Chemistry 3PA3 - Sample Final Questions

A Casio FX991 calculator, and 1 $8\frac{1}{2} \times 11$" sheet written on both sides, are the only aids allowed.

$$h = 4.136 \times 10^{-15} \text{ eV s}$$

1. Each of the following wavefunctions is an eigenfunction of one of the Hamiltonians listed below.

a. Which Hamiltonian is associated with each eigenfunction?

b. What is the associated eigenvalue?

Eigenfunctions:

i.

$$\psi(u) = \frac{1}{\sqrt{\pi}} \sin(3u)$$

$-\ -\ -\ -\ -\ -\ -\ -\ -\ -$

a. This is a particle in a box energy eigenfunction. It is an eigenfunction of Hamiltonian a. Note that $\sin(3u) = 0$ for $u = 0$ and $u = \pi$. Verify:

$$-\frac{1}{2}\frac{d^2}{du^2}\frac{1}{\sqrt{\pi}}\sin(3u) = -\frac{1}{2}\frac{1}{\sqrt{\pi}}\frac{d}{du}3\cos(3u)$$

$$= \frac{1}{2}\frac{1}{\sqrt{\pi}}9\sin(3u)$$

$$= \frac{9}{2}\psi(u).$$

b. The associated eigenvalue is $9/2$.

$-\ -\ -\ -\ -\ -\ -\ -\ -\ -$

ii.

$$\psi(u) = \frac{1}{\sqrt{2\pi}} \exp(2iu)$$

$-\ -\ -\ -\ -\ -\ -\ -\ -\ -$

a. This is a particle in a ring energy eigenfunction. It is an eigenfunction of Hamiltonian b - the same as Hamiltonian a, except for the boundary conditions - periodic boundary conditions in this case. Verify:

$$-\frac{1}{2}\frac{d^2}{du^2}\frac{1}{\sqrt{2\pi}}\exp(2iu) = -\frac{1}{2}\frac{1}{\sqrt{2\pi}}\frac{d}{du}2i\exp(2iu)$$

$$= \frac{1}{2}\frac{1}{\sqrt{2\pi}}4\exp(2iu)$$

$$= 2\psi(u).$$

b. The associated eigenvalue is 2.

– – – – – – – – – –

iii.

$$\psi(u) = u\exp(-u)$$

– – – – – – – – – –

a. This is a hydrogen atom scaled radial energy eigenfunction. It is an eigenfunction of Hamiltonian d. Verify:

$$\left(-\frac{1}{2}\frac{d^2}{du^2} - \frac{1}{u}\right)u\exp(-u)$$

$$= -\frac{1}{2}\frac{d}{du}(\exp(-u) - u\exp(-u)) - \exp(-u)$$

$$= -\frac{1}{2}(-\exp(-u) - \exp(-u) + u\exp(-u)) - \exp(-u)$$

$$= \exp(-u) - \frac{1}{2}u\exp(-u) - \exp(-u)$$

$$= -\frac{1}{2}\psi(u)$$

b. The associated eigenvalue is $-1/2$. $\psi(u)$ is the 1s scaled radial wavefunction.

– – – – – – – – – –

iv.

$$\psi(u) = \frac{1}{\sqrt{\pi}}\exp\left(-\frac{u^2}{2}\right)$$

– – – – – – – – – –

a. This is a harmonic oscillator energy eigenfunction. It is an eigenfunction of Hamiltonian c. Verify:

$$\left(-\frac{1}{2}\frac{d^2}{du^2} + \frac{1}{2}u^2\right)\frac{1}{\sqrt{\pi}}\exp\left(-\frac{u^2}{2}\right)$$

$$= \frac{1}{\sqrt{\pi}} \left[-\frac{1}{2} \frac{d}{du} \left(-u \exp\left(-\frac{u^2}{2}\right) \right) + \frac{1}{2} u^2 \exp\left(-\frac{u^2}{2}\right) \right]$$

$$= \frac{1}{\sqrt{\pi}} \left[-\frac{1}{2} \left(-\exp\left(-\frac{u^2}{2}\right) + u^2 \exp\left(-\frac{u^2}{2}\right) \right) + \frac{1}{2} u^2 \exp\left(-\frac{u^2}{2}\right) \right]$$

$$= \frac{1}{\sqrt{\pi}} \left[\frac{1}{2} \exp(-u^2) - \frac{1}{2} u^2 \exp(-u^2) + \frac{1}{2} u^2 \exp(-u^2) \right]$$

$$= \frac{1}{2} \psi(u)$$

b. The associated eigenvalue is $1/2$.

– – – – – – – – – –

v.

$$\psi(u) = \frac{1}{\sqrt{\pi}} \exp(5iu)$$

– – – – – – – – – –

a. This is a particle in a ring energy eigenfunction. It is an eigenfunction of Hamiltonian b - the same as Hamiltonian a, except for the boundary conditions - periodic boundary conditions in this case. Verify:

$$-\frac{1}{2} \frac{d^2}{du^2} \frac{1}{\sqrt{2\pi}} \exp(5iu) = -\frac{1}{2} \frac{1}{\sqrt{2\pi}} \frac{d}{du} 5i \exp(2iu)$$

$$= \frac{1}{2} \frac{1}{\sqrt{2\pi}} 25 \exp(2iu)$$

$$= \frac{25}{2} \psi(u).$$

b. The associated eigenvalue is $25/2$.

