

Homework 6

PHYSICS 342
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Kevin Evans
ID: 11571810

1. In hydrogenic atoms, the shielding effects of outer electrons breaks down the degeneracy. Essentially, the inner electrons in filled shells “blocks” the effects of the nuclear electronic charge, and the outer electrons are pushed outward more by the electronic repulsion of inner electrons. From Fig. 6.22 in the book, the energy ranking would be $2s, 2p, 3s, 3p, 3d...$
2. (a) In the ground state, the total energy is minimized. This is done with the valence electrons in the triplet states, where the spins are parallel to one another. This is only allowable (due to the Pauli principle) when the spins are in separate subshells.
(b) The spins are added to the lowest empty subshell. If there's no non-empty subshells left, it goes with the first non-paired electron, but with an opposite spin orientation.
(c) $1^2S_{1/2}$, as $n = 1, s = 1/2, j = 1/2$
 $2^2S_{1/2}$, as $n = 2, s = 1/2, j = 1/2$
 2^1S_0 , as $n = 2, s = 0$ (spins are opposite), $j = 0$
 $2^2P_{3/2}$, as $n = 2, s = 1/2, j = 1 + 1/2$. Is the book wrong here?
 2^3P_2 , as $n = 2, s = 1, j = 2$

3. (a) Since the kinetic energy for a rotating thing is

$$T = I\omega^2/2$$

But angular momentum is just $L = I\omega \implies \omega^2 = (L/I)^2$,

$$\begin{aligned} T &= \frac{L^2}{2I} \\ &= \frac{\hbar^2 \ell(\ell + 1)}{2I} \end{aligned}$$

- (b) At lower temperatures, we would expect more electrons to fall to the ground singlet state. So it should have more para hydrogen at low temperatures.
4. This is due to the relative proportion of singlet to triplet states for each molecule. For hydrogen, we would expect the singlet state to be a third of the triplet probability. For oxygen and by Hund's rule, the ground state must have aligned spins and therefore must be in the triplet state. The singlet state is missing because it's energetically unfavorable (I think but could use some clarification!).
5. (a) If we impose the Pauli principle, the singlet state must have a symmetric spatial function (and an antisymmetric spin function), so now

$$\begin{aligned} |1s\rangle |2s\rangle &\rightarrow \frac{1}{\sqrt{2}} (|1s\rangle |2s\rangle + |2s\rangle |1s\rangle) \\ \langle \mathbf{r}_1 | \langle \mathbf{r}_2 | \frac{1}{\sqrt{2}} (|1s\rangle |2s\rangle + |2s\rangle |1s\rangle) &= \frac{1}{\sqrt{2}} (\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) + \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2)) \end{aligned}$$

(b) For the triplet state, the spatial function must be antisymmetric,

$$|1s\rangle|2s\rangle \rightarrow \frac{1}{\sqrt{2}}(|1s\rangle|2s\rangle - |2s\rangle|1s\rangle)$$

$$\langle \mathbf{r}_1 | \langle \mathbf{r}_2 | \frac{1}{\sqrt{2}}(|1s\rangle|2s\rangle - |2s\rangle|1s\rangle) = \frac{1}{\sqrt{2}}(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) - \psi_{2s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2))$$

6. (a) The expectation becomes

$$\begin{aligned} \langle \hat{U} \rangle &= \langle 1s | \hat{U} | 1s \rangle \\ &= \int \langle 1s | \mathbf{r} \rangle \hat{U} \langle \mathbf{r} | 1s \rangle d^3\mathbf{r} \end{aligned}$$

(b) There's a $1/2$ as a normalization constant, as it would double count the energy. The expectation for the two electron is now

$$\begin{aligned} \langle \hat{U} \rangle &= \langle a | \langle b | \left(\frac{1}{2} \iint |\mathbf{r}_1\rangle |\mathbf{r}_2\rangle \frac{e^2}{r_{12}} \langle \mathbf{r}_1 | \langle \mathbf{r}_2 | \right) | a \rangle | b \rangle d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\ &= \frac{1}{2} \iint \psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2) \frac{e^2}{r_{12}} \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \end{aligned}$$

7. Using the singlet state

$$\frac{1}{\sqrt{2}}(|a\rangle|b\rangle + |b\rangle|a\rangle)$$

(a) The average potential energy is

$$\begin{aligned} \langle \hat{U} \rangle &= \frac{1}{4} (\langle a | \langle b | + \langle b | \langle a |) \iint |\mathbf{r}_1\rangle |\mathbf{r}_2\rangle \frac{e^2}{r_{12}} \langle \mathbf{r}_1 | \langle \mathbf{r}_2 | d^3\mathbf{r}_1 d^3\mathbf{r}_2 (|a\rangle |b\rangle + |b\rangle |a\rangle) \\ &= \frac{1}{4} \iint (\langle a | \mathbf{r}_1 \rangle \langle b | \mathbf{r}_2 \rangle + \langle b | \mathbf{r}_1 \rangle \langle a | \mathbf{r}_2 \rangle) \frac{e^2}{r_{12}} (\langle \mathbf{r}_1 | a \rangle \langle \mathbf{r}_2 | b \rangle + \langle \mathbf{r}_1 | b \rangle \langle \mathbf{r}_2 | a \rangle) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\ &= \frac{1}{4} \iint (\psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2) + \psi_b^*(\mathbf{r}_1)\psi_a^*(\mathbf{r}_2)) \frac{e^2}{r_{12}} (\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \end{aligned}$$

