

H.W. #7 Chem 1410

8-10. Show $E = I_1 + I_2 + J_{12}$ for He atom

$$E = \int \phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \left(-\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{2}{r_2} + \frac{1}{r_{12}} \right) \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

$$\left(-\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} \right) \phi_1(\vec{r}_1) = I_1 \phi_1(\vec{r}_1)$$

$$\left(-\frac{1}{2} \nabla_2^2 - \frac{2}{r_2} \right) \phi_2(\vec{r}_2) = I_2 \phi_2(\vec{r}_2)$$

$$J_{12} = \int \phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \frac{1}{r_{12}} \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

$$\Rightarrow E = I_1 + I_2 + J_{12}$$

$$\text{Note } J_{12} = \int \frac{|\phi_1(\vec{r}_1)|^2 |\phi_2(\vec{r}_2)|^2}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

This is just the classical Coulomb interaction between two charge distributions, $|\phi_1|^2$ and $|\phi_2|^2$.

8-11 Using the expression for \hat{H}_1^{eff} , show

$$E_1 = I_1 + J_{12} = E - I$$

$$\hat{H}_1^{\text{eff}} \phi_1(\vec{r}_1) = E_1 \phi_1(\vec{r}_1)$$

$$\int \phi_1^*(\vec{r}_1) \hat{H}_1^{\text{eff}} \phi_1(\vec{r}_1) d\vec{r}_1 = E_1 \int \phi_1^*(\vec{r}_1) \phi_1(\vec{r}_1) d\vec{r}_1 = E_1$$

$$\int \phi_1^*(\vec{r}_1) \left[\underbrace{-\frac{1}{2} \nabla_1^2 - \frac{2}{r_1}}_{I_1} + V_1^{\text{eff}}(\vec{r}_1) \right] \phi_1(\vec{r}_1) d\vec{r}_1$$

$$\int \phi_1^*(\vec{r}_1) V_1^{\text{eff}}(\vec{r}_1) \phi_1(\vec{r}_1) d\vec{r}_1 =$$

$$\int \phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \frac{1}{r_{12}} \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 = J_{12}$$

Thus

$$I_1 + J_{12} = \epsilon_1$$

$$\text{from 8-10 } E = I_1 + I_2 + J_{12}$$

$$E = \epsilon_1 + I_2 \Rightarrow \epsilon_1 = E - I_2 = E - I_1$$

Note: for He atom $I_1 = I_2 = I$

$$8-25. \quad \phi_1 = |1s2s|, \quad \phi_2 = |\bar{1}s\bar{2}s|, \quad \phi_3 = |1s\bar{2}s|, \\ \phi_4 = |\bar{1}s2s|, \quad \text{where "-" denotes } \beta \text{ spin.}$$

Consider a trial function $\psi = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + c_4 \phi_4$.

$$\begin{aligned} \text{integrate over spin} \quad H_{11} &= \frac{1}{2} \int (1s2s - 2s1s) d\alpha d\beta \hat{H} (1s2s - 2s1s) d\alpha d\beta d\vec{r}_1 d\vec{r}_2 \\ &= \frac{1}{2} \int (1s2s - 2s1s) \hat{H} (1s2s - 2s1s) d\vec{r}_1 d\vec{r}_2 \\ &= \frac{1}{2} \left\{ \int 1s2s \hat{H} 1s2s d\vec{r}_1 d\vec{r}_2 + \int 2s1s \hat{H} 2s1s d\vec{r}_1 d\vec{r}_2 \right. \\ &\quad \left. - 2 \int 1s2s \hat{H} 2s1s d\vec{r}_1 d\vec{r}_2 \right\} \\ &= \underbrace{\int 1s2s \hat{H} 1s2s d\vec{r}_1 d\vec{r}_2}_{E_0 + J} - \underbrace{\int 1s2s \hat{H} 2s1s d\vec{r}_1 d\vec{r}_2}_K \end{aligned}$$

$$H_{11} = E_0 + J - K$$

$$H_{22} = E_0 + J - K \quad \leftarrow \text{identical to } H_{11} \text{ once spin is integrated out.}$$

