Priciple of indistinguishability

Consider two quantum states labeled by the quantum numbers *a* and *b* and filled with two non-interacting particles, 1 and 2. The Schrödinger equation of the system will be:
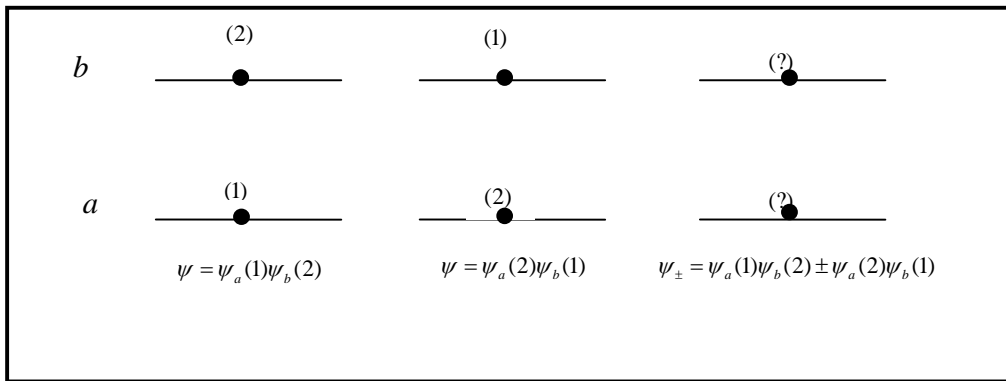
$$\hat{H}\psi = E\psi \tag{1}$$

where

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\nabla^2(1) + \nabla^2(2)\right] \tag{2}$$

and

$$\psi(1,2) = \psi_a(1)\psi_b(2) \tag{3}$$

Is $\psi(1,2)$ in (3) acceptable? Answer is No, since we can also have:

$$\psi(1,2) = \psi_b(1)\psi_a(2) \tag{4}$$

that satisfies $\hat{H}$. Any other superposition will be solution, for example

$$\psi_+(1,2) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)\right] \tag{5}$$

$$\psi_-(1,2) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)\right] \tag{6}$$

Use the permutation operator $\hat{P}(1,2)$, which exchange 1 and 2,we have:

$$\hat{P}(1,2)\psi_+(1,2) = \frac{1}{\sqrt{2}}\left[\psi_a(2)\psi_b(1) + \psi_b(2)\psi_a(1)\right] = \psi_+(1,2) \qquad \text{Symmetric} \tag{7}$$

$$\hat{P}(1,2)\psi_-(1,2) = \frac{1}{\sqrt{2}}\left[\psi_a(2)\psi_b(1) - \psi_b(2)\psi_a(1)\right] = -\psi_-(1,2) \qquad \text{Antisymmetric} \tag{8}$$

Watch for the behavior for $\psi_+(1,2)$ and $\psi_-(1,2)$ at small distance, what is your comment? We reach to what so called ***Pauli Exclusion Principle.***

Pauli Exclusion Principle

Weaker statement: No two electrons can have the same set of quantum numbers.

Stronger statement: Indistinguishable fermions must have total antisymmetric wavefunction.
- **fermion** – particle with half-integral spin, i.e., electron, positron, proton, ^{3}He .
- **boson** – particle with integral spin, photon, photons, phonons, ^{4}He , π -meson,.
Symmetric for Bosons, and antisymmetric for Fermions.

Comments:

1- **Antisymmetric wavefunction** is a wavefunction that changes sign when two particles are exchanged.

   For the ground state Helium atom, the antisymmetric wave function is expressed in the spin portion of the wavefunction.

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left\{\psi_{1s_\alpha}(1)\psi_{1s_\beta}(2) - \psi_{1s_\beta}(1)\psi_{1s_\alpha}(2)\right\}$$

$$= \psi_{1s}(1)\psi_{1s}(2)\frac{1}{\sqrt{2}}\left\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\right\}$$

- where α, β are spin portion of the functions.

