Assignment 8 Solutions

8.1 Problem 21.10: The fundamental expression for the energy of a magnetic nucleus with spin component quantum number \( m_I \) in a magnetic field \( B \) (neglecting shielding and spin–spin coupling) is

\[
E = -g_N \mu_N B m_I.
\]

For protons, \( g_N = 5.5857 \) and \( m_I = \pm 1/2 \). Transitions follow the selection rule \( \Delta m_I = \pm 1 \), so the transition energy \( \Delta E \) is given by

\[
\Delta E = -g_N \mu_N B \left( -\frac{1}{2} \right) - \left[ -g_N \mu_N B \left( +\frac{1}{2} \right) \right] = g_N \mu_N B.
\]

This transition energy is related to the transition frequency \( \nu \) in the usual way:

\[
\nu = \frac{\Delta E}{h}\quad \text{or} \quad B = \frac{\nu g_N \mu_N}{h}.
\]

Substituting values for \( g_N, \mu_N, \) and \( h \) gives \( B = (2.3487 \times 10^{-8} \text{ T Hz}^{-1}) \nu \). This is equivalent to \( B/nT = 23.487 \left( \nu/\text{Hz} \right) \).

Problem 21.11: Again using the fundamental relationship

\[
\nu = \frac{\Delta E}{h} = \frac{g_N \mu_N B}{h},
\]

we see that the NMR frequency at a constant field is directly proportional to the nuclear g factor, \( g_N \). If \( B = 5.875 \text{ T} \) for protons resonating at 250 MHz, then \( ^{13}\text{C} \), with a \( g \) factor of 1.4047, requires a frequency

\[
\nu_{^{13}\text{C}} = \frac{g_{^{13}\text{C}}}{g_{^{1}\text{H}}} \nu_{^{1}\text{H}} = \frac{1.4047}{5.5857} (250 \text{ MHz}) = 62.87 \text{ MHz}.
\]

If 2-propanol has two peaks with TMS chemical shifts of 63.4 and 24.7 ppm, then we can use the definition of chemical shift,

\[
\delta_i = 10^6 \frac{\nu_i - \nu_{\text{ref}}}{\nu_{\text{ref}}},
\]

to write

\[
\delta_1 - \delta_2 = 10^6 \left( \frac{\nu_1 - \nu_{\text{ref}}}{\nu_{\text{ref}}} - \frac{\nu_2 - \nu_{\text{ref}}}{\nu_{\text{ref}}} \right) = 10^6 \frac{\nu_1 - \nu_2}{\nu_{\text{ref}}} = 38.7 \text{ ppm},
\]

or \( \nu_1 - \nu_2 = 2433 \text{ Hz with } \nu_{\text{ref}} = 62.87 \text{ MHz} \).

Problem 21.12: TMS has four carbon atoms, but since \( ^{13}\text{C} \) has a natural abundance of only 1.1\%, those TMS molecules with more than one \( ^{13}\text{C} \) nucleus are too scarce to be seen. Thus, with proton decoupling, the TMS \( ^{13}\text{C} \) spectrum consists of a single line. Without proton decoupling, however, the three protons bound to the \( ^{13}\text{C} \) produce a quartet signal with a 1:3:3:1 intensity ratio and a separation of \( J_{\text{CH}} = 118 \text{ Hz} \). The protons bound to \( ^{12}\text{C} \) atoms in the same TMS molecule are too far from the \( ^{13}\text{C} \)
nucleus to show an observable splitting. If $^{13}\text{C}$ had a 50% abundance, the TMS spectrum would not change. All the C atoms in TMS are equivalent, and equivalent magnetic nuclei cannot split each other’s resonances.

