HW #6 Chem 1410

(1) Express in atomic units

a) the energy of the $1s \to 2p$ transition of H.

$$E = -\frac{1}{2n^2} \Rightarrow E(1s) = -\frac{1}{2}, \quad E(2p) = -\frac{1}{8}$$

$$\Delta E = 1/2 - 1/8 = 3/8 \text{ a.u.}$$

b) the ground state energy of an electron in a box of width 5Å

$$E = \frac{h^2}{8ma^2} = \frac{4\pi^2\hbar^2}{8ma^2} = \frac{\pi^2\hbar^2}{2ma^2} = \frac{\pi^2}{2(1)[5/.529]^2}$$

change to a.u.

$$E = \frac{\pi^2}{2(9.45)^2} = 0.055 \text{ au}$$

Note: the conversion of the width "a" to a.u.

(2) Expand out the Slater determinant for the ground state of the Li atom.

$$|1s\bar{1s}2s| = \frac{1}{\sqrt{6}}\{1s\bar{1s}2s - \bar{1s}1s2s - 1s2s\bar{1s} - 2s\bar{1s}1s + 2s1s\bar{1s} + \bar{1s}2s1s\}$$

(3) Consider the $1s^2 \to 1s2s$ excited states of the He atom

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$$\phi_1 = |1s2s|, \quad \phi_2 = |\bar{1s}\bar{2s}|, \quad \phi_3 = |1s\bar{2s}|, \quad \phi_4 = |\bar{1s}2s|$$

$\uparrow\uparrow$ $\quad\downarrow\downarrow$ $\quad\uparrow\downarrow$ $\quad\downarrow\uparrow$

Calculate the energies possible for a wavefunction of the form $\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} \end{vmatrix} = 0$$

$S_{ii} = 1$, $S_{ij} = 0, i \neq j$ by spin or spatial orbital orthogonality

$$\left.\begin{aligned} H_{12} &= 0 \\ H_{13} &= 0 \\ H_{14} &= 0 \\ H_{23} &= 0 \\ H_{24} &= 0 \end{aligned}\right\} \text{by spin orthognality}$$

$H_{ij} = H_{ji}$

$$\begin{vmatrix} H_{11}-E & 0 & 0 & 0 \\ 0 & H_{22}-E & 0 & 0 \\ 0 & 0 & H_{33}-E & H_{34} \\ 0 & 0 & H_{34} & H_{44}-E \end{vmatrix} = 0 = (H_{11}-E)(H_{22}-E)\begin{vmatrix} H_{33}-E & H_{34} \\ H_{34} & H_{44}-E \end{vmatrix}$$

$$\begin{aligned} H_{11} &= \langle |1s2s| \,|H|\, |1s2s| \rangle \\ &= \tfrac{1}{2}\left\langle (1s2s-2s1s) \middle| H^\circ + \tfrac{1}{r_{12}} \middle| (1s2s-2s1s) \right\rangle \\ &= \langle 1s2s | H^\circ | 1s2s \rangle + \left\langle 1s2s \middle| \tfrac{1}{r_{12}} \middle| 1s2s \right\rangle - \left\langle 1s2s \middle| \tfrac{1}{r_{12}} \middle| 2s1s \right\rangle \\ &= E_0 + J - K \end{aligned}$$

Here we made use of:

$$\langle 1s2s | H^0 | 1s2s \rangle = \langle 2s1s | H^0 | 2s1s \rangle$$

$$\langle 1s2s | \frac{1}{r_{12}} | 1s2s \rangle = \langle 2s1s | \frac{1}{r_{12}} | 2s1s \rangle$$

$$\langle 1s2s | \frac{1}{r_{12}} | 2s1s \rangle = \langle 2s1s | \frac{1}{r_{12}} | 1s2s \rangle$$

Also spin is simply integrated out since both spins are α, and $\langle 1s2s | H^0 | 2s1s \rangle = 0$.

