General Theorem:

eigenfunctions with different eigenvalues
are orthogonal (and can always be normalized)

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$

$$\langle \alpha | \beta \rangle = 0$$

Helium ground state, and singlet vs triplet excited state

The notation of ***spin orbital*** is often used for compactness: Examples are:

$$\varphi_{1s}(1) = 1s(1)\alpha(1)$$
$$\overline{\varphi}_{1s}(1) = 1s(1)\beta(1)$$

For example the ground state function for He can be written as:

$$\varphi_{1s}(1)\overline{\varphi}_{1s}(2) - \overline{\varphi}_{1s}(1)\varphi_{1s}(2)$$

$$or$$

$$= 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The ***space-spin separated*** form is convenient for understanding the triplet state of a ***2-electron*** system. This factorization, however, cannot be done for 3 or more electrons.

Now consider the excited state of He, 1s2s, and example of an open shell system.

Here one must consider that electron exchange is also between the spatial orbitals as well as the spin functions.

Because we may factor into a space x spin functions, it is obvious that one may achieve an antisymmetric function two general ways:

(1) space = sym, spin= antisymmetric to permutation

2) space = antisym, spin= symmetric to permutation

There is **only 1 way to achieve the (1),** so it is called a **singlet state**:

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

There are 3 ways to have a symmetric spin function while having an antisymmetric space function, however:

$$\Psi_{triplet} =$$

$$[1s(1)2s(2) - 2s(1)1s(2)][\alpha(1)\alpha(2)], \qquad M = 1/2 \quad + \quad 1/2 \quad = 1$$

$$[1s(1)2s(2) - 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)], \quad M = 1/2 \quad - \quad 1/2 \quad = 0$$

$$[1s(1)2s(2) - 2s(1)1s(2)][\beta(1)\beta(2)], \qquad M = -1/2 \quad - \quad 1/2 = -1$$

Helium ground state energy:

Hamiltonian: $H = T_1 + T_2 - \frac{2}{r_{1n}} - \frac{2}{r_{2n}} + \frac{1}{r_{12}}$

kinetic E | e-n attraction | e-e repulsion

one-electron operators | **two-electron operator**

The ONLY KIND we ever have!

$$< E >= \left\langle 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \middle| H \middle| 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \right\rangle$$

$$= \left\langle 1s(1)1s(2) \middle| H \middle| 1s(1)1s(2) \right\rangle \left\langle \alpha(1)\beta(2) - \beta(1)\alpha(2) \middle| \alpha(1)\beta(2) - \beta(1)\alpha(2) \right\rangle$$

because H is purely a spatial operator (ignoring spin orbit coupling)

$$< T_1 >= \left\langle 1s(1) \middle| T_1 \middle| 1s(1) \right\rangle \times \left\langle 1s(2) \middle| 1s(2) \right\rangle = T_{1s}$$

$$< T_2 >=< T_1 > \text{so} < T > = 2\mathrm{T}_{1\mathrm{s}}$$

The same will be true for any one-electron operator, so for the e-n attraction

$$< -\frac{2}{r_{1n}} > = < -\frac{2}{r_{2n}} > = 2 < -\frac{2}{r_{1n}} >$$

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

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

$$< \frac{1}{r_{12}} >= \int 1s(1)1s(2)\frac{1}{r_{12}}1s(1)1s(2)d\tau_1 d\tau_2 = J_{1s,1s}$$

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

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:

$$\mathbf{E_{ground} = 2h_{1s} + J_{1s,1s}}$$

where h_{1s}= is the KE + electron-nuclear attraction for a 1s electron

Next consider the Helium 1s2s configuration

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

$$E_{1s2s}\ \text{singlet} = \langle [1s(1)1s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] | H | [1s(1)1s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \rangle$$

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 $\mathbf{h_{1s} + h_{2s}}$ but appears to be twice that at this point. Must normalize the linear combination,

Normalization

Whenever two orthonormal functions are added $|A\rangle + |B\rangle$, the overlap is no longer 1, but $(\langle A| + \langle B|) \mid (|A\rangle + |B\rangle)$

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

$= \quad 1 \quad + \quad 1 \quad + \quad 0 \quad + \quad 0 = 2$

So normalization constant square =1/2

N = $\mathbf{2^{-1/2} = 0.707}$

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

$$<1/r_{12}>=\frac{1}{2}\left\langle 1s(1)2s(2)+2s(1)1s(2)\left|\frac{1}{r_{12}}\right|1s(1)2s(2)+2s(1)1s(2)\right\rangle$$

$$=\left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|1s(1)2s(2)\right\rangle+\left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|2s(1)1s(2)\right\rangle$$

$$=\left\langle 1s(1)1s(1)\left|\frac{1}{r_{12}}\right|2s(2)2s(2)\right\rangle+\left\langle 1s(1)2s(1)\left|\frac{1}{r_{12}}\right|1s(2)2s(2)\right\rangle$$

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

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

Triplet

$$<1/r_{12}>=\frac{1}{2}\langle 1s(1)2s(2)-2s(1)1s(2)|\frac{1}{r_{12}}|1s(1)2s(2)-2s(1)1s(2)\rangle$$

$$=\langle 1s(1)2s(2)|\frac{1}{r_{12}}|1s(1)2s(2)\rangle-\langle 1s(1)2s(2)|\frac{1}{r_{12}}|2s(1)1s(2)\rangle$$

$$=\langle 1s(1)1s(1)|\frac{1}{r_{12}}|2s(2)2s(2)\rangle-\langle 1s(1)2s(1)|\frac{1}{r_{12}}|1s(2)2s(2)\rangle$$

= $J_{1s,2s}$ minus $K_{1s,2s}$

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

At this level of theory, the triplet state is lowest by a large amount because of less electron repulsion. **Make sure you understand the reason for this**: the antisymmetric space function becomes small when the two electrons are near each other (going to zero in the limit of the 2 electrons being a the same point), i.e., the probability to be near each other is much reduced. This is opposite the behavior of the singlet state.

Slater Determinants notation for the same functions:

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

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

Generically:

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

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

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

Generically:

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

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

$$\left\langle \left|ABC\right| \middle| \left|ABC\right| \right\rangle$$

Note that it does not matter whether:
columns have same electron number and rows have same orbital,
or vice versa.

We will try to consistently use the above notation.