C455A – Quantum Chemistry and Spectroscopy
Midterm 1 Version 2
April 21, 2006
Exams will be collected promptly at 9:20:00 am
1 8.5x11" page of notes is allowed

-SIT IN ASSIGNED SEAT
-ALL ANSWERS MUST BE IN THE ANSWER BOXES
-CROSSED OUT/PARTIALLY ERASED WORK WILL BE IGNORED
-NO PARTIAL CREDIT ON NUMERICAL PROBLEMS WITHOUT A FORMULA
-NO PARTIAL CREDIT ON "PHYSICALLY IMPLAUSIBLE" ANSWERS UNLESS THE ERROR IS RECOGNIZED BY THE STUDENT
-SHOW ALL WORK

Your name: __________________________

Student ID#: _________________________

I have neither received nor provided assistance of any kind on this exam.

Signature: ____________________________

In the following, u and v are functions of x, and a and n are real numbers

\[ \int u \, dv = uv - \int v \, du \]

\[ \int x^a \, dx = \frac{x^{a+1}}{a+1} \text{ except } n = -1 \]

\[ \int \frac{1}{x} \, dx = \ln x \]

\[ \int e^x \, dx = e^x \]

\[ \int \sin ax \, dx = -\frac{1}{a} \cos ax \]

\[ \int \cos ax \, dx = \frac{1}{a} \sin ax \]

\[ \int (\sin ax)^k \, dx = \frac{1}{a} \cos ax (\sin ax)^{-1} \, dx \]

\[ \int (\cos ax)^k \, dx = \frac{1}{a} \sin ax (\cos ax)^{-1} \, dx \]

\[ \int x^n \, dx = \frac{x^{n+1}}{n+1} \quad (a > 0, n \text{ positive integer}) \]

\[ \int x^n \, dx = \frac{n!}{n} (x^n) \quad (a > 0, n \text{ positive integer}) \]

\[ \int e^{ax} \, dx = \frac{1}{a} e^{ax} \quad (a > 0, n \text{ positive integer}) \]

\[ \int e^{ax} \, dx = \frac{1}{a} e^{ax} \quad (a > 0, n \text{ positive integer}) \]

\[ \int \cos ax \, dx = \frac{1}{a} \sin ax \quad (a > 0, n \text{ positive integer}) \]
Spin Operators and Eigenfunctions:

\[ S_z \alpha = \frac{1}{2} \alpha \]
\[ S_z \beta = \frac{1}{2} \beta \]
\[ S_y \alpha = i \frac{h}{2} \beta \]
\[ S_y \beta = -i \frac{h}{2} \alpha \]
\[ S_x \alpha = \frac{1}{2} \beta \]
\[ S_x \beta = \frac{1}{2} \alpha \]
\[ S^2 \alpha = \frac{1}{2} (1 + \frac{1}{2}) \hbar^2 \alpha \]
\[ S^2 \beta = \frac{1}{2} (1 + \frac{1}{2}) \hbar^2 \beta \]

