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Course: **8.421 - AMO I**
Problem set: **#7**
Due: Friday, April 1, 2022.

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

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

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

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

Now consider the function

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

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

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

(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

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

From the equation above we find that

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

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

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

(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

$$\begin{aligned}
\langle J' m_{J'} | \mathcal{H} | J m_J \rangle &= BJ(J+1)\delta_{JJ'}\delta_{m_{J'} m_J} - dE \langle J' m_{J'} | C_{10} | J m_J \rangle \\
&= BJ(J+1)\delta_{JJ'}\delta_{m_{J'} m_J} - dE \sqrt{\frac{4\pi}{3}} \underbrace{\int d\Omega\, Y^*_{J' m_{J'}} Y_{10} Y_{J m_J}} \\
&= BJ(J+1)\delta_{JJ'}\delta_{m_{J'} m_J} - dE \sqrt{\frac{(2J+1)(2+1)}{3(2J'+1)}} \langle (J,0)(1,0) | (J',0) \rangle \langle J' m_{J'} | (J m_J)(1,0) \rangle \\
&= BJ(J+1)\delta_{JJ'}\delta_{m_{J'} m_J} - dE \sqrt{\frac{(2J+1)(2+1)}{3(2J'+1)}} \langle (J,0)(1,0) | (J',0) \rangle \langle J' m_{J'} | (J m_J)(1,0) \rangle .
\end{aligned}$$

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:

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

which with we write the Hamiltonian matrix elements as

$$\begin{aligned}
\langle J' m_{J'} | \mathcal{H} | J m_J \rangle &= BJ(J+1)\delta_{JJ'}\delta_{m_{J'} m_J} \\
&\quad - dE \sqrt{\frac{(2J+1)(2+1)}{3(2J'+1)}} (-1)^{-J+1} (-1)^{-J+1-m_{J'}} \sqrt{2J'+1}\sqrt{2J'+1} \begin{pmatrix} J & 1 & J' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ m_J & 0 & -m_{J'} \end{pmatrix} \\
&= BJ(J+1)\delta_{JJ'}\delta_{m_{J'} m_J} - dE(-1)^{-m_{J'}} \sqrt{\frac{(2J+1)(2+1)(2J'+1)}{3}} \begin{pmatrix} J & 1 & J' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ m_J & 0 & -m_{J'} \end{pmatrix} .
\end{aligned}$$

Using MATLAB, we can generate this matrix and diagonalize to find the eigenstates and their energies. Since it is convenient, I actually generated the Hamiltonian and carried out exact diagonalization in MATLAB but then plotted the probabilities in using `SphericalPlot3D[]` in Mathematica. Perhaps the grader will tell me that this solution is *cursed*. Figure 1 shows the first six energy levels up to an electric field $E \approx 10B/d$. For this calculation, I have picked $J_{\max} = 10$.

Using Mathematica, we plot $\left|\langle \theta, \phi | \Psi \rangle\right|^2$ of the lowest state for $dE/B = 0, 1, 10$. To do this, I have used MATLAB to find the lowest energy eigenstate for each value of dE/B. Then, I express these states in terms of spherical harmonics by identifying each entry of the state vector with the correct $|Jm_J\rangle$ state in the basis. For this part of the problem, I have used $J_{\max} = 4$. See Figures 2a, 2b, 3 for the results.

