① 14.33

know $\sigma_i\sigma_j = -\sigma_j\sigma_i \quad i \neq j \quad (1)$

$\sigma_i\sigma_j = i\sigma_k$ for $\varepsilon_{ijk}=1 \quad (2)$

Using (1), can turn (2) into $\sigma_j\sigma_i = -i\sigma_k$ for $\varepsilon_{ijk}=1$.

So $\sigma_i\sigma_j = i\varepsilon_{ijk}\sigma_k$

Now $Tr(\sigma_i\sigma_j) = Tr(\sigma_j\sigma_i)$ (see Ex.17.1)

But if $\sigma_i\sigma_j = -\sigma_j\sigma_i$ then

$$Tr(\sigma_i\sigma_j) = -Tr(\sigma_j\sigma_i)$$

so $Tr(\sigma_i\sigma_j) = 0$ for $i \neq j$

Now

$$0 = Tr(i\varepsilon_{ijk}\sigma_k) = i\varepsilon_{ijk}Tr(\sigma_k)$$

$\rightarrow Tr(\sigma_k) = 0$ for all k.

② 14.3.4 Show $(\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{B}) = \vec{A}\cdot\vec{B} + i\hat{\sigma}\cdot\vec{A}\times\vec{B}$

$$\sigma_i\sigma_j = \frac{1}{2}\left([\hat{\sigma}_i,\hat{\sigma}_j]_+ + [\hat{\sigma}_i,\hat{\sigma}_j]\right) = \underbrace{\delta_{ij}\mathbb{1} + i\sum_k \varepsilon_{ijk}\hat{\sigma}_k}_{\text{see p. 384}}$$

(1) $$(\hat{\vec{\sigma}}\cdot\vec{A})(\hat{\vec{\sigma}}\cdot\vec{B}) = \left(\sum_i \hat{\sigma}_i A_i\right)\left(\sum_j \hat{\sigma}_j B_j\right) = \sum_{i,j}\hat{\sigma}_i\hat{\sigma}_j A_i B_j$$

$$= \sum_{i,j}\left[\delta_{ij}\mathbb{1} + i\sum_k \varepsilon_{ijk}\hat{\sigma}_k\right]A_i B_j$$

$$= \sum_i A_i B_i \mathbb{1} + i\sum_{ijk}\varepsilon_{ijk}A_i B_j \hat{\sigma}_k$$

$$= A\cdot B + i\hat{\vec{\sigma}}\cdot(\vec{A}\times\vec{B})$$ ✓

(2) Let $\hat{M} = (\hat{\vec{\sigma}}\cdot\vec{A})(\hat{\vec{\sigma}}\cdot\vec{B}) = \sum_{ij}\hat{\sigma}_i\hat{\sigma}_j A_i B_j$ as above.

if $\hat{M} = \sum_i m_i \sigma_i$, $m_i = \frac{1}{2}\mathrm{Tr}(\hat{M}\hat{\sigma}_i)$

$$\hat{M} = \sum_{ij}\left(\delta_{ij}\mathbb{1} + \sum_k i\varepsilon_{ijk}\sigma_k\right)A_i B_j$$

$$\Rightarrow M_0 = \frac{1}{2}\mathrm{Tr}(\hat{M}\mathbb{1}) = \frac{1}{2}\mathrm{Tr}(\hat{M}) = \sum_{ij}\delta_{ij}A_i B_j = \vec{A}\cdot\vec{B}$$

$$M_x = \frac{1}{2}\mathrm{Tr}(\hat{M}\sigma_x) = i\sum_{ij}\varepsilon_{ijx}A_i B_j = i[A_y B_z - A_z B_y]$$

+ cyc perm.

$$\Rightarrow M = \vec{A}\cdot\vec{B} + i(\vec{A}\times\vec{B})\cdot\hat{\vec{\sigma}}$$ ✓

③ 14.3.7

(1) Recall rotations effectively add:

$$\hat{R}(a)\hat{R}(b) = \hat{R}(a+b)$$

so $\left[\hat{R}_{\vec{n}}(a)\right]^{\frac{1}{2}} = R_{\vec{n}}\left(\frac{a}{2}\right)$

Now $\sqrt{2}(\mathbb{1} + i\hat{\sigma}_x) = \hat{R}_x\left(\frac{-\pi}{2}\right)$

$$\longrightarrow \quad (\mathbb{1} + i\sigma_x)^{\frac{1}{2}} = 2^{\frac{1}{4}}\hat{R}_x\left(\frac{-\pi}{4}\right)$$

$$= 2^{\frac{1}{4}}\left[\mathbb{1}\cos\frac{\pi}{8} + i\hat{\sigma}_x \sin\frac{\pi}{8}\right]$$

