Assignment (16)

(1) a) $[A,B] = AB - BA = -(BA - AB) = -[B,A]$.

b) $[A^n, A^m] = 0 \quad \forall\, n, m$

$[A^1, A^1] = AA - AA = 0$

$[A^n, A^m] = A^n A^m - A^m A^n = A^{n+m} - A^{m+n} = 0$.

c) $[A^2, B] = AAB - BAA = A[A,B] + [A,B]A = A(AB-BA) + (AB-BA)A = AAB - \cancel{ABA} + \cancel{ABA} - BAA$

$AAB - BAA = AAB - BAA$

d) $[A,[B,C]] + [B,[C,A]] + [C,[A,B]] = 0$.

$[A,(BC-CB)] + [B,(CA-AC)] + [C,(AB-BA)] = 0$.

$[ABC - ACB - \cancel{BCA} + \cancel{CBA} + \cancel{BCA} - BAC - \cancel{CAB} + \cancel{ACB} + \cancel{CAB} - \cancel{CBA} - \cancel{ABC} + BAC] = 0$.

$0 = 0$

(2) $M_+ = \hat{M}_x + i\hat{M}_y \quad \rightarrow \quad \hat{M}_+ Y_\ell^m = \hbar\sqrt{\ell(\ell+1) - m(m+1)}\, Y_\ell^{m+1}$

$M_- = \hat{M}_x - i\hat{M}_y \quad \rightarrow \quad \hat{M}_- Y_\ell^m = \hbar\sqrt{\ell(\ell+1) - m(m-1)}\, Y_\ell^{m-1}$

a) $\hat{M}_x = \dfrac{\hat{M}_+ + \hat{M}_-}{2}$; $\hat{M}_y = \dfrac{\hat{M}_+ - \hat{M}_-}{2i}$

b) $\hat{M}^2 = \frac{1}{2}(\hat{M}_+\hat{M}_- + \hat{M}_-\hat{M}_+) + \hat{M}_z^2$

$\hat{M}_x^2 + \hat{M}_y^2 + \cancel{\hat{M}_z^2} = \frac{1}{2}(\hat{M}_+\hat{M}_- + \hat{M}_-\hat{M}_+) + \cancel{\hat{M}_z^2}$

$\left(\dfrac{\hat{M}_+ + \hat{M}_-}{2}\right)^2 + \left(\dfrac{\hat{M}_+ - \hat{M}_-}{2i}\right)^2 = \frac{1}{2}(\hat{M}_+\hat{M}_- + \hat{M}_-\hat{M}_+)$

$\dfrac{\hat{M}_+\hat{M}_+ + \hat{M}_+\hat{M}_- + \hat{M}_-\hat{M}_+ + \hat{M}_-\hat{M}_-}{4} + \dfrac{\hat{M}_+\hat{M}_+ - \hat{M}_+\hat{M}_- - \hat{M}_-\hat{M}_+ + \hat{M}_-\hat{M}_-}{4(-1)} = \frac{1}{2}(\hat{M}_+\hat{M}_- + \hat{M}_-\hat{M}_+)$

$\dfrac{\cancel{\hat{M}_+\hat{M}_+} + \hat{M}_+\hat{M}_- + \hat{M}_-\hat{M}_+ + \cancel{\hat{M}_-\hat{M}_-} - \cancel{\hat{M}_+\hat{M}_+} + \hat{M}_+\hat{M}_- + \hat{M}_-\hat{M}_+ - \cancel{\hat{M}_-\hat{M}_-}}{4} = \frac{1}{2}(\hat{M}_+\hat{M}_- + \hat{M}_-\hat{M}_+)$

