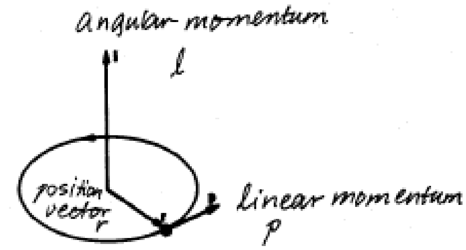
Problem Set 8 Answers
On angular momentum

1.



The classical definition of angular momentum, $\mathbf{l} = \mathbf{r} \wedge \mathbf{p}$.

CLASSICAL MECHANICS

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} \quad \text{or} \quad \mathbf{r} \wedge \mathbf{p}$$

"cross product" or "vector product"

position vector

$$\mathbf{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

linear momentum

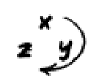
$$\mathbf{p} = p_x\hat{i} + p_y\hat{j} + p_z\hat{k}$$

angular momentum

$$\mathbf{l} = (yp_z - zp_y)\hat{i} + (zp_x - xp_z)\hat{j} + (xp_y - yp_x)\hat{k}$$

$$\mathbf{r}\times\mathbf{p} = \begin{vmatrix} \hat{i} & \hat{j} & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$l_x = yp_z - zp_y$$
$$l_y = zp_x - xp_z$$
$$l_z = xp_y - yp_x$$



$$\mathbf{l}\cdot\mathbf{l} = l^2 = l_x^2 + l_y^2 + l_z^2$$

dot product
or scalar product

QUANTUM MECHANICS

Replace p_x, p_y, and p_z by operators to find

$$l_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$l_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$
$$l_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$[\ell_x, \ell_y] = \frac{\hbar}{i}\cdot\frac{\hbar}{i}\left\{ \begin{array}{l} \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ -\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \end{array} \right\}$$

$$= \frac{\hbar}{i}\frac{\hbar}{i}\left\{ \begin{array}{l} y\frac{\partial}{\partial z}\, z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\, z\frac{\partial}{\partial y} \\ + z\frac{\partial}{\partial y}\, x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\, y\frac{\partial}{\partial z} \end{array} \right\} \quad \text{all others drop out}$$

$$y\frac{\partial}{\partial z}\, z\frac{\partial}{\partial x}\psi(x,y,z) = y\frac{\partial}{\partial z}\left(z\frac{\partial\psi}{\partial x}\right) = y\frac{\partial\psi}{\partial x} + yz\frac{\partial^2\psi}{\partial z\partial x}$$

($\frac{\partial\psi}{\partial x}$ itself is a function of z)

$$z\frac{\partial}{\partial y}\, x\frac{\partial\psi}{\partial z} = zx\frac{\partial^2\psi}{\partial y\partial z}$$

On the other hand, the negative terms:

$$x\frac{\partial}{\partial z}\, z\frac{\partial\psi(x,y,z)}{\partial y} = x\frac{\partial}{\partial z}\left(z\frac{\partial\psi}{\partial y}\right) = x\frac{\partial\psi}{\partial y} + xz\frac{\partial^2\psi}{\partial z\partial y}$$

($\frac{\partial\psi}{\partial y}$ a function of z)

$$z\frac{\partial}{\partial x}\, y\frac{\partial\psi}{\partial z} = zy\frac{\partial^2\psi}{\partial x\partial z}$$

Leaving only:

$$[\ell_x, \ell_y] = \frac{\hbar}{i}\underbrace{\frac{\hbar}{i}\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)}_{-\ell_z} = i\hbar\,\ell_z$$

The others can be shown similarly.

$$[\ell^2, \ell_x] = \ell^2\ell_x - \ell_x\ell^2 = (\ell_x^2 + \ell_y^2 + \ell_z^2)\ell_x - \ell_x(\ell_x^2 + \ell_y^2 + \ell_z^2)$$

$$= \ell_x^3 + \ell_y\underbrace{\ell_y\ell_x}_{\ell_x\ell_y - i\hbar\ell_z} + \ell_z\underbrace{\ell_z\ell_x}_{\ell_x\ell_z + i\hbar\ell_y} - \ell_x^3 - \underbrace{\ell_x\ell_y}_{\ell_y\ell_x + i\hbar\ell_z}\ell_y - \underbrace{\ell_x\ell_z}_{\ell_z\ell_x - i\hbar\ell_y}\ell_z$$

$$= \ell_y\ell_x\ell_y - i\hbar\ell_y\ell_z + \ell_z\ell_x\ell_z + i\hbar\ell_z\ell_y - \ell_y\ell_x\ell_y - i\hbar\ell_z\ell_y - \ell_z\ell_x\ell_z + i\hbar\ell_y\ell_z$$

$$[\ell^2, \ell_x] = 0$$

Similarly, one can show that

$$[\ell^2, \ell_y] = 0$$

$$[\ell^2, \ell_z] = 0$$

$L_+ \equiv L_x + i\,L_y \qquad\qquad L_- \equiv L_x - i\,L_y$

adding, we get $L_+ + L_- = 2\,L_x$ Thus, $L_x = \frac{1}{2}[L_+ + L_-]$.

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

$$[\ell^2, \ell_+]\psi = \ell^2(\ell_x + i\ell_y)\psi - (\ell_x + i\ell_y)\ell^2\psi$$

$$= \underbrace{(\ell^2\ell_x - \ell_x\ell^2)}_{\text{zero}}\psi + i\underbrace{(\ell^2\ell_y - \ell_y\ell^2)}_{\text{zero}}\psi$$

$$[\ell^2, \ell_+] = 0$$

$$[\ell_+, \ell_z]\psi = (\ell_x + i\ell_y)\ell_z\psi - \ell_z(\ell_x + i\ell_y)\psi$$

$$= \underbrace{(\ell_x\ell_z - \ell_z\ell_x)}_{-i\hbar\ell_y}\psi + i\underbrace{(\ell_y\ell_z - \ell_z\ell_y)}_{i\hbar\ell_x}\psi$$

$$= -\hbar(\ell_x + i\ell_y)\psi$$

$$[\ell_+, \ell_z] = -\hbar\,\ell_+$$ Similarly, can show $[\ell_-, \ell_z] = +\hbar\ell_-$

Note that we can write l_x and l_y in terms of these RAISING and LOWERING operators:

$$l_+ \equiv l_x + i l_y$$

$$l_- \equiv l_x - i l_y$$

ADD: $\frac{1}{2}(l_+ + l_-) = l_x$

SUBTRACT: $\frac{l_+ - l_-}{2i} = l_y$

Example:
What is the result of applying l_+ to an eigenfunction of l_z?

$$l_+ Y_{lm}(\theta,\phi) = \text{? function?}$$

Let us find out by applying the l_z operator on it:

$$l_z l_+ Y_{lm}(\theta,\phi) \underset{\substack{\text{commutator} \\ [l_+, l_z] = -\hbar l_+}}{\overset{\text{using}}{=}} (l_+ l_z + \hbar l_+) Y_{lm}(\theta,\phi)$$

$$= l_+ m\hbar Y_{lm}(\theta,\phi) + \hbar l_+ Y_{lm}(\theta,\phi)$$

$$l_z \boxed{l_+ Y_{lm}(\theta,\phi)} = (m+1)\hbar \boxed{l_+ Y_{lm}(\theta,\phi)}$$