– – – – – – – – – –

vi.

$$\psi(u) = u\left(1 - \frac{u}{2}\right) \exp\left(-\frac{u}{2}\right)$$

– – – – – – – – – –

a. This is a hydrogen atom scaled radial energy eigenfunction. It is an eigenfunction of Hamiltonian d. Verify:

$$\left(-\frac{1}{2} \frac{d^2}{du^2} - \frac{1}{u}\right)\left(u - \frac{u^2}{2}\right) \exp\left(-\frac{u}{2}\right)$$

$$= -\frac{1}{2}\frac{d}{du}\left(\left(1-u\right)\exp\left(-\frac{u}{2}\right) - \frac{1}{2}\left(u - \frac{u^2}{2}\right)\exp\left(-\frac{u}{2}\right)\right) - \left(1 - \frac{u}{2}\right)\exp\left(-\frac{u}{2}\right)$$

$$= -\frac{1}{2}\left(-\exp\left(-\frac{u}{2}\right) - \frac{1}{2}(1-u)\exp\left(-\frac{u}{2}\right) - \frac{1}{2}(1-u)\exp\left(-\frac{u}{2}\right) + \frac{1}{4}\left(u - \frac{u^2}{2}\right)\exp\left(-\frac{u}{2}\right)\right.$$
$$\left. - \left(1 - \frac{u}{2}\right)\exp\left(-\frac{u}{2}\right)\right.$$

$$= \left[-\frac{1}{2}\left(-1 - \frac{1}{2}(1-u) - \frac{1}{2}(1-u) + \frac{1}{4}\left(u - \frac{u^2}{2}\right)\right) - 1 + \frac{u}{2}\right]\exp\left(-\frac{u}{2}\right)$$

$$= \left[-\frac{1}{2}\left(-2 + \frac{5}{4}u - \frac{u^2}{8}\right) - 1 + \frac{u}{2}\right]\exp\left(-\frac{u}{2}\right)$$

$$= -\frac{1}{2}\left(\frac{1}{4}u - \frac{u^2}{8}\right)\exp\left(-\frac{u}{2}\right)$$

$$= -\frac{1}{8}\psi(u)$$

b. The associated eigenvalue is $-1/8$. $\psi(u)$ is the 2s scaled radial wavefunction.

– – – – – – – – – – –

Hamiltonians:

    a.

$$\hat{H} = -\frac{1}{2}\frac{d^2}{du^2} \qquad 0 < u < \pi$$

        Hard wall boundary conditions: $\qquad \psi(0) = \psi(\pi) = 0$

    b.

$$\hat{H} = -\frac{1}{2}\frac{d^2}{du^2} \qquad 0 \le u < 2\pi$$

        Periodic boundary conditions: $\qquad \psi(0) = \psi(2\pi)$

    c.

$$\hat{H} = -\frac{1}{2}\frac{d^2}{du^2} + \frac{1}{2}u^2 \qquad -\infty < u < \infty$$

    d.

$$\hat{H} = -\frac{1}{2}\frac{d^2}{du^2} - \frac{1}{u} \qquad 0 \le u < \infty$$

  2. Which of the eigenfunctions of question 1 are normalized. For the function(s) which is(are) not normalized, what is the correct normalized eigenfunction?

– – – – – – – – – – –

Check normalizations:

    a.   **i.**

$$\int_0^\pi \left(\frac{1}{\sqrt{\pi}} \sin(3u) \right)^2 du$$

$$= \frac{1}{\pi} \int_0^\pi \sin^2(3u)\, du$$

$$= \frac{1}{\pi} \frac{\pi}{2} \qquad \text{from integrals provided}$$

$$= \frac{1}{2}$$

This wavefunction is not normalized. The normalized wavefunction is

$$\sqrt{\frac{2}{\pi}} \sin(3u).$$

ii.

$$\int_0^{2\pi} \left| \frac{1}{\sqrt{2\pi}} \exp(2iu) \right|^2 du$$

$$= \frac{1}{2\pi} \int_0^{2\pi} \exp(-2iu + 2iu)\, du$$

$$= \frac{1}{2\pi} \int_0^{2\pi} du$$

$$= \frac{2\pi}{2\pi} = 1$$

This wavefunction is normalized.

iii.

$$\int_0^\infty (u \exp(-u))^2\, du$$

$$= \int_0^\infty u^2 \exp(-2u)\, du$$

$$= \frac{2!}{2^{2+1}} \qquad \text{from integrals provided}$$

$$= \frac{2}{8} = \frac{1}{4}$$

This wavefunction is not normalized. The normalized wavefunction is

$$\sqrt{4}\, u \exp(-u)$$

$$= 2u \exp(-u).$$

iv.

$$\int_{-\infty}^{\infty} \left(\frac{1}{\sqrt{\pi}} \exp\left(-\frac{u^2}{2}\right) \right)^2 du$$

$$= \frac{1}{\pi} \int_{-\infty}^{\infty} \exp(-u^2)\,du$$

$$= \frac{1}{\pi} \sqrt{\pi} \qquad \text{from integrals provided}$$

$$= \frac{1}{\sqrt{\pi}}$$

This wavefunction is not normalized. The normalized wavefunction is

$$\frac{1}{\pi^{1/4}} \exp\left(-\frac{u^2}{2}\right).$$

v.

$$\int_0^{2\pi} \left| \frac{1}{\sqrt{\pi}} \exp(5iu) \right|^2 du$$

$$= \frac{1}{\pi} \int_0^{2\pi} 1\,du$$

$$= \frac{2\pi}{\pi} = 2$$

This wavefunction is not normalized. The normalized wavefunction is

$$\frac{1}{\sqrt{2\pi}} \exp(5iu).$$

vi.

