Name ______________________

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February 28th, 2025

Chemistry 120A - First Midterm Exam

This exam consists of five questions for a total of 100 points. **An equation sheet is given in the back of this exam.** Review the point distribution before starting the exam and read the entire question prompt - it may contain hints. **Your solutions need to be on the front pages of the exam - the back of the pages can be used as scratch paper, but will not be considered for grading.**

1. 32pts - **Multiple Choice.** Circle the **ONE** correct answer. Scratch paper is provided on the next page; **only provide the circled answer** on this sheet. Any answers on other sheets will not be graded.

   (a) **The de Broglie wavelength of two particles with identical linear momentum, but different masses is...**

   (i) different.

   (ii) always identical.

   (iii) identical, but only for some masses.

   (b) **A quantum particle is in infinite space without any potentials acting on it. What is true about the momentum of this particle?**

   (i) it can be measured with arbitrarily high precision while its position is known

   (ii) it must come from a particle with finite mass.

   (iii) its momentum is not quantized

(c) **Consider the spectrum of hydrogen as described by Rydberg's formula. Lines in the optical spectrum...**

(i) ...are observed if the quantum numbers of the initial and final states are the same ($n_1 = n_2$).

(ii) ...have an increasing frequency (shorter wavelength) with increasing difference between n_1 and n_2.

(iii) ...don't exist, unless the hydrogen is negatively charged.

(d) **Two operators $\hat{A}$ and $\hat{B}$ commute, that is $[\hat{A}, \hat{B}] = 0$. The observables corresponding to these operators can be measured...**

(i) ...simultaneously with infinite precision.

(ii) ...only simultaneously.

(iii) ...simultaneously with limited precision.

(iv) ...sequentially with limited precision.

(e) **A quantum harmonic oscillator exists in a state $|\Psi\rangle$ which would give energy measurements of $\frac{1}{2}\hbar\omega$ and $\frac{3}{2}\hbar\omega$ 50% of the time, respectively. What is the properly normalized wavefunction if $|n\rangle$ is the n^{th} Eigenstate of the Hamiltonian?**

(i) $|\Psi\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |3\rangle)$

(ii) $|\Psi\rangle = \frac{1}{\sqrt{2}}(|1\rangle - i\,|3\rangle)$

(iii) $|\Psi\rangle = \frac{1}{\sqrt{2}}(|1\rangle + i\,|0\rangle)$

(iv) $|\Psi\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |2\rangle)$

(g) **Some wavefunction $\Psi(x)$ is written as a super-position of Eigenfunctions of the Hamiltonian of a system with quantum numbers n: $\Psi(x) = \sum_n c_n \phi_n(x)$. The time-dependence is added correctly in...**

(i) ... $\Psi(x,t) = \sum_n c_n \phi_n(x) e^{\frac{-i\langle E\rangle t}{\hbar}}$, where $\langle E\rangle$ is the energy expectation value of $\Psi(x)$.

(ii) ...$\Psi(x,t) = \sum_n c_n \phi_n(x) e^{\frac{-iE_n t}{\hbar}}$, where E_n are the energy eigenvalues of $\phi_n(x)$.

(iii) ...$\Psi(x,t) = \sum_n c_n \phi_n(x) e^{-i\omega t}$ with ω a frequency of choice, for example that of light.

(h) **A one-dimensional wavefunction $\Psi(x)$ is perfectly symmetric around $x = 0$ and non-zero for some $x \neq 0$. The expectation value of the position operator squared $\hat{x}^2$, defined as $\int \Psi^*(x)\hat{x}^2\Psi(x)dx$, is...**

(i) zero.

(ii) strictly positive.

(iii) not enough information to tell.

(h) **The Eigenfunctions of the Hamiltonian for the 1D quantum harmonic oscillator $\phi_v(x)$...**

(i) ...have a non-zero overlap integral $\int \phi_v^*(x)\phi_w(x)dx$ for different functions v and w, that is $v \neq w$.

