Name_____Student Number_____

Midterm #1 KEY

Show your work clearly. I will give partial credit in some cases, but *only* to the extent that I can clearly understand your work. There is extra paper at the front of the room if you need it.

There are seven (7) short-answer questions (10 points each) and one (1) "long problem" (worth 30 points) on this midterm. There are two bonus questions.

Key integrals and identities:

$$\left(\frac{a}{2}\right)\delta_{mm} = \int_{0}^{a} \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx$$

$$\left(\frac{a}{2}\right)\delta_{mm} = \int_{0}^{a} \cos\left(\frac{n\pi x}{a}\right) \cos\left(\frac{m\pi x}{a}\right) dx$$

$$0 = \int_{0}^{a} \cos\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx$$

$$\frac{a^{2}}{4} = \int_{0}^{a} \left(\sin\left(\frac{n\pi x}{a}\right)\right)^{2} x dx$$

$$\left(\frac{a}{2\pi n}\right)^{3} \left(\frac{4\pi^{3}n^{3}}{3} - 2\pi n\right) = \int_{0}^{a} \left(\sin\left(\frac{n\pi x}{a}\right)\right)^{2} x^{2} dx$$

$$\frac{1}{2}\sqrt{\frac{\pi}{a}} = \int_{0}^{\infty} e^{-ax^{2}} dx$$

$$\left(\frac{1}{2}\sqrt{\frac{\pi}{a}}\right) \left(\frac{(2n-1)(2n-3)\cdots(3)(1)}{(2\alpha)^{n}}\right) = \int_{0}^{\infty} x^{2n} e^{-ax^{2}} dx$$

$$n = 1, 2, 3, \dots$$

$$\left(\frac{1}{2}\right) \left(\frac{n!}{a^{n+1}}\right) = \int_{0}^{\infty} x^{2n+1} e^{-ax^{2}} dx$$

$$n = 0, 1, 2, \dots$$

$$2\sin(x)\sin(y) = \cos(x-y) - \cos(x+y) \rightarrow 2\sin^{2}x = 1 - \cos(2x)$$

$$2\cos(x)\cos(y) = \cos(x-y) + \cos(x+y) \rightarrow 2\cos^{2}x = 1 + \cos(2x)$$

$$2\sin(x)\cos(y) = \sin(\alpha+\beta) + \sin(\alpha-\beta) \rightarrow 2\sin x \cos x = \sin(2x)$$

$$\sin(x+y) = \sin x \cos y + \cos x \sin y \rightarrow \sin(2x) = 2\sin x \cos x$$

$$\cos(x+y) = \cos x \cos y - \sin x \sin y \rightarrow \cos(2x) = \cos^{2}x - \sin^{2}x$$

VALUES OF SOME PHYSICAL CONSTANTS	SICAL CONSTA	ANTS
Constant	Symbol	Value
Avogadro's number	N_0	$6.02205 \times 10^{23} \mathrm{mol^{-1}}$
Proton charge	e	$1.60219 \times 10^{-19} \mathrm{C}$
Planck's constant	<i>ה</i> ה	$6.62618 \times 10^{-34} \text{ J} \cdot \text{s}$ $1.05459 \times 10^{-34} \text{ J} \cdot \text{s}$
Speed of light in vacuum	c	$2.997925 \times 10^8 \mathrm{m \cdot s^{-1}}$
Atomic mass unit	amu	$1.66056 \times 10^{-27} \mathrm{kg}$
Electron rest mass	m _e	$9.10953 \times 10^{-31} \mathrm{kg}$
Proton rest mass	m_p	$1.67265 \times 10^{-27} \mathrm{kg}$
Boltzmann constant	k_B	$1.38066 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ 0.69509 cm^{-1}
Molar gas constant	R	8.31441 J·K ⁻¹ ·mol ⁻¹
Permittivity of a vacuum	$\frac{\varepsilon_0}{4\pi\varepsilon_0}$	$8.854188 \times 10^{-12} \text{ C}^2 \cdot \text{s}^2 \cdot \text{kg}^{-1} \cdot \text{m}^{-3}$ $1.112650 \times 10^{-10} \text{ C}^2 \cdot \text{s}^2 \cdot \text{kg}^{-1} \cdot \text{m}^{-3}$
Rydberg constant (infinite nuclear mass)	R_{∞}	$2.179914 \times 10^{-23} \text{ J}$ 1.097373 cm^{-1}
First Bohr radius	a_0	$5.29177 \times 10^{-11} \text{ m}$
Bohr magneton	μ_B	$9.27409 \times 10^{-24} \text{J} \cdot \text{T}^{-1}$
Stefan-Boltzmann constant	g	$5.67032 \times 10^{-8} \mathrm{J \cdot m^{-2} \cdot K^{-4} \cdot s^{-1}}$
CONVERSION FACTORS FOR ENERGY UNITS	S FOR ENERGY	UNITS
joule kJ·mol ⁻¹	-1 eV	au cm ⁻¹ Hz
1 joule 6.022 × 10 ²⁰) ²⁰ 6.242×10 ¹⁸	2.2939×10^{17} 5.035×10^{22} 1.509×10^{33}
$= 1.661 \times 10^{-21}$	1.036×10^{-2}	3.089×10^{-4} 83.60 2.506×10^{12}
=1.602×10 ⁻¹⁹ 96.48	-	3.675×10^{-2} 8065 2.418×10^{14}
= 4.359 × 10 ⁻¹⁸ 2625	27.21	1 2.195×10^5 6.580×10^{15}
1.19	1.240×10^{-4}	4.556×10 ° 1 2.998×10°

