

## Exam 2 Solution

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,  $\mu = \frac{1.008 \cdot 34.97}{1.008 + 34.97} * \frac{10^{-3} \text{kg}}{\text{mole}} = 1.626 * 10^{-27} \text{kg/molecule}$ ,  $r = 0.1275 \text{ nm}$ , so

$$I = \mu r^2 = 1.626 * 10^{-27} * (0.1275 * 10^{-9})^2 = 2.64 * 10^{-47} \text{kgm}^2$$

For J=1 to J=2 transition,

$$\Delta E = \frac{\hbar^2}{2I} (6 - 2) \quad (1)$$

$$= \frac{(6.626 * 10^{-34})^2 * 4}{2 * 4 * \pi^2 * 2.64 * 10^{-47}}$$

$$= 8.42 * 10^{-22} \text{J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 * 10^{-34} * 3 * 10^8}{8.42 * 10^{-22}} = 2.36 * 10^{-4} \text{m}$$

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:

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

- 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  $\hat{H}_{rot}$ :

$$\begin{aligned} \hat{H}_{rot} &= -\frac{\hbar^2}{2mr^2} \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right\} \\ &= -\frac{\hbar^2}{2mr^2} \left\{ \frac{1}{\sin\theta} \left( \cos\theta \frac{\partial}{\partial\theta} + \sin\theta \frac{\partial^2}{\partial\theta^2} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right\} \end{aligned}$$

$$= -\frac{\hbar^2}{2mr^2} \left\{ \cot\theta \frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right\}$$

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:

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

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  $\frac{\hbar^2}{mr^2} = \frac{\hbar^2 1 \cdot 2}{2mr^2}$  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  $\hat{I} = \sum_n |n\rangle\langle n|$  in Dirac notation or by  $\hat{I} = \sum_n \varphi_n(x) \int dx \varphi_n^*(x)$  in ordinary function notation.
- Show** by operating in function notation that  $\hat{I} \psi(x) = \psi(x)$  for any wavefunction  $\psi$ .
  - Show** by operating in Dirac notation that  $\hat{I} |\psi\rangle = |\psi\rangle$  for any ket  $|\psi\rangle$ .

**Solution:**

a)

$$\begin{aligned}\hat{I}\psi(x) &= \left( \sum_n \varphi_n \int dx \varphi_n^*(x) \right) \psi(x) \\ &= \sum_n \varphi_n \int dx \varphi_n^*(x) \psi(x) \\ &= \sum_n c_n \varphi_n(x) = \psi(x)\end{aligned}$$

b)

$$\begin{aligned}\hat{I}|\psi\rangle &= \left( \sum_n |n\rangle\langle n| \right) |\psi\rangle \\ &= \sum_n |n\rangle\langle n|\psi\rangle \\ &= \sum_n c_n |n\rangle = |\psi\rangle\end{aligned}$$

4. [5+5+5 pts] Consider the matrix

$$\tilde{M} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

- Find** the eigenvalues  $\lambda_1$  and  $\lambda_2$ , of the matrix by solving the equation  $\det\|\tilde{M} - \tilde{\Lambda}\| = 0$ , where  $\tilde{\Lambda}$  is the diagonal eigenvalue matrix.
- Plug each of these eigenvalues (one at a time) back into the equation  $(\tilde{M} - \tilde{\Lambda}) * \mathbf{v} = 0$ , to **find** the eigenvectors  $\mathbf{v}_{\lambda_1}$  and  $\mathbf{v}_{\lambda_2}$ ; no need to normalize.
- 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

$$\lambda = \pm 1 \rightarrow \lambda_1 = -1 \text{ and } \lambda_2 = 1$$

b)

$$\begin{aligned}\lambda_1 &= -1 : \\ \begin{pmatrix} 1 & -i \\ i & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} &= 0\end{aligned}$$

Gives to the two equations

$$\begin{aligned}c_1 - ic_2 &= 0 \\ ic_1 + c_2 &= 0\end{aligned}$$

Letting  $c_1 = 1$  yields  $c_2 = -i$  and we arrive at the first eigenvector

$$\mathbf{v}_{\lambda_1} = \begin{pmatrix} 1 \\ -i \end{pmatrix}$$

$\lambda_1 = 1$  :

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

Gives the two equations

$$\begin{aligned} -c_1 - ic_2 &= 0 \\ ic_1 - c_2 &= 0 \end{aligned}$$

Letting  $c_1 = 1$  yields  $c_2 = i$  and we arrive at the second eigenvector

$$\mathbf{v}_{\lambda_2} = \begin{pmatrix} 1 \\ i \end{pmatrix}$$

c)

$$\mathbf{v}_{\lambda_1}^\dagger \cdot \mathbf{v}_{\lambda_2} = \begin{pmatrix} 1 \\ -i \end{pmatrix}^\dagger \cdot \begin{pmatrix} 1 \\ i \end{pmatrix} = (1 \ i) \begin{pmatrix} 1 \\ i \end{pmatrix} = 1 - 1 = 0$$

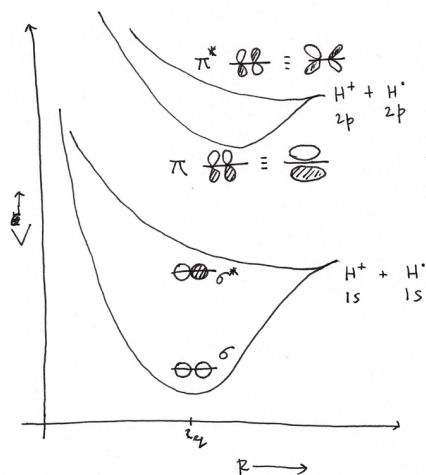
Therefore the eigenvectors are orthogonal.

5. [10+10 pts] a. **Draw**  $V(R)$  for  $H^+$  and  $H$  approaching one another to form an  $H_2^+$  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  $H_2^+$  molecule with  $\pi$  bonding and  $\pi^*$  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  $\pi$  and  $\pi^*$ .

[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  $\pi$  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)