Name_____ Student Number_____

Mid-Term #4

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.

12 questions @ 8 points each.

2 Bonus questions worth 8 points each.

Key integrals and identities:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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Pad $x + \beta$ $x + \beta$ β β β β β $m(n - 1)(n - 2)$ $3!$ $m(n - 1)(n - 2)$ $3!$ $m(n + 2)$ $3!$ $m(n + 2)$ $3!$ $m(n + 2)$ $3!$ $m(n + 2)$ $3!$ $m(n + 2)$ $m(n + 2)$ $3!$ $m(n + 2)$		010					$\int_0^{\infty} a^{-\frac{1}{2}}$		$\int_0^a \sin \frac{m\pi x}{a} \sin \frac{n\pi x}{a}$	Jo ; ,	$\int_{0}^{\infty} \chi^{2n+1} e^{-a\chi^2}$	ì

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

1,2. Write the electronic and nuclear Schrödinger equations for the triply-ionized Helium dimer, He2³⁺. You can use atomic units.

Electronic:

$$\left(-\frac{1}{2}\nabla^{2}+\frac{4}{\left|\mathbf{R}_{1}-\mathbf{R}_{2}\right|}-\frac{2}{\left|\mathbf{r}-\mathbf{R}_{1}\right|}-\frac{2}{\left|\mathbf{r}-\mathbf{R}_{2}\right|}\right)\psi_{e}\left(\mathbf{r}\left|\mathbf{R}_{1},\mathbf{R}_{2}\right)=U\left(\mathbf{R}_{1},\mathbf{R}_{2}\right)\psi_{e}\left(\mathbf{r}\left|\mathbf{R}_{1},\mathbf{R}_{2}\right)$$

Nuclear:

$$\left(-\frac{1}{2m_{\mathrm{He}}}\nabla_{\mathbf{R}_{1}}^{2}-\frac{1}{2m_{\mathrm{He}}}\nabla_{\mathbf{R}_{1}}^{2}+U\left(\mathbf{R}_{1},\mathbf{R}_{2}\right)\right)\chi\left(\mathbf{R}_{1},\mathbf{R}_{2}\right)=E_{\mathrm{total}}\chi\left(\mathbf{R}_{1},\mathbf{R}_{2}\right)$$

3,4. What is the ground-state electronic energy and wavefunction for He_2^{3+} in the unitedatom limit?

In the united-atom limit, this is the Beryllium +3 ion (1-electron; Z = 4). So:

$$E = \frac{-(4)^2}{2(n=1)^2} = -8 \text{ a.u.}$$

$$\psi(\mathbf{r}) = \psi_{1s}^{Z=4}(\mathbf{r}) = \sqrt{\frac{4^3}{\pi}}e^{-4r}$$

5,6. What are the ground-state electronic energy and wavefunctions for ${\rm He2^{3+}}$ in the separated-atom limit? Write all four degenerate ground-state wavefunctions.

In the separated atom limit, the energy is the energy of a 1-electron He atom. The wavefunction is the symmetric and asymmetric combinations of the He-atom wavefunctions (with spin). So the energy is

$$E = -\frac{2^2}{2} = -2$$
 a.u.

Defining
$$\psi_{\text{He-l}s}(r) = \sqrt{\frac{2^3}{\pi}}e^{-2r}$$
, we have:

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{2}} (\psi_{\text{He-1s}} (\mathbf{r} - \mathbf{R}_1) + \psi_{\text{He-1s}} (\mathbf{r} - \mathbf{R}_2)) \alpha$$

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{2}} (\psi_{\text{He-1s}} (\mathbf{r} - \mathbf{R}_1) + \psi_{\text{He-1s}} (\mathbf{r} - \mathbf{R}_2)) \beta$$

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{2}} (\psi_{\text{He-1s}} (\mathbf{r} - \mathbf{R}_1) - \psi_{\text{He-1s}} (\mathbf{r} - \mathbf{R}_2)) \alpha$$

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7,8. Label the following approximate (unnormalized) molecular orbitals using the σ, π, δ , u, g, and +,- designations. Here, we denote the 1s orbital on the "left-hand" atom as $\psi_{1s}^{(l)}(\mathbf{r})$, with the obvious generalization of notation to the other orbitals and the "right-hand" atom. Bonuses are 2-pts.