8.3 Problem 21.15: Raising and lowering operators were first defined in Eq. (12.38), and for nuclear angular momentum operators, they are

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

Thus we have

$$\hat{I}_{+,1} + \hat{I}_{+,2} + \hat{I}_{-,1} + \hat{I}_{-,2} = \hat{I}_{x,1} + i \hat{I}_{y,1} + \hat{I}_{x,2} + i \hat{I}_{y,2} + \hat{I}_{x,1} - i \hat{I}_{y,1} + \hat{I}_{x,2} - i \hat{I}_{y,2}$$

$$= \hat{I}_{x,1} + \hat{I}_{x,2} + \hat{I}_{y,1} + \hat{I}_{y,2} = 2\hat{I}_{x,T}.$$ 

Next, we recall the basic rules for raising and lowering operator algebra:

$$\hat{I}_+ a = 0$$ $$\hat{I}_+ b = a$$ $$\hat{I}_- a = b$$ $$\hat{I}_- b = 0.$$ 

This shows us that

$$\left(\hat{I}_{+,1} + \hat{I}_{+,2} + \hat{I}_{-,1} + \hat{I}_{-,2}\right) a a = \hat{I}_{+,1} a a + \hat{I}_{+,2} a a + \hat{I}_{-,1} a a + \hat{I}_{-,2} a a$$

$$= 0 + 0 + 0 + 0$$

$$\left(\hat{I}_{+,1} + \hat{I}_{+,2} + \hat{I}_{-,1} + \hat{I}_{-,2}\right) b b = \hat{I}_{+,1} b b + \hat{I}_{+,2} b b + \hat{I}_{-,1} b b + \hat{I}_{-,2} b b$$

$$= 0 + 0 + 0 + 0$$

$$\left(\hat{I}_{+,1} + \hat{I}_{+,2} + \hat{I}_{-,1} + \hat{I}_{-,2}\right) a b = \hat{I}_{+,1} a b + \hat{I}_{+,2} a b + \hat{I}_{-,1} a b + \hat{I}_{-,2} a b$$

$$= 0 + 0 + 0 + 0$$

$$\left(\hat{I}_{+,1} + \hat{I}_{+,2} + \hat{I}_{-,1} + \hat{I}_{-,2}\right) b a = \hat{I}_{+,1} b a + \hat{I}_{+,2} b a + \hat{I}_{-,1} b a + \hat{I}_{-,2} b a$$

$$= 0 + 0 + 0 + 0$$

Note how this operator gives new spin functions that seem to have flipped either of the two spins, one at a time, e.g., $aa$ becomes $ba + ab$, etc.

Problem 21.16: Following the notation of the previous problem, in which $\Box\Box$ means $a(1)a(2)$, etc., and ignoring normalization constants, we have the four spin states for $H_2$ in the form

$$\Psi_1 = \Box\Box \quad \Psi_2 = \Box\Box \quad \Psi_3 = \Box\Box + \Box\Box \quad \Psi_4 = \Box\Box - \Box\Box.$$ 

Now we use the results of the previous problem to find the six matrix elements $H_{12} - H_{34}$. For $H_{12}$, done here in detail, we first substitute the operator expression from the previous problem into the integral (second line, with the spin quantum numbers explicitly labeled with the nucleus each refers to), then expand the integrand into two integrals (third line), and finally note that both integrals are zero: the first has orthogonal spins on nucleus 2 while the second has orthogonal spins on nucleus 1.
Thus, transitions between state $f_1$ and state $f_2$ are forbidden, which should be no surprise, since such a transition would require the simultaneous flip of both spins.

\[
H_{12} = \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \mathbf{d}_a \mathbf{d}_b
\]
\[
= \int \left( \mathbf{d}_1(1) \mathbf{d}_2(2) \left( \mathbf{d}_1(1) \mathbf{d}_2(2) + \mathbf{d}_1(1) \mathbf{d}_2(2) \right) \right) \mathbf{d}_a \mathbf{d}_b
\]
\[
= \int \left( \mathbf{d}_1(1) \mathbf{d}_2(2) \right) \mathbf{d}_a \mathbf{d}_b + \int \left( \mathbf{d}_1(1) \mathbf{d}_2(2) \right) \mathbf{d}_a \mathbf{d}_b = 0 + 0 .
\]