(ii) ...are also Eigenfunctions of the momentum operator $\hat{p}$.

(iii) ... have exactly v nodes (zero-crossings).

2. 15pts - **Sequential Measurements**. An operator $\hat{A}$ has two normalized eigenstates ψ_1 and ψ_2, with corresponding eigenvalues a_1 and a_2. Likewise, operator $\hat{B}$ has two normalized eigenstates ϕ_1 and ϕ_2, with eigenvalues b_1 and b_2. The eigenstates are related by

$$\psi_1 = \frac{3\phi_1 + 4\phi_2}{5}, \quad \psi_2 = \frac{4\phi_1 - 3\phi_2}{5}.$$

(a) Observable A (associated with the operator $\hat{A}$) is measured, and the value a_1 is obtained. What is the state of the system immediately after this measurement in terms of Eigenfunctions of $\hat{A}$?

The system is in ψ_1 right after the eigenvalue a_1 is measured.

(b) Continued from (a), if observable B is now measured, what are the possible outcomes and their probabilities?

After a_1 is measured, the system is collapsed in ψ_1. The possible outcome of measuring B corresponds to the eigenvalues of $\hat{B}$ which are b_1 and b_2. The probability of measuring those values are given by the modular square of the inner product between ψ_1 and ϕ_1 or ϕ_2:

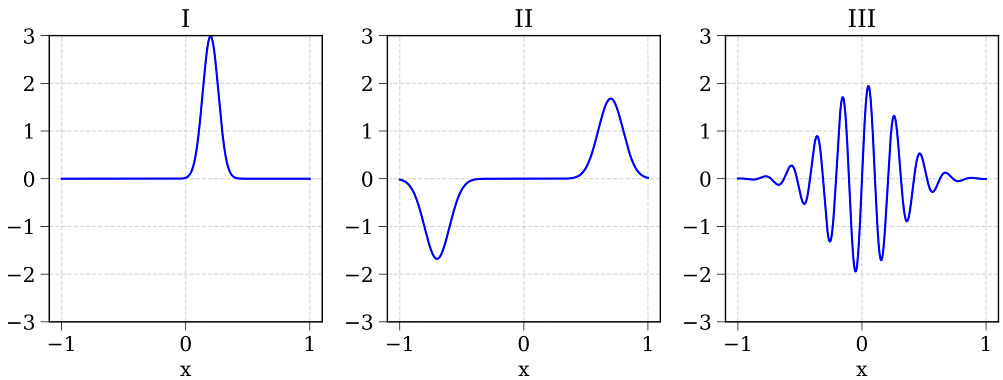
$$\mathsf{P}(\text{outcome} = b_1) = |\langle\phi_1|\psi_1\rangle|^2 = \left(\frac{3}{5}\right)^2 = \frac{9}{25}$$

$$\mathsf{P}(\text{outcome} = b_2) = |\langle\phi_2|\psi_1\rangle|^2 = \left(\frac{4}{5}\right)^2 = \frac{16}{25}$$

(c) Right after, a subsequent measurement of B resulted in a value b_1. B is measured again right away (measuring the same observable twice). What is the probability of getting b_2 and why? Explain in just a few words.

Sequentially measuring the same observable will yield the same result. In this case, if the first measurement gives b_1, the the subsequent measurement will also give b_1 with probability 1. This means the probability of getting b_2 is 0.

3. 18pts - **Properties of wavefunctions**. Look at the following normalized (real) wavefunctions, plotted as $\Psi(x)$ for a particle confined in space so that $-1 < x < 1$:



Answer the following questions. Hint: You do not have to perform any calculations.

(a) Which of the wavefunctions (I,II, or III) will give the largest value for the expectation value of $\langle \hat{x} \rangle$? Briefly give your reason.