↖ THIS is an EIGENFUNCTION of l_z with eigenvalue $(m+1)\hbar$

Let us find out more by applying the l^2 operator on it:

$$l^2 l_+ Y_{lm}(\theta,\phi) \underset{\text{COMMUTE}}{\overset{\text{THEY}}{=}} l_+ l^2 Y_{lm}(\theta,\phi)$$

$$= l_+ l(l+1)\hbar^2 Y_{lm}(\theta,\phi)$$

$$l^2 \boxed{l_+ Y_{lm}(\theta,\phi)} = l(l+1)\hbar^2 \boxed{l_+ Y_{lm}(\theta,\phi)}$$

↖ THIS is an EIGENFUNCTION of l^2 with eigenvalue $l(l+1)\hbar^2$

Therefore,

$$l_+ Y_{lm}(\theta,\phi) = \overbrace{N^+_{lm}}^{\text{a constant}} Y_{l\,m+1}(\theta,\phi)$$

an EIGENFUNCTION of l^2 with eigenvalue $l(l+1)\hbar^2$
an EIGENFUNCTION of l_z with eigenvalue $(m+1)\hbar$

Example:
What is the result of applying l_- to an eigenfunction of l_z?

$$l_- Y_{lm}(\theta,\phi) = \text{what function?}$$

Let us find out by applying the l_z operator:

$$l_z l_- Y_{lm}(\theta,\phi) \underset{\substack{\text{commutator} \\ [l_-, l_z] = \hbar l}}{\overset{\text{using}}{=}} \underbrace{(l_- l_z - \hbar l_-) Y_{lm}(\theta,\phi)}_{l_- m\hbar Y_{lm} - \hbar l_- Y_{lm}}$$

$$l_z \boxed{\mathbf{l}_- Y_{lm}(\theta,\phi)} = (m-1)\hbar \boxed{\mathbf{l}_- Y_{lm}(\theta,\phi)}$$

This is an EIGENFUNCTION of l_z with eigenvalue $(m-1)\hbar$

Also,

$$l^2 \mathbf{l}_- Y_{lm}(\theta,\phi) \underset{\text{commute}}{\overset{\text{they}}{=}} \mathbf{l}_- l^2 Y_{lm}(\theta,\phi) = \mathbf{l}_- l(l+1)\hbar^2 Y_{lm}(\theta\phi)$$

$$l^2 \boxed{\mathbf{l}_- Y_{lm}(\theta,\phi)} = l(l+1)\hbar^2 \boxed{\mathbf{l}_- Y_{lm}(\theta,\phi)}$$

This is an EIGENFUNCTION of l^2 with eigenvalue $l(l+1)\hbar^2$

Therefore,

$$\mathbf{l}_- Y_{lm}(\theta,\phi) = \overset{\text{a constant}}{N_{lm}^-} Y_{lm-1}(\theta,\phi)$$

an EIGENFUNCTION of l^2 with eigenvalue $l(l+1)\hbar^2$

an EIGENFUNCTION of l_z with eigenvalue $(m-1)\hbar$

Example:

What is the result of applying $\mathbf{l}_-\mathbf{l}_+$ to an eigenfunction of l_z?

$$\mathbf{l}_-\mathbf{l}_+ = (l_x - il_y)(l_x + il_y) =$$
$$= \underbrace{l_x^2 + l_y^2} + \underbrace{il_x l_y - il_y l_x}$$
$$= l^2 - l_z^2 + i\underbrace{[l_x, l_y]}_{i\hbar l_z}$$

$$\mathbf{l}_-\mathbf{l}_+ = l^2 - l_z^2 - \hbar l_z$$

Therefore, $\int Y_{lm}^* \mathbf{l}_-\mathbf{l}_+ Y_{lm}\, d\tau = l(l+1)\hbar^2 - m^2\hbar^2 - m\hbar^2$
$= [l(l+1) - m(m+1)]\hbar^2$

Now relate this to the constants N_{lm}^+ and N_{lm}^-:

$$\int Y_{lm}^* \mathbf{l}_- \underbrace{\mathbf{l}_+ Y_{lm}}\, d\tau = \int Y_{lm}^* \mathbf{l}_- (N_{lm}^+ Y_{lm+1})\, d\tau$$
$$= N_{lm}^+ \int Y_{lm}^* \underbrace{\mathbf{l}_- Y_{lm+1}}\, d\tau = N_{lm}^+ \int Y_{lm}^* N_{lm+1}^- Y_{lm}\, d\tau$$
$$[l(l+1) - m(m+1)]\hbar^2 = N_{lm}^+ \; N_{lm+1}^-$$

Question: What are these constants N_{lm}^+ and N_{lm}^-? We need one more relationship, which we can get as follows:

Consider the integral

$$\int Y_{lm}^* \underbrace{\mathbf{l}_- Y_{lm+1}}\, d\tau = N_{lm+1}^- \int Y_{lm}^* Y_{lm}\, d\tau = N_{lm+1}^-$$

$$\Downarrow \; \mathbf{l}_- = l_x - il_y$$

$$\int Y_{lm}^* l_x Y_{lm+1}\, d\tau - i\int Y_{lm}^* l_y Y_{lm+1}\, d\tau$$

↓ Hermitian operator ↓ Hermitian operator

$$\left(\int Y_{lm+1}^* l_x Y_{lm}\, d\tau\right)^* - i\left(\int Y_{lm+1}^* l_y Y_{lm}\, d\tau\right)^*$$

$$\left(\int Y_{lm+1}^* l_x Y_{lm}\, d\tau + i\int Y_{lm+1}^* l_y Y_{lm}\, d\tau\right)^*$$

$$\left(\int Y_{lm+1}^* (l_x + il_y) Y_{lm}\, d\tau\right)^*$$

$$\left(\int Y_{lm+1}^* \underbrace{\mathbf{l}_+ Y_{lm}}\, d\tau\right)^*$$

$$\left(\int Y_{lm+1}^* N_{lm}^+ Y_{lm+1}\, d\tau\right)^*$$

$$(N_{lm}^+)^* = N_{lm+1}^-$$

Finally, we combine the two relationships that we have found:

$$\left.\begin{aligned}[\ell(\ell+1) - m(m+1)]\hbar^2 &= N^+_{\ell m} N^-_{\ell m+1} \\ (N^+_{\ell m})^* &= N^-_{\ell m+1}\end{aligned}\right\}$$

to get:

$$[\ell(\ell+1) - m(m+1)]\hbar^2 = N^+_{\ell m} (N^+_{\ell m})^*$$

$$\text{or} \quad N^+_{\ell m} = \sqrt{\ell(\ell+1) - m(m+1)}\,\hbar$$

and $[\ell(\ell+1) - m(m+1)]\hbar^2 = (N^-_{\ell m+1})^* N^-_{\ell m+1}$

from which we get, upon $m' = m+1$

$$[\ell(\ell+1) - (m'-1)m']\hbar^2 = (N^-_{\ell m'})^* N^-_{\ell m'}$$

$$\text{or} \quad N^-_{\ell m} = \sqrt{\ell(\ell+1) - m(m-1)}\,\hbar$$

Summarizing:

$$N^{\pm}_{\ell m} = \sqrt{\ell(\ell+1) - m(m\pm 1)}\,\hbar$$

$$\boxed{\ell_{\pm} Y_{\ell m} = \sqrt{\ell(\ell+1) - m(m\pm 1)}\,\hbar\, Y_{\ell\, m\pm 1}}$$

