Answers to the Problems in Chapter 9

Problem 9.1.

We recall that $$\hat{I}_{x} = \sum_{r}\hat{I}_{rx} = \frac{1}{2}\sum_{r}(\hat{I}_{r+} + \hat{I}_{r-})$$

Therefore,

$$\left\langle \Psi_{S}\middle|\hat{I}_{x}\middle|\Psi_{T}\right\rangle = \frac{1}{2}\sum_{r}\left\langle \Psi_{S}\middle|(\hat{I}_{r+} + \hat{I}_{r-})\middle|\Psi_{T}\right\rangle$$

Taking the triplet |+½ +½> as our example we have:

$$\frac{1}{2}\sum_{r}\left\langle \Psi_{S}\middle|(\hat{I}_{r+} + \hat{I}_{r-})\middle|\Psi_{T}\right\rangle$$

$$= \frac{1}{2\sqrt{2}}\sum_{r=1,2}\left\langle\left\langle +\frac{1}{2} -\frac{1}{2}\right| - \left\langle -\frac{1}{2} +\frac{1}{2}\right|\right|(\hat{I}_{r+} + \hat{I}_{r-})\left|+\frac{1}{2} +\frac{1}{2}\right\rangle$$

Because <+½|–½> = <–½|+½> = 0, the four possible contributions reduce to:

$$= \frac{1}{2\sqrt{2}}\left\{\left\langle +\frac{1}{2}\middle| +\frac{1}{2}\right\rangle\left\langle -\frac{1}{2}\middle|\hat{I}_{2+} + \hat{I}_{2-}\middle| +\frac{1}{2}\right\rangle - \left\langle +\frac{1}{2}\middle| +\frac{1}{2}\right\rangle\left\langle -\frac{1}{2}\middle|\hat{I}_{1+} + \hat{I}_{1-}\middle| +\frac{1}{2}\right\rangle\right\}$$

$$= \frac{1}{2\sqrt{2}}\left\{\left\langle +\frac{1}{2}\middle| +\frac{1}{2}\right\rangle\left\langle -\frac{1}{2}\middle|\hat{I}_{2-}\middle| +\frac{1}{2}\right\rangle - \left\langle -\frac{1}{2}\middle|\hat{I}_{1-}\middle| +\frac{1}{2}\right\rangle\left\langle +\frac{1}{2}\middle| +\frac{1}{2}\right\rangle\right\}$$

$$= \frac{1}{2\sqrt{2}}\left\{\left\langle +\frac{1}{2}\middle| +\frac{1}{2}\right\rangle\left\langle -\frac{1}{2}\middle| -\frac{1}{2}\right\rangle - \left\langle -\frac{1}{2}\middle| -\frac{1}{2}\right\rangle\left\langle +\frac{1}{2}\middle| +\frac{1}{2}\right\rangle\right\} = 0$$

Problem 9.2.

The only terms in the Hamiltonian, Equation 9.6.1, which can give rise to off-diagonal matrix elements are those which link two different basis states, i.e. only terms arising from the operator

$$\sum_{r<s} J_{rs}\mathbf{I}_r \cdot \mathbf{I}_s = \sum_{r<s} J_{rs}\{\hat{I}_{rz}\hat{I}_{sz} + \frac{1}{2}(\hat{I}_{r+}\hat{I}_{s-} + \hat{I}_{r-}\hat{I}_{s+})\}$$

The term in $\hat{I}_{rz}\hat{I}_{sz}$ does not change the m_I value of any component of a spin state and therefore never changes the sum total of m_I values.

Suppose we have a general matrix element of the form

$$<m_{Ia}, m_{Ib} \ldots m_{Ir}, \ldots m_{Is}, \ldots m_{Iz}| \hat{I}_{r+}\hat{I}_{s-} |m_{Ia}, m_{Ib} \ldots m'_{Ir}, \ldots m'_{Is}, \ldots m_{Iz}>$$

where the m_I values for nuclei r and s in the bra are not the same as those in the ket. All the others must be the same for a non-zero result, because we have:

$$<m_{Ia}|m_{Ia}><m_{Ib}|m_{Ib}>\ldots<m_{Ir}, m_{Is}| \hat{I}_{r+}\hat{I}_{s-} |m'_{Ir}\ m'_{Is}>\ldots<m_{Iz}|m_{Iz}>$$

$$= <m_{Ia}|m_{Ia}><m_{Ib}|m_{Ib}>\ldots<m_{Ir}, m_{Is}|(m'_I+1)_r,(m'_I-1)_s>\ldots<m_{Iz}|m_{Iz}>$$

because the raising and lowering operators always take the spin up or down one unit of m_I. (Unless, of course, they annihilate the spin function).