$$\int_0^{\infty} \left(u\left(1 - \frac{u}{2}\right) \exp\left(-\frac{u}{2}\right) \right)^2 du$$

$$= \int_0^{\infty} u^2 \left(1 - \frac{u}{2}\right)^2 \exp(-u)\,du$$

$$= \int_0^{\infty} u^2 \left(1 - u + \frac{u^2}{4}\right) \exp(-u)\,du$$

$$= \int_0^{\infty} u^2 \exp(-u)\,du - \int_0^{\infty} u^3 \exp(-u)\,du + \frac{1}{4} \int_0^{\infty} u^4 \exp(-u)\,du$$

$$= \frac{2!}{1^{2+1}} - \frac{3!}{1^{3+1}} + \frac{1}{4}\frac{4!}{1^{4+1}} \qquad \text{from integrals provided}$$

$$= 2 - 6 + 6 = 2$$

This wavefunction is not normalized. The normalized wavefunction is

$$\frac{1}{\sqrt{2}} u\left(1 - \frac{u}{2}\right) \exp\left(-\frac{u}{2}\right).$$

- - - - - - - - - - -

3. The angular momentum raising and lowering operators are given by

$$\hat{L}_+ = \hbar \exp(i\phi)\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi} \right)$$

and

$$\hat{L}_- = \hbar \exp(-i\phi)\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi} \right),$$

respectively.

a. Given that the eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ have the form,

$$Y_{\ell,m_\ell}(\theta,\phi) = \Theta_{\ell,m_\ell}(\theta)\frac{1}{\sqrt{2\pi}}\exp(im_\ell\phi),$$

find the top state for the $\ell = 2$ ladder of states.

-- -- -- -- -- -- --

The top state for the $\ell = 2$ ladder of states is

$$Y_{2,2}(\theta,\phi) = \Theta_{2,2}(\theta)\frac{1}{\sqrt{2\pi}}\exp(i2\phi).$$

It is such that, if you try to raise the m_ℓ quantum number by an application of $\hat{L}_+$, the result must be zero. Specifically,

$$\hat{L}_+Y_{2,2}(\theta,\phi) = 0$$

$$\hbar\exp(i\phi)\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi} \right)\Theta_{2,2}(\theta)\frac{1}{\sqrt{2\pi}}\exp(i2\phi) = 0$$

$$\frac{\partial}{\partial\theta}\Theta_{2,2}(\theta)\exp(i2\phi) + i\cot\theta\frac{\partial}{\partial\phi}\Theta_{2,2}(\theta)\exp(i2\phi) = 0$$

$$\exp(i2\phi)\frac{d}{d\theta}\Theta_{2,2}(\theta) + i\cot\theta\Theta_{2,2}(\theta)\frac{d}{d\phi}\exp(i2\phi) = 0$$

$$\exp(i2\phi)\frac{d}{d\theta}\Theta_{2,2}(\theta) + i\cot\theta\Theta_{2,2}(\theta)(2i)\exp(i2\phi) = 0$$

$$\frac{d}{d\theta}\Theta_{2,2}(\theta) - 2\cot\theta\Theta_{2,2}(\theta) = 0$$

which gives

$$\frac{1}{\Theta_{2,2}(\theta)}\frac{d}{d\theta}\Theta_{2,2}(\theta) = 2\frac{\cos\theta}{\sin\theta}$$

$$\frac{d\Theta_{2,2}(\theta)}{\Theta_{2,2}(\theta)} = 2\frac{\cos\theta}{\sin\theta}d\theta$$

$$\int\frac{d\Theta_{2,2}(\theta)}{\Theta_{2,2}(\theta)} = 2\int\frac{\cos\theta}{\sin\theta}d\theta$$

$$\ln\Theta_{2,2}(\theta) = 2\int\frac{d\sin\theta}{\sin\theta} + C' \qquad C' = \text{constant}$$

$$= 2\ln\sin\theta + C'$$

$$= \ln\sin^2\theta + C'$$

$$\Theta_{2,2}(\theta) = e^{C'}\sin^2\theta = C\sin^2\theta$$

The top state we seek is given by
$$\frac{C}{\sqrt{2\pi}}\sin^2\theta\exp(i2\phi).$$

– – – – – – – – – – –

b. Use the lowering operator to determine $Y_{2,1}(\theta,\phi)$, to within a multiplicative constant.

– – – – – – – – – – –

$$Y_{2,1}(\theta,\phi) = A''\hat{L}_- Y_{2,2}(\theta,\phi) \qquad A'' = \text{constant}$$

$$= A''\hbar\exp(-i\phi)\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)\frac{C}{\sqrt{2\pi}}\sin^2\theta\exp(i2\phi)$$

$$= A'\exp(-i\phi)\left(-\frac{\partial}{\partial\theta}\sin^2\theta\exp(i2\phi) + i\cot\theta\frac{\partial}{\partial\phi}\sin^2\theta\exp(i2\phi)\right)$$

$$= A'\exp(-i\phi)\left(-\exp(i2\phi)\frac{d}{d\theta}\sin^2\theta + i\frac{\cos\theta}{\sin\theta}\sin^2\theta\frac{d}{d\phi}\exp(i2\phi)\right)$$

$$= A'\exp(-i\phi)(-\exp(i2\phi)2\cos\theta\sin\theta + i\cos\theta\sin\theta(i2)\exp(i2\phi))$$

$$= A'\exp(i\phi)(-2\cos\theta\sin\theta - 2\cos\theta\sin\theta)$$

$$= A\cos\theta\sin\theta\exp(i\phi)$$

– – – – – – – – – – –

4. Suppose the vibrational state of a diatomic molecule is represented by the wavefunction,
$$\psi(x) = \frac{1}{\sqrt{2}}\psi_0(x) + \frac{1}{2}\psi_1(x) + \frac{1+i}{2\sqrt{2}}\psi_2(x),$$
where $\psi_0(x)$, $\psi_1(x)$ and $\psi_2(x)$ are the normalized ground, and first two excited, vibrational states of the diatomic molecule. Also, suppose that these states are well approximated by the energy eigenstates of a harmonic oscillator.

a. Show that ψ is normalized.

