Problem Set 8
On angular momentum

1. Angular momentum is a vector, call it **L**. The components of the angular momentum vector are defined classically as follows:

$L_x \equiv yp_z - zp_y$ $\quad$ $L_y \equiv zp_x - xp_z$ $\quad$ $L_z \equiv xp_y - yp_x$

Replace the linear momentum components p_x, p_y, p_z by their quantum mechanical operators to find the operators L_x , L_y , L_z , then *prove* that

$[L_y, L_z] = i\hbar L_x$ $\quad$ $[L_z, L_x] = i\hbar L_y$ $\quad$ $[L_x, L_y] = i\hbar L_z$

Prove also that $[L^2, L_x] = 0$ $\quad$ $[L^2, L_y] = 0$ $\quad$ $[L^2, L_z] = 0$

2. Consider an operator L_+ which is a combination of the components of angular momentum $\quad L_+ \equiv L_x + i L_y$

find $[L^2, L_+]$.

Now consider the other combination: $\quad L_- \equiv L_x - i L_y$

find $[L^2, L_-]$.

Prove that $L^2 = L_+ L_- - \hbar L_z + L_z^2$ and that $L^2 = L_- L_+ + \hbar L_z + L_z^2$

L_+ and L_- are called "ladder operators" .

Prove that you can write L_x in terms of the ladder operators

$L_x = \frac{1}{2} [L_+ + L_-]$.

3. Elementary particles have been found to have an intrinsic angular momentum, i.e., they have this fundamental property even when **L** = 0 (no rotational or orbital motion). For example an electron, a neutron, a proton, a deuteron, has intrinsic angular momentum called, for historic reasons, "spin" angular momentum. <u>All angular momentum</u> operators follow the same rules, such as those you derived in problem 1 :

$[L_y, L_z] = i\hbar L_x$ $\quad$ $[L_z, L_x] = i\hbar L_y$ $\quad$ $[L_x, L_y] = i\hbar L_z$

$[L^2, L_x] = 0$ $\quad$ $[L^2, L_y] = 0$ $\quad$ $[L^2, L_z] = 0$

and those we will derive in class:

$L_z Y_{\ell m} = m\hbar Y_{\ell m}$ $\quad$ $L^2 Y_{\ell m} = \ell(\ell+1)\hbar^2 Y_{\ell m}$ $\quad$ such that $m = -\ell, -\ell+1, \ldots, +\ell$

$L_\pm Y_{\ell m}(1) = [\ell(\ell+1) - m(m\pm1)]^{1/2} \hbar Y_{\ell\, m\pm1}$

Consider <u>electron spin</u> angular momentum vector **S**. Since it is angular momentum, its operators follows the rules:

$[S_y, S_z] = i\hbar S_x$ $\quad$ $[S_z, S_x] = i\hbar S_y$ $\quad$ $[S_x, S_y] = i\hbar S_z$

$[S^2, S_x] = 0$ $\quad$ $[S^2, S_y] = 0$ $\quad$ $[S^2, S_z] = 0$

$S_z \psi_{sm} = m\hbar \psi_{s\,m}$ $\quad$ $S^2 \psi_{sm} = s(s+1)\hbar^2 \psi_{s\,m}$ $\quad$ such that $m = -s, -s+1, \ldots, +s$

$\mathcal{S}_\pm \psi_{s\,m}(1) = [s(s+1) - m(m\pm1)]^{1/2} \hbar \psi_{s\,m\pm1}$

For one electron, call it electron 1, s = ½. Thus, we can immediately write, from the above rules:

$S_z(1)\varphi_{½}(1) = ½\,\hbar\,\varphi_{½}(1)$ (1)

$S_z(1)\varphi_{-½}(1) = -½\,\hbar\,\varphi_{-½}(1)$ (2)

$S^2(1)\,\varphi_{½}(1) = ½\,(½+1)\,\hbar^2\varphi_{½}(1)$

$S^2(1)\,\varphi_{-½}(1) = ½\,(½+1)\,\hbar^2\varphi_{-½}(1)$

$\mathcal{S}_+(1)\varphi_{-½}(1) = \hbar\,\varphi_{½}(1)$ the raising operator

$\mathcal{S}_-(1)\,\varphi_{½}(1) = \hbar\,\varphi_{-½}(1)$ the lowering operator

$\mathcal{S}_+(1)\,\varphi_{½}(1) = 0$ m can't go any higher than +½

$\mathcal{S}_-(1)\,\varphi_{-½}(1) = 0$ m can't go any lower than -½

for electron 2, we can write similar equations, for example

$S_z(2)\varphi_{½}(2) = ½\,\hbar\,\varphi_{½}(2)$ (3)

$S_z(2)\varphi_{-½}(2) = -½\,\hbar\,\varphi_{-½}(2)$ (4)

and so on.

