Physics 780.04 Winter 2009
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Answers To Assignment #3

(1) a) $^2S + ^2P$ $L_A = 0$ $L_B = 1$ $M_{L,A} = 0$ $M_{L,B} = 1, 0, -1$

$\Lambda = M_{L,A} + M_{L,B} = 1, 0, -1 \Rightarrow \Pi\ (\Lambda = \pm 1),\ \Sigma\ (\Lambda = 0)$

$S_A = S_B = 1/2$ $S = 1, 0$ $2S+1 = 3, 1$

$\therefore\ ^3\Pi\ ^3\Sigma\ ^1\Pi\ ^1\Sigma$ order unknown

b) $^3P + ^1D$ $M_L^A = 1, 0, -1$ $M_L^B = 2, 1, 0, -1, -2$

$\Lambda = 3, 2, 1, 0, -1\ ;\ 2, 1, 0, -1, -2\ ;\ 1, 0, -1, -2, -3$

$\Rightarrow\ \Phi\ (\Lambda = \pm 3)$ $\Delta\ (\Lambda = \pm 2,$ 2 terms) $\Pi\ (\Lambda = \pm 1,$ 3 terms)

$\Sigma\ (\Lambda = 0,$ 3 terms) $S_A = 1$ $S_B = 0 \Rightarrow S = 1$

$\therefore\ ^3\Phi\ ^3\Delta(2)\ ^3\Pi(3)\ ^3\Sigma(3)$

c) $^3P + ^2S$ $\Lambda = M_{L,A} = 1, 0, -1 \Rightarrow \Pi, \Sigma$

$S_A = 1$ $S_B = 1/2$ $S = 3/2, 1/2$ $2S+1 = 4, 2$

$^4\Pi\ ^4\Sigma\ ^2\Pi\ ^2\Sigma$

(2) OH (9 electrons) $KK\ (\sigma_{2s_0})^2\ (\pi_{2p_0})^3$ (π_{2p_0}: open shell)

λ	1	$\uparrow\downarrow$	$\uparrow$	$\uparrow\downarrow$	$\downarrow$
	−1	$\downarrow$	$\uparrow\downarrow$	$\downarrow$	$\uparrow\downarrow$
Λ		1	−1	1	−1
Σ		1/2	1/2	−1/2	−1/2

$\Lambda = \pm 1$ $\Sigma = \pm 1/2 \Rightarrow S = 1/2 \Rightarrow X\ ^2\Pi$

Ground state atoms: $O\ (1s^2 2s^2 2p^4)\ ^3P$ $H(1s)\ ^2S$

See (1c): $^3P + ^2S \Rightarrow ^2\Pi$ $\therefore$ $X\ ^2\Pi$ can correlate with $O(^3P) + H(^2S)$

CO^+ (13 electrons) $KK(\sigma 2s_o)^2(\sigma 2s_c)^2(\pi 2p_o)^4 : (\sigma 2p_o)^1$ ($\sigma 2p_o$: open shell)

$\sigma^1 \Rightarrow X\,^2\Sigma$

Ground State Atoms: $C^+ (1s^2 2s^2 2p^1)\ ^2P$

$O\ (1s^2 2s^2 2p^4)\ ^3P$

$^2P + {}^3P \quad L_A = 1 \quad M_{L,A} = 1,0,-1 \quad L_B = 1 \quad M_{L,B} = 1,0,-1$

$\Lambda = 2,1,0\ ;\ 1,0,-1\ ;\ 0,-1,-2$

$\Lambda = \pm 2\ (\Delta),\ \pm 1\ (\Pi),\ 0\ (\Sigma)$

$S_A = \frac{1}{2} \quad S_B = 1 \quad S = 3/2, 1/2 \quad 2S+1 = 4, 2$

$C^+(^2P) + O(^3P) \Rightarrow {}^4\Delta, {}^2\Delta, {}^4\Pi(2), {}^2\Pi(2), {}^4\Sigma(3), {}^2\Sigma(3)$

$\therefore X\,^2\Sigma$ can correlate with ground state C^+ and O atoms.