(2) $(2+\hat{\sigma}_x)^{-1} = \dfrac{\mathbb{1}}{(2+\hat{\sigma}_x)}\,\dfrac{2-\hat{\sigma}_x}{2-\hat{\sigma}_x} = \dfrac{2-\hat{\sigma}_x}{\underbrace{4-\hat{\sigma}_x^2}_{\hat{\sigma}_x^2=1}} = \frac{1}{3}(2-\hat{\sigma}_x)$

Or you could do it with $\hat{M}(2+\hat{\sigma}_x) = \mathbb{1}$ and solve for components of $\hat{M}$.

(3) $\hat{\sigma}_x^2 = \mathbb{1}$, so $\hat{\sigma}_x^{-1} = \hat{\sigma}_x$.

14.3.8

$\vec{\sigma} = \sigma_x + \sigma_y + \sigma_z$

(1)

$$= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= \begin{pmatrix} 1 & (1-i) \\ (1+i) & -1 \end{pmatrix}$$

$$\begin{pmatrix} 1 & (1-i) \\ (1+i) & -1 \end{pmatrix}\begin{pmatrix} a & b \\ c & d \end{pmatrix} - \begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} 1 & (1-i) \\ (1+i) & -1 \end{pmatrix}$$

$$\begin{pmatrix} a + (1-i)c & b + (1-i)d \\ (1+i)a - c & (1+i)b - d \end{pmatrix} - \begin{pmatrix} a + (1+i)b & a(1-i) - b \\ c + (1+i)d & c(1-i) - d \end{pmatrix}$$

$$= \begin{pmatrix} [c(1-i) - b(1+i)] & [d(1-i) - a(1-i)] \\ [(1+i)a - (1+i)d] & [(1+i)b - (1-i)c] \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$\Longrightarrow$

$$\left.\begin{array}{l} c(1-i) - b(1+i) = 0 \\ -c(1-i) + b(1+i) = 0 \end{array}\right\} \text{same eqn}$$

and

$$\left.\begin{array}{l} -a(1-i) + d(1-i) = 0 \\ a(1+i) - (1+i)d = 0 \end{array}\right\} \Rightarrow a = d$$

$$c - ic - b - ib = 0$$

$$(c-b) + i(-c-b) = 0 \Rightarrow c = b = 0$$

thus $\begin{array}{l} a = d = s \\ c = b = 0 \end{array} \Longrightarrow \boxed{s\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}$

14.4.1 let $H = -\gamma \vec{L}\cdot\vec{B} = \sum_j -\gamma L_j B_j$

$$i\hbar \frac{d}{dt}\langle \vec{L}\rangle = \langle[\vec{L}, H]\rangle$$

$$[\vec{L},H] = -\gamma[\vec{L}, \vec{L}\cdot\vec{B}] = -\gamma\Big[\vec{L}, \sum_j L_jB_j\Big] = -\gamma\sum_{ij}[L_i, L_jB_j]$$

Now $-[L_jB_j, L_i] = -\{L_j[B_j,L_i] + [L_j,L_i]B_j\}$

$$= -[L_j,L_i]B_j \quad ; \text{ But } [L_j,L_i] = -i\hbar\sum_k \epsilon_{ijk}L_k$$

Thus $[L_i, L_jB_j] = i\hbar\sum_k \epsilon_{ijk}L_kB_j =$

So $[\vec{L},H] = -\gamma i\hbar \sum_i\sum_j\sum_k \epsilon_{ijk}L_kB_j$

But $\sum_j\sum_k \epsilon_{ijk}L_kB_j = (\vec{L}\times\vec{B})_i$

$\therefore$ $[\vec{L},H] = -\gamma i\hbar\sum_i(\vec{L}\times\vec{B})_i = -i\hbar\gamma(\vec{L}\times\vec{B})$

So $\frac{d}{dt}\langle\vec{L}\rangle = \langle -\gamma\vec{L}\times\vec{B}\rangle = -\gamma\langle\vec{L}\rangle\times\vec{B}$

(6) 14.4.3 Let $R_z(\omega t) = e^{-\frac{i\omega t \hat{S}_z}{\hbar}}$ $\Rightarrow |\psi_r\rangle = \hat{R}_z(\omega t)|\psi\rangle$

