

The same will be true for any **one-electron** operator, so for the **electron-nuclear** attraction

$$\left\langle -\frac{2}{r_{1n}} \right\rangle = \left\langle -\frac{2}{r_{2n}} \right\rangle = 2 \left\langle -\frac{1}{r_{1n}} \right\rangle$$

The 2-electron operator $1/r_{12}$ is different:

$$\left\langle \frac{1}{r_{12}} \right\rangle = \int 1s(1)1s(2) \frac{1}{r_{12}} 1s(1)1s(2) d\tau_1 d\tau_2 = J_{1s,1s}$$

J_{ij} repulsion integrals are called “Coulomb integrals”;

Here they are simply the repulsion of two 1s clouds of negative charge, that happen to be superimposed in this case.

Thus, for the He ground state:

$$\mathbf{E}_{\text{ground}} = \mathbf{2h}_{1s} + \mathbf{J}_{1s,1s}$$

where h_{1s} is a sum of one-electron operators:

the KE + electron-nuclear attraction for a 1s electron

Next consider the Helium 1s2s configuration

$$\Psi_{\text{singlet}} = [1s(1)2s(2) + 2s(1)1s(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\Psi_{\text{singlet}} = [1s(1) 2s(2) + 2s(1) 1s(2)] \{ \alpha(1)\beta(2) - \beta(1) \alpha(2) \}$$

$$\langle E \rangle_{\text{singlet}} = \langle [1s(1) 2s(2) + 2s(1) 1s(2)] \{ \alpha(1)\beta(2) - \beta(1) \alpha(2) \} | H | [1s(1) 2s(2) + 2s(1) 1s(2)] \{ \alpha(1)\beta(2) - \beta(1) \alpha(2) \} \rangle$$

$$\langle E \rangle_{\text{singlet}} = \langle [1s(1) 2s(2) + 2s(1) 1s(2)] \{ \alpha(1)\beta(2) - \beta(1) \alpha(2) \} | H | [1s(1) 2s(2) + 2s(1) 1s(2)] \{ \alpha(1)\beta(2) - \beta(1) \alpha(2) \} \rangle$$

Again, H does not have spin coordinates, ignoring spin-orbit coupling, so:

$$E_{\text{singlet}} = \langle s(1)2s(2) + 2s(1)1s(2) | H | s(1)2s(2) + 2s(1)1s(2) \rangle$$

Now the 1-electron part has to be $\mathbf{h}_{1s} + \mathbf{h}_{2s}$ but appears to be twice that at this point. Must normalize the linear combination,

Normalization

Whenever two orthonormal functions are added, e.g., $|A\rangle + |B\rangle$, the overlap is no longer 1,

but $(\langle A| + \langle B|) (|A\rangle + |B\rangle)$

$$= N^2(\langle A|A\rangle + \langle B|B\rangle + \langle A|B\rangle + \langle B|A\rangle)$$

$$= 1 + 1 + 0 + 0 = 2$$

So normalization constant **squared** = 1/2

$$\text{norm const} = 2^{-1/2} = \mathbf{0.707}$$

Generally, adding N orthonormal functions with equal weight gives norm const = $N^{-1/2}$

but the 2-electron part has an extra part due to **electron exchange**

$$\begin{aligned}
 \langle 1/r_{12} \rangle &= \frac{1}{2} \langle 1s(1)2s(2) + 2s(1)1s(2) | \frac{1}{r_{12}} | 1s(1)2s(2) + 2s(1)1s(2) \rangle \\
 &= \langle 1s(1)2s(2) | \frac{1}{r_{12}} | 1s(1)2s(2) \rangle + \langle 1s(1)2s(2) | \frac{1}{r_{12}} | 2s(1)1s(2) \rangle \\
 &= \langle 1s(1)1s(1) | \frac{1}{r_{12}} | 2s(2)2s(2) \rangle + \langle 1s(1)2s(1) | \frac{1}{r_{12}} | 1s(2)2s(2) \rangle
 \end{aligned}$$

Order does not matter (just multiplying by 1/r₁₂). Writing this way makes it easier to visualize

$$= \mathbf{J}_{1s,2s} + \mathbf{K}_{1s,2s}$$

where $\mathbf{K}_{1s,2s}$ is called an **exchange integral** because it arises only because of the requirement that the electrons must exchange.