MATLAB code for calculating:

```
clear all
close all

J = 10;
strength = 0:0.05:10;
size = (J+1)^2;
H = zeros(size,size);

% creat a basis for the Hamiltonian
basis = [];

for j = 0:1:J
for mj = -j:1:j
basis = [basis; [j mj]];
end
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

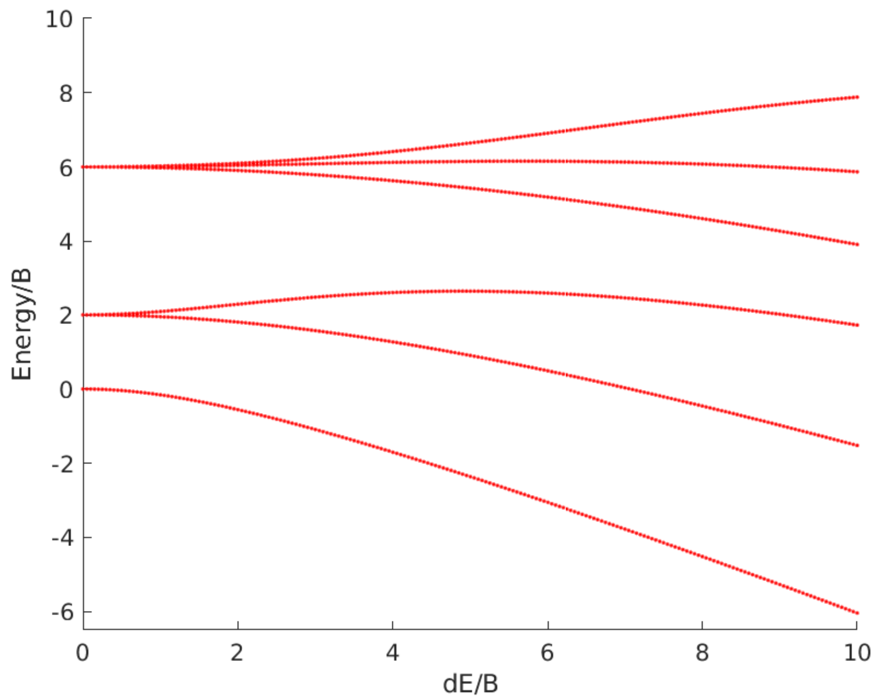
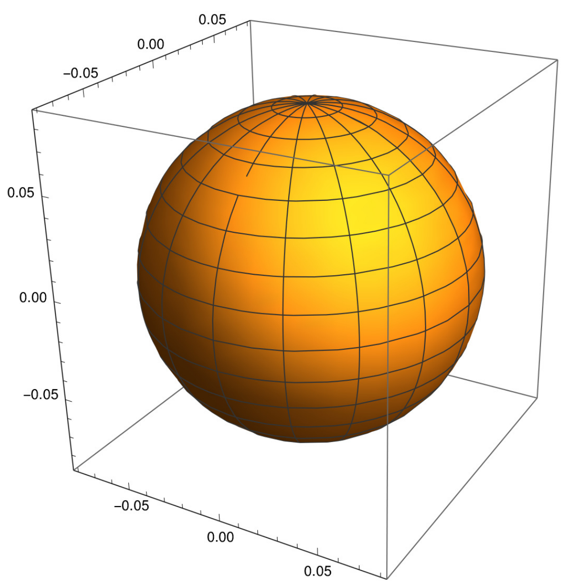
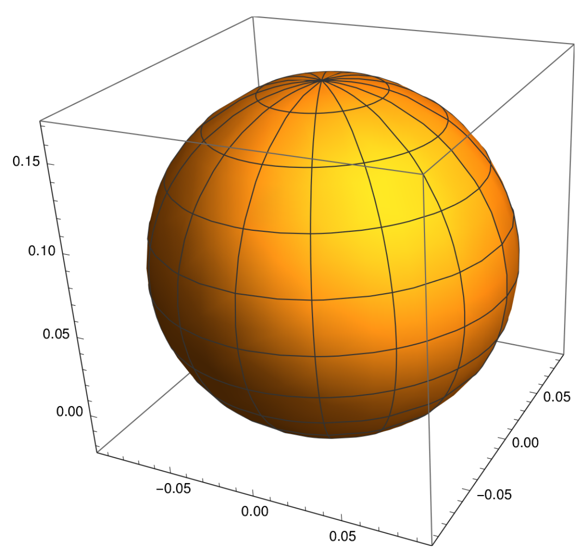


Figure 1: Energies of the first six energy levels p to an electric field $E \approx 10B/d$.



(a) $|\langle\theta,\phi|\Psi\rangle|^2$ for $dE/B = 0$.



(b) $|\langle\theta,\phi|\Psi\rangle|^2$ for $dE/B = 1$.

