Problem Set 10
On Solving H $\Psi = E\Psi$ for a Spin System, Comparison with NMR Experiments

1. Consider particles 1 and 2. Given the operators I_x, I_y, I_z which have the following properties:

$I_z(1)\alpha(1) = \frac{1}{2}\hbar\,\alpha(1)$ $\qquad$ $I_z(1)\,\beta(1) = -\frac{1}{2}\hbar\,\beta(1)$
$I_x(1)\alpha(1) = \frac{1}{2}\hbar\,\beta(1)$ $\qquad$ $I_x(1)\,\beta(1) = \frac{1}{2}\hbar\,\alpha(1)$
$I_y(1)\alpha(1) = \frac{1}{2}i\hbar\,\beta(1)$ $\qquad$ $I_y(1)\,\beta(1) = -\frac{1}{2}i\hbar\,\alpha(1)$

$\alpha(1)$ and $\beta(1)$ are functions associated with particle 1.

$\mathbf{I}(1) \equiv I_x(1)\,\mathbf{i} + I_y(1)\,\mathbf{j} + I_z(1)\,\mathbf{k}$ $\qquad$ **i**, **j**, and **k** are unit vectors along the x, y, and z directions.

Find the simultaneous eigenfunctions of the operators

$$F_z \equiv I_z(1) + I_z(2) \quad \text{and} \quad F^2 \equiv F_x^2 + F_y^2 + F_z^2$$

2. Now consider <u>three</u> particles of the same type as the two in problem 1.
Prepare an orthonormal complete set of functions which are eigenfunctions of the operator

$$F_z \equiv I_z(1) + I_z(2) + I_z(3)$$

which can be used as the basis for constructing a matrix representation of operators involving all 3 spins. Arrange them according to decreasing eigenvalues of F_z., i.e., function ψ_1 for eigenvalue $+(3/2)\hbar$, ψ_2, ψ_3, ψ_4, for eigenvalue $+\frac{1}{2}\hbar$, ..., and ψ_8 for eigenvalue $-(3/2)\hbar$.

Using these 8 functions as your orthonormal complete set, *find the matrix representations of the following operators*:

$I_z(1)/\hbar \qquad I_z(2)/\hbar \qquad I_z(3)/\hbar$
$F_x \equiv I_x(1) + I_x(2) + I_x(3)$
$I_x(1)\,I_x(2)/\hbar^2 \qquad I_x(1)\,I_x(3)/\hbar^2 \qquad I_x(2)\,I_x(3)/\hbar^2$
$I_y(1)\,I_y(2)/\hbar^2 \qquad I_y(1)\,I_y(3)/\hbar^2 \qquad I_y(2)\,I_y(3)/\hbar^2$
$I_z(1)\,I_z(2)/\hbar^2 \qquad I_z(1)\,I_z(3)/\hbar^2 \qquad I_z(2)\,I_z(3)/\hbar^2$

Given the Hamiltonian operator (expressed in Hz) in a magnetic field B:

$$\mathrm{H}_{op}/h = -(\nu_0 + \nu_1)I_z(1)/\hbar - (\nu_0 + \nu_2)I_z(2)/\hbar - (\nu_0 + \nu_3)I_z(3)/\hbar$$
$$+ J_{12}\mathbf{I}(1)\bullet\mathbf{I}(2)/\hbar^2 + J_{13}\mathbf{I}(1)\bullet\mathbf{I}(3)/\hbar^2 + J_{23}\mathbf{I}(2)\bullet\mathbf{I}(3)/\hbar^2$$

[where $h(\nu_0 + \nu_1) \equiv g_1(1-\sigma_1)\mu_N B/\hbar$,
$h(\nu_0 + \nu_2) \equiv g_2(1-\sigma_2)\mu_N B/\hbar$,

$$h(\nu_0 + \nu_3) \equiv g_3 (1-\sigma_3)\mu_N B/\hbar \;]$$

Find the matrix representation H *of the* (H_{op}/h) *operator in the complete orthonormal set of 8 functions.*

3. Use the Hamiltonian matrix of problem 2 to solve the problem

$$\mathsf{H}\,\Psi = E\,\Psi$$

The magnitudes of the constants in the Hamiltonian are given below

$\nu_0 =$ 60×10^6 Hz $\nu_1 =$ 0.0 $\nu_2 =$ 46.8 Hz $\nu_3 =$ 52.2 Hz

$J_{12} =$ 14.8 Hz $J_{23} =$ -1.3 Hz $J_{13} =$ 7.4 Hz

The energy eigenvalues will be clustered around

90×10^6, 30×10^6, -30×10^6, and -90×10^6 Hz.

Block out your H *matrix elements and solve each block* *<u>separately</u>*.

For each block the energy values will be clustered around one of these very large numbers. Therefore, for each block USE THAT VERY LARGE NUMBER TEMPORARILY AS AN ARTIFICIAL ZERO OF ENERGY, [except for the block centered around 0.0] so as to maintain digital accuracy to better than 0.1 Hz. For each block compute your H matrix elements to better than 0.1 Hz accuracy, relative to that block's own "zero" of energy.

Solve the 1×1 matrices separately, that is write out E and Ψ directly.

