QM II
Phys 652

Solutions of HW #5 (cont'd) 8

Problem #1

(a) From Lecture #12, $\vec{S}\cdot\vec{n} \doteq \frac{\hbar}{2}\vec{\sigma}\cdot\vec{n}$

$\vec{n} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$

↑ arbitrary unit vector

$$\vec{S}\cdot\vec{n} \doteq \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\sin\theta\cos\varphi + \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\sin\theta\sin\varphi +$$

$$+ \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\cos\theta = \frac{\hbar}{2}\begin{pmatrix} \cos\theta & \sin\theta\, e^{-i\varphi} \\ e^{i\varphi}\sin\theta & -\cos\theta \end{pmatrix}$$

Now find eigenvalues:

$$\det\begin{vmatrix} \frac{\hbar}{2}\cos\theta - \lambda & \frac{\hbar}{2}\sin\theta\, e^{-i\varphi} \\ \frac{\hbar}{2}e^{i\varphi}\sin\theta & -\frac{\hbar}{2}\cos\theta - \lambda \end{vmatrix} = 0 \Rightarrow -\frac{\hbar^2}{4}\cos^2\theta + \lambda^2 -$$

$$-\frac{\hbar^2}{4}\sin^2\theta = 0 \Rightarrow$$

$$\boxed{\lambda = \pm\frac{\hbar}{2}}$$

Eigenstates:

$|S_n = +\frac{\hbar}{2}\rangle$:
$$\begin{bmatrix} \frac{\hbar}{2}(\cos\theta - 1) & \frac{\hbar}{2}\sin\theta\, e^{-i\varphi} \\ \frac{\hbar}{2}e^{i\varphi}\sin\theta & -\frac{\hbar}{2}(\cos\theta + 1) \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

$$c_1(\cos\theta - 1) + c_2\sin\theta\, e^{-i\varphi} = 0$$

Recall: $1-\cos\theta = 2\sin^2\frac{\theta}{2}$, $\sin\theta = 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}$

Then, $c_1 \cdot \cancel{2}\sin^{\cancel{2}}\frac{\theta}{2} = c_2 \cancel{2}\cancel{\sin\frac{\theta}{2}}\cos\frac{\theta}{2}e^{-i\varphi} \Rightarrow$

$$\underline{c_2 = e^{i\varphi}\tan\frac{\theta}{2}\, c_1}$$

$$|S_n = +\frac{\hbar}{2}\rangle = \begin{bmatrix} 1 \\ e^{i\varphi}\tan\frac{\theta}{2}\end{bmatrix} \cdot \frac{1}{\sqrt{1+\tan^2\frac{\theta}{2}}} = \begin{bmatrix}\cos\frac{\theta}{2} \\ e^{i\varphi}\sin\frac{\theta}{2}\end{bmatrix}$$

$$|S_n = -\frac{\hbar}{2}\rangle \underset{\substack{\uparrow \\ \text{similarly}}}{=} \begin{bmatrix}-\sin\frac{\theta}{2} \\ e^{i\varphi}\cos\frac{\theta}{2}\end{bmatrix}$$

(b) $\langle S_n = +\frac{\hbar}{2} | \vec{S}\cdot\vec{n} | S_n = +\frac{\hbar}{2}\rangle = ?$

$= \langle S_n = +\frac{\hbar}{2} | S_x n_x + S_y n_y + S_z n_z | S_n = +\frac{\hbar}{2}\rangle =$

$= \frac{\hbar}{2}\langle S_n = +\frac{\hbar}{2} | \underbrace{\sigma_x n_x + \sigma_y n_y + \sigma_z n_z}_{\begin{pmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z\end{pmatrix} = \begin{pmatrix}\cos\theta & \sin\theta e^{-i\varphi} \\ e^{i\varphi}\sin\theta & -\cos\theta\end{pmatrix}} | S_n = +\frac{\hbar}{2}\rangle =$

$$= \frac{\hbar}{2}\left[\cos\frac{\theta}{2} \;\; e^{-i\varphi}\sin\frac{\theta}{2}\right]\begin{bmatrix}\cos\theta & \sin\theta e^{-i\varphi} \\ e^{i\varphi}\sin\theta & -\cos\theta\end{bmatrix}\begin{bmatrix}\cos\frac{\theta}{2} \\ e^{i\varphi}\sin\frac{\theta}{2}\end{bmatrix}$$

$$= \frac{\hbar}{2}\left[\cos\frac{\theta}{2}\;\; e^{-i\varphi}\sin\frac{\theta}{2}\right]\begin{bmatrix}\cos\theta\cos\frac{\theta}{2} + \sin\theta\sin\frac{\theta}{2} \\ e^{i\varphi}\sin\theta\cos\frac{\theta}{2} - \cos\theta\sin\frac{\theta}{2}e^{i\varphi}\end{bmatrix} =$$

