

Chemistry 455A

Second Exam
May 25, 2007

Name _____ KEY _____

Helpful Information:

$H\Psi = E\Psi$ $\hat{H} = \hat{T} + \hat{V}(x)$ $T = \frac{\hat{p}^2}{2m}$ $\hat{p} = -i\hbar \frac{d}{dx}$ $e^{i\phi} = \cos \phi + i \sin \phi$ $1 = \sin^2 \phi + \cos^2 \phi$ $\sigma_x^2 \sigma_p^2 \geq \left(\frac{\hbar}{2}\right)^2$ $[p, x] = -i\hbar$	$\hbar = 1.054 \cdot 10^{-34} \text{ J} \cdot \text{sec}$ $m_e = 9.109 \cdot 10^{-31} \text{ Kg}$ $c = 3.00 \cdot 10^8 \text{ m/sec}$ $N_A = 6.022 \cdot 10^{23} \text{ molecules/mole}$ $E_n = \frac{1}{2m} \left(\frac{\hbar \pi n}{a} \right)^2$ $V = \frac{q_1 q_2}{(4\pi\epsilon_0) r}$ $E_n = -22 \cdot 10^{-19} \left(\frac{Z}{n} \right)^2 \text{ J}$	$E_n = \hbar \omega_{os} \left(n + \frac{1}{2} \right)$ $\omega_{os} = \sqrt{\frac{k_s}{\mu}}$ $\langle T \rangle_n = \langle V \rangle_n$ $\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$ $\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2\alpha} \sqrt{\frac{\pi}{\alpha}}$ $E_J = \frac{\hbar^2}{2I} J(J+1)$	$\hat{H}\phi_m = E_m \phi_m$ $\int_x \phi_n^* \phi_m dx = \delta_{m,n}$ $1 = \int_x \Psi^* \Psi dx$ $\langle A \rangle = \frac{\int_x \Psi^* \hat{A} \Psi dx}{\int_x \Psi^* \Psi dx}$ $i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi$
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There are 6 pages; with 8 (multi part) problems. Be sure you have all the pages before you start.

Be sure your name is on the exam before you start.

This is a timed 50 minute exam.

To receive full credit on all problems you must show your work or reasoning.

$$\omega = ck$$

$$\lambda \nu = c$$

$$E = \hbar \omega = h\nu$$

$$E^2 = (cp)^2 + (mc^2)^2$$

$$p = \hbar k$$

$$[A, B + C] = [A, B] + [A, C]$$

$$[A, BC] = B[A, C] + [A, B]C$$

Q1) (P5.3) Linear C_6H_8 has a π bonding network over the length of this molecule. Assume that the molecule is 660 pm in length. Use the particle in the box model, and determine the wavelength of light needed to induce a transition from the ground state to the first excited state (for an electron in a one dimensional box).

$$E = h\nu = \frac{hc}{\lambda} = \Delta E_{n \rightarrow n+1} = \frac{1}{2m} \left(\frac{\hbar\pi}{a} \right)^2 (2n+1)$$

$$\frac{hc}{\lambda} = \frac{2\pi \cdot 1 \cdot 10^{-34} \cdot 3 \cdot 10^8}{\lambda} = \frac{1}{2 \cdot 10^{-30}} \left(\frac{\pi \cdot 10^{-34}}{660 \cdot 10^{-12}} \right)^2 (2n+1)$$

$$\frac{2 \cdot 3 \cdot 10^8}{\lambda} = \frac{1\pi \cdot 10^{-34}}{2 \cdot (0.66)^2 10^{-30-18}} (2n+1)$$

$$\frac{0.436 \cdot 12 \cdot 10^{8-30-18}}{\pi \cdot 10^{-34} (2n+1)} = \lambda$$

$$\lambda = \frac{1.7 \cdot 10^{-6}}{(2n+1)} m = \frac{1.7}{(2n+1)} \mu$$

Any $n > 0$ is OK.

