1. Employ the commutation relation: $\frac{d\langle Q\rangle}{dt} = \frac{i}{\hbar}\langle [H,Q]\rangle + \langle \frac{\partial Q}{\partial t}\rangle$, where $\langle\frac{\partial Q}{\partial t}\rangle = 0$ since the operators are time-independent

$$\frac{d\langle J_x\rangle}{dt} = \frac{i}{\hbar}\langle [H,J_x]\rangle \; ; \; H \equiv \omega J_z$$

$$= \frac{i\omega}{\hbar}\langle [J_z,J_x]\rangle = \frac{i\omega}{\hbar}\langle i\hbar J_y\rangle = -\omega\langle J_y\rangle$$

Similarly $\frac{d\langle J_y\rangle}{dt} = \frac{i\omega}{\hbar}\langle [J_z,J_y]\rangle = +\omega\langle J_x\rangle$

$$\frac{d\langle J_z\rangle}{dt} = \frac{i\omega}{\hbar}\langle [J_z,J_z]\rangle = 0$$

These are coupled, first order differential equations. We can uncouple them by taking another derivative, but the price is that they become second-order.

$$\frac{d}{dt}\left[\frac{d\langle J_x\rangle}{dt}\right] = -\omega\frac{d\langle J_y\rangle}{dt} \quad \text{and} \quad \frac{d}{dt}\left[\frac{d\langle J_y\rangle}{dt}\right] = \omega\frac{d\langle J_x\rangle}{dt}$$

$$\frac{d^2\langle J_x\rangle}{dt^2} = -\omega^2\langle J_x\rangle \qquad\qquad \frac{d^2\langle J_y\rangle}{dt^2} = -\omega^2\langle J_y\rangle$$

If we guess $\langle J_x\rangle = A\cos(\alpha t) + B\sin(\beta t)$ $\qquad \langle J_y\rangle = C\cos(\delta t) + D\sin(\delta t)$

$$\frac{d\langle J_x\rangle}{dt} = A\alpha\sin(\alpha t) - B\beta\cos(\beta t) \qquad \frac{d\langle J_y\rangle}{dt} = C\delta\sin(\delta t) - D\delta\cos(\delta t)$$

$\therefore \alpha = \beta = \gamma = \delta = \omega$ and $A = -D$, $B = C$ and $A = \langle J_x(0)\rangle$, $C = \langle J_y(0)\rangle$

So $\langle J_x(t)\rangle = \langle J_x(0)\rangle\cos(\omega t) + \langle J_y(0)\rangle\sin(\omega t)$ and $\langle J_y(t)\rangle = \langle J_y(0)\rangle\cos(\omega t) - \langle J_x(0)\rangle\sin(\omega t)$

$$\vec{J} = \langle J_x(t)\rangle\hat{i} + \langle J_y(t)\rangle\hat{j} + \langle J_z(t)\rangle\hat{k} = [\langle J_x(0)\rangle + \langle J_y(0)\rangle]\cos(\omega t) + [\langle J_y(0)\rangle - \langle J_x(0)\rangle]\sin(\omega t)$$

This motion is an ellipse about the z-axis (which may be a circle depending on the initial conditions). The average expectation value precesses in the classical and quantum case, as Ehrenfest's Theorem requires. The difference in the quantum case is that only certain values of J_z are observed (quantization) and non-commuting operators $(J_x, J_y$ or $J_y, J_z,$ or $J_z, J_x)$ cannot simultaneously be known to arbitrary precision (uncertainty).

2. The key to doing this is to express the angular wavefunction as a linear combination of spherical harmonics with simple expectation values. This can be done mechanically by computing overlap integrals

$$|\psi\rangle = |R\rangle|\Theta\rangle \; ; \; \langle\theta,\phi|\Theta\rangle = N(1-\cos^3\theta)\sin\theta\cos\phi \; ; \; |\Theta\rangle = \sum_\ell\sum_m (\langle Y_{\ell m}|\Theta\rangle)|Y_{\ell m}\rangle$$

Radical part ↑   Angular part ↑

But let's eyeball it: $\underbrace{\sin\theta\cos\phi}_{\substack{\text{Looks like} \\ Y_1^{-1}-Y_1^1}} - \underbrace{\cos^3\theta\sin\theta\cos\phi}_{\substack{\text{Looks like} \\ Y_4^{-1}-Y_4^1}}$