$$= \frac{\hbar}{2}\Big(\underbrace{\cos^2\frac{\theta}{2}\cos\theta} + \underbrace{\sin\theta\cos\frac{\theta}{2}\sin\frac{\theta}{2}} +$$

$$+ \underline{\sin\theta\sin\frac{\theta}{2}\cos\frac{\theta}{2}} - \underbrace{\sin^2\frac{\theta}{2}\cos\theta}\Big) = \frac{\hbar}{2}\left(\cos^2\theta +\right.$$

$$\left. + \sin^2\theta\right) = \underbrace{\frac{\hbar}{2}}$$

↑ which is of course expected, since $(\vec{S}\cdot\vec{n}) = S_n \Rightarrow S_n|S_n = +\frac{\hbar}{2}\rangle =$
$= \frac{\hbar}{2}|S_n = \frac{\hbar}{2}\rangle$

What about

$$\langle S_z = +\frac{\hbar}{2}|S_n|S_z = +\frac{\hbar}{2}\rangle\ ? \Rightarrow$$

$$|S_z = +\frac{\hbar}{2}\rangle \doteq \begin{pmatrix}1\\0\end{pmatrix} \Rightarrow$$

$$\frac{\hbar}{2}\begin{bmatrix}1 & 0\end{bmatrix}\begin{bmatrix}\cos\theta & \sin\theta\, e^{-i\varphi}\\ e^{i\varphi}\sin\theta & -\cos\theta\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix}1 & 0\end{bmatrix}\cdot$$

$$\cdot\begin{bmatrix}\cos\theta\\ e^{i\varphi}\sin\theta\end{bmatrix} = \frac{\hbar}{2}\cos\theta = \frac{\hbar}{2}\underbrace{n_z}$$

Problem #4

$$H = \frac{a}{\hbar^2}\left(\vec{S}_x^{\,2} + \vec{S}_y^{\,2} - 2\vec{S}_z^{\,2}\right) - \frac{b}{\hbar} S_z =$$

$$= \frac{a}{\hbar^2}\left(\vec{S}^{\,2} - 3\vec{S}_z^{\,2}\right) - \frac{b}{\hbar} S_z$$ ← obviously, H is diagonal in the $\{|s, m_s\rangle\}$ basis

$$E_{m_s} = \langle s, m_s | H | s, m_s \rangle =$$

$$= \frac{a}{\hbar^2}\left(\hbar^2 s(s+1) - 3\hbar^2 m_s^2\right) - \frac{b}{\hbar}\hbar m_s =$$

$$= a\left(s(s+1) - 3m_s^2\right) - b\, m_s \underset{s=\frac{3}{2}}{=} a\left(\frac{15}{4} - 3m_s^2\right) - b m_s$$

Since $|m_s| \leq s \Rightarrow$

$$m_s = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$$

Then, $E_{m_s=-\frac{3}{2}} = \frac{15}{4}a - 3a\cdot\frac{9}{4} - b\cdot\left(-\frac{3}{2}\right) = -3a + \frac{3}{2}b$

$$E_{m_s=-\frac{1}{2}} = \frac{15}{4}a - 3a\cdot\frac{1}{4} - b\cdot\left(-\frac{1}{2}\right) = 3a + \frac{b}{2}$$

$$E_{m_s=+\frac{1}{2}} = \frac{15}{4}a - 3a\cdot\frac{1}{4} - b\cdot\frac{1}{2} = 3a - \frac{b}{2}$$

$$E_{m_s=+\frac{3}{2}} = \frac{15}{4}a - 3a\cdot\frac{9}{4} - b\cdot\frac{3}{2} = -3a - \frac{3}{2}b$$

Problem #3

(red) or 3.26 (grey)

Problem 3.22 of Sakurai (3.38 in the newest (3rd) edition)

(a) Consider $j=1$

$\langle 1,m' | J_y | 1,m \rangle = ?$ $\Rightarrow$ obviosly, diagonal elements (i.e. $m'=m$) are 0

$J_y = \frac{J_+ - J_-}{2i}$; $\quad J_\pm |j,m\rangle = \hbar\sqrt{j(j+1)-m(m\pm1)}\,|j,m\pm1\rangle$

