

Chemistry 691 Homework 3

18) $B \ 1s^2 2s^2 2p$

$\chi(1,2,3,4,5) = 1 \ 1s \ 1s \ 2s \ 2s \ 2p \ 1$

where $2p$ can be $2p_x$, $2p_y$ or $2p_z$

$E = 2h_{1s} + 2h_{2s} + h_{2p}$ [one electron energies]

$+ [1s^2 | 1s^2] + 4 [1s^2 | 2s^2] + [2s^2 | 2s^2] + 2 [1s^2 | 2p^2] + 2 [2s^2 | 2p^2]$

(repulsion between all pairs of electrons; 10 pairs thus 10 $[a^2 | b^2]$ integrals)

$-2 [1s 2s | 2s 1s] - [1s 2p | 2p 1s] - [2s 2p | 2p 2s]$

[exchange integrals between all pairs with same spin]

19)

$|^3P_{0,1}\rangle = |P_{0,1}\rangle$

we L-raise $L_-|^3P_{0,1}\rangle = \sqrt{2} |^3P_{-1,1}\rangle$

$= (L_{1-} + L_{2-}) |P_{0,1}\rangle = \sqrt{2} |P_{0,1}\rangle$

$\approx |^3P_{-1,1}\rangle = |P_{0,1}\rangle$

similarly

$L^+|^3P_{0,1}\rangle = \sqrt{2} |^3P_{1,1}\rangle = (L_{1+} + L_{2+}) |P_{0,1}\rangle = \sqrt{2} |P_{0,1}\rangle$

$\sqrt{2} |^3P_{1,1}\rangle = |P_{0,1}\rangle$

and, $S_-|^3P_{0,1}\rangle = \sqrt{2} |^3P_{0,0}\rangle = (S_{1-} + S_{2-}) |P_{0,1}\rangle = |\bar{P}_{0,1}\rangle + |P_{0,\bar{1}}\rangle$

so $|^3P_{0,0}\rangle = \frac{1}{\sqrt{2}} [|\bar{P}_{0,1}\rangle + |P_{0,\bar{1}}\rangle]$

similarly $S_-|^3P_{-1,1}\rangle = \sqrt{2} |^3P_{-1,0}\rangle = (S_{1-} + S_{2-}) |P_{0,1}\rangle = |\bar{P}_{0,1}\rangle + |P_{0,\bar{1}}\rangle$

so $|^3P_{-1,0}\rangle = \frac{1}{\sqrt{2}} [|\bar{P}_{0,1}\rangle + |P_{0,\bar{1}}\rangle]$

by symmetry

$|^3P_{1,0}\rangle = \frac{1}{\sqrt{2}} [|\bar{P}_{0,1}\rangle + |P_{0,\bar{1}}\rangle]$

and, also by symmetry

$|^3P_{0,-1}\rangle = |P_{-1,0}\rangle$ etc.

for D states, you've been given $|^1D_{2,2}\rangle$, $|^1D_{1,0}\rangle$, $|^1D_{0,0}\rangle$
 $|^1D_{-2,-2}\rangle$ and $|^1D_{-2,0}\rangle$ are obvious by symmetry

(2)

$$|D_{10}\rangle = \frac{1}{\sqrt{2}} [|p_0 \bar{p}_{-1}\rangle + |p_{-1} \bar{p}_0\rangle] \quad (\text{take } |D_{10}\rangle \text{ and change } m_x \text{ to } -m_x)$$

$$|D_{20}\rangle = |p_{-1} \bar{p}_{-1}\rangle$$

$$|S_{00}\rangle = a |p_1 \bar{p}_{-1}\rangle + b |p_{-1} \bar{p}_1\rangle + c |p_0 \bar{p}_0\rangle$$

this has to be orthogonal to $|D_{00}\rangle = \frac{1}{\sqrt{2}} [|p_1 \bar{p}_{-1}\rangle + |p_{-1} \bar{p}_1\rangle]$
 $= \frac{1}{\sqrt{2}} [|p_{-1} \bar{p}_1\rangle + |p_1 \bar{p}_{-1}\rangle]$

