Physics 780.04 Winter 2009

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Answers To HW Set 2

1. Bernath p. 154, prob. 10 $E_n = -R_{He} Z^2/n^2 \cong -4R/n^2$

R/hc (Bernath, p. 406) $=$ 109737 cm^{-1} $\tilde{E}_n = -4\tilde{R}/n^2$

$$\frac{1}{\lambda} = -4\tilde{R}\left(\frac{1}{n_u^2} - \frac{1}{n_\ell^2}\right) = 438948\left(1/n_\ell^2 - 1/n_u^2\right)$$

$$\lambda(\text{Å}) = 10^8 \lambda(\text{cm}) = 227.82\left[1/n_\ell^2 - 1/n_u^2\right]^{-1}$$

Try $n_\ell = 1$ $n_u = 2,3,4,5$ $\lambda(\text{Å}) = 303.76, 256.29, 243.01, 237.31$ ✓

2. Bernath p. 154, prob. 11

(a) $\hat{O}(r)$: any radial operator $\langle \hat{O}(r)\rangle = \int_{r=0}^{\infty} \underbrace{|N_{n,\ell}|^2}_{\text{see Table 5.2 (p.117)}} R^*_{n,\ell}\, \hat{O}\, R_{n,\ell}\, r^2 dr$

since spherical harmonics separately normalized over θ, φ.

$$R_{1,0}(r) = R_{1s}(r) = (1/a_0)^{3/2}\, 2 \cdot e^{-r/a_0}$$

$$\langle \hat{O}(r)\rangle_{1s} = \frac{4}{a_0^3}\int_{r=0}^{\infty} e^{-2r/a_0}\, \hat{O}(r)\, r^2 dr$$

$$\int_0^{\infty} x^n e^{-ax} dx = n!/a^{n+1}$$

$$\therefore \langle r\rangle = \frac{4}{a_0^3}\int_{r=0}^{\infty} r^3 e^{-2r/a_0} dr = \frac{4}{a_0^3}\frac{3!}{(2/a_0)^4} = 1.5\, a_0$$

$$\langle 1/r\rangle = \frac{4}{a_0^3}\int_{r=0}^{\infty} r\, e^{-2r/a_0} dr = \frac{4}{a_0^3}\frac{1!}{(2/a_0)^2} = \frac{1}{a_0}$$

(b) Table 5.3 $\psi_{1s} = \frac{1}{\pi^{1/2}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{5/2} r\, e^{-r/2a_0} \cos\theta$$

$\vec{\mu} = -e\vec{r} \qquad \mu_x = -er\sin\theta\cos\varphi \qquad \mu_y = -er\sin\theta\sin\varphi \qquad \mu_z = -er\cos\theta$

$$\begin{pmatrix}\mu_{\begin{smallmatrix}x\\y\\z\end{smallmatrix}}\end{pmatrix}_{2p_z-1s} = -e\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\psi^*_{2p_z}\left\{\begin{matrix} r\sin\theta\cos\varphi \\ r\sin\theta\sin\varphi \\ r\cos\theta\end{matrix}\right\}\psi_{1s}\, r^2\sin\theta\, dr\, d\theta\, d\varphi$$

$$\begin{pmatrix}\mu_{\begin{smallmatrix}x\\y\\z\end{smallmatrix}}\end{pmatrix}_{2p_z-1s} = \frac{-e}{4\pi\sqrt{2}\,a_0^4}\int_{r=0}^{\infty} r^4 e^{-3r/2a_0}\,dr \int_{\theta=0}^{\pi}\begin{bmatrix}\cos\theta\sin^2\theta \\ \cos\theta\sin^2\theta \\ \cos^2\theta\sin\theta\end{bmatrix} d\theta$$

$$\times\int_{\varphi=0}^{2\pi}\left\{\begin{matrix}\cos\varphi\\ \sin\varphi \\ 1\end{matrix}\right\} d\varphi$$

Since $\int_{\varphi=0}^{2\pi}\cos\varphi\, d\varphi = \int_0^{2\pi}\sin\varphi\, d\varphi = 0$,

μ_z only non-zero component.