\mathbf{J}_{ij} is classical; It is simply the Coulombic repulsion of $1s(1)^2$ and $2s(2)^2$ negative clouds of charge.

\mathbf{K}_{ij} is the repulsion of two ij clouds: $1s(1)2s(1)$ and $1s(2)2s(2)$

Triplet State

$$\begin{aligned}
 \langle 1/r_{12} \rangle &= \frac{1}{2} \langle 1s(1)2s(2) - 2s(1)1s(2) | \frac{1}{r_{12}} | 1s(1)2s(2) - 2s(1)1s(2) \rangle \\
 &= \langle 1s(1)2s(2) | \frac{1}{r_{12}} | 1s(1)2s(2) \rangle - \langle 1s(1)2s(2) | \frac{1}{r_{12}} | 2s(1)1s(2) \rangle \\
 &= \langle 1s(1)1s(1) | \frac{1}{r_{12}} | 2s(2)2s(2) \rangle - \langle 1s(1)2s(1) | \frac{1}{r_{12}} | 1s(2)2s(2) \rangle
 \end{aligned}$$

Now the cross terms are negative, because the space function is antisymmetric.

$$= J_{1s,2s} \quad \text{minus} \quad K_{1s,2s}$$

The triplet state is LOWER than the singlet state!!!

because it can be proved that all J_{ij} and K_{ij} integrals are positive, but $K_{ij} < J_{ij}$.

J_{ij} is classical; It is simply the Coulombic repulsion of two negative clouds of charge described by the squares of the orbitals
 K_{ij} is the repulsion of two ij clouds e.g., $1s(1)2s(1)$

Slater Determinants notation for the same functions:

$$\Psi_{ground} = \varphi_{1s}(1)\bar{\varphi}_{1s}(2) - \bar{\varphi}_{1s}(1)\varphi_{1s}(2)$$

$$\Psi_{ground} = \begin{vmatrix} \varphi_{1s}(1) & \bar{\varphi}_{1s}(1) \\ \varphi_{1s}(2) & \bar{\varphi}_{1s}(2) \end{vmatrix}$$

$$\Psi = A(1)B(2) - B(1)A(2)$$

$$\Psi_{ground} = \begin{vmatrix} A(1) & B(1) \\ A(2) & B(2) \end{vmatrix} = \begin{vmatrix} A(1) & A(2) \\ B(1) & B(2) \end{vmatrix} \equiv |AB|$$

For 4 electrons:

$|ABCD|$ means a Slater determinant and the electron numbering in each term is 1,2,3,4

Antisymmetry for more than 2 electrons

Generic 3 electron case:

$$\Psi = A(1)B(2)C(3)\dots - B(1)A(2)C(3)\dots - C(1)B(2)A(3)\dots$$

$$\Psi = \begin{vmatrix} A(1) & A(2) & A(3) \\ B(1) & B(2) & B(3) \\ C(1) & C(2) & C(3) \end{vmatrix} \equiv \begin{vmatrix} A(1) & B(1) & C(1) \\ A(2) & B(2) & C(2) \\ A(3) & B(3) & C(3) \end{vmatrix} \equiv |ABC|$$

$$\Psi^* \Psi = \langle |ABC| || |ABC| \rangle$$

Note that it does not matter whether:

columns have same electron number and rows have same orbital,
or vice versa

Normalization (assuming orthonormal orbitals)

There are $N!$ (N factorial) terms for an N -electron Slater determinant

Example of 3 electrons: $3! = 6$

$$ABC - ACB + BCA - BAC + CAB - CBA$$

Overlap integral is:

$$\langle ABC - ACB + BCA - BAC + CAB - CBA | ABC - ACB + BCA - BAC + CAB - CBA \rangle = ?$$

$$= \langle ABC | ABC \rangle = \langle A | A \rangle \langle B | B \rangle \langle C | C \rangle = (1)(1)(1) \text{ because orbitals are } \mathbf{1\text{-electron functions}}$$

but, if there is only one mismatch, e.g., $\langle ABC | ACB \rangle$

$$= \langle A | A \rangle \langle \mathbf{B} | \mathbf{C} \rangle \langle \mathbf{C} | \mathbf{B} \rangle = (1) (0) (0) = 0$$

ab initio Calculations

meaning literally: from the beginning

In practice means: no approximations are made in the mathematical operations, although all calculations are more or less approximate, depending on the number of variational parameters chosen.