FIND ANY ONE EIGEN-FUNCTION of ℓ_z, FIND ALL OTHERS by $\ell_{\pm}$

Note that if we apply the STEP DOWN op. to the function with the lowest eigenvalue of ℓ_z

$$\ell_- Y_{\ell\, -\ell} \xrightarrow[\text{get}]{\text{we}} [\ell(\ell+1) - (-\ell)(-\ell-1)]^{1/2} \cdots = \text{ZERO}$$

Similarly, if we apply the STEP UP op. to the function with the highest eigenvalue of ℓ_z

$$\ell_+ Y_{\ell\ell} \xrightarrow[\text{get}]{\text{we}} [\ell(\ell+1) - \ell(\ell+1)]^{1/2} \cdots = \text{ZERO}$$

3. (a) For the biradical, *the complete orthonormal set of eigenfunctions* of S_z, the z component of the <u>total</u> spin angular momentum, *and the corresponding eigenvalues*

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

$S_z(1)\varphi_{1/2}(1) = ½\,\hbar\,\varphi_{1/2}(1)$ etc.

Using the separation of variables, we can write the eigenfunctions as

$\Psi_1(1,2) = \varphi_{1/2}(1)\bullet\varphi_{1/2}(2)$

or $\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2)$

or $\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2)$

or $\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)$

$S_z\,\Psi(1,2) = [S_z(1) + S_z(2)]\Psi(1,2)$

$= [S_z(1) + S_z(2)]\varphi_{1/2}(1)\bullet\varphi_{1/2}(2) = ½\hbar\,\varphi_{1/2}(1)\bullet\varphi_{1/2}(2) + ½\hbar\varphi_{1/2}(1)\bullet\varphi_{1/2}(2)$

$= \hbar\,\varphi_{1/2}(1)\bullet\varphi_{1/2}(2)$ eigenvalue $=\hbar$

Similarly can do the other 3 functions:

$[S_z(1) + S_z(2)]\,\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2) = -½\hbar\,\varphi_{1/2}(1)\bullet\varphi_{1/2}(2) - ½\hbar\varphi_{1/2}(1)\bullet\varphi_{1/2}(2)$

$= -\hbar\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2)$ eigenvalue $= -\hbar$

$[S_z(1) + S_z(2)]\,\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) = -½\hbar\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) + ½\hbar\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2)$

$= 0\,\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2)$

$[S_z(1) + S_z(2)]\,\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2) = ½\hbar\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2) - ½\hbar\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)$

$= 0\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)$

The last two are degenerate with same eigenvalue 0.

(b)

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

$\mathcal{S}_+(1)\,\mathcal{S}_-(2) =[S_x(1)+ i\, S_y(1)][S_x(2) - i\, S_y(2)]$

$= S_x(1)\, S_x(2)- iS_x(1)\, S_y(2) + i\, S_y(1)\, S_x(2) + S_y(1)S_y(2)$

$\mathcal{S}_-(1)\,\mathcal{S}_+(2) =[S_x(1)- i\, S_y(1)][S_x(2) + i\, S_y(2)]$

$= S_x(1)\, S_x(2)+ iS_x(1)\, S_y(2) - i\, S_y(1)\, S_x(2) + S_y(1)S_y(2)$

$\mathcal{S}_+(1)\,\mathcal{S}_-(2) + \mathcal{S}_-(1)\,\mathcal{S}_+(2) = 2\, S_x(1)\, S_x(2)+2\, S_y(1)S_y(2)$

Definition of a dot product of two vectors:

$\mathbf{S}(1)\bullet\mathbf{S}(2) = S_x(1)\, S_x(2) + S_y(1)\, S_y(2) + S_z(1)\, S_z(2)$

From $\mathcal{S}_+(1)\,\mathcal{S}_-(2) + \mathcal{S}_-(1)\,\mathcal{S}_+(2) = 2\, S_x(1)\, S_x(2)+2\, S_y(1)S_y(2)$ we can replace the first two terms to get,

$\mathbf{S}(1)\bullet\mathbf{S}(2) = \{ ½\, \mathcal{S}_+(1)\mathcal{S}_-(2) + ½\, \mathcal{S}_-(1)\mathcal{S}_+(2) + S_z(1)S_z(2) \}$ Q.E.D.

(c) Any linear combination of the degenerate eigenfunctions of S_z also satisfies the operator equation for S_z , for example, we use the sum

$(1/\sqrt{2})[\varphi_{-½}(1)\bullet \varphi_{½}(2) + \varphi_{½}(1)\bullet \varphi_{-½}(2)]$

$[S_z(1) + S_z(2)]\, (1/\sqrt{2})[\varphi_{-½}(1)\bullet \varphi_{½}(2) + \varphi_{½}(1)\bullet \varphi_{-½}(2)]$

$= 0\, (1/\sqrt{2})\, [\varphi_{-½}(1)\bullet \varphi_{½}(2) + \varphi_{½}(1)\bullet \varphi_{-½}(2)]$

$[S_z(1) + S_z(2)]\, (1/\sqrt{2})[\varphi_{-½}(1)\bullet \varphi_{½}(2) - \varphi_{½}(1)\bullet \varphi_{-½}(2)]$

$= 0\, (1/\sqrt{2})\, [\varphi_{-½}(1)\bullet \varphi_{½}(2) - \varphi_{½}(1)\bullet \varphi_{-½}(2)]$

(d) To prove that the nondegenerate eigenfunctions of S_z are also eigenfunctions of S^2:

$\mathbf{S}^2 = \mathbf{S}(1)^2 + 2\, \mathbf{S}(1)\bullet\mathbf{S}(2) + \mathbf{S}(2)^2$ where $\mathbf{S}(1)^2 = S_x(1)^2 + S_y(1)^2 + S_z(1)^2$

$\mathcal{S}_+(1)\,\mathcal{S}_-(1) =[S_x(1)+ i\, S_y(1)][S_x(1) - i\, S_y(1)] = S_x(1)^2 - iS_x(1)\, S_y(1) + i\, S_y(1)\, S_x(1) + S_y(1)^2$

$\mathcal{S}_-(1)\,\mathcal{S}_+(1) =[S_x(1)- i\, S_y(1)][S_x(1) + i\, S_y(1)] = S_x(1)^2 + iS_x(1)\, S_y(1) - i\, S_y(1)\, S_x(1) + S_y(1)^2$

$½\, \mathcal{S}_+(1)\,\mathcal{S}_-(1) +½\, \mathcal{S}_-(1)\,\mathcal{S}_+(1) = S_x(1)^2 + S_y(1)^2$

$\mathbf{S}(1)^2 = ½\, \mathcal{S}_+(1)\,\mathcal{S}_-(1) +½\, \mathcal{S}_-(1)\,\mathcal{S}_+(1) + S_z(1)^2$

$\mathbf{S}(2)^2 = ½\, \mathcal{S}_+(2)\,\mathcal{S}_-(2) +½\, \mathcal{S}_-(2)\,\mathcal{S}_+(2) + S_z(2)^2$

$2\mathbf{S}(1)\bullet\mathbf{S}(2) = \{\mathcal{S}_+(1)\mathcal{S}_-(2) + \mathcal{S}_-(1)\mathcal{S}_+(2) + 2S_z(1)S_z(2)\}$ from proof in part (c)

Therefore, the $\mathbf{S}^2$ operator is

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

$+ ½\, \mathcal{S}_+(2)\,\mathcal{S}_-(2) +½\, \mathcal{S}_-(2)\,\mathcal{S}_+(2) + S_z(2)^2 +\{\mathcal{S}_+(1)\mathcal{S}_-(2) + \mathcal{S}_-(1)\mathcal{S}_+(2) + 2S_z(1)S_z(2)\}$

Note that $\mathcal{S}_+(1)\, \varphi_{½}(1) = 0$ since $+½\hbar$ is the highest eigenvalue, cannot raise it.

and $\mathcal{S}_-(1)\, \varphi_{-½}(1) = 0$ since $-½\hbar$ is the lowest eigenvalue, cannot lower it.