Let us observe what happens to this two-particle wavefunction when we exchange the labels 1 and 2, where $(i) \equiv (r_i, \theta_i, \phi_i)$.

$$\psi(2,1) = \psi_{1s}(1)\psi_{1s}(2)\frac{1}{\sqrt{2}}\left\{\alpha(2)\beta(1) - \beta(2)\alpha(1)\right\} = \psi_{1s}(1)\psi_{1s}(2)\frac{1}{\sqrt{2}}\left\{-\beta(2)\alpha(1) + \alpha(2)\beta(1)\right\}$$

$$= -\psi_{1s}(1)\psi_{1s}(2)\frac{1}{\sqrt{2}}\left\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\right\} = -\psi(1,2)$$

2- **Symmetric wavefunction** is a wavefunction whose sign remains unchanged when particles are exchanged.

Examples of symmetric spin functions for two particles

$$\alpha(1)\alpha(2) \quad \Rightarrow \quad \psi_{1s_\alpha}(1)\psi_{2s_\alpha}(2)$$

$$\alpha(1)\beta(2) + \beta(1)\alpha(2) \quad \Rightarrow \quad \frac{1}{\sqrt{2}}\left\{\psi_{1s_\alpha}(1)\psi_{2s_\beta}(2) + \psi_{2s_\beta}(1)\psi_{1s_\alpha}(2)\right\} \quad \beta(1)\beta(2) \quad \Rightarrow \quad \psi_{1s_\beta}(1)\psi_{2s_\beta}(1)$$

What about the antisymmetric wavefunction for three or more particles? Thank goodness for *Slater determinants*.

Slater determinants

Reconsider

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\right\} = \frac{1}{\sqrt{2}}\begin{vmatrix}\alpha(1) & \alpha(2)\\ \beta(1) & \beta(2)\end{vmatrix}$$

We note that the antisymmetric wavefunction can be written as a determinant. This pattern follows wavefunctions of three or more particles.

Properties of the determinant:

 a-   If two columns are the same, the determinant will be zero.

$$\frac{1}{\sqrt{2}}\begin{vmatrix} \alpha(1) & \beta(2) \\ \alpha(1) & \beta(2) \end{vmatrix} = 0$$

 b-   Changing the positions of the columns will change the sign of the determinant.

The wavefunction for three particles (such as the ground state Li atom) (note we need to explicitly include the **spatial wavefunction**.)

$$\psi(1,2,3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} 1s\,\alpha(1) & 1s\,\alpha(2) & 1s\,\alpha(3) \\ 1s\,\beta(1) & 1s\,\beta(2) & 1s\,\beta(3) \\ 2s\,\alpha(1) & 2s\,\alpha(2) & 2s\,\alpha(3) \end{vmatrix}$$

$$= \frac{1}{\sqrt{6}}\left\{ \begin{array}{l} 1s\,\alpha(1)1s\,\beta(2)2s\,\alpha(3) + 1s\,\alpha(2)1s\,\beta(3)2s\,\alpha(1) + 1s\,\alpha(3)1s\,\beta(1)2s\,\alpha(2) + \\ -1s\,\alpha(3)1s\,\beta(2)2s\,\alpha(1) - 1s\,\alpha(2)1s\,\beta(1)2s\,\alpha(3) - 1s\,\alpha(1)1s\,\beta(3)2s\,\alpha(2) \end{array} \right\}$$

An antisymmetric wavefunction for n particles can be written as

$$\psi(1,2,3,\ldots,n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \alpha(1) & \alpha(2) & \alpha(3) & \cdots & \alpha(n) \\ \beta(1) & \beta(2) & \beta(3) & \cdots & \beta(n) \\ \gamma(1) & \gamma(2) & \gamma(3) & \cdots & \gamma(n) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \omega(1) & \omega(2) & \omega(3) & \cdots & \omega(n) \end{vmatrix}$$

The Pauli's exclusion principle imposes an additional complication in calculating the energy. In general for the electron-electron repulsion integral, we have:

$$V(\overline{r_1}) = \int \psi^*(\overline{r_2})\frac{1}{r_{12}}\psi(\overline{r_2})d\overline{r_2}$$

If the wavefunction is an antisymmetric wavefunction (as it should be), then the integral is broken into two portions:

$$V(\overline{r_1}) = \int \psi_\alpha^*(\overline{r_2})\frac{1}{r_{12}}\psi_\alpha(\overline{r_2})d\overline{r_2} + \int \psi_\alpha^*(\overline{r_2})\frac{1}{r_{12}}\psi_\beta(\overline{r_2})d\overline{r_2}$$

The first integral is called the **Coulomb integral**. The second integral is called the **exchange integral**. The **exchange interaction** is a consequence of quantum effect, due to that the electrons are indistinguishable (or due to **<u>Pauli Exclusion Principle</u>** We can see that the antisymmetry property of the wavefunction has a measurable effect on the energy.