1 J(oule) = $1 \text{ kg} \cdot \text{m}^2/\text{s}^2 = 1 \text{ C(oulomb)} \cdot \text{V(olt)}$

The following information is used in problems 1-3.

The red laser pointers that are ubiquitous in conference presentations are He/Ne (Helium-Neon) lasers. They produce photons with a wavelength of $632.8 \text{ nm} = 6.328 \cdot 10^{-7} \text{ m}$.

1. What is the frequency of the light from a He/Ne laser?

$$v = c/\lambda = (2.998 \cdot 10^8 \frac{m}{s})/(6.328 \cdot 10^{-7} \text{ m}) = 4.738 \cdot 10^{14} \text{ s}^{-1} = 4.738 \cdot 10^{14} \text{ Hz}$$

2. What is the energy of one photon from a He/Ne laser?

$$E = hv = (6.626 \cdot 10^{-34} \,\mathrm{J \cdot s})(4.738 \cdot 10^{14} \,\mathrm{s}^{-1}) = 3.139 \cdot 10^{-19} \,\mathrm{J}$$

3. What is the momentum of one photon from a He/Ne laser?

$$p = h/\lambda = (6.626 \cdot 10^{-34} \frac{\text{kg·m}^2}{\text{s}})/(6.328 \cdot 10^{-7} \text{ m}) = 1.047 \cdot 10^{-27} \frac{\text{kg·m}}{\text{s}}$$

4. Write the time-independent Schrödinger equation.

$$\hat{H}(x)\Psi_n(x) = E_n\Psi_n(x)$$

5. Write the time-dependent Schrödinger equation.

$$\hat{H}(x,t)\Psi_n(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

6. Write a Slater determinant wavefunction (write out all the rows and columns) for the ground state of the Lithium atom, with electron configuration $1s^22s^1$.

$$\Psi(x_{1}, x_{2}, x_{3}) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{1s}(x_{1})\alpha(1) & \psi_{1s}(x_{1})\beta(1) & \psi_{2s}(x_{1})\alpha(1) \\ \psi_{1s}(x_{2})\alpha(2) & \psi_{1s}(x_{2})\beta(2) & \psi_{2s}(x_{2})\alpha(2) \\ \psi_{1s}(x_{3})\alpha(3) & \psi_{1s}(x_{3})\beta(3) & \psi_{2s}(x_{3})\alpha(3) \end{vmatrix}$$

Problem 1. The harmonic oscillator box.

