14.E: Nuclear Magnetic Resonance Spectroscopy (Exercises)

These are homework exercises to accompany Chapter 14 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q14.1

Write the equation for a magnetic dipole in the angular momentum form starting from $\mu = \frac{q(\mathbf{r}\ x\ \mathbf{v})}{2}$.

S14.1

μ can be expressed in terms of angular momentum by using the fact $\mathbf{L} = \mathbf{r}\ \text{ x }\mathbf{p}$ and that $\mathbf{p} = m\mathbf{v}$.

By substituting $\mathbf{p} = m\mathbf{v}$ in to $\mathbf{L}$ gives :

$$\mathbf{L} = \mathbf{r}\ \text{ x } m\mathbf{v}$$

by dividing out the m becuse it is a scalar μ becomes:

$$\mu = \frac{q}{2m}\mathrm{L}.$$

Q14.3

Show that the frequency from $\nu_{1\to 3}$ given in Table 14.6 reduces to Equation 14.66 when $J \ll \nu_0(\sigma_1 - \sigma_2)$

S14.35

$$\nu_{1\to 3} = \frac{\nu_0}{2}(2 - \sigma_1 - \sigma_2) - \frac{J}{2} + \frac{1}{2}\left[\nu_0^2(\sigma_1 - \sigma_2)^2 + J^2\right]^{\frac{1}{2}}$$

$$= \frac{\nu_0}{2}(2 - \sigma_1 - \sigma_2) - \frac{J}{2} + \frac{\nu_0(\sigma_1 - \sigma_2)}{2}\left[1 + \frac{J^2}{\nu_0^2(\sigma_1 - \sigma_2)^2}\right]^{\frac{1}{2}}$$

Since $J \ll \nu_0(\sigma_1 - \sigma_2)$, we can use a Taylor expansion and keeping only the terms that are linear in J gives

$$\frac{\nu_0}{2}(2 - \sigma_1 - \sigma_2) - \frac{J}{2} + \frac{\nu_0(\sigma_1 - \sigma_2)}{2} - O(J^2)$$

$$= \nu_0(1 - \sigma_2) - \frac{J}{2}$$

Q14.18

Nuclear spin operators I_x, I_y, I_z all obey the commutation relations, that

$$[I_x, I_y] = ihI_z$$

$$[I_y, I_z] = ihI_x$$

$$[I_z, I_x] = ihI_y$$

Show that

$$I_zI_+ = I_+I_z + hI_+ \qquad and \qquad I_zI_- = I_-I_z - hI_-$$

S14.18

We know that the commutation relations are as follows:

$$I_xI_y - I_yI_x = ihI_z$$

$$I_yI_z - I_zI_y = ihI_x$$

$$I_zI_x - I_xI_z = ihI_y$$

Therefore,

$$I_zI_+ = I_z(I_x + iI_y) = ihI_y + I_xI_z + iI_zI_y = ihI_y + I_xI_z + i(I_yI_z - ihI_x) = I_xI_z + iI_yI_z + hI_x + ihI_y = I_+I_z + hI_+$$

and

$$I_zI_- = I_z(I_x - iI_y) = ihI_y + I_xI_z - iI_zI_y = ihI_y + I_xI_z - i(I_yI_z - ihI_x) = I_xI_z - iI_yI_z - hI_x + ihI_y = I_-I_z - hI_-$$

Q14.19

Given:

$$\hat{I}_+\hat{I}_- = \hat{I}_x^2 + i\hat{I}_x\hat{I}_y - i\hat{I}_x\hat{I}_y + \hat{I}_y^2$$

and

$$\hat{I}^2 = \hat{I}_x^2 + \hat{I}_y^2 + \hat{I}_z^2$$

Show:

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

and

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

S14.19

$\hat{I}^2 - \hat{I}_z^2 = \hat{I}_x^2 + \hat{I}_y^2$, so

$$\begin{aligned}\hat{I}_+\hat{I}_- &= \hat{I}^2 - \hat{I}_z^2 + i\hat{I}_y\hat{I}_x - i\hat{I}_x\hat{I}_y \\ &= \hat{I}^2 - \hat{I}_z^2 - i(i\hbar\hat{I}_z) \\ &= \hat{I}^2 - \hat{I}_z^2 + \hbar\hat{I}_z\end{aligned}$$

and

$$\begin{aligned}\hat{I}_-\hat{I}_+ &= \hat{I}_x^2 + \hat{I}_y^2 + i\hat{I}_x\hat{I}_y - i\hat{I}_y\hat{I}_x \\ &= \hat{I}^2 - \hat{I}_z^2 + i(i\hbar\hat{I}_z) \\ &= \hat{I}^2 - \hat{I}_z^2 - \hbar\hat{I}_z\end{aligned}$$

