the coordinates of two electrons}}$

$$\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} g_{ij} = g_{12} + g_{13} + \dots + g_{1N} + g_{23} + g_{24} + \dots + g_{N-1\,N}$$

- only the identity and P_{ij} operators can give non-zero matrix elements with g_{ij} operators

terms arising from the identity operator:

$$\langle \Pi | g_{12} | \Pi \rangle =$$

acts on the coordinates of electrons 1 and 2

$$= \langle \chi_1(1)\chi_2(2)\cdots\chi_N(N) | g_{12} | \chi_1(1)\chi_2(2)\cdots\chi_N(N)\rangle$$

$$= \underbrace{\langle \chi_1(1)\chi_2(2) | \frac{1}{r_{12}} | \chi_1(1)\chi_2(2)\rangle}_{J_{12}} \underbrace{\langle \chi_3(3)|\chi_3(3)\rangle}_{=1} \cdots$$

$$= J_{12}$$

Analogously:

$$\langle \Pi | g_{13} | \Pi \rangle = J_{13}$$

- - - - - - -

$$\langle \Pi | g_{ij} | \Pi \rangle = J_{ij}$$

J_{ij} - Coulomb bielectronic integrals
- represent the classical repulsion energy between two charge densities described by χ_i and χ_j spin orbitals

The total electrostatic interaction between the electron in orbital χ_i and the other $N-1$ electrons is a sum of such integrals.

Integral form of J_{ij}:

$$J_{ij} = \iint \chi_i^2(1) \frac{1}{r_{12}} \chi_j^2(2)\, d\tau_1\, d\tau_2$$

This means that:

The exact bielectronic potential $\frac{1}{r_{12}}$ felt by e^-1, due to the instantaneous position of e^-2 is replaced by an averaged monoelectronic potential $V_i(1)$ obtained by averaging the interaction between the two electrons over the spatial and spin coordinates of e^-2.

Summing over $j \neq i$ one obtained the medium potential acting on electron in χ_i and which is due to the other $N-1$ electrons.

$$V_i(1) = \sum_{\substack{j=1 \\ j \neq i}}^{N} \int |\chi_j(2)|^2 \frac{1}{r_{12}} d\tau_2$$

terms arising from the P_{ij} operators

$$\langle \Pi | g_{12} | P_{12} \Pi \rangle =$$

$$= \langle \chi_1(1) \cdots \chi_N(N) \left| \frac{1}{r_{12}} \right| \left[-\chi_2(1) \chi_1(2) \chi_3(3) \cdots \chi_N(N) \right] \rangle$$

$$= -\underbrace{\langle \chi_1(1) \chi_2(2) \left| \frac{1}{r_{12}} \right| \chi_2(1) \chi_1(2) \rangle}_{K_{12}} \underbrace{\langle \chi_3 | \chi_3 \rangle}_{=1} \cdots \underbrace{\langle \chi_N | \chi_N \rangle}_{=1}$$

$$= -K_{12}$$

$$\langle \Pi | \overbrace{g_{12}}^{\equiv 1/r_{12}} | P_{13} \Pi \rangle =$$

$$= \langle \chi_1(1) \cdots \chi_N(N) | g_{12} | [-\chi_3(1)\chi_2(2)\chi_1(3)\chi_4(4) \cdots \chi_N(N)] \rangle$$

$$= -\langle \chi_1(1)\chi_2(2) | g_{12} | \chi_3(1)\chi_2(2) \rangle \underbrace{\langle \chi_3(3) | \chi_1(3) \rangle}_{=0} \underbrace{\langle \chi_4(4) | \chi_4(4) \rangle}_{=1} \cdots$$

$$\cdots \underbrace{\langle \chi_N(N) | \chi_N(N) \rangle}_{=1}$$

$$= 0$$

Analogously:

$$\langle \Pi | g_{13} | P_{13} \Pi \rangle = -K_{13}$$

- - -

$$\langle \Pi | g_{ij} | P_{ij} \Pi \rangle = -K_{ij}$$

$$\langle \Pi | g_{ij} | P_{kl} \Pi \rangle = 0 \text{ if } i \neq k \text{ and } j \neq l$$

K_{ij} - exchange integrals
- they have no classical analogy
- appear due to the fact that in a determinantal wavefunction the electrons are allowed to be exchanged between different spin-orbitals