```
%%% first plot energies as a fn of dE/B

stark = figure(1);
for a = strength % loop over field strengths
% create the Hamiltonian, element-by-element
for r = 1:size
j = basis(r,1);
mj = basis(r,2);
```

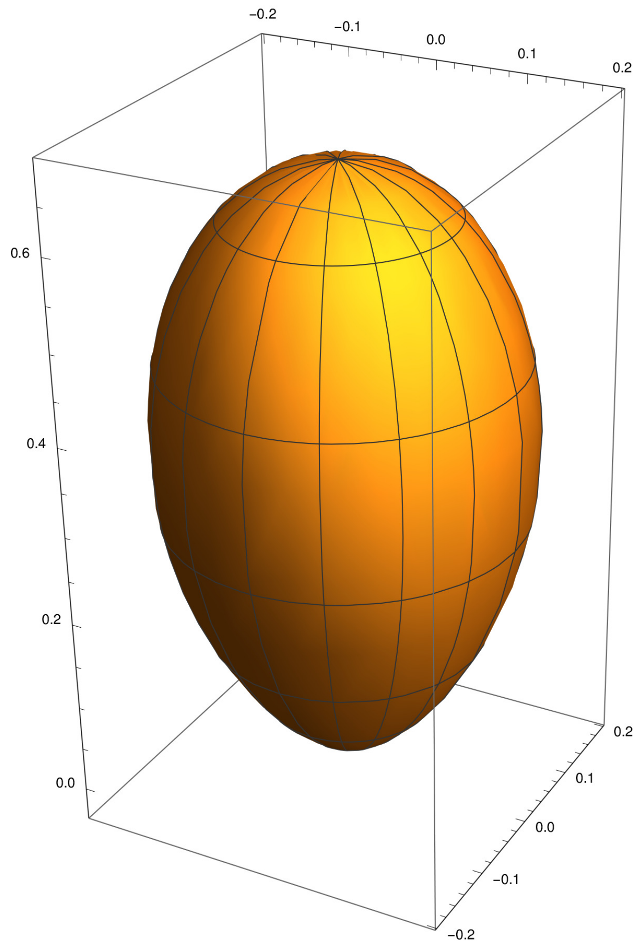


Figure 3: $\left|\left\langle\theta,\phi\middle|\Psi\right\rangle\right|^2$ for $dE/B = 10$.

```
for c = 1:size
jj = basis(c,1);
mjj = basis(c,2);

H(r,c) = j*(j+1)*(j==jj)*(mj==mjj)...
-a*(-1)^(-mjj)*sqrt((2*j+1)*(2*1+1)*(2*jj+1)/3)...
*Wigner3j([j,1,jj],[0,0,0])*Wigner3j([j,1,jj],[mj,0,-mjj]);
end
end
% diag n plot eigenvalues associated with field strength a = dE/B
energies = eig(H);
hold on
plot(a*ones(size), energies, '.', 'Color', 'red', 'MarkerSize',4);
end

% disp(H)

% plot includes up to 6 lowest energies only

hold off
%title('Energy vs dE/B')
ylim([-6.5 10])
xlabel('dE/B')
ylabel('Energy/B')


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
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%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

```
% now find the lowest state and associated energy for various a = dE/B
% then take result over to mathematica to plot wavefunction^2

strength = [0 1 10];
wavefunction = 0;

for a = strength % loop over field strengths
% create the Hamiltonian, element-by-element
for r = 1:size
j = basis(r,1);
mj = basis(r,2);
for c = 1:size
jj = basis(c,1);
mjj = basis(c,2);

H(r,c) = j*(j+1)*(j==jj)*(mj==mjj)...
-a*(-1)^(-mjj)*sqrt((2*j+1)*(2*1+1)*(2*jj+1)/3)...
*Wigner3j([j,1,jj],[0,0,0])*Wigner3j([j,1,jj],[mj,0,-mjj]);
end
end
% diag n plot eigenvalues associated with field strength a = dE/B
[state,energy] = eigs(H,1,'SA');
disp('Ground state energy:')
disp(energy)
disp('Ground state:')
disp(state)

end
```