The other matrix elements are found in a similar way:

\[
H_{13} = \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \left( \mathbf{d}_a + \mathbf{d}_b \right) \mathbf{d}_a
\]
\[
= \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \mathbf{d}_a \mathbf{d}_b + \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \mathbf{d}_a \mathbf{d}_b
\]
\[
= 2 \int \left( \mathbf{d}_1(1) \mathbf{d}_2(2) \mathbf{d}_a \mathbf{d}_b + 2 \int \left( \mathbf{d}_1(1) \mathbf{d}_2(2) \right) \mathbf{d}_a \mathbf{d}_b = 2 + 0 = 2 .
\]

\[
H_{14} = \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \left( \mathbf{d}_a - \mathbf{d}_b \right) \mathbf{d}_a
\]
\[
= \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \mathbf{d}_a \mathbf{d}_b - \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \mathbf{d}_a \mathbf{d}_b
\]
\[
= \int \left( \mathbf{d}_1(1) \mathbf{d}_2(2) \mathbf{d}_a \mathbf{d}_b - \int \left( \mathbf{d}_1(1) \mathbf{d}_2(2) \mathbf{d}_a \mathbf{d}_b = 0 .
\]

\[
H_{23} = \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \left( \mathbf{d}_a + \mathbf{d}_b \right) \mathbf{d}_a
\]
\[
= \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \mathbf{d}_a \mathbf{d}_b + \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \mathbf{d}_a \mathbf{d}_b
\]
\[
= 2 \int \left( \mathbf{d}_1(1) \mathbf{d}_2(2) \mathbf{d}_a \mathbf{d}_b = 0 + 2 = 2 .
\]

\[
H_{24} = \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \left( \mathbf{d}_a - \mathbf{d}_b \right) \mathbf{d}_a
\]
\[
= \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \mathbf{d}_a \mathbf{d}_b - \int \left( \hat{\mathbf{f}}_{1,l} + \hat{\mathbf{f}}_{2,l} + \hat{\mathbf{f}}_{1,r} + \hat{\mathbf{f}}_{2,r} \right) \mathbf{d}_a \mathbf{d}_b
\]
\[
= 0 .
\]
$$H_{34} = \int (\hat{\sigma}_1 + \hat{\sigma}_2) (\hat{\sigma}_{+1,1} + \hat{\sigma}_{+1,2} + \hat{\sigma}_{-1,1} + \hat{\sigma}_{-1,2}) (\hat{\sigma}_1 - \hat{\sigma}_2) d\sigma$$

$$= \int (\hat{\sigma}_1 + \hat{\sigma}_2) (\hat{\sigma}_{+1,1} + \ldots + \hat{\sigma}_{-1,2}) d\sigma - \int (\hat{\sigma}_1 + \hat{\sigma}_2) (\hat{\sigma}_{+1,1} + \ldots + \hat{\sigma}_{-1,2}) d\sigma$$

$$= \int (\hat{\sigma}_1 + \hat{\sigma}_2) (\hat{\sigma}_1 + \hat{\sigma}_2) d\sigma - \int (\hat{\sigma}_1 + \hat{\sigma}_2) (\hat{\sigma}_1 + \hat{\sigma}_2) d\sigma$$

$$= 0 .$$

Only two of these six matrix elements are non-zero, $H_{13}$ and $H_{23}$. Now we have to figure out what this means. Note that states $f_1$, $f_2$, and $f_3$ represent $I = 1$ (the triplet spin combinations) while $f_4$ represents $I = 0$ (the singlet combination). Since neither of the non-zero transition matrix elements involves state 4, the $D_I = 0$ selection rule is established; no transition is possible between state 4 with $I = 0$ and any of the $I = 1$ states. Next, note that state 1 ($\uparrow\uparrow$) has $m_I = +1$ (both spins up), state 2 has $m_I = -1$ (both down), and state 3 has $m_I = 0$. The allowed 1 $\uparrow\uparrow$ 3 transition has $\Delta m_I = 0 - (+1) = -1$, and the allowed 2 $\uparrow\uparrow$ 3 transition has $\Delta m_I = 0 - (-1) = +1$, establishing the $\Delta m_I = \pm 1$ selection rule.