$$\therefore (\mu_z)_{2p_z-1s} = \frac{-e}{4\pi\sqrt{2}\,a_0^4}\underbrace{\int_{r=0}^{\infty} r^4 e^{-3r/2a_0}\,dr}_{\frac{4!}{(3/2a_0)^5}}\ \underbrace{\int_{\theta=0}^{\pi}\cos^2\theta\sin\theta\, d\theta}_{\underbrace{-\frac{1}{3}\cos^3\theta\Big|_0^{\pi}}_{2/3}}\ \underbrace{\int_{\varphi=0}^{\pi} d\varphi}_{2\pi}$$

$$\therefore (\mu_z)_{2p_z-1s} = \frac{-e a_0}{4\pi\sqrt{2}}\ \frac{4\times3\times2}{3^5}\ 2^5\ \frac{2}{3}\ 2\pi = \frac{-e a_0}{\sqrt{2}}\frac{2^8}{3^5}$$

$(\mu_z)_{2p_z-1s} = -0.745\, e a_0 \qquad e = 4.803\times10^{-10}\text{ esu} \quad a_0 = 0.5292\times10^{-8}\text{ cm}$

$(\mu_z)_{2p_z-1s} = -1.893\times10^{-18}\text{ esu-cm} = -1.893\text{ Debye}$

3. Li (3 electrons) $Z=3$ $R = 13.6057\text{ eV}$ (Bernath appendix)

$$E_{n_1n_2n_3} = -9R\left[1/n_1^2 + 1/n_2^2 + 1/n_3^2\right]$$

$1s^2 2s^1$ lowest configuration $E_{1,1,2} = -9R\underbrace{[1+1+1/4]}_{2.25} = -275.52\text{ eV}$

$$E_{1,1,\infty}\ (Li^{+}\ 1s^2 + e^-) = -9R(2) = -244.90\ eV$$

$$E_{1,\infty,\infty}\ (Li^{2+}\ 1s + 2e^-) = -9R = -122.45\ eV$$

$$E_{\infty,\infty,\infty}\ (Li^{3+} + 3e^-) = 0\ eV$$

Li^{3+} ——— 0 eV

$\uparrow IP_3 \downarrow$

Li^{2+} ——— 1s −122.45eV

$\uparrow IP_2 \downarrow$

Li^{+} ——— $1s^2$ −244.90eV

$\uparrow IP_1 \downarrow$

Li ——— $1s^2 2s^1$ −275.52eV

Ionization Potentials (eV)

IP	'Theory'	Expt
1	30.62	5.392
2	122.45	75.638
3	122.45	122.45 ✓

Screening Approach

2s electron screened by 1s electrons. Assume it 'sees' $Z' = 3-2 = 1$

$$E'_{n_1=n_2=1,\ n_3=2} = -R\left(\frac{Z^2}{1^2} + \frac{Z^2}{1^2} + \frac{Z'^2}{2^2}\right)$$

$$= -248.30\ eV$$

$$IP_1' = E_{1,1,\infty}(Li^+) - E'_{1,1,2}(Li) = 3.40\ eV$$

much closer to expt value

Of course, 1s electrons will be partially screened as well. This will help IP_2.

4. Bernath p. 153 prob. 8 ns n's ns n'd np n'p n''p

Use vector algebra since no need to invoke PEP

a) $\ell_1 = \ell_2 = 0$ $s_1 = s_2 = 1/2$ $L = 0$ $S = 1, 0$ ^3S, ^1S

ns n's

ns n'd $\ell_1 = 0\ \ell_2 = 2 \Rightarrow L = 2$ $S = 1, 0 \Rightarrow$ ^3D, ^1D

$\underbrace{np\ n'p}\ n''p$

$\ell_1 = \ell_2 = 1 \Rightarrow L' = 2,1,0 \quad + \ell_3 = 1 \Rightarrow L = 3,2,1,2,1,0,1$

$S' = 1,0 \quad + s_3 = 1/2 \Rightarrow S = 3/2, 1/2, 1/2$

$L = 3 \quad S = 3/2,\ 1/2,\ 1/2 \Rightarrow {}^4F,\ {}^2F,\ {}^2F$

(2) $L = 2 \quad S = 3/2,\ 1/2,\ 1/2 \Rightarrow {}^4D,\ {}^2D,\ {}^2D$ (2 each)