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by symmetry $H_{22} = H_{11} = E_0 + J - K$

$$H_{33} = \frac{1}{2} \langle 1s\bar{2s} - \bar{2s}1s | H^0 + \frac{1}{r_{12}} | 1s\bar{2s} - \bar{2s}1s \rangle$$

$$= \langle 1s\bar{2s} | H^0 | 1s\bar{2s} \rangle + \underbrace{\langle 1s\bar{2s} | \frac{1}{r_{12}} | 1s\bar{2s} \rangle}_{\to J}$$

$$- \langle 1s\bar{2s} | \frac{1}{r_{12}} | \bar{2s}1s \rangle \to 0 \text{ by spin orthogonality}$$

$$= E_0 + J$$

By symmetry $H_{44} = H_{33} = E_0 + J$

$$H_{34} = \frac{1}{2} \langle 1s\bar{2s} - \bar{2s}1s | H^0 + \frac{1}{r_{12}} | \bar{1s}2s - 2s\bar{1s} \rangle$$

$$= \langle 1s\bar{2s} | \frac{1}{r_{12}} | 2s\bar{1s} \rangle = -K$$

Here we used the fact that the integrals over H^0 are 0 by spin or spatial orbital orthogonality and $\langle 1s\bar{2s} | \frac{1}{r_{12}} | \bar{1s}2s \rangle = 0$ by spin orthogonality

$$0 = H_{11} - E \rightarrow \quad E = E_0 + J - K$$
$$0 = H_{22} - E \rightarrow \quad E = E_0 + J - K$$

$$\begin{vmatrix} H_{33}-E & H_{34} \\ H_{34} & H_{44}-E \end{vmatrix} = 0 = \begin{vmatrix} E_0+J-E & -K \\ -K & E_0+J-K \end{vmatrix}$$

$$\Rightarrow (E_0 + J - E)^2 = K^2$$
$$E = E_0 + J - K \text{ and } E = E_0 + J + K$$

So we get three roots with energy $E_0 + J - K$ and one with energy $E_0 + J + K$. The former correspond to the three components of the <u>triplet</u> state and the latter to the <u>singlet</u> state.

Why is J (+)?

$$J = \langle 1s2s | \frac{1}{r_{12}} | 1s2s \rangle = \int |1s(r_1)|^2 \frac{1}{r_{12}} |1s(r_2)|^2 d\vec{r}_1 d\vec{r}_2$$

This is just the classical interaction between two (negative) charge distributions, and, hence, is positive.

Show that $E = E_0 + J + K \longrightarrow \psi_3 = 1/\sqrt{2}\,(\phi_3 - \phi_4)$

$E = E_0 + J - K \longrightarrow \psi_4 = 1/\sqrt{2}\,(\phi_3 + \phi_4)$

From the system of linear eq's.

$$(E_0 + J - \mathbf{E})\, c_3 - K c_4 = 0$$
$$(E_0 + J - E_0 - J - K)\, c_3 - K c_4 = 0 \Rightarrow -K c_3 - K c_4 = 0$$
$$\Rightarrow c_3 = -c_4 \Rightarrow \psi_3 = (\phi_3 - \phi_4) \longrightarrow 1/\sqrt{2}\,(\phi_3 - \phi_4) \leftarrow \text{Normalized}$$

if $E = E_0 + J - K$

$$Kc_3 - Kc_4 = 0 \Rightarrow c_3 = c_4$$

$$\psi_4 = (\varphi_3 + \varphi_4) \rightarrow \tfrac{1}{\sqrt{2}}(\varphi_3 + \varphi_4) \leftarrow \text{Normalized}$$