Orbital Symmetry Label	Molecular Orbital
σ_g^+ *+ designation is optional for σ -states.*	$\psi_{2s}^{(l)}(\mathbf{r}) + \psi_{2s}^{(r)}(\mathbf{r})$
σ_u^+	$\psi_{2s}^{(l)}(\mathbf{r})$ $-\psi_{2s}^{(r)}(\mathbf{r})$
π_u^+ (or -, but if you use - for x you must use + for y.)	$\psi_{2p_x}^{(l)}(\mathbf{r})+\psi_{2p_x}^{(r)}(\mathbf{r})$
π_g^+	$\psi_{2p_x}^{(l)}(\mathbf{r}) - \psi_{2p_x}^{(r)}(\mathbf{r})$
σ_g^+	$\psi_{3d_{z^2}}^{(l)}(\mathbf{r})+\psi_{3d_{z^2}}^{(r)}(\mathbf{r})$
σ_u^+	$\psi_{3d_{z^2}}^{(l)}\left(\mathbf{r}\right) - \psi_{3d_{z^2}}^{(r)}\left(\mathbf{r}\right)$
σ_u^+	$\psi_{2p_z}^{(l)}(\mathbf{r})+\psi_{2p_z}^{(r)}(\mathbf{r})$
σ_g^+	$\psi_{2p_z}^{(l)}(\mathbf{r}) - \psi_{2p_z}^{(r)}(\mathbf{r})$
π_u^-	$\psi_{3d_{yz}}^{(l)}(\mathbf{r}) - \psi_{3d_{yz}}^{(r)}(\mathbf{r})$ (bonus)
π_{g}^{-}	$\psi_{3d_{yz}}^{(l)}(\mathbf{r}) + \psi_{3d_{yz}}^{(r)}(\mathbf{r})$ (bonus)
δ_u^-	$\psi_{3d_{xy}}^{(l)}(\mathbf{r}) - \psi_{3d_{xy}}^{(r)}(\mathbf{r})$ (bonus)
$\delta_{ m g}^-$	$\psi_{3d_{xy}}^{(l)}(\mathbf{r}) + \psi_{3d_{xy}}^{(r)}(\mathbf{r})$ (bonus)

9. The ground-state term symbols for the ground state of the Nickel atom, [Ar]4s²3d⁸ are ¹S, ³P, ¹D, ³F, ¹G. What are the term symbols for the excited states of the Vanadium atom with electron configuration [Ar]4s²3d²4d¹?

The term symbols for $[Ar]4s^23d^2$ are the same as for $[Ar]4s^23d^8$. So we need only couple the existing terms to L=2,S=1/2 (for the $4d^1$ electron). This gives the following terms:

10,11. The ground-state term symbol for the Holmium atom is ⁴I. What are the possible values of the J quantum number of Holmium? Circle the J value that is predicted to be lowest in energy according to Hund's Rules.

The spin-multiplicity of 4 indicates that S=3/2. The L-symbol of I indicates that L=6. Possible values of J are therefore: 9/2,11/2,13/2,15/2. The Holmium atom has electron configuration [Xe]6s²4f¹¹; this is more than half-filled so the lowest-energy J value is 15/2.

12. The ground-state term symbols for the 1s²2s²2p¹3d¹ configuration of the Carbon atom are ³P, ³D, ³F, ¹P, ¹D, ¹F. **List the terms in their Hund's Rule order.**

BONUS: (8 pts) What would be the order of terms based on the Russell-Meggers and Kutzelnigg-Morgan Rules?