Q2) (P6.6) For the Harmonic oscillator, one needs to evaluate the commutator of $T = \frac{1}{2m} \hat{p}^2$ with x and x^2 .

a) Evaluate the commutator of $[T, x]$ using a test function f as needed.

$$[T, x]f = \frac{1}{2m} [\hat{p}^2, x]f = \frac{1}{2m} \{ \hat{p}[\hat{p}, x]f + [\hat{p}, x]\hat{p}f \} = \frac{1}{2m} \{ \hat{p}(-i\hbar)f - i\hbar\hat{p}f \} = \frac{-i\hbar}{m} \hat{p}f$$

$$[T, x] = \frac{-i\hbar}{m} \hat{p}$$

b) Use the result of part a) to evaluate the commutator of $[T, x^2]$

$$[T, x^2] = [T, x]x + x[T, x] = \frac{-i\hbar}{m} \hat{p}x + x \frac{-i\hbar}{m} \hat{p} = \frac{-i\hbar}{m} (\hat{p}x + x\hat{p})$$

$$[T, x^2] = \frac{-i\hbar}{m} (-i\hbar + 2x\hat{p})$$

Q3) (P6.15) Consider the particle in a one dimensional box. If we assume that the uncertainty in the particle position is less than the length of the box, use the HUP, to find the lowest possible energy of the particle in the box.

$$a^2 \sigma_p^2 \geq \sigma_x^2 \sigma_p^2 \geq \left(\frac{\hbar}{2} \right)^2$$

$$\langle p \rangle = 0 \quad E = \frac{p^2}{2m} = \frac{\sigma_p^2}{2m} \Rightarrow 2ma^2 E = a^2 \sigma_p^2 \geq \left(\frac{\hbar}{2} \right)^2$$

$$E \geq \frac{1}{2m} \left(\frac{\hbar}{2a} \right)^2$$

Q4) (7.22) a) Show by carrying out the necessary integration that the eigenfunctions of the Schrödinger equation for rotation in two dimensions

$$\frac{1}{\sqrt{2\pi}} e^{im\phi} \quad \text{and} \quad \frac{1}{\sqrt{2\pi}} e^{-in\phi} \quad \text{for } m \neq -n$$

are orthogonal:

$$\int_{\phi=0}^{2\pi} \left(\frac{1}{\sqrt{2\pi}} e^{im\phi} \right)^* \left(\frac{1}{\sqrt{2\pi}} e^{-in\phi} \right) d\phi = \frac{1}{2\pi} \int_{\phi=0}^{2\pi} \left(e^{-i(n+m)\phi} \right) d\phi = \frac{1}{2\pi} \cdot \frac{e^{-i(n+m)\phi} \Big|_0^{2\pi}}{-i(n+m)} = \frac{i}{2\pi} \cdot \frac{(1-1)}{(n+m)} = 0$$

This is only true if $n + m \neq 0$, otherwise one has zero divided by zero, which is indeterminate.

b) Show that the first eigenfunction is properly normalized.

$$\int_{\phi=0}^{2\pi} \left(\frac{1}{\sqrt{2\pi}} e^{im\phi} \right)^* \left(\frac{1}{\sqrt{2\pi}} e^{im\phi} \right) d\phi = \frac{1}{2\pi} \int_{\phi=0}^{2\pi} \left(e^{i(m-m)\phi} \right) d\phi = \frac{1}{2\pi} \cdot \int_{\phi=0}^{2\pi} d\phi = 1$$

Q5) (7.24/8.16-17) The oxygen (diatomic) molecule has an O-O bond length of 120pm and the mass of O is 16 amu.

a) Calculate the moment of inertia of the oxygen molecule:

$$\mu = \frac{mM}{m+M} = 8$$

$$I = \mu r^2 = \frac{8(120 \cdot 10^{-12})^2}{6 \cdot 10^{23}} \cdot 10^{-3} \text{ kg} \cdot \text{m}^2 = 1.9 \cdot 10^{+4-24-3-23} \text{ kg} \cdot \text{m}^2 = 1.9 \cdot 10^{-46} \text{ kg} \cdot \text{m}^2$$

b) Calculate the rotational energy of the molecule in the J=5 rotational state:

$$E_J = \frac{\hbar^2}{2I} J(J+1) = \frac{1}{2 \cdot 1.9} \left(\frac{1 \cdot 10^{-34}}{1 \cdot 10^{-23}} \right)^2 \cdot 5 \cdot 6 = \frac{30}{3.8} \cdot 10^{-22} \text{ J} = 8 \cdot 10^{-22} \text{ J}$$

FYI: This rotational energy is comparable to (about 1/5 that of) room temperature.

