Name_____ Student Number_____

Mid-Term #3

Show your work clearly. I will give partial credit in some cases, but *only* to the extent that I can clearly understand your work. The exam is marked out of 100 points.

You may use any non-internet-enabled calculator for the exam. You may not use any internet-enabled device (including e-readers, tablets, laptops, cellular phones, …). You may not use any notes, books, or other materials.

7 questions @ 14 points each. [There are 2 "free points"]
2 Bonus questions worth 10 points each (see the last page).

Key integrals and identities:

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx$$

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \cos\left(\frac{n\pi x}{a}\right)\cos\left(\frac{m\pi x}{a}\right)dx$$

$$0 = \int_0^a \cos\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx$$

$$\frac{a^2}{4} = \int_0^a \left(\sin\left(\frac{n\pi x}{a}\right)\right)^2 xdx$$

$$\left(\frac{a}{2\pi n}\right)^3\left(\frac{4\pi^3 n^3}{3} - 2\pi n\right) = \int_0^a \left(\sin\left(\frac{n\pi x}{a}\right)\right)^2 x^2 dx$$

$$\frac{1}{2}\sqrt{\frac{\pi}{\alpha}} = \int_0^\infty e^{-\alpha x^2}dx$$

$$\left(\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\right)\left(\frac{(2n-1)(2n-3)\cdots(3)(1)}{(2\alpha)^n}\right) = \int_0^\infty x^{2n}e^{-\alpha x^2}dx \qquad n = 1,2,3,\ldots$$

$$\left(\frac{1}{2}\right)\left(\frac{n!}{\alpha^{n+1}}\right) = \int_0^\infty x^{2n+1}e^{-\alpha x^2}dx \qquad n = 0,1,2,\ldots$$

$$\int x\sin(bx)dx = \frac{\sin(bx)}{b^2} - \frac{x\cos(bx)}{b} + \text{constant}$$

$$\int x^2 \sin(bx)dx = -\left(\frac{x^2\cos(bx)}{b} + \frac{2x\cos(bx+\frac{1}{2}\pi)}{b^2} + \frac{2\cos(bx+\pi)}{b^3}\right) + \text{constant}$$

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

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

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

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

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

VALUES OF SOME PHYSICAL CONSTANTS

Constant	Symbol	Value
Avogadro's number	N_0	6.02205×10^{23} mol^{-1}
Proton charge	e	1.60219×10^{-19} C
Planck's constant	h	6.62618×10^{-34} J·s
	$\hbar$	1.05459×10^{-34} J·s
Speed of light in vacuum	c	2.997925×10^{8} m·s^{-1}
Atomic mass unit	amu	1.66056×10^{-27} kg
Electron rest mass	m_e	9.10953×10^{-31} kg
Proton rest mass	m_p	1.67265×10^{-27} kg
Boltzmann constant	k_B	1.38066×10^{-23} J·K^{-1}
		0.69509 cm^{-1}
Molar gas constant	R	8.31441 J·K^{-1}·mol^{-1}
Permittivity of a vacuum	ε_0	8.85188×10^{-12} C^2·s^2·kg^{-1}·m^{-3}
	$4\pi\varepsilon_0$	1.112650×10^{-10} C^2·s^2·kg^{-1}·m^{-3}
Rydberg constant (infinite nuclear mass)	R_∞	2.179914×10^{-23} J
		1.097373 cm^{-1}
First Bohr radius	a_0	5.29177×10^{-11} m
Bohr magneton	μ_B	9.27409×10^{-24} J·T^{-1}
Stefan-Boltzmann constant	σ	5.67032×10^{-8} J·m^{-2}·K^{-4}·s^{-1}

CONVERSION FACTORS FOR ENERGY UNITS

	joule	kJ·mol^{-1}	eV	au	cm^{-1}	Hz
1 joule =1	1	6.022×10^{20}	6.242×10^{18}	2.2939×10^{17}	5.035×10^{22}	1.509×10^{33}
1 kJ·mol^{-1} =1.661×10^{-21}		1	1.036×10^{-2}	3.089×10^{-4}	83.60	2.506×10^{12}
1 eV =1.602×10^{-19}		96.48	1	3.675×10^{-2}	8065	2.418×10^{14}
1 au =4.359×10^{-18}		2625	27.21	1	2.195×10^{5}	6.580×10^{15}
1 cm^{-1} =1.986×10^{-23}		1.196×10^{-2}	1.240×10^{-4}	4.556×10^{-6}	1	2.998×10^{10}
1 Hz =6.626×10^{-34}		3.990×10^{-13}	4.136×10^{-15}	1.520×10^{-16}	3.336×10^{-11}	1