So let's subtract $Y_1^{-1}, Y_1^1, Y_4^{-1}, Y_4^1$ from the function and see what's leftover:

What's leftover?

$$\begin{array}{c|cc}
 & |\Theta\rangle & \sin\theta\cos\phi - \cos^3\theta\sin\theta\cos\phi \\
\text{(add)}\downarrow & -n_1(|Y_1^{-1}\rangle + |Y_1^1\rangle) & -n_1\sqrt{\frac{3}{2\pi}}(e^{-i\phi}+e^{i\phi})\sin\theta \\
 & -n_2(|Y_4^{-1}\rangle + |Y_4^1\rangle) & -\frac{3n_2}{8}\sqrt{\frac{5}{\pi}}(e^{-i\phi}+e^{i\phi})\sin\theta(7\cos^3\theta - 3\cos\theta) \\
\hline
 & |\Theta\rangle - n_1(Y_1^{-1}+Y_1^1) - n_2(Y_4^{-1}+Y_4^1) & \sin\theta\cos\phi(1-\sqrt{\frac{3}{2\pi}}n_1) - (1+\frac{21}{4}\sqrt{\frac{5}{\pi}}n_2)\cos^3\theta\sin\theta\cos\phi \\
 & & \frac{9n_2}{4}\sqrt{\frac{5}{\pi}}\cos\theta\sin\theta\cos\phi
\end{array}$$

So if $n_1 = \sqrt{\frac{2\pi}{3}}$ and $n_2 = -\frac{4}{21}\sqrt{\frac{\pi}{5}}$, the we are left with a term that looks like $Y_2^{-1} + Y_2^1$

Remainder: $-\frac{3}{7}\cos\theta\sin\theta\cos\phi = n_3(Y_2^{-1} + Y_2^1) = n_3(\sqrt{\frac{15}{2\pi}}\cos\theta\sin\theta\cos\phi)$; $n_3 = -\frac{1}{7}\sqrt{\frac{6\pi}{5}}$

$\therefore |\Theta\rangle = -\frac{4}{21}\sqrt{\frac{\pi}{5}}(|Y_4^{-1}\rangle + |Y_4^1\rangle) - \frac{1}{7}\sqrt{\frac{6\pi}{5}}(|Y_2^{-1}\rangle + |Y_2^1\rangle) + \sqrt{\frac{2\pi}{3}}(|Y_1^{-1}\rangle + |Y_1^1\rangle)$

2a. If one performs a measurement of L^2, the possible outcomes are $\ell(\ell+1)\hbar^2$ for each spherical harmonic basis state or $20\hbar^2$ (if $\ell=4$ from $Y_4^{\pm1}$), $6\hbar^2$ (if $\ell=2$ from $Y_2^{\pm1}$), or $2\hbar^2$ (if $\ell=1$ from $Y_1^{\pm1}$).

If one performs a measurement of L_z, the possible outcomes are $+\hbar$ (if $m=1$ from $Y_4^1, Y_2^1,$ or Y_1^1) or $-\hbar$ (if $m=-1$ from $Y_4^{-1}, Y_2^{-1},$ or Y_1^{-1}).

b. The dipole moment operator $\hat{\mu}=e\hat{r}$ and the question is when is the expectation value $\langle n'\ell'm'|e\hat{r}|n\ell m\rangle \neq 0$

If we can express $\hat{r}$ as a spherical tensor or linear combination of spherical tensors, we can use the Wigner-Eckart theorem: $\langle n'\ell'm'|T_q^{(k)}|n\ell m\rangle = \dfrac{\langle n'\ell'\|T^{(k)}\|n\ell\rangle}{\sqrt{2\ell+1}}\langle \ell k; mq|\ell k; \ell'm'\rangle$

Since we're only worried about selection rules, we'll ignore the double-bar matrix element.