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$$

$$\Rightarrow i\hbar \frac{d}{dt}|\psi(t)\rangle = \hat{H}\hat{R}_z^+(\omega t)|\psi_r(t)\rangle$$

$$i\hbar \frac{d}{dt}\hat{R}_z^+(\omega t)|\psi_r(t)\rangle = \hat{H}\hat{R}_z^+(\omega t)|\psi_r(t)\rangle$$

$$i\hbar\left(\frac{d\hat{R}_z^+(\omega t)}{dt}\right)|\psi_r(t)\rangle + i\hbar \hat{R}_z^+(\omega t)\frac{d}{dt}|\psi_r(t)\rangle = \hat{H}\hat{R}_z^+(\omega t)|\psi_r(t)\rangle$$

$$\Rightarrow i\hbar \frac{d}{dt}|\psi_r(t)\rangle = -i\hbar \hat{R}_z(\omega t)\left(\frac{d}{dt}\hat{R}_z^+(\omega t)\right)|\psi_r\rangle + \hat{R}_z(\omega t)\hat{H}\hat{R}_z^+(\omega t)|\psi_r(t)\rangle$$

$$= \hat{H}_r|\psi_r(t)\rangle$$

Now $\hat{R}_z(\omega t) = e^{-\frac{i\omega t}{\hbar}\hat{S}_z} = e^{-\frac{i\omega t}{2}\hat{\sigma}_z}$

$$= \cos\frac{\omega t}{2} - i\hat{S}_z \sin\frac{\omega t}{2}$$

so $-i\hbar \hat{R}_z(\omega t)\frac{d}{dt}\hat{R}_z^+(\omega t) = -i\hbar \frac{i\omega}{2}\cancel{e^{\frac{i\omega t \sigma_z}{2}}}\,\hat{\sigma}_z\,\cancel{e^{-\frac{i\omega t}{2}\sigma_z}}$

$$= \frac{\hbar\omega}{2}\hat{\sigma}_z$$

$$\Rightarrow \hat{H}_r = \frac{\hbar\omega}{2}\hat{\sigma}_z + \hat{R}_z(\omega t)\hat{H}\hat{R}_z^+(\omega t)$$

$$\hat{R}_z(\omega t)\hat{H}\hat{R}_z^+(\omega t) = -\frac{\hbar}{2}\left(\cos\frac{\omega t}{2} - i\sigma_z \sin\frac{\omega t}{2}\right)\left[\gamma B_0\sigma_z + \gamma B\vec{\sigma}\cdot(\vec{e}_x\cos\omega t - \vec{e}_y \sin\omega t)\right]\cdot$$
$$\cdot\left(\cos\frac{\omega t}{2} + i\sigma_z \sin\frac{\omega t}{2}\right)$$

Terms proportional to $B_0\gamma$ is $\frac{\hbar B_0 \gamma}{2}\hat{\sigma}_z$

" " " " $-\frac{\hbar\gamma B}{2}\left(\cos\frac{\omega t}{2} - i\hat{\sigma}_z \sin\frac{\omega t}{2}\right)\left(\sigma_x \cos\omega t - \sigma_y \sin\omega t\right)\cdot$

$\cdot\left(\frac{\cos\omega t}{2} + i\hat{\sigma}_z \sin\frac{\omega t}{2}\right)$

Now, use $\sigma_i\sigma_j = -\sigma_j\sigma_i$:

$$= -\frac{\hbar\gamma B}{2}\left(\cos^2\frac{\omega t}{2}\left(\hat{\sigma}_x\cos\omega t - \hat{\sigma}_y \sin\omega t\right) + \sin^2\frac{\omega t}{2}\hat{\sigma}_z\left(\hat{\sigma}_x\cos\omega t - \hat{\sigma}_y\sin\omega t\right)\hat{\sigma}_z\right.$$

$$\left. - 2i\frac{\cos\omega t}{2}\sin\frac{\omega t}{2}\hat{\sigma}_z\left(\hat{\sigma}_x\cos\omega t - \hat{\sigma}_y \sin\omega t\right)\right]$$

(Now $\hat{\sigma}_z\hat{\sigma}_x\hat{\sigma}_z = -\hat{\sigma}_z\hat{\sigma}_z\hat{\sigma}_x = -\hat{\sigma}_x$

$\hat{\sigma}_z\hat{\sigma}_y\hat{\sigma}_z = -\hat{\sigma}_y$

$\sigma_z\sigma_x = i\sigma_y$ + cyc. perm.)