$j=1 \Rightarrow J_\pm |1,m\rangle = \hbar\sqrt{2-m(m\pm1)}\,|1,m\pm1\rangle$

$\Downarrow$

$m=-1,0,1 \Rightarrow J_\pm|1,\pm1\rangle \Rightarrow J_-|1,-1\rangle = 0$

$J_+|1,+1\rangle = 0$

$J_+|1,-1\rangle = \hbar\sqrt{2}\,|1,0\rangle$

$J_-|1,1\rangle = \hbar\sqrt{2}\,|1,0\rangle \quad \Leftarrow \quad J_\pm|1,\mp1\rangle = \hbar\sqrt{2\pm1\underbrace{(\mp1\pm1)}_{=0}}\cdot|1,\mp1\pm1\rangle$

$\langle 1,\mp1 | J_y | 1,\pm1\rangle = 0$

The only non-zero elements are:

$\langle 1,0 | \frac{J_+ - J_-}{2i} | 1,-1\rangle = \frac{1}{2i}\hbar\sqrt{2}$

$\langle 1,0 | \frac{J_+ - J_-}{2i} | 1,1\rangle = \frac{-1}{2i}\hbar\sqrt{2}$

and their conjugates (i.e. $\langle 1,\pm1 | J_y | 1,0\rangle$)

$\Downarrow$

$$J_y^{(j=1)} = \frac{\hbar}{2}\begin{array}{c|c} m= \;\; 1 \quad\quad 0 \quad\quad -1 & m'= \\ \begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix} & \begin{array}{c} 1 \\ 0 \\ -1 \end{array} \end{array}$$

(b) Expand $e^{-\frac{i}{\hbar}J_y\beta}$ into Taylor series $\Rightarrow$

$$e^{-\frac{i}{\hbar}J_y\beta} = 1 - \frac{i}{\hbar}J_y\beta + \left(\frac{i}{\hbar}J_y\beta\right)^2\cdot\frac{1}{2!} + \left(-\frac{i}{\hbar}J_y\beta\right)^3\cdot\frac{1}{3!} + \dots$$

$$e^x = \sum_{n=0}^{\infty}\frac{x^n}{n!}$$

Consider $\underbrace{\left(\frac{J_y^{(j=1)}}{\hbar}\right)^3}$ $\underset{\text{from (a)}}{=}$ $\frac{1}{8}\begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix}\begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix}\cdot$

$$\cdot\begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix} = \frac{1}{8}\begin{pmatrix} 2 & 0 & -2 \\ 0 & 4 & 0 \\ -2 & 0 & 2 \end{pmatrix}\begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix} =$$

$$= \frac{1}{8}\begin{pmatrix} 0 & -4i\sqrt{2} & 0 \\ 4i\sqrt{2} & 0 & -4i\sqrt{2} \\ 0 & 4i\sqrt{2} & 0 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix} = \underbrace{\frac{J_y^{(j=1)}}{\hbar}}$$

Then, $e^{-\frac{i}{\hbar}J_y\beta} = 1 - \frac{i}{\hbar}J_y\beta + \left(-\frac{i}{\hbar}J_y\right)^2\frac{\beta^2}{2!} + \left(+\frac{i}{\hbar}J_y\right)\frac{\beta^3}{3!} +$

$$+ \left(\frac{J_y}{\hbar}\right)^2\frac{\beta^4}{4!} + \dots = 1 - \frac{i}{\hbar}J_y\underbrace{\left(\beta - \frac{\beta^3}{3!} + \dots\right)}_{\sin\beta} - \left(\frac{J_y}{\hbar}\right)^2\underbrace{\left(\frac{\beta^2}{2!} - \frac{\beta^4}{4!} + \dots\right)}_{1-\cos\beta}$$

$$= \underline{1 - \frac{i}{\hbar}J_y\sin\beta - \left(\frac{J_y}{\hbar}\right)^2(1-\cos\beta)}$$

(c) $d^{(j=1)}_{m'm}(\beta) = \langle j,m'|\, e^{-\frac{i}{\hbar}J_y\beta}\,|j,m\rangle =$

$$= \langle j,m'|\, 1 - \left(\frac{J_y}{\hbar}\right)^2(1-\cos\beta) - i\left(\frac{J_y}{\hbar}\right)\sin\beta\,|j,m\rangle =$$

$$= \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} - \frac{1}{\hbar^2}\cdot\left(\frac{\hbar}{2}\right)^2\cdot \underbrace{\begin{pmatrix}2&0&-2\\0&4&0\\-2&0&2\end{pmatrix}}_{J_y^2 \text{ from (b)}}\cdot(1-\cos\beta) -$$