If the integral over the two spin functions above is to be non-zero we must have:

$$m_{Ir} = (m'_I+1)_r, \text{ and } m_{Is} = (m'_I-1)_s$$

So that $m_{Ir} + m_{Is} = m'_{Ir} + 1 + m'_{Is} - 1 = m'_{Ir} + m'_{Is}$ and the sums of m_I values in the bra and the ket are equal.

Problem 9.3.

We have to diagonalise the matrix

$$\begin{matrix} -\tfrac{1}{2}\delta\nu - \tfrac{1}{4}J & +\tfrac{1}{2}J \\ +\tfrac{1}{2}J & +\tfrac{1}{2}\delta\nu - \tfrac{1}{4}J \end{matrix}$$

where $\delta\nu = \nu_a - \nu_b$ and $J = J_{ab}$.

Using Appendix 3 we find

$$\Sigma = \tfrac{1}{2}\{-\tfrac{1}{2}\delta\nu - \tfrac{1}{4}J + \tfrac{1}{2}\delta\nu - \tfrac{1}{4}J\} = -\tfrac{1}{4}J$$

$$\Delta = \tfrac{1}{2}\{-\tfrac{1}{2}\delta\nu - \tfrac{1}{4}J - \tfrac{1}{2}\delta\nu + \tfrac{1}{4}J\} = -\tfrac{1}{2}\delta\nu$$

$$\Omega = \tfrac{1}{2}\{\tfrac{1}{4}\delta\nu^2 + \tfrac{1}{4}J^2\}^{\frac{1}{2}} = +\tfrac{1}{2}\{\delta\nu^2 + J^2\}^{\frac{1}{2}}$$

Therefore

$$E_1 = \Sigma + \Omega = -\tfrac{1}{4}J + \tfrac{1}{2}\{\delta\nu^2 + J^2\}^{\frac{1}{2}} = \tfrac{1}{2}\{[\nu_a - \nu_b]^2 + J^2\}^{\frac{1}{2}} - \tfrac{1}{4}J$$

$$= +\tfrac{1}{2}D - \tfrac{1}{4}J$$

$$E_2 = \Sigma - \Omega = -\tfrac{1}{4}J - \tfrac{1}{2}\{\delta\nu^2 + J^2\}^{\frac{1}{2}} = -\tfrac{1}{2}\{[\nu_a - \nu_b]^2 + J^2\}^{\frac{1}{2}} - \tfrac{1}{4}J$$

$$= -\tfrac{1}{2}D - \tfrac{1}{4}J$$

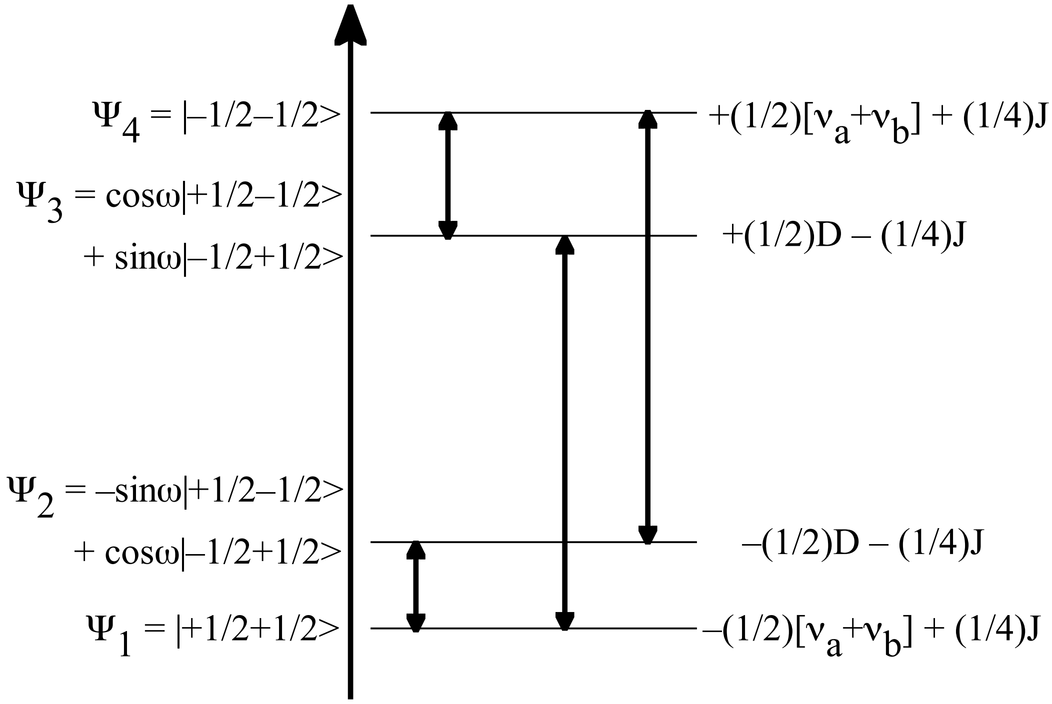
Where $D = \{[\nu_a - \nu_b]^2 + J^2\}^{\frac{1}{2}}$.