$\frac{1}{2}(\hat{M}_+\hat{M}_- + \hat{M}_-\hat{M}_+) = \frac{1}{2}(\hat{M}_+\hat{M}_- + \hat{M}_-M_+)$

c) $[\hat{M}_+, \hat{M}_-] = 2\hbar\hat{M}_z$

$\hat{M}_+\hat{M}_- - \hat{M}_-\hat{M}_+ = 2\hbar\hat{M}_z$

$[\hat{M}_+\hat{M}_- - \hat{M}_-\hat{M}_+]Y_\ell^m = \hat{M}_+\left[\hbar\sqrt{\ell(\ell+1) - m(m-1)}\, Y_\ell^{m-1}\right] - \hat{M}_-\left[\hbar\sqrt{\ell(\ell+1) - m(m+1)}\, Y_\ell^{m+1}\right]$

$= \hbar^2\sqrt{\ell(\ell+1) - m(m-1)}\sqrt{\ell(\ell+1) - (m-1)m}\, Y_\ell^m - \hbar^2\sqrt{\ell(\ell+1) - m(m+1)}\sqrt{\ell(\ell+1) - (m+1)m}\, Y_\ell^m$

$= \hbar^2[\cancel{\ell(\ell+1)} - m(m-1) - \cancel{\ell(\ell+1)} + m(m+1)]Y_\ell^m$

$= \hbar^2[\cancel{m^2} + m - \cancel{m^2} + m]Y_\ell^m = 2\hbar^2 m Y_\ell^m = 2\hbar\hat{M}_z Y_\ell^m$

d) $[\hat{M}_+, \hat{M}_x] = [\hat{M}_x + i\hat{M}_y, \hat{M}_x] = [\hat{M}_x, \hat{M}_x] + i[\hat{M}_y, \hat{M}_x] = 0 + i[-i\hbar\hat{M}_z] = \hbar\hat{M}_z$

$[\hat{M}_+, \hat{M}_y] = [\hat{M}_x + i\hat{M}_y, \hat{M}_y] = [\hat{M}_x, \hat{M}_y] + 0i = i\hbar\hat{M}_z$

$[\hat{M}_+, \hat{M}_z] = [\hat{M}_x + i\hat{M}_y, \hat{M}_z] = [\hat{M}_x, \hat{M}_z] + i[\hat{M}_y, \hat{M}_z] = -i\hbar\hat{M}_y + i[i\hbar\hat{M}_x] = -\hbar[\hat{M}_x + i\hat{M}_y]$

$= -\hbar\hat{M}_+$

$[M^2, M_+] = [M_x^2 + M_y^2 + M_z^2, M_+] = [\hat{M}_x^2, M_+] + [M_y^2, M_+] + [M_z^2, M_+]$

$= \hat{M}_x[\hat{M}_x, M_+] + [\hat{M}_x, \hat{M}_+]\hat{M}_x + \hat{M}_y[\hat{M}_y, \hat{M}_+] + [\hat{M}_y, \hat{M}_+]\hat{M}_y + \hat{M}_z[\hat{M}_z, \hat{M}_+] + [\hat{M}_z, \hat{M}_+]\hat{M}_z$

$= \hat{M}_x(-\hbar\hat{M}_z) + (-\hbar\hat{M}_z)\hat{M}_x + \hat{M}_y(-i\hbar\hat{M}_z) + (-i\hbar\hat{M}_z)\hat{M}_y + \hat{M}_z(\hbar\hat{M}_+) + (\hbar\hat{M}_+)\hat{M}_z$

$= -\hbar[\hat{M}_x, \hat{M}_z] - i\hbar[\hat{M}_y, \hat{M}_z] + \hbar[\hat{M}_z, \hat{M}_+]$

$= -\hbar[-i\hbar\hat{M}_y] - i\hbar[i\hbar\hat{M}_x] + \hbar[-\hbar\hat{M}_+] = \hbar^2\hat{M}_x + i\hbar^2\hat{M}_y - \hbar^2[\hat{M}_x + i\hat{M}_y] = 0$