$\mathcal{S}_-(1)\, \varphi_{½}(1) = \hbar\varphi_{-½}(1)$ and $\mathcal{S}_+(1)\, \varphi_{-½}(1) = \hbar\varphi_{½}(1)$ using $[s(s+1)- m(m\pm1)]^{½}\,\hbar$

$\mathbf{S}^2\varphi_{½}(1)\bullet\varphi_{½}(2) = ½\hbar^2\varphi_{½}(1)\bullet\varphi_{½}(2)+0+(½\hbar)^2\varphi_{½}(1)\bullet\varphi_{½}(2) +½\hbar^2\varphi_{½}(1)\bullet\varphi_{½}(2)+0$
$+(½\hbar)^2\varphi_{½}(1)\bullet\varphi_{½}(2)+0+0+2(½\hbar)^2\varphi_{½}(1)\bullet\varphi_{½}(2) = 2\hbar^2\varphi_{½}(1)\bullet\varphi_{½}(2)$

$= s(s+1)\,\hbar^2\varphi_{1/2}(1)\bullet\varphi_{1/2}(2)$ where s=1 Yes, an eigenfunction of $\mathbf{S}^2$

Similarly

$\mathbf{S}^2\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2) = 0 + \tfrac{1}{2}\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2) + (-\tfrac{1}{2})^2\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2) + 0 + \tfrac{1}{2}\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2)$
$+ (-\tfrac{1}{2})^2\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2) + 0 + 0 + 2(-\tfrac{1}{2})^2\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2) = 2\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2)$

$= s(s+1)\,\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2)$ where s=1 Yes, an eigenfunction of $\mathbf{S}^2$

Check if $(1/\sqrt{2})[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$ is an eigenfunction of $\mathbf{S}^2$,
we find,

$[\tfrac{1}{2}\mathcal{S}_+(1)\mathcal{S}_-(1) + \tfrac{1}{2}\mathcal{S}_-(1)\mathcal{S}_+(1) + S_z(1)^2$
$+ \tfrac{1}{2}\mathcal{S}_+(2)\mathcal{S}_-(2) + \tfrac{1}{2}\mathcal{S}_-(2)\mathcal{S}_+(2) + S_z(2)^2 + \{\mathcal{S}_+(1)\mathcal{S}_-(2) + \mathcal{S}_-(1)\mathcal{S}_+(2) + 2S_z(1)S_z(2)\}]$
$(1/\sqrt{2})[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = ?$

$\tfrac{1}{2}\mathcal{S}_+(1)\mathcal{S}_-(1)[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = \tfrac{1}{2}[0 - \hbar^2\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$

$\tfrac{1}{2}\mathcal{S}_-(1)\mathcal{S}_+(1)[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = \tfrac{1}{2}[\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - 0]$

$\tfrac{1}{2}\mathcal{S}_+(2)\mathcal{S}_-(2)[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = \tfrac{1}{2}[\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - 0]$

$\tfrac{1}{2}\mathcal{S}_-(2)\mathcal{S}_+(2)[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = \tfrac{1}{2}[0 - \hbar^2\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$

$\mathcal{S}_+(1)\mathcal{S}_-(2)[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = \hbar^2\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2) - 0$

$\mathcal{S}_-(1)\mathcal{S}_+(2)[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = 0 - \hbar^2\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2)$

$\{\tfrac{1}{2}\mathcal{S}_+(1)\mathcal{S}_-(1) + \tfrac{1}{2}\mathcal{S}_-(1)\mathcal{S}_+(1)\}[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$
$= \tfrac{1}{2}\hbar^2[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$

$\{\tfrac{1}{2}\mathcal{S}_+(2)\mathcal{S}_-(2) + \tfrac{1}{2}\mathcal{S}_-(2)\mathcal{S}_+(2)\}[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$
$= \tfrac{1}{2}\hbar^2[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$

$\{\mathcal{S}_+(1)\mathcal{S}_-(2) + \mathcal{S}_-(1)\mathcal{S}_+(2)\}[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$
$= -\hbar^2[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$

$S_z(1)^2[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = (-\tfrac{1}{2})(-\tfrac{1}{2})\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - (\tfrac{1}{2})(\tfrac{1}{2})\hbar^2\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)$
$= \tfrac{1}{4}\hbar^2[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$

$S_z(2)^2[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = (\tfrac{1}{2})(\tfrac{1}{2})\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - (-\tfrac{1}{2})(-\tfrac{1}{2})\hbar^2\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)$
$= \tfrac{1}{4}\hbar^2[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$

$2S_z(1)S_z(2)[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = 2\{(-\tfrac{1}{2})(\tfrac{1}{2})\hbar^2\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2)$
$- (\tfrac{1}{2})(-\tfrac{1}{2})\hbar^2\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)\} = -\tfrac{1}{2}\hbar^2[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) - \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$

altogether we get 0. Yes, an eigenfunction of $\mathbf{S}^2$ with eigenvalue 0.

Check if $(1/\sqrt{2})[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) + \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$ is an eigenfunction of $\mathbf{S}^2$
we find,

$[\tfrac{1}{2}\mathcal{S}_+(1)\mathcal{S}_-(1) + \tfrac{1}{2}\mathcal{S}_-(1)\mathcal{S}_+(1) + S_z(1)^2$
$+ \tfrac{1}{2}\mathcal{S}_+(2)\mathcal{S}_-(2) + \tfrac{1}{2}\mathcal{S}_-(2)\mathcal{S}_+(2) + S_z(2)^2 + \{\mathcal{S}_+(1)\mathcal{S}_-(2) + \mathcal{S}_-(1)\mathcal{S}_+(2) + 2S_z(1)S_z(2)\}]$
$(1/\sqrt{2})[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) + \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = ?$

$\tfrac{1}{2}\mathcal{S}_+(1)\mathcal{S}_-(1)[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) + \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)] = \tfrac{1}{2}[0 + \hbar^2\varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$

$\frac{1}{2}\, S_-(1)\, S_+(1)\, [\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)] = \frac{1}{2}[\hbar^2\varphi_{-½}(1)\bullet\varphi_{½}(2)+0]$

$\frac{1}{2}\, S_+(2)\, S_-(2)\, [\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)] = \frac{1}{2}[\hbar^2\varphi_{-½}(1)\bullet\varphi_{½}(2)+0]$