I. All the other functions will have symmetric distribution $|\Psi(x)|^2$ so the $\langle \hat{x} \rangle$ becomes zero.

(b) Which of the wavefunctions (I,II, or III) will give the larget value for the expectation value of $\langle \hat{x}^2 \rangle$? Briefly give your reason.

II. $|\Psi(x)|^2$ so the $\langle \hat{x} \rangle$ has larger contribution from large x. (or it has larger variation)

(c) Which of the wavefunctions (I,II, or III) will have the highest expectation value for the kinetic energy $\frac{\langle \hat{p}^2 \rangle}{2m}$? Briefly give your reason.

III. $|\Psi(x)|^2$ for III has large frequency components (fast oscillation) which correspond to large kinetic energy.

4. 25pts - **Particle in a 2D potential well**. A particle of mass m is confined in a potential $V(x, y)$ defined as:

$$V(x,y) = \begin{cases} \infty, & \text{for } x < -a \text{ and } x > a, \\ V_0 + \frac{1}{2}ky^2, & \text{for } -a \leq x \leq a, \end{cases} \tag{1}$$

where k and $V_0 \geq 0$ are real positive constants. The total Hamiltonian $\hat{H}(x, y)$ can be written as the sum of two components, $\hat{H}(x)$ and $\hat{H}(y)$, where:

$$\hat{H}(x,y) = \hat{H}(x) + \hat{H}(y) + \hat{V}_0 \tag{2}$$

The potential corresponds to a particle-in-a-box (PIB) potential in the x-direction (with boundaries at $x = -a$ and $x = a$) and a quantum harmonic oscillator (QHO) potential in the y-direction.

(a) Write $\hat{H}(x)$ and $\hat{H}(y)$ explicitly in terms of derivatives and potential terms.

$$\hat{H}(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_1(x), \quad V_1(x) = \begin{cases} \infty, & x < -a \text{ or } x > a, \\ 0, & -a \leq x \leq a. \end{cases}$$

$$\hat{H}(y) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + V_2(y), \quad V_2(y) = \frac{1}{2}ky^2.$$

$\hat{H}(x)$ describes a PIB system, and $\hat{H}(y)$ describes a QHO with a potential minimum at $y = 0$.

(b) Show that $\phi_n(x) = \sqrt{\frac{1}{a}}\sin\left(\frac{n\pi x}{2a}\right)$, $-a \leq x \leq a$ is an Eigenfunction of $\hat{H}(x)$. Hint: The energy Eigenvalues are $E_n = \frac{n^2h^2}{32ma^2}$.

Within the interval $-a \leq x \leq a$, differentiating twice gives

$$\frac{d^2}{dx^2}\phi_n(x) = -\left(\frac{n\pi}{2a}\right)^2 \phi_n(x).$$

Thus,

$$\hat{H}_x\phi_n(x) = -\frac{\hbar^2}{2m}\left[-\left(\frac{n\pi}{2a}\right)^2\phi_n(x)\right] = \frac{\hbar^2}{2m}\left(\frac{n\pi}{2a}\right)^2\phi_n(x).$$

Since

$$\left(\frac{n\pi}{2a}\right)^2 = \frac{n^2\pi^2}{4a^2},$$

we have

$$\hat{H}\phi_n(x) = \frac{n^2\pi^2\hbar^2}{8ma^2}\phi_n(x).$$

$$E_n = \frac{n^2\pi^2\hbar^2}{8ma^2} = \frac{n^2h^2}{32ma^2}.$$

Thus, $\phi_n(x)$ is indeed an eigenfunction of $\hat{H}(x)$ with eigenvalue E_n.

(c) The principle of separation of variables permits product wavefunctions $\Psi_{n,v}(x,y) = \phi_n(x)\psi_v(y)$ as solutions to $\hat{H}(x,y)$, where $\psi_v(y)$ are Eigenfunctions of $\hat{H}(y)$. Show that the total energy is given by $E_{n,v} = E_n + E_v + V_0$.

