

BCMB/CHEM 8190
ANSWERS TO PROBLEM SET 3

1) We worked out the energy levels for the pair of weakly coupled spin 1/2 nuclei in class. Below is a sketch of the predicted spectrum with lines labeled as to transition and energy difference for the one quantum transitions.



$$\frac{\Delta E}{\alpha\beta - \beta\beta} = h\nu_1 + \frac{1}{2} J_{12} h$$

$$\frac{\Delta E}{\alpha\alpha - \beta\alpha} = h\nu_1 - \frac{1}{2} J_{12} h$$

$$\frac{\Delta E}{\beta\alpha - \beta\beta} = h\nu_2 + \frac{1}{2} J_{12} h$$

$$\frac{\Delta E}{\alpha\alpha - \alpha\beta} = h\nu_2 - \frac{1}{2} J_{12} h$$

2)

$$I_{z \text{ tot}} = I_{z1} + I_{z2}$$

$$M_{z \text{ tot}}(\alpha\alpha) = \gamma \hbar \langle \alpha\alpha | I_{z1} + I_{z2} | \alpha\alpha \rangle = \gamma \hbar \left(\frac{1}{2} + \frac{1}{2} \right) = \gamma \hbar$$

$$M_{z \text{ tot}}(\alpha\beta) = \gamma \hbar \langle \alpha\beta | I_{z1} + I_{z2} | \alpha\beta \rangle = \gamma \hbar \left(\frac{1}{2} - \frac{1}{2} \right) = 0$$

$$I_{\text{tot}}^2 = (I_{x1} + I_{x2} + I_{y1} + \dots)(I_{x1} + I_{x2} + I_{y1} + \dots)$$

all cross products will change ψ \therefore only auto terms survive.

$$M_{\text{tot}}^2(\alpha\alpha) = \gamma \hbar \langle \alpha\alpha | I_{x1}I_{x1} + I_{y1}I_{y1} + \dots | \alpha\alpha \rangle = \gamma \hbar \left(\frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} \right) = \frac{3}{2} \gamma \hbar$$

$$M_{\text{tot}}^2(\alpha\beta) = \frac{3}{2} \gamma \hbar$$

$$\overline{M_{z1}} M_{z1}(\alpha\alpha) = \gamma \hbar \langle \alpha\alpha | I_{z1} | \alpha\alpha \rangle = \frac{\gamma \hbar}{2}$$

$$M_{z1}(\alpha\beta) = \gamma \hbar \langle \alpha\beta | I_{z1} | \alpha\beta \rangle = \frac{\gamma \hbar}{2}$$

3)

		<u>ideal - couplings</u>	
	<u>trans</u>	<u>gauche⁻</u>	<u>gauche⁺</u>
${}^3J_{PH'}$	3.0	18.8	3.0
${}^3J_{PH''}$	3.0	3.0	18.8

experimental

$$J_{PH'} = f_t(3.0) + f_{g^+}(3.0) + f_{g^-}(18.8)$$
$$= 6.0$$

$$J_{PH''} = f_t(3.0) + f_{g^+}(18.8) + f_{g^-}(3.0)$$
$$= 8.0$$

$$f_t + f_{g^+} + f_{g^-} = 1$$

$$\Rightarrow f_t = 0.5, f_{g^+} = 0.3, f_{g^-} = 0.2$$