22.3.4: iv. Review Exercise Solutions

Q1

a. For non-degenerate point groups one can simply multiply the representations (since only one representation will be obtained):

$$a_1 \otimes b_1 = b_1$$

Constructing a "box" in this case is unnecessary since it would only contain a single row. Two unpaired electrons will result in a singlet (S=0, M_S=0), and three triplets (S=1, M_S=1, S=1, M_S=0, S=1, $M_S = -1$). The states will be: ${}^3B_1(M_S$=1), ${}^3B_1(M_S = 0)$, (^3B_1(M_S=-1\)), and ${}^1B_1(M_S = 0)$.

b. Remember that when coupling non-equivalent linear molecule angular momenta, one simple adds the individual Lz values and vector couples the electron spin. So, in this case $(1\pi_u^1 2\pi_u^1)$, we have M_L values of 1+1, 1-1, -1+1, and -1-1 (2,0,0, and -2). The term symbol Δ is used to denote the spatially doubly degenerate level $(M_L = \pm 2)$ and there are two distinct spatially non-degenerate levels denote by the term symbol $\sum(M_L = 0)$. Again, two unpaired electrons will result in a singlet ($S = 0$, $M_S = 0$), and three triplets ($S = 1$, $M_S = 1$; $S = 1$, $M_S = 0$; $S = 1$, $M_S = -1$). The states generate are then:

$${}^1\Delta\ (M_L = 2);\ \text{one states}\ (M_S = 0),$$

$${}^1\Delta\ (M_L = -2);\ \text{one states}\ (M_S = 0),$$

$${}^3\Delta\ (M_L = 2);\ \text{one states}\ (M_S = 1,\ 0,\ \text{and -1}),$$

$${}^3\Delta\ (M_L = -2);\ \text{one states}\ (M_S = 1,\ 0,\ \text{and -1}),$$

$${}^1\Delta\ (M_L = 0);\ \text{one states}\ (M_S = 0),$$

$${}^1\Delta\ (M_L = 0);\ \text{one states}\ (M_S = 0),$$

$${}^3\Delta\ (M_L = 0);\ \text{one states}\ (M_S = 1,\ 0,\ \text{and -1}),\ \text{and}$$

$${}^3\Delta\ (M_L = 0);\ \text{one states}\ (M_S = 1,\ 0,\ \text{and -1})$$

c. Constructing the "box" for two equivalent π electrons one obtains:

M_S \ M_L	2	1	0
1			$\lvert\pi_1\alpha\pi_{-1}\alpha\rvert$
0	$\lvert\pi_1\alpha\pi_1\beta\rvert$		$\lvert\pi_1\alpha\pi_{-1}\beta\rvert$, $\lvert\pi_{-1}\alpha\pi_1\beta\rvert$

From this "box" one obtains six states:

$${}^1\Delta(M_L = 2);\ \text{one state}\ (M_S = 0),$$

$$^1\Delta(M_L = -2);\ \text{one state}\ (M_S = 0),$$

$$^1\Delta(M_L = 0);\ \text{one state}\ (M_S = 0),$$

$$^3\Delta(M_L = 0);\ \text{three states}\ (M_S = 1,\ 0,\ \text{and -1}),$$

d. It is not necessary to construct a "box" when coupling non-equivalent angular momenta since the vector coupling results in a range from the sum of the two individual angular momenta to the absolute value of their difference. In this case, $3d^14d^1$, L=4, 3, 2, 1, 0, and S=1, 0. The term symbol are: $^3G,^1G,^3F,^1F,^3D,^1D,^3P,^1P,^3S$, and ^1S. THe L and S angular momenta can be vector coupled to produce further splitting into levels:

$$\text{J} = \text{L} + \text{S} \dots |\text{L - S}|.$$

Denoting J as a term symbol subscript one can identify all the levels and the subsequent (2J + 1) states:

$$^3G_5\ \text{(11 states)},$$

$$^3G_4\ \text{(9 states)},$$

$$^3G_3\ \text{(7 states)},$$

$$^1G_4\ \text{(9 states)},$$

$$^3F_4\ \text{(9 states)},$$

$$^3F_3\ \text{(7 states)},$$

$$^3F_2\ \text{(5 states)},$$

$$^1F_3\ \text{(7 states)},$$

$$^3D_3\ \text{(7 states)},$$

$$^3D_2\ \text{(5 states)},$$

$$^3D_1\ \text{(3 states)},$$

$$^1D_2 \text{ (5 states)},$$

$$^3P_2 \text{ (5 states)},$$

$$^3P_1 \text{ (3 states)},$$

$$^3P_0 \text{ (1 states)},$$

$$^1P_1 \text{ (3 states)},$$

$$^3S_5 \text{ (3 states), and}$$

$$^1S_0 \text{ (1 states)}.$$

e. Construction of a "box" for the two equivalent d electrons generates (note the "box" has been turned side ways for convenience):

M_L \ M_S	1	0
4		$\lvert d_2\alpha d_2\beta\rvert$
3	$\lvert d_2\alpha d_1\alpha\rvert$	$\lvert d_2\alpha d_1\beta\rvert$, $\lvert d_2\beta d_1\alpha\rvert$
2	$\lvert d_2\alpha d_0\alpha\rvert$	$\lvert d_2\alpha d_0\beta\rvert$, $\lvert d_2\beta d_0\alpha\rvert$, $\lvert d_1\alpha d_1\beta\rvert$
1	$\lvert d_1\alpha d_0\alpha\rvert$, $\lvert d_2\alpha d_{-1}\alpha\rvert$	$\lvert d_1\alpha d_0\beta\rvert$, $\lvert d_1\beta d_0\alpha\rvert$, $\lvert d_2\alpha d_{-1}\beta\rvert$, $\lvert d_2\beta d_{-1}\alpha\rvert$
0	$\lvert d_2\alpha d_{-2}\alpha\rvert$, $\lvert d_1\alpha d_{-1}\alpha\rvert$	$\lvert d_2\alpha d_{-2}\beta\rvert$, $\lvert d_2\beta d_{-2}\alpha\rvert$, $\lvert d_1\alpha d_{-1}\beta\rvert$, $\lvert d_1\beta d_{-1}\alpha\rvert$, $\lvert d_0\alpha d_0\beta\rvert$

The term symbols are: ^1G, ^3F, ^1D, ^3P, and ^1S. The L and S angular momenta can be vector coupled to produce further splitting into levels:

$$^1G_4 \text{ (9 states)},$$

$$^3F_4 \text{ (9 states)},$$

$$^3F_3 \text{ (7 states)},$$

$$^3F_2 \text{ (5 states)},$$

$$^1D_2 \text{ (5 states)},$$

$$^3P_2 \text{ (5 states)},$$

$$^3P_1 \text{ (3 states)},$$

$$^3P_0 \text{ (1 states), and}$$

$$^1S_0 \text{ (1 states).}$$