Only $[M^2, M_\pm] = 0$

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e) $\hat{M}^2|Y_\ell^m\rangle = \ell(\ell+1)\hbar^2|Y_\ell^m\rangle$

f) i) $\langle P_x|\hat{L}_z|P_y\rangle = \langle \frac{1}{\sqrt{2}}(P_{-1} - P_{+1})|\hat{L}_z|\frac{i}{\sqrt{2}}(P_{-1} + P_{+1})\rangle = \frac{i}{2}\langle P_{-1} - P_{+1}|\hat{L}_z P_{-1} + \hat{L}_z P_{+1}\rangle$

$= \frac{i}{2}\langle P_{-1} - P_{+1}|\hbar(-1)P_{-1} + \hbar(+1)P_{+1}\rangle = \frac{i\hbar}{2}\langle P_{-1} - P_{+1}|P_{+1} - P_{-1}\rangle$

$= \frac{i\hbar}{2}[\cancel{\langle P_{-1}|P_{+1}\rangle}^{0} - \cancel{\langle P_{-1}|P_{-1}\rangle}^{1} - \cancel{\langle P_{+1}|P_{+1}\rangle}^{1} + \cancel{\langle P_{+1}|P_{-1}\rangle}^{0}] = \frac{i\hbar}{2}[-1-1] = -i\hbar$

ii) $\langle P_x|\hat{L}_+|P_y\rangle = \langle \frac{1}{\sqrt{2}}(P_{-1} - P_{+1})|\hat{L}_+|\frac{i}{\sqrt{2}}(P_{-1} + P_{+1})\rangle = \frac{i}{2}\langle P_{-1} - P_{+1}|\hat{L}_+P_{-1} + \hat{L}_+P_{+1}\rangle$

$= \frac{i}{2}\langle P_{-1} - P_{+1}|\hbar\sqrt{1(1+1) - (-1)(0)}\, P_0 + \cancel{\hbar\sqrt{1(1+1) - (1)(1+1)}\, P_{+2}}\rangle$ cannot happen and square root is 0

$= \frac{i}{2}\langle P_{-1} - P_{+1}|\hbar\sqrt{2}P_0\rangle = \frac{i\hbar}{\sqrt{2}}[\cancel{\langle P_{-1}|P_0\rangle}^{0} - \cancel{\langle P_{-1}|P_0\rangle}^{0}] = 0$

iii) $\langle P_z|\hat{L}_y|P_x\rangle = \langle P_0|\hat{L}_y|\frac{1}{\sqrt{2}}(P_{-1} - P_{+1})\rangle = \langle P_0|\frac{1}{\sqrt{2}}(\hat{L}_yP_{-1} - \hat{L}_yP_{+1})\rangle$

$= \frac{1}{\sqrt{2}}\langle P_0|(\hat{L}_+ - \hat{L}_-)(\frac{1}{2i})P_{-1} + (\hat{L}_- - \hat{L}_+)(\frac{1}{2i})P_{+1}\rangle$

$= \frac{-\hbar}{2i\sqrt{2}}\langle P_0|\sqrt{1(1+1) - (-1)(0)}\, P_0 - \cancel{\sqrt{1(1+1) - (-1)(-1-1)}\, P_{-2}}$ cannot happen $+ \sqrt{1(1+1) - 1(1-1)}\, P_0 - \cancel{\sqrt{1(1+1) - (1)(1+1)}\, P_{+2}}\rangle$ cannot happen

$= \frac{-\hbar}{2i\sqrt{2}}\langle P_0|\sqrt{2}P_0 + \sqrt{2}P_0\rangle = -\frac{\hbar}{2i}(2)\langle P_0|P_0\rangle = i\hbar$

iv) $\langle P_z|\hat{L}_x|P_y\rangle = \langle P_0|\hat{L}_x|\frac{i}{\sqrt{2}}(P_{-1} + P_{+1})\rangle = \frac{i}{\sqrt{2}}\langle P_0|\hat{L}_x(P_{-1} + P_{+1})\rangle$

