PHYS261 Atomic Physics and Physical Optics

Lecture Thursday 18. September 2008

Topics:

Helium; The Triplet – Singlet Story

Exchange Interaction final touch

Helium; Perturbation Theory, Variational Theory

Comment:

After the lecture - preliminary version;

From last time: Functions of operators

$$e^{i\alpha\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}} = I\cos\alpha + i\sin\alpha\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$$

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Pauli Matrices

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The story you should learn to perform: (three slides follow in the ODP file)

The two electron atoms have the spin symmetry feature. You can make the total wavefunction antisymmetric by taking symmetric spin and space function antisymmetric. Or you can take antisymmetric spin and then this aplies space function is symmetric. Symmetric spins are called triplet, because there are 3 of them, antisymmetric is a singlet.

Two electrons repel each other. **The repulsion adds energy, positive potential.**

We will explain HOW to see that the **repulsion is larger for singlets than for corresponding triplet.**

Think e.g. about 1s 2p orbitals, as states a and b. Then schematically

Psi(antisym) -> a(1) b(2) – b(1) a(2) Psi(sym) -> a(1) b(2) + b(1) a(2)

when the repulsion is greatest? It is when r1->r2 - and then Psi(sym) is BIG, Psi(antisym) is very small ...

So HERE IS THE STORY:

triplet -> spin SYM -> space ASYM -> for r1->r2 Psi(antisym) is very small -> the repulsion is very small .
singlet -> spin ASYM -> space SYM -> for r1->r2 Psi(sym) is BIG, the repulsion is BIG,

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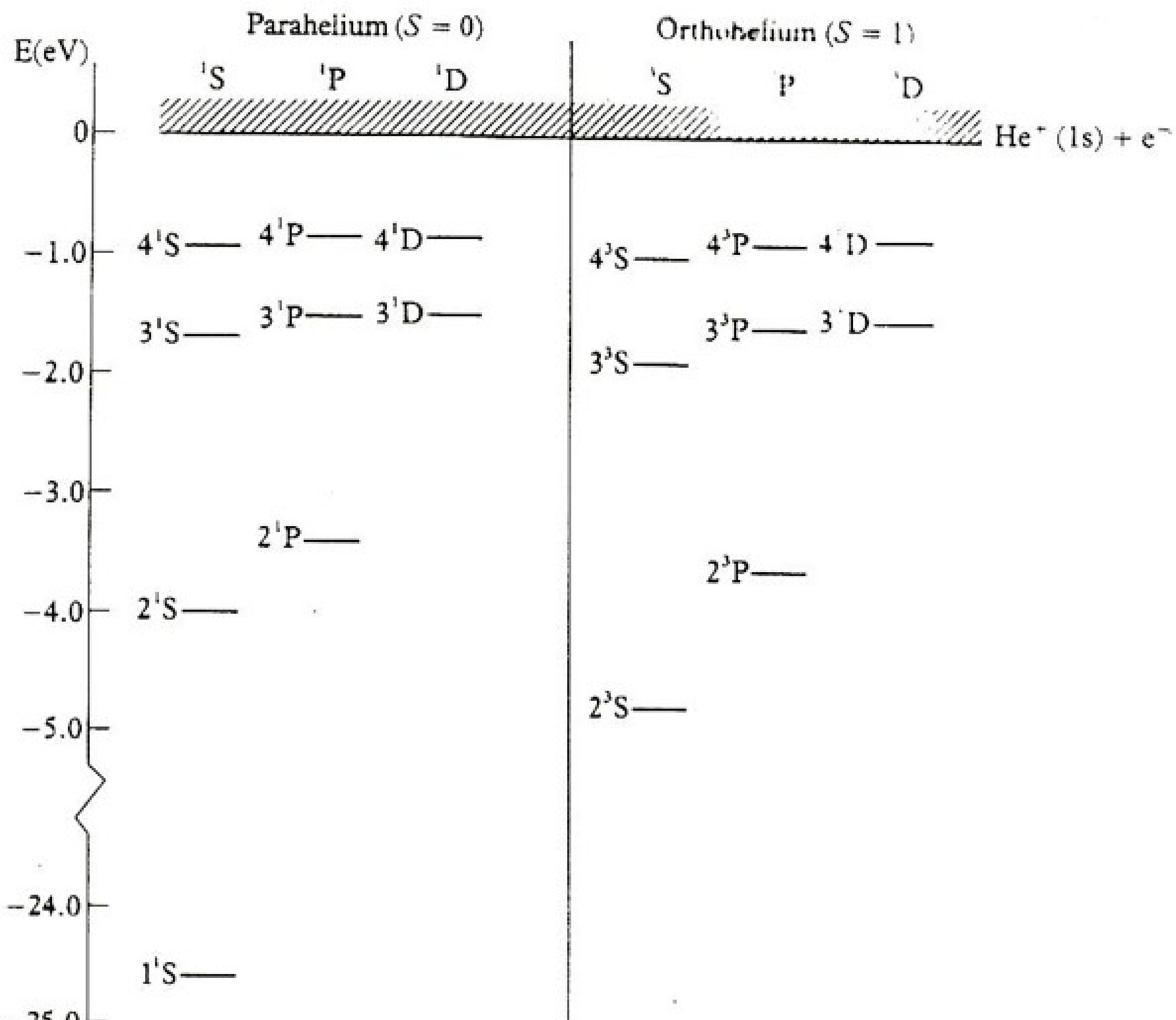
Experiment – Level scheme for Helium