Examples:

A-   For $1s^2$, the wavefunction, including the spin, is represented by

(1) $$u_0(r_1, r_2) = \phi_{100}(\vec{r}_1)\, \phi_{100}(\vec{r}_2)\, \chi_{\sin glet}$$

where the spin part is antisymmetric, and the spatial part is symmetric, under exchange of electron 1 and 2. The wavefunction in (1) does not include the e-e interaction. It can be calculated by doing this integral

(2) $$\Delta E = \int d^3 r_1 d^3 r_2\ |\phi_{100}(\vec{r}_1)|^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|}|\ \phi_{100}(\vec{r}_2)|^2$$

Note that the spin function is integrated to one directly.

B-   For two electrons designated by $1s2\ell$, for example, we can have singlet or triplet states,

(3a) $$u_1^{(s)} = \frac{1}{\sqrt{2}}\left[\phi_{100}(r_1)\, \phi_{2lm}(r_2) + \phi_{2lm}(r_1)\, \phi_{100}(r_2)\right]\chi_{singlet}$$

(3b) $$u_1^{(t)} = \frac{1}{\sqrt{2}}\left[\phi_{100}(r_1)\, \phi_{2lm}(r_2) - \phi_{2lm}(r_1)\, \phi_{100}(r_2)\right]\chi_{triplet}$$

Note that the spatial and spin functions are combined to give total antisymmetric wavefunctions. Using first-order perturbation theory, the integral can be expressed by

$$\Delta E_1^{(s,t)} = \frac{1}{2}\int d^3 r_1 \int d^3 r_2 \left[\phi_{100}(r_1)\, \phi_{2l0}(r_2) \pm\ \phi_{2l0}(r_1)\, \phi_{100}(r_2)\ \right]^*$$

$$\times \frac{1}{|r_1 - r_2|}\ \left[\phi_{100}(r_1)\, \phi_{2l0}(r_2) \pm\ \phi_{2l0}(r_1)\, \phi_{100}(r_2)\ \right]$$

$$= \int d^3 r_1 \int d^3 r_2\ |\phi_{100}(r_1)|^2\ \frac{1}{|r_1 - r_2|}|\phi_{2l0}(r_2)|^2$$

$$\pm \int d^3 r_1 \int d^3 r_2\ \phi_{100}^*(r_1)\ \phi_{2l0}^*(r_2)\frac{1}{|r_1 - r_2|}\phi_{2l0}(r_1)\, \phi_{100}(r_2)$$

$$= J \pm K$$

where the first integral, J, is the classical expression for the interaction energy between two electron clouds represented by the modulus square of each wavefunction. The second term has no classical analog-- it is the **exchange interaction** (K). The latter is a consequence of quantum effect, due to that the electrons are indistinguishable (or due to **Pauli Exclusion Principle)**.

$$\rho_1 = -\psi_{1s}^*(1)\psi_{1s}(1) = -|\psi_{1s}(1)|^2,$$

$$\rho_2 = -\psi_{1s}^*(2)\psi_{1s}(2) = -|\psi_{1s}(2)|^2$$

$$K = \int\int \psi_a^*(1)\psi_b(1)\frac{1}{r_{12}}\psi_b^*(2)\psi_a(2)d\tau_1 d\tau_2$$

K, which is always positive, represents the interaction energy between the two electrons whose distributed charge densities ρ_1 and ρ_2.

The electrostatic repulsion $\dfrac{1}{r_{12}}$ between the electrons has partly removed the degeneracy.