$\frac{1}{2}\, S_-(2)\, S_+(2)\, [\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)] = \frac{1}{2}[0+ \hbar^2\varphi_{½}(1)\bullet\varphi_{-½}(2)]$

$S_+(1)S_-(2)\, [\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)] = \hbar^2\varphi_{½}(1)\bullet\varphi_{-½}(2)+0$

$S_-(1)S_+(2)\, [\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)] =0 + \hbar^2\varphi_{-½}(1)\bullet\varphi_{½}(2)$

$\{\frac{1}{2}\, S_+(1)\, S_-(1)+\frac{1}{2}\, S_-(1)\, S_+(1)\}\, [\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$

$=\frac{1}{2}\hbar^2[\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$

$\{\frac{1}{2}\, S_+(2)\, S_-(2) +\frac{1}{2}\, S_-(2)\, S_+(2)\}\, [\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$

$= \frac{1}{2}\hbar^2[\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$

$\{S_+(1)S_-(2) + S_-(1)S_+(2)\}\, [\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$

$= \hbar^2[\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$

$S_z(1)^2\, [\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)] = (-\frac{1}{2})(-\frac{1}{2})\hbar^2\varphi_{-½}(1)\bullet\varphi_{½}(2) + (\frac{1}{2})(\frac{1}{2})\hbar^2\varphi_{½}(1)\bullet\varphi_{-½}(2)$

$= \frac{1}{4}\hbar^2[\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$

$S_z(2)^2\, [\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)] = (\frac{1}{2})(\frac{1}{2})\hbar^2\varphi_{-½}(1)\bullet\varphi_{½}(2) + (-\frac{1}{2})(-\frac{1}{2})\hbar^2\varphi_{½}(1)\bullet\varphi_{-½}(2)$

$= \frac{1}{4}\hbar^2[\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$

$2S_z(1)S_z(2)[\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)] =2\{(-\frac{1}{2})(\frac{1}{2})\hbar^2\varphi_{-½}(1)\bullet\varphi_{½}(2)$

$+ (\frac{1}{2})(-\frac{1}{2})\hbar^2\varphi_{½}(1)\bullet\varphi_{-½}(2)\}= -\frac{1}{2}\hbar^2[\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$

altogether we get $2\hbar^2[\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$. Yes, an eigenfunction of $\mathbf{S}^2$ with eigenvalue $2\hbar^2$.

Collecting all eigenfunctions of BOTH $\mathbf{S}^2$ and $\mathbf{S}_z$:

	eigenvalue of $\mathbf{S}_z$	M_s	eigenvalue of $\mathbf{S}^2$	S
$\varphi_{½}(1)\bullet\varphi_{½}(2)$	$\hbar$	1	$2\hbar^2$	1
$\varphi_{-½}(1)\bullet\varphi_{-½}(2)$	$-\hbar$	-1	$2\hbar^2$	1
$(1/\sqrt{2})[\varphi_{-½}(1)\bullet\varphi_{½}(2) + \varphi_{½}(1)\bullet\varphi_{-½}(2)]$	0	0	$2\hbar^2$	1
$(1/\sqrt{2})[\varphi_{-½}(1)\bullet\varphi_{½}(2) - \varphi_{½}(1)\bullet\varphi_{-½}(2)]$	0	0	0	0

(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)

To find out if it is possible to simultaneously know S_z for the biradical and also R, we need to find out if S_z commutes with R_{op}.

$[S_z, R_{op}] = a_1\, [S_z, S_z(1)] + a_2\, [S_z, S_z(1)] + J[S_z, \mathbf{S}(1)\bullet\mathbf{S}(2)]$

Since $S_z = S_z(1) + S_z(2)$, then S_z commutes with both $S_z(1)$ and with $S_z(2)$.

We proved that $\mathbf{S}(1)\bullet\mathbf{S}(2) = \{\, \frac{1}{2}\, S_+(1)S_-(2) + \frac{1}{2}\, S_-(1)S_+(2) + S_z(1)S_z(2)\, \}$

We need to find out, does S_z commute with $S_+(1)S_-(2)$?

$[S_z(1) + S_z(2), S_+(1)S_-(2)]$=? We have seen that $[L_+, L_z] = -i\hbar L_+$ Therefore, we can write $[S_+(1), S_z(1)] = -i\hbar S_+(1)$ or $[S_z(1), S_+(1)] = i\hbar S_+(1)$

$[\mathcal{S}_-(1), S_z(1)] = i\hbar\mathcal{S}_-(1)$ or $[S_z(1), \mathcal{S}_-(1)] = -i\hbar\mathcal{S}_-(1)$

$[S_z(1) + S_z(2), \mathcal{S}_+(1)\mathcal{S}_-(2)] = [S_z(1), \mathcal{S}_+(1)\mathcal{S}_-(2)] + [S_z(2), \mathcal{S}_+(1)\mathcal{S}_-(2)]$

$= i\hbar S_+(1)\mathcal{S}_-(2) - i\hbar\mathcal{S}_+(1)\mathcal{S}_-(2) = 0.$

Similarly, $[S_z(1) + S_z(2), \mathcal{S}_-(1)\mathcal{S}_+(2)] = [S_z(1), \mathcal{S}_-(1)\mathcal{S}_+(2)] + [S_z(2), \mathcal{S}_-(1)\mathcal{S}_+(2)]$

$= -i\hbar\mathcal{S}_-(1)\mathcal{S}_+(2) + i\hbar\mathcal{S}_-(1)\mathcal{S}_+(2) = 0$

Although neither $S_z(1)$ nor $S_z(2)$ individually commute with $\mathcal{S}_+(1)\mathcal{S}_-(2)$, the sum $S_z(1)+S_z(2)$ does commute with $\mathcal{S}_+(1)\mathcal{S}_-(2)$!

Finally $[S_z(1) + S_z(2), S_z(1)S_z(2)] = 0$ since each of Sz(1) and Sz(2) commute with this operator. Since S_z commutes with every term in R_{op}, then $[S_z, R_{op}] = 0$

The zero commutator means that there are no limitations to the errors in their simultaneous measurements since the uncertainty principle states that

$\sigma_S \sigma_R \geq \frac{1}{2}\langle \mathbf{[S, R]}/i\rangle$.

(f) Find the average value of R under various conditions:

(i) The average value of R 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 $1\hbar$.

$R_{op} = a_1S_z(1) + a_2S_z(2) + J\mathbf{S}(1)\bullet\mathbf{S}(2)$ In part (d) we found the eigenstate of S_z corresponding to the eigenvalue $1\hbar$ is

$\varphi_{1/2}(1)\bullet\varphi_{1/2}(2)$

$\langle R\rangle = \int \varphi_{1/2}(1)^*\bullet\varphi_{1/2}(2)^*[a_1S_z(1) + a_2S_z(2) + J\mathbf{S}(1)\bullet\mathbf{S}(2)]\,\varphi_{1/2}(1)\bullet\varphi_{1/2}(2)d\tau_1d\tau_2$

$= a_1\frac{1}{2}\hbar + a_2\frac{1}{2}\hbar$

$+ J\int\varphi_{1/2}(1)\bullet\varphi_{1/2}(2)\{\frac{1}{2}\mathcal{S}_+(1)\mathcal{S}_-(2) + \frac{1}{2}\mathcal{S}_-(1)\mathcal{S}_+(2) + S_z(1)S_z(2)\}\varphi_{1/2}(1)\bullet\varphi_{1/2}(2)d\tau_1d\tau_2$

$= a_1\frac{1}{2}\hbar + a_2\frac{1}{2}\hbar + J[0 + 0 + (\frac{1}{2}\hbar)^2]$ where $a_1 = 2/\hbar$, $a_2 = 2/\hbar$, $J = 4/\hbar^2$.