$= \frac{i}{\sqrt{2}}\langle P_0|(\hat{L}_+ + \hat{L}_-)P_{-1} + (\hat{L}_+ + \hat{L}_-)P_{+1}\rangle(\frac{1}{2})$

$= \frac{i\hbar}{2\sqrt{2}}\langle P_0|\cancel{\sqrt{1(1+1) - (-1)(-1+1)}\, P_0}^{0} + 0 + 0 + \sqrt{1(2) - (1)(0)}\, P_0\rangle = \frac{i\hbar}{2\sqrt{2}}\langle P_0|\sqrt{2}P_0 + \sqrt{2}P_0\rangle$

$= \frac{i\hbar}{2}\langle P_0|P_0\rangle(2) = i\hbar$

v) $\langle P_z|\hat{L}_x|P_x\rangle = \langle P_0|\hat{L}_x|\frac{1}{\sqrt{2}}(P_{-1} - P_{+1})\rangle = \frac{1}{\sqrt{2}}\langle P_0|\hat{L}_xP_{-1} - \hat{L}_xP_{+1}\rangle = \frac{1}{\sqrt{2}}\langle P_0|(\hat{L}_+ + \hat{L}_-)(\frac{1}{2})P_{-1} - \frac{1}{2}(\hat{L}_+ + \hat{L}_-)P_{+1}\rangle$

$= \frac{\hbar}{2\sqrt{2}}\langle P_0|\sqrt{1(2) - (-1)(0)}\, P_0 + 0 - 0 + \sqrt{1(2) - (1)(0)}\, P_0\rangle = \frac{\hbar}{2\sqrt{2}}\langle P_0|\sqrt{2}P_0 + \sqrt{2}P_0\rangle = \hbar$

3a. What are the term symbols associated with the ground state electron configuration of the Vanadium atom, $[\mathrm{Ar}]4s^2 3d^3$? You do not need to show the "J labels". (10 points)