The experimental values of the lowest energy levels of helium.
$E = 0$ corresponds to the ionisation threshold.

The Perturbation Theory (see next slide – work)

$$\left[-\frac{\hbar^2}{2m_e}\nabla_{r_1}^{\,2} - \frac{Z\,e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_{r_2}^{\,2} - \frac{Z\,e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\Psi\left(\mathbf{r}_1,\mathbf{r}_2\right) = E\,\Psi\left(\mathbf{r}_1,\mathbf{r}_2\right)$$

Repulsion expectation Value

Evaluation of the repulsion term using the multipole expansion

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} = \sum_{LM}\frac{4\pi}{2L+1}\,\frac{r_<^L}{r_>^{L+1}}\,Y_{LM}^{\star}\left(\hat{r}_1\right)Y_{LM}\left(\hat{r}_2\right)$$

where

$$r_< = r_1, \quad r_> = r_2 \quad \text{for} \quad |\mathbf{r}_1| < |\mathbf{r}_2|$$
$$r_< = r_2, \quad r_> = r_1 \quad \text{for} \quad |\mathbf{r}_1| > |\mathbf{r}_2|$$

Perturbation theory result:

$$\int d^3\mathbf{r}_1\int d^3\mathbf{r}_2\;\psi_{100}^{\star}\left(\mathbf{r}_1\right)\psi_{100}^{\star}\left(\mathbf{r}_2\right)\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_{100}\left(\mathbf{r}_1\right)\psi_{100}\left(\mathbf{r}_2\right) = \frac{5}{8}\frac{Ze^2}{a_0}$$

$$E(Z, 1s, 1s) = -\frac{1}{2}Z^2 - \frac{1}{2}Z^2 + \frac{5}{8}Z \quad [a.u.]$$

The Variational Method

Perturbation theory

$$H = H_0 + H_1$$

$$H_0 \varphi = E_0 \varphi \quad \left(H_0 |\varphi\rangle = E_0 |\varphi\rangle \right)$$

H_1 "is not essential"

H_1 is small (nonsense)

$$E = E_0 + \langle \varphi | H_1 | \varphi \rangle \quad E_1$$

$$= \langle \varphi | H | \varphi \rangle = \langle \varphi | H_0 | \varphi \rangle + \langle \varphi | H_1 | \varphi \rangle$$

(first order......)

[Repeat Pert. Th or read in Wikip.]

$$E_0 = E_{electron}(Z, n_1) + E_{electron}(Z, n_2)$$

(in a.u. E) $-\frac{1}{2}\frac{Z^2}{n_1^2} + \left(-\frac{1}{2}\frac{Z^2}{n_2^2}\right)$ $\quad E_1^{n=1} = \frac{5Z}{8}$

$$E(z) = \left(z^2 - 2z \cdot Z + \frac{5}{8} z\right) E_0$$

find z by $\frac{\partial E(z)}{\partial z} = 0$

$$2z - 2Z + \frac{5}{8} = 0$$

$$z = Z - \frac{5}{16} \approx 0.3$$

$$z = Z - 0.3$$

Derivation of "EXTREMUM"

$$\varphi = \sum c_i \varphi_i$$

$$E(\varphi) \geq E(\varphi_0)$$

To remember ...... in preliminary version

Carousel (pictures t include??)
Flogiston - Look it up

The joke about Who wrote Hamlet - for remembering
Stern-Gerlach (see wikipedia)

Quantiki (Quantum wiki) - very bad QM intro
Quantum Computation