Q14.20

Using

$$\hat{I}_z\hat{I}_+ = \hat{I}_+\hat{I}_z + \hbar\hat{I}_+$$

$$\hat{I}_z\beta = -\frac{\hbar}{2}\beta$$

$$\hat{I}_+\beta = \hbar\alpha$$

and $c = \hbar$,
derive $\hat{I}_x\alpha$, $\hat{I}_y\alpha$, $\hat{I}_x\beta$, and $\hat{I}_y\beta$ in terms of $\alpha, \beta, \hbar$.

S14.20

We know

$$\hat{I}_+ = \hat{I}_x + i\hat{I}_y \text{ and } \hat{I}_- = \hat{I}_x - i\hat{I}_y$$

So we can show that

$$\hat{I}_{+}\alpha = \hat{I}_{x}\alpha + i\hat{I}_{y}\alpha = 0 \text{ and } \hat{I}_{-}\alpha = \hat{I}_{x}\alpha - i\hat{I}_{y}\alpha = \hbar\beta$$

by adding the equations we can show that

$$\hat{I}_{x}\alpha = \frac{\hbar}{2}\beta \text{ and } \hat{I}_{y}\alpha = \frac{i\hbar}{2}\beta$$

if we apply the same methodology as above but with \(\beta)\ we can see that

$$\hat{I}_{x}\beta = \frac{\hbar}{2}\alpha \text{ and } \hat{I}_{y}\beta = \frac{i\hbar}{2}\alpha$$

Q14.21

This problem shows that the proportionality constant c in

$$\hat{I}_{+}\beta = c\alpha \; or \; \hat{I}_{-}\alpha = c\beta$$

is equal to $\hbar$. Start with

$$\int \alpha^{*}\alpha d\tau = 1 = \frac{1}{c^{2}}\int (\hat{I}_{+}\beta)^{*}(\hat{I}_{+}\beta)d\tau$$

Let $\hat{I}_{+} = \hat{I}_{x} + i\hat{I}_{y}$ in the second factor in the above integral and use the fact that $\hat{I}_{x}$ and $\hat{I}_{y}$ are Hermitian to get

$$\int (\hat{I}_{x}\hat{I}_{+}\beta)^{*}\beta d\tau + i\int (\hat{I}_{y}\hat{I}_{+}\beta)^{*}\beta d\tau = c^{2}$$

Now take the complex conjugate of both sides to get

$$\int \beta^{*}\hat{I}_{x}\hat{I}_{+}\beta d\tau - i\int \beta^{*}\hat{I}_{y}\hat{I}_{+}\beta d\tau = c^{2} = \int \beta^{*}\hat{I}_{-}\hat{I}_{+}\beta d\tau$$

Using the given equation:

$$\hat{I}_{-}\hat{I}_{+} = \hat{I}^{2} - \hat{I}_{z}^{2} - \hbar\hat{I}_{z}$$

Show that:

$$c^{2} = \int \beta^{*}\hat{I}_{-}\hat{I}_{+}\beta d\tau = \int \beta^{*}(\hat{I}^{2} - \hat{I}_{z}^{2} - \hbar\hat{I}_{z})\beta d\tau = \int \beta^{*}\left(\frac{3}{4}\hbar^{2} - \frac{1}{4}\hbar^{2} + \frac{\hbar^{2}}{2}\right)\beta d\tau = \hbar^{2}$$

or that $c = \hbar$

S14.21

Recall that for a Hermitian operator $\hat{A}$,

$$\int f^{*}(x)\hat{A}g(x)dx = \int g(x)\hat{A}^{*}f^{*}(x)dx$$

Begin with the expression

$$\int \alpha^{*}\alpha d\tau = 1 = \frac{1}{c^{2}}\int (\hat{I}_{+}\beta)^{*}(\hat{I}_{+}\beta)d\tau$$

Solving for c^{2} gives

$$c^{2} = \int (\hat{I}_{+}\beta)^{*}(\hat{I}_{+}\beta)d\tau = \int (\hat{I}_{+}\beta)^{*}(\hat{I}_{x}\beta + i\hat{I}_{y}\beta)d\tau = \int (\hat{I}_{+}\beta)^{*}(\hat{I}_{+}\beta d\tau + i\int (\hat{I}_{+}\beta)^{*}\hat{I}_{y}\beta d\tau$$