$$H = \sum_i -\frac{1}{2} \nabla_i^2 - \sum_{i,\mu} \frac{Z_\mu}{r_{i\mu}} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_i -\frac{1}{2} \nabla_\mu^2 + \sum_{\mu,\nu} \frac{Z_{\mu\nu}}{r_{\mu\nu}}$$

electron kinetic E	electron- nuclear attraction	electron- electron repulsion	nuclear kinetic E	nuclear- nuclear repulsion
-----------------------	------------------------------------	------------------------------------	----------------------	----------------------------------

$$H = \sum_i -\frac{1}{2} \nabla_i^2 - \sum_{i,\mu} \frac{Z_\mu}{r_{i\mu}} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_i -\frac{1}{2} \nabla_\mu^2 + \sum_{\mu,\nu} \frac{Z_{\mu\nu}}{r_{\mu\nu}}$$

electron
kinetic E

electron-
nuclear
attraction

electron-
electron
repulsion

nuclear
kinetic E

nuclear-
nuclear
repulsion

ONE-electron
operators

TWO-electron
operators

= **0** for electronic
energy at a **fixed
geometry**

= a **constant**
for electronic
energy at a fixed
geometry
Is added to the
electronic energy
at the end

“Electronic” Energy

Hartree Self-Consistent Field (SCF)

Wavefunction = single product of orthonormal spin orbitals

$$A \bar{A} B \bar{B} C \bar{C} \dots$$

where bar on top means β spin

This preceded the Hartree-Fock SCF.

What is wrong with this?

Not anti-symmetric to interchange of electron coordinates,
Fock was the one who extend the method for Slater
Determinants.

Hartree-Fock Self Consistent Field (SCF)

Wavefunction = single Slater determinant of orthonormal spin orbitals

$$(N!)^{-1/2} \left| A \bar{A} B \bar{B} C \bar{C} \dots \right|$$


HF-SCF total energy: ***

Simplifications:

1. *** Unnecessary to have a determinant on both sides because of double counting of permutations
2. Integrate over **electrons ONLY** because :
nuclear kinetic energy assumed zero (Born-Oppenheimer)
3. and therefore **nuclear-nuclear repulsion is a constant to be added after** the purely electronic energy is determined.
4. H does not contain spin (a good approximation for light atoms)

Consider the example where there are $6! = 720$ permutations on the right, showing only the **permutation of electrons 1 and 2**

$$E_{trial} = (N!)^{-1/2} \langle A\bar{A}B\bar{B}C\bar{C} | H | A\bar{A}B\bar{B}C\bar{C} \rangle$$

$$= \langle A\bar{A}B\bar{B}C\bar{C} | H | A\bar{A}B\bar{B}C\bar{C} - \bar{A}A\bar{B}B\bar{C}C - \dots \rangle$$


$\langle A(1) | h(1) | A(1) \rangle \langle A(2) | A(2) \rangle \langle \alpha | \beta \rangle \langle \beta | \alpha \rangle \langle A(3) | A(3) \rangle \langle A(4) | A(4) \rangle \dots$
 just for the **one-electron part of H** for electron 1.

This illustrates most of the permutations give **zero** because of either **spin or space orthogonality mismatches** (when an electron is in a different spin-orbital on the two sides of the integral).

Such mismatches may only be non zero if the corresponding operator in the Hamiltonian intervenes.

Slater Condon Rules

Slater and Condon articulated rules for the few cases on non zero element.

11.8 The Condon–Slater Rules

pp 320-321 Levine 7th E.

In the Hartree–Fock approximation, the wave function of an atom (or molecule) is a Slater determinant or a linear combination of a few Slater determinants [for example, Eq. (10.44)]. A configuration-interaction wave function such as (11.17) is a linear combination of many Slater determinants. To evaluate the energy and other properties of atoms and molecules using Hartree–Fock or configuration-interaction wave functions, we must be able to evaluate integrals of the form $\langle D' | \hat{B} | D \rangle$, where D and D' are Slater determinants of orthonormal spin-orbitals and \hat{B} is an operator.

