Name: **Huan Q. Bui**
Course: **8.421 - AMO I**
Problem set: **#7**
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1. Spherical Harmony. We want to evaluate matrix elements

$$\langle J' m_J' | Y_{LM} | J m_J \rangle = \int d\Omega \, Y^*_{J' m_J'} Y_{LM} Y_{J m_J}.$$

To do this, we consider two particles with angular momenta $\boldsymbol{j}_1$ and $\boldsymbol{j}_2$. The total angular momentum is $\boldsymbol{J} = \boldsymbol{j}_1 + \boldsymbol{j}_2$. We can go between the coupled and uncoupled basis via

$$\begin{aligned} |(j_1 j_2) J M\rangle &= \sum_{m_1, m_2} |j_1 m_1\rangle |j_2 m_2\rangle \langle j_1 m_1 j_2 m_2 | J M\rangle \\ |j_1 m_1\rangle |j_2 m_2\rangle &= \sum_{J, M} |(j_1 j_2) J M\rangle \langle J M | j_1 m_1 j_2 m_2\rangle. \end{aligned}$$

The sum over M has only one nonzero term $M = m_1 + m_2$, and $|j_1 - j_2| < J < j_1 + j_2$. We also have the wavefunction of each particle at polar angle $\Omega_i = (\theta_1, \phi_i)$ is

$$\langle \Omega_i | j_i m_i \rangle = Y_{j_i m_i}(\Omega_i).$$

For the state of definite total angular momentum, we have

$$\Phi_{JM}(\Omega_1, \Omega_2) = \langle \Omega_1, \Omega_2 | (j_1 j_2) J M\rangle.$$

Now consider the function

$$F_{JM}(\Omega) \equiv \langle \Omega, \Omega | (j_1 j_2) J M\rangle$$

where $\Omega_1 = \Omega_2 = \Omega$. This is a wavefunction of an effective particle with angular momentum quantum numbers J, M. Indeed, it inherits its eigenvalues $\boldsymbol{J}^2$ and J_z from $\Phi_{JM}(\Omega_1, \Omega_2)$. We conclude that $F_{JM}(\Omega)$ must be proportional to the spherical harmonic $Y_{JM}(\Omega)$. Let us call

$$F_{JM}(\Omega) = A_{(j_1 j_2) J} Y_{JM}(\Omega).$$

The factor $A_{(j_1 j_2)J}$ cannot depend on M as F_{JM} must behave exactly like Y_{JM}, in particular when acted upon by $J_\pm$ which changes M. From here we have that

$$A_{(j_1 j_2)J} Y_{JM}(\Omega) = \sum_{m_1, m_2} \langle j_1 m_1 j_2 m_2 | J M\rangle Y_{j_1 m_1}(\Omega) Y_{j_2 m_2}(\Omega).$$

(a) To find $A_{(j_1 j_2)J}$ we consider the special case where $\Omega = (\theta = 0, \phi)$. In this case, we have that

$$Y_{j_i m_i}(\Omega) = Y_{j_i m_i}(\theta = 0, \phi) = \sqrt{\frac{2j_i + 1}{4\pi}} \delta_{m_i 0}.$$

From the equation above we find that

$$A_{(j_1 j_2)J} \sqrt{\frac{2J+1}{4\pi}} \delta_{M0} = \sum_{m_1, m_2} \langle j_1 m_1 j_2 m_2 | J M\rangle \sqrt{\frac{2j_1 + 1}{4\pi}} \delta_{m_1 0} \sqrt{\frac{2j_2 + 1}{4\pi}} \delta_{m_2 0}.$$

This equation is nontrivial if $M = m_1 = m_2 = 0$, in which case we can solve for $A_{(j_1 j_2)J}$:

$$\boxed{A_{(j_1, j_2)J} = \sqrt{\frac{(2j_1+1)(2j_2+1)}{4\pi(2J+1)}} \langle j_1 0 j_2 0 | J 0\rangle}$$