– – – – – – – – – – –

$$\|\psi\|^2 = \left\langle \frac{1}{\sqrt{2}}\psi_0 + \frac{1}{2}\psi_1 + \frac{1+i}{2\sqrt{2}}\psi_2 \middle| \frac{1}{\sqrt{2}}\psi_0 + \frac{1}{2}\psi_1 + \frac{1+i}{2\sqrt{2}}\psi_2 \right\rangle$$

$$= \frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\langle\psi_0|\psi_0\rangle + \frac{1}{2}\frac{1}{2}\langle\psi_1|\psi_1\rangle + \left(\frac{1+i}{2\sqrt{2}}\right)^*\left(\frac{1+i}{2\sqrt{2}}\right)\langle\psi_2|\psi_2\rangle + \text{cross terms}$$

There are six cross terms (6 = the binomial factor, "3 choose 2").
Each cross term has a factor, $\langle\psi_v|\psi_{v'}\rangle$, where $v \neq v'$. Since the distinct vibrational states are orthogonal, all the cross terms are zero. Thus,

$$\|\psi\|^2 = \frac{1}{2}\underbrace{\langle\psi_0|\psi_0\rangle}_{=1} + \frac{1}{4}\underbrace{\langle\psi_1|\psi_1\rangle}_{=1} + \frac{(1-i)(1+i)}{4\times 2}\underbrace{\langle\psi_2|\psi_2\rangle}_{=1}$$

$$= \frac{1}{2} + \frac{1}{4} + \frac{1-i^2}{8} \qquad \text{the vibrational states are normalized}$$

$$= \frac{1}{2} + \frac{1}{4} + \frac{2}{8} = 1.$$

- - - - - - - - - - -

b. If the vibrational energy of the molecule is measured, what is the probability of each of the following outcomes - in units of $h\nu_{\text{vib}}$, where $\nu_{\text{vib}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ is the vibrational frequency of the molecule?

i.
$$\frac{1}{2}$$

ii.
$$\frac{3}{2}$$

iii.
$$\frac{5}{2}$$

iv.
$$\frac{7}{2}$$

- - - - - - - - - - -

The probability of an energy measurement yielding $E_\upsilon = (\upsilon + \frac{1}{2})h\nu_{\text{vib}}$ is given by

$$|\langle\psi_\upsilon|\psi\rangle|^2 = \left|\langle\psi_\upsilon\left|\frac{1}{\sqrt{2}}\psi_0 + \frac{1}{2}\psi_1 + \frac{1+i}{2\sqrt{2}}\psi_2\right.\rangle\right|^2$$

$$= \left|\frac{1}{\sqrt{2}}\langle\psi_\upsilon|\psi_0\rangle + \frac{1}{2}\langle\psi_\upsilon|\psi_1\rangle + \frac{1+i}{2\sqrt{2}}\langle\psi_\upsilon|\psi_2\rangle\right|^2.$$

The given energies correspond to $\upsilon = 0, 1, 2$ and 3. For $\upsilon = 0$ (energy $= 1/2$ in units of $h\nu_{\text{vib}}$), the probability equals

$$|\langle\psi_0|\psi\rangle|^2 = \left|\frac{1}{\sqrt{2}}\underbrace{\langle\psi_0|\psi_0\rangle}_{=1} + \frac{1}{2}\underbrace{\langle\psi_0|\psi_1\rangle}_{=0} + \frac{1+i}{2\sqrt{2}}\underbrace{\langle\psi_0|\psi_2\rangle}_{=0}\right|^2$$

$$= \left|\frac{1}{\sqrt{2}}\right|^2 = \frac{1}{2}.$$

For $\upsilon = 1$ (energy $= 3/2$), the probability is

$$|\langle \psi_1 | \psi \rangle|^2 = \left|\frac{1}{2}\right|^2 = \frac{1}{4}.$$

For $v = 2$ (energy $= 5/2$), the probability is

$$|\langle \psi_2 | \psi \rangle|^2 = \left|\frac{1+i}{2\sqrt{2}}\right|^2$$

$$= \frac{1+1}{4 \times 2} = \frac{1}{4}.$$

For $v = 3$ (energy $= 7/2$), the probability is zero.

$-----------$

c. If $\psi(x)$ is the vibrational state of the system at time $= 0$, what is the vibrational state at time,

$$t = \frac{1}{2v_{\text{vib}}}?$$

Are the probabilities of the above energy-measurement-outcomes different, if the energy is measured at this time?

$-----------$

The state of the system is given by solving the time dependent Schrodinger equation with $\psi(x)$ as the initial state. Each of the energy eigenfunction components of $\psi(x)$ time evolves by picking up a phase factor, $\exp(-iE_v t/\hbar)$. Thus, the state of the system at time $= t$, is

$$\frac{\exp(-iE_0 t/\hbar)}{\sqrt{2}}\psi_0 + \frac{\exp(-iE_1 t/\hbar)}{2}\psi_1 + \frac{(1+i)\exp(-iE_2 t/\hbar)}{2\sqrt{2}}\psi_2$$

$$= \frac{\exp(-2\pi i(\frac{1}{2}hv_{\text{vib}})t/h)}{\sqrt{2}}\psi_0 + \frac{\exp(-2\pi i(\frac{3}{2}hv_{\text{vib}})t/h)}{2}\psi_1 + \frac{(1+i)\exp(-2\pi i(\frac{5}{2}hv_{\text{vib}})t/h)}{2\sqrt{2}}\psi_2$$