Each spin-orbital u_i is a product of a spatial orbital θ_i and a spin function σ_i , where σ_i is either α or β . We have $u_i = \theta_i \sigma_i$ and $\langle u_i(1) | u_j(1) \rangle = \delta_{ij}$, where $\langle u_i(1) | u_j(1) \rangle$ involves a sum over the spin coordinate of electron 1 and an integration over its spatial coordinates. If u_i and u_j have different spin functions, then (10.12) ensures the orthogonality

of u_i and u_j . If u_i and u_j have the same spin function, their orthogonality is due to the orthogonality of the spatial orbitals θ_i and θ_j .

For an n -electron system, D is

$$D = \frac{1}{\sqrt{n!}} \begin{vmatrix} u_1(1) & u_2(1) & \dots & u_n(1) \\ u_1(2) & u_2(2) & \dots & u_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ u_1(n) & u_2(n) & \dots & u_n(n) \end{vmatrix} \quad (11.76)$$

An example with $n = 3$ is Eq. (10.40). D' has the same form as D except that u_1, u_2, \dots, u_n are replaced by u'_1, u'_2, \dots, u'_n .

of u_i and u_j . If u_i and u_j have the same spin function, their orthogonality is due to the orthogonality of the spatial orbitals θ_i and θ_j .

For an n -electron system, D is

$$D = \frac{1}{\sqrt{n!}} \begin{vmatrix} u_1(1) & u_2(1) & \dots & u_n(1) \\ u_1(2) & u_2(2) & \dots & u_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ u_1(n) & u_2(n) & \dots & u_n(n) \end{vmatrix} \quad (11.76)$$

An example with $n = 3$ is Eq. (10.40). D' has the same form as D except that u_1, u_2, \dots, u_n are replaced by u'_1, u'_2, \dots, u'_n .

We shall assume that the columns of D and D' are arranged so as to have as many as possible of their left-hand columns match. For example, if we were working with the Slater determinants $|1s\bar{1}s2s3p_0|$ and $|1s\bar{1}s3p_04s|$, we would interchange the third and fourth columns of the first determinant (thereby multiplying it by -1) and let $D = |1s\bar{1}s3p_02s|$ and $D' = |1s\bar{1}s3p_04s|$.

The operator \hat{B} typically has the form

$$\hat{B} = \sum_{i=1}^n \hat{f}_i + \sum_{i=1}^{n-1} \sum_{j>i} \hat{g}_{ij} \quad (11.77)$$

where the *one-electron operator* \hat{f}_i involves only coordinate and momentum operators of electron i and the *two-electron operator* \hat{g}_{ij} involves electrons i and j . For example, if \hat{B} is the atomic Hamiltonian operator (11.1), then $\hat{f}_i = -(\hbar^2/2m_e)\nabla_i^2 - Ze^2/4\pi\epsilon_0r_i$ and $\hat{g}_{ij} = e^2/4\pi\epsilon_0r_{ij}$.

Condon and Slater showed that the n -electron integral $\langle D'|\hat{B}|D \rangle$ can be reduced to¹⁶

Condon and Slater showed that the n -electron integral $\langle D' | \hat{B} | D \rangle$ can be reduced to sums of certain one- and two-electron integrals. The derivation of these Condon–Slater formulas uses the determinant expression of Prob. 8.22 together with the orthonormality of the spin-orbitals. (See *Parr*, pp. 23–27 for the derivation.) **Table 11.3** gives the Condon–Slater formulas.

In Table 11.3, each matrix element of \hat{g}_{12} involves summation over the spin coordinates of electrons 1 and 2 and integration over the full range of the spatial coordinates of electrons 1 and 2. Each matrix element of \hat{f}_1 involves summation over the spin coordinate of electron 1 and integration over its spatial coordinates. The variables in the sums and definite integrals are dummy variables.