Integral form: $K_{ij} = \iint \chi_i(1)\chi_j(2) \frac{1}{r_{12}} \chi_i(2)\chi_j(1) d\tau_1 d\tau_2$

The exchange energy between the electron in spin orbital χ_i and the other N-1 electrons is summing over $j \neq i \Rightarrow$:

$$E_i^{exch.} = \sum_{j \neq i}^{N} \iint d\tau_1 d\tau_2 \chi_i(1)\chi_j(2) \frac{1}{r_{12}} \chi_i(2)\chi_j(1)$$

▣ terms arising from P_{ijk} operators

permutations

first

$$\begin{array}{ccc} 1 & 2 & 3 \\ 1 & 2 & 3 \end{array} \begin{array}{l} \leftarrow \text{electrons} \\ \leftarrow \text{orbitals} \end{array}$$

second

$$\Rightarrow \begin{array}{ccc} 2 & 1 & 3 \\ 1 & 2 & 3 \end{array} = \begin{array}{ccc} 2 & 3 & 1 \\ 1 & 2 & 3 \end{array}$$

$$\langle \Pi | g_{12} | P_{123} \Pi \rangle =$$

$$= \langle \chi_1(1) \cdots \chi_N(N) | \frac{1}{r_{12}} | \chi_3(1) \chi_1(2) \chi_2(3) \cdot \chi_4(4) \cdots \chi_N(N) =$$

$$= \langle \chi_1(1) \chi_2(2) | \frac{1}{r_{12}} | \chi_3(1) \chi_1(2) \rangle \cdot$$

$$\cdot \underbrace{\langle \chi_3(3) | \chi_2(3) \rangle}_{=0} \cdot \underbrace{\langle \chi_4(4) | \chi_4(4) \rangle}_{=1} \cdots \underbrace{\langle \chi_N(N) | \chi_N(N) \rangle}_{=1} =$$

$$= 0$$

All the terms of this type are zero.

Thus:

$$\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} g_{ij} = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} (J_{ij} - K_{ij})$$

and

$$E_e = \sum_{i=1}^{N} H_i + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} (J_{ij} - K_{ij})$$

What about J_{ii} and K_{ii}?

$$J_{ij} = \langle \chi_i(1)\chi_j(2) | \frac{1}{r_{12}} | \chi_i(1)\chi_j(2) \rangle$$

$$K_{ij} = \langle \chi_i(1)\chi_j(2) | \frac{1}{r_{12}} | \chi_i(2)\chi_j(1) \rangle$$

For $i=j \Rightarrow J_{ii} = K_{ii}$

J_{ii} means a Coulomb self-interaction but this contribution is eliminated from E_e because $K_{ii} = J_{ii}$ and thus, $J_{ii} - K_{ii} = 0$

Also: $J_{ij} = J_{ji}$ and $K_{ij} = K_{ji}$

It may be shown that:

$$J_{ij} \geq K_{ij} \geq 0 \quad \text{and} \quad \frac{1}{2}(J_{ii} + J_{jj}) \geq J_{ij}$$

Considering that:

$$J_{ii} = K_{ii} \; ; \; J_{ij} = J_{ji} \; ; \; K_{ij} = K_{ji}$$

the expression for E_e can be written in a more symmetrical form:

$$\boxed{E_e = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} (J_{ij} - K_{ij})}$$

The old expression was:

$$E_e = \sum_{i=1}^{N} H_i + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} (J_{ij} - K_{ij})$$

- the factor $\frac{1}{2}$ allows the double sum to run over all possible pairs of electrons (12, 13, ... 21, 31, ...) not only on distinct electron pairs.
- Also, the pairs of type 11, 22, ... give no contribution to the energy since $J_{ii} = K_{ii}$

Later, we will see that $K_{ij} \neq 0$ only for pairs in which electrons have the same spin.