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H.W. Check the normalization of the function:

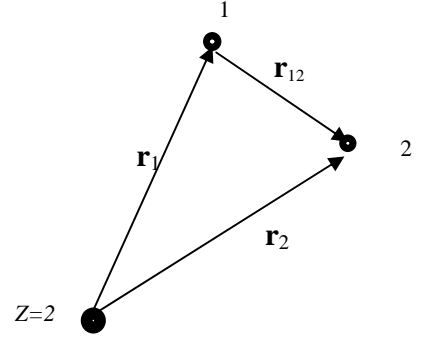$$\psi_{\pm} = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) \pm \psi_b(1)\psi_a(2)\right]$$

Example: work out the Helium atom in the ground state:

Answer: For the ground state of Helium atom, **t**he expected wave functions are:

$$\psi_1 = \psi_{1s}(1)\psi_{1s}(2)\alpha(1)\alpha(2)$$

$$\psi_2 = \psi_{1s}(1)\psi_{1s}(2)\alpha(1)\beta(2)$$

$$\psi_3 = \psi_{1s}(1)\psi_{1s}(2)\beta(1)\alpha(2)$$

$$\psi_4 = \psi_{1s}(1)\psi_{1s}(2)\beta(1)\beta(2)$$

which are the solutions of the equation:

$$\left(-\frac{1}{2}\left[\nabla_1^2 + \nabla_2^2\right] - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}\right)\psi_i = E_o\psi_i$$

But they will not satisfy Pauli's exclusion principle, since:

$$\hat{P}(1,2)\psi_1 = \psi_{1s}(2)\psi_{1s}(1)\alpha(2)\alpha(1) = \psi_1$$

$$\hat{P}(1,2)\psi_2 = \psi_3$$

$$\hat{P}(1,2)\psi_3 = \psi_2$$

$$\hat{P}(1,2)\psi_4 = \psi_4$$

So, we have to define:

$$\psi_+(1,2) = \frac{1}{\sqrt{2}}\psi_{1s}(1)\psi_{1s}(2)\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]$$

$$\psi_-(1,2) = \frac{1}{\sqrt{2}}\psi_{1s}(1)\psi_{1s}(2)\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

Then,

$$\hat{P}(1,2)\psi_+(1,2) = +\psi_+(1,2)$$

$$\hat{P}(1,2)\psi_-(1,2) = -\psi_-(1,2)$$

H.W. Prove that ψ_- take the form of Slater determinant:

$$\psi_-(1,2) = \frac{1}{\sqrt{2!}}\begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(2)\alpha(2) \\ \psi_{1s}(1)\beta(1) & \psi_{1s}(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2!}}\begin{vmatrix} \psi_{1s}^\alpha(1) & \psi_{1s}^\alpha(2) \\ \psi_{1s}^\beta(1) & \psi_{1s}^\beta(2) \end{vmatrix}$$

H.W. Using the wavefunction $\psi_{\pm} = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)\right]$ for the e-e interaction,

$$\hat{H}_{12} = \frac{1}{r_{12}} = \frac{1}{\left|\mathbf{r}_2 - \mathbf{r}_1\right|},$$

Prove that:

$$\int \psi_{\pm}^* \hat{H}_{12}\psi_{\pm} d\tau_1 d\tau_2 = J \pm K$$

where

$$J = \iint \left|\psi_a^*(1)\right|^2 \frac{e^2}{r_{12}} \left|\psi_b^*(2)\right|^2 d\tau_1 d\tau_2, \qquad K = \iint \psi_a^*(1)\psi_b(1)\frac{1}{r_{12}}\psi_b^*(2)\psi_a(2)d\tau_1 d\tau_2$$

For the operator:

$$\left(-\frac{1}{2}\left[\nabla_1^2 + \nabla_2^2\right] - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}\right)\psi = E_o\psi$$

Use the H-equation:

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right)\psi = E_o\psi, \qquad E_o = -\frac{Z^2}{n^2}$$

$$\hat{H}_{12} = \frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}$$

Use the function:

$$\psi_\pm = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)\right] = \frac{1}{\sqrt{2}}[C \pm D],$$

then

$$\langle H_1 + H_2 \rangle = \frac{1}{2}\langle C \pm D \,|\, H_1 + H_2 \,|\, C \pm D \rangle$$