TABLE 11.3 The Condon–Slater Rules

D and D' differ by	$\langle D' \sum_{i=1}^n \hat{f}_i D \rangle$	$\langle D' \sum_{i=1}^{n-1} \sum_{j>1} \hat{g}_{ij} D \rangle$
no spin-orbitals	$\sum_{i=1}^n \langle u_i(1) \hat{f}_1 u_i(1) \rangle$	$\sum_{i=1}^{n-1} \sum_{j>1} [\langle u_i(1)u_j(2) \hat{g}_{12} u_i(1)u_j(2) \rangle - \langle u_i(1)u_j(2) \hat{g}_{12} u_j(1)u_i(2) \rangle]$
one spin-orbital $u'_n \neq u_n$	$\langle u'_n(1) \hat{f}_1 u_n(1) \rangle$	$\sum_{j=1}^{n-1} [\langle u'_n(1)u_j(2) \hat{g}_{12} u_n(1)u_j(2) \rangle - \langle u'_n(1)u_j(2) \hat{g}_{12} u_j(1)u_n(2) \rangle]$
two spin-orbitals $u'_n \neq u_n, u'_{n-1} \neq u_{n-1}$	0	$\langle u'_n(1)u'_{n-1}(2) \hat{g}_{12} u_n(1)u_{n-1}(2) \rangle - \langle u'_n(1)u'_{n-1}(2) \hat{g}_{12} u_{n-1}(1)u_n(2) \rangle$
three or more spin-orbitals	0	0

TABLE 11.3 The Condon–Slater Rules

D and D' differ by	$\left\langle D' \left \sum_{i=1}^n \hat{f}_i \right D \right\rangle$	$\left\langle D' \left \sum_{i=1}^{n-1} \sum_{j>1} \hat{g}_{ij} \right D \right\rangle$
no spin-orbitals	$\sum_{i=1}^n \langle u_i(1) \hat{f}_1 u_i(1) \rangle$	$\sum_{i=1}^{n-1} \sum_{j>1} [\langle u_i(1)u_j(2) \hat{g}_{12} u_i(1)u_j(2) \rangle - \langle u_i(1)u_j(2) \hat{g}_{12} u_j(1)u_i(2) \rangle]$
one spin-orbital $u'_n \neq u_n$	$\langle u'_n(1) \hat{f}_1 u_n(1) \rangle$	$\sum_{j=1}^{n-1} [\langle u'_n(1)u_j(2) \hat{g}_{12} u_n(1)u_j(2) \rangle - \langle u'_n(1)u_j(2) \hat{g}_{12} u_j(1)u_n(2) \rangle]$
two spin-orbitals $u'_n \neq u_n, u'_{n-1} \neq u_{n-1}$	0	$\langle u'_n(1)u'_{n-1}(2) \hat{g}_{12} u_n(1)u_{n-1}(2) \rangle - \langle u'_n(1)u'_{n-1}(2) \hat{g}_{12} u_{n-1}(1)u_n(2) \rangle$
three or more spin-orbitals	0	0