$$H_{33} = \frac{1}{2} \int (1s2s \alpha\beta - 2s1s \beta\alpha) \hat{H} (1s2s \alpha\beta - 2s1s \beta\alpha) d\tau_1 d\tau_2$$

$$= \int 1s2s \hat{H} 1s2s d\vec{r}_1 d\vec{r}_2 = E_0 + J$$

$$\left(\text{Here we used: } \int \alpha(1)\beta(2) \beta(1)\alpha(2) d\sigma_1 d\sigma_2 = 0 \right)$$

$$H_{44} = E_0 + J, \text{ since it is equivalent to } H_{33}.$$

$H_{12}, H_{13}, H_{14}, H_{23}, H_{24}$ are ϕ by spin orthogonality.

$$H_{34} = \frac{1}{2} \int (1s2s \alpha\beta - 2s1s \beta\alpha) \hat{H} (1s2s \beta\alpha - 2s1s \alpha\beta) d\tau_1 d\tau_2$$

$$= - \int 1s2s \hat{H} 2s1s d\vec{r}_1 d\vec{r}_2 = -K$$

$$\underline{\underline{H}} = \begin{pmatrix} E_0 + J - K & 0 & 0 & 0 \\ 0 & E_0 + J - K & 0 & 0 \\ 0 & 0 & E_0 + J & -K \\ 0 & 0 & -K & E_0 + J \end{pmatrix}$$

$$\begin{vmatrix} E_0 + J - E & -K \\ -K & E_0 + J - E \end{vmatrix} = 0 \Rightarrow \begin{cases} (E_0 + J - E)^2 - K^2 = 0 \\ E_0 + J - E = \pm K \end{cases}$$

$$E = E_0 + J \pm K$$

So three levels have the energy

$$E_0 + J - K \quad (\text{triplet})$$

and one level has the energy

$$E_0 + J + K \quad (\text{singlet})$$

$$E_0 = \int 1s2s \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} \right) 1s2s \, d\vec{r}_1 \, d\vec{r}_2$$

$$= \int 1s \left(-\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} \right) 1s \, d\vec{r}_1 + \int 2s \left(-\frac{1}{2} \nabla_2^2 - \frac{2}{r_2} \right) 2s \, d\vec{r}_2$$

$$\left(E(\text{H-like atom}) = -\frac{Z^2}{2n^2} E_H \right)$$

$$E_0 = -\frac{4}{2(1)} E_H - \frac{4}{8} E_H = -\left(2 + \frac{1}{2}\right) E_H = -\frac{5}{2} E_H$$

$$J = \int |1s(\vec{r}_1)|^2 \frac{1}{r_{12}} |2s(\vec{r}_2)|^2 \, d\vec{r}_1 \, d\vec{r}_2$$

just the classical coulomb interaction between two spherical charge distributions.

$$K = \int 1s(\vec{r}_1) 2s(\vec{r}_1) \frac{1}{r_{12}} 1s(\vec{r}_2) 2s(\vec{r}_2) \, d\vec{r}_1 \, d\vec{r}_2$$

This is called exchange because it results from the exchange of the coordinates of the two electrons.

Backing up

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

$$= (E_0+J-K-E)^2 \begin{vmatrix} E_0+J-E & -K \\ -K & E_0+J-E \end{vmatrix}$$

from two successive applications of the cofactor expansion method, in both cases expanding using the (1,1) element.

$$\text{Show } \begin{cases} E_0+J+K \rightarrow \psi_3 = \frac{1}{\sqrt{2}}(\phi_3 - \phi_4) \\ E_0+J-K \rightarrow \psi_4 = \frac{1}{\sqrt{2}}(\phi_3 + \phi_4) \end{cases}$$

$$(E_0+J-E)c_3 - Kc_4 = 0$$

$$(E_0+J-(E_0+J+K))c_3 - Kc_4 = 0 \Rightarrow -Kc_3 - Kc_4 = 0$$

$$\Rightarrow c_3 = -c_4 \Rightarrow \psi_3 = \frac{1}{\sqrt{2}}(\phi_3 - \phi_4)$$