Foiling out the two groups,

$$\begin{aligned} \langle \hat{U} \rangle &= \frac{1}{4} \iint \frac{e^2}{r_{12}} \left(\psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2) \right. \\ &\quad \left. + \psi_b^*(\mathbf{r}_1)\psi_a^*(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2) + \psi_b^*(\mathbf{r}_1)\psi_a^*(\mathbf{r}_2)\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \right) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \end{aligned}$$

As the labels r_1 and r_2 are arbitrary, we can reorder and combine the integrals,

$$\langle \hat{U} \rangle = \frac{1}{2} \iint \frac{e^2}{r_{12}} \left(\underbrace{\psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)}_J + \underbrace{\psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)}_K \right) d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

From Problem 5, we have the direct integral J , then the exchange integral K is

$$K = \frac{1}{2} \iint \frac{e^2}{r_{12}} \psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

(b) For the triplet state, it's about the same as (a), but with a $-$ sign,

$$\begin{aligned}
 \langle \hat{U} \rangle &= \frac{1}{4} (\langle a | \langle b | - \langle b | \langle a |) \iint |\mathbf{r}_1\rangle |\mathbf{r}_2\rangle \frac{\ell^2}{r_{12}} \langle \mathbf{r}_1 | \langle \mathbf{r}_2 | d^3\mathbf{r}_1 d^3\mathbf{r}_2 (|a\rangle |b\rangle - |b\rangle |a\rangle) \\
 &= \frac{1}{4} \iint (\langle a | \mathbf{r}_1 \rangle \langle b | \mathbf{r}_2 \rangle - \langle b | \mathbf{r}_1 \rangle \langle a | \mathbf{r}_2 \rangle) \frac{\ell^2}{r_{12}} (\langle \mathbf{r}_1 | a \rangle \langle \mathbf{r}_2 | b \rangle - \langle \mathbf{r}_1 | b \rangle \langle \mathbf{r}_2 | a \rangle) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
 &= \frac{1}{4} \iint (\psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) - \psi_b^*(\mathbf{r}_1) \psi_a^*(\mathbf{r}_2)) \frac{\ell^2}{r_{12}} (\psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) - \psi_b(\mathbf{r}_1) \psi_a(\mathbf{r}_2)) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
 &= \frac{1}{4} \iint \frac{\ell^2}{r_{12}} \left(\psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) - \psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \psi_b(\mathbf{r}_1) \psi_a(\mathbf{r}_2) \right. \\
 &\quad \left. + \psi_b^*(\mathbf{r}_1) \psi_a^*(\mathbf{r}_2) \psi_b(\mathbf{r}_1) \psi_a(\mathbf{r}_2) - \psi_b^*(\mathbf{r}_1) \psi_a^*(\mathbf{r}_2) \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \right) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
 &= \frac{1}{2} \iint \frac{\ell^2}{r_{12}} (\psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) - \psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \psi_b(\mathbf{r}_1) \psi_a(\mathbf{r}_2)) d^3\mathbf{r}_1 d^3\mathbf{r}_2
 \end{aligned}$$

Between the singlet and triplet state, the energy differs by K (or is it $2K$?).

8. At least in the book, the assumption is made by the ansatz which approximates the screening effects of inner electrons. It assumes the screening effects are spherically symmetric, and therefore the potential must be spherically symmetric too.
9. (a) To scale/normalize the sum of N permutations, it requires the factor of $\frac{1}{N!}$. I think it's rooted because it requires the expectation (which would square it) to be normalized.
- (b)
- (c)
10. (a) To show that it's real, we can check if $K^* = K$,

$$\begin{aligned}
 K^* &= \left(\frac{1}{2} \iint \frac{\ell^2}{r_{12}} \psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \psi_b(\mathbf{r}_1) \psi_a(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \right)^* \\
 &= \frac{1}{2} \iint \frac{\ell^2}{r_{12}} \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \psi_b^*(\mathbf{r}_1) \psi_a^*(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2
 \end{aligned}$$

Swapping the labels, it's equal to K . □

$$K^* = \frac{1}{2} \iint \frac{\ell^2}{r_{12}} \psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

(b) The eigenvalues are found as

$$\begin{aligned}
 \det \begin{bmatrix} J/2 - E & K/2 \\ K/2 & J/2 - E \end{bmatrix} &= 0 \\
 (J/2 - E)^2 - (K/2)^2 &= 0 \\
 J/2 - E &= \pm K/2 \\
 E &= \frac{1}{2} (J \pm K)
 \end{aligned}$$

- (c) For the basis vectors, the associated eigenvectors can be solved with WolframAlpha and normalized as

$$\frac{1}{\sqrt{2}} \begin{bmatrix} -1 \\ 1 \end{bmatrix}, \quad E = \frac{J - K}{2}$$

This vector can be expanded using the provided basis as

$$\Rightarrow \frac{1}{\sqrt{2}} (|2s\rangle |1s\rangle - |1s\rangle |2s\rangle)$$

And that's basically the triplet state. For the other eigenvector, it expands to the singlet state,

$$\begin{aligned} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad E = \frac{J + K}{2} \\ \Rightarrow \frac{1}{\sqrt{2}} (|1s\rangle |2s\rangle + |2s\rangle |1s\rangle) \end{aligned}$$