Total energy:

In the Born-Oppenheimer approximation:

$$\hat{H} = -\frac{1}{2}\sum_{i}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \underbrace{\sum_{A=1}^{M-1}\sum_{B=A+1}^{M}\frac{Z_A Z_B}{R_{AB}}}_{V_{NN}}$$

But, since V_{NN} does not depend on electronic coordinates,

$$\langle \Psi | V_{NN} | \Psi \rangle = V_{NN}\langle \Psi | \Psi \rangle = V_{NN}$$

Thus, total energy is:

$$E = E_e + V_{NN}$$

$$E = \sum_{i=1}^{N} H_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}(J_{ij} - K_{ij}) + V_{NN}$$

Coulomb and exchange operators

The electronic energy can be expressed in terms of the operators J_i and K_i, defined as:

$$\hat{J}_i(1)|\chi_j(2)\rangle = \langle\chi_i(1)|\frac{1}{r_{12}}|\chi_i(1)\rangle|\chi_j(2)\rangle$$

$$\hat{K}_i(1)|\chi_j(2)\rangle = \langle\chi_i(1)|\frac{1}{r_{12}}|\chi_j(1)\rangle|\chi_i(2)\rangle$$

$\hat{J}$ - involves a multiplication by a matrix element with the same orbital on both sides of $\frac{1}{r_{12}}$ (is a local operator since the result of its application on a spin-orb. depends solely on value of χ_i at x_1)

$$\hat{J}_i(1) = \int\left[dx_2\,|\chi_j(2)|^2 \cdot \frac{1}{r_{12}}\right]$$ - average local potential at x_1 arising from an electron in x_2

$\hat{K}$ - exchanges the two functions on the right-hand side of $1/r_{12}$.

- non-local operator since the result of operating with $K_i(x_1)$ on $\chi_i(x_1)$ depends on the value of χ_i on all points in space (χ_i is related to x_2 - variable of integration

$\hat{J}_i$ and $\hat{K}_i$ - Introduced for the purpose of deriving the variation of energy as a result of varying the wavefunction

With these operators:

$$E_e = \sum_{i=1}^{N}\langle\chi_i|\hat{h}_i|\chi_i\rangle + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\langle\chi_j|J_i|\chi_j\rangle - \langle\chi_j|K_i|\chi_j\rangle\right)$$

More about K_{ij}

Let's consider the H_2 molecule

Ψ – total wavefunction

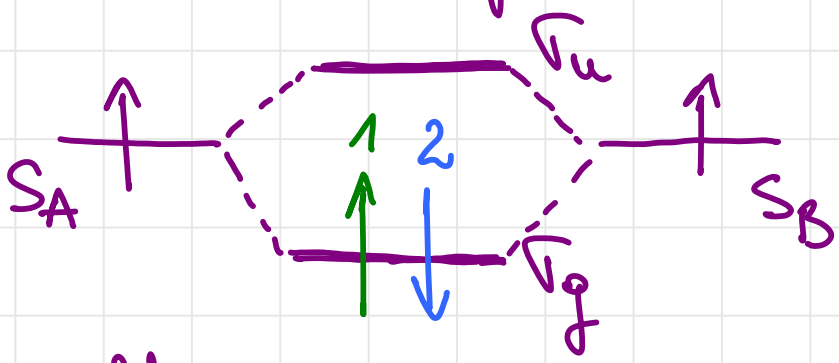
χ – spin orbitals

$\chi = \phi \cdot \eta$

ϕ – spatial MO (σ_g or σ_u)

σ – spin function: α or β

Consider the ground state of H_2:
(singlet state)



$\chi_1 = \sigma_g \cdot \alpha$

$\chi_2 = \sigma_g \cdot \beta$

$$\Psi^{singlet} = \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = \chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)$$

$$\chi_1(1) = \sigma_g(1)\,\alpha(1) \qquad \chi_2(1) = \sigma_g(1)\,\beta(1)$$

$$\chi_1(2) = \sigma_g(2)\,\alpha(2) \qquad \chi_2(2) = \sigma_g(2)\,\beta(2)$$

$$J_{12} = \langle \chi_1(1)\chi_2(2) | \frac{1}{r_{12}} | \chi_1(1)\chi_2(2) \rangle =$$

$$= \iint d\tau_1\, d\tau_2\, \chi_1(1)\chi_2(2) \cdot \frac{1}{r_{12}} \cdot \chi_1(1)\chi_2(2) =$$

$$= \iint \overbrace{d\tau_1\, d\tau_2}^{\text{spatial \& spin coordinates}} \sigma_g(1)\alpha(1)\,\sigma_g(2)\beta(2)\cdot\frac{1}{r_{12}}\cdot\sigma_g(1)\alpha(1)\,\sigma_g(2)\beta(2) =$$

$$= \iint \overbrace{dr_1\, dr_2}^{\text{spatial coordinates}} \sigma_g(1)\sigma_g(2)\cdot\frac{1}{r_{12}}\sigma_g(1)\sigma_g(2)\ \cdot$$

$$\cdot \underbrace{\int ds_1\, \alpha(1)\alpha(1)}_{=1} \cdot \underbrace{\int ds_2\, \beta(2)\beta(2)}_{=1}$$

spin coordinates

$$\Rightarrow J_{ij} = \iint dr_1\, dr_2\, \sigma_g(1)\sigma_g(2)\,\frac{1}{r_{12}}\,\sigma_g(1)\sigma_g(2) \neq 0$$