SOME MATHEMATICAL FORMULAS

$$\sin\alpha\sin\beta = \tfrac{1}{2}\cos(\alpha-\beta) - \tfrac{1}{2}\cos(\alpha+\beta)$$
$$\cos\alpha\cos\beta = \tfrac{1}{2}\cos(\alpha-\beta) + \tfrac{1}{2}\cos(\alpha+\beta)$$
$$\sin\alpha\cos\beta = \tfrac{1}{2}\sin(\alpha+\beta) + \tfrac{1}{2}\sin(\alpha-\beta)$$

$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$
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$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta$$
$$\cos\theta = \frac{e^{i\theta}+e^{-i\theta}}{2}$$
$$\sin\theta = \frac{e^{i\theta}-e^{-i\theta}}{2i}$$

$$f(x) = f(a) + f'(a)(x-a) + \frac{1}{2!}f''(a)(x-a)^2 + \frac{1}{3!}f'''(a)(x-a)^3 + \cdots$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots$$
$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots$$
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$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \cdots \qquad x^2 < 1$$
$$(1\pm x)^n = 1 \pm nx + \frac{n(n-1)}{2!}x^2 \pm \frac{n(n-1)(n-2)}{3!}x^3 \pm \cdots \qquad x^2 <$$

$$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}} \qquad (n\ \text{positive integer})$$

$$\int_0^\infty e^{-ax^2}\,dx = \left(\frac{\pi}{4a}\right)^{1/2}$$

$$\int_0^\infty x^{2n}e^{-ax^2}\,dx = \frac{1\cdot 3\cdot 5\cdot\cdots\cdot(2n-1)}{2^{n+1}a^n}\left(\frac{\pi}{a}\right)^{1/2} \qquad (n\ \text{positive integer})$$

$$\int_0^\infty x^{2n+1}e^{-ax^2}\,dx = \frac{n!}{2a^{n+1}} \qquad (n\ \text{positive integer})$$

$$\int_0^a \sin\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = \int_0^a \cos\frac{n\pi x}{a}\cos\frac{m\pi x}{a}\,dx = \frac{a}{2}\delta_{nm}$$

$$\int_0^a \cos\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = 0 \qquad (m\ \text{and}\ n\ \text{integers})$$

1 J(oule) = 1 kg·m^2/s^2 = 1 C(oulomb)·V(olt)

1. **Write the molecular Hamiltonian for P-atom N-electron molecule, including the dependence on constants like** $\hbar, e, \varepsilon_0, m_e, \ldots$.

2,3. **Write the electronic and nuclear Schrödinger equations for the LiH⁺ molecular cation.** You can use atomic units.

4. Suppose that one chooses to neglect electron-electron repulsion in the Boron atom. **What is the momentum of the photon associated with the transition from the $1s^2 2s^2 3d^1$ excited state to the $1s^2 2s^2 2p^1$ ground state, in $\frac{kg \cdot m}{s}$?** A conversion factor from page 2 may be helpful.

5. The ground state of the Vanadium atom has total orbital angular momentum quantum number L = 3 and total spin quantum number $S = 3/2$. **List all possible choices for the eigenvalues of the following operators (you can use atomic units).**

$$\hat{L}_z \Psi_{L=3;S=\frac{3}{2}} = \underline{\hspace{6cm}} \Psi_{L=3;S=\frac{3}{2}}$$

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$$\hat{J}^2 \Psi_{L=3;S=\frac{3}{2}} = \underline{\hspace{6cm}} \Psi_{L=3;S=\frac{3}{2}}$$