This is zero unless $m'=q+m$ and $|\ell-k|\leq\ell'\leq\ell+k$

If we realize $Q_1^1=\frac{1}{\sqrt{2}}(\hat{x}+i\hat{y})$; $Q_1^0=\hat{z}$; $Q_1^{-1}=\frac{1}{\sqrt{2}}(\hat{x}-i\hat{y})$

then $\hat{x}=Q_1^1+Q_1^{-1}$; $\hat{y}=Q_1^1-Q_1^{-1}$; $\hat{z}=Q_1^0$

For Q_1^0, $m'=0+m$ and $|\ell-1|\leq\ell'\leq\ell+1$, which is satisfied for $m'=m, \ell'=\ell$

For Q_1^1, $m'=1+m$, which can never be satisfied since $m,m'\in\{-1,1\}$ (we'd need $m=0$ or $m=2$)

For Q_1^{-1}, $m'=-1+m$, which also can never be satisfied.

Only Q_1^0 gives a non-zero matrix element, which means that only $\hat{z}$ can be non-zero and only a $\hat{z}$ dipole is allowed.

c. $M=e(3\hat{z}^2-\hat{r}^2)$ is already in spherical tensor form: $M=Q_2^0$

Thus, $m'=0+m$ and $|\ell-2|\leq\ell'\leq\ell+2$, which is satisfied for $m'=m, \ell'=\ell$.

This quadrupole moment is non-zero.

3a. Here we have four atoms and thus $2^4=16$ possible uncoupled states that will be mixed by the Hamiltonian to form coupled states. Since the Hamiltonian only "exchanges" spins or leaves them alone, it will be block diagonal. (ie, no spins are created without another annihilated)

This is clear in the isolated case:
$$\hat{H}_{isolated} = J\,\hat{S}_i\cdot\hat{S}_j = J(S_{ix}S_{jx}+S_{iy}S_{jy}+S_{iz}S_{jz})$$
$$= JS_{iz}S_{jz} + \frac{J}{2}(2S_{ix}S_{jx}+2S_{iy}S_{jy}+\underbrace{iS_{ix}S_{jy}-iS_{ix}S_{jy}}_{=0}+\underbrace{iS_{iy}S_{jx}-iS_{iy}S_{jx}}_{})$$
$$= JS_{iz}S_{jz} + \frac{J}{2}[(S_{ix}+iS_{iy})(S_{jx}-iS_{jy}) + \underbrace{(S_{ix}-iS_{iy})(S_{jx}+iS_{jy})}{}]$$
$$= JS_{iz}S_{jz} + \frac{J}{2}(S_i^+S_j^- + S_i^-S_j^+)$$

$\uparrow$ Moves an up spin from j to i $\quad$ $\uparrow$ Moves an up spin from i to j

Now in the molecule, $\hat{H}=J\hat{S}_1\cdot\hat{S}_2 +J'\hat{S}_2\cdot\hat{S}_3 + J\hat{S}_3\cdot\hat{S}_4+J'\hat{S}_4\cdot\hat{S}_1$; $J'\geq J$
$$=J(S_{1z}S_{2z}+S_{3z}S_{4z}+\tfrac{1}{2}(S_1^+S_2^-+S_1^-S_2^++S_3^+S_4^-+S_3^-S_4^+))$$
$$+J'(S_{2z}S_{3z}+S_{4z}S_{1z}+\tfrac{1}{2}(S_2^+S_3^-+S_2^-S_3^++S_4^+S_1^-+S_4^-S_1^+))$$

So since spin is "conserved", only matrix elements between two states with the same number of up spins are non-zero. Also, the Hamiltonian is Hermitian and completely symmetrical with respect to $\uparrow/\downarrow$, ie $\langle\uparrow\uparrow\uparrow\uparrow|\hat{H}|\uparrow\uparrow\uparrow\uparrow\rangle=\langle\downarrow\downarrow\downarrow\downarrow|\hat{H}|\downarrow\downarrow\downarrow\downarrow\rangle$ and $\langle\uparrow\uparrow--|\hat{H}|\uparrow\uparrow--\rangle=\langle-\uparrow\uparrow-|\hat{H}|-\uparrow\uparrow-\rangle$ etc

Finally, these matrix elements are simple to eyeball. There are two contributions:

$$H = \underbrace{J(S_{1z}S_{2z} + S_{3z}S_{4z}) + J'(S_{2z}S_{3z} + S_{4z}S_{1z})}_{} + \frac{J}{2}(S_1^+S_2^- + S_1^-S_2^+ + S_3^+S_4^- + S_3^-S_4^+) + \frac{J'}{2}(S_2^+S_3^- + S_2^-S_3^+ + S_4^+S_1^- + S_4^-S_1^+)$$