Now, let's calculate K_{12}

$$K_{12} = \iint d\tau_1\, d\tau_2\, \chi_1(1)\chi_2(2)\cdot\frac{1}{r_{12}}\cdot\chi_2(1)\chi_1(2) =$$

$\chi_1(1) = \sigma_g(1)\beta(1)$, $\chi_2(2) = \sigma_g(2)\alpha(2)$

$$= \iint dr_1\, dr_2\, \sigma_g(1)\sigma_g(2)\cdot\frac{1}{r_{12}}\,\sigma_g(1)\sigma_g(2)\ \cdot$$

$$\cdot \underbrace{\int ds_1\, \alpha(1)\beta(1)}_{=0} \cdot \underbrace{\int ds_2\, \beta(2)\cdot\alpha(2)}_{=0} = 0$$

Conclusion:

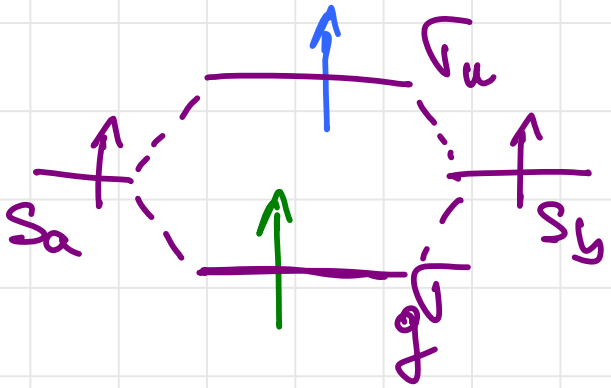
- for singlet state: $K_{12} = 0$; $J_{12} \neq 0$

Opposing spins are orthogonal (by definition)

⇨ integration over the α-β cross term is zero

⇨ exchange integral is eliminated

Now, let's consider the triplet excited state of H_2:



$$\psi^{triplet} = \begin{vmatrix} \sigma_g(1)\alpha(1) & \sigma_u(1)\alpha(1) \\ \sigma_g(2)\alpha(2) & \sigma_u(2)\alpha(2) \end{vmatrix}$$

$\chi_1 = \sigma_g \cdot \alpha$

$\chi_2 = \sigma_u \cdot \alpha$

$$\chi_1(1) = \sigma_g(1)\alpha(1) \qquad \chi_2(1) = \sigma_u(1)\alpha(1)$$

$$\chi_1(2) = \sigma_g(2)\alpha(2) \qquad \chi_2(2) = \sigma_u(2)\alpha(2)$$

$$J_{12} = \iint d\tau_1 d\tau_2\, \chi_1(1)\chi_2(2)\frac{1}{r_{12}}\chi_1(1)\chi_2(2)$$

$$= \iint dr_1 dr_2\, \sigma_g(1)\sigma_u(2)\cdot\frac{1}{r_{12}}\cdot\sigma_g(1)\sigma_u(2)\cdot$$

$$\cdot\int d\sigma_1\, \alpha(1)\alpha(1)\cdot\int d\sigma_2\, \alpha(2)\alpha(2)$$

$$= \iint dr_1 dr_2\, \sigma_g(1)\sigma_u(2)\frac{1}{r_{12}}\sigma_g(1)\sigma_u(2) \neq 0$$

$$K_{12} = \iint d\tau_1 d\tau_2\, \chi_1(1)\chi_2(2)\frac{1}{r_{12}}\chi_2(1)\chi_1(2)$$

$$= \iint dr_1 dr_2\, \sigma_g(1)\sigma_u(2)\cdot\frac{1}{r_{12}}\sigma_u(1)\sigma_g(2)\cdot$$