6. Consider the ground state of the Carbon atom, specificially the state with $L = M_L = S = M_S = 1$. **Use the Heisenberg Uncertainty Principle to provide a lower bound for the product of the angular momenta uncertainty for the atoms in the other directions.** You can use atomic units.

$$\sigma^2_{\hat{L}_x} \sigma^2_{\hat{L}_y} \geq \underline{\hspace{5cm}}$$

7. When one integrates a spherical function in 3 dimensions, integration has the form
$$\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} f(r,\theta,\phi) r^2 \sin\theta \, dr \, d\theta \, d\phi$$
Recall that the orthonormalization convention for spherical harmonics is
$$\int_0^{2\pi} \int_0^{\pi} \left(Y_l^m(\theta,\phi)\right)^* Y_{l'}^{m'}(\theta,\phi) \sin\theta \, d\theta \, d\phi = \delta_{ll'}\delta_{mm'}$$
What is the average distance of an electron from the nucleus in the 3d^1 excited state of the Hydrogen atom? Integral(s) provided on the data sheet will be helpful.

Bonus: A nearly exact measurement of the energy of the Lithium cation, Li^+, gives the lower bound $E_{Li^+} > -7.280$ a.u.. Give a lower bound to the energy of the neutral Lithium atom (the tighter your bound, the more points you get).

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1 Hz	6.626×10^{-34}	3.990×10^{-13}	4.136×10^{-15}	1.520×10^{-16}	3.336×10^{-11}	1

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$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \cdots \quad x^2 < 1$$

$$(1\pm x)^n = 1 \pm nx + \frac{n(n-1)}{2!}x^2 \pm \frac{n(n-1)(n-2)}{3!}x^3 \pm \cdots \quad x^2 <$$

$$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}} \quad \text{(n positive integer)}$$

$$\int_0^\infty e^{-ax^2}\,dx = \left(\frac{\pi}{4a}\right)^{1/2}$$

$$\int_0^\infty x^{2n}e^{-ax^2}\,dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\left(\frac{\pi}{a}\right)^{1/2} \quad \text{(n positive integer)}$$

$$\int_0^\infty x^{2n+1}e^{-ax^2}\,dx = \frac{n!}{2a^{n+1}} \quad \text{(n positive integer)}$$

$$\int_0^a \sin\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = \int_0^a \cos\frac{n\pi x}{a}\cos\frac{m\pi x}{a}\,dx = \frac{a}{2}\delta_{nm}$$

$$\int_0^a \cos\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = 0 \quad \text{(m and n integers)}$$

1   J(oule) = 1 kg·m^2/s^2 = 1 C(oulomb)·V(olt)

1. **Write the molecular Hamiltonian for P-atom N-electron molecule, including the dependence on constants like** $\hbar, e, \varepsilon_0, m_e, \ldots$.

$$\sum_{i=1}^{N} -\frac{\hbar^2}{2}\nabla_i^2 + \sum_{\alpha=1}^{P} -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + \sum_{\alpha=2}^{P}\sum_{\beta=1}^{\alpha-1} \frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0 |\mathbf{R}_\alpha - \mathbf{R}_\beta|} + \sum_{i=2}^{P}\sum_{j=1}^{i-1} \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\alpha=1}^{P}\sum_{i=1}^{N} \frac{-Z_\alpha e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{R}_\alpha|}$$

2,3. **Write the electronic and nuclear Schrödinger equations for the LiH⁺ molecular cation. You can use atomic units.**

$$\left(-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \tfrac{1}{2}\nabla_3^2 - \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} - \frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_3} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|} + \frac{3}{|\mathbf{R}_H - \mathbf{R}_{Li}|} \right) \psi_e\left(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 | \mathbf{R}_H, \mathbf{R}_{Li}\right)$$

$$= U\left(\mathbf{R}_H, \mathbf{R}_{Li}\right) \psi_e\left(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 | \mathbf{R}_H, \mathbf{R}_{Li}\right)$$

$$\left(-\frac{1}{2M_H}\nabla_H^2 - \frac{1}{2M_{Li}}\nabla_{Li}^2 + U\left(\mathbf{R}_H, \mathbf{R}_{Li}\right) \right) \chi\left(\mathbf{R}_H, \mathbf{R}_{Li}\right) = E_{mol}\chi\left(\mathbf{R}_H, \mathbf{R}_{Li}\right)$$

4. Suppose that one chooses to neglect electron-electron repulsion in the Boron atom. **What is the momentum of the photon associated with the transition from the 1s²2s²3d¹ excited state to the 1s²2s²2p¹ ground state, in** $\frac{\text{kg·m}}{\text{s}}$**?** A conversion factor from page 2 may be helpful.