③ C_2 (12 electrons) ground configuration: $KKLL(\pi_u 2p)^4 \quad X\,^1\Sigma_g$

1^{ST} excited configuration: $KKLL : (\pi_u 2p)^3 (\sigma_g 2p)^1$

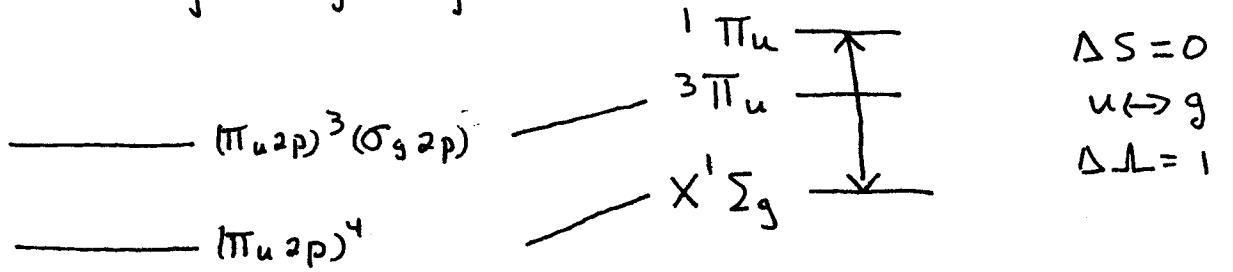
$\pi^3 = \pi^1 \Rightarrow \Lambda' = \pm 1,\ S' = 1/2 \qquad \sigma^1 \Rightarrow \Lambda'' = 0,\ S'' = 1/2$

$u^3 = u$

$\therefore$ Terms are $(\Lambda = \pm 1,\ S = 1,0)\ {}^3\Pi_u < {}^1\Pi_u$

2^{nd} excited configuration: $(\pi_u 2p)^2 (\sigma_g 2p)^2$ (π_u^2; closed shell) $\qquad u \times u = g$

${}^3\Sigma_g < {}^1\Delta_g < {}^1\Sigma_g \Leftarrow \pi_u^2$



N_2 (14 electrons) $KK(\sigma_g 2s)^2(\pi_u 2p)^4(\sigma_u^* 2s)^2(\sigma_g 2p)^2$ $X\,^1\Sigma_g$
ground conf.

1ST excited conf: $(\sigma_g 2p)^1(\pi_g^* 2p)^1$ } $^3\Pi_g < {}^1\Pi_g$

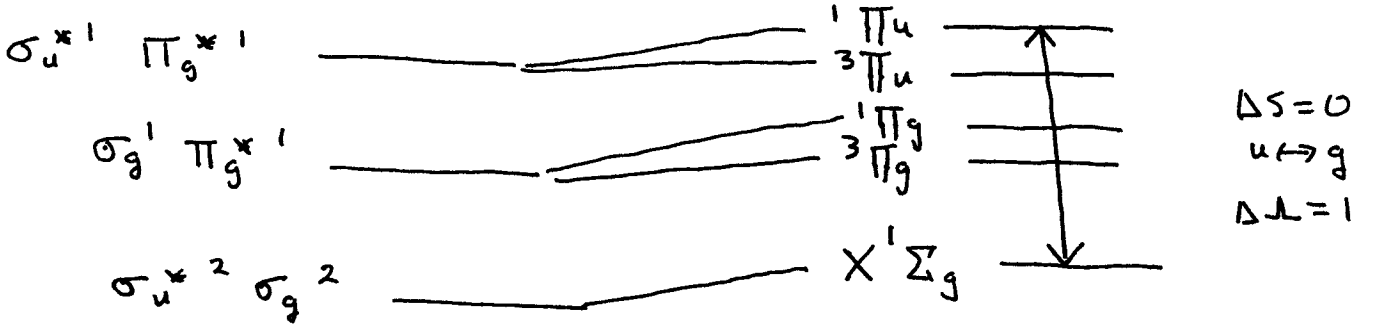
$g = g \times g$ $\quad S = 1, 0$ $\quad \Lambda = \pm 1$

$g \not\leftrightarrow g$

2nd excited conf.: $(\sigma_u^* 2s)^1(\underline{\sigma_g 2p})^2(\pi_g^* 2p)^1$
closed shell