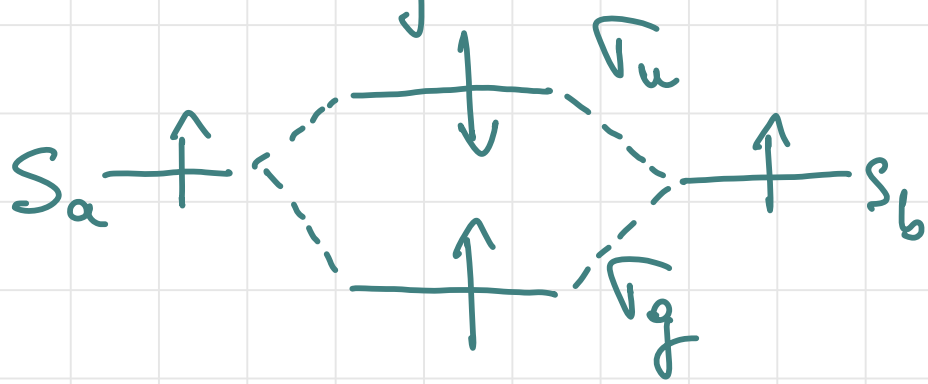
$$\cdot\int d\sigma_1\, \alpha(1)\alpha(1)\cdot\int d\sigma_2\, \alpha(2)\alpha(2) \neq 0$$

Conclusion

- for triplet state: $K_{12} \neq 0$, $J_{12} \neq 0$

Exercise

Prove that for the singlet excited state given in the figure below, $K_{ij} = 0$



$K_{ij} = 0$ for spin orbitals χ_i and χ_j describing a pair of antiparallel spins.

$K_{ij} \neq 0$ for spin orbitals χ_i and χ_j describing a pair of parallel spins.

Since K_{ij} is substracted from J_{ij} in the expression for E_e, it means that this exchange term, K_{ij}, can be considered as a correction to J_{ij} for electrons of the same spin.

Less Coulomb repulsion for these electrons

$\Rightarrow$

- electrons with parallel spin can be considered as avoiding each other (spin correlation)

or, in other words

- electrons with parallel spin can be considered as having a lower charge or as having a "hole" associated with them (exchange hole or "Fermi hole")

Homework

1) Derive the expression of the electronic energy using a simple Hartree product as wave function:

$$\Psi = \prod = \chi_1(1)\chi_2(2)\cdots\chi_N(N)$$

2) Show that matrix elements arising from P_{ijkl} operators are zero

3) Consider the first excited state of the helium atom. One possible wave function is given by:

$2s \; \uparrow$

$1s \; \uparrow$

$$\Psi_1 = \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix}$$

where:

$\chi_1(1) = 1s(1)\alpha(1)$ $\qquad$ $\chi_2(1) = 2s(1)\alpha(1)$

$\chi_1(2) = 1s(2)\alpha(2)$ $\qquad$ $\chi_2(2) = 2s(2)\alpha(2)$

Introduce new spin orbitals χ' as linear combinations of the original ones:

$$\chi_1' = \frac{1s + 2s}{\sqrt{2}}\alpha \qquad \chi_2' = \frac{1s - 2s}{\sqrt{2}}\alpha$$

Prove that the total wavefunction in this case is: $\Psi_2 = -\Psi_1$

! The conclusion of this exercises will be that a linear combination of MOs used to construct a given Ψ leads to the same Ψ (eventually with different sign) and the same energy.

In this particular case,

χ – are localized orbitals

χ' – are orbitals delocalized over the entire molecule.

$$K_j(x_1)\,|\chi_i(x_1)\rangle$$

$$= \int \underbrace{\chi_j(x_2)\,\frac{1}{r_{12}}\,\chi_i(x_2)\,dx_2}_{\text{here:}}\,|\chi_j(x_1)\rangle$$

$\frac{1}{r_{12}}$ – is spin independent

$\Rightarrow$ the integral over the spin coordinate can be separated

χ_i & χ_i depend on the same spatial coordinate ($\vec{r}_2$)

because spin functions are orthonormal

$\Rightarrow$ exchange contribution $\neq 0$ only for electrons with the same spin.