The coefficients, $\sin\omega$ and $\cos\omega$, and the wave functions are obtained by direct substitution into the formulae of Appendix 3.

$$\cos\omega = \left\{\frac{\Omega + \Delta}{2\Omega}\right\}^{\frac{1}{2}} = \left[\frac{\frac{1}{2}\left\{(\nu_a - \nu_b)^2 + J^2\right\}^{\frac{1}{2}} - \frac{1}{2}(\nu_a - \nu_b)}{\left\{(\nu_a - \nu_b)^2 + J^2\right\}^{\frac{1}{2}}}\right]^{\frac{1}{2}}$$

$$\sin\omega = \left\{\frac{\Omega - \Delta}{2\Omega}\right\}^{\frac{1}{2}} = \left[\frac{\frac{1}{2}\left\{(\nu_a - \nu_b)^2 + J^2\right\}^{\frac{1}{2}} - \frac{1}{2}(\nu_a - \nu_b)}{\left\{(\nu_a - \nu_b)^2 + J^2\right\}^{\frac{1}{2}}}\right]^{\frac{1}{2}}$$

The energy level diagram is given below for $\nu_a > \nu_b$. Since the spin of only one proton can be changed in a transition, the possible transitions are: $\Psi_1 \leftrightarrow \Psi_2$, $\Psi_1 \leftrightarrow \Psi_3$, $\Psi_4 \leftrightarrow \Psi_2$ and $\Psi_4 \leftrightarrow \Psi_3$.



The energies of the transitions are simply the differences in the eigenvalues, e.g.

$$\Delta E_{12} = -\tfrac{1}{2}D - \tfrac{1}{4}J + \tfrac{1}{2}[\nu_a + \nu_b] - \tfrac{1}{4}J = -\tfrac{1}{2}D - \tfrac{1}{2}J + \tfrac{1}{2}[\nu_a + \nu_b]$$

The intensities are calculated as follows:

$$\left|\left\langle \Psi_1 \middle| \hat{I}_x \middle| \Psi_2 \right\rangle\right|^2 = \left|\left\langle +\frac{1}{2} + \frac{1}{2}\middle| \frac{1}{2}(\hat{I}_+ + \hat{I}_-) \middle| -\sin\omega\,| +\frac{1}{2} - \frac{1}{2} > + \cos\omega\,| -\frac{1}{2} + \frac{1}{2} > \right\rangle\right|^2$$

$$\hat{I}_+ |+\frac{1}{2}-\frac{1}{2}> \;=\; \hat{I}_{a+} |+\frac{1}{2}-\frac{1}{2}> + \hat{I}_{b+} |+\frac{1}{2}-\frac{1}{2}> \;=\; 0 + |+\frac{1}{2}+\frac{1}{2}>$$

$$\hat{I}_- |+\frac{1}{2}-\frac{1}{2}> \;=\; \hat{I}_{a-} |+\frac{1}{2}-\frac{1}{2}> + \hat{I}_{b-} |+\frac{1}{2}-\frac{1}{2}> \;=\; |-\frac{1}{2}-\frac{1}{2}> + 0$$

$$\hat{I}_+ |-\frac{1}{2}+\frac{1}{2}> \;=\; \hat{I}_{a+} |-\frac{1}{2}+\frac{1}{2}> + \hat{I}_{b+} |-\frac{1}{2}+\frac{1}{2}> \;=\; |+\frac{1}{2}+\frac{1}{2}> + 0$$

$$\hat{I}_- |-\frac{1}{2}+\frac{1}{2}> \;=\; \hat{I}_{a-} |-\frac{1}{2}+\frac{1}{2}> + \hat{I}_{b-} |-\frac{1}{2}+\frac{1}{2}> \;=\; 0 + |-\frac{1}{2}-\frac{1}{2}>$$