**Values of Some Physical Constants**

<table>
<thead>
<tr>
<th>Constant</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic mass constant</td>
<td>( m_u )</td>
<td>1.660 5402 x 10^{-27} kg</td>
</tr>
<tr>
<td>Avogadro constant</td>
<td>( N_A )</td>
<td>6.022 1367 x 10^{23} mol^{-1}</td>
</tr>
<tr>
<td>Bohr magneton</td>
<td>( \mu B )</td>
<td>9.274 0154 x 10^{-24} J \cdot T^{-1}</td>
</tr>
<tr>
<td>Bohr radius</td>
<td>( a_0 )</td>
<td>5.291 772 49 x 10^{-10} m</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>( k_B )</td>
<td>1.380 650 x 10^{-23} J \cdot K^{-1}</td>
</tr>
<tr>
<td>Electron rest mass</td>
<td>( m_e )</td>
<td>9.109 3897 x 10^{-28} kg</td>
</tr>
<tr>
<td>Gravitational constant</td>
<td>( G )</td>
<td>6.672 59 x 10^{-11} \cdot m^3 \cdot kg^{-1} \cdot s^{-2}</td>
</tr>
<tr>
<td>Molar gas constant</td>
<td>( R )</td>
<td>8.314 5101 J \cdot K^{-1} \cdot mol^{-1}</td>
</tr>
<tr>
<td>Molar volume, ideal gas</td>
<td>(one bar, 0(^\circ)C)</td>
<td>22.711 08 L \cdot mol^{-1}</td>
</tr>
<tr>
<td></td>
<td>(one atm, 0(^\circ)C)</td>
<td>22.414 09 L \cdot mol^{-1}</td>
</tr>
<tr>
<td>Nuclear magneton</td>
<td>( \mu_B = \mu_0 / 2m_p )</td>
<td>5.050 7866 x 10^{-27} J \cdot T^{-1}</td>
</tr>
<tr>
<td>Permittivity of vacuum</td>
<td>( \varepsilon_0 )</td>
<td>8.854 187 816 x 10^{-12} C^2 \cdot m^{-1}</td>
</tr>
<tr>
<td></td>
<td>( \varepsilon_0 )</td>
<td>1.112 650 056 x 10^{-12} C^2 \cdot m^{-1}</td>
</tr>
<tr>
<td>Planck constant</td>
<td>( h )</td>
<td>6.626 0755 x 10^{-27} J \cdot s</td>
</tr>
<tr>
<td></td>
<td>( h )</td>
<td>1.054 726 65 x 10^{-34} J \cdot s</td>
</tr>
<tr>
<td>Proton charge</td>
<td>( e )</td>
<td>1.602 177 33 x 10^{-19} C</td>
</tr>
<tr>
<td>Proton magnetogyratic ratio</td>
<td>( g_p )</td>
<td>2.675 221 28 x 10^{-5} s^{-1} \cdot T^{-1}</td>
</tr>
<tr>
<td>Proton rest mass</td>
<td>( m_p )</td>
<td>1.672 6231 x 10^{-27} kg</td>
</tr>
<tr>
<td>Rydberg constant (Bohr)</td>
<td>( R_B = m_e e^4 / 8\varepsilon_0^2 h^2 )</td>
<td>2.179 8736 x 10^{-23} m \cdot s^{-1}</td>
</tr>
<tr>
<td>Rydberg constant for H</td>
<td>( R_B )</td>
<td>109 737.3154 cm \cdot s^{-1}</td>
</tr>
<tr>
<td>Speed of light in vacuum</td>
<td>( c )</td>
<td>10677.581 cm \cdot s^{-1} (defined)</td>
</tr>
<tr>
<td>Stefan-Boltzmann constant</td>
<td>( \sigma = 2\pi k_B^2 / 15\hbar^2 c^5 )</td>
<td>5.670 51 x 10^{-8} J \cdot m^{-2} \cdot K^4 \cdot s^{-1}</td>
</tr>
</tbody>
</table>
1) Back to Basics (21 points)
A) The European Union has developed the “Teramobil” system, a terawatt laser mounted in a mobile truck platform. This laser has a peak power of $5 \times 10^{12} \text{ W}$ at a wavelength of 800 nm. How many photons are contained in a short $70 \times 10^{12} \text{ s}$ burst from the Teramobil laser?

\[
5 \times 10^{10} \text{ J/s} \times 70 \times 10^{-12} \text{ s} = 350 \text{ J} \times \frac{1 \text{ photon}}{2.48 \times 10^{-19} \text{ J}} = 1.41 \times 10^{21} \text{ photons}
\]

\[E_{\text{photon}} = \frac{kc}{2} = \frac{1.34 \times 10^4 \text{ eV} \cdot \text{nm}}{800 \text{ nm}} = 2.48 \times 10^{-19} \text{ J/photon}\]

Photons/burst:

\[
1.41 \times 10^{21} \text{ photons}
\]

1B) A frequency tripled YAG laser with a wavelength of 354.7 nm and a power of 3 mW is directed at a clean sodium surface in a vacuum. What is the maximum speed of an ejected photoelectron?

\[
KE = \frac{1}{2} m v^2 = E_{\text{photon}} - \phi_{\text{metal}} = \left(\frac{1.34 \times 10^4 \text{ eV}}{354.7 \text{ nm}} - 2.38 \text{ eV}\right) \times 10^{-19} \text{ J/ev}
\]

\[
V = \sqrt{\frac{2E}{m}} = \sqrt{\frac{1.94 \times 10^{-19} \text{ J}}{9.11 \times 10^{-31} \text{ kg}}} = 6.53 \times 10^5 \text{ m/s}
\]

Speed:

\[
6.53 \times 10^5 \text{ m/s}
\]

1C) Shown at right are two identical diffraction patterns taken by passing an x-ray beam (left) and an electron beam (right) through a very thin Al foil in the exact same geometry for both beams. If the x-rays have an energy of 8.04 keV, what is the kinetic energy of the electrons used to make the diffraction pattern (in eV)?