Does not flip any spins. Thus, these only contribute on the diagonal. Also, you can show that if there are an odd number of spins up, they will cancel to zero.

only contribute off-diagonal

$= \hbar^2$ if spin 1 is down and spin 2 is up on the ket and flipped on the bra,

since $S_1^+ S_2^- |-+\rangle = \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1)-(\frac{1}{2})(\frac{1}{2}-1)}$ $S_1^+ |--\rangle$

$= \hbar^2 \sqrt{\frac{1}{2}(\frac{1}{2}+1)-(-\frac{1}{2})(-\frac{1}{2}+1)}|+-\rangle$

$= \hbar^2 |+-\rangle$

etc··

So: $\langle ++++| H |++++\rangle = \frac{J+J'}{2}\hbar^2$

$$\begin{array}{c c} & \begin{matrix} +++- & ++-+ & +-++ & -+++ \end{matrix} \\ \begin{matrix} +++- \\ ++-+ \\ +-++ \\ -+++ \end{matrix} & \begin{bmatrix} 0 & \frac{J}{2}\hbar^2 & 0 & \frac{J'}{2}\hbar^2 \\ & 0 & \frac{J'}{2}\hbar^2 & 0 \\ & & 0 & \frac{J}{2}\hbar^2 \\ & & & 0 \end{bmatrix} \end{array}$$

$$\begin{array}{c c} & \begin{matrix} ++-- & +-+- & +--+ \end{matrix} \\ \begin{matrix} ++-- \\ +-+- \\ +--+ \end{matrix} & \begin{bmatrix} \frac{J-J'}{2}\hbar^2 & \frac{J'}{2}\hbar^2 & 0 \\ & -\frac{J+J'}{2}\hbar^2 & \frac{J}{2}\hbar^2 \\ & & \frac{J'-J}{2}\hbar^2 \end{bmatrix} \end{array}$$

That's all you need to evaluate!

(in units of $\hbar^2/2$):

$$H = \begin{pmatrix}
J+J' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & J & 0 & J' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & J & 0 & J' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & J' & 0 & J & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & J' & 0 & J & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & J-J' & J' & 0 & 0 & J' & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & J' & -J-J' & J & J & 0 & J' & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & J & -J+J' & 0 & J & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & J & 0 & -J+J' & J & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & J' & 0 & J & J & -J-J' & J' & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & J' & 0 & 0 & J & J-J' & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & J & 0 & J' & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & J & 0 & J' & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & J' & 0 & J & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & J' & 0 & J & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & J+J'
\end{pmatrix}
\begin{matrix}
++++ \\ +++- \\ ++-+ \\ +-++ \\ -+++ \\ ++-- \\ +-+- \\ +--+ \\ -++- \\ -+-+ \\ --++ \\ +--- \\ -+-- \\ --+- \\ ---+ \\ ----
\end{matrix}$$

Computing the eigenvalues & eigenvectors is straightforward. (a+b)

c) There are many ways to do this. Here is one way. Look at the lowest energy state in each part a, b

J	J'	Lowest Energy	++-- Coefficient	+--+ Coefficient	$\|$++-- Coefficient$\|^2$	$\|$+--+ Coefficient$\|^2$
1	2	-3.12	-0.437	-0.158	0.191	0.0249
$\frac{3}{2}$	$\frac{3}{2}$	-3.00	0.289	0.289	0.0833	0.0833

The ++-- state has electrons (2,3) and (1,4) paired. The ++-- state has electrons (1,2) and (3,4) paired. Thus, the ++-- state prefers the J' bonding while ++-- prefers J.

In part a, more electron density is in the J' favoring state, meaning that C_2-C_3 and C_4-C_1 contribute more to the stability. In part b, both states contribute equally and so the bonds are all equivalent, and overall weaker as shown by the less stable state.

Cyclobutadiene is anti-aromatic and is observed to have a rectangular structure.

4. Considering the transition state has no rotational angular momentum, $J = L + S = 0 + \frac{1}{2} = \frac{1}{2}$
The transition state is natural to describe in the coupled basis, while the product O atom is natural to describe in the uncoupled basis.

