1. [5+5 pts] The equilibrium internuclear distance in HCl is 0.1275 nm. Calculate the difference in rotational energy between the J=1 and J=2 levels. Then calculate the wavelength of radiation that will be absorbed in promoting the molecule from J=1 to J=2. The atomic masses of H and Cl are 1.008 amu and 34.97 amu, respectively.

Solution:

For HCl, \( \mu = \frac{1.008 \cdot 34.97}{1.008 + 34.97} \cdot \frac{10^{-3}}{kg/mole} \) = 1.626 \( \times \) 10^{-27} kg/molecule, \( r = 0.1275 \) nm, so

\[ I = \mu r^2 = 1.626 \times 10^{-27} \times (0.1275 \times 10^{-9})^2 = 2.64 \times 10^{-47} kgm^2 \]

For J=1 to J=2 transition,

\[ \Delta E = \frac{\hbar^2}{2I} (6 - 2) \]

\[ = \frac{(6.626 \times 10^{-34})^2 \times 4}{2 \times 4 \times \pi^2 \times 2.64 \times 10^{-47}} \]

\[ = 8.42 \times 10^{-22} J \]

\[ \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{8.42 \times 10^{-22}} = 2.36 \times 10^{-4} m \]

2. [5+10 pts] The rotational Hamiltonian in spherical co-ordinates is given by

\[ \hat{H}_{rot} = -\frac{\hbar^2}{2mr^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} \]

a. Show that you can express the Hamiltonian as:

\[ \hat{H}_{rot} = -\frac{\hbar^2}{2mr^2} \left\{ \cot \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \varphi^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} \]

b. Operate with the Hamiltonian on \( Y_{1,-1} = \frac{1}{2}\sqrt{3/(2\pi)} e^{-i\varphi} \sin \theta \), to verify that this is an eigenfunction, and find its eigenvalue.

Solution:

a) We need to perform the chain rule on the first term in brackets of the original \( \hat{H}_{rot} \):

\[ \hat{H}_{rot} = -\frac{\hbar^2}{2mr^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} \]

\[ = -\frac{\hbar^2}{2mr^2} \left\{ \frac{1}{\sin \theta} \left( \cos \theta \frac{\partial}{\partial \theta} + \sin \theta \frac{\partial^2}{\partial \theta^2} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} \]
\[
\begin{align*}
\frac{\hbar^2}{2mr^2} \left\{ \cot \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} = -\frac{\hbar^2}{2mr^2} \left\{ \cot \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} =
\end{align*}
\]

which is what we set out to prove.

**b)** Inserting \( Y_{1,-1} \) and dividing by the normalization and kinetic energy factor \( \frac{\hbar^2}{2mr^2} \) so they do not have to be carried through everywhere:

\[
\begin{align*}
(2/\sqrt{3/(2\pi)}) \frac{\hbar^2}{2mr^2} \hat{H}_{rot} Y_{1,-1} &= -\left\{ \cot \theta \frac{\partial}{\partial \theta} \left( e^{-i\varphi} \sin \theta \right) + \frac{\partial^2}{\partial \theta^2} \left( e^{-i\varphi} \sin \theta \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \left( e^{-i\varphi} \sin \theta \right) \right\} \\
&= -\left\{ \cot \theta \cos \theta \left( e^{-i\varphi} \right) - \sin \theta \left( e^{-i\varphi} \right) - \frac{1}{\sin^2 \theta} \left( e^{-i\varphi} \sin \theta \right) \right\} \\
&= -\left\{ \left( \frac{\cos^2 \theta}{\sin \theta} - \sin \theta - \frac{1}{\sin \theta} \right) \right\} \\
&= \left( \frac{\sin \theta}{\sin \theta} + \frac{(\sin \theta)^2 - 1}{\sin \theta} \right) \\
&= \left( \frac{1}{\sin \theta} \right) \\
&= \left( \frac{(\sin \theta)^2 + 1 - (\cos \theta)^2}{\sin \theta} \right) \\
&= +2 \left( e^{-i\varphi} \sin \theta \right)
\end{align*}
\]

Multiplying by the normalization and kinetic energy factor on both sides again, we see that \( Y_{1,-1} \) is an eigenfunction of \( \hat{H}_{rot} \), with eigenvalue \( \frac{\hbar^2}{2mr^2} = \frac{\hbar^2 \cdot 2}{2mr^2} \) or \( \ell = 1 \).