Therefore,

$$\left\langle\Psi_1\middle|\hat{I}_x\middle|\Psi_2\right\rangle = \frac{1}{2}\{< +\frac{1}{2}+\frac{1}{2}|-\sin\omega|+\frac{1}{2}+\frac{1}{2}> + \frac{1}{2} < +\frac{1}{2}+\frac{1}{2}|-\sin\omega|-\frac{1}{2}-\frac{1}{2}>$$

$$+ < +\frac{1}{2}+\frac{1}{2}|\cos\omega|+\frac{1}{2}+\frac{1}{2}> + \frac{1}{2} < +\frac{1}{2}+\frac{1}{2}|\cos\omega|-\frac{1}{2}-\frac{1}{2}>\}$$

$$= \frac{1}{2}\{-\sin\omega + 0 + \cos\omega + 0\} = \frac{1}{2}\{\cos\omega - \sin\omega\}$$

Therefore,

$$\left|\left\langle\Psi_1\middle|\hat{I}_x\middle|\Psi_2\right\rangle\right|^2 = \frac{1}{4}\{\cos\omega - \sin\omega\}^2 = \frac{1}{4}\{1 - \sin 2\omega\}$$

Problem 9.4.

The Hamiltonian is:

$$h^{-1}\hat{H} = -\nu_H\hat{I}_{Hz} - \nu_N\hat{I}_{Nz} + J_{HN}\{\hat{I}_{Hz}\hat{I}_{Nz} + \tfrac{1}{2}(\hat{I}_{H+}\hat{I}_{N-} + \hat{I}_{H-}\hat{I}_{N+})\}$$

If we write the spin states in the form $|m_I(\mathrm{H}), m_I(\mathrm{N})>$ the energy matrix is:

$\hat{H}$	$\|-½,-1>$	$\|+½,-1>$	$\|-½,0>$	$\|+½,0>$	$\|-½,+1>$	$\|+½,+1>$
$<-½,-1\|$	$+½\nu_H+\nu_N$ $+½J$	0	0	0	0	0
$<+½,-1\|$	0	$-½\nu_H+\nu_N$ $-½J$	$\sqrt{2}J$	0	0	0
$<-½,0\|$	0	$\sqrt{2}J$	$+½\nu_H$	0	0	0
$<+½,0\|$	0	0	0	$-½\nu_H$	$\sqrt{2}J$	0
$<-½,+1\|$	0	0	0	$\sqrt{2}J$	$+½\nu_H-\nu_N$ $-½J$	0
$<+½,+1\|$	0	0	0	0	0	$-½\nu_H-\nu_N$ $+½J$

The first order energy levels are obtained by taking the diagonal elements of the matrix, neglecting the off-diagonal elements of $\sqrt{2}J$.

The proton transitions are found (in Hz) at:

$\Delta E_H(1) = -½J + ½\nu_H - \nu_N - ½J + ½\nu_H + \nu_N = \nu_H - J$ [$m_I(\mathrm{N}) = +1$]

$\Delta E_H(2) = ½\nu_H + ½\nu_H = \nu_H$ [$m_I(\mathrm{N}) = 0$]

$\Delta E_H(3) = ½J + ½\nu_H + \nu_N + ½J + ½\nu_H - \nu_N = \nu_H + J$ [$m_I(\mathrm{N}) = -1$]

The three lines are equally spaced and all of the same intensity because each corresponds to the transition |+½, m_I(N)> → |–½, m_I(N)>

The ^{14}N transitions are found (in Hz) at:

$\Delta E_N(1) = -\frac{1}{2}\nu_H + \frac{1}{2}\nu_H + \nu_N - \frac{1}{2}J = \nu_N - \frac{1}{2}J$ |+½ +1> → |+½ 0>

$\Delta E_N(2) = -\frac{1}{2}\nu_H + \nu_N - \frac{1}{2}J + \frac{1}{2}\nu_H = \nu_N - \frac{1}{2}J$ |+½ 0> → |+½ –1>

$\Delta E_N(3) = \frac{1}{2}\nu_H - \frac{1}{2}\nu_H + \nu_N + \frac{1}{2}J = \nu_H + \frac{1}{2}J$ |–½ +1> → |–½ 0>

$\Delta E_N(4) = \frac{1}{2}\nu_H + \nu_N + \frac{1}{2}J - \frac{1}{2}\nu_H = \nu_N + \frac{1}{2}J$ |–½ 0> → |–½ –1>

The four lines are equally spaced and of the same intensity because each corresponds to either |m_I(H),+1> → |m_I(H),0> or |m_I(H),0> → |m_I(H),–1>.

If the applied magnetic field is such that ν_H = 100.0 MHz then
$\nu_N = 100.0 \times \gamma(^{14}N)/\gamma(H) = 100.0 \times 1.934/26.75 = 7.230$ MHz.

Therefore, the difference between the resonance frequencies of the two nuclei in this field, i.e. $\nu_H - \nu_N$ is ~ 93 MHz but the coupling is only 50 Hz. Therefore, the first-order treatment is amply justified.