so $$= \frac{-\hbar\gamma B}{2}\left[\cos\omega t\left(\hat{\sigma}_x\cos\omega t - \hat{\sigma}_y\sin\omega t\right) + \sin\omega t\left(\sigma_y\cos\omega t + \sigma_x \sin\omega t\right)\right]$$

$$= -\frac{\hbar\gamma B}{2}\left[\hat{\sigma}_x + \sigma_y\left(\sin\omega t\cos\omega t - \sin\omega t\cos\omega t\right)\right]$$

$$= \frac{-\hbar\gamma B}{2}\hat{\sigma}_x$$

So $\hat{H}_r = \frac{\hbar\omega}{2}\hat{\sigma}_z - \frac{\hbar B_0\gamma}{2}\hat{\sigma}_z - \frac{\hbar B\gamma}{2}\hat{\sigma}_x$ = time-independent.

$$\hat{U}_r(t) = \exp\left(\frac{-i\hat{H}_r t}{\hbar}\right) = \exp\left(-it\left[\frac{\omega - B_0\gamma}{2}\hat{\sigma}_z - \frac{B\gamma}{2}\hat{\sigma}_x\right]\right)$$

$$|\psi_r\rangle = \hat{U}_r(t)|\psi_r(0)\rangle = \exp\left[-it\left(\frac{\omega - B_0\gamma}{2}\hat{\sigma}_z - \frac{B\gamma}{2}\hat{\sigma}_x\right)\right]|\psi_r(0)\rangle$$

Start with $|\psi_r(0)\rangle = |+_z\rangle \leftrightarrow \begin{pmatrix}1\\0\end{pmatrix}$ so $\hat{\sigma}_z|\psi_r(0)\rangle = |\psi_r(0)\rangle$

$$|\psi_r(t)\rangle = e^{-it\left(\frac{\omega-B_0\gamma}{2}\right)\hat{\sigma}_z} e^{-\frac{itB\gamma}{2}\hat{\sigma}_x}\begin{pmatrix}1\\0\end{pmatrix}$$

$$|\psi(t)\rangle = \hat{R}^\dagger|\psi_r(t)\rangle = \hat{R}^\dagger\hat{U}_r|\psi_r(t)\rangle$$

$$= \left(\cos\frac{\omega t}{2} - i\hat{\sigma}_z\sin\frac{\omega t}{2}\right)\left(\cos\frac{\omega_r t}{2} + i\frac{\vec{\hat{\sigma}}\cdot\vec{\omega}_r}{|\vec{\omega}_r|}\sin\frac{\omega_r t}{2}\right)\begin{pmatrix}1\\0\end{pmatrix}$$

where $\vec{\omega}_r = -(\omega - B_0\gamma)\vec{e}_z + B\gamma\vec{e}_x$

In matrix form:

$$\begin{pmatrix}\psi_+(t)\\ \psi_-(t)\end{pmatrix} = \begin{pmatrix}e^{\frac{i\omega t}{2}} & 0\\ 0 & e^{-\frac{i\omega t}{2}}\end{pmatrix}\cdot\left[\begin{pmatrix}\cos\frac{\omega_r t}{2} & 0\\ 0 & \cos\frac{\omega_r t}{2}\end{pmatrix} + \frac{-i(\omega - B_0\gamma)}{\omega_r}\begin{pmatrix}\sin\frac{\omega_r t}{2} & 0\\ 0 & -\sin\frac{\omega_r t}{2}\end{pmatrix} + \frac{i\gamma B}{\omega_r}\begin{pmatrix}0 & \sin\frac{\omega_r t}{2}\\ \sin\frac{\omega_r t}{2} & 0\end{pmatrix}\right]\begin{pmatrix}1\\0\end{pmatrix}$$

$$= \begin{pmatrix}\left[\cos\frac{\omega_r t}{2} - i\frac{(\omega - B_0\gamma)}{\omega_r}\sin\frac{\omega_r t}{2}\right]e^{i\omega t/2}\\ \frac{i\gamma B}{\omega_r}\sin\frac{\omega_r t}{2}\, e^{-i\omega t/2}\end{pmatrix}$$

$$\langle\mu_z(t)\rangle = \mu\langle\hat{S}_z(t)\rangle = \frac{\mu\hbar}{2}\langle\hat{\sigma}_z(t)\rangle$$

$$= \left(|\psi_+(t)|^2 - |\psi_-(t)|^2\right)\frac{\mu\hbar}{2} = \cos^2\frac{\omega_r t}{2} + \frac{(\omega - B_0\gamma)^2}{\omega_r^2}\sin^2\frac{\omega_r t}{2} - \left(\frac{\gamma B}{\omega_r}\right)^2\sin^2\frac{\omega_r t}{2}$$

$$= \frac{(\omega - B_0\gamma)^2 + \gamma^2B^2\cos\omega_r t}{(\omega - B_0\gamma)^2 + \gamma^2B^2}\langle\mu_z(t=0)\rangle$$