Thus, we do a C-G decomposition, assuming no rotational angular momentum.
$$j_1 = \frac{1}{2}, \; j_2 = 1, \; J = \frac{1}{2}, \; m_J = -\frac{1}{2}, \frac{1}{2} \;\rightarrow\; j_1 = \frac{1}{2}, \; m_{j_1} = -\frac{1}{2}, \frac{1}{2}, \; j_2 = 1, \; m_{j_2} = -1, 0, 1$$

Transition state   ·OH   O

$$|J, m_J\rangle \iff |m_{j_1}, m_{j_2}\rangle$$

$$|\tfrac{1}{2}, +\tfrac{1}{2}\rangle \iff \sqrt{\tfrac{2}{3}}\,|-\tfrac{1}{2}, 1\rangle - \sqrt{\tfrac{1}{3}}\,|+\tfrac{1}{2}, 0\rangle$$

$$|\tfrac{1}{2}, -\tfrac{1}{2}\rangle \iff \sqrt{\tfrac{1}{3}}\,|-\tfrac{1}{2}, 0\rangle - \sqrt{\tfrac{2}{3}}\,|+\tfrac{1}{2}, -1\rangle$$

Total $m_{j_2} = 0$ $\frac{1}{2} \times |-\sqrt{\tfrac{1}{3}}|^2 + \frac{1}{2} \times |\sqrt{\tfrac{1}{3}}|^2 = \frac{1}{3}$

$m_{j_2} = -1$ $\frac{1}{2} \times |-\sqrt{\tfrac{2}{3}}|^2 = \frac{1}{3}$ Each equally likely

$m_{j_2} = +1$ $\frac{1}{2} \times |\sqrt{\tfrac{2}{3}}|^2 = \frac{1}{3}$

Notice that although there are more possible $m_{j_2} = 0$ states $(0 + \frac{1}{2}, 0 - \frac{1}{2})$, each is less likely to occur so in the end each possibility is equally likely.

We can also consider the possibility that the OH radical carries off some rotational angular momentum, $L = 1$. The total spin $S = \frac{1}{2} + 1 = \frac{3}{2}$. To conserve total $J = \frac{1}{2}$, either $\substack{L = -1 \\ S = \frac{3}{2}}$ or $\substack{L = 1 \\ S = -\frac{1}{2}}$ keeping in mind $m_J = -\frac{1}{2}$ or $\frac{1}{2}$, we can C-G decompose this:

Now $j_1 = 1, \; m_{j_1} = -1, 0, 1, \; j_2 = \frac{3}{2}, \; m_{j_2} = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

$$\underset{\text{rotational ang mom}}{|J, m_J\rangle \iff |m_S, m_L\rangle} \qquad \underset{\text{spin ang mom}}{}$$

$\left(\substack{S = \frac{3}{2} \\ L = -1}\right)$

$$|\tfrac{1}{2}, +\tfrac{1}{2}\rangle \iff \sqrt{\tfrac{1}{2}}\,|-1, \tfrac{3}{2}\rangle - \sqrt{\tfrac{1}{3}}\,|0, \tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{6}}\,|1, -\tfrac{1}{2}\rangle \quad Ⓐ$$

$$|\tfrac{1}{2}, -\tfrac{1}{2}\rangle \iff \sqrt{\tfrac{1}{6}}\,|-1, \tfrac{1}{2}\rangle - \sqrt{\tfrac{1}{3}}\,|0, -\tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{2}}\,|1, -\tfrac{3}{2}\rangle \quad Ⓑ$$

$\left(\substack{S = -\frac{1}{2} \\ L = 1}\right)$

$$|\tfrac{1}{2}, \tfrac{1}{2}\rangle \iff \sqrt{\tfrac{2}{3}}\,|1, -\tfrac{1}{2}\rangle - \sqrt{\tfrac{1}{3}}\,|0, \tfrac{1}{2}\rangle \quad Ⓒ$$

$$|\tfrac{1}{2}, -\tfrac{1}{2}\rangle \iff \sqrt{\tfrac{1}{3}}\,|0, -\tfrac{1}{2}\rangle - \sqrt{\tfrac{2}{3}}\,|-1, \tfrac{1}{2}\rangle \quad Ⓓ$$

These expansions are still in a spin-coupled basis (although, decoupled from rotational ang mom).