$= 2/\hbar\frac{1}{2}\hbar + 2/\hbar\frac{1}{2}\hbar + 4/\hbar^2(\frac{1}{2}\hbar)^2 = 1+1+1 = 3$

(ii) The average value of R 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 $-1\hbar$.

In part (d) we found the eigenstate of S_z corresponding to the eigenvalue $-1\hbar$ is

$\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2)$.

$\langle R\rangle = \int \varphi_{-1/2}(1)^*\bullet\varphi_{-1/2}(2)^*[a_1S_z(1) + a_2S_z(2) + J\mathbf{S}(1)\bullet\mathbf{S}(2)]\,\varphi_{-1/2}(1)\bullet\varphi_{-1/2}(2)d\tau_1d\tau_2$

$= -a_1\frac{1}{2}\hbar - a_2\frac{1}{2}\hbar + J[0+0+(-\frac{1}{2}\hbar)^2] = -1-1+1 = -1$

(iii) The average value of R 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 $0\hbar$ and in an eigenstate of S^2 corresponding to the eigenvalue $2\hbar^2$.

In part (d) we found this eigenstate: $(1/\sqrt{2})[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) + \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]$

$\langle R\rangle = \frac{1}{2}\int [\varphi_{-1/2}(1)^*\bullet\varphi_{1/2}(2)^* + \varphi_{1/2}(1)^*\bullet\varphi_{-1/2}(2)^*]\,[a_1S_z(1) + a_2S_z(2) + J\mathbf{S}(1)\bullet\mathbf{S}(2)]$

$[\varphi_{-1/2}(1)\bullet\varphi_{1/2}(2) + \varphi_{1/2}(1)\bullet\varphi_{-1/2}(2)]\,d\tau_1d\tau_2$

$= \frac{1}{2}\{-a_1 \frac{1}{2}\hbar + a_1 \frac{1}{2}\hbar + a_2 \frac{1}{2}\hbar - a_2 \frac{1}{2}\hbar + J \int[\varphi_{-1/2}(1)^* \bullet \varphi_{1/2}(2)^* + \varphi_{1/2}(1)^* \bullet \varphi_{-1/2}(2)^*]\{\frac{1}{2} S_+(1) S_-(2)$
$+ \frac{1}{2} S_-(1) S_+(2) + S_z(1)S_z(2)\} [\varphi_{-1/2}(1) \bullet \varphi_{1/2}(2) + \varphi_{1/2}(1) \bullet \varphi_{-1/2}(2)]\, d\tau_1 d\tau_2 \}$
$= \frac{1}{2} J \{\frac{1}{2}\hbar^2 + \frac{1}{2}\hbar^2 + (-\frac{1}{2})(\frac{1}{2})\hbar^2 + (\frac{1}{2})(-\frac{1}{2})\hbar^2 \} = \frac{1}{4} J\hbar^2 = 1$ for $J = 4/\hbar^2$.

4. (a) Find the eigenvalues of $R_{op} = a_1 I_z(1)/\hbar + a_2 I_z(2)/\hbar + J\mathbf{I}(1) \bullet \mathbf{I}(2) / \hbar^2$ such that $\langle R_{op} \rangle$ is in Hz. We start with a complete orthonormal set of functions that we already know: the eigenfunctions of S_z. These are

eigenfunctions of $I_{z,total} = [I_z(1) + I_z(2)]$	eigenvalues of $I_{z,total} = [I_z(1) + I_z(2)]$
$\varphi_1 = \alpha(1) \bullet \alpha(2)$	$\hbar$
$\varphi_2 = \alpha(1) \bullet \beta(2)$	0
$\varphi_3 = \beta(1) \bullet \alpha(2)$	0
$\varphi_4 = \beta(1) \bullet \beta(2)$	$-\hbar$

(b) Since R_{op} and S_z have been shown to commute in part 3e above, the eigenfunctions of S_z which are non-degenerate are also eigenfunctions of R_{op}. Thus, $\Psi_1 = \psi_1$ and $\Psi_4 = \psi_{-1}$. Since R_{op} and S_z have been shown to commute, a suitable linear combination of the degenerate functions of S_z can be found which are eigenfunctions of R_{op}. Any linear combination of degenerate eigenfunctions of S_z are also eigenfunctions of S_z. We have to do the work to find these linear combinations so they are eigenfunctions of R_{op}. Let the combination be written (as suggested in the problem set) as $\Psi_2 = (\cos x)\psi_{0a} - (\sin x)\psi_{0b}$ and $\Psi_3 = (\sin x)\psi_{0a} + (\cos x)\psi_{0b}$. This is a useful strategy to ensure that the linear combinations are orthogonal and also normalized, using the properties of sin and cos ($\sin^2 x + \cos^2 x = 1$). There is no significance to the angle x, it is merely a crutch to ensure orthonormality.
After we do matrix representations of operators and operator equations, we will be able to solve for the eigenfunctions and eigenvalues (in Problem Set 9).

The eigenstates	eigenvalues of R_{op}
$\Psi_1 = \varphi_1 = \alpha(1) \bullet \alpha(2)$	$\frac{1}{2} a_1 + \frac{1}{2} a_2 + (\frac{1}{2})^2 J$
$\Psi_2 = \cos x\, \alpha(1) \bullet \beta(2) + \sin x\, \beta(1) \bullet \alpha(2)$	$\frac{1}{2} D - \frac{1}{4} J$
$\Psi_3 = -\sin x\, \alpha(1) \bullet \beta(2) + \cos x\, \beta(1) \bullet \alpha(2)$	$-\frac{1}{2} D - \frac{1}{4} J$
$\Psi_4 = \varphi_4 = \beta(1) \bullet \beta(2)$	$-\frac{1}{2} a_1 - \frac{1}{2} a_2 + (\frac{1}{2})^2 J$

where $D = [(a_2 - a_1)^2 + J^2]^{1/2}$ $\sin 2x = J/D$, $\cos 2x = (a_1 - a_2)/D$. In the limit $J << |(a_1 - a_2)|$, $x = 0°$, the $\alpha(1) \bullet \beta(2)$ and $\beta(1) \bullet \alpha(2)$ functions are not mixed.
(c) The order of the energy levels depend on signs of a_1, a_2. For protons,