Use the integral:

$$\langle \psi_a(i)\psi_b(2)|H_i|\psi_a(i)\psi_b(2)\rangle = E_i \langle \psi_a(i)\psi_b(2)_i \,|\, \psi_a(i)\psi_b(2)\rangle = E_i \delta_{aa}\delta_{bb}$$

and

$$\langle \psi_a(1)\psi_b(i)|H_i|\psi_a(i)\psi_b(1)\rangle = E_i \langle \psi_a(1)\psi_b(i)_i \,|\, \psi_a(i)\psi_b(1)\rangle = E_i \delta_{ab}\delta_{ab} = 0$$

we will have:

$$\langle H_1 + H_2 \rangle = \frac{1}{2}\left[\underbrace{\langle C|H_1 + H_2|C\rangle}_{=2E_{o1}} + \underbrace{\langle D|H_1 + H_2|D\rangle}_{=2E_{o2}} \pm \underbrace{\langle C|H_1 + H_2|D\rangle}_{=0} \pm \underbrace{\langle D|H_1 + H_2|C\rangle}_{=0}\right]$$

$$= E_{o1} + E_{o2}$$

and

$$\langle H_{12}\rangle = \frac{1}{2}\langle C \pm D \,|\, H_{12} \,|\, C \pm D \rangle = \frac{1}{2}\left[\langle C|H_{12}|C\rangle + \langle D|H_{12}|D\rangle \pm \langle C|H_{12}|D\rangle \pm \langle D|H_{12}|C\rangle\right]$$

Note that: Due to symmetry, i.e. of exchanging 1 and 2, we have:

$$J = \langle C|H_{12}|C\rangle = \langle D|H_{12}|D\rangle; \qquad K = \langle C|H_{12}|D\rangle = \langle D|H_{12}|C\rangle$$

Then:

$$\langle H_{12}\rangle = \frac{1}{2}\langle C \pm D \,|\, H_{12} \,|\, C \pm D \rangle = J \pm K$$

$$\langle H \rangle = E_{o1} + E_{o2} + J(1\ell, 2\ell) \pm K(1\ell, 2\ell)$$

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Example: Neglecting the interaction term in Helium atom, the single electron energy will be (Z=2)

$$E_{nl} = -13.6\frac{Z^2}{n^2} \approx -\frac{54}{n^2} \ \text{eV}$$

For 1s^2
$$E_{nl} = -54\left(\frac{1}{1}+\frac{1}{1}\right) = -108 \ \text{eV}$$

For single ionized Helium:
$$E_{nl}(\text{He}^+) = -54\left(\frac{1}{1}+\frac{1}{\infty}\right) = -54 \ \text{eV}$$

For 1s 2s and 1s 2p
$$E_{nl} = -54\left(\frac{1}{1}+\frac{1}{2^2}\right) = -68 \ \text{eV}$$

The J and K re in a.u. , we will use $Z = 2, \ \text{a.u.} = (27.2 \ \text{eV})$

$$J(1s,2s) = \frac{17}{81}Z = 11.42 \ \text{eV}, \quad J(1s,2p) = \frac{59}{243}Z = 13.21 \ \text{eV}$$

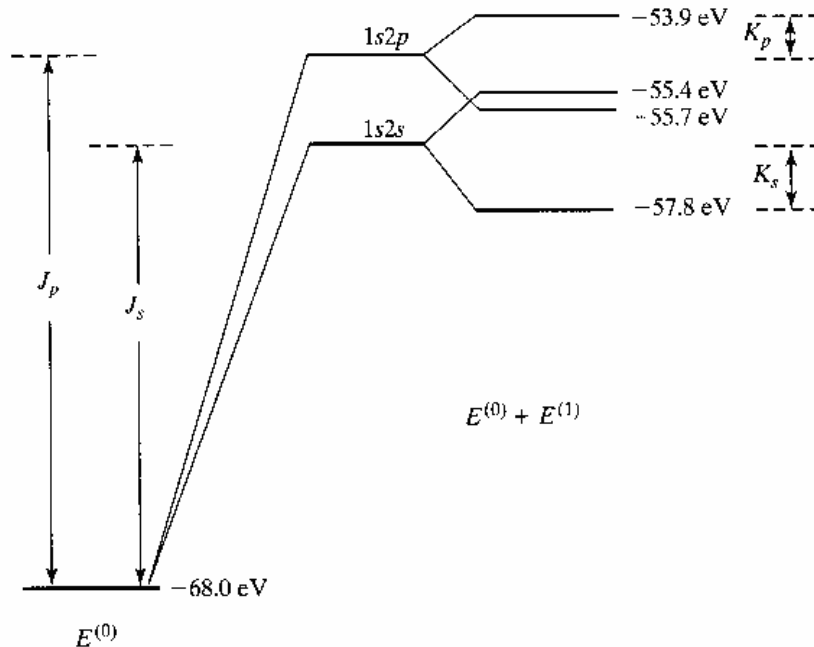$$K(1s,2s) = \frac{16}{729}Z = 1.19 \ \text{eV}, \quad K(1s,2p) = \frac{112}{6561}Z = 0.93 \ \text{eV}$$