$u \times g = u$

$\sigma\pi \Rightarrow {}^3\Pi_u < {}^1\Pi_u$

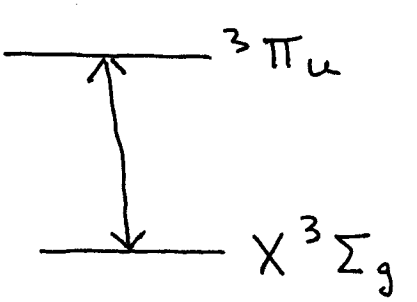


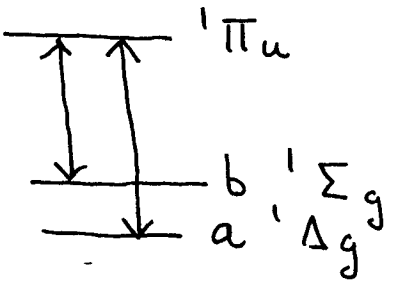
O_2 (16 electrons) ground configuration $KKLL(\underline{\pi_u 2p})^4(\sigma_g 2p)^2 : (\pi_g^* 2p)^2$
order unclear but unimportant

$\pi_g^2 \Rightarrow X\,^3\Sigma_g < a\,^1\Delta_g < b\,^1\Sigma_g$

one excited conf.: $(\pi_g^* 2p)^1(\sigma_u^* 2p)^1$ $\quad {}^3\Pi_u < {}^1\Pi_u$

a second possibility: $(\sigma_g 2p)^1(\pi_g^* 2p)^3$ $\quad {}^3\Pi_g < {}^1\Pi_g$





(4) $\mathcal{H}' = \gamma \vec{N}\cdot\vec{S}$ $\quad \vec{J} = \vec{N} + \vec{S}$ $\quad \vec{J}^2 = (\vec{N}+\vec{S})^2 = \vec{N}^2 + \vec{S}^2 + 2\vec{N}\cdot\vec{S}$

$$\gamma \vec{N}\cdot\vec{S} = \frac{\gamma}{2}\left(\vec{J}^2 - \vec{N}^2 - \vec{S}^2\right)$$

$$E^{(1)} = \langle \alpha N S J | \gamma \vec{N}\cdot\vec{S} | \alpha N S J\rangle = \frac{\gamma}{2}\left\langle \vec{J}^2 - \vec{N}^2 - \vec{S}^2 \right\rangle$$

$$E^{(1)} = \frac{\gamma}{2}\left(J(J+1) - N(N+1) - S(S+1)\right)$$

$(\gamma \equiv \hbar^2\langle\gamma\rangle)$ $\quad J = N+1/2,\ N-1/2$ $\quad {}^2\Sigma$ $\quad S = 1/2$

$J = N + 1/2 \quad (N \geq 0)$

$$E^{(1)}_{N+1/2} = \frac{\gamma}{2}\left[(N+1/2)(N+3/2) - N(N+1) - 1/2\cdot 3/2\right]$$

$$= \frac{\gamma}{2}\left[N\right]$$

$J = N - 1/2 \quad (N \geq 1)$

$$E^{(1)}_{N-1/2} = \frac{\gamma}{2}\left[(N-1/2)(N+1/2) - N(N+1) - 3/4\right]$$

$$= -\frac{\gamma}{2}\left[N+1\right]$$

$N \neq 0$ $\quad \gamma/2\, N$

$\quad\quad\quad -\gamma/2\,(N+1)$

$N = 0 \quad J = 1/2$ ——————

$\gamma > 0$

$\text{Splitting} = \frac{\gamma}{2}(2N+1)$

(5) ${}^2\Delta \quad \Lambda = \pm 2 \quad S = 1/2 \quad \Sigma = \pm 1/2 \quad E^{(1)}_{SO} = A\Lambda\Sigma$

Λ	Σ	$A\Lambda\Sigma$	$\Omega = \Lambda + \Sigma$	
2	1/2	A	5/2	${}^2\Delta_{5/2}$
−2	−1/2	A	−5/2	
2	−1/2	−A	3/2	${}^2\Delta_{3/2}$
−2	1/2	−A	−3/2	

$A > 0$: A — ${}^2\Delta_{5/2}$; $-A$ — ${}^2\Delta_{3/2}$

$A < 0$: $-A$ — ${}^2\Delta_{3/2}$; A — ${}^2\Delta_{5/2}$