----------$\beta(1) \bullet \beta(2)$

----------$\alpha(1) \bullet \alpha(2)$

(d) Intensities depend on the square of the transition integral
$\int\Psi_1 * \{½ [I_+(1) + I_-(1)] + ½ [I_+(2) + I_-(2)] \}\Psi_2 \, d\tau_1 d\tau_2$ for the transition between eigenstates Ψ_1 and Ψ_2
$\iint\alpha (1)^*\bullet\alpha(2)^* \{½ [I_+(1) + I_-(1)] + ½ [I_+(2) + I_-(2)] \} [\cos x\, \alpha(1)\bullet\beta(2) + \sin x\, \beta(1)\bullet\alpha(2)] \, d\tau_1 d\tau_2$
Note that $I_+(1)\alpha(1)\bullet\beta(2)$ gives zero. $I_-(1)\, \alpha(1)\bullet\beta(2)$ gives $\beta(1)\bullet\beta(2)$ and so on. However, it is not necessary to look at every term,. Because of orthonormality of the eigenfunctions of a Hermitian operator such as $[I_z(1) + I_z(2)]$, only those ladder operations which turn the function on the right into $\alpha(1)\bullet\alpha(2)$ can contribute to the integral. In this case, only $I_+(2)\alpha(1)\bullet\beta(2)$ and $I_+(1)\beta(1)\bullet\alpha(2)$ give non-zero contributions.
$\iint\alpha (1)^*\bullet\alpha(2)^*\, ½ \cos x\, \alpha(1)\bullet\alpha(2) + ½ \sin x\,\alpha(1)\bullet\alpha(2)\, d\tau_1 d\tau_2 = ½ [\cos x + \sin x]$
The square of this integral is $¼ \cos^2 x+\sin^2 x+2\sin x\cos x = ¼[1+\sin 2x]$
using the identity $2\sin x\cos x =\sin 2x$

Transition	Transition integral	intensity of peak
$\Psi_1 \rightarrow \Psi_2$	$\iint\alpha (1)^*\bullet\alpha(2)^* \{½ [I_+(1) + I_-(1)] + ½ [I_+(2) + I_-(2)]\} [\cos x\, \alpha(1)\bullet\beta(2) + \sin x\, \beta(1)\bullet\alpha(2)]\, d\tau_1 d\tau_2 = ½ [\cos x+ \sin x]$	$¼[1+\sin 2x]$
$\Psi_1 \rightarrow \Psi_3$	$\iint\alpha (1)^*\bullet\alpha(2)^* \{½ [I_+(1) + I_-(1)] + ½ [I_+(2) + I_-(2)]\} [-\sin x\, \alpha(1)\bullet\beta(2) + \cos x\, \beta(1)\bullet\alpha(2)]\, d\tau_1 d\tau_2 = ½ [-\sin x+ \cos x]$	$¼[1-\sin 2x]$
$\Psi_1 \rightarrow \Psi_4$	$\iint\alpha (1)^*\bullet\alpha(2)^* \{½ [I_+(1) + I_-(1)] + ½ [I_+(2) + I_-(2)]\}\beta(1)\bullet\beta(2)\, d\tau_1 d\tau_2 = 0$	0
$\Psi_2 \rightarrow \Psi_3$	$\iint [\cos x\, \alpha(1)\bullet\beta(2) + \sin x\, \beta(1)\bullet\alpha(2)] \{½ [I_+(1) + I_-(1)] + ½ [I_+(2) + I_-(2)]\} [-\sin x\, \alpha(1)\bullet\beta(2) + \cos x\, \beta(1)\bullet\alpha(2)] = 0$	0
$\Psi_2 \rightarrow \Psi_4$	$\iint\beta(1)^*\bullet\beta(2)^* \{½ [I_+(1) + I_-(1)] + ½ [I_+(2) + I_-(2)]\} [\cos x\, \alpha(1)\bullet\beta(2) + \sin x\, \beta(1)\bullet\alpha(2)]\, d\tau_1 d\tau_2 = ½ [\cos x+ \sin x]$	$¼[1+\sin 2x]$
$\Psi_3 \rightarrow \Psi_4$	$\iint\beta(1)^*\bullet\beta(2)^* \{½ [I_+(1) + I_-(1)] + ½ [I_+(2) + I_-(2)]\} [-\sin x\, \alpha(1)\bullet\beta(2) + \cos x\, \beta(1)\bullet\alpha(2)]\, d\tau_1 d\tau_2 =½ [-\sin x+ \cos x]$	$¼[1-\sin 2x]$

(e) See next pages for spectra
(f) When $a_1 = a_2$, this makes x = 45° maximum mixing

The eigenstates	eigenvalues of R_{op}	transition freqs
$\Psi_1 = \varphi_1 = \alpha (1)\bullet\alpha(2)$	$a_1 + (½)^2 J$	$1 \rightarrow 2 = - a_1$
$\Psi_2 = [\alpha(1)\bullet\beta(2) + \beta(1)\bullet\alpha(2)]\sqrt{2}$	¼J	$2 \rightarrow 4= - a_1$
$\Psi_3 = [- \alpha(1)\bullet\beta(2) + \beta(1)\bullet\alpha(2)]\sqrt{2}$	¼J	$1 \rightarrow 3 =- a_1$
$\Psi_4 = \varphi_4 = \beta (1)\bullet\beta(2)$	$- a_1 + (½)^2 J$	$3 \rightarrow 4= - a_1$

A single peak is observed and although J is non-zero, its value can not be observed.

Simple example: The AX system

- Equation 4 is the secular determinant that needs to be solved to obtain the eigenvalues (energies) and eigenfunctions (wave functions)
- The elements $<\Psi_m|\mathcal{H}|\Psi_n>$ are given from Eq. 2 and the wave functions Ψ are the basic wave functions for this system, *ie* the states αα, αβ etc
- The secular determinant for this AB system will be a 4 × 4 determinant which is shown schematically below

A	B	m_T	αα	αβ	βα	ββ
α	α	1	<αα | H | αα> - E	0	0	0
α	β	0	0			0
β	α	0	0			0
β	β	-1	0	0	0	

= 0

The diagonal elements of this determinant are computed from Eq. 3. All off-diagonal elements between wave functions with different m_T equal zero.

The determinant has now been broken down to two single determinants (elements) and one 2 × 2 determinant for the αβ and βα wave functions

Using the variational method of quantum mechanics we obtain the coefficients for the linear combination of wave functions αβ and βα

Continuing with the variational method and using an angle, θ, which is related to the mixing coefficients we obtain

$$\sin 2\theta = \frac{J}{D}$$

$$\cos 2\theta = \frac{(\nu_A - \nu_B)}{D}$$

$$D = \sqrt{(\nu_B - \nu_A)^2 + J^2}$$

The stationary states and the corresponding energies are easily calculated using these new terms

See http://cartwright.chem.ox.ac.uk/tlab/603/ab2.html for an example of the changing NMR spectrum for two protons, as you change the values of J and chemical shift.