Same diffraction pattern \(\Rightarrow\) same wavelength

\[
\lambda_{\text{x-ray}} = \frac{hc}{E} = \frac{1.34 \times 10^4 \text{ eV mm}}{8040 \text{ eV}} = 0.154 \text{ nm}
\]

\[
\lambda_e = \frac{h}{mc} = 0.154 \times 10^{-7} \text{ m} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{1.6 \times 10^{-19} \text{ kg m/s}} \Rightarrow p = \frac{4.3 \times 10^{-24} \text{ kg m/s}}{p^2}
\]

\[
E = \frac{p^2}{2m} = \left(\frac{4.3 \times 10^{-24} \text{ kg m/s}}{2 \times 9.11 \times 10^{-31} \text{ kg}}\right)^2 = 1.01 \times 10^{-17} \text{ J} \times \frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}} = \text{63.5 eV}
\]

Energy:

\[
63.5 \text{ eV}
\]
2) Particle in a box (8 Pts). An electron confined to an infinitely deep 1-dimensional box 2 nm long has the following wave function:

$$\psi(x) = C[\phi_1(x) + 2i\phi_2(x) - 3\phi_3(x)]$$

Where, as usual, $$\phi_n$$ denotes the n\textsuperscript{th} normalized energy eigenfunction for the particle in a box with energy $$E_n$$.

A) Is this wave function normalized? If not, find the normalization constant C that normalizes this wave function.

$$\int_{-1}^{1} |\psi|^2 \, dx = \left( \frac{1}{14} \right)^2 \left( 1^2 + 2^2 + 3^2 \right)$$

Normalizing constant C:

$$C = \frac{1}{\sqrt{14}}$$

B) What is the probability of measuring the electron energy to be $$E=0.85 \text{ eV}$$ for the electron with this wave function?

$$E = \frac{0.85 \text{ eV}}{1.36 \times 10^{-19} \text{ J}} = \frac{n^2 \hbar^2}{8mL^2} = \frac{n^2 \left( 6.63 \times 10^{-34} \text{ J s} \right)}{8 \left( 9.11 \times 10^{-31} \text{ Kg m}^2 \text{s}^{-1} \right) \left( 2 \times 10^{-9} \text{ nm} \right)^2}$$

$$n = \sqrt{\frac{8 \times 10^{-31} \times 0.85 \times 10^{-19}}{6.63 \times 10^{-34}}} = \sqrt{1.2} = 1.1$$

$$n = 3$$

The probability of measuring the energy is:

$$P(E_3) = |C_3|^2 = 0$$

$$P(E=0.85 \text{ eV}) = 0$$
2) Particle in a box (cont.).
2C) Draw a histogram (bar graph) with the y-axis being probability, and the x-axis being energy that summarizes the results you'd get from experimentally measuring the energy for many identical systems with above wavefunction. (In other words, graphically show—and label your graph—what the odds of measuring $E_1, E_2, \ldots$ etc. are). What is the expectation value for the energy?

![Graph of the histogram with energy levels]

\[ P(E_n) \propto |c_n|^2 \]

\[
\langle E \rangle = \frac{1}{14}E_2 + \frac{1}{14}E_4 + \frac{9}{14}E_6 = \frac{1}{14}4E_1 + \frac{1}{14}16E_1 + \frac{9}{14}36E_1
\]

\[
= 28E_1, \quad E_1 = 0.694 \text{ eV (from)} \frac{28}{28}
\]

\[
\langle E \rangle = 2.64 \text{ eV} \cdot 4.23 \times 10^{-19} \text{ J}
\]

2D) What will the average value for the position of the particle (i.e. $\langle x \rangle$) if the ends of the box are at $x=-1$ nm and $x=+1$ nm (For credit you should set up then evaluate the appropriate integral by hand, and you must get the right answer for the right reasons).

\[
\langle x \rangle = \frac{1}{14} \int_{-y_2}^{y_2} \left( \varphi_2 - 2 \varphi_4 - 3 \varphi_6 \right) \left( \varphi_2 + 2 \varphi_4 + 3 \varphi_6 \right) dx
\]

\[
= \frac{1}{14} \int_{-y_2}^{y_2} \varphi_2^2 dx + 2 \varphi_2 \varphi_4 dx - 3 \varphi_2 \varphi_6 dx + 2 \varphi_4 \varphi_2 dx - 2 \varphi_4 \varphi_4 dx + 6 \varphi_4 \varphi_6 dx - 3 \varphi_6 \varphi_2 dx - 6 \varphi_6 \varphi_4 dx + 9 \varphi_6^2 dx
\]

\[
= \frac{1}{14} \int_{-y_2}^{y_2} \varphi_2^2 dx - 6 \varphi_2 \varphi_2 dx + 9 \varphi_2^2 dx + 4 \varphi_4^2 dx + 4 \varphi_6^2 dx + 4 \varphi_4 \varphi_6 dx
\]

all $\varphi_n^2$ are even, $\varphi_2 \varphi_4$ are even and $x = \text{odd}$ about center of box \Rightarrow even $\times$ odd

\[
\langle x \rangle = 0 + 1
\]
3) Uncertainty, Operators, Eigenfunctions (30 pts)