then

$$E(1s,2s)^3\text{S} = -68 + J(1s,2s) - K(1s,2s) = -57.8 \ \text{eV}$$
$$E(1s,2s)^1\text{S} = -68 + J(1s,2s) + K(1s,2s) = -55.4 \ \text{eV}$$
$$E(1s,2p)^3\text{P} = -68 + J(1s,2p) - K(1s,2p) = -55.7 \ \text{eV}$$
$$E(1s,2p)^1\text{P} = -68 + J(1s,2p) + K(1s,2p) = -53.9 \ \text{eV}$$

The first excited levels of the helium atom.

The first-order energy corrections seem to indicate that the lower of the two levels of the ls2p configuration lies below the higher of the two levels of the ls2s configuration. Study of the helium spectrum reveals that this is not so. The error is due to neglect of the higher-order perturbation-energy corrections.
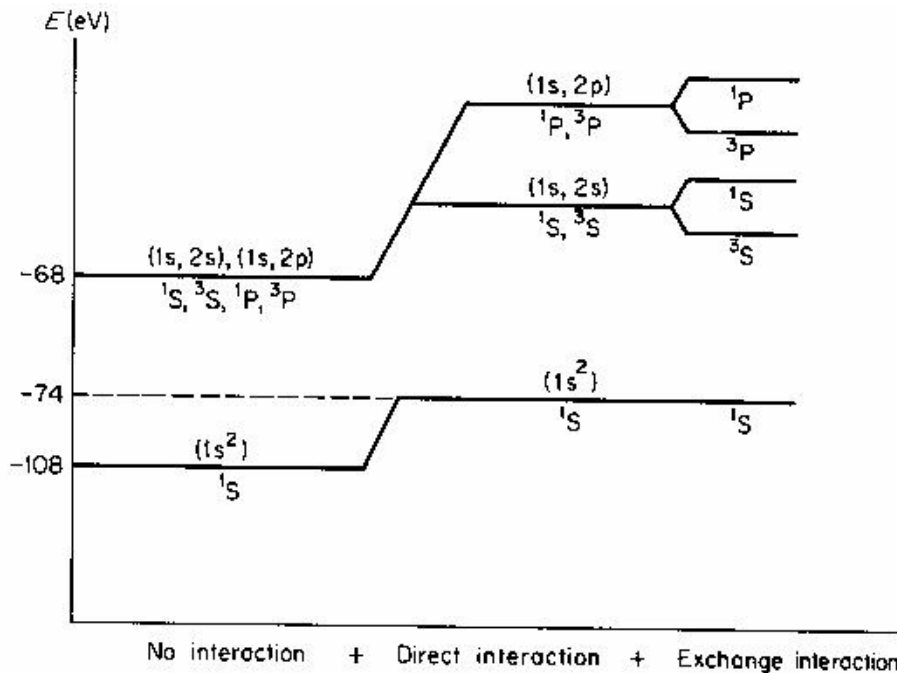
The shifts in energy of the ideal atomic states in helium when the electron interaction is taken into account.