$M_L \setminus M_S$	$M_S = \frac{1}{2}$		$M_S = \frac{3}{2}$
$M_L = 5$ 2+2+1	$\lvert 3d_2\alpha \quad 3d_2\beta \quad 3d_1\alpha \rvert$		
$M_L = 4$ 2+2+0 2+1+1	$\lvert 3d_2\alpha \quad 3d_2\beta \quad 3d_0\alpha \rvert$ $\lvert 3d_2\alpha \quad 3d_1\alpha \quad 3d_1\beta \rvert$		
$M_L = 3$ 2+1+0 2+2+-1	$\lvert 3d_2\alpha \quad 3d_1\alpha \quad 3d_0\beta \rvert$ $\lvert 3d_2\beta \quad 3d_1\alpha \quad 3d_0\alpha \rvert$	$\lvert 3d_2\alpha \quad 3d_1\beta \quad 3d_0\alpha \rvert$ $\lvert 3d_2\alpha \quad 3d_2\beta \quad 3d_{-1}\alpha \rvert$	$\lvert 3d_2\alpha \quad 3d_1\alpha \quad 3d_0\alpha \rvert$
$M_L = 2$ 2+0+0 1+1+0 2+1+-1 2+2+-2	$\lvert 3d_2\alpha \quad 3d_0\alpha \quad 3d_0\beta \rvert$ $\lvert 3d_2\alpha \quad 3d_1\alpha \quad 3d_{-1}\beta \rvert$ $\lvert 3d_2\beta \quad 3d_1\alpha \quad 3d_{-1}\alpha \rvert$	$\lvert 3d_1\alpha \quad 3d_1\beta \quad 3d_0\alpha \rvert$ $\lvert 3d_2\alpha \quad 3d_1\beta \quad 3d_{-1}\alpha \rvert$ $\lvert 3d_2\alpha \quad 3d_2\beta \quad 3d_{-2}\alpha \rvert$	$\lvert 3d_2\alpha \quad 3d_1\alpha \quad 3d_{-1}\alpha \rvert$
$M_L = 1$ 1+0+0 2+0+-1 1+1+-1 2+1+-2	$\lvert 3d_1\alpha \quad 3d_0\alpha \quad 3d_0\beta \rvert$ $\lvert 3d_2\alpha \quad 3d_0\beta \quad 3d_{-1}\alpha \rvert$ $\lvert 3d_1\alpha \quad 3d_1\beta \quad 3d_{-1}\alpha \rvert$ $\lvert 3d_2\alpha \quad 3d_1\beta \quad 3d_{-2}\alpha \rvert$	$\lvert 3d_2\alpha \quad 3d_0\alpha \quad 3d_{-1}\beta \rvert$ $\lvert 3d_2\beta \quad 3d_0\alpha \quad 3d_{-1}\alpha \rvert$ $\lvert 3d_2\alpha \quad 3d_1\alpha \quad 3d_{-2}\beta \rvert$ $\lvert 3d_2\beta \quad 3d_1\alpha \quad 3d_{-2}\alpha \rvert$	$\lvert 3d_2\alpha \quad 3d_0\alpha \quad 3d_{-1}\alpha \rvert$ $\lvert 3d_2\alpha \quad 3d_1\alpha \quad 3d_{-2}\alpha \rvert$
$M_L = 0$ 2+-1+-1 1+0+-1 1+1+-2 2+0+-2	$\lvert 3d_2\alpha \quad 3d_{-1}\alpha \quad 3d_{-1}\beta \rvert$ $\lvert 3d_1\alpha \quad 3d_0\beta \quad 3d_{-1}\alpha \rvert$ $\lvert 3d_1\alpha \quad 3d_1\beta \quad 3d_{-2}\alpha \rvert$ $\lvert 3d_2\alpha \quad 3d_0\beta \quad 3d_{-2}\alpha \rvert$	$\lvert 3d_1\alpha \quad 3d_0\alpha \quad 3d_{-1}\beta \rvert$ $\lvert 3d_1\beta \quad 3d_0\alpha \quad 3d_{-1}\alpha \rvert$ $\lvert 3d_2\alpha \quad 3d_0\alpha \quad 3d_{-2}\beta \rvert$ $\lvert 3d_2\beta \quad 3d_0\alpha \quad 3d_{-2}\alpha \rvert$	$\lvert 3d_1\alpha \quad 3d_0\alpha \quad 3d_{-1}\alpha \rvert$ $\lvert 3d_2\alpha \quad 3d_0\alpha \quad 3d_{-2}\alpha \rvert$

$^2\mathrm{H}$, $^2\mathrm{G}$, $^4\mathrm{F}$, $^2\mathrm{F}$, $^2\mathrm{D}$, $^2\mathrm{D}$, $^4\mathrm{P}$, $^2\mathrm{P}$

So, the term symbols are: $^4\mathrm{F}$, $^4\mathrm{P}$, $^2\mathrm{H}$, $^2\mathrm{G}$, $^2\mathrm{F}$, $2\left(^2\mathrm{D}\right)$, $^2\mathrm{P}$.

3b. According to Hund's Rules, what is the ground-state term symbol for Vanadium?(2pts.)

$^4\mathrm{F}$

3c. For the ground state term symbol from #3b, what are the possible values of J? List these in order of increasing energy. (3 points)

$\left|L-S\right| = \left|3-\frac{3}{2}\right| = \frac{3}{2} \le J \le \frac{9}{2} = 3+\frac{3}{2}$; $J = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$. Since the shell is less than half filled:

$$E\left(^4\mathrm{F}_{3/2}\right) < E\left(^4\mathrm{F}_{5/2}\right) < E\left(^4\mathrm{F}_{7/2}\right) < E\left(^4\mathrm{F}_{9/2}\right)$$