⏟ normalization factor

$$(E_0+J-(E_0+J-K))c_3 - Kc_4 = 0 \Rightarrow Kc_3 - Kc_4 = 0$$

$$\Rightarrow c_3 = c_4 \Rightarrow \psi_4 = \frac{1}{\sqrt{2}}(\phi_3 + \phi_4)$$

$$\psi_3 = \frac{1}{\sqrt{2}} \left\{ \frac{1}{\sqrt{2}}(1s2s\alpha\beta - 2s1s\beta\alpha) - \frac{1}{\sqrt{2}}(1s2s\beta\alpha - 2s1s\alpha\beta) \right\}$$

$$= \frac{1}{2} \left\{ (1s2s+2s1s)\alpha\beta - (1s2s+2s1s)\beta\alpha \right\}$$

$$= \frac{1}{2} (1s2s+2s1s)(\alpha\beta - \beta\alpha) \leftarrow \text{the wave function factors}$$

$$\begin{aligned}
 \psi_4 &= \frac{1}{2} \left\{ (1s2s\alpha\beta - 2s1s\beta\alpha) + (1s2s\beta\alpha - 2s1s\alpha\beta) \right\} \\
 &= \frac{1}{2} \left\{ (1s2s + 2s1s)\alpha\beta + (1s2s - 2s1s)\beta\alpha \right\} \\
 &= \frac{1}{2} (1s2s - 2s1s) (\alpha\beta + \beta\alpha)
 \end{aligned}$$

This wavefunction also factors.

$$\begin{aligned}
 \psi_1 &= 1s2s\alpha\alpha - 2s1s\alpha\alpha = (1s2s - 2s1s)\alpha\alpha \\
 \psi_2 &= (1s2s\beta\beta - 2s1s\beta\beta) = (1s2s - 2s1s)\beta\beta
 \end{aligned}
 \left. \vphantom{\begin{aligned} \psi_1 \\ \psi_2 \end{aligned}} \right\} \text{Also factor}$$

$$E_T = E_0 + J - K$$

$$= -\frac{5}{2} E_H + \frac{34}{81} E_H - \frac{32}{(27)^2} E_H = -2.124 \text{ a.u.}$$

$$E_S = E_0 + J + K = \left(-\frac{5}{2} + \frac{34}{81} + \frac{32}{(27)^2} \right) E_H = -2.036 \text{ a.u.}$$

The ground state energy from the text is -2.750 a.u.

So the excitation energies are:

$$\text{a) to the triplet } (1s2s) = .626 \text{ a.u.} = 137397 \text{ cm}^{-1}$$

$$\text{b) to the singlet } (1s2s) = .714 \text{ a.u.} = 156630 \text{ cm}^{-1}$$

8-27

Why do np^2 and np^4 give rise to the same electronic configurations. The former places two electrons in the three p orbitals and the latter two "holes". This will result in the same electronic states

8-31 ns nd configuration

ns $m_l = 0, m_s = \pm 1/2$

nd $m_l = 2, 1, 0, -1, -2, m_s = \pm 1/2$

So there are $2 \times 10 = 20$ arrangements.

$L = 2, S = 1, 0 \Rightarrow {}^3D, {}^1D$ states.

Accounting for the J quantum #.

${}^3D_3, {}^3D_2, {}^3D_1, {}^1D_2$ states

8-35 $4d^2 4s^2 \rightarrow {}^1S, {}^1D, {}^1G, {}^3P, {}^3F$ states

from the table in the text (nd² entry)

3F is lowest in energy by Hund's rule

${}^3F \rightarrow {}^3F_4, {}^3F_3, {}^3F_2$

3F_2 is lowest by Hund's rule #3.

8-47 Halogens: $p^5 \rightarrow {}^2P_{1/2}, {}^2P_{3/2}$

The ${}^2P_{3/2}$ is lower in energy according to Hund's rule.

$E^{(1)} \propto Z^4$ which explains why the spin-orbit splitting increases as one moves down a column of the periodic table.