Chemistry 3PA3 - Sample Midterm Questions

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

$$h = 4.136 \times 10^{-15} \text{ eV s}^{-1}$$

1. Which of the following statements are **true**, according to the postulates of quantum mechanics? For statements that are false, add or change one (or a few) word(s) to make it a true statement. [1 mark each + 1 mark for each corrected false statement]

a. If an observable is measured, only certain values are possible outcomes of the measurement.

b. The time dependent Schrodinger equation determines the time evolution of the state of a system.

c. The probability of an outcome of the measurement of an observable is given by

$$|\langle \varphi | \psi \rangle|^2,$$

where ψ represents the state of the system (before the measurement), and φ is a normalized eigenfunction of the operator that represents the observable.

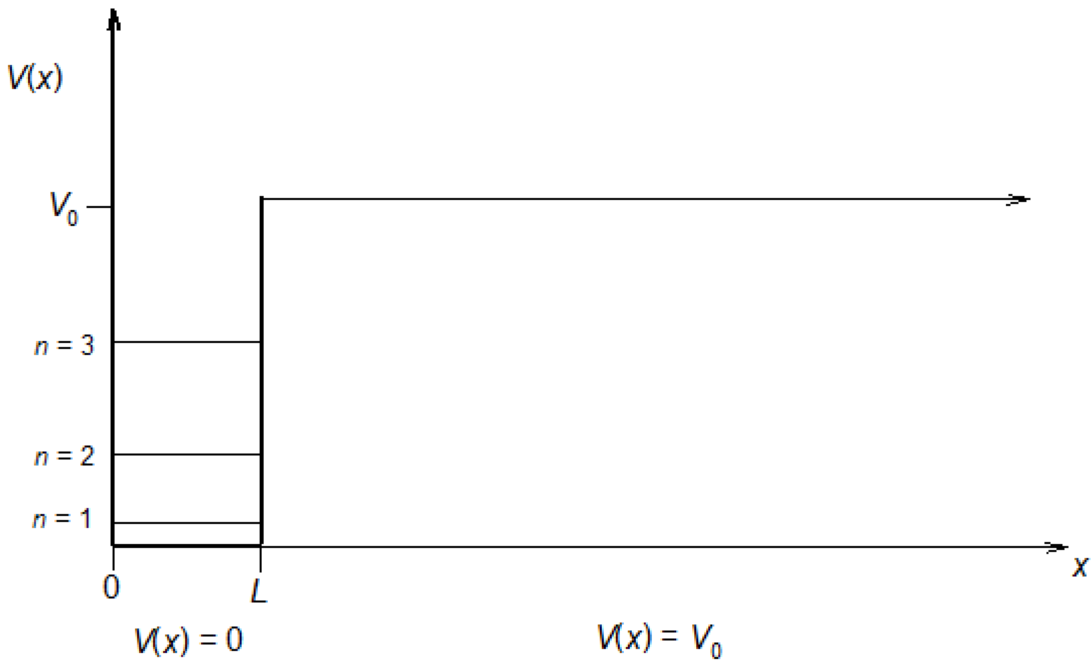
d. Eigenvalues of a Hermitian linear operator are almost always observed, upon measurement of an observable.

e. Eigenvalues of operators that represent observables always come in discrete sets with each eigenvalue labeled by an integer quantum number.

2. Consider an electron in a well of finite depth, $V_0 = 15.0$ eV, and width, L, such that $\hbar^2/(2mL^2) = 1.00$ eV. The potential energy for this well is given by

$$V(x) = \begin{cases} \infty & x \leq 0 \\ 0 & 0 < x < L \\ V_0 & L < x \end{cases},$$

and shown in the figure below along with the lowest three energy levels of the particle-in-a-box with the same width, L.



a. Sketch the lowest **energy eigenstate**. Show where the boundary conditions are applied, and how they are satisfied in your plot. [6 marks]

b. Draw the lowest three **energy levels** of the above finite-depth well in the figure - i.e., just show their positions relative to the particle-in-a-box levels already shown. [6 marks]

c. Suppose an electron is in the ground state of this well. The probability density for finding this electron at $x = 2L$ is 4.46×10^{-7} L^{-1}. What is the **probability density** for finding the electron at $x = 3L$?. [4 marks]

d. In what ways (state two) are the energy eigenstates **above the well** - i.e., with $E > V_0$ - **different** from the bound states considered above?

3. With certain choices of units for distance and energy, the harmonic oscillator Hamiltonian can take the form,

$$\hat{H} = \frac{1}{2}\left(-\frac{d^2}{dy^2} + y^2\right),$$

a. Find the commutator, $\left[\hat{H}, \hat{a}^\dagger\right]$, where

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}}\left(-\frac{d}{dy} + y\right),$$

and use it to **show** that $\hat{a}^\dagger \psi_3$ is an eigenfunction of $\hat{H}$, if ψ_3 is the third excited state of the harmonic oscillator. What is the associated **eigenvalue**? [10 marks]

b. **Evaluate** the transition matrix element,

$$\langle \psi_4 | y \psi_3 \rangle.$$

where ψ_3 and ψ_4 are the third and fourth excited states of the harmonic oscillator. [5 marks]

4. Consider a particle in a $a \times b$ two dimensional box such that $\hbar^2/(2ma^2) = 1.00$ eV and $b = 2a$.

a. **Write** the expression for the normalized energy eigenstate associated with quantum numbers, $n_x = 1$, $n_y = 2$ (x is the a direction, and y is the $b = 2a$ direction.) **Sketch** this wavefunction (as a contour or perspective plot). Indicate the (x, y) **points** where the probability density is largest, and any **lines** where the wavefunction is zero - i.e., nodal lines. [8 marks]

b. For **two** non-interacting **electrons** (the particle such that $\hbar^2/(2ma^2) = 1.00$ eV) in the two dimensional box, what are the **two lowest** energy levels? [5 marks]