3. [5+5 pts] Remember from basic matrix algebra that multiplying any vector by the identity matrix, leaves the vector unchanged. You learned in lecture that the identity operator is given by \( I = \sum_n |n\rangle \langle n| \) in Dirac notation or by \( I = \sum_n \varphi_n(x) \int dx \varphi_n^*(x) \) in ordinary function notation.

a. **Show** by operating in function notation that \( \hat{I} \psi(x) = \psi(x) \) for any wavefunction \( \psi \).

b. **Show** by operating in Dirac notation that \( \hat{I} |\psi\rangle = |\psi\rangle \) for any ket \( |\psi\rangle \).

**Solution:**
4. [5+5+5 pts] Consider the matrix 
\[ \mathbf{M} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \]

a. **Find** the eigenvalues \( \lambda_1 \) and \( \lambda_2 \), of the matrix by solving the equation 
\[ \det(\mathbf{M} - \mathbf{\Lambda}) = 0 \]
where \( \mathbf{\Lambda} \) is the diagonal eigenvalue matrix.

b. Plug each of these eigenvalues (one at a time) back into the equation \( (\mathbf{M} - \mathbf{\Lambda}) \mathbf{v} = 0 \), to **find** the eigenvectors \( \mathbf{v}_{\lambda_1} \) and \( \mathbf{v}_{\lambda_2} \); no need to normalize.

c. **Verify** that the eigenvectors are orthogonal, i.e. show that \( \mathbf{v}_{\lambda_1}^\dagger \cdot \mathbf{v}_{\lambda_2} = 0 \).

**Solution:**

a) We start by solving the determinant equation
\[ \begin{vmatrix} -\lambda & -i \\ i & -\lambda \end{vmatrix} = 0 \]
which gives
\[ \lambda^2 - 1 = 0 \]
and so
\[ \lambda = \pm 1 \rightarrow \lambda_1 = -1 and \lambda_2 = 1 \]

b) \( \lambda_1 = -1 : \)
\[
\begin{pmatrix}
1 & -i \\
i & 1
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix} = 0
\]

Gives to the two equations
\[
c_1 - ic_2 = 0 \\
ic_1 + c_2 = 0
\]

Letting \(c_1 = 1\) yields \(c_2 = -i\) and we arrive at the first eigenvector
\[
v_{\lambda_1} = \begin{pmatrix} 1 \\ -i \end{pmatrix}
\]

\(\lambda_1 = 1\) :

\[
\begin{pmatrix}
-1 & -i \\
i & -1
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix} = 0
\]

Gives the two equations
\[
-c_1 - ic_2 = 0 \\
ic_1 - c_2 = 0
\]

Letting \(c_1 = 1\) yields \(c_2 = i\) and we arrive at the second eigenvector
\[
v_{\lambda_2} = \begin{pmatrix} 1 \\ i \end{pmatrix}
\]

\(c)\)
\[
v_{\lambda_1}^\dagger \cdot v_{\lambda_2} = \left(\begin{pmatrix} 1 \\ -i \end{pmatrix}\right)^\dagger \cdot \left(\begin{pmatrix} 1 \\ i \end{pmatrix}\right) = (1 \ i)\left(\begin{pmatrix} 1 \\ i \end{pmatrix}\right) = 1 - 1 = 0
\]

Therefore the eigenvectors are orthogonal.
5. [10+10 pts] a. **Draw** V(R) for H+ and H approaching one another to form an H2+ molecule in its lowest energy state and in its first excited state. **Sketch** polar plots of the two electronic wavefunctions (orbitals) at the equilibrium geometry and **name** them correctly.

b. Now assume the H atom is excited to the 2p state and forms an excited H2+ molecule with π bonding and π* antibonding states. **Draw** those two V(R) approximately on the same plot as in (a), at the correct relative energy. **Sketch** polar plots of these two electronic wavefunctions and label them π and π*.

[Hint: the excited H atom in the 2p state is higher in energy than the ground state H atom in the 1s state.]

**Solution:**

The V(R) curve for H in the 2p state is higher in energy since the 2p orbital is a higher energy state for the H atom. Remember that the ‘well’ shape in the bonding orbitals arises out of the nuclear-electron attraction term in the Hamiltonian; hence the well is shallower for the π orbital, since an electron in the 2p state feels a lower attraction from the nucleus.

Next, the bonding orbital has no node (higher probability of finding e between nuclei) and the antibonding orbital has a node (lower probability of finding e between nuclei).