(b) By applying $\langle \Omega, \Omega|$ to the LHS of

$$|j_1 m_1\rangle|j_2 m_2\rangle = \sum_{J,M} |(j_1 j_2)JM\rangle\langle JM|j_1 m_1 j_2 m_2\rangle$$

we find that

$$\begin{aligned}
\boxed{Y_{j_1 m_1}(\Omega) Y_{j_2 m_2}(\Omega)} &= \sum_{J,M} F_{JM}(\Omega)\langle JM|j_1 m_1 j_2 m_2\rangle \\
&= \sum_{J,M} A_{(j_1 j_2)J} Y_{JM}(\Omega)\langle JM|j_1 m_1 j_2 m_2\rangle \\
&= \boxed{\sum_{J,M} \sqrt{\frac{(2j_1+1)(2j_2+1)}{4\pi(2J+1)}}\langle j_1 0 j_2 0|J0\rangle\langle JM|j_1 m_1 j_2 m_2\rangle Y_{JM}(\Omega)}
\end{aligned}$$

(c) It remains to find the matrix element given at the top. To do this, we simply plug things in and use orthonormality of spherical harmonics:

$$\begin{aligned}
\boxed{\langle j_3 m_3|Y_{j_2 m_2}|j_1 m_1\rangle} &= \int d\Omega\, Y^*_{j_3 m_3}(\Omega) Y_{j_2 m_2}(\Omega) Y_{j_1 m_1}(\Omega) \\
&= \int d\Omega\, Y^*_{j_3 m_3}(\Omega) \sum_{J,M} \sqrt{\frac{(2j_1+1)(2j_2+1)}{4\pi(2j_3+1)}}\langle j_1 0 j_2 0|j_3 0\rangle\langle j_3 m_3|j_1 m_1 j_2 m_2\rangle Y_{JM}(\Omega) \\
&= \sqrt{\frac{(2j_1+1)(2j_2+1)}{4\pi(2j_3+1)}}\langle j_1 0 j_2 0|j_3 0\rangle\langle j_3 m_3|j_1 m_1 j_2 m_2\rangle \underbrace{\int d\Omega Y^*_{j_3 m_3}(\Omega) Y_{j_3 m_3}(\Omega)}_{1} \\
&= \boxed{\sqrt{\frac{(2j_1+1)(2j_2+1)}{4\pi(2j_3+1)}}\langle j_1 0 j_2 0|j_3 0\rangle\langle j_3 m_3|j_1 m_1 j_2 m_2\rangle}
\end{aligned}$$

2. Dipole Operator. A symmetric top molecule has a Hamiltonian $\mathcal{H} = B\boldsymbol{J}^2$, with B the rotational constant. The dipole moment operator is $\hat{\boldsymbol{d}} = d\hat{\boldsymbol{r}}$, with d the value of the "permanent dipole moment" (in the molecular frame).

(a) We will prove the spherical tensor decomposition:

$$\sum_m C^*_{1m}\hat{\boldsymbol{e}}_m = \sum_m C_{1m}\hat{\boldsymbol{e}}_m = \hat{\boldsymbol{r}}$$

where $C_{1m}(\theta,\phi) = \sqrt{4\pi/3}Y_{1m}(\theta,\phi)$,

$$\hat{\boldsymbol{e}}_\pm = \mp\frac{\hat{\boldsymbol{e}}_x \pm i\hat{\boldsymbol{e}}_y}{\sqrt{2}} \qquad \hat{\boldsymbol{e}}_0 = \hat{\boldsymbol{e}}_z$$

To this end, we simply write everything out explicitly. We will show that the left-most term is equal to $\hat{\boldsymbol{r}}$. Once done, the other equality follows immediately from the fact that $\hat{\boldsymbol{r}}$ is real (and therefore the second term is equal to the (conjugate of) the first term).