$$-\frac{i}{\cancel{\hbar}}\cdot\frac{\cancel{\hbar}}{2}\begin{pmatrix}0&-i\sqrt{2}&0\\i\sqrt{2}&0&-i\sqrt{2}\\0&i\sqrt{2}&0\end{pmatrix}\sin\beta = \begin{pmatrix}1-\frac{1}{2}(1-\cos\beta) & -\frac{\sqrt{2}}{2}\sin\beta & \frac{1}{2}(1-\cos\beta)\\ \frac{\sqrt{2}}{2}\sin\beta & \cancel{1}-\cancel{1}+\cos\beta & -\frac{\sqrt{2}}{2}\sin\beta\\ \frac{1}{2}(1-\cos\beta) & \frac{\sqrt{2}}{2}\sin\beta & 1-\frac{1}{2}(1-\cos\beta)\end{pmatrix} =$$

$$= \underline{\begin{pmatrix}\frac{1}{2}(1+\cos\beta) & -\frac{\sqrt{2}}{2}\sin\beta & \frac{1}{2}(1-\cos\beta)\\ \frac{\sqrt{2}}{2}\sin\beta & \cos\beta & -\frac{\sqrt{2}}{2}\sin\beta\\ \frac{1}{2}(1-\cos\beta) & \frac{\sqrt{2}}{2}\sin\beta & \frac{1}{2}(1+\cos\beta)\end{pmatrix}}$$

Solutions of HW #6 (ctd)

Problem #4

$$H_{total} = H_{Coulomb} + \underbrace{H_{hf}}_{A\vec{S}_1\cdot\vec{S}_2}$$

(a) The state of the system is described by

$$|\Psi\rangle = |1,0,0\rangle \otimes |S, m_s\rangle$$

$$H_{total}|\Psi\rangle = E|\Psi\rangle$$

$$\Downarrow$$

$$\left(H_{Coulomb} + H_{hf}\right)|\Psi\rangle = -E_I|\Psi\rangle + A\underbrace{\vec{S}_1\cdot\vec{S}_2}_{\frac{\vec{S}^2 - \vec{S}_1^{\,2} - \vec{S}_2^{\,2}}{2}}|\Psi\rangle$$

ground-state energy of H-atom

$$= \left(-E_I + \frac{A}{2}\hbar^2\left(S(S+1) - \frac{3}{4}\cdot 2\right)\right)|\Psi\rangle$$

$$\Downarrow$$

$$E = -E_I + \frac{A\hbar^2}{2}\left(S(S+1) - \frac{3}{2}\right)$$

Singlet: $s=0 \Rightarrow \underline{E = -E_I - \frac{3}{4}A\hbar^2}$

Triplet: $s=1 \Rightarrow \underline{E = -E_I + \frac{A\hbar^2}{4}}$

(b) $A \sim \frac{e}{mc}\,\frac{5.6e}{2Mc}\,\frac{1}{a_0^3}$

$\Delta E = E_{triplet} - E_{singlet} = \underline{A\hbar^2}$

Ground-state energy $\Rightarrow |-E_I| = \frac{me^4}{2\hbar^2} = \frac{e^2}{2a_0}$ ← Bohr radius

Energy correction:

$$\left|\frac{\Delta E}{-E_I}\right| = \frac{A\hbar^2}{e^2}\cdot 2a_0 = \frac{e}{mc}\,\frac{5.6\cancel{e}}{2Mc}\,\frac{1}{a_0^{3\,2}}\,\frac{\hbar^2\cdot \cancel{2a_0}}{\cancel{e^2}} = 5.6\frac{\hbar^2}{mMc^2a_0^2} =$$

$$= 5.6\frac{\hbar^2}{\cancel{m}Mc^2}\cdot\frac{m^2e^4}{\hbar^4} = 5.6\frac{m}{M}\underbrace{\frac{e^4}{\hbar^2c^2}}_{\alpha^2} = 5.6\frac{m}{M}\alpha^2$$

$a_0 = \frac{\hbar^2}{me^2}$

α^2 ← fine-structure constant ($\alpha = \frac{1}{137}$)

(c) From (b):

$$\Delta E \sim 5.6\frac{m}{M}\alpha^2 E_I = 5.6\cdot\frac{1}{1836}\cdot\left(\frac{1}{137}\right)^2\cdot 13.6\ eV$$

$$\nu = \frac{\Delta E}{h} = \frac{5.6\cdot\frac{1}{1836}\left(\frac{1}{137}\right)^2\cdot 13.6\cdot 1.6\cdot 10^{-19}}{6.6\cdot 10^{-34}} = \underline{5.4\cdot 10^8\ Hz}$$

$\lambda_{exp} = 21.4\ cm \longleftrightarrow \lambda_{theor} = \frac{c}{\nu} \sim 56\ cm$

(d) Since there are 3 states with $E_{triplet}$ and one with $E_{singlet}$, statistically $\frac{P_{triplet}}{P_{singlet}} = \frac{3}{1} \Rightarrow$ out of 20 H-atoms 15 will be in triplet and 5 in a singlet state