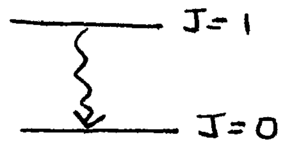
Physics 780.04 Winter Quarter 2009

Answers To Midterm Exam

1.

(a)



$B = 57.8975 \text{ GHz}$

$\nu(1-0) = 2B = 115.795 \text{ GHz}$

$$A_{10} = \frac{32\pi^3 \nu_{10}^3}{3\hbar c^3} \left| \langle\mu\rangle_{10} \right|^2$$

$\mu_{10} = 0.04\text{D} = 4 \times 10^{-20} \text{ esu-cm}$

$A_{1-0} = 2.891 \times 10^{-8} \text{ s}^{-1}$ $\quad n = n_0 e^{-A_{10}t}$

$0.1 = e^{-A_{10}\tau}$ $\quad \ln 0.1 = -A_{10}\tau = -2.303 = -A_{10}\tau$

$$\tau = A_{10}^{-1}\, 2.303 = 7.965 \times 10^7 \text{ s} \cong 2.5 \text{ yr}$$

1(b) $A_{ul} = B_{ul}\, \rho_r(\nu)$ $\quad \dfrac{A_{ul}}{B_{ul}} = \dfrac{32\pi^3 \nu_{ul}^3 |\mu_{ul}|^2 / 3\hbar c^3}{2\pi/3\hbar^2\, |\mu_{ul}|^2}$

$$\frac{A_{ul}}{B_{ul}} = 16\pi^2\, 3\hbar^2 \nu_{ul}^3 / 3\hbar c^3 = \frac{16\pi^2}{c^3} \hbar \nu_{ul}^3$$

$$\frac{A_{ul}}{B_{ul}} = \frac{8\pi h \nu_{ul}^3}{c^3} = \frac{8\pi h \nu_{ul}^3}{c^3} \frac{1}{e^{h\nu_{ul}/kT} - 1}$$

$$\therefore\ e^{h\nu_{ul}/kT} - 1 = 1$$

$$h\nu_{ul}/kT = \ln 2 \Rightarrow T = \frac{h\nu_{ul}}{k \ln 2}$$

② (a) Li $1s^2 2s^1$ $\quad$ ^2S

$$\Psi_A = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)|1:+\rangle & 1s(2)|2:+\rangle & 1s(3)|3:+\rangle \\ 1s(1)|1:-\rangle & 1s(2)|2:-\rangle & 1s(3)|3:-\rangle \\ 2s(1)|1:\pm\rangle & 1s(2)|2:\pm\rangle & 1s(3)|3:\pm\rangle \end{vmatrix}$$

2 determinants

(b) $1s3d^2$ $\quad$ First do $3d^2$ $\quad$ $\omega = \dfrac{10!}{2!\,8!} = 45$ determinants

Maximum L

$$\begin{array}{rc} 2 & \underline{\uparrow\downarrow} \\ 1 & \underline{\quad} \\ 0 & \underline{\quad} \\ -1 & \underline{\quad} \\ -2 & \underline{\quad} \\ M_L & 4 \\ M_S & 0 \end{array} \Rightarrow \begin{array}{c} L=4 \\ S=0 \end{array} \Rightarrow {}^1G \text{ (9 diagrams, determinants)}$$

Maximum S

$$\begin{array}{rc} 2 & \underline{\uparrow} \\ 1 & \underline{\uparrow} \\ 0 & \underline{\quad} \\ -1 & \underline{\quad} \\ -2 & \underline{\quad} \\ M_L & 3 \\ M_S & 1 \end{array} \Rightarrow \begin{array}{c} L=3 \\ S=1 \end{array} \Rightarrow {}^3F \; (3\times 7 = 21 \text{ diagrams})$$

Next max. L

$$\begin{array}{rc} 2 & \underline{\quad} \\ 1 & \underline{\uparrow\downarrow} \\ 0 & \underline{\quad} \\ -1 & \underline{\quad} \\ -2 & \underline{\quad} \\ M_L & 2 \\ M_S & 0 \end{array} \Rightarrow \begin{array}{c} L=2 \\ S=0 \end{array} \Rightarrow {}^1D \; (1\times 5 = 5 \text{ diagrams})$$