Expand ψ_3

$$\psi_3 = \tfrac{1}{\sqrt{2}}\{\varphi_3 - \varphi_4\} = \tfrac{1}{\sqrt{2}}\left\{\tfrac{1}{\sqrt{2}}(1s\,\overline{2s} - \overline{2s}\,1s) - (\overline{1s}\,2s - 2s\,\overline{1s})\tfrac{1}{\sqrt{2}}\right\}$$

$$= \tfrac{1}{2}\{1s2s\,\alpha\beta - 2s1s\,\beta\alpha - 1s2s\,\beta\alpha + 2s1s\,\alpha\beta\}$$

$$= \tfrac{1}{2}\{1s2s(\alpha\beta - \beta\alpha) + 2s1s(\alpha\beta - \beta\alpha\}$$

$$= \tfrac{1}{2}(1s2s + 2s1s)(\alpha\beta - \beta\alpha)$$

Expand ψ_4

$$\psi_4 = \tfrac{1}{\sqrt{2}}\{\varphi_3 + \varphi_4\} = \tfrac{1}{2}\{(1s\,\overline{2s} - \overline{2s}\,1s) + (\overline{1s}\,2s - 2s\,\overline{1s})\}$$

$$= \tfrac{1}{2}\{1s2s\,\alpha\beta - 2s1s\,\beta\alpha + 1s2s\,\beta\alpha - 2s1s\,\alpha\beta\}$$

$$= \tfrac{1}{2}\{(1s2s)(\alpha\beta + \beta\alpha) - (2s1s)(\alpha\beta + \beta\alpha)\}$$

$$= \tfrac{1}{2}(1s2s - 2s1s)(\alpha\beta + \beta\alpha)$$

From above

$$^1E = E_0 + J + K$$

$$^3E = E_0 + J - K$$

$J > 0$ and $K > 0$

So the triplet is lower in energy

$J = \frac{34}{81}$, $K = \frac{32}{(27)^2}$

$E_{GS} = -11/4$ = energy of ground state

$\epsilon_{1s} = -\frac{1}{2}\frac{2^2}{1^2} = -2$

$\epsilon_{2s} = -\frac{1}{2}\left(\frac{2^2}{2^2}\right) = -\frac{1}{2}$

$E_{GS} = \underset{\substack{\uparrow \\ 2e^- \text{ in } 1s}}{-4} + 2\left(\frac{5}{8}\right) = -11/4$

from 1^{st} order PT.

$^1E = E_0 + J + K$

$= \underset{\substack{\uparrow \\ 1s}}{-2} \underset{\substack{\uparrow \\ 2s}}{-\frac{1}{2}} + \frac{34}{81} + \frac{32}{(27)^2} = -2.04$ a.u.

$^3E = E_0 + J - K$

$= -2 - \frac{1}{2} + \frac{34}{81} - \frac{32}{(27)^2} = -2.12$ au

$E_{gs} \rightarrow {}^1E = 2.75 - 2.04 = 0.71$ au $= 19.3$ eV

$E_{gs} \rightarrow {}^3E = 2.75 - 2.12 = 0.63$ au $= 17.1$ eV

8-29.

4 What is the # of sets of m_ℓ and m_s for nd^8

$$\frac{G!}{N!(G-N)!} = \frac{10!}{8!\,2!} = \frac{10 \cdot 9}{2} = 45 \text{ sets}$$

^1S	^1D	^3P	^3F	^1G	
1×1	1×5	3×3	3×7	1×9	
1 +	5 +	9 +	21 +	9	= 45

(5)
8-32 $nd^2 \rightarrow {}^1S, {}^1D, {}^1G, {}^3P, {}^3F$

What are the possible J states?

${}^1S \rightarrow J = 0$

${}^1D \rightarrow J = 2$

${}^1G \rightarrow J = 4$

${}^3P \rightarrow J = 2, 1, 0$

${}^3F \rightarrow J = 4, 3, 2$

Expect ${}^3F_2$ to be lowest in energy based on Hund's rules.

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(6)
8-47 $ns^2np^5 \rightarrow {}^2P_{1/2}, {}^2P_{3/2}$

which is the ground state?

${}^2P_{3/2}$ by Hund's rules

$E({}^2P_{1/2}) - E({}^2P_{3/2}) >$ along the sequence F, Cl, Br, I.

Suggests that the spin-orbit interaction grows with > at #. (see problem 8-46.)