This examination consists of 7 consecutively numbered pages. Please check that your paper is complete before starting work. All work must be shown in this booklet.

Name: ____________________________ Student number: ____________________________

(print, surname first)

Signature: ____________________________

University of British Columbia

Midterm Examination
Sample

**CHEMISTRY 312**
Quantum Chemistry

**Time: 1 hour 20 minutes**

NON-PROGRAMMABLE NON-GRAPHING CALCULATORS ARE PERMITTED

READ AND OBSERVE THE FOLLOWING EXAM RULES

1. Each candidate must be prepared to produce, upon request, a UBCcard for identification.
2. Candidates are not permitted to ask questions of the invigilators, except in cases of supposed errors or ambiguities in examination questions.
3. No candidate shall be permitted to enter the examination room after the expiration of one-half hour from the scheduled starting time, or to leave during the first half hour of the examination.
4. Candidates suspected of any of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action.
   - Having at the place of writing any books, papers or memoranda, calculators, computers, sound or image players/recorders/transmitters (including telephones), or other memory aid devices, other than as authorized by the examiners.
   - Speaking or communicating with other candidates.
   - Purposely exposing written papers to the view of other candidates or imaging devices.
     The Plea of accident or forgetfulness shall not be received.
5. Candidates must not destroy or mutilate any examination material; must hand in all examination papers; and must not take any examination material from the examination room without permission of the invigilator.
6. Candidates must follow any additional examination rules or directions communicated by the instructor or invigilator.

| Part | Max | Mark |
|---|---|---|
| I | 10 | |
| II | 10 | |
| III | 8 | |
| IV | 12 | |
| Total | 40 | |

**Part I** [10 marks]

For each numbered statement below, select the letter corresponding to the best answer. There is only one correct answer per question. Each correct answer is worth 2 marks.

1. Which of the following operators is not Hermitian?

   (a) $i\partial/\partial x$

   (b) $\partial/\partial x$

   (c) $\hat{x}$

   (d) $\partial^2/\partial x^2$

**Answer:**
(b) $\partial/\partial x$ is not a Hermitian operator. Note that all the other operators in this question correspond (up to a constant factor of $\hbar$ or $m$) to a physical observable. But (b) is different by a factor of $i$. Multiplying a Hermitian operator by $i$ results in an operator that is not Hermitian. Prove this!

2. Which of the following is an eigenfunction of the Hamiltonian for a two-dimensional harmonic oscillator?

   (a) $e^{(x^2+y^2)}$

   (b) $e^{-x^2}$

   (c) $e^{-(x^2+y^2)}$

   (d) $e^{-x^2+y^2}$

**Answer:**
The answer is (c). The Hamiltonian depends on two variables, so the eigenfunction has to be a function of two variables $x$ and $y$. The wavefunction should be normalizable. Options (a) and (d) diverge when $x$ and $y$ goes to infinity, so they are not normalizable. But option (c) approaches zero at inifinity.

3. Which of the following operators do not commute?

   (a) Hamiltonian and momentum for a particle in free motion

   (b) Hamiltonian and coordinate for a particle in free motion

   (c) Kinetic energy and momentum for a particle in a box

   (d) Hamiltonian and kinetic energy for a particle in free motion

**Answer:**
(b) The Hamiltonian contains $\hat{p}^2$ and does not commute with $\hat{x}$.

4. Which of the following particles has the highest zero point energy?

(a) Electron confined to a cubic box with edges equal to 2 Å.

(b) Proton confined to a cubic box with edges equal to 1 Å.

(c) Lithium atom confined to a cubic box with edges equal to 1 Å.

(d) Lithium atom confined to a cubic box with edges equal to 10 Å.

**Answer:**
Zero point energy is the energy of the ground state. The energy is proportional to the inverse of mass and the inverse square of length. The mass of the electron is about 2000 times smaller than that of the proton and even smaller than that of lithium. So an electron confined in a 2Å box has the highest energy.

5. Which of the following particles has the lowest zero point energy?

(a) Electron confined to a one-dimensional box with size equal to 1 Å.

(b) Electron confined to a two-dimensional box with both edges equal to 1 Å.

(c) Electron confined to a three-dimensional box with all edges equal to 1 Å.

(d) Electron confined to a one-dimensional box with size equal to 2 Å.

**Answer:**
(d) The ground state energy of a particle in the one-dimensional, two-dimensional and three-dimensional boxes is

$$E_{1d} = n_x^2 h^2/8ma^2$$

$$E_{2d} = (n_x^2 + n_y^2)h^2/8ma^2 = 2E_{1d}$$

$$E_{3d} = (n_x^2 + n_y^2 + n_z^2)h^2/8ma^2 = 3E_{1d}$$

So for the same particle mass and confinement length, a particle confined only along one dimension has the lowest energy. The size of the box in (d) is larger so it has the lowest energy.