Solve the 3×3 matrices on a computer.

Find the eigenvalues E_i *and the corresponding eigenvectors* C_i .

Draw the energy level diagram for this system and write out the eigenfunction Ψ_i *for each level* E_i. *Write out the matrix* C which contains all the eigenvectors arranged in columns. This should also appear blocked out in 1×1, 4×4, etc. blocks.

4. The transitions which can be induced between these energy levels are in the radiofrequency region. All frequencies will be clustered around 60×10^6 Hz in this example.

The probability of a transition occurring between levels *s* and *t* is proportional to the <u>square of the integral</u>

$$\iiint \Psi_s^*[(I_x(1) + I_x(2) + I_x(3)]/\hbar\; \Psi_t\, d\tau_1\, d\tau_2\, d\tau_3$$

Find these integrals for each *s* and *t* pair, and thus determine not only $h\nu = (E_s - E_t)$ for each pair of eigenstates *s* and *t* , but also the intensity of the transition between them. How to do it? Here is a hint:

Note that the above integrals are the elements in the matrix representation of the operator $[(I_x(1) + I_x(2) + I_x(3)]/\hbar$ IN THE BASIS SET WHICH ARE THE EIGENFUNCTIONS OF THE HAMILTONIAN.

The transformation

$$C^{-1} H C = \mathbf{H} = \begin{bmatrix} E_1 & & O \\ & E_i & \\ O & & E_8 \end{bmatrix}$$

created from H (in the original basis set) a new matrix representation, that which uses as basis functions the correct eigenfunctions of the Hamiltonian, in which complete orthonormal set the matrix $\mathbf{H}$ is diagonal.

You can also use the same transformation to convert the matrix F_x in the original basis set to a new matrix $\mathbf{F_x}$ in the basis set of the eigenfunctions of the Hamiltonian

$$C^{-1} F_x C = \mathbf{F_x}$$

where the matrix elements of $\mathbf{F_x}$ are the integrals

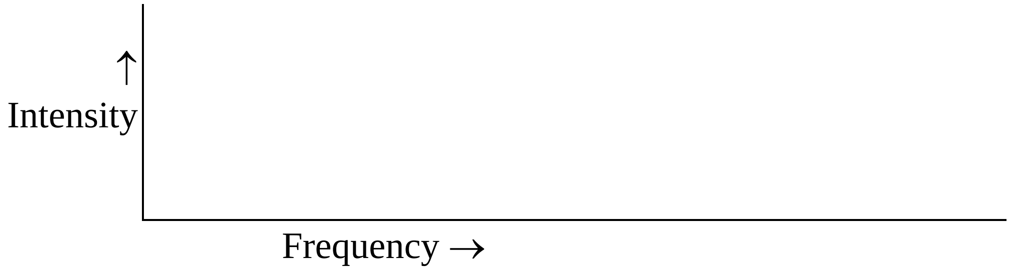
$$\iiiint \Psi_s^* [(I_x(1) + I_x(2) + I_x(3)]/\hbar \, \Psi_t \, d\tau_1 \, d\tau_2 \, d\tau_3$$

that is, just exactly those ones which when squared gives a number which is directly proportional to the intensity of the NMR peak resulting from the transition between energy levels E_s and E_t. *Use the computer to do the matrix multiplication*

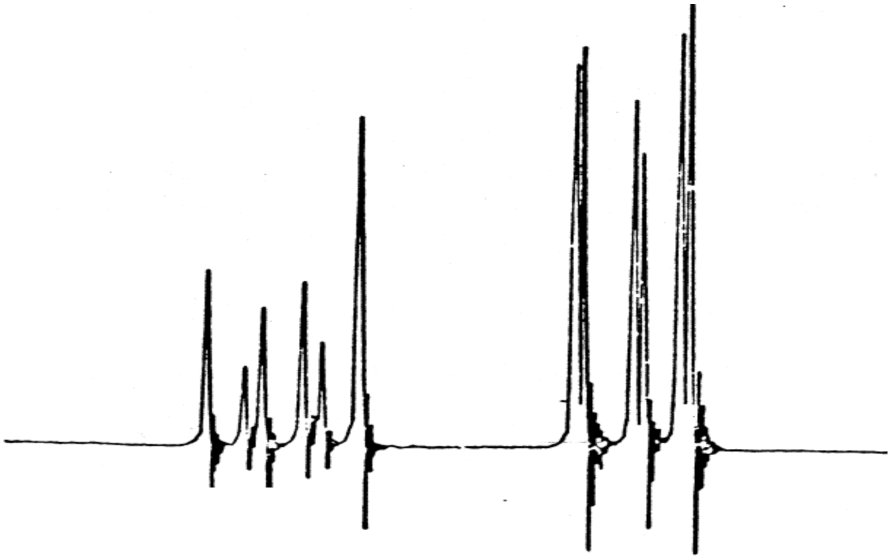
$$C^{-1} F_x C = \mathbf{F_x}$$

Every non-zero intensity is an observable transition. *Draw these transitions on your energy level diagram.*

Make a stick plot of your predicted spectrum, as shown below:



Compare your prediction with the actual NMR spectrum



frequency →