Level number	Spin function	Energy (in frequency units)
4	$\beta\beta$	$\frac{\nu_A + \nu_B}{2} + \frac{J}{4}$
3	$\cos\theta\ \alpha\beta + \sin\theta\ \beta\alpha$	$\frac{D}{2} - \frac{J}{4}$
2	$-\sin\theta\ \alpha\beta + \cos\theta\ \beta\alpha$	$-\frac{D}{2} - \frac{J}{4}$
1	$\alpha\alpha$	$-\frac{\nu_A + \nu_B}{2} + \frac{J}{4}$

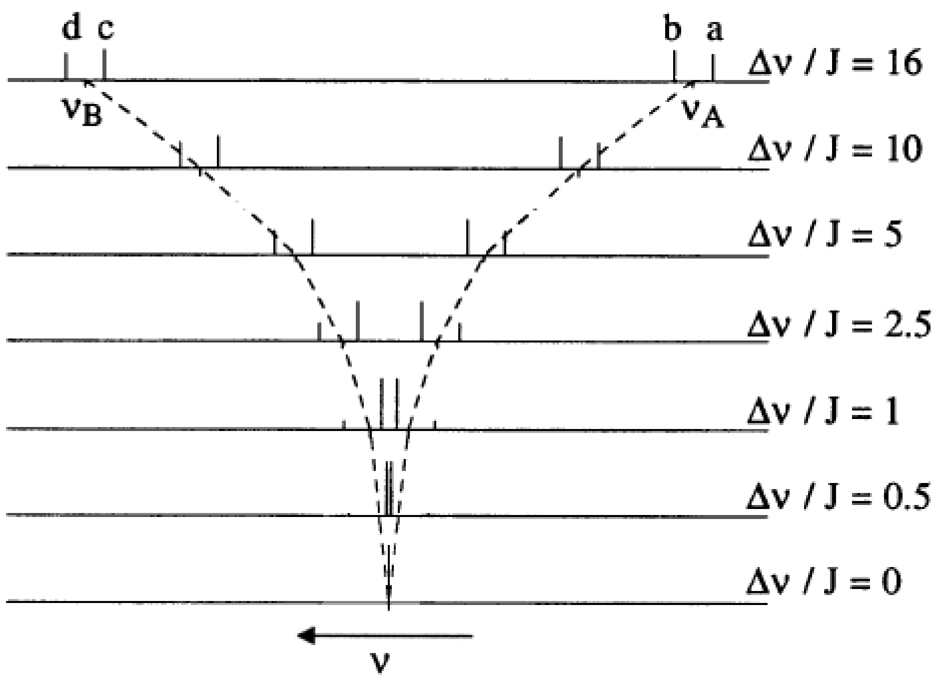
If $\delta\nu >> J$ (an AX system) then the term $D \approx \delta\nu$ and $\frac{J}{D} \approx 0$. Then follows that $\theta = 0°$ and the $\alpha\beta$ and $\beta\alpha$ spin functions are not mixed at all

If $\delta\nu = 0$ (an A_2 system) then the mixing is maximal and $\theta = 45°$

The same angle can be used to express the relative intensities of the resonance lines

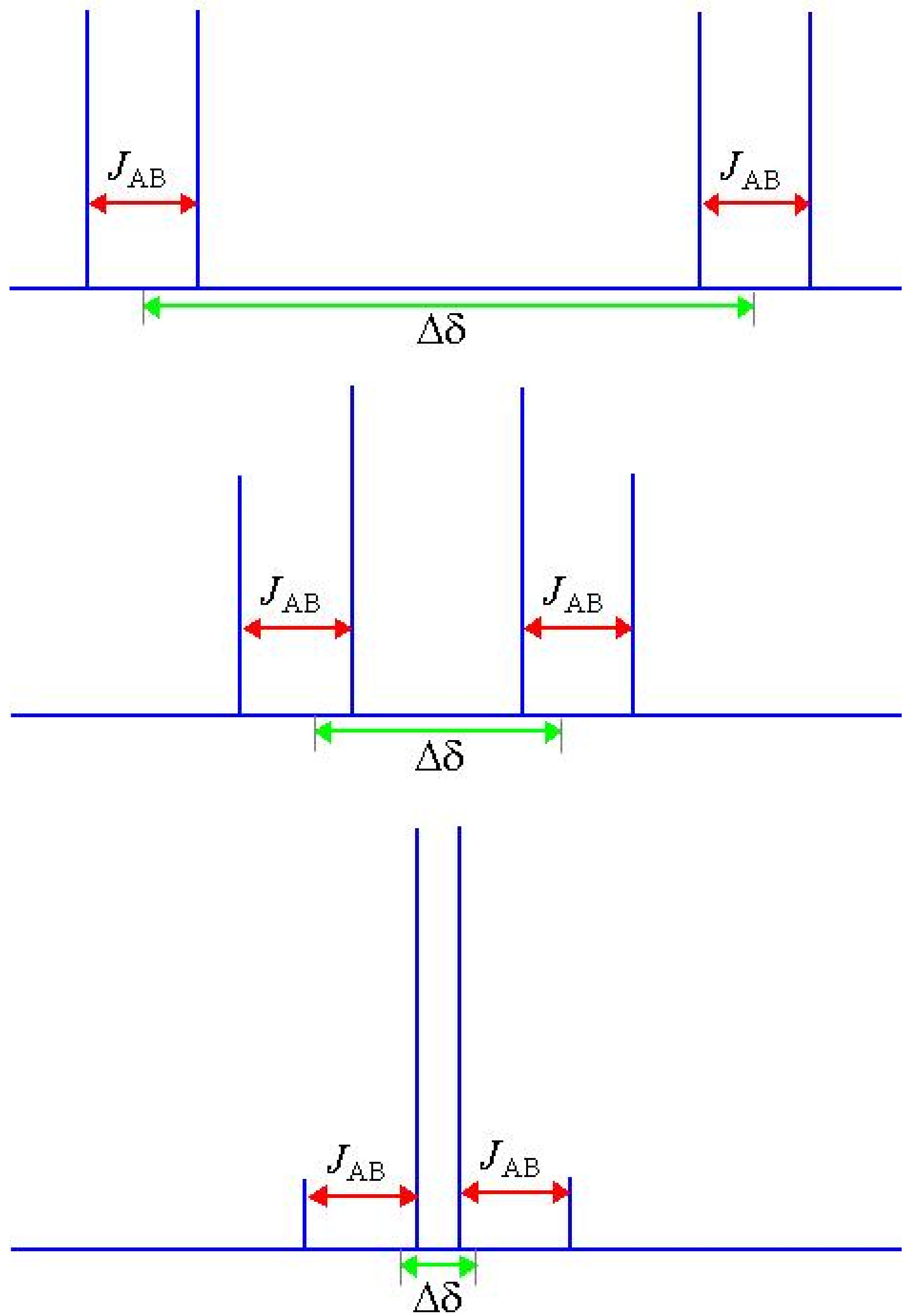
- The simple rules involving binomial coefficients (Pascal's triangle) are not useful in strongly coupled systems

Transition		Frequency	Relative Intensity
d	$2 \rightarrow 4$	$\frac{\nu_A + \nu_B}{2} + \frac{J}{2} + \frac{D}{2}$	$1 - \sin 2\theta$
b	$3 \rightarrow 4$	$\frac{\nu_A + \nu_B}{2} + \frac{J}{2} - \frac{D}{2}$	$1 + \sin 2\theta$
c	$1 \rightarrow 3$	$\frac{\nu_A + \nu_B}{2} - \frac{J}{2} + \frac{D}{2}$	$1 + \sin 2\theta$
a	$1 \rightarrow 2$	$\frac{\nu_A + \nu_B}{2} - \frac{J}{2} - \frac{D}{2}$	$1 - \sin 2\theta$



Simulated NMR spectra with a constant J of 5 Hz and varying ν_A and ν_B.

$\Delta\nu$ varies between 80 Hz and 0 Hz. Note the changes of intensities as well as the relative positions of the resonance lines and ν



J_{AB}
J_{AB}
$\Delta\delta$
J_{AB}
J_{AB}
$\Delta\delta$
J_{AB}
J_{AB}
$\Delta\delta$