Chem 442
Fall 2015
Hour Exam 2

1. (10 pts) **Calculate** the energy in Joules required to excite an electron in the hydrogen atom from the *n*=2 to *n*=4 state, given that the Rydberg constant converted to Joule units is $\approx 2.18 \cdot 10^{-18} J$.

2. (10 pts) **Show** that the Gaussian stationary state $\Psi(x) \sim e^{-m\omega x^2/2\hbar}$ of the vibrating molecule that we derived in lecture really is the lowest energy state, or 'ground state': the Heisenberg principle forbids the wavefunction from having a smaller Δx and 'squeezing down further' in energy.

[Hint: The lowering operator is $\hat{a} = \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{2}} \left(\hat{x} + \frac{i}{m\omega}\hat{p}\right)$, and you should remember what $\hat{p}$ =?]

3. (15 pts) If $Y_{2,-2} \sim sin^2\theta e^{-2i\varphi}$ and $Y_{2,+2} \sim sin^2\theta e^{+2i\varphi}$ are degenerate eigenfunctions of the Hamiltonian $\widehat{H}_{rot}$ with eigenvalue $E_{2,\pm 2} = 6\hbar^2/(2mR^2)$,

a) **Write down** the real function $d_{xy}(\theta, \varphi) \sim i(Y_{2,+2} - Y_{2,-2})$, and **prove** that it is also an eigenfunction of $\widehat{H}_{rot}$.

b) **Plot** a polar plot of $d_{xy}(\theta, \varphi)$ in the x-y plane (θ = π/2, plot as function of φ). Cross-hatch the negative lobes of the function.

c) Given the trigonometric identity $sin2\varphi \sim cos\varphi sin\varphi$, and knowing that $x = cos\varphi$ and $y = sin\varphi$ if *r*=1, **why** do you think this function is called d_{xy}?

4. (25 pts) The technique of finding the eigenvalues and eigenvectors of the Hamiltonian in matrix form is called "diagonalization". You will diagonalize the Hamiltonian matrix

$$\mathrm{H} = \begin{pmatrix} 3 & \sqrt{5}/2 \\ \sqrt{5}/2 & 1 \end{pmatrix}$$

The starting point is the equation H **v** = E **v** or (H– IE) · **v** = 0, where H is your non-diagonal Hamiltonian matrix, I is the identity matrix, E is one of the eigenvalues, and **v** is one of the eigenvectors. In order to obtain a non-trivial solution, we need the condition det $\|\mathrm{H} - \mathrm{I}E\| = 0$.

a. **Multiply out** the determinant of the matrix H − IE, to get a quadratic equation for the

two eigenvalues *E*. **Solve** for *E*. This gives you the 2 eigenvalues of the 2x2 matrix.

b. **Plug one** of these eigenvalues into the equation $(H - IE) \cdot \mathbf{v} = 0$, writing the vector **v** as a column vector $\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$.

c. **Solve** for c_1 in terms of c_2 or *vice versa*, so you know your eigenvector within a constant factor.

d. **Normalize** the eigenvector. Remember that $\mathbf{v}^\dagger \cdot \mathbf{v} = c$, then divide by $\sqrt{c}$ to normalize, just like for wavefunctions.

e. **Check** that your eigenvector satisfies $H\mathbf{v} = E\mathbf{v}$. If the basis set used to calculate the Hamiltonian matrix was $\varphi_1 = \sqrt{\frac{1}{\pi}} sin\phi$ and $\varphi_2 = \sqrt{\frac{1}{\pi}} cos\phi$, **what is** the wavefunction $\psi(\phi)$ that corresponds to your eigenvector **v**?

5. (10 pts) In lecture, Gruebele started with $\hat{A}\psi(x) = \chi(x)$, expanded in a complete basis $\psi(x) = \sum c_n \varphi_n(x)$ and $\chi(x) = \sum c'_n \varphi_n(x)$, and showed that this is equivalent to A**v**=**u** or $\sum A_{mn} c_n = c'_m$ for vectors, where A is a matrix with elements $A_{mn} = \int dx \varphi^*_m(x)\, \hat{A} \varphi_n(x)$.

Now do the same derivation in bracket notation. Start with $\hat{A}|\psi> = |\chi>$, **expand** the kets in a basis |*n*>, and **prove** again that $\sum A_{mn} c_n = c'_m$, this time with $A_{mn} = < m|\hat{A}|n >$