$\leftarrow$ distinct from diagram for ^1G

2(b) cont. Next max. S:

m_l	
2	↑
1	↑
0	
−1	
−2	

$\Rightarrow$ $L=1$, $S=1$ $\quad {}^3P$ ($3 \times 3 = 9$ diagrams)

M_L 1
M_S 1 $\leftarrow$ distinct from diagram for ${}^3F$

Final diagram: ${}^1S$ $\quad (M_L = M_S = 0 \Rightarrow L = S = 0)$

1s electron $S' = 1/2 \quad L' = 0$

$\Rightarrow \quad {}^1G \rightarrow {}^2G \qquad {}^3F \rightarrow {}^4F, {}^2F \qquad {}^1D \rightarrow {}^2D$

$(S = 1 + 1/2,\ 1 - 1/2)$

${}^3P \rightarrow {}^4P, {}^2P \qquad {}^1S \rightarrow {}^2S$

Order: ${}^4F < {}^4P < {}^2G < {}^2F < {}^2D < {}^2P < {}^2S$

$1s^2 2s^1$ ${}^2S$ $\qquad$ Allowed transitions:

$$\frac{1s^2 2s^1}{{}^2S} \longleftrightarrow \frac{1s\,3d^2}{{}^2P}$$

2(c) N_2^+ $\quad (\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\sigma_g 2p)^2 [\pi_u (2p)]^3$

$\Rightarrow X\ {}^2\Pi_u \qquad (\pi^3 = \pi)$

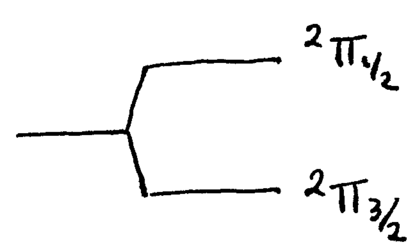
OR $\quad KKLL(\pi_u 2p)^4 (\sigma_g 2p)^1 \Rightarrow X\ {}^2\Sigma_g$

<u>Spin-orbit Splitting</u>

only ${}^2\Pi_u \quad S = 1/2 \quad \Sigma = \pm 1/2 \quad \Lambda = \pm 1$

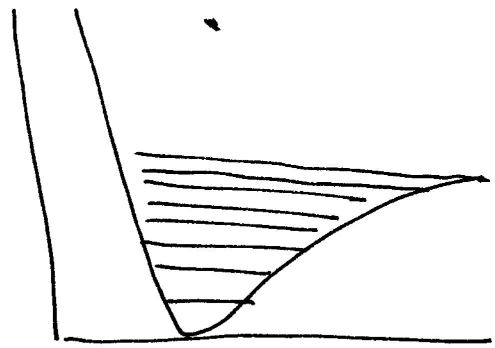
$E_{so} = \langle A L_z S_z \rangle = A \Lambda \Sigma \qquad A < 0 \quad \pi^3$

Λ	Σ	E_{so}	$\Omega = \Lambda + \Sigma$	
1	1/2	A/2	3/2	$\}\ {}^2\Pi_{3/2}$
−1	−1/2	A/2	−3/2	
1	−1/2	−A/2	1/2	$\}\ {}^2\Pi_{1/2}$
−1	1/2	−A/2	−1/2	



${}^2\Pi_i$

3.



at $E = D_e$, vibrational levels are no longer increasing in energy.

I:
$$E_v/h = \omega_e(v+\tfrac{1}{2}) - \omega_e x_e (v+\tfrac{1}{2})^2$$

$$\frac{1}{h}\frac{dE_v}{dv} = 0 = \omega_e - 2\omega_e x_e (v+\tfrac{1}{2})$$

$$v_{max} + \tfrac{1}{2} = \omega_e/2\omega_e x_e$$

$$\frac{1}{h}E_v^{max} = \frac{D_e}{h} = \omega_e \frac{\omega_e}{2\omega_e x_e} - \frac{\omega_e x_e \, \omega_e^2}{4\omega_e^2 x_e^2}$$

$$\frac{D_e}{h} = \frac{\omega_e}{4x_e} = \frac{\omega_e^2}{4\omega_e x_e}$$

$$D_e = h\omega_e/4x_e$$

II:
$$\Delta E_{v+1,v} = \omega_e - 2\omega_e x_e (v+1) = 0$$

$$v_{max} + 1 = \omega_e/2\omega_e x_e$$

$E_{v_{max}} = D_e =$ etc.