**Part II** [10 marks] Signature: ________________

In the boxes provided, briefly answer the following questions.

Why is the energy of a particle in a box quantized?

Because the particle is confined. Mathematically, this is expressed as the boundary conditions. The boundary conditions impose restrictions and select only certain solutions (corresponding to certain – and not all – energies) out of the manifold of the possible solutions of the Schrödinger equation.

Why is the energy of an electron in the hydrogen atom quantized?

Because the electron is confined (bound) by the Columb potential generated by the proton.

Why does the energy separation between the energy levels of the electron in hydrogen become smaller with increasing energy?

As the energy of the electron increases it is less confined.

What is the expectation value of momentum for the particle in the ground state of the particle in a box?

The particle moves in all directions with equal probability, giving the zero net result for the expectation (average) value of linear momentum.

$$\langle p_x \rangle = \frac{2}{a}\int_0^a \sin\frac{n\pi x}{a}(-i\hbar\frac{d}{dx})\sin\frac{n\pi x}{a}dx = -\frac{i2n\pi\hbar}{a^2}\int_0^a \sin\frac{n\pi x}{a}\cos\frac{n\pi x}{a}dx$$

$$= -\frac{in\pi\hbar}{a^2}\int_0^a \sin\frac{2n\pi x}{a}dx = \frac{i\hbar}{2a}(\cos 2n\pi - 1) = 0$$

**Part III** [8 marks]

Incident light of wavelength 400 nm causes electrons to be emitted from some metal surface. Half the energy of the incident light is absorbed by the metal, and the other half becomes the energy of the emitted electron. What is the de Broglie wavelength of the emitted electron?

$$h\nu = \phi + T$$

$$\phi = T = h\nu/2 = \frac{hc}{2\lambda}$$

$$T = \frac{6.63 \times 10^{-34} \times 3 \times 10^{8}}{2 \times 400 \times 10^{-9}} = 2.4848 \times 10^{-19}$$

$$T = p^2/2m$$

$$p = \sqrt{2mT} = \sqrt{2 \times 9.11 \times 10^{-31} \times 2.4848 \times 10^{-19}} = 6.7283 \times 10^{-25}$$

$$\lambda_e = h/p = 6.63 \times 10^{-34}/6.7283 \times 10^{-25} = 0.98 \text{ nm}$$

A better way is to write all the equations first and insert the numbers at the end:

$$\frac{hc}{2\lambda} = p^2/2m$$

$$p = h/\lambda_e = \sqrt{hmc/\lambda}$$

$$\lambda_e = \sqrt{h\lambda/mc} = \sqrt{\frac{6.63 \times 10^{-34} \times 400 \times 10^{-9}}{9.11 \times 10^{-31} \times 3 \times 10^{8}}} = 0.98 \text{ nm}$$

**Part IV** [12 marks] Signature: ____________________

Consider a particle moving freely in a one-dimensional box between $0 \leq x \leq a$. The Hamiltonian has the eigenvalues $E_n$ and orthonormal eigenfunctions $\psi_n = \sqrt{2/a}\sin(\pi n x/a)$ . Consider that the particle is in a state described by the function $\Psi(x) = Ax(x-a)$ where $A$ is a normalization constant.

1. Show that the normalization constant $A = \sqrt{30/a^5}$.

$$\int_0^a |\Psi(x)|^2 dx = 1$$

$$\int_0^a A^2(x^4 + a^2x^2 - 2ax^3)dx = 1$$

$$A^2(a^5/5 + a^5/3 - 2a^5/4) = 1$$

$$A^2a^5/30 = 1$$

$$A = \sqrt{\frac{30}{a^5}}$$

2. The state $\Psi(x)$ above can be written as a linear combination of the energy eigenfunctions $\psi_n$: $\Psi(x) = \sum_n c_n\psi_n$. Show that the superposition coefficients are:

$$c_n = -\frac{8\sqrt{15}}{(n\pi)^3} \qquad (n \text{ odd});$$
$$c_n = 0 \qquad (n \text{ even})$$