(3) $L = 1 \quad S = 3/2,\ 1/2,\ 1/2 \Rightarrow {}^4P,\ {}^2P,\ {}^2P$ (3 each)

$L = 0 \quad S = 3/2,\ 1/2,\ 1/2 \Rightarrow {}^4S,\ {}^2S,\ {}^2S$

(b) $J = L+S,\ L+S-1,\ \cdots\ |L-S|$ $\quad {}^1S: J=0 \quad {}^3S: J=1 \quad {}^1D: J=2 \quad {}^3D: J=3,2,1$

${}^4F: J = 9/2,\ 7/2,\ 5/2,\ 3/2 \qquad {}^2F: J = 7/2,\ 5/2$

${}^4D: J = 7/2,\ 5/2,\ 3/2,\ 1/2 \qquad {}^2D: J = 5/2,\ 3/2$

${}^4P: J = 5/2,\ 3/2,\ 1/2 \qquad {}^2P: J = 3/2,\ 1/2$

${}^4S: J = 3/2 \qquad {}^2S: J = 1/2$

5. $np^4 \quad W = \dfrac{6!}{2!\,4!} = 15$ (same as p^2) diagrams

In class, terms for np^2 shown to be ${}^3P < {}^1D < {}^1S$. But, the 15 diagrams for np^2 and np^4 are related in the following sense:

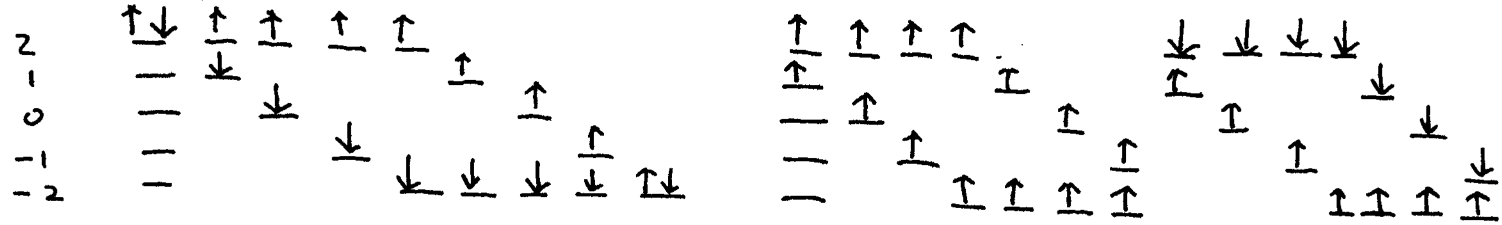
m_ℓ 1	↑↓		o o		↑ o		o ↓
0	↑↓	⟷	o o	or	↑↓	⟷	o o
−1	o o ← hole		↑↓		↑ o		o ↓
M_L	2		−2	M_L	0		0
M_S	0		0	M_S	1		−1

For any np^4 diagram, construct an np^2 diagram such that their sum is np^6 ($M_L = M_S = 0$).

$np^2 \Rightarrow M_L\ M_S \qquad np^4 \Rightarrow -M_L,\ -M_S$

Changing signs does not change L, S values enumerated.

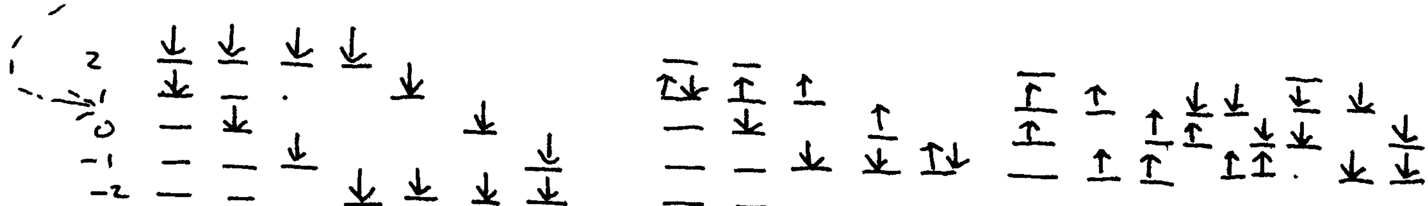
$\underline{nd^2} \quad W = \dfrac{10!}{2!\,8!} = 45 \quad \ell = 2 \quad m_\ell = 2, 1, 0, -1, -2$