3A) Explicitly evaluate the commutator $[\hat{x}, \hat{p}_x]$

\[
\begin{align*}
[\hat{x}, \hat{p}_x]f &= (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})f \\
&= x \left(\frac{-i\hbar}{\hbar \frac{d}{dx}} \right) f - \left(\frac{-i\hbar}{\hbar \frac{d}{dx}}\right) (xf) \\
&= -i\hbar \frac{df}{dx} + i\hbar \frac{dx}{dx} f + i\hbar f \\
&= -i\hbar \frac{df}{dx} + i\hbar f + i\hbar f \\
&= i\hbar f \\
\end{align*}
\]

\[ [\hat{x}, \hat{p}_x] = i\hbar \]

3B) Why does your result from A suggest that you can never know both the position and momentum of a particle exactly at the same time? (don’t restate the uncertainty principle—explain WHY 3A implies there must be an uncertainty principle in 1-3 sentences).

To know an observable exactly $y$ must be an eigenfunction of the corresponding operator. However, two operators $\hat{A}$ and $\hat{B}$ have simultaneous eigenfunctions $\mathcal{F}$ if $\hat{A} \mathcal{F} = \hat{B} \mathcal{F}$, since $\mathcal{F}[\hat{A}, \hat{B}] = 0$, you can’t have $y$ that is an eigenfunction of both.

3C) Is the ground state wave function for a particle in an infinite depth box of length $L$ an eigenfunction of the momentum operator? If yes, what is the eigenvalue. Verify by explicit application of the momentum operator to the wave function.

\[ -i\hbar \frac{d}{dx} \left( \sqrt{\frac{2}{L}} \sin \left( \frac{\pi x}{L} \right) \right) \equiv C \sqrt{\frac{2}{L}} \sin \left( \frac{\pi x}{L} \right) \]

\[ -i\hbar \sqrt{\frac{2}{L}} \left( \frac{\pi}{L} \right) \cos \left( \frac{\pi x}{L} \right) \not\equiv C \sqrt{\frac{2}{L}} \sin \left( \frac{\pi x}{L} \right) \]

$\Rightarrow$ Not an eigenfn

Yes/No=? NO

Eigenvalue if yes= N/A
3D) Find the momentum eigenfunctions by solving the momentum eigenvalue equation, $\hat{p}_x \psi(x) = C \psi(x)$.

$$-i \hbar \frac{d\psi}{dx} = C \psi$$

$$\int \frac{d\psi}{\psi} = \int \frac{C e^{i \lambda x}}{\lambda} \, dx$$

$$e^{i \lambda x} = \frac{C x}{\lambda} \psi$$

$$\psi = e^{i \frac{C}{\lambda} x}$$

$\lambda$ is eigenvalue (can be $+\pi$, $-\pi$)

3E) One electron is placed in an infinitely deep box, and another electron in a box of depth $V = 5 \text{ eV}$. If each box is 2 Angstroms wide, for which electron will we have more uncertainty about its momentum if both are in the ground state (lowest energy eigenstate)? You should draw both potentials and both wave functions as part of your answer.
4) Short Answer Concept Questions (24):
4A) Below are four wave functions for a particle in a 2D circular box. Rank them from LOW to HIGH energy. EXPLAIN.

A) 
B) 
C) 
D)

further nodes
most nodes

C < A < B < D

more nodes = higher energy
3/6 for right ans no expl

4B) Circle which of the following pairs is more likely to cross the barrier (unless specified otherwise, the barrier is 1 eV high, and 0.1 nm wide). EXPLAIN EACH CHOICE WITH ONE SENTENCE OR LESS

i) 0.5 eV electron or 0.5 eV proton

T \propto e^{-\frac{1}{\nu m}}

ii) 0.9 eV electron or 0.5 eV electron

T \propto e^{-\frac{1}{\nu m}}

iii) 2 eV Carbon atom or 0.9 eV electron

Energy is greater than barrier height \Rightarrow no tunneling required

iv) 0.9 eV electron and 0.1 nm barrier or 0.9 eV electron and a 0.2 nm barrier

T \propto e^{-\frac{1}{\nu m}}

4C) Below is plotted |\psi(x)|^2 for the first excited state for the particle in the box. How can the particle move from the left side of the box to the right side of the box if there is no chance of finding it in the middle of the box?

The particle is not "moving" back and forth in the classical sense but is best described as a standing wave occupying the whole box - |\psi(x)|^2 gives us the probability of finding it somewhere if we look but does not describe motion

4D) Will the infrared absorption bands of D₂O be at higher or lower energies than for H₂O? Explain using an equation

\Delta E_{IR} = h \nu = h \sqrt{\frac{k}{m}}

\text{increase mass increases}

\nu \Rightarrow \text{lower Energy for D₂O}