so, clearly, $a = b$

also $\langle S_{00} | D_{00} \rangle = 0$ so, since $|D_{00}\rangle = \frac{1}{\sqrt{2}} [|p_1 \bar{p}_{-1}\rangle + |p_{-1} \bar{p}_1\rangle + 2 |p_0 \bar{p}_0\rangle]$

we have $\langle S_{00} | D_{00} \rangle = \frac{1}{\sqrt{2}} [a + a + 2c] = 0$

thus $\boxed{c = -a}$

$$|S_{00}\rangle = a [|p_1 \bar{p}_{-1}\rangle + |p_{-1} \bar{p}_1\rangle - |p_0 \bar{p}_0\rangle]$$

to normalize, a must be $\frac{1}{\sqrt{3}}$

(2) $|D_{00}\rangle = \frac{1}{\sqrt{2}} [|p_x \bar{p}_x\rangle - |p_y \bar{p}_y\rangle]$

by symmetry

$$|S_{00}\rangle = \frac{1}{\sqrt{3}} [|p_x \bar{p}_x\rangle + |p_y \bar{p}_y\rangle + |p_z \bar{p}_z\rangle]$$

$|D_{00}\rangle$ must be orthogonal

$$\text{so } |D_{00}\rangle = \frac{1}{\sqrt{3}} [|p_x \bar{p}_x\rangle + |p_y \bar{p}_y\rangle - 2 |p_z \bar{p}_z\rangle]$$

see subsection 6 of the new notes (3/27/17)

(2) $|D_{10}\rangle$ totally symmetric
 similarly for $|S_{00}\rangle$

(3)

22a)

 $z p$

$$L_z = L_z S_z + \frac{1}{2}(L_+ S_- + L_- S_+)$$

for example $\langle p_1 | L_z S_z | p_1 \rangle = \langle p_1 | 1 \cdot \frac{1}{2} | p_1 \rangle + \frac{1}{2} \langle p_1 | 0 \rangle + \frac{1}{2} \langle p_1 | 0 \rangle$

$$= \frac{1}{2}$$

$$\langle p_1 | L_z S_z | p_1 \rangle = \langle p_1 | 0 | p_0 \rangle + \frac{1}{2} \langle p_1 | p_1 \rangle + \frac{1}{2} \langle p_1 | p_{-1} \rangle = 0$$

$$\langle p_1 | L_z S_z | \bar{p}_0 \rangle = \langle p_1 | 0 | \bar{p}_0 \rangle + \frac{1}{2} \langle p_1 | 0 \rangle + \frac{1}{2} \langle p_1 | p_{-1} \rangle = 0$$

the only non-zero elements are

$$\langle p_{-1} | L_z S_z | \bar{p}_0 \rangle = \frac{\sqrt{2}}{2} \quad \langle \bar{p}_1 | L_z S_z | p_1 \rangle = \frac{\sqrt{2}}{2} \quad \text{etc}$$

matrix is

	p_1	p_0	p_{-1}	$\bar{p}_1$	$\bar{p}_0$	$\bar{p}_{-1}$
p_1	$\frac{1}{2}$	0	0	0	0	0
p_0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0
p_{-1}	0	0	$-\frac{\sqrt{2}}{2}$	0	$\frac{\sqrt{2}}{2}$	0
$\bar{p}_1$	0	$\frac{\sqrt{2}}{2}$	0	$-\frac{1}{2}$	0	0
$\bar{p}_0$	$\frac{\sqrt{2}}{2}$	0	0	0	0	0
$\bar{p}_{-1}$	0	0	0	0	0	$\frac{1}{2}$

eigenvalues are

$$-a, -a, \frac{a}{2}, \frac{a}{2}, \frac{a}{2}, \frac{a}{2}$$