One more step is needed:
$$|S, m_S\rangle \iff |m_{S_1}, m_{S_2}\rangle$$

$\substack{S = \frac{3}{2} \\ = 1 + \frac{1}{2}}$ $\Bigg($

$$|\tfrac{3}{2}, \tfrac{3}{2}\rangle = |1, \tfrac{1}{2}\rangle \quad Ⓔ$$

$$|\tfrac{3}{2}, \tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}\,|1, -\tfrac{1}{2}\rangle + \sqrt{\tfrac{2}{3}}\,|0, \tfrac{1}{2}\rangle \quad Ⓕ$$

$$|\tfrac{3}{2}, -\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\,|0, -\tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{3}}\,|1, \tfrac{1}{2}\rangle \quad Ⓖ$$

$$|\tfrac{3}{2}, -\tfrac{3}{2}\rangle = |-1, -\tfrac{1}{2}\rangle \quad Ⓗ$$

$\substack{S = -\frac{1}{2} \\ = -1 + \frac{1}{2}}$ $\Bigg($

$$|\tfrac{1}{2}, \tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\,|1, -\tfrac{1}{2}\rangle - \sqrt{\tfrac{1}{3}}\,|0, \tfrac{1}{2}\rangle \quad Ⓘ$$

$$|\tfrac{1}{2}, -\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}\,|0, -\tfrac{1}{2}\rangle - \sqrt{\tfrac{2}{3}}\,|-1, \tfrac{1}{2}\rangle \quad Ⓙ$$

Ⓐ, Ⓑ, Ⓒ, Ⓓ are each equally likely $(\frac{1}{4})$

The $m_{S_2} = 0$ terms give: $\frac{1}{4}\left(\frac{1}{3} \times \frac{2}{3} + \frac{1}{6} \times \frac{2}{3} + \frac{1}{6} \times \frac{2}{3} + \frac{1}{3} \times \frac{2}{3} + \frac{2}{3} \times \frac{1}{3} + \frac{1}{3} \times \frac{1}{3} + \frac{1}{3} \times \frac{1}{3} + \frac{2}{3} \times \frac{1}{3}\right) = \frac{1}{3}$

Ⓐ+Ⓕ   Ⓐ+Ⓖ   Ⓑ+Ⓕ   Ⓑ+Ⓖ   Ⓒ+Ⓙ   Ⓒ+Ⓘ   Ⓓ+Ⓙ   Ⓓ+Ⓘ

$m_{S_2} = 1$ terms give: $\frac{1}{4}\left(\frac{1}{2} \times 1 + \frac{1}{3} \times \frac{1}{3} + \frac{1}{6} \times \frac{1}{3} + \frac{1}{3} \times \frac{2}{3} + \frac{2}{3} \times \frac{2}{3}\right) = \frac{1}{3}$ and $m_{S_2} = -1$ must also be $\frac{1}{3}$

Ⓐ+Ⓔ   Ⓐ+Ⓕ   Ⓑ+Ⓕ   Ⓒ+Ⓘ   Ⓓ+Ⓘ   Since total $= 100\%$

So even considering rotational angular momentum, no preference for m_J of 0 is seen.

$OH (m_J = \frac{1}{2}) + O(m_J = 1)$ is possible (case Ⓔ) when the rotational angular momentum adds as -1 (first term in Ⓐ).

5. $V(\hat{q}) = \frac{1}{2} k \hat{q}^2 - \alpha \hat{q}^3 + \beta \hat{q}^4$; $H_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} k \hat{q}^2$, $H' = -\alpha \hat{q}^3 + \beta \hat{q}^4$ $(\hbar\omega = 1)$

and from perturbation theory:

$E_n^{(0)} = (n + \frac{1}{2})$, trivially

$E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle$

$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle|^2}{E_n - E_m}$

In the first order, only diagonal elements of H' contribute, but the diagonal elements of $\hat{q}^3$ are all zero since an odd number of raising/lowering operators must change the number of quanta. Only even powers of $\hat{q}$ can contribute to first order.