Mathematica code for plotting:

```
(*dE/B=0 ---> |0,0> state*)

Energy1 = 0;

State1 = SphericalHarmonicY[0, 0, \[Theta], \[Phi]];

SphericalPlot3D[
Conjugate[State1]*State1, {\[Theta], 0, Pi}, {\[Phi], 0, 2 Pi},
PlotRange -> All]


(*dE/B=1 ---> get superposition state*)

Jmax2 = 4;

Base2 = Flatten[
Table[SphericalHarmonicY[J, mJ, \[Theta], \[Phi]], {J, 0,
Jmax2}, {mJ, -J, J}], 1];

Energy2 = -0.1577;

State2 = {-0.9644, 0.0000, -0.2634, -0.0000, -0.0000,
0.0000, -0.0222, -0.0000, -0.0000, 0.0000, 0.0000,
0.0000, -0.0009, -0.0000, 0.0000, 0.0000, 0.0000, -0.0000, -0.0000,
0.0000, -0.0000, -0.0000, 0.0000, -0.0000, 0.0000};

State2 = State2/Norm[State2];

wfn2 = Dot[Base2, State2]

-0.27206 - 0.128702 Cos[\[Theta]] -
0.0070019 (-1 + 3 Cos[\[Theta]]^2) -
0.000335869 (-3 Cos[\[Theta]] + 5 Cos[\[Theta]]^3)

SphericalPlot3D[
Conjugate[wfn2]*wfn2, {\[Theta], 0, Pi}, {\[Phi], 0, 2 Pi},
AspectRatio -> Full]


(*dE/B=10 ---> get superposition state*)

Jmax3 = 4;

Base3 = Flatten[
Table[SphericalHarmonicY[J, mJ, \[Theta], \[Phi]], {J, 0,
Jmax2}, {mJ, -J, J}], 1];

Energy3 = -6.0448;
```

```
State3 = {-0.6477, 0.0000, -0.6782, -0.0000,
0.0000, -0.0000, -0.3323, -0.0000, 0.0000, -0.0000, 0.0000,
0.0000, -0.0987, -0.0000, -0.0000, 0.0000, 0.0000, 0.0000, -0.0000,
0.0000, -0.0191, -0.0000, 0.0000, -0.0000, 0.0000};

State3 = State3/Norm[State3];

wfn3 = Dot[Base3, State3]

-0.182713 - 0.33137 Cos[\[Theta]] -
0.104805 (-1 + 3 Cos[\[Theta]]^2) -
0.0368325 (-3 Cos[\[Theta]] + 5 Cos[\[Theta]]^3) -
0.0020205 (3 - 30 Cos[\[Theta]]^2 + 35 Cos[\[Theta]]^4)

SphericalPlot3D[
Conjugate[wfn3]*wfn3, {\[Theta], 0, Pi}, {\[Phi], 0, 2 Pi},
PlotRange -> All, AspectRatio -> Full]
```

3. The Stark Effect in Hydrogen.

(a) **Stark quenching of the** $2S$ **state.** In hydrogen, the $2S$ state is metastable. In the absence of external electric fields, its lifetime is 1/8 seconds. When an external electric field is applied, the $2S$ becomes mixed with the $2P$ state, which is strongly coupled to the ground state. The $2P$ state lifetime is only 1.6 ns. Depending on the strength of the electric field, the lifetime of the $2S$ state can be shortened by many orders og magnitude. This process is known as "quenching." To see how this works, we will look at how the amplitude $a(t)$ of $|a\rangle$ ($2S$ state) evolves ocer time in the presenece of a DC Stark perturbation with matrix element $\hbar V = \langle b| e\boldsymbol{E}\cdot\boldsymbol{r}\,|a\rangle$ where $|b\rangle$ stands for the $2P$ state.