We can use the fact that $\hat{I}_{x}$ and $\hat{I}_{y}$ are Hermitian to write this as

$$c^{2} = \int \beta\hat{I}_{+}^{*}(\hat{I}_{+}\beta)^{*}d\tau + i\int \beta\hat{I}_{y}^{*}(\hat{I}_{+}\beta)^{*}d\tau$$

Take the complex conjugate of both sides of the last equation to find

$$c^2 = \int \beta^* \hat{I}_x \hat{I}_+ \beta d\tau - i \int \beta^* \hat{I}_y \hat{I}_+ \beta d\tau = \int \beta^* (\hat{I}_x - i\hat{I}_y) \hat{I}_+ \beta d\tau = \int \beta^* \hat{I}_- \hat{I}_+ \beta d\tau$$

Substituting $\hat{I}_- \hat{I}_+ = \hat{I}^2 - \hat{I}_z^2 - \hbar \hat{I}_z$, we obtain

$$c^2 = \int \beta^* \hat{I}_- \hat{I}_+ \beta d\tau = \int \beta^* (\hat{I}^2 - \hat{I}_z^2 - \hbar \hat{I}_z) \beta d\tau = \int \beta^* \left(\frac{3\hbar^2}{4} - \frac{1\hbar^2}{4} + \frac{\hbar^2}{2} \right) \beta d\tau = \hbar^2$$

where we have used the given equation to evaluate the various terms involving $\hat{I}^2$ and $\hat{I}_z$.

Taking the squareroot of both sides of the final equation proves that $c = \hbar$.

Q14.22

Show that $H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha *(1) \alpha*(2) \hat{I}_{y1} \hat{I}_{y2} \alpha(1) \alpha(2) = 0$.

S14.22

$$H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \hat{I}_{y1} \hat{I}_{y2} \alpha(1) \alpha(2)$$

$$H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) [\hat{I}_{y1} \alpha(1)] [\hat{I}_{y2} \alpha(2)]$$

$$H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \left[\frac{i\bar{h}}{2} \beta(1) \right] \left[\frac{i\bar{h}}{2} \beta(2) \right]$$

$$= -\frac{hJ_{12}}{4} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \beta(1) \beta(2) = 0$$

Orthogonality of spin functions is used so that the equation equates to zero.

Q14-23 Nice work! Correct

The energy levels of a two-spin system can be calculated using first-order perturbation theory. Show this for the first energy level.

S14-23

$$E_j = E_j^{(0)} + \int d\tau_1 d\tau_2 \psi_j^* H^{(1)} \psi_j \tag{14.E.1}$$

$$H^{(0)} \psi_j = E_j^{(0)} \psi_j \tag{14.E.2}$$

$$E_j = E_j^{(0)} + H_{xjj}^{(1)} + H_{yjj}^{(1)} + H_{zjj}^{(1)} \tag{14.E.3}$$

The unperturbed first-order energy is calculated using

$$I_{zj} \alpha(j) = \frac{\hbar}{2} \alpha(j) \tag{14.E.4}$$

$$H^{(0)} \psi_1 = H^{(0)} \alpha(1) \alpha(2) \tag{14.E.5}$$

$$= -\gamma B_0 (1 - \sigma_1) I_{z1} \alpha(1) \alpha(2) - \gamma B_0 (1 - \sigma_2) I_{z2} \alpha(1) \alpha(2) \tag{14.E.6}$$

$$E_1^{(0)} \alpha(1) \alpha(2) = E_1^{(0)} \psi_1 \tag{14.E.7}$$

$$E_1^{(0)} = -\hbar \gamma B_0 (1 - \frac{\sigma_1 + \sigma_2}{2}) \tag{14.E.8}$$

The first-order correction is defined as

$$H_{ii} = \frac{hJ_{12}}{\hbar^2} \int d\tau_1 d\tau_2 \psi_i^* I_1 I_2 \psi_i \tag{14.E.9}$$

with the x and y terms in I1 and I2 not contributing to the first-order energy.