$$= \frac{\exp\left(-2\pi i \frac{(\frac{1}{2}hv_{\text{vib}})}{2hv_{\text{vib}}}\right)}{\sqrt{2}}\psi_0 + \frac{\exp\left(-2\pi i \frac{(\frac{3}{2}hv_{\text{vib}})}{2hv_{\text{vib}}}\right)}{2}\psi_1 + \frac{(1+i)\exp\left(-2\pi i \frac{(\frac{5}{2}hv_{\text{vib}})}{2hv_{\text{vib}}}\right)}{2\sqrt{2}}\psi_2$$

$$= \frac{\exp(-2\pi i\frac{1}{4})}{\sqrt{2}}\psi_0 + \frac{\exp(-2\pi i\frac{3}{4})}{2}\psi_1 + \frac{(1+i)\exp(-2\pi i\frac{5}{4})}{2\sqrt{2}}\psi_2$$

$$= \frac{\exp(-\frac{\pi i}{2})}{\sqrt{2}}\psi_0 + \frac{\exp(-\frac{3\pi i}{2})}{2}\psi_1 + \frac{(1+i)\exp(-\frac{5\pi i}{2})}{2\sqrt{2}}\psi_2 \qquad \text{an acceptable answer}$$

$$= \frac{-i}{\sqrt{2}}\psi_0 + \frac{i}{2}\psi_1 + \frac{(1+i)(-i)}{2\sqrt{2}}\psi_2 = \frac{-i}{\sqrt{2}}\psi_0 + \frac{i}{2}\psi_1 + \frac{(1-i)}{2\sqrt{2}}\psi_2$$

$-----------$

d. Suppose the outcome of a measurement of the energy is $3hv_{\text{vib}}/2$. What is the vibrational state of the diatomic molecule after the measurement?

When the energy is measureed to be $3h\nu_{vib}/2$, the system state is subsequently equal to the energy eigenstate associated with this energy eigenvalue. Thus, the state of the system will be

$$\psi_1(x).$$

----

e. Suppose the absorption spectrum of a collection of molecules in state ψ is measured. What would the spectrum look like? If anharmonicity were not negligible - in particular, the potential has an x^3 term with negative coefficient - what would the spectrum look like in this case? Label the "hot bands".

Because of the selection rule, $\Delta v = \pm 1$ ($\Delta v = +1$ for absorption), there are three transitions possible: $0 \to 1$, $1 \to 2$ and $2 \to 3$. These are possible because the initial state is a superposition of $v = 0, 1$ and 2 states. Because the harmonic oscillator has equal spacings between energy levels, these transitions all correspond to the same frequency and only one absorption peak is seen in the spectrum. If there is anharmonicity, as described, then the energy level spacings decrease slightly with energy. In this case, there are three absorption peaks. The $1 \to 2$ transition occurs at a slightly lower frequency than $0 \to 1$, and its intensity is $1/2$ that of $0 \to 1$. The intensity is proportional to the probability that the molecule is in the $v = 1$ state. Similarly, the $2 \to 3$ transition occurs at another slightly lower frequency (lower than $1 \to 2$), and its intensity is $1/2$ that of $0 \to 1$ (i.e, the same as the $1 \to 2$ peak).

----

5. A certain quantum dot can be modeled as a two dimensional $L \times L$ box, such that

$$\frac{\hbar^2 \pi^2}{2m_e L^2} = 1 \text{ eV}.$$

a. What is the degeneracy of the three lowest energy eigenvalues for one electron in this quantum dot?

The energy eigenfunctions of one electron in this two dimensional quantum dot are given by

$$E_{n_x,n_y} = \frac{\hbar^2 \pi^2}{2m_e L^2}(n_x^2 + n_y^2), \qquad n_x = 1, 2, \dots \text{ and } n_y = 1, 2, \dots.$$

$$= n_x^2 + n_y^2 \text{ eV}$$

The lowest energy level corresponds to $(n_x, n_y) = (1, 1)$. The energy

is

$$E_{1,1} = 1^2 + 1^2 \text{ eV}$$
$$= 2 \text{ eV}.$$

The $(1,2)$ and $(2,1)$ states have the same energy (i.e., the second lowest energy is doubly degenerate),

$$E_{1,2} = E_{2,1} = 2^2 + 1^2 \text{ eV}$$
$$= 5 \text{ eV}.$$

The $(2,2)$ state has energy

$$E_{2,2} = 2^2 + 2^2 \text{ eV}$$
$$= 8 \text{ eV},$$

while the $(1,3)$ and $(3,1)$ states have energy,

$$E_{1,3} = E_{3,1} = 3^2 + 1^2 \text{ eV}$$
$$= 10 \text{ eV}.$$

Thus, the third lowest energy is 8 eV, and it has a degeneracy of 1. In summary, the lowest three energy levels and degeneracies are

given by

2,2	8 eV	degeneracy = 1
1,2 and 2,1	5 eV	degeneracy = 2
1,1	2 eV	degeneracy = 1

– – – – – – – – – – –

b. Suppose there are six electrons in the quantum dot, and electron-electron repulsion can be neglected.

   i. What is the ground state energy of this quantum dot?

  ii. What are the two lowest transition frequencies of this quantum dot?