15.1.1 Derive $S^2 \xrightarrow[\text{Prod. basis}]{} \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix}$

So $S^2 = S_1^2 \otimes \mathbb{1}_2 + \mathbb{1}_1 \otimes S_2^2 + 2\{S_{1x} \otimes S_{2x} + S_{1y} \otimes S_{2y} + S_{1z} \otimes S_{2z}\}$

Now act on the following basis to get columns of S^2 $\Rightarrow \{|++\rangle, |+-\rangle, |-+\rangle, |--\rangle\}$

$S^2|++\rangle = \frac{3}{4}\hbar^2|++\rangle + \frac{3}{4}\hbar^2|++\rangle + \frac{2\hbar^2}{4}\{|--\rangle - \cancel{|--\rangle} + |++\rangle\}$

$= \frac{3}{2}\hbar^2|++\rangle + \frac{\hbar^2}{2}|++\rangle = 2\hbar^2|++\rangle \Rightarrow \hbar^2\begin{pmatrix} 2 \\ 0 \\ 0 \\ 0 \end{pmatrix}$

$S^2|+-\rangle = \frac{3}{4}\hbar^2|+-\rangle + \frac{3}{4}\hbar^2|+-\rangle + \frac{2\hbar^2}{4}\{|-+\rangle + |-+\rangle - |+-\rangle$

$= \frac{3}{2}\hbar^2|+-\rangle - \frac{1}{2}\hbar^2|+-\rangle + \hbar^2|-+\rangle$

$= \hbar^2|+-\rangle + \hbar^2|-+\rangle \Rightarrow \hbar^2\begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix}$

carrying out the same calculation w/ the last two you get

$$S^2 = \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix}$$

15.1.2

$$H_{HF} = A\vec{S}_1\cdot\vec{S}_2 \qquad \vec{S} \equiv \vec{S}_1 + \vec{S}_2$$

$$S^2 = S_1^2 + S_2^2 + 2S_1\cdot S_2$$

$$\vec{S}_1\cdot\vec{S}_2 = \frac{1}{2}\left(S^2 - S_1^2 - S_2^2\right)$$

$$\langle E_{hf}\rangle = \langle A\vec{S}_1\cdot\vec{S}_2\rangle = A\langle\vec{S}_1\cdot\vec{S}_2\rangle$$

$$= \frac{A}{2}\langle S^2 - S_1^2 - S_2^2\rangle$$

$$= \frac{A}{2}\left[\langle S^2\rangle - \langle S_1^2\rangle - \langle S_2^2\rangle\right]$$

But $\langle S_1^2\rangle = \langle S_2^2\rangle = \frac{3}{4}\hbar^2$

And if we are in singlet state

$$\langle S^2\rangle = 0$$

And in triplet state

$$\langle S^2\rangle = 2\hbar^2$$

Thus we have

$$E_T = -13.6\text{eV} + \langle E_{HF}\rangle$$

$$= -13.6\text{eV} + \frac{A\hbar^2}{4} \quad (\text{triplet})$$

$$= -13.6\text{eV} - \frac{A\hbar^2 3}{4} \quad (\text{singlet})$$

② Assume $A = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$

(i) $\sigma_x A + A\sigma_x = 0 \Rightarrow \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a & b \\ c & d \end{pmatrix} + \begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} c & d \\ a & b \end{pmatrix} + \begin{pmatrix} b & a \\ d & c \end{pmatrix}$

$$= \begin{pmatrix} [c+b] & [d+a] \\ [a+d] & [c+b] \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

(ii) $\sigma_y A + A\sigma_y = 0 \Rightarrow \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} a & b \\ c & d \end{pmatrix} + \begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} -ic & -id \\ ia & ib \end{pmatrix} + \begin{pmatrix} ib & -ia \\ id & -ic \end{pmatrix}$

$$= \begin{pmatrix} i(b-c) & -i(a+d) \\ i(a+d) & i(b-c) \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

(iii) $\sigma_z A + A\sigma_z = 0 \Rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} a & b \\ c & d \end{pmatrix} + \begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} a & b \\ -c & -d \end{pmatrix} + \begin{pmatrix} a & -b \\ c & -d \end{pmatrix}$

$$= \begin{pmatrix} 2a & 0 \\ 0 & -2d \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$\Rightarrow$ $a = d = 0$ from (iii)

$$\left.\begin{array}{l} \text{(ii)} \Rightarrow b = c \\ \text{(i)} \Rightarrow b = -c \end{array}\right\} \Rightarrow b = c = 0$$

$$\boxed{\text{Thus } A = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}}$$

(9) Math is done exactly as in lecture. Answers are on p. 667 in Shankar.