no mismatches = leading term of identical determinants

TABLE 11.3 The Condon–Slater Rules

D and D' differ by

$$\left\langle D' \left| \sum_{i=1}^n \hat{f}_i \right| D \right\rangle$$

no spin-orbitals

$$\sum_{i=1}^n \langle u_i(1) | \hat{f}_1 | u_i(1) \rangle$$

one spin-orbital

$$\langle u'_n(1) | \hat{f}_1 | u_n(1) \rangle$$

$$u'_n \neq u_n$$

two spin-orbitals

0

$$u'_n \neq u_n, u'_{n-1} \neq u_{n-1}$$

three or more
spin-orbitals

0

**leading terms of
identical
determinants**

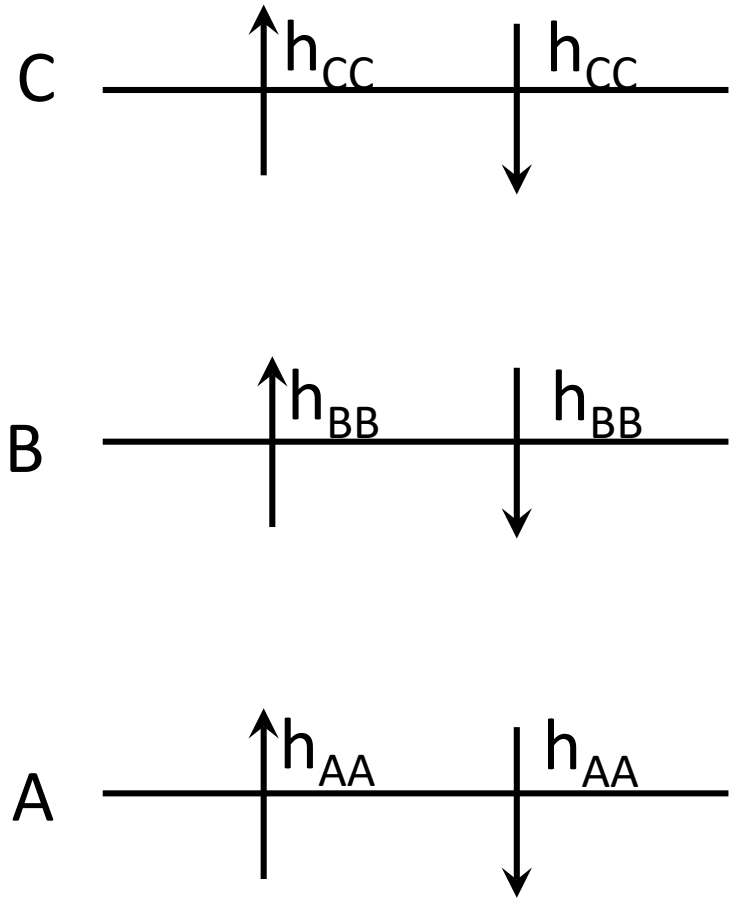
1 – electron operators give

$$2h_{AA} + 2h_{BB} + 2h_{CC}$$

where h_{AA} is:

$$h_{AA} = \langle A(1) | -\frac{1}{2} \nabla_1^2 - \sum_{\mu} \frac{Z_{1\mu}}{r_{1\mu}} | A(1) \rangle$$

= the kinetic energy and potential energy of attraction to all nuclei for an electron in orbital A



D and D' differ by

no spin-orbitals

leading terms of
identical determinants

one spin-orbital

$$u'_n \neq u_n$$

two spin-orbitals

$$u'_n \neq u_n, u'_{n-1} \neq u_{n-1}$$

three or more
spin-orbitals

$$\left\langle D' \left| \sum_{i=1}^{n-1} \sum_{j>1} \hat{g}_{ij} \right| D \right\rangle$$