– – – – – – – – – – –

i. The six electrons are placed in the one-electron states - the orbitals of the quantum dot - starting with the lowest energy orbital, moving upwards once an orbital has two electrons (one spin up and one spin down). Thus, the ground state electron configuration is

$$[1,1]^2[1,2]^4,$$

where $[1,2]$ represents the $(1,2)$ and $(2,1)$ shell. The ground state energy is given by summing the one-electron energies:

$$E_{\text{g.s.}} = 2 \times 2 + 4 \times 5 \text{ eV}$$
$$= 24 \text{ eV}.$$

ii. The two lowest transitions are the

$[1,1]^2[1,2]^4 \rightarrow [1,1]^2[1,2]^3[2,2]$ and
$[1,1]^2[1,2]^4 \rightarrow [1,1]^2[1,2]^3[1,3]$ transitions. In these
transitions, one electron in $[1,2]$ is promoted to $[2,2]$
(lowest energy transition) or $[1,3]$ (next lowest). The
frequencies associated with these transitions are given by

$$v = \frac{\Delta E}{h} = \begin{cases} \frac{(2\times2+3\times5+8)-24 \text{ eV}}{h} & \text{lowest} \\[2mm] \frac{(2\times2+3\times5+10)-24 \text{ eV}}{h} & \text{next} \end{cases}$$

$$= \begin{cases} \frac{3 \text{ eV}}{h} \\[2mm] \frac{5 \text{ eV}}{h} \end{cases} = \begin{cases} 725 \text{ THz} \\[2mm] 1209 \text{ THz} \end{cases}.$$

– – – – – – – – – –

6. Consider a diatomic molecule with moment of inertia, I, such that the rotational constant in wavenumbers,

$$\bar{B} = \frac{\hbar^2}{2Ihc} = 50 \text{ cm}^{-1}.$$

a. Neglecting centrigual distortion, sketch the rotational spectrum of this molecule with wavenumbers (in cm^{-1}) along the horizontal axis. What is the spacing between peaks? What is the origin of the peak intensities? How would centrifugal distortion affect this spectrum?

– – – – – – – – – –

The lines occur at all multiples of $2\bar{B} = 100$ cm^{-1}, weighted by the populations of the distinct J th levels ($J = 0, 1, 2, \ldots$) which is proportional to

$$(2J + 1)\exp\left(-\frac{J(J+1)B}{k_B T}\right).$$

The spectrum has the following form:
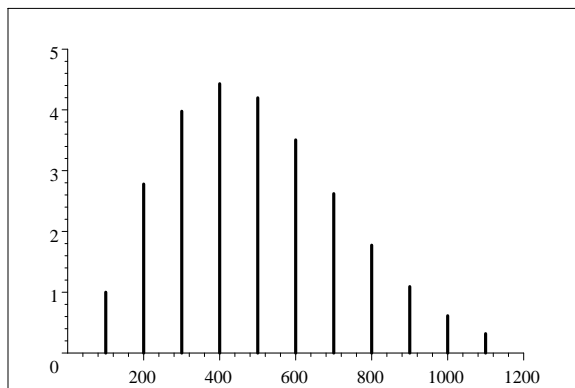
Centrifugal distortion causes the spacings between peaks ($\Delta\Delta E$) to decrease with increasing J - i.e., the high frequency peaks would be closer together. Note that the overall envelope of the peaks would

be same. A decreasing spacing results from the larger moment of inertia associated with a rapidly rotating molecule. The effect is quite small, however, and would not be evident without careful measrement of the peak positions.

— — — — — — — — — —

b. Rotational structure is seen in the fundamental vibrational transition of this molecule. Sketch this detailed structure of the fundamental vibrational transition with the horizontal axis showing $\bar{\nu} - \bar{\nu}_{vib}$, the difference of the absorption line wavenumbers from the fundamental vibrational transition frequency. Label all "branches" shown. Which branches that do not appear in this spectrum appear in a Raman spectrum?

— — — — — — — — — —
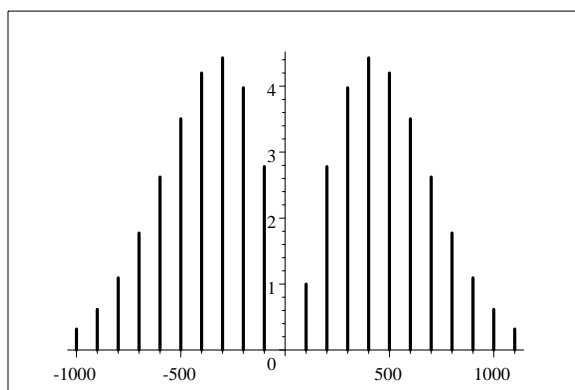
The branch on the left (the peaks with negative $\bar{\nu} - \bar{\nu}_{vib}$) is called the P branch. These peaks result from $\Delta J = -1$ transitions. The branch on the left (the peaks with positive $\bar{\nu} - \bar{\nu}_{vib}$) is called the R branch. These peaks result from $\Delta J = +1$ transitions.

— — — — — — — — — —

c. Which peak in the R branch of the above spectrum has the same intensity as the first peak (the peak with $\bar{\nu}$ closest to $\bar{\nu}_{vib}$) of the P branch?

— — — — — — — — — —

The second peak in the R branch has the same intensity as the first peak in the P branch. This intensity is determined by the population of the $J = 1$ level, in both cases. This is the first peak in the P branch because the first $\Delta J = -1$ transition is the $1 \rightarrow 0$ transition.

— — — — — — — — — —

d. What are the selection rules for ro-vibrational transitions?

— — — — — — — — — —

$\Delta v = \pm 1$, $\Delta J = \pm 1$ and $\Delta M_J = 0, \pm 1$.

- - - - - - - - - - -

7. Consider the normalized scaled radial wavefunction (i.e., the radial wavefunction is $rR(r)$),

$$\varphi(r) = 2a^{3/2}r\exp(-ar),$$

for a hydrogen atom. Here, a is a parameter that can be varied.

a. Determine the expectation value of the $\ell = 0$ radial Hamiltonian (associated with the scaled radial wavefunction),

$$\hat{H} = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r},$$

for a hydrogen atom in state $\varphi(r)$.