Summary

$\hat{J}$ & $\hat{K}$ operators:

$$J_j(1)\,\chi_i(1) = \left[\int \chi_j^*(2)\,\frac{1}{r_{12}}\,\chi_j(2)\,d\tau_2\right]\cdot\chi_i(1)$$

or:

$$J_j(1)\,\chi_i(1) = \langle \chi_j^*(2)\,|\,\frac{1}{r_{12}}\,|\,\chi_j(2)\rangle \cdot |\chi_i(1)\rangle$$

$$K_j(1)\,\chi_i(1) = \left[\int \chi_j^*(2)\,\frac{1}{r_{12}}\,\chi_i(2)\,d\tau_2\right]\chi_j(1)$$

or:

$$K_j(1)\,\chi_i(1) = \langle \chi_j^*(2)\,|\,\frac{1}{r_{12}}\,|\,\chi_i(2)\rangle \cdot |\chi_j(1)\rangle$$

$\hat{J}$ – local operator

– its value as a result of application on $\chi_i(1)$ depends on the value of χ_i in $\vec{x}_1$ only

$\hat{K}$ – non-local operator

– its value as a result of application on $\chi_i(1)$ depends on the values of χ_i in all points in space (χ_i is part of the integrand)

$\hat{J}$ & $\hat{K}$ were introduced for deriving the variation of E_e as a function of the variations of the monoelectronic wavefunctions χs.

$$E_e = \sum_{i=1}^{N} \langle \chi_i | \hat{h}_i | \chi_i \rangle + \frac{1}{2}\sum_i^N \sum_j^N \left[\langle \chi_i | \hat{J}_j | \chi_i \rangle - \langle \chi_i | \hat{K}_j | \chi_i \rangle\right]$$

Kij Integrals: Example

Let's consider the H_2 molecule.

Ψ – total wavefunction

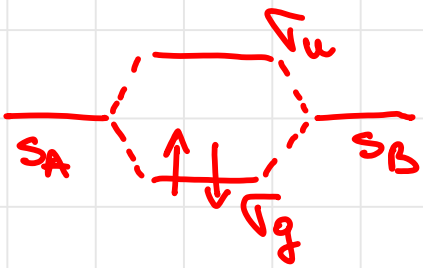
χ – spin orbitals $\qquad \chi = \phi \cdot \eta$

$\eta \to$ spin wf: α or β

$\phi \to$ spatial wf (MO) (σ_g or σ_u)

Ground state of H_2

– singlet state



$$\chi_1 = \sigma_g \cdot \alpha$$
$$\chi_2 = \sigma_g \cdot \beta$$

$$\Rightarrow \Psi^S = \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = \chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)$$

$$\chi_1(1) = \sigma_g(1)\alpha(1) \qquad \chi_2(1) = \sigma_g(1)\beta(1)$$
$$\chi_1(2) = \sigma_g(2)\alpha(2) \qquad \chi_2(2) = \sigma_g(2)\beta(2)$$

$$\Rightarrow J_{12} = \left\langle \chi_1(1)\chi_2(2) \frac{1}{r_{12}} \chi_1(1)\chi_2(2) \right\rangle =$$

$$= \iint d\tau_1 d\tau_2 \, \chi_1(1)\chi_2(2) \frac{1}{r_{12}} \chi_1(1)\chi_2(2) =$$

$$= \iint d\tau_1 d\tau_2 \, \sigma_g(1)\alpha(1)\sigma_g(2)\beta(2) \frac{1}{r_{12}} \sigma_g(1)\alpha(1)\sigma_g(2)\beta(2)$$

$$= \iint dr_1 dr_2 \, \sigma_g(1)\sigma_g(2) \frac{1}{r_{12}} \sigma_g(1)\sigma_g(2) \cdot \underbrace{\int ds_1 \, \alpha(1)\alpha(1)}_{=1} \cdot \underbrace{\int ds_2 \, \beta(2)\beta(2)}_{=1}$$

$$\Rightarrow J_{12} = \iint dr_1 dr_2 \, \sigma_g(1)\sigma_g(2) \frac{1}{r_{12}} \sigma_g(1)\sigma_g(2) \neq 0$$

$$\boxed{J_{12} \neq 0}$$

$$K_{12} = \iint d\tau_1 d\tau_2\, \chi_1(1)\chi_2(2)\, \frac{1}{r_{12}}\, \chi_2(1)\chi_1(2)$$