The configuration $(1s^1, 2p^1)$ in helium is twelvefold degenerate. According to the vector model, we can couple the magnetic configuration into atomic states with $L = 1$, $S = 0$ (^1P) and $L = 1$, $S = 1$ (^3P). Since the latter is ninefold degenerate and the former is threefold degenerate, the total degeneracy is twelvefold. Again, since the electrons are nonequivalent, none of the atomic states above are ruled out. Because of the accidental degeneracy, the $(1s^1, 2s^1)$ and $(1s^1, 2p^1)$ configurations both have the same energies; consequently, the ^1S, ^3S, ^1P, and ^3P states all have energy $E = -68$ eV. When first-order perturbation theory is applied to the electrostatic interaction the energies of these states shift according to their L and S values the Pauli exclusion principle causes the higher multiplicity states to be of lower energy for a given configuration. Hence in the $(1s^1, 2s^1)$ configuration, the ^3S is of lower energy than the ^1S state. Also in the $(1s^1, 2p^1)$ configuration, the ^3P resides below the ^1P state

Helium terms

Triplet (Orthohelium) states are lower in energy than the singlet (**parahelium)** states. Explanation for this is:

1- Parallel spins make the spin part of the wavefunction symmetric.

2- Total wavefunction for electrons must be antisymmetric since electrons are fermions.

3- This forces space part of wavefunction to be antisymmetric.

4- Antisymmetric space wavefunction implies a larger average distance between electrons than a symmetric function. Results as square of antisymmetric function must go to zero at the origin $\Rightarrow$ probability for small separations of the two electrons is smaller than for a symmetric space wavefunction.

5- If electrons are on the average further apart, then there will be less shielding of the nucleus by the ground state electron, and the excited state electron will therefore be more exposed to the nucleus. This implies that it will be more tightly bound and of lower energy.

H.W. **For the ground state of Li atom** $1s^2 2s$:
1- Write down the full Hamiltonian,
2- Use Slater's determinant for the ground state of Li atom in the form:

$$\psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\,\alpha(1) & 1s\,\alpha(2) & 1s\,\alpha(3) \\ 1s\,\beta(1) & 1s\,\beta(2) & 1s\,\beta(3) \\ 2s\,\alpha(1) & 2s\,\alpha(2) & 2s\,\alpha(3) \end{vmatrix}$$

$$= \frac{1}{\sqrt{6}} \left\{ \begin{array}{l} 1s\,\alpha(1)1s\,\beta(2)2s\,\alpha(3) + 1s\,\alpha(2)1s\,\beta(3)2s\,\alpha(1) + 1s\,\alpha(3)1s\,\beta(1)2s\,\alpha(2) + \\ -1s\,\alpha(3)1s\,\beta(2)2s\,\alpha(1) - 1s\,\alpha(2)1s\,\beta(1)2s\,\alpha(3) - 1s\,\alpha(1)1s\,\beta(3)2s\,\alpha(2) \end{array} \right\}$$

To proof:

$$\langle H \rangle = 2E_o(1s) + E_o(2s) + 2J(1s,2s) + J(1s,1s) - K(1s,2s)$$

Where

$$2E_o(1s) + E_o(2s) = -\left(\frac{1}{1^2} + \frac{1}{1^2} + \frac{1}{2^2} \right) \text{a.u.} = -275.5 \ \text{eV}$$

$$2J(1s,2s) + J(1s,1s) - K(1s,2s) = \frac{5965}{972} \text{a.u.} = 83.5\,\text{eV}$$

$\frac{1}{6}$ <1sα(1)1sβ(2)2sα(3) + 2sα(1)1sα(2)1sβ(3) + 1sβ(1)2sα(2)1sα(3) − 1sα(1)2sα(2)1sβ(3)

      − 1sβ(1)1sα(2)2sα(3) − 2sα(1)1sβ(2)1sα(3)|$\hat{\mathcal{H}}^0$(1) + $\hat{\mathcal{H}}^0$(2) + $\hat{\mathcal{H}}^0$(3)|1sα(1)1sβ(2)2sα(3)

      + 2sα(1)1sα(2)1sβ(3) + 1sβ(1)2sα(2)1sα(3) − 1sα(1)2sα(2)1sβ(3)

