

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.

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

ii.

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

iii.

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

iv.

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

v.

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

vi.

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

Hamiltonians:

a.

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

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

b.

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

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

c.

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

d.

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

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?

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.

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

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.

b. If the vibrational energy of the molecule is measured, what is the probability of each of the following outcomes - in units of $\hbar \nu_{\text{vib}}$,

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.

$$\frac{7}{2}$$

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

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

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

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

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?
- 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?

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 centrifugal 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?
- 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 $\bar{\nu} - \bar{\nu}_{\text{vib}}$, 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?
- 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 $\bar{\nu}_{\text{vib}}$) of the P branch?
- d. What are the selection rules for ro-vibrational transitions?

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 $\varphi(r)$.

- 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.
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?
9. What are the term symbols associated with the electron configurations, $2p^1 3p^1$ and $2p^2$?

Useful Integrals:

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

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

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

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

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

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