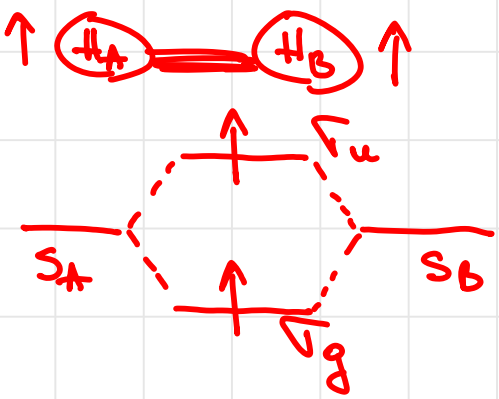
$$= \iint d\tau_1 d\tau_2\, \sigma_g(1)\alpha(1)\sigma_g(2)\beta(2)\, \frac{1}{r_{12}}\, \sigma_g(1)\beta(1)\, \sigma_g(2)\alpha(2) =$$

$$= \iint d\tau_1 d\tau_2\, \sigma_g(1)\sigma_g(2)\, \frac{1}{r_{12}}\, \sigma_g(1)\sigma_g(2) \cdot \underbrace{\int ds_1\, \alpha(1)\beta(1)}_{=0} \cdot \underbrace{\int ds_2\, \beta(2)\alpha(2)}_{=0}$$

$$\Rightarrow \boxed{K_{12} = 0}$$

$\Rightarrow$ H_2 ground state, singlet : $J_{12} \neq 0$, $K_{12} = 0$

Excited state of H_2 – triplet



$\chi_1 = \sigma_g \cdot \alpha$ $\quad$ $\chi_1(1) = \sigma_g(1)\alpha(1)$

$\chi_2 = \sigma_u \cdot \alpha$ $\quad$ $\chi_2(2) = \sigma_u(2)\alpha(2)$

$$\psi^t = \begin{vmatrix} \sigma_g(1)\alpha(1) & \sigma_u(1)\alpha(1) \\ \sigma_g(2)\alpha(2) & \sigma_u(2)\alpha(2) \end{vmatrix}$$

$$J_{12} = \iint d\tau_1 d\tau_2\, \sigma_g(1)\alpha(1)\sigma_u(2)\alpha(2)\, \frac{1}{r_{12}}\, \sigma_g(1)\alpha(1)\sigma_u(2)\alpha(2) =$$

$$= \iint d\tau_1 d\tau_2\, \sigma_g(1)\sigma_u(2)\, \frac{1}{r_{12}}\, \sigma_g(1)\sigma_u(2) \cdot \underbrace{\int ds_1\, \alpha(1)\alpha(1)}_{=1} \cdot \underbrace{\int ds_2\, \alpha(2)\alpha(2)}_{=1}$$

$$= \iint d\tau_1 d\tau_2\, \sigma_g(1)\sigma_u(2)\, \frac{1}{r_{12}}\, \sigma_g(1)\sigma_u(2) \neq 0$$

$$\Rightarrow \boxed{J_{12} \neq 0}$$

$$K_{12} = \iint d\tau_1 d\tau_2 \, \chi_1(1)\chi_2(2) \frac{1}{r_{12}} \chi_2(1)\chi_1(2) =$$

$$= \iint d\tau_1 d\tau_2 \, \sigma_g(1)\alpha(1)\sigma_u(2)\alpha(2) \frac{1}{r_{12}} \sigma_u(1)\alpha(1)\sigma_g(2)\alpha(2) =$$

$$= \underbrace{\iint d\tau_1 d\tau_2 \, \sigma_g(1)\sigma_u(2) \frac{1}{r_{12}} \sigma_u(1)\sigma_g(2)}_{\neq 0} \cdot \underbrace{\int ds_1 \, \alpha(1)\alpha(1)}_{=1} \cdot \underbrace{\int ds_2 \, \alpha(2)\alpha(2)}_{=1}$$

$$\Rightarrow \boxed{K_{12} \neq 0}$$

$\Rightarrow$ H_2 triplet state (excited state): $J_{12} \neq 0$, $K_{12} \neq 0$

In general:

$K_{ij} = 0$ for pairs of spin orbitals χ_i & χ_j describing a pair of electrons with antiparallel spins

$K_{ij} \neq 0$ for pairs of spin orbitals χ_i & χ_j describing a pair of electrons with parallel spins

Interpretation

in E_e, K_{ij} is substracted from J_{ij}

$\hookrightarrow$ Coulombian repulsion

$\Rightarrow$ K_{ij} – correction to J_{ij} for spin paired electrons ($\alpha\alpha$ or $\beta\beta$)

$\Rightarrow$ spin-paired electrons avoid each other

$\rightarrow$ spin correlation

or

the spin-paired electrons can be considered as having a lower charge (or as having an associated "hole" with $q < |e|$)

$\rightarrow$ "Fermi hole"