Considering the unperturbed wave function for a two-spin system

$$\psi_1 = \alpha(1)\alpha(2) \tag{14.E.10}$$

$$I_{z1}I_{z2}\alpha(1)\alpha(2) = \frac{\hbar^2}{4}\alpha(1)\alpha(2) \tag{14.E.11}$$

Furthermore, the perturbation to the first-order energy becomes

$$H_{z,11} = \frac{hJ_{12}}{\hbar^2}\int d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2)I_{z1}I_{z2}\alpha(1)\alpha(2) = \frac{hJ_{12}}{4} \tag{14.E.12}$$

As a result the first order energy energy can be represented by

$$E_1 = -h\nu_0(1-\frac{\sigma_1+\sigma_2}{2}) + \frac{hJ_{12}}{4} \tag{14.E.13}$$

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Q14.24

Derive the frequencies associated with the allowed transitions between nuclear spin up to n = 4.

S14.24

(its good that you started from the beginning to derive the frequencies good job--RM)

$$E = h\nu \tag{14.E.14}$$

$$E_{1=>2} = E_2 - E_1 \tag{14.E.15}$$

$$= \frac{h\nu}{2}(\sigma_2-\sigma_1) - \frac{hJ_{12}}{4} + h\nu_0(1-\frac{\sigma_1+\sigma_2}{2}) - \frac{hJ_{12}}{4} \tag{14.E.16}$$

$$= h\nu_0(1-\sigma_1) - \frac{hJ_{12}}{2} \tag{14.E.17}$$

$$\nu_{1=>2} = \nu_0(1-\sigma_1) - \frac{hJ_{12}}{2} \tag{14.E.18}$$

$$E_{1=>3} = E_3 - E_1 \tag{14.E.19}$$

$$= \frac{h\nu}{2}(\sigma_1-\sigma_2) - \frac{hJ_{12}}{4} + h\nu_0(1-\frac{\sigma_1+\sigma_2}{2}) - \frac{hJ_{12}}{4} \tag{14.E.20}$$

$$= h\nu_0(1-\sigma_3) - \frac{hJ_{12}}{2} \tag{14.E.21}$$

$$\nu_{1=>3} = \nu_0(1-\sigma_2) - \frac{hJ_{12}}{2} \tag{14.E.22}$$

$$E_{2=>4} = E_4 - E_2 \tag{14.E.23}$$

$$= h\nu(\sigma_1+\sigma_2) - \frac{hJ_{12}}{4} - \frac{h\nu_0}{2}(\sigma_2-\sigma_1) + \frac{hJ_{12}}{4} \tag{14.E.24}$$

$$= h\nu_0(1-\sigma_2) + \frac{hJ_{12}}{2} \tag{14.E.25}$$

$$\nu_{2=>4} = \nu_0(1-\sigma_2) + \frac{hJ_{12}}{2} \tag{14.E.26}$$

$$E_{3=>4} = E_4 - E_3 \tag{14.E.27}$$

$$= h\nu(1-\frac{\sigma_1+\sigma_2}{2}) + \frac{hJ_{12}}{4} - \frac{h\nu_0}{2}(\sigma_1-\sigma_2) + \frac{hJ_{12}}{4} \tag{14.E.28}$$

$$= h\nu_0(1-\sigma_1) + \frac{hJ_{12}}{2} \tag{14.E.29}$$

$$\nu_{2=>4} = \nu_0(1-\sigma_1) + \frac{hJ_{12}}{2} \tag{14.E.30}$$

Q14.28

Using the Hamiltonian for an H_2 molecule with 2 nonequivalent hydrogen atoms, prove that $H_{13} = \iint d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2)\hat{H}\beta(1)\alpha(2) = 0$.

S14.28

The necessary Hamiltonian is:

$$\hat{H} = -\gamma B_0(1-\sigma_1)\hat{I}_1 - \gamma B_0(1-\sigma_2)\hat{I}_2 + \frac{hJ_{12}}{\hbar^2}\hat{I}_1 \cdot \hat{I}_2.$$

We can then plug in the Hamiltonian and write the second half of the equation as:

$$\begin{aligned}\hat{H}\beta(1)\beta(2) &= -\gamma B_0(1-\sigma_1)(-\frac{\hbar}{2})\beta(1)\alpha(2) - \gamma\beta_0(1-\sigma_2)(\frac{\hbar}{2})\beta(1)\beta(2) \\ &+ \frac{hJ_{23}}{\hbar^2}[\frac{\hbar^2}{4}\alpha(1)\beta(2) + \frac{h^2}{4}\alpha(1)\beta(2) - \frac{\hbar^2}{4}\beta(1)\alpha(2)] \\ &= \frac{\hbar}{2}\gamma B_0\beta(1)\alpha(2)[(1-\sigma_1)-(1-\sigma_2)] + \frac{hJ_{12}}{4}[2\alpha(1)\beta(2) - \beta(1)\alpha(2)]\end{aligned}$$