- - - - - - - - - - -

$$\langle\varphi|\hat{H}\varphi\rangle = \int_0^\infty 2a^{3/2}r\exp(-ar)\left(-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\right)2a^{3/2}r\exp(-ar)\,dr$$

$$= 4a^3\int_0^\infty r\exp(-ar)\left(-\frac{1}{2}\frac{d}{dr}(\exp(-ar) - ar\exp(-ar)) - \exp(-ar)\right)dr$$

$$= 4a^3\int_0^\infty r\exp(-ar)\left(-\frac{1}{2}(-a\exp(-ar) - a\exp(-ar) + a^2r\exp(-ar)) - \exp(-ar)\right)dr$$

$$= 4a^3\int_0^\infty r\exp(-2ar)\left(-\frac{1}{2}(-2a + a^2r) - 1\right)dr$$

$$= 4a^3(a-1)\int_0^\infty r\exp(-2ar)\,dr - 2a^5\int_0^\infty r^2\exp(-2ar)\,dr$$

$$= 4a^3(a-1)\frac{1!}{(2a)^{1+1}} - 2a^5\frac{2!}{(2a)^{2+1}}$$

$$= a(a-1) - \frac{a^2}{2} = \frac{a^2}{2} - a$$

- - - - - - - - - - -

b. Minimize the expectation value found in part a, with respect to parameter a, and thereby determine the best estimate of the ground state of hydrogen, and associated radial wavefunction $R(r)$, using this variational wavefunction. This calculation gives the exact ground state energy and radial wavefunction.

- - - - - - - - - - -

Set the derivative of the energy expectation value to zero to find the value of a that gives the minimum expectation.

$$\frac{d}{da}\left(\frac{a^2}{2} - a\right) = a - 1 = 0;$$

i.e., $a = 1$ gives the minimum energy expectation. This minimum energy - the estimate of the ground state energy of hydrogen (exact in this case) is

$$\frac{a^2}{2} - a \bigg|_{a=1} = -\frac{1}{2}.$$

– – – – – – – – – –

8. Estimate the energies of the first triplet and singlet excited states of helium associated with the $1s^1 2s^1$ electron configuration. Why does the triplet state have the lower energy?

– – – – – – – – – –

Here, we use the approximate energy eigenstates,

$$\psi_{\text{sing}} = \frac{1}{\sqrt{2}}((1s)(1)(2s)(2) + (1s)(2)(2s)(2)),$$

for the singlet, and

$$\psi_{\text{trip}} = \frac{1}{\sqrt{2}}((1s)(1)(2s)(2) - (1s)(2)(2s)(2)),$$

for the triplet. These are just the spatial parts of the the eigenstates. The singlet spatial function is symmetric with respect to exchange because the assocated spin function,

$$\chi_{\text{sing}} = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(2))$$

is antisymmetric. The triplet spatial function is antisymmetric with respect to exchange because its associated spin functions,

$$\chi_{\text{trip}} = \begin{cases} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(2)) \\ \beta(1)\beta(2) \end{cases}$$

are symmetric with respect to exchange. The spatial and spin states must have opposite symmetry with respect to exchange in order for the total state - product of spatial and spin functions - to be antisymmetric. These approximate states correspond to neglecting the electron-electron repulsion. The energy of these states is estimated by the associated expectation values of the Hamiltonian. These estimates are at the level of 1st order perurbation theory with respect to electron-electron repulsion. In terms of the symmetrizer, $\hat{B}$, the singlet energy estimate is given by

$$E^{(0)}_{\text{He 1st sing}} = \left\langle \psi^{(0)}_{\text{He 1st sing.}} \middle| \hat{H}\psi^{(0)}_{\text{He 1st sing}} \right\rangle$$

$$= \left\langle \hat{B}(1\text{s})(1)(2\text{s})(2) \middle| \left(\hat{H}_1 + \hat{H}_2 + \tfrac{1}{r_{12}}\right)\hat{B}(1\text{s})(1)(2\text{s})(2) \right\rangle \quad \text{two-spin state is normalized}$$

$$= \left\langle (1\text{s})(1)(2\text{s})(2) \middle| \hat{B}\left(\hat{H}_1 + \hat{H}_2 + \tfrac{1}{r_{12}}\right)\hat{B}(1\text{s})(1)(2\text{s})(2) \right\rangle \quad \hat{B} \text{ is Hermitian}$$

$$= \left\langle (1\text{s})(1)(2\text{s})(2) \middle| \left(\hat{H}_1 + \hat{H}_2 + \tfrac{1}{r_{12}}\right)\hat{B}^2(1\text{s})(1)(2\text{s})(2) \right\rangle \quad \hat{B} \text{ commutes with Hamiltonia}$$

$$= \left\langle (1\text{s})(1)(2\text{s})(2) \middle| \left(\hat{H}_1 + \hat{H}_2 + \tfrac{1}{r_{12}}\right)\sqrt{2}\,\hat{B}(1\text{s})(1)(2\text{s})(2) \right\rangle \quad \hat{B}^2 = \sqrt{2}\,\hat{B}$$

$$= \left\langle (1\text{s})(1)(2\text{s})(2) \middle| \left(\hat{H}_1 + \hat{H}_2 + \tfrac{1}{r_{12}}\right)((1\text{s})(1)(2\text{s})(2) + (1\text{s})(2)(2\text{s})(2)) \right\rangle$$