Q6) (4.25) Suppose that the wave function for a system can be written:

$$\psi(x) = \frac{1}{2}\phi_1(x) + i\frac{\sqrt{3}}{2}\phi_2(x)$$

where $\phi_1(x)$ and $\phi_2(x)$ are the normalized eigenfunctions of the Hamiltonian, \hat{H} , with eigenvalues E_1 and $E_2 = 5E_1$

a) Verify that $\psi(x)$ is normalized:

$$\begin{aligned} \psi(x)^* \psi(x) &= \left(\frac{1}{2}\phi_1(x) + i\frac{\sqrt{3}}{2}\phi_2(x) \right)^* \left(\frac{1}{2}\phi_1(x) + i\frac{\sqrt{3}}{2}\phi_2(x) \right) = \left(\frac{1}{2}\phi_1^*(x) - i\frac{\sqrt{3}}{2}\phi_2^*(x) \right) \left(\frac{1}{2}\phi_1(x) + i\frac{\sqrt{3}}{2}\phi_2(x) \right) \\ &= \left(\frac{1}{4}\phi_1^*(x)\phi_1(x) + i\frac{\sqrt{3}}{4}\phi_1^*(x)\phi_2(x) \right) - \left(\frac{1}{2}i\frac{\sqrt{3}}{2}\phi_2^*(x)\phi_1(x) + i\frac{\sqrt{3}}{2}i\frac{\sqrt{3}}{2}\phi_2^*(x)\phi_2(x) \right) \\ \int \psi(x)^* \psi(x) dx &= \frac{1}{4} \int \phi_1^*(x)\phi_1(x) dx - \left(i\frac{\sqrt{3}}{2}i\frac{\sqrt{3}}{2} \right) \int \phi_2^*(x)\phi_2(x) dx = \frac{1}{4} + \frac{3}{4} = 1 \end{aligned}$$

b) What is the average energy obtained as a result of measuring the energy a large number of times with replicate copies of this system? (postulate 4).

$$\begin{aligned} \langle E \rangle &= \int \psi(x)^* H\psi(x) dx = \frac{1}{4} \int \phi_1^*(x) E_1 \phi_1(x) dx - \left(i\frac{\sqrt{3}}{2}i\frac{\sqrt{3}}{2} \right) \int \phi_2^*(x) E_2 \phi_2(x) dx \\ &= \frac{1}{4} E_1 + \frac{3}{4} E_2 = 4E_1 \end{aligned}$$

c) (W4.6) Verify that $\Psi(x,t) = c \cdot e^{-i\omega_1 t} \phi_1(x) + d \cdot e^{-i\omega_2 t} \phi_2(x)$ is a wave function for all time based on the assumption that at time zero the wave function is $\psi(x)$ (i.e. assume $\Psi(x,t=0) = \psi(x)$, of part a) by showing that it is a solution to the time dependent Schrödinger equation (of postulate 5).

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi \quad \text{where } \Psi(x,t) = c \cdot e^{-i\omega_1 t} \phi_1(x) + d \cdot e^{-i\omega_2 t} \phi_2(x)$$

$$i\hbar \frac{\partial}{\partial t} \{ c \cdot e^{-i\omega_1 t} \phi_1(x) + d \cdot e^{-i\omega_2 t} \phi_2(x) \} = \{ c \cdot \hbar \omega_1 e^{-i\omega_1 t} \phi_1(x) + d \cdot \hbar \omega_2 e^{-i\omega_2 t} \phi_2(x) \}$$

$$H \{ c \cdot e^{-i\omega_1 t} \phi_1(x) + d \cdot e^{-i\omega_2 t} \phi_2(x) \} = \{ c \cdot e^{-i\omega_1 t} E_1 \phi_1(x) + d \cdot e^{-i\omega_2 t} E_2 \phi_2(x) \}$$

These two operations (the lower two lines are equal, regardless of c and d) if:

$$\hbar \omega_1 = E_1 \quad \text{and} \quad \hbar \omega_2 = E_2$$

d) Identify the constants c and d $c = \frac{1}{2}$ and $d = i\frac{\sqrt{3}}{2}$

e) Identify the frequencies ω_1 and ω_2 in terms of E_1 and E_2

$$\hbar \omega_1 = E_1 \quad \text{and} \quad \hbar \omega_2 = E_2$$

Q7) (P7.6/8) The two lowest (normalized) eigenstates for the harmonic oscillator are:

$$\alpha = \frac{\sqrt{k_s \mu}}{\hbar} \quad \phi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha x^2} \quad \phi_1(x) = \sqrt{2\alpha} \cdot x \cdot \phi_0(x)$$

a) Evaluate the integrals. If you know the value of an integral, write it and explain why. (Do not evaluate the integrals if you can avoid it.)