Doing some algebra, we get that:

$$H_{13} = \iint d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2)\left[\frac{\hbar}{2}\gamma B_0\beta(1)\alpha(2)[(1-\sigma_1)-(1-\sigma_2)] + \frac{hJ_{12}}{4}[2\alpha(1)\beta(2)-\beta(1)\alpha(2)]\right]$$

Because α and β are orthonormal, **the integral goes to zero**. Therefore, we have proved that $H_{13} = 0$.

Q14.29

Prove that

$$\begin{aligned}H_{44} &= \iint d\tau_(1)d\tau_(2)\beta^*(1)\beta^*(2)\hat{H}\beta(1)\beta(2) \\ &= -\frac{1}{2}h\nu_0(1-\sigma_1) - \frac{1}{2}h\nu_0(1-\sigma_2) + \frac{hJ_12}{4}\end{aligned}$$

with

$$\hat{H} = -\gamma B_0(1-\sigma_1)\hat{I}_1 - \gamma B_0(1-\sigma_2)\hat{I}_2 + \frac{hJ_{12}}{\hbar^2}\hat{I}_1 \cdot \hat{I}_2.$$

S14.29

$$\begin{aligned}\hat{H}\beta(1)\beta(2) &= -\gamma B_0(1-\sigma_1)(\frac{\hbar}{2})\beta(1)\beta(2) - \gamma\beta_0(1-\sigma_2)(\frac{\hbar}{2})\beta(1)\beta(2) \\ &+ \frac{hJ_{12}}{\hbar^2}[\frac{\hbar^2}{4}\beta(1)\beta(2) - \frac{h^2}{4}\beta(1)\beta(2) + \frac{\hbar^2}{4}\alpha(1)\alpha(2)] \\ &= \left[\frac{-\hbar\gamma B_0}{2}(1-\sigma_1) - \frac{-\hbar\gamma B_0}{2}(1-\sigma_2) + \frac{hJ_{12}}{4}][2\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\beta(1)\beta(2)\end{aligned}$$

Calculated with matlab,

$$\begin{aligned}H_{44} &= \iint d\tau_1 d\tau_2 \left[\frac{-\hbar\gamma B_0}{2}(1-\sigma_1) - \frac{-\hbar\gamma B_0}{2}(1-\sigma_2) + \frac{hJ_{12}}{4}][2\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\beta(1)\beta(2) \\ &= \frac{1}{2}h\nu_0(1-sigma_1) - \frac{1}{2}h\nu_0(1-\sigma_2) + h\frac{J_{12}}{4}\end{aligned}$$

Q14.30

Using Equation 14.58, prove that

$$H_{44} = -\frac{1}{2}hv_0(1-\sigma_1) + \frac{1}{2}h_v0(1-\sigma_2) + \frac{hJ_{12}}{4}$$

S14.30

To find this matrix element, you must complete the integral given by $\langle\psi_4|H|\psi_4\rangle$. By using the relationships in Table 14.4 to evaluate parts of the integral, Equation 14.45 and Equation 14.58, algebra, and calculus, this integral can be solved to give the final answer above.

Q14.31

Given the following matrix, expand the determinants to solve for the energies:

$$\begin{pmatrix} \alpha-E & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha-E \end{pmatrix}$$

S14.31

\[x_{i} = \frac{\alpha E}{\beta}\nonumber \]

$$E_j = \alpha - \beta x_j$$

$$x_j = -2cos(\frac{j\pi}{n_c+1})$$

$$E_j = \alpha + 2\beta * cos(\frac{j\pi}{n_c}+1)$$

$$E_1 = \alpha + 2\beta * cos(\frac{\pi}{6+1}) = \alpha + 1.8\beta$$

$$E_2 = \alpha + 2\beta * cos(\frac{2\pi}{6+1}) = \alpha + 1.24\beta$$

$$E_3 = \alpha + 2\beta * cos(\frac{3\pi}{6+1}) = \alpha + 0.44\beta$$

$$E_4 = \alpha + 2\beta * cos(\frac{4\pi}{6+1}) = \alpha - 0.44\beta$$

$$E_5 = \alpha + 2\beta * cos(\frac{5\pi}{6+1}) = a - 1.25\beta$$

$$E_6 = \alpha + 2\beta * cos(\frac{6\pi}{6+1}) = \alpha - 1.8\beta$$

Q14.33

Show that a two-spin system with $J = 0$ consists of only two peaks with frequencies $v_0(1-\sigma_1)$ and $v_0(1-\sigma_2)$.