To find the total energy, we apply the total Hamiltonian $\hat{H}(x,y)$ on the product wavefunction $\Psi_{n,v}(x,y) = \phi_n(x)\psi_v(y)$,

$$\hat{H}(x,y)\Psi_{n,v}(x,y) = \left[\hat{H}(x) + \hat{H}(y) + \hat{V_0}\right][\phi_n(x)\psi_v(y)]$$

This can be simplified since $\hat{H}(x)$ only operates on $\phi_n(x)$, and $\hat{H}(y)$ only operates on $\phi_n(x)$,

$$\begin{aligned}
&\hat{H}(x,y)\Psi_{n,v}(x,y) \\
&= \left[\hat{H}(x)\phi_n(x)\right]\psi_v(y) + \left[\hat{H}(y)\psi_v(y)\right]\phi_n(x) + V_0\Psi_{n,v}(x,y) \\
&= E_n\phi_n(x)\psi_v(y) + E_v\psi_v(y)\phi_n(x) + V_0\Psi_{n,v}(x,y) \\
&= (E_n + E_v + V_0)\,\Psi_{n,v}(x,y)
\end{aligned}$$

Thus, the total energy is given by

$$E_{n,v} = E_n + E_v + V_0$$

(d) What is the zero-point energy of the particle? Hint: E_n and E_v are the Eigenenergies of the particle in a box and the quantum harmonic oscillator, respectively.

The zero-point energy corresponds to the ground state energy ($n = 1$, $v = 0$):

$$E_{\text{zero-point}} = E_{n=1} + E_{v=0} + V_0 = \frac{h^2}{32ma^2} + \frac{1}{2}\hbar\omega + V_0,$$

where $\omega = \sqrt{\frac{k}{m}}$.

5. 20pts - **Particle on a ring**. $\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$, $(m = 0, \pm 1, \pm 2, \dots)$ are the normalized Eigenfunctions of the angular momentum operator $\hat{L}_z = -i\hbar \frac{d}{d\phi}$ for the particle on a ring model system, where ϕ is the angular coordinate of the particle. We consider the case where the particle's orbit is in the x-y plane, so that $L_x = L_y = 0$.

   (a) The particle is prepared in a state with $\Psi(\phi) = A \sum_{m=-2}^{m=2} e^{im\phi}$. A is a normalization constant so that $\langle \Psi(\phi) | \Psi(\phi) \rangle = 1$. If L_z is measured, what are the possible values and their probabilities?

   The wavefunction is a linear combination of 5 eigenstates of $\hat{L}_z$ with the same coefficients. Therefore, the possible observed values from measuring $\hat{L}_z$ are the corresponding eigenvalues, each with 1/5 probability of observation.

   I.e., the possible values from measuring $\hat{L}_z$ are $0, \pm\hbar, \pm 2\hbar$, each with 1/5 probability.

   (b) What is the expectation value $\langle \hat{L}_z \rangle$ of the state $\Psi(\phi)$? Hint: Consider the symmetry of the wavefunction.

   The wavefunction is a sum of eigenstates with angular momentum quantum numbers $m = -2, -1, 0, 1, 2$. Each of these eigenfunctions contributes an angular momentum of $-2\hbar, -\hbar, 0, \hbar, 2\hbar$.

   Since the coefficients in front of each eigenstate are the same, the expectation value of the angular momentum will be zero. Positive and negative contributions of angular momentum will cancel each other out.

   (c) The Hamiltonian is defined as $\hat{H}(\phi) = \frac{\hat{L}_z^2}{2I}$, where I is the moment of inertia. What is the expectation value for the energy for the state $\Psi(\phi)$ in (a)?

   Similarly, each of the eigenstates with angular momentum quantum numbers $m = -2, -1, 0, 1, 2$ has energy of contributes an angular momentum of $\frac{4\hbar^2}{2I}, \frac{\hbar^2}{2I}, 0, \frac{\hbar^2}{2I}, \frac{4\hbar^2}{2I}$.