$$= \underbrace{-\frac{2^2}{2 \times 1^2}}_{\text{1s e}^-\text{ in He}^+} \underbrace{-\frac{2^2}{2 \times 2^2}}_{\text{2s e}^-\text{ in He}^+} + J_{1\text{s},2\text{s}} + K_{1\text{s},2\text{s}}$$

$$= -\frac{5}{2} + J_{1\text{s},2\text{s}} + K_{1\text{s},2\text{s}},$$

The triplet energy estimate consists of an almost identical calculation, except that $\hat{B}$ is replaced by the symmetrizer, $\hat{A}$. The antisymmetrizer is the same as the symmetrizer, except for the sign in front of the exchange operator. Specifically,

$$\hat{A} = \frac{1}{\sqrt{2}}\left(1 - \hat{P}_{12}\right)$$

and

$$\hat{B} = \frac{1}{\sqrt{2}}\left(1 + \hat{P}_{12}\right).$$

The calculation of the energy estimate for the triplet state takes the form,

$$E^{(0)}_{\text{He 1st trip}} = \left\langle (1\text{s})(1)(2\text{s})(2) \middle| \left(\hat{H}_1 + \hat{H}_2 + \tfrac{1}{r_{12}}\right)\sqrt{2}\,\hat{A}(1\text{s})(1)(2\text{s})(2) \right\rangle \quad \hat{A}^2 = \sqrt{2}\,\hat{A}$$

$$= \left\langle (1\text{s})(1)(2\text{s})(2) \middle| \left(\hat{H}_1 + \hat{H}_2 + \tfrac{1}{r_{12}}\right)((1\text{s})(1)(2\text{s})(2) - (1\text{s})(2)(2\text{s})(2)) \right\rangle$$

$$= \underbrace{-\frac{2^2}{2 \times 1^2}}_{\text{1s e}^-\text{ in He}^+} \underbrace{-\frac{2^2}{2 \times 2^2}}_{\text{2s e}^-\text{ in He}^+} + J_{1\text{s},2\text{s}} - K_{1\text{s},2\text{s}}$$

$$= -\frac{5}{2} + J_{1\text{s},2\text{s}} - K_{1\text{s},2\text{s}}.$$

The triplet state has lower in energy than the singlet state because the exchange integral ($K_{1\text{s},2\text{s}}$), which is positive, appears here with a minus sign, whereas it appears in the singlet energy estimate with a plus sign. Another way to think of this is to note that because the spatial (orbital) part of the triplet state is antisymmetric, the two electrons are kept away from each other, reducing the associated repulsion energy, whereas the spatial part of the singlet state is symmetric, allowing the electrons to be close with large repulsion energy.

– – – – – – – – – – –

9. What are the term symbols associated with the electron configurations,

$2p^1 3p^1$ and $2p^2$?

$-\ -\ -\ -\ -\ -\ -\ -\ -\ -\ -$

For 2p3p, there are no restictions on the way spin and orbital angular momenta of the two electrons add together. In this case, the possible total orbital angular momentum quantum numbers are

$$L = |L_1 - L_2|, |L_1 - L_2| + 1, \ldots, L_1 + L_2$$

$$= |1 - 1|, \ldots, 1 + 1 \qquad L_1 = L_2 = 1 \text{ (both electrons are in p orbitals)}$$

$$= 0, 1, 2 \qquad \text{i.e., the terms are S, P and D.}$$

The possible total spin quantum numbers are

$$S = |S_1 - S_2|, |S_1 - S_2| + 1, \ldots, S_1 + S_2$$

$$= \left| \frac{1}{2} - \frac{1}{2} \right|, \ldots, \frac{1}{2} + \frac{1}{2} \qquad S_1 = S_2 = \frac{1}{2}$$

$$= 0, 1 \qquad \text{the multiplicities are 1 and 3.}$$

Both spin multiplicities are possible for each of the three orbital terms. So, the possible terms are ^{1}S, ^{3}S, ^{1}P, ^{3}P, ^{1}D and ^{3}D. The complete term specifications require the J values also - though, I would not require these unless I specifically asked for them. The J values are

$$J = |L - S|, |L - S| + 1, \ldots, L + S$$

$$= \begin{cases} |L - 0|, \ldots, L + 0 & \text{singlets} \\ |L - 1|, \ldots, L + 1 & \text{triplets} \end{cases}$$

$$= \begin{cases} L & \text{singlets} \\ 1 & \text{triplet S} \\ L - 1, L, L + 1 & \text{triplet P and D} \end{cases} ,$$

and the complete terms for the $2p^1 3p^1$ configuration are ^{1}S$_0$, ^{3}S$_1$, ^{1}P$_1$, ^{3}P$_0$, ^{3}P$_1$, ^{3}P$_2$, ^{1}D$_2$, ^{3}D$_1$, ^{3}D$_2$ and ^{3}D$_3$.

$-\ -\ -\ -\ -\ -\ -\ -\ -\ -\ -$

Useful Integrals:

$$\int_0^\infty \exp(-ar)\, dr = \frac{1}{a}$$

$$\int_0^\infty r^n \exp(-ar)\, dr = \frac{n!}{a^{n+1}}$$

$$\int_{-\infty}^\infty \exp(-ax^2)\, dx = \left(\frac{\pi}{a} \right)^{1/2}$$

$$\int_{-\infty}^\infty x^{2n} \exp(-ax^2)\, dx = \frac{\pi^{1/2}(2n-1)(2n-3)\cdots 3 \times 1}{2^n a^{n+1/2}}$$

$$\int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{L}{2}$$

$$\int_0^L x \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n'\pi x}{L}\right) dx = \frac{L^2}{2\pi^2}\left(\frac{1}{(n-n')^2} + \frac{1}{(n+n')^2}\right)\left((-1)^{n-n'} - 1\right)$$