i and j are different
spin orbitals but may
be same space orbital

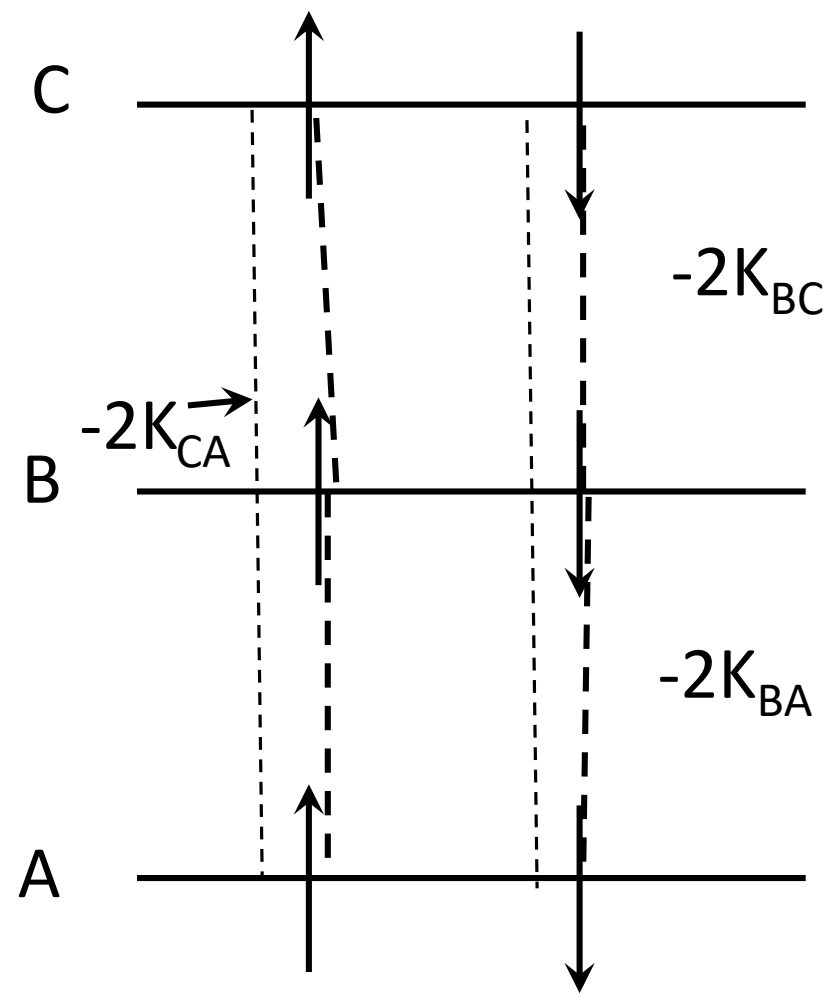
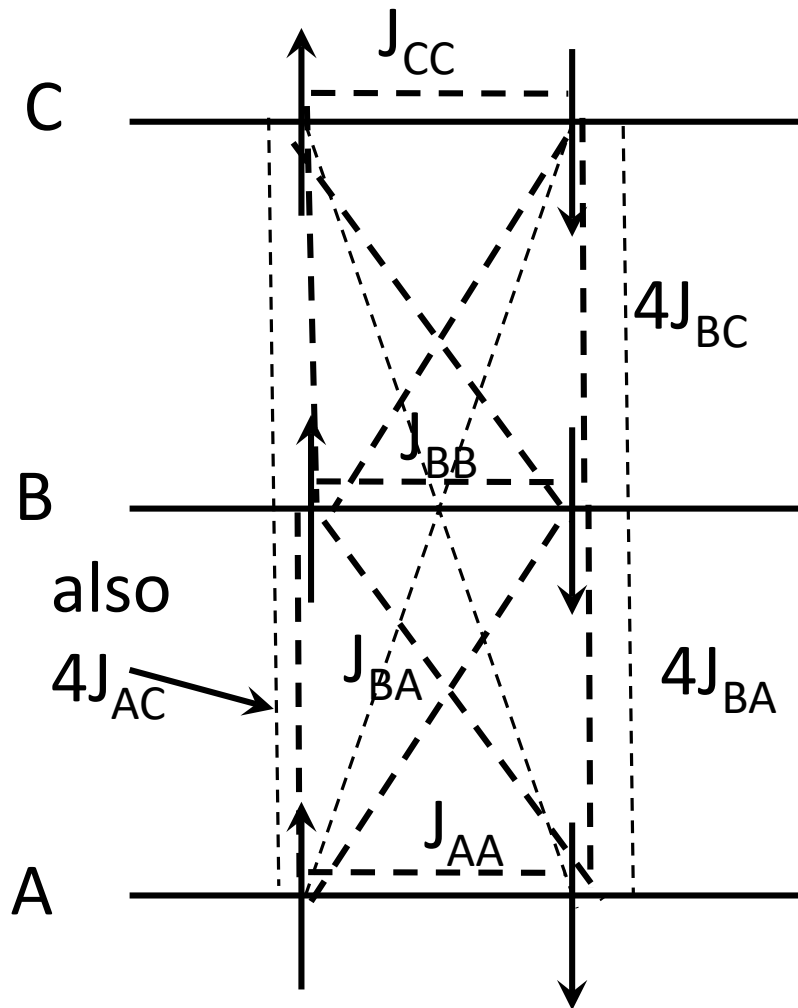
$$\sum_{i=1}^{n-1} \sum_{j>1} \left[\langle u_i(1)u_j(2) | \hat{g}_{12} | u_i(1)u_j(2) \rangle \right. \\ \left. - \langle u_i(1)u_j(2) | \hat{g}_{12} | u_j(1)u_i(2) \rangle \right]$$

No self-interaction

$$\sum_{j=1}^{n-1} \left[\langle u'_n(1)u_j(2) | \hat{g}_{12} | u_n(1)u_j(2) \rangle \right. \\ \left. - \langle u'_n(1)u_j(2) | \hat{g}_{12} | u_j(1)u_n(2) \rangle \right]$$

$$\langle u'_n(1)u'_{n-1}(2) | \hat{g}_{12} | u_n(1)u_{n-1}(2) \rangle \\ - \langle u'_n(1)u'_{n-1}(2) | \hat{g}_{12} | u_{n-1}(1)u_n(2) \rangle$$

0



2 – electron operators give

$$J_{AA} + J_{BB} + J_{CC} + 4J_{BA} + 4J_{AC} + 4J_{BC} - 2K_{BA} - 2K_{CA} - 2K_{BC}$$

Electron repulsion is reduced between electron with same m_s as seen for He(1s,2s)