      − 1sβ(1)1sα(2)2sα(3) − 2sα(1)1sβ(2)1sα(3)>

Using the orthogonality conditions for the space and spin function, <u>i.e.</u>

     <$u_i \chi_k$(1)|$u_j \chi_\ell$(1)> = <u_i(1)|u_j(1)><χ_k(1)|χ_ℓ(1)> = $\delta_{ij} \delta_{k\ell}$

we can reduce (1) to:

    $\frac{1}{6} \sum\limits_{i=1}^{3}$ [4<1s(i)|$\hat{\mathcal{H}}^0$(i)|1s(i)> + 2<2s(i)|$\hat{\mathcal{H}}^0$(i)|2s(i)>] = 2I(1s) + I(2s)

    The two-electron integrals are more difficult. In order to simplify this calculation
we factor out the common spin functions. Thus

     $\Psi = \psi_1 \alpha(1)\beta(2)\alpha(3) + \psi_2 \beta(1)\alpha(2)\alpha(3) + \psi_3 \alpha(1)\alpha(2)\beta(3) = \sum\limits_i \psi_i S_i$

where

    $\psi_1 = \frac{1}{\sqrt{6}}$ [1s(1)1s(2)2s(3) − 2s(1)1s(2)1s(3)]

    $\psi_2 = \frac{1}{\sqrt{6}}$ [1s(1)2s(2)1s(3) − 1s(1)1s(2)2s(3)]

    $\psi_3 = \frac{1}{\sqrt{6}}$ [2s(1)1s(2)1s(3) − 1s(1)2s(2)1s(3)]

The $\hat{\mathcal{H}}'$ integral then becomes:

    <Ψ|$\hat{\mathcal{H}}'$|Ψ> = <$\psi_1 S_1$ + $\psi_2 S_2$ + $\psi_3 S_3$|$\sum\limits_{i<j}^{3}$ 2/r_{ij}|$\psi_1 S_1$ + $\psi_2 S_2$ + $\psi_3 S_3$>

The orthogonality of the spin functions gives $\langle S_i | S_j \rangle = \delta_{ij}$ and we are left with

$$\langle \Psi | \hat{\mathcal{H}}' | \Psi \rangle = \langle \psi_1 | \hat{\mathcal{H}}' | \psi_1 \rangle + \langle \psi_2 | \hat{\mathcal{H}}' | \psi_2 \rangle + \langle \psi_3 | \hat{\mathcal{H}}' | \psi_3 \rangle$$

Evaluating $\langle \psi_1 | \hat{\mathcal{H}}' | \psi_1 \rangle$ explicitly gives

$$6\langle \psi_1 | \hat{\mathcal{H}}' | \psi_1 \rangle = \langle 1s(1)1s(2)2s(3) - 2s(1)1s(2)1s(3) | 2/r_{12} + 2/r_{13} + 2/r_{23} |$$
$$1s(1)1s(2)2s(3) - 2s(1)1s(2)1s(3) \rangle$$
$$= \langle 1s(1)1s(2) | 2/r_{12} | 1s(1)1s(2) \rangle + \langle 2s(1)1s(2) | 2/r_{12} | 2s(1)1s(2) \rangle$$
$$+ \langle 1s(1)2s(3) | 2/r_{13} | 1s(1)2s(3) \rangle + \langle 2s(1)1s(3) | 2/r_{13} | 2s(1)1s(3) \rangle$$
$$+ \langle 1s(2)2s(3) | 2/r_{23} | 1s(2)2s(3) \rangle + \langle 1s(2)1s(3) | 2/r_{23} | 1s(2)1s(3) \rangle$$
$$- 2\langle 1s(1)2s(3) | 2/r_{13} | 2s(1)1s(3) \rangle$$

The terms $\langle \psi_2 | \hat{\mathcal{H}}' | \psi_2 \rangle$ and $\langle \psi_3 | \hat{\mathcal{H}}' | \psi_3 \rangle$ give exactly the same results and we conclude that:

$$\langle \Psi | \hat{\mathcal{H}}' | \Psi \rangle = J(1s, 1s) + 2J(1s, 2s) - K(1s, 2s)$$

The expectation value of the energy using a single Slater determinant is thus

$$E = 2I(1s) + I(2s) + J(1s, 1s) + 2J(1s, 2s) - K(1s, 2s)$$