Assuming that the atom is initially in the $2S$ state, i.e., $a(0) = 1, b(0) = 0$. Working in the interaction picture, we can derive the following differential equations for $a(t)$ and $b(t)$:

$$
\begin{aligned}
i\dot{a} &= V^* e^{i\omega_0 t} b - i\frac{\Gamma_a}{2}a \\
i\dot{b} &= V e^{-i\omega_0 t} a - i\frac{\Gamma_b}{2}b
\end{aligned}
$$

where $\Gamma_a = 8\ \mathrm{s}^{-1}$ and $\Gamma_b = 6.3\times 10^8\ \mathrm{s}^{-1}$. Here, $\hbar\omega_0$ is the energy difference $E_a - E_b$. To solve these equations, we make the following ansatz

$$
\begin{aligned}
a(t) &= a_1 e^{-\mu_1 t} + a_2 e^{-\mu_2 t} \\
b(t) &= b_1 e^{-(\mu_1 + i\omega_0)t} + b_2 e^{-(\mu_2 + i\omega_0)t}
\end{aligned}
$$

where a_1, a_2, b_1, b_2 are constants. Applying the initial condition $a(0) = 1, b(0) = 0$ we find that

$$
a_1 + a_2 = 1 \qquad b_1 + b_2 = 0.
$$

With this, we may write our ansatz as

$$
\begin{aligned}
a(t) &= a_1 e^{-\mu_1 t} + (1 - a_1)e^{-\mu_2 t} \\
b(t) &= b_1 e^{-(\mu_1 + i\omega_0)t} - b_1 e^{-(\mu_2 + i\omega_0)t}
\end{aligned}
$$

From this point, we may proceed using Mathematica. Plugging this ansatz into the system of differential equations above and set $t = 0$, we can solve for μ_1 and μ_2 in terms of a_1, b_1. The result is

$$
\mu_1 = \frac{\Gamma_a}{2} - \frac{i(a_1 - 1)V}{b_1} \qquad \mu_2 = \frac{\Gamma_a}{2} - \frac{i a_1 V}{b_1}
$$

It remains to find a_1, b_1. To this end, we pick $t = 1/V$. By writing μ_1, μ_2 in terms of a_1, b_1, we can solve for a_1, b_1. The result is

$$
\begin{aligned}
a_1 &= \frac{1}{2} + \frac{i(\Gamma_a - \Gamma_b) - 2\omega_0}{2\sqrt{-(\Gamma_a - \Gamma_b - 4V + 2i\omega_0)(\Gamma_a - \Gamma_b + 4V + 2i\omega_0)}} \\
b_1 &= -\frac{2V}{\sqrt{-(\Gamma_a - \Gamma_b - 4V + 2i\omega_0)(\Gamma_a - \Gamma_b + 4V + 2i\omega_0)}}
\end{aligned}
$$

We should simplify this even more by writing the denominator as

$$
\begin{aligned}
\sqrt{-(\Gamma_a - \Gamma_b - 4V + 2i\omega_0)(\Gamma_a - \Gamma_b + 4V + 2i\omega_0)} &= \sqrt{16V^2 - ((\Gamma_a - \Gamma_b) + 2i\omega_0)^2} \\
&= \sqrt{16V^2 - (\Gamma_a - \Gamma_b)^2 + 4\omega_0^2 - 4i\omega_0(\Gamma_a - \Gamma_b)}.
\end{aligned}
$$

Now recall that for $x, y \in \mathbb{R}$,

$$
\sqrt{x + iy} = \sqrt{\frac{\sqrt{x^2 + y^2} + x}{2}} + i\operatorname{sgn}(y)\sqrt{\frac{\sqrt{x^2 + y^2} - x}{2}}.
$$

Let $x = 16V^2 - (\Gamma_a - \Gamma_b)^2 + 4\omega_0^2$ and $y = -4\omega_0(\Gamma_a - \Gamma_b) > 0$, then we have

$$
\begin{aligned}
\sqrt{-(\Gamma_a - \Gamma_b - 4V + 2i\omega_0)(\Gamma_a - \Gamma_b + 4V + 2i\omega_0)} &= \sqrt{x + iy} \\
&= \sqrt{\frac{\sqrt{x^2 + y^2} + x}{2}} + i\sqrt{\frac{\sqrt{x^2 + y^2} - x}{2}}.
\end{aligned}
$$