$$\begin{aligned}
& C^*_{1-}\hat{\boldsymbol{e}}_- + C^*_{10}\hat{\boldsymbol{e}}_0 + C^*_{1+}\hat{\boldsymbol{e}}_+ \\
&= \frac{1}{2}e^{+i\phi}\sqrt{\frac{3}{2\pi}}\sqrt{\frac{4\pi}{3}}\sin\theta\frac{\hat{\boldsymbol{e}}_x - i\hat{\boldsymbol{e}}_y}{\sqrt{2}} + \frac{1}{2}\sqrt{\frac{3}{\pi}}\sqrt{\frac{4\pi}{3}}\cos\theta\hat{\boldsymbol{e}}_z + \frac{1}{2}e^{-i\phi}\sqrt{\frac{3}{2\pi}}\sqrt{\frac{4\pi}{3}}\sin\theta\frac{\hat{\boldsymbol{e}}_x + i\hat{\boldsymbol{e}}_y}{\sqrt{2}} \\
&= \sin\theta\cos\phi\,\hat{\boldsymbol{e}}_x + \sin\theta\sin\phi\,\hat{\boldsymbol{e}}_y + \cos\theta\,\hat{\boldsymbol{e}}_z \\
&= \hat{\boldsymbol{r}}. \qquad \checkmark
\end{aligned}$$

(b) Now we will show that

$$\hat{\boldsymbol{e}}_m^* \cdot \hat{\boldsymbol{e}}_n = \sum_p \delta_{mp}\delta_{np} = \delta_{mn}.$$

It suffices to demonstrate the following cases:

$$\hat{\boldsymbol{e}}_+^* \cdot \hat{\boldsymbol{e}}_- = -\frac{\hat{\boldsymbol{e}}_x - i\hat{\boldsymbol{e}}_y}{\sqrt{2}} \cdot \frac{\hat{\boldsymbol{e}}_x - i\hat{\boldsymbol{e}}_y}{\sqrt{2}} = 0 \iff \hat{\boldsymbol{e}}_-^* \cdot \hat{\boldsymbol{e}}_+ = 0$$

and

$$\hat{\boldsymbol{e}}_\pm^* \cdot \hat{\boldsymbol{e}}_\pm = \frac{\hat{\boldsymbol{e}}_x \mp i\hat{\boldsymbol{e}}_y}{\sqrt{2}} \cdot \frac{\hat{\boldsymbol{e}}_x \mp i\hat{\boldsymbol{e}}_y}{\sqrt{2}} = \frac{2}{2} = 1.$$

With these we are done.

(c) Suppose we have two unit vectors $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{r}}'$ pointing in the direction of solid angle (θ, ϕ) and (θ', ϕ'). Let us call Θ the angle between the vectors, then we have

$$\begin{aligned}
\cos\Theta &= \hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{r}}' \\
&= \sum_{m,n} C_{1m}(\theta,\phi) C_{1n}^*(\theta',\phi')\, \hat{\boldsymbol{e}}_m^* \cdot \hat{\boldsymbol{e}}_n \\
&= \sum_{m,n} C_{1m}(\theta,\phi) C_{1n}^*(\theta',\phi') \delta_{mn} \\
&= \sum_{m} C_{1m}(\theta,\phi) C_{1m}^*(\theta',\phi') \\
&= \cos\theta\cos\theta' + \frac{1}{2} e^{-i\phi - i\phi'} \sin\theta\sin\theta' + \frac{1}{2} e^{i\phi + i\phi'} \sin\theta\sin\theta' \\
&= \cos\theta\cos\theta' + \cos\big(\phi - \phi'\big)\sin\theta\sin\theta',
\end{aligned}$$

as expected from standard geometry. A generalization of this result (for which $l = 1$) is

$$P_l(\cos\Theta) = \sum_m C_{lm}^*(\theta,\phi) C_{lm}(\theta',\phi')$$

where

$$C_{lm}(\theta,\phi) = \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\theta,\phi).$$

The proof is done by setting one of the unit vectors the z-axis, and the angles simplify.