S14.33

The resonance frequencies is given by

$v_1 \rightarrow_2$ = $\frac{v_0}{2}$ $(2-\sigma_1-\sigma_2)$ - $\frac{J}{2}$-$\frac{1}{2}$ $[v_0^2(\sigma_1-\sigma_2)^2 + J^2]^{\frac{1}{2}}$

with J = 0, this leads to

$v_1 \rightarrow_2$ = $\frac{v_0}{2}$ $(2-\sigma_1-\sigma_2)$ - $\frac{0}{2}$-$\frac{1}{2}$ $[v_0^2(\sigma_1-\sigma_2)^2 + 0^2]^{\frac{1}{2}}$

$$= \frac{v_0}{2}\ (2-\sigma_1-\sigma_2\ )\ \text{-}\frac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2]^{\frac{1}{2}}$$
$$= v_0(1-\sigma_1\ )$$

Similarly, for the other transitions:

$$v_1 \rightarrow_3\ =\ \frac{v_0}{2}\ (2-\sigma_1-\sigma_2\ )\ \text{-}\ \frac{J}{2}+\frac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2+J^2]^{\frac{1}{2}}$$
$$= \frac{v_0}{2}\ (2-\sigma_1-\sigma_2\ )\ \text{-}\ \frac{0}{2}+\frac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2+0^2]^{\frac{1}{2}}$$
$$= \frac{v_0}{2}\ (2-\sigma_1-\sigma_2\ )+\frac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2]^{\frac{1}{2}}$$
$$= v_0(1-\sigma_2\ )$$

$$v_2 \rightarrow_4\ =\ \frac{v_0}{2}\ (2-\sigma_1-\sigma_2\ )\ +\ \frac{J}{2}+\frac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2+J^2]^{\frac{1}{2}}$$
$$= \frac{v_0}{2}\ (2-\sigma_1-\sigma_2\ )\ +\ \frac{0}{2}+\frac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2+0^2]^{\frac{1}{2}}$$
$$= \frac{v_0}{2}\ (2-\sigma_1-\sigma_2\ )+\frac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2]^{\frac{1}{2}}$$
$$= v_0(1-\sigma_2\ )$$

$$v_3 \rightarrow_4\ =\ \frac{v_0}{2}\ (2-\sigma_1-\sigma_2\ )\ +\ \frac{J}{2}\text{-}\frac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2+J^2]^{\frac{1}{2}}$$
$$= \frac{v_0}{2}\ (2-\sigma_1-\sigma_2\ )\ +\ \frac{0}{2}\text{-}\frac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2+0^2]^{\frac{1}{2}}$$
$$= \frac{v_0}{2}\ (2-\sigma_1-\sigma_2\ )\ \text{-}\frac{1}{2}\ [v_0^2(\sigma_1-\sigma_2)^2]^{\frac{1}{2}}$$
$$= v_0(1-\sigma_1\ )$$

Q14.34

Show that

$$\nu_{2\to 4} = \frac{\nu_0}{2}(2-\sigma_1-\sigma_2)+\frac{J}{2})+\frac{1}{2}[\nu_0^2()\sigma_1-\sigma_2)^2+J^2]^{1/2}$$

for a general two-spin system.

S14.34

$$E_4-E_2 = [h\nu_0(1-\frac{\sigma_1+\sigma_2}{2})+\frac{hJ}{4}]-[-\frac{hJ}{4}-\frac{h}{2}[\nu_0^2(\sigma_1-\sigma_2)^2+J^2]^{1/2}]$$
$$= h\nu_0(1-\frac{\sigma_1+\sigma_2}{2})+\frac{hJ}{2}-\frac{h}{2}[\nu_0^2(\sigma_1-\sigma_2)^2+J^2]^{1/2}$$
$$\frac{E_4-E_2}{2} = \frac{\nu_0}{2}(2-\sigma_1-\sigma_2)+\frac{J}{2})+\frac{1}{2}[\nu_0^2()\sigma_1-\sigma_2)^2+J^2]^{1/2}$$