$$\int_{-\infty}^{\infty} \phi_0^*(x) \phi_0(x) dx = 1 \text{ normalized}$$

$$\int_{-\infty}^{\infty} \phi_1^*(x) \phi_1(x) dx = 1, \text{ also normalized}$$

$$\int_{-\infty}^{\infty} \phi_0^*(x) \phi_1(x) dx = 0, \text{ orthogonal}$$

$$\langle x^2 \rangle_0 = \int_{-\infty}^{\infty} \phi_0^*(x) x^2 \phi_0(x) dx = \int_{-\infty}^{\infty} (x \phi_0^*(x))^* (x \phi_0(x)) dx$$

$$\langle x^2 \rangle_0 = \int_{-\infty}^{\infty} \left(\frac{\phi_1(x)}{\sqrt{2\alpha}}\right)^* \left(\frac{\phi_1(x)}{\sqrt{2\alpha}}\right) dx = \frac{1}{2\alpha}$$

b) Evaluate the following integrals. (Again avoid doing the integral if possible) If you know the value of an integral, write it and explain why.

$$\int_{-\infty}^{\infty} \phi_0^*(x) x \phi_0(x) dx = 0 \text{ by symmetry, an odd function, even interval}$$

$$\int_{-\infty}^{\infty} \phi_1^*(x) x \phi_1(x) dx = 0, \text{ same reason}$$

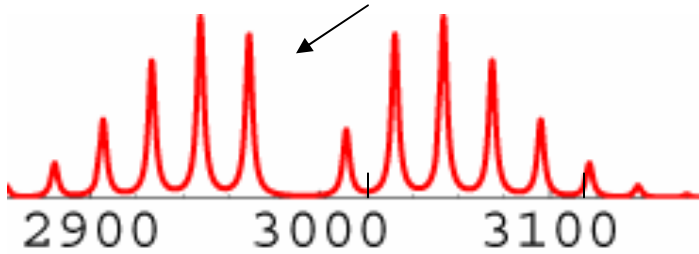
$$\int_{-\infty}^{\infty} \phi_0^*(x) x \phi_1(x) dx = \int_{-\infty}^{\infty} \left(\frac{1}{\sqrt{2\alpha}} \phi_1(x)\right)^* \phi_1(x) dx = \frac{1}{\sqrt{2\alpha}}$$

c) The selection rule for vibration excitations of the Harmonic oscillator is $\Delta n = \pm 1$.

How does the integral $\int_{-\infty}^{\infty} \phi_0^*(x) x \phi_1(x) dx$ relate to the selection rule?

This is an example of how the selection rule works. This integral is nonzero as indicated by the selection rule: $1 = 0 = 1 = \Delta n$

Q8) (8.20) The infrared spectra of HCl is shown below:



You should explain the origin of the first peak to the left of 3000cm^{-1} (where the arrow is pointing) in terms of the n and J quantum numbers outlined in the following questions.

a) What is the rotational and vibrational state before the transition:
 $n=0$ or (really any value of n), and $J=1$ (first excited rotational state)

b) What is the rotational and vibrational state after the transition?
 This transition is to $n=1$ (or just 1 plus the ground state vibration), and $J=0$

c) In the absorption process (associated with this particular line) has the vibrational energy increased or decreased? explain

The vibration energy increased by one quantum of vibration energy: $\hbar\omega_{os}$

d) In the absorption process (associated with this particular line) has the rotational energy increased or decreased? Explain

The rotational energy dropped by one quantum or: $\Delta E_{rot} = E_0 - E_1 = -2 \frac{\hbar^2}{2I}$. The total energy increased, when absorbing a photon but the energy of this photon is less than that needed to (hypothetically) just excite the vibrational state by one level $\nu_o = \frac{1}{2\pi} \omega_{os}$

e) (Q8.7) What is the explanation for the absence of a peak in the above spectrum near 3000cm^{-1} , between the line marked with the arrow and the one to the right of it.

As suggested in part d, there is a missing transition due to the $\Delta n = 1; \Delta J = 0$ energy transition. But this is forbidden so the line is not there.

f) (Q8.8) Qualitatively explain why the intensities (or peak heights) increase in the series of lines above 3000cm^{-1} and then decrease.

The intensities of the lines are roughly proportional to the (relative) populations of the different levels. There are two terms that determine level population. They have different effects. The first is that: the increase in degeneracy of the levels as one goes up (in J number) provides more occupation of those levels. The second term dictates that the populations must decrease because the levels are getting high relative to the temperature of the system. So the intensities increase as one goes up in J but then decrease at higher J .