(d) The electric field can be written

$$\begin{aligned}
\boldsymbol{E} &= E_z\hat{\boldsymbol{e}}_z + E_x\hat{\boldsymbol{e}}_x + E_y\hat{\boldsymbol{e}}_y \\
&= E_0\hat{\boldsymbol{e}}_0 + E_+\hat{\boldsymbol{e}}_+ + E_-\hat{\boldsymbol{e}}_- \\
&= \sum_m E_m^* \hat{\boldsymbol{e}}_m = \sum_m E_m \hat{\boldsymbol{e}}_m^*
\end{aligned}$$

where $E_0, E_\pm$ defined in terms of $E_{x,y,z}$ in a similar way as the $\hat{e}_m$'s are defined in terms of $\hat{e}_{x,y,z}$. The dipole operator may be decomposed into spherical harmonics as

$$\begin{aligned}
-\hat{\boldsymbol{d}} \cdot \boldsymbol{E} &= -d\hat{\boldsymbol{r}} \cdot \mathbf{E} \\
&= -d \sum_{m,n} C_{1m}^* E_n \hat{\boldsymbol{e}}_m \cdot \hat{\boldsymbol{e}}_n^* = -d \sum_{m,n} C_{1m} E_n^* \hat{\boldsymbol{e}}_m^* \cdot \hat{\boldsymbol{e}}_n \\
&= -d \sum_m C_{1m}^* E_m = -d \sum_m C_{1m} E_m^*.
\end{aligned}$$

(e) (Extra credit) Take $\boldsymbol{E} = E\hat{\boldsymbol{e}}_z$. The matrix elements of the Hamiltonian $\mathcal{H} = B\boldsymbol{J}^2 - \hat{\boldsymbol{d}} \cdot \boldsymbol{E}$ in the $\{|Jm_J\rangle\}$ basis are given by

$$\begin{aligned}
\langle J'm_{J'}|\mathcal{H}|Jm_J\rangle &= BJ(J+1)\delta_{JJ'}\delta_{m_{J'}m_J} - dE^*\langle J'm_{J'}|C_{10}|Jm_J\rangle \\
&= BJ(J+1)\delta_{JJ'}\delta_{m_{J'}m_J} - dE\underbrace{\int d\Omega\, Y^*_{J'm_{J'}} C_{10} Y_{Jm_J}} \\
&= BJ(J+1)\delta_{JJ'}\delta_{m_{J'}m_J} - dE\sqrt{\frac{(2J+1)(2+1)}{4\pi(2J'+1)}}\langle (J,0)(1,0)|(J',0)\rangle\langle J'm_{J'}|(Jm_J)(1,0)\rangle \\
&= BJ(J+1)\delta_{JJ'}\delta_{m_{J'}m_J} - dE\sqrt{\frac{(2J+1)(2+1)}{4\pi(2J'+1)}}\langle (J,0)(1,0)|(J',0)\rangle\langle J'm_{J'}|(Jm_J)(1,0)\rangle.
\end{aligned}$$

where we have used the fact that $C_{10} = C_{10}^*$ and remove the conjugation symbol. To get the matrix elements in the second term, we must use Wigner's 3-j symbols:

$$\langle j_1 m_1 j_2 m_2 | JM\rangle = (-1)^{-j_1+j_2-M}\sqrt{2J+1}\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix}$$

which with we write the Hamiltonian matrix elements as

$$\begin{aligned}
\langle J'm_{J'}|\mathcal{H}|Jm_J\rangle &= BJ(J+1)\delta_{JJ'}\delta_{m_{J'}m_J} \\
&\quad - dE\sqrt{\frac{(2J+1)(2+1)}{4\pi(2J'+1)}}(-1)^{-J+1}(-1)^{-J+1-m_{J'}}\sqrt{2J'+1}\sqrt{2J'+1}\begin{pmatrix} J & 1 & J' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} J & 1 & J' \\ m_J & 0 & -m_{J'} \end{pmatrix} \\
&= BJ(J+1)\delta_{JJ'}\delta_{m_{J'}m_J} - dE(-1)^{-m_{J'}}\sqrt{\frac{(2J+1)(2+1)(2J'+1)}{4\pi}}\begin{pmatrix} J & 1 & J' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} J & 1 & J' \\ m_J & 0 & -m_{J'} \end{pmatrix}.
\end{aligned}$$

Using Mathematica, we can generate this matrix and diagonalize to find the eigenstates and their energies.

3. The Stark Effect in Hydrogen.

(a) **Stark quenching of the $2S$ state**

(b) **Effect of the Lamb shift on quenching**