Because electron-electron repulsion is neglected, this is equal to the energy of the transition between the $n=3$ and $n=2$ states of the 1-electron atom with $Z = 5$. They have not

$$\Delta E = -\frac{Z^2}{2(n=3)^2} - \left(-\frac{Z^2}{2(n=2)^2} \right) = \frac{-Z^2}{18} + \frac{Z^2}{8} = (Z=5)^2\left(\frac{1}{8} - \frac{1}{18}\right) = 1.736 \text{ Hartree}$$

$$= 1.736 \text{ Hartree} \cdot \left(2.2939 \cdot 10^{17} \tfrac{\text{Hartree}}{\text{Joules}}\right)^{-1}$$

$$= 7.568 \cdot 10^{-18} \text{ J}$$

The momentum is related to the wavelength by $p = h\lambda^{-1}$ and then using the link between wavelength and frequency and the link between frequency and energy, $p = h\left(cv^{-1}\right)^{-1} = hvc^{-1} = Ec^{-1}$. So

$$p = \frac{7.568 \cdot 10^{-18} \text{ J}}{2.998 \cdot 10^8 \tfrac{\text{m}}{\text{s}}} = 2.524 \cdot 10^{-26} \tfrac{\text{kg·m}}{\text{s}}$$

5. The ground state of the Vanadium atom has total orbital angular momentum quantum number L = 3 and total spin quantum number $S = 3/2$. **List all possible choices for the eigenvalues of the following operators (you can use atomic units).**

$$\hat{L}_z \Psi_{L=3;S=\frac{3}{2}} = \{-3,-2,-1,0,1,2,3\} \Psi_{L=3;S=\frac{3}{2}}$$

$$\hat{S}_z \Psi_{L=3;S=\frac{3}{2}} = \{-\tfrac{3}{2},\tfrac{-1}{2},\tfrac{1}{2},\tfrac{3}{2}\} \Psi_{L=3;S=\frac{3}{2}}$$

$$\hat{J}^2 \Psi_{L=3;S=\frac{3}{2}} = \{(\tfrac{9}{2})(\tfrac{11}{2});(\tfrac{7}{2})(\tfrac{9}{2});(\tfrac{5}{2})(\tfrac{7}{2});(\tfrac{3}{2})(\tfrac{5}{2})\} \Psi_{L=3;S=\frac{3}{2}}$$

$$= \{\tfrac{99}{4};\tfrac{63}{4};\tfrac{35}{4};\tfrac{15}{4}\} \Psi_{L=3;S=\frac{3}{2}}$$

$$\left(\text{because } J = |L-S|,|L-S|+1,\ldots,L+S-1,L+S = \tfrac{3}{2},\tfrac{5}{2},\tfrac{7}{2},\tfrac{9}{2}\right)$$

6. Consider the ground state of the Carbon atom, specificially the state with $L = M_L = S = M_S = 1$. **Use the Heisenberg Uncertainty Principle to provide a lower bound for the product of the angular momenta uncertainty for the atoms in the other directions.** You can use atomic units.

$$\sigma_{\hat{L}_x}^2 \sigma_{\hat{L}_y}^2 \geq \tfrac{1}{4}\left|\left\langle\left[\hat{L}_x,\hat{L}_y\right]\right\rangle\right|^2 = \tfrac{1}{4}\left|\left\langle\hat{L}_z\right\rangle\right|^2 = \tfrac{1}{4}M_L^2 = \tfrac{1}{4}(1)$$

$$\sigma_{\hat{L}_x}^2 \sigma_{\hat{L}_y}^2 \geq \tfrac{1}{4}$$

7. When one integrates a spherical function in 3 dimensions, integration has the form

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} f(r,\theta,\phi)r^2\sin\theta\,dr\,d\theta\,d\phi$$

Recall that the orthonormalization convention for spherical harmonics is

$$\int_0^{2\pi}\int_0^{\pi}\left(Y_l^m(\theta,\phi)\right)^* Y_{l'}^{m'}(\theta,\phi)\sin\theta\,d\theta\,d\phi = \delta_{ll'}\delta_{mm'}$$

What is the average distance of an electron from the nucleus in the $3d^1$ excited state of the Hydrogen atom? Integral(s) provided on the data sheet will be helpful.