You are given a system containing electrons which are confined by a harmonic restoring force with force constant κ in the x direction and confined within an infinite box in the y direction. That is, the confining potential is,

$$V(x, y) = \frac{1}{2}\kappa x^{2} + \begin{cases} 0 & 0 < y < a \\ +\infty & y \le 0 \\ +\infty & y \ge a \end{cases}$$

I call this the harmonic-oscillator-box potential. It is helpful to know the eigenvalues and eigenfunctions for the particle-in-a-box (which I assume you know) and for the harmonic oscillator (which I don't assume you know). For the harmonic oscillator, with the Hamiltonian

$$\hat{H}_{ho}(x) = -\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} + \frac{1}{2}\kappa x^2$$

the eigenfunctions and eigenvalues are:

$$\hat{H}_{ho}\psi_{k}(x) = E_{k}\psi_{k}(x)$$

$$E_{k} = \hbar\omega(k + \frac{1}{2}) \qquad k = 0,1,2,...$$

$$\psi_{0}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega x^{2}}{2\hbar}}$$

$$\psi_{1}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega x^{2}}{2\hbar}} \left(x\sqrt{\frac{2m\omega}{\hbar}}\right)$$

$$\psi_{2}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega x^{2}}{2\hbar}} \left(\frac{1}{\sqrt{2}}\right) \left(2x^{2}\left(\frac{m\omega}{\hbar}\right) - 1\right)$$

where, for convenience, we have introduced the angular frequency of the oscillation,

$$\omega = 2\pi v = \sqrt{\kappa/m_e}$$

1a. What is the Hamiltonian for two electrons confined in the harmonic-oscillator box? (10 points)

$$\begin{split} \hat{H}_{\text{ho-box}}\left(x_{1},y_{1};x_{2},y_{2}\right) &= -\frac{\hbar^{2}}{2m_{e}}\left(\frac{\partial^{2}}{\partial x_{1}^{2}} + \frac{\partial^{2}}{\partial y_{1}^{2}} + \frac{\partial^{2}}{\partial x_{2}^{2}} + \frac{\partial^{2}}{\partial y_{2}^{2}}\right) + V\left(x_{1},y_{1}\right) + V\left(x_{2},y_{2}\right) \\ &+ \frac{e^{2}}{4\pi\varepsilon_{0}\sqrt{\left(x_{1}-x_{2}\right)^{2} + \left(y_{1}-y_{2}\right)^{2}}} \\ \hat{H}_{\text{ho-box}}\left(\mathbf{r}_{1},\mathbf{r}_{2}\right) &= -\frac{\hbar^{2}}{2m_{e}}\left(\nabla_{1}^{2} + \nabla_{2}^{2}\right) + V\left(\mathbf{r}_{1}\right) + V\left(\mathbf{r}_{2}\right) + \frac{e^{2}}{4\pi\varepsilon_{0}\left|\mathbf{r}_{1}-\mathbf{r}_{2}\right|} \end{split}$$
 When I use the short form I am defining $\mathbf{r} = \left(x,y\right)$ and $|\mathbf{r}_{1}-\mathbf{r}_{2}| = \sqrt{\left(x_{1}-x_{2}\right)^{2} + \left(y_{1}-y_{2}\right)^{2}}$.

1b. Write an expression for the ground-state energy for two electrons confined in the aforementioned harmonic-oscillator box, assuming it is permissible to neglect the electron-electron repulsion. (15 points)

The system can be written as a sum of four Hamiltonians: each of the two electrons is described by an identical Hamiltonian which is itself the sum of a harmonic-oscillator Hamiltonian and a particle-in-a-box Hamiltonian. So the energy for *one* electron in the lowest-energy orbital is the sum of the particle-in-a-box and the Harmonic Oscillator energies,

$$\varepsilon_{1 \text{ electron}} = \varepsilon_{\text{ho}} + \varepsilon_{\text{box}} = \frac{1}{2}\hbar\omega + \frac{h^2}{8m_e a^2} = \frac{\hbar}{2}\sqrt{\frac{\kappa}{m_e}} + \frac{h^2}{8m_e a^2}$$

The total ground-state energy is the sum of the (identical) energies of the two electrons. So you have

$$E_{g.s.} = 2\left(\frac{1}{2}\hbar\omega + \frac{h^2}{8m_e a^2}\right) = \hbar\sqrt{\frac{\kappa}{m_e}} + \frac{h^2}{4m_e a^2}$$

1c. Write an expression for the ground-state wavefunction for two electrons confined in the aforementioned harmonic-oscillator box, assuming it is permissible to neglect the electron-electron repulsion. (15 points)