$\beta \langle n | \hat{q}^4 | n \rangle = \frac{\beta}{4} \langle n | (a^\dagger + a)^4 | n \rangle$, also there must be an equal number of a and $a^\dagger$

$= \frac{\beta}{4} \langle n | a^\dagger a^\dagger a a + a a a^\dagger a^\dagger + a^\dagger a a a^\dagger + a a^\dagger a^\dagger a + a a^\dagger a a^\dagger + a^\dagger a a^\dagger a | n \rangle$

Also, remember $a^\dagger a = \hat{N}$ and $a a^\dagger = (1 + \hat{N})$

$= \frac{\beta}{4} \langle n | a^\dagger \hat{N} a + a(1+N)a^\dagger + N(1+N) + (1+N)N + (1+N)^2 + N^2 | n \rangle$

$= \frac{\beta}{4} \left(n(n-1) + (n+1)(n+2) + n(1+n) + (1+n)n + (1+n)^2 + n^2 \right)$

$= \frac{\beta}{4} (6n^2 + 6n + 3)$

We want it to look like $X (n + \frac{1}{2})^2 + y = \frac{\beta}{4} (6n^2 + 6n + 3)$

$X n^2 + X n + \frac{X}{4} + y = \frac{\beta}{4} (6n^2 + 6n + 3)$

$X = \frac{3}{2}\beta$ and $y = \frac{3\beta}{4} - \frac{3}{8}\beta = \frac{3}{8}\beta$

$E_n^{(1)} = \frac{3}{2}\beta(n+\frac{1}{2})^2 + \frac{3}{8}\beta$

In the second order, $n \neq m$ and so $\hat{q}^3$ terms can contribute:

$-\alpha \langle m | \hat{q}^3 | n \rangle = \frac{-\alpha}{\sqrt{8}} \langle m | a^\dagger a^\dagger a^\dagger + a a a + a^\dagger a a + a a^\dagger a + a a a^\dagger + a a^\dagger a^\dagger + a^\dagger a a^\dagger + a^\dagger a^\dagger a | n \rangle$

$= \frac{-\alpha}{\sqrt{8}} \langle m | a^\dagger a^\dagger a^\dagger + a a a + \hat{N} a + a \hat{N} + a(1+\hat{N}) + (1+\hat{N})a^\dagger + \hat{N} a^\dagger + a^\dagger \hat{N} | n \rangle$

$= \frac{-\alpha}{\sqrt{8}} \left(\sqrt{(n+1)(n+2)(n+3)} \, \delta_{n+3,m} + \sqrt{n(n-1)(n-2)} \, \delta_{n-3,m} + (n-1)\sqrt{n} \, \delta_{n-1,m} \right.$

$+ n\sqrt{n} \, \delta_{n-1,m} + (1+n)\sqrt{n} \, \delta_{n-1,m} + (2+n)\sqrt{n+1} \, \delta_{n+1,m} + (1+n)\sqrt{n+1} \, \delta_{n+1,m}$

$\left. + n\sqrt{n+1} \, \delta_{n+1,m} \right)$

Only $m = n+3$, $m = n-3$, $m = n+1$, $m = n-1$ will contribute

$E_n^{(2)} = \frac{\alpha^2}{8} \left[\frac{(n+1)(n+2)(n+3)}{-3} + \frac{n(n-1)(n-2)}{3} + \frac{n(n-1)^2 + n^3 + n(1+n)^2}{1} + \frac{(2+n)^2(n+1) + (1+n)^2(n+1) + n^2(n+1)}{-1} \right]$

$= \frac{\alpha^2}{8} \left[\frac{n^3 + 6n^2 + 11n + 6}{-3} + \frac{n^3 - 3n^2 + 2n}{3} + 3n^3 + 2n - 3n^3 - 9n^2 - 11n - 5 \right]$

$= \frac{\alpha^2}{8} \left[-12n^2 - 12n - 7 \right]$ and the preferred form is $X(n+\frac{1}{2})^2 + y = X n^2 + X n + \frac{X}{4} + y$

$X = -\frac{3}{2}\alpha^2 , y = -\frac{\alpha^2}{2}$

$\therefore E_n \approx E_n^{(0)} + E_n^{(1)} + E_n^{(2)} = \left(\frac{3}{8}\beta - \frac{\alpha^2}{2} \right) + (n+\frac{1}{2}) + \frac{3}{2}(\beta - \alpha^2)(n+\frac{1}{2})^2$