M_L: 4 3 2 +1 0 −1 −2 −3 −4 | 3 2 1 0 −1 −2 −3 3 2 1 0 −1 −2 −3

M_S: 0 0 0 0 0 0 0 0 0 | 1 1 1 1 1 1 1 0 0 0 0 0 0 0

9 determinants $L=4$ $S=0$ ^1G



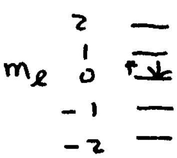
M_L: 3 2 1 0 −1 −2 −3 | 2 1 0 −1 −2 | 1 0 −1 1 0 −1 1 0 −1

M_S: −1 −1 −1 −1 −1 −1 −1 | 0 0 0 0 0 | 1 1 1 0 0 0 −1 −1 −1

$L=3$ $S=1$ ^3F
21 determinants

$L=2$ $S=0$ ^1D
5 determinants

$L=1$ $S=1$ ^3P
9 determinants



M_L 0
M_S 0

$L=S=0$ ^1S
1 determinant

Order: $^3F < {}^3P < {}^1G < {}^1D < {}^1S$

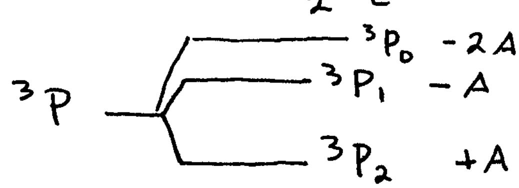
p^4 Spin-Orbit Splitting

$^1S \rightarrow {}^1S_0$ $\quad {}^1D \rightarrow {}^1D_2$ $\quad {}^3P \rightarrow {}^3P_0, {}^3P_1, {}^3P_2$

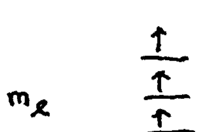
For ^3P $L=1$ $S=1$ $J=2,1,0$

$$E_{fs}^{(1)} = \frac{A}{2}\left[J(J+1) - L(L+1) - S(S+1)\right] = \frac{A}{2}\left[J(J+1) - 4\right]$$

$A<0$



6. N $(1s^2 2s^2 2p^3)$ ground configuration $W = \frac{6!}{3!\,3!} = 20$



$M_L = 0$ $M_S = 3/2$ $\Rightarrow$ ^4S ground term

Two possible first excited configurations: $1s^2\,2s\,2p^4$
$1s^2\,2s^2\,2p^2\,3s$

Terms for $1s^2 \vdots \underbrace{2s2p^4}_{sp^4}$ = Terms for $1s^2\,2s^2 \vdots \underbrace{2p^2\,3s}_{sp^2}$

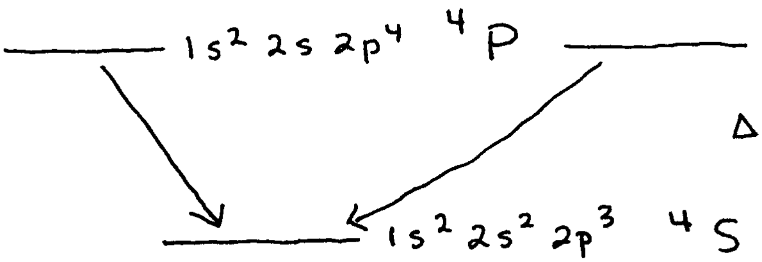
Terms for $p^2 = p^4$ $\quad {}^3P\,(L' = S' = 1)$ $\quad {}^1D\,(L' = 2 \;\; S' = 0)$
${}^1S\,(L' = S' = 0)$

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

$${}^3P\,(L' = 1 \;\; S' = 1) + S'' = 1/2 \Rightarrow L = 1 \quad S = 3/2,\ 1/2 \quad {}^4P \;\; {}^2P$$

$${}^1D\,(L' = 2 \;\; S' = 0) + S'' = 1/2 \Rightarrow L = 2 \quad S = 1/2 \quad {}^2D$$

$${}^1S\,(L' = 0 \;\; S' = 0) + S'' = 1/2 \Rightarrow L = 0 \quad S = 1/2 \quad {}^2S$$