   Since the coefficients in front of each eigenstate are the same, the expectation value for the energy is:

$$\frac{2}{5} \cdot \frac{4\hbar^2}{2I} + \frac{2}{5} \cdot \frac{\hbar^2}{2I} = \frac{\hbar^2}{I}$$

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Equation Sheet

Constants:

$$
\begin{aligned}
h &= 6.626 \times 10^{-34}\, J \cdot s \\
c &= \lambda\nu = 2.998 \times 10^{8}\, m/s
\end{aligned}
$$

Spherical Coordinates:

$$
\begin{aligned}
r &= \sqrt{x^2 + y^2 + z^2} \\
\theta &= \arccos \frac{z}{r} \\
\phi &= \arctan \frac{y}{x} \\
x &= r \cos\phi \sin\theta \\
y &= r \sin\phi \sin\theta \\
z &= r \cos\theta \\
dx\, dy\, dz &= r^2 \sin\theta\, dr\, d\theta\, d\phi
\end{aligned}
$$

Euler's Formula:

$$
\begin{aligned}
e^{\pm i\theta} &= \cos\theta \pm i \sin\theta \\
\cos\theta &= \frac{1}{2}\left(e^{i\theta} + e^{-i\theta}\right) \\
\sin\theta &= \frac{1}{2i}\left(e^{i\theta} - e^{-i\theta}\right)
\end{aligned}
$$

Linear Position and Momentum Operators (1D):

$$
\begin{aligned}
\hat{x} &= x \\
\hat{p} &= -i\hbar \frac{\partial}{\partial x}
\end{aligned}
$$

Commutator:

$$\left[\hat{A},\hat{B}\right] = \hat{A}\hat{B}-\hat{B}\hat{A}$$

Particle in a 1D Box:

For a box of length L:

$$\begin{aligned} E_n &= \frac{h^2n^2}{8mL^2}\,,\ n=1,2,\ldots \\ \psi_n(x) &= \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), \quad 0\le x\le L \end{aligned}$$

Quantum Harmonic Oscillator (1D):

For a particle of mass m and frequency ω:

$$\begin{aligned} \hat{H} &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2x^2 \\ \omega &= \sqrt{\frac{k}{m}} \\ E_v &= \left(v+\frac{1}{2}\right)\hbar\omega\,,\ v=0,1,2,\ldots \\ \psi_v(x) &= \frac{1}{\sqrt{2^v v!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} H_v\left(\sqrt{\frac{m\omega}{\hbar}}x\right)e^{-\frac{m\omega}{2\hbar}x^2}, \end{aligned}$$

with H_v as the Hermite Polynominals given below.

$$\begin{aligned} H_{v=0}(x) &= 1 \\ H_{v=1}(x) &= 2x \end{aligned}$$

$$\begin{aligned} \psi_0(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}, \\ \psi_1(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\sqrt{2}\left(\sqrt{\frac{m\omega}{\hbar}}x\right)e^{-\frac{m\omega}{2\hbar}x^2}. \end{aligned}$$

Energy Levels of Hydrogenic Atoms with Nuclear Charge Z:

$$E_n = \frac{-Z^2 e^2}{2a_0 n^2}, \; n = 1, 2, \ldots$$

Angular Momentum:

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\begin{aligned} \hat{L}^2 \left| l, m_l \right\rangle &= \hbar^2 l\,(l+1) \left| l, m_l \right\rangle \\ \hat{L}_z \left| l, m_l \right\rangle &= \hbar m_l \left| l, m_l \right\rangle \end{aligned}$$

Particle on a ring:

For a particle of mass m moving on a ring of radius R:

$$\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} \quad \text{with } I = mR^2,$$

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots,$$

$$E_m = \frac{\hbar^2 m^2}{2I} \quad \text{for } m = 0, \pm 1, \pm 2, \ldots,$$