We know that the wavefunction form for the *3d* orbital is, up to a normalization factor,

$$\psi_{3d}(r,\theta,\phi) = r^{l=2}e^{-\left(\frac{Z=1}{n=3}\right)r}Y_l^m(\theta,\phi) \qquad\qquad m = -2,-1,0,1,2$$

The average distance of the electron from the nucleus is then

$$\langle r\rangle = \frac{\int \psi_{3d}^*(\mathbf{r})r\psi_{3d}(\mathbf{r})d\mathbf{r}}{\int \psi_{3d}^*(\mathbf{r})r\psi_{3d}(\mathbf{r})d\mathbf{r}} = \frac{\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}r^2e^{-\left(\frac{1}{3}\right)r}\left(Y_l^m(\theta,\phi)\right)^*\cdot r\cdot r^2e^{-\left(\frac{1}{3}\right)r}\left(Y_l^m(\theta,\phi)\right)r^2\sin\theta\,dr\,d\theta\,d\phi}{\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}r^2e^{-\left(\frac{1}{3}\right)r}\left(Y_l^m(\theta,\phi)\right)^* r^2e^{-\left(\frac{1}{3}\right)r}\left(Y_l^m(\theta,\phi)\right)r^2\sin\theta\,dr\,d\theta\,d\phi}$$

$$= \frac{\int_0^{\infty}r^7e^{-\frac{2}{3}r}dr}{\int_0^{\infty}r^6e^{-\frac{2}{3}r}dr} = \frac{\frac{7!}{\left(\frac{2}{3}\right)^8}}{\frac{6!}{\left(\frac{2}{3}\right)^7}} = \frac{21}{2} = 10.5$$

Bonus: A nearly exact measurement of the energy of the Lithium cation, Li$^+$, gives the lower bound $E_{Li^+} > -7.280$ a.u.. Give a lower bound to the energy of the neutral Lithium atom (the tighter your bound, the more points you get).

Consider the Hamiltonian for the problem,

$$\hat{H}_{Li} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \tfrac{1}{2}\nabla_3^2 - 3r_1^{-1} - 3r_2^{-1} - 3r_3^{-1} + |\mathbf{r}_1 - \mathbf{r}_2|^{-1} + |\mathbf{r}_1 - \mathbf{r}_3|^{-1} + |\mathbf{r}_2 - \mathbf{r}_3|^{-1}$$

$$= \hat{H}_{Li^+} - \tfrac{1}{2}\nabla_3^2 - \tfrac{Z}{r_3} + |\mathbf{r}_1 - \mathbf{r}_3|^{-1} + |\mathbf{r}_2 - \mathbf{r}_3|^{-1}$$

Now if I neglect the electron-electron repulsion between the first two electrons and the third electron, I have a lower bound to the energy. That is, the Hamiltonian of the Lithium atom is greater than the sum of the Hamiltonians of the Lithium cation and the Lithium dication,

$$\hat{H}_{Li} \geq \hat{H}_{Li^+} + \hat{H}_{Li^{+2}}$$

So its energy must be greater than the sum of the energies of these two systems, which is

$$E_{Li} > E_{Li^+} + E_{Li^{+2}} = -7.280 - \tfrac{3^2}{2} = -11.780 \text{ a.u.}$$

A slightly more intelligent (but less rigorous) bound is to consider that the third electron is in a *2s* orbital. so you have

$$E_{Li} > E_{Li^+} + E_{Li^{+2}}\left(2s^1\right) = -7.280 - \tfrac{3^2}{2\cdot4} = -8.405 \text{ a.u.}$$

This is still not very good compared to the true answer $E_{Li} \approx -7.478$ a.u., but lower bounds are hard....