Possibly useful integrals:

$$\int x\sin(x)\,dx = \sin(x) - x\cos(x)$$

$$\int x^2\sin(x)\,dx = 2x\sin(x) - (x^2-2)\cos(x)$$

$$\Psi = \sum_k c_k\psi_k$$

We multiply both sides by $\psi_n^*$ and integrate

$$\int_0^a \psi_n^*\Psi dx = \sum_k c_k \int_0^a \psi_n^*\psi_k dx \tag{1}$$

where $\psi_k$ and $\psi_n$ functions are the eigenfunction of the Hamiltonian with quantum number $k$ and $n$. Since these are the eigenfunctions of a Hermitian operator, they are orthonormal meaning that

$$\int_0^a \psi_n^*\psi_k dx = 0$$

when $n \neq k$ and

$$\int_0^a \psi_n^*\psi_n dx = 1$$

when $k = n$. The only term that survives on the right hand side of equation **??** is $c_n$. So

$$c_n = \int_0^a \psi_n^*\Psi dx = \sqrt{\frac{60}{a^6}}\int_0^a x(x-a)\sin\frac{n\pi x}{a}dx$$
$$= \sqrt{\frac{60}{a^6}}\left[\int_0^a x^2\sin\frac{n\pi x}{a}dx - a\int_0^a x\sin\frac{n\pi x}{a}dx\right]$$

Using the substituiton $u = n\pi x/a$, we have $dx = adu/n\pi$. The limits of the integration are $u = 0$ and $u = n\pi$.

$$c_n = \sqrt{\frac{60}{a^6}}\left[\frac{a^3}{n^3\pi^3}\int_0^{n\pi} u^2\sin u du - \frac{a^3}{n^2\pi^2}\int_0^{n\pi} u\sin u du\right]$$

The integrals are

$$\int_0^{n\pi} u^2\sin u du = (2n\pi\sin n\pi - (n^2\pi^2-2)\cos n\pi) - 2 = -(n^2\pi^2-2)(-1)^n - 2$$

$$\int_0^{n\pi} u\sin u du = (\sin n\pi - n\pi\cos n\pi) = -n\pi(-1)^n$$

Notice that $\sin n\pi = 0$ for any integers, and $\cos n\pi = 1$ if $n$ is even and $\cos n\pi = -1$ if $n$ is odd. In short we can write $\cos n\pi = (-1)^n$

$$c_n = \sqrt{60}\left[\frac{1}{n^3\pi^3}(-(n^2\pi^2-2)(-1)^n-2) - \frac{1}{n^2\pi^2}(-n\pi(-1)^n)\right]$$

$$c_n = \frac{\sqrt{60}}{n^3\pi^3}\left[-(n^2\pi^2-2)(-1)^n - 2 + n^2\pi^2(-1)^n\right]$$

$$c_n = \frac{\sqrt{60}}{n^3\pi^3}\left[2(-1)^n-2\right]$$

If $n$ is even, the above expression is equal to zero. Otherwise, for odd $n$,

$$c_n = -\frac{4\sqrt{60}}{n^3\pi^3} = -\frac{8\sqrt{15}}{n^3\pi^3}$$

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3. What is the probability of an observer to find the particle in the lowest energy state?

   The probability of finding energy equal to $E_n$ is $|c_n|^2$. The probability of finding the particle in the ground state is

$$P(E_1) = |c_1|^2 = \frac{64 \times 15}{\pi^6} = 0.9986$$

4. What is the probability of an observer to find the particle in the first excited energy state?

   For the first excited state $n = 2$, $c_2 = 0$. So the probability of measuring energy to be $E_2$ is zero.

5. Using the answers in question 3 and 4 above and assuming that all $c_n = 0$ for $n \geq 3$, evaluate the average value of the energy of the system in the state $\Psi(x)$. Give your answer in units of $\frac{\hbar^2}{ma^2}$.

$$E = n^2 h^2 / 8ma^2 = n^2 \pi^2 \hbar^2 / 2ma^2$$

   The average energy is

$$\langle E \rangle = P(E_1)E_1 + P(E_2)E_2 = 0.9986 \; E_1 = 4.92\hbar^2/ma^2$$

6. Calculate the expectation value of energy using the formula: $\langle E \rangle = \int_0^a \Psi(x)^* \hat{H} \Psi(x) \, dx$, with $\Psi(x) = Ax(x-a)$, and the normalization constant $A$ from question 1 above.

$$\langle E \rangle = \int_0^a \sqrt{\frac{30}{a^5}} x(x-a)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{30}{a^5}} x(x-a) dx = -\frac{15\hbar^2}{ma^5} \int_0^a x(x-a)\frac{d^2}{dx^2} x(x-a) dx$$

$$= -\frac{30\hbar^2}{ma^5} \int_0^a x(x-a) dx = \frac{5\hbar^2}{ma^2}$$