CHM 442
Spring 2015

Exam 2

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.

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.

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.
a. **Show** by operating in function notation that $\hat{I}\,\psi(x) = \psi(x)$ for any wavefunction ψ.
b. **Show** by operating in Dirac notation that $\hat{I}\,|\psi >= |\psi >$ for any ket $|\psi >$.

4. [5+5+5 pts] Consider the matrix
$$\tilde{M} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

a. **Find** the eigenvalues λ_1 and λ_2, of the matrix by solving the equation $\det\|\tilde{M} - \tilde{\Lambda}\| = 0$, where $\tilde{\Lambda}$ is the diagonal eigenvalue matrix.
b. 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.
c. **Verify** that the eigenvectors are orthogonal, i.e. show that $\mathbf{v}_{\lambda_1}{}^{\dagger} \cdot \mathbf{v}_{\lambda_2} = 0$.

5. [10+10 pts] a. **Draw** V(R) for H^+ and $H^\cdot$ approaching one another to form an H_2^+ molecule in its lowest energy state and in its first excited state. **Sketch** qualitative polar plots of the two electronic wavefunctions (orbitals) at the equilibrium geometry and **name** them correctly.

b. Now assume the $H^\cdot$ atom is excited to the 2p state and forms an excited H_2^+ molecule with π bonding and π* antibonding states. **Draw** those two V(R) curves on the same plot as in (a), at the correct relative energy. **Sketch** qualitative 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.]