The wavefunction is a product of the wavefunctions for the different electrons, but antisymmetrized to obey the Pauli exclusion principle. You can write this as a Slater determinant,

$$\Psi(x_{1}, y_{1}, x_{2}, y_{2}) = \frac{1}{\sqrt{2}} \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} \sqrt{\frac{2}{a}} e^{-\frac{m\omega x_{1}^{2}}{2\hbar}} \sin\left(\frac{\pi y_{1}}{a}\right) \alpha(1) \quad \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \sqrt{\frac{2}{a}} e^{-\frac{m\omega x_{1}^{2}}{2\hbar}} \sin\left(\frac{\pi y_{1}}{a}\right) \beta(1) \right) \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} \sqrt{\frac{2}{a}} e^{-\frac{m\omega x_{2}^{2}}{2\hbar}} \sin\left(\frac{\pi y_{2}}{a}\right) \alpha(2) \quad \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \sqrt{\frac{2}{a}} e^{-\frac{m\omega x_{2}^{2}}{2\hbar}} \sin\left(\frac{\pi y_{2}}{a}\right) \beta(2) \right)$$

or explicitly,

$$\Psi(x_1, y_1; x_2, y_2) = \frac{2}{a} \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} e^{-\frac{m\omega(x_1^2 + x_2^2)}{2\hbar}} \sin\left(\frac{\pi y_1}{a}\right) \sin\left(\frac{\pi y_2}{a}\right) \left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}\right)$$

BONUS: (5 points) You are told that the ground-state for <u>FOUR</u> electrons confined in a harmonic-oscillator box is degenerate in the absence of electron-electron repulsion. (That is, there are two states with the same energy, assuming that it is permissible to neglect the electron-electron repulsion.) **Derive a relationship between** a **and** κ **for which this is true.**

In the first part of this problem we had to fill only one orbital. Now we need to fill two orbitals. The first orbital we filled had the quantum numbers (k = 0; n = 1). The second orbital we could fill could be (k = 1; n = 1) or could be (k = 0; n = 2). Degeneracy will happen when these two expressions have the same energy, so that there are two possible states with the same energy. So we need to determine when

$$\frac{h^{2}(1)^{2}}{8ma^{2}} + \left(\frac{1}{2} + 1\right)\hbar\omega = \frac{h^{2}(2)^{2}}{8ma^{2}} + \frac{1}{2}\hbar\omega$$

this occurs when:

$$\hbar\omega = \frac{3h^{2}}{8m_{e}a^{2}}$$

$$\omega = \frac{3h^{2}}{8\hbar m_{e}a^{2}} = \frac{6\pi h}{8m_{e}a^{2}} = \frac{3\pi h}{4m_{e}a^{2}}$$

$$\sqrt{\frac{\kappa}{m_{e}}} = \frac{3\pi h}{4m_{e}a^{2}}$$

$$\kappa = \left(\frac{3\pi h}{4\sqrt{m_{e}}a^{2}}\right)^{2} = \frac{9\pi^{2}h^{2}}{16m_{e}a^{4}}$$

When $\kappa < \frac{9\pi^2h^2}{16m_ea^4}$, the (k=1;n=1) state will be lower in energy. When $\kappa > \frac{9\pi^2h^2}{16m_ea^4}$, the (k=0;n=2) state will be lower in energy.

BONUS: (5 points) The box is placed in a uniform electric field in the x direction. The new potential is then

$$V(x,y) = \frac{1}{2}kx^{2} + Fx + \begin{cases} 0 & 0 < y < a \\ +\infty & y \le 0 \\ +\infty & y \ge a \end{cases}$$

How does the lowest orbital energy (the energy of the first orbital) depend on the field strength, F? Assume that the field is weak enough that 1st-order perturbation theory is valid. The wavefunction for the lowest orbital is

$$\phi_{0,1}(\mathbf{r}) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{2}{a}} e^{-\frac{m\omega x_1^2}{2\hbar}} \sin\left(\frac{\pi y_1}{a}\right)$$

and the first-order perturbation correction to the energy is given by

$$E'(0) = \int \Psi_0^*(\mathbf{r}) V'(\mathbf{r}) \Psi_0(\mathbf{r}) d\mathbf{r}$$

which in this case gives the expression

$$E'(0) = \int_{-\infty}^{\infty} \int_{0}^{a} \phi_{0,1}^{*}(x,y) x \phi_{0,1}(x,y) dy dx = \langle x \rangle$$

This expression is zero since it is the expectation value for x, $\langle x \rangle$, and the average position of x in a symmetric system like this is clearly zero.