$\boxed{{}^4P < {}^2D < {}^2P < {}^2S}$

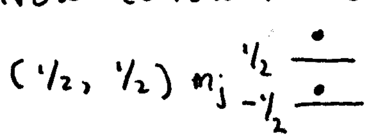
$\Delta \ell_i = 1 \quad \Delta L = 1 \quad \Delta S = 0$

7. np^2 jj coupling $\quad$ For each electron $\ell = 1 \;\; s = 1/2 \quad j = 3/2,\ 1/2$

$(3/2,\ 1/2) \Rightarrow J = 2, 1$ vector addition allowed

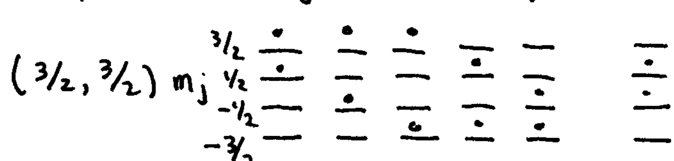
Note: no distinction between $(3/2, 1/2)$ + $(1/2, 3/2)$
states: $2(3/2, 1/2)$ and $1(3/2, 1/2)$

Now consider $(1/2, 1/2)$ + $(3/2, 3/2)$ diagramatically:



$M_J \quad 0 \Rightarrow J = 0$

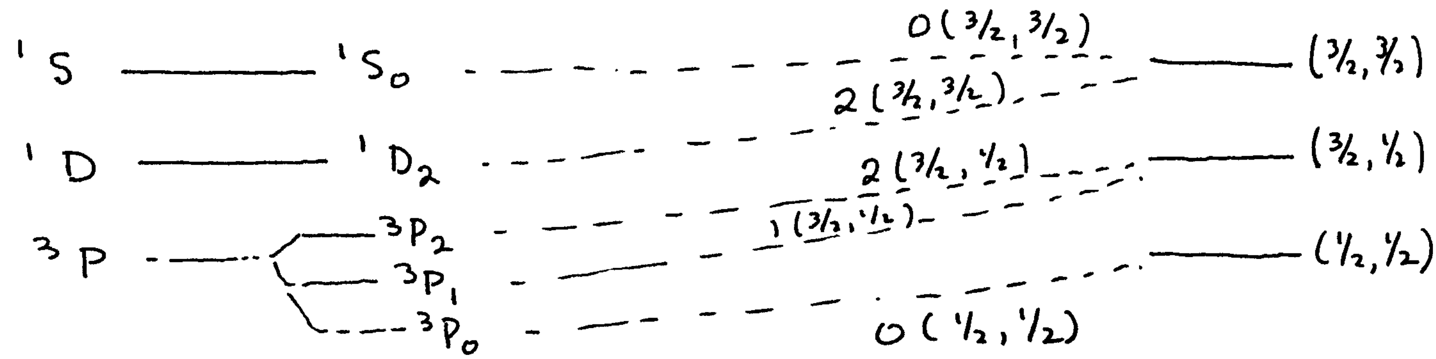
$\Rightarrow 0\,(1/2, 1/2)$



$M_J \quad \underbrace{2 \quad 1 \quad 0 \quad -1 \quad -2}_{J = 2} \qquad 0 \quad J = 0$

$2\,(3/2, 3/2) \qquad 0\,(3/2, 3/2)$

Correlation Diagram



8. $$E^{(1)}_{M_L M_S} = \mu_b B_z (M_L + 2M_S) + A M_L M_S \quad \text{(in class)}$$

$^2P \quad L = 1 \quad S = 1/2 \quad M_L = 1, 0, -1 \quad M_S = \pm 1/2$

M_L	M_S	$E^{(1)}_{M_L M_S}$
1	1/2	$2\mu_b B_z + A/2$
0	1/2	$\mu_b B_z$
−1	1/2	$-A/2$
1	−1/2	$-A/2$
0	−1/2	$-\mu_b B_z$
−1	−1/2	$-2\mu_b B_z + A/2$