From here we can calculate μ_1, μ_2:

$$
\begin{aligned}
\mu_1 &= \frac{\Gamma_a}{4} + \frac{\Gamma_b}{4} + \frac{i}{4}\sqrt{x + iy} - \frac{i\omega_0}{2} \\
\mu_2 &= \frac{\Gamma_a}{4} + \frac{\Gamma_b}{4} - \frac{i}{4}\sqrt{x + iy} - \frac{i\omega_0}{2}
\end{aligned}
$$

From here, we can find the real and imaginary parts of μ_1, μ_2:

$$
\begin{aligned}
\operatorname{Re}(\mu_1) &= \frac{\Gamma_a}{4} + \frac{\Gamma_b}{4} - \frac{1}{4}\sqrt{\frac{\sqrt{x^2 + y^2} - x}{2}} \\
\operatorname{Im}(\mu_1) &= \frac{1}{4}\sqrt{\frac{\sqrt{x^2 + y^2} + x}{2}} - \frac{\omega_0}{2} \\
\operatorname{Re}(\mu_2) &= \frac{\Gamma_a}{4} + \frac{\Gamma_b}{4} + \frac{1}{4}\sqrt{\frac{\sqrt{x^2 + y^2} - x}{2}} \\
\operatorname{Im}(\mu_2) &= -\frac{1}{4}\sqrt{\frac{\sqrt{x^2 + y^2} + x}{2}} - \frac{\omega_0}{2}
\end{aligned}
$$

Here, the real parts of μ_1, μ_2 give the decay rate of the $2S$ state, and the imaginary parts tell us the level shifts. With these expressions, we can write down the full solution for $a(t)$. While it is possible, I won't do that here since this is simply plugging things into the ansatz.

In the small V limit, we may Taylor expand these expressions about $V = 0$ to second order in V to find

$$\mathrm{Re}(\mu_1) \approx \frac{\Gamma_a}{4} + \frac{\Gamma_b}{4} + \frac{\Gamma_a}{4} - \frac{\Gamma_b}{4} - \frac{8(\Gamma_b - \Gamma_a)}{(\Gamma_b - \Gamma_a)^2 + 4\omega_0^2} V^2$$

$$\mathrm{Im}(\mu_1) \approx 2\omega_0 + \frac{16\omega_0}{(\Gamma_b - \Gamma_a)^2 + 4\omega_0^2} - \frac{\omega_0}{2} = \frac{3\omega_0}{2} + \frac{16\omega_0}{(\Gamma_b - \Gamma_a)^2 + 4\omega_0^2} V^2$$

$$\mathrm{Re}(\mu_2) \approx \frac{\Gamma_a}{4} + \frac{\Gamma_b}{4} - \frac{\Gamma_a}{4} + \frac{\Gamma_b}{4} + \frac{8(\Gamma_b - \Gamma_a)}{(\Gamma_b - \Gamma_a)^2 + 4\omega_0^2} V^2$$

$$\mathrm{Im}(\mu_2) \approx -2\omega_0 - \frac{16\omega_0}{(\Gamma_b - \Gamma_a)^2 + 4\omega_0^2} - \frac{\omega_0}{2} = \frac{-5\omega_0}{2} + \frac{16\omega_0}{(\Gamma_b - \Gamma_a)^2 + 4\omega_0^2} V^2$$

On the other hand, we have in the large V limit, $x \to 16V^2$ and $x \gg y$, and so

$$\mathrm{Re}(\mu_1) \approx \frac{\Gamma_a}{4} + \frac{\Gamma_b}{4}$$

$$\mathrm{Im}(\mu_1) \approx V - \frac{\omega_0}{2}$$

$$\mathrm{Re}(\mu_2) \approx \frac{\Gamma_a}{4} + \frac{\Gamma_b}{4}$$

$$\mathrm{Im}(\mu_2) \approx -V - \frac{\omega_0}{2}$$

We see that these results agree well with perturbation theory results for Stark shift energies.

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