Vectors add by adding their components. The total spin angular momentum vector for two electrons is the vector sum:

$\mathbf{S} = \mathbf{S}(1) + \mathbf{S}(2),$ (5)

with total z component

$S_z = S_z(1) + S_z(2).$ (6)

The other components of the vectors add similarly.

The problem: Now consider a biradical (that is, two unpaired electron spins).

(a) For the biradical, *determine the complete orthonormal set of eigenfunctions* of S_z, the z component of the total spin angular momentum, *and the corresponding eigenvalues. Are any of them degenerate? Which ones?*

(b) Note, for the square of a vector, we can write

$\mathbf{S}^2 = \{\mathbf{S}(1) + \mathbf{S}(2)\}^2 = \mathbf{S}(1)^2 + 2\,\mathbf{S}(1)\bullet\mathbf{S}(2) + \mathbf{S}(2)^2.$ (7)

Prove that $\mathbf{S}(1)\bullet\mathbf{S}(2) = \{\, ½\,\mathcal{S}_+(1)\,\mathcal{S}_-(2) + ½\,\mathcal{S}_-(1)\,\mathcal{S}_+(2) + S_z(1)\,S_z(2)\,\}$ (8)

Start from the definitions $\mathcal{S}_+ \equiv S_x + i\,S_y$ $\quad\mathcal{S}_- \equiv S_x - i\,S_y$ (9)

(c) *Prove* that any linear combination of the degenerate eigenfunctions of S_z also satisfies the operator equation for S_z. You may use a sum of degenerate functions to try.

(d) Using Eq. (7) *demonstrate* that the nondegenerate functions of S_z that you found in part (a) are also eigenfunctions of S^2, and *find the corresponding eigenvalues*. *Find the correct linear combinations of the degenerate functions of* S_z *that are also eigenfunctions of* S^2. When you are done, you should have a complete list of functions that are simultaneously eigenfunctions of both S_z and S^2. *Write out the complete list of simultaneous eigenfunctions, and the corresponding eigenvalues of* S_z *and* S^2.

(e) Suppose we wish to measure the observable that corresponds to the operator

$R_{op} = a_1S_z(1) + a_2S_z(2) + J\mathbf{S}(1)\bullet\mathbf{S}(2)$ where $a_1 = 2/\hbar$, $a_2 = 2/\hbar$, $J = 4/\hbar^2$. (10)

Determine whether or not it is possible to simultaneously know S_z for the biradical and also R. That is, determine whether there are any limitations to the errors in their simultaneous measurements.

(f) *Find the average value* of R

(i) that would be found in a series of measurements if the biradical system is prepared in an eigenstate of S_z corresponding to the eigenvalue $1\hbar$.

(ii) that would be found in a series of measurements if the biradical system is prepared in an eigenstate of S_z corresponding to the eigenvalue $-1\hbar$.

(iii) that would be found in a series of measurements if the biradical system is prepared such that it is simultaneously in an eigenstate of S_z corresponding to the eigenvalue $0\hbar$ <u>and</u> in an eigenstate of S^2 corresponding to the eigenvalue $2\hbar^2$.

The eigenstates of R are also the states of the biradical in a magnetic field, thus this problem is relevant to electron spin resonance (ESR) spectroscopy of organic free radicals.

4. In high-resolution NMR spectroscopy, the observed transitions are between eigenstates of the nuclear spin angular momentum operators for the NMR nuclei, such as protons. Suppose there are only two protons in a molecule, and they are in non-equivalent electronic environments, and all the other nuclei have zero intrinsic angular momentum (or else effectively so). An example of such a molecule would be 2-bromo-5-chlorothiopene. Here you have a situation which is identical to problem 3. The R_{op} given there was,

$$R_{op} = a_1S_z(1) + a_2S_z(2) + J\mathbf{S}(1)\bullet\mathbf{S}(2)$$

For NMR the symbols used for the nuclear angular momentum operators are used:

$$R_{op} = a_1I_z(1) + a_2I_z(2) + J\mathbf{I}(1)\bullet\mathbf{I}(2)$$

R_{op} determines the energy states of the two-proton-spin system in an NMR magnet, where, a_1 is a measure of the chemical shift of proton (1) , a_2 is a measure of the chemical shift of proton (2) , and J is the 'spin-spin coupling' between the two protons. For this example, let a_1 and a_2 be respectively, $-(\nu_0 - 150)$ Hz and $-(\nu_0 - 350)$ Hz where the resonance frequency of the reference substance (tetramethylsilane liquid) is ν_0 , and let the spin-spin coupling constant J be 20 Hz. With a_1, a_2, and J in these units, we write

$$R_{op} = a_1I_z(1)/\hbar + a_2I_z(2)/\hbar + J\mathbf{I}(1)\bullet\mathbf{I}(2)/\hbar^2 \qquad \text{such that } \langle R_{op}\rangle \text{ is in Hz}$$

As in problem 3, you can determine all the states corresponding to the eigenvalues of this operator R_{op}. You have already done the work in the previous problem, now simply write down the answers appropriate to this problem:

(a) If for proton 1

$I_z(1)\ \alpha(1) = ½\ \hbar\ \alpha(1)$ (1)

$I_z(1)\ \beta(1) = -\ ½\ \hbar\ \beta(1)$ (2)

and for proton 2

$I_z(2)\ \alpha(2) = ½\ \hbar\ \alpha(2)$ (3)

$I_z(2)\ \beta(2) = -\ ½\ \hbar\ \beta(2)$ (4)

Applying separation of variables, what are the eigenvalues and eigenfunctions of $I_{z,total} = [I_z(1) + I_z(2)]$? call them φ_1, φ_2, φ_3, φ_4, such as to arrange them in order of increasing eigenvalue.

(b) Two of the eigenfunctions are nondegenerate in $I_{z,total}$ and are already eigenfunctions of R_{op}. Call the eigenfunctions of R_{op} Ψ_1, Ψ_2, Ψ_3, Ψ_4.
Thus, $\Psi_1 = \varphi_1$, $\Psi_4 = \varphi_4$, Any linear combination of the two that are degenerate in $I_{z,total}$ are also acceptable solutions for the $I_{z,total}$ eigenfunction-eigenvalue equation. The particular linear combinations that are also eigenfunctions of R_{op} are:
$\Psi_2 = (\cos x)\ \varphi_2 - (\sin x)\ \varphi_3$ and $\Psi_3 = (\sin x)\ \varphi_2 + (\cos x)\ \varphi_3$, where:
$\cos 2x \equiv \delta / [J^2 + \delta^2]^{½}$, $\sin 2x \equiv J / [J^2 + \delta^2]^{½}$, and $\delta = (350\text{-}150)$ Hz.
Show that these four functions Ψ_1, Ψ_2, Ψ_3, Ψ_4 are indeed eigenfunctions of R_{op} and *find the corresponding eigenvalues* (in Hz). You may leave the ν_0 in the expressions for the eigenvalues.

(c) Now *draw the energy level diagram* (the eigenvalues of R_{op}) for the two protons in the NMR magnet; label each level with eigenvalues and eigenfunctions.

(d) The intensities of the NMR transitions are given by the square of the transition integral. In NMR the transition integral is: ($I_{x\ total}$) integrated between the two nuclear spin state functions involved in the transition.
For example, the transition integral between states 3 and 4 = $\int \Psi_3{}^* I_{x\ total} \Psi_4\, d\tau$.
To evaluate this integral, first write out the operator $I_{x\ total} = I_x(1) + I_x(2)$ in terms of raising and lowering operators, e.g., start with $I_x(1) = ½\ [I_+(1) + I_-(1)]$ analogous to $L_x = ½\ [L_+ + L_-]$ in problem 2.
Now you are ready to *calculate the intensities of the transitions between the energy levels* of the two protons in the NMR magnet. Do this for all pairs of levels in absorption mode, i.e., transition from lower energy to higher energy. Hint: although there are 6 such unique pairs, some transition integrals are zero (transition is not allowed) !

(e) Using your calculated eigenvalues, calculate the energy differences (in Hz) and use the calculated intensities to *draw the NMR spectrum* of the two protons.

(f) *Prove* that if the chemical shifts of the two protons are identical (same electronic environment, say $a_1 = a_2 = -(\nu_0 - 350)$ Hz, only one peak can be observed even if the spin spin coupling J is still 20 Hz.