However, we can also work this out explicitly:

$$E'(0) = \int_{-\infty}^{\infty} \int_{0}^{a} \phi_{0,1}^{*}(x,y) x \phi_{0,1}(x,y) dy dx$$

$$= \int_{-\infty}^{\infty} \int_{0}^{a} \left[\left(\frac{m\omega}{\pi \hbar} \right)^{\frac{1}{4}} \sqrt{\frac{2}{a}} e^{-\frac{m\omega x^{2}}{2\hbar}} \sin\left(\frac{\pi y}{a}\right) \right]^{*} x \left[\left(\frac{m\omega}{\pi \hbar} \right)^{\frac{1}{4}} \sqrt{\frac{2}{a}} e^{-\frac{m\omega x^{2}}{2\hbar}} \sin\left(\frac{\pi y}{a}\right) \right] dy dx$$

$$= \left(\left(\frac{m\omega}{\pi \hbar} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} e^{-\frac{m\omega x^{2}}{\hbar}} \cdot x dx \right) \left(\sqrt{\frac{2}{a}} \int_{0}^{a} \sin\left(\frac{\pi y}{a}\right)^{2} dy \right)$$

$$= 0.1$$

$$= 0$$

The second factor is 1 because of the normalization of the particle-in-a-box eigenfunctions. The first factor is zero because it is the integral of an odd function over all space:

$$\int_{-\infty}^{\infty} e^{-\frac{m\omega x^2}{\hbar}} \cdot x dx = \int_{-\infty}^{\infty} [\text{even function}] \cdot [\text{odd function}] dx = \int_{-\infty}^{\infty} [\text{odd function}] dx = 0$$

(You could also deduce that the integral was zero using the formula sheet for the exam.) Recall that a function is even if f(x) = f(-x) and odd if f(x) = -f(-x). The integral of odd functions over a symmetric interval is zero because one can write

$$\int_{-\infty}^{\infty} f_{\text{odd}}(x) dx = \int_{-\infty}^{0} f_{\text{odd}}(x) dx + \int_{0}^{\infty} f_{\text{odd}}(x) dx$$

$$= \int_{-\infty}^{0} -f_{\text{odd}}(-x) dx + \int_{0}^{\infty} f_{\text{odd}}(x) dx$$

$$= -\int_{0}^{\infty} f_{\text{odd}}(u) du + \int_{0}^{\infty} f_{\text{odd}}(x) dx$$

$$= 0$$

The conclusion of this analysis is that, to first order, the energy of the first orbital is not affected by a uniform external electric field.

BONUS: (5 points) Consider a beam of electrons, accelerated through a potential of 100. Volts. What is the de Broglie wavelength of electrons in the beam?

This is directly from Randy's book, exercise 1.1. The energy after the electrons are accelerated through the potential is entirely potential, and is equal to the voltage drop times the charge. So we start by computing the energy as

$$E = e_{\text{charge on the electron}} \cdot (100. \text{ V}) = (1.609 \cdot 10^{-19} \text{ C}) \cdot (100 \text{ V}) = 1.609 \cdot 10^{-17} \text{ C} \cdot \text{V}$$

The kinetic energy can then be determined, and we use the conversion 1 C-V = 1 J. So

$$T = 1.609 \cdot 10^{-17} \,\text{J} = \frac{p^2}{2m_e}$$
$$p = \sqrt{2m_e \cdot 1.609 \cdot 10^{-17} \cdot \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}}$$

This gives that the momentum of the electron is

$$p = \sqrt{2 \cdot \left(9.11 \cdot 10^{-31} \,\mathrm{kg}\right) \cdot 1.609 \cdot 10^{-17} \,\frac{\mathrm{kg \cdot m}^2}{\mathrm{s}^2}} = 5.41 \cdot 10^{-24} \,\frac{\mathrm{kg \cdot m}}{\mathrm{s}}$$

and then the De Broglie relation gives the wavelength to be:

$$p = h/\lambda$$

$$\lambda = h/p = \left(6.626 \cdot 10^{-34} \, \frac{\text{kg} \cdot \text{m}^2}{\text{s}}\right) / \left(5.41 \cdot 10^{-24} \, \frac{\text{kg} \cdot \text{m}}{\text{s}}\right) = 1.22 \cdot 10^{-10} \, \text{m} = 0.122 \, \text{nm}$$