We first assign the terms to odd- or even-parity.

F; L=3;
$$(-1)^{3+1+2} = 1$$
 (even)

D; L=2;
$$(-1)^{2+1+2} = -1$$
 (odd)

P; L=1;
$$(-1)^{1+1+2} = 1$$
 (even)

The Kutzelnigg-Morgan rule says the optimal value of L is

$$L_{\rm opt} = \frac{1+2}{\sqrt{2}} = 2.12$$

Then remember that odd-parity singlets come before triplets come before even-parity singlets, and the L=2 states are going to be best energetically within a family, with F (L=3) slightly preferred over P (L=1). So the prediction is:

Name_____ Student Number_____

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12 questions @ 8 points each.

2 Bonus questions worth 8 points each.

Key integrals and identities:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

		No.
Constant Constant Symbol	CAL CONSTA	NTS
Avogadro's number	N _o	$6.02205 \times 10^{23} \mathrm{mol^{-1}}$
Proton charge	e	$1.60219 \times 10^{-19} \mathrm{C}$
Planck's constant	<i>ከ</i>	$6.62618 \times 10^{-34} \text{ J} \cdot \text{s}$ $1.05459 \times 10^{-34} \text{ J} \cdot \text{s}$
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	$\frac{\varepsilon_0}{4\pi\varepsilon_0}$	$\begin{array}{l} 8.854188 \times 10^{-12} \text{C}^2 \cdot \text{s}^2 \cdot \text{kg}^{-1} \cdot \text{m}^{-3} \\ 1.112650 \times 10^{-10} \text{C}^2 \cdot \text{s}^2 \cdot \text{kg}^{-1} \cdot \text{m}^{-3} \end{array}$
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	q	$5.67032 \times 10^{-8} \text{ J} \cdot \text{m}^{-2} \cdot \text{K}^{-4} \cdot \text{s}^{-1}$
CONVERSION FACTORS FOR ENERGY UNITS	OR ENERGY	SEINU
joule kJ·mol-1	eV	au cm ⁻¹ Hz
1 joule 6.022×10 ²⁰	6.242 × 10 ¹⁸	2.2939×10^{17} 5.035×10^{22} 1.509×10^{33}
$kJ \cdot mol^{-1}$ = 1.661 × 10 ⁻²¹ 1	1.036×10^{-2}	3.089×10^{-4} 83.60 2.506×10^{12}
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

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

1,2.	Write the electronic and nuclear Schrödinger equations for the triply-ionized Helium dimer, He2 ³⁺ . You can use atomic units.
3,4.	What is the ground-state electronic energy and wavefunction for He_2^{3+} in the unitedatom limit?
5,6.	What are the ground-state electronic energy and wavefunctions for He_2^{3+} in the separated-atom limit? Write all four degenerate ground-state wavefunctions.

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Orbital Symmetry Label	Molecular Orbital
	$\psi_{2s}^{(l)}(\mathbf{r}) + \psi_{2s}^{(r)}(\mathbf{r})$
	$\psi_{2s}^{(l)}(\mathbf{r}) - \psi_{2s}^{(r)}(\mathbf{r})$
	$\psi_{2p_x}^{(l)}(\mathbf{r})+\psi_{2p_x}^{(r)}(\mathbf{r})$
	$\psi_{2p_x}^{(l)}(\mathbf{r}) - \psi_{2p_x}^{(r)}(\mathbf{r})$
	$\psi_{3d_{z^2}}^{(l)}(\mathbf{r})+\psi_{3d_{z^2}}^{(r)}(\mathbf{r})$
	$\psi_{3d_{z^2}}^{(l)}(\mathbf{r}) - \psi_{3d_{z^2}}^{(r)}(\mathbf{r})$
	$\psi_{2p_z}^{(l)}(\mathbf{r}) + \psi_{2p_z}^{(r)}(\mathbf{r})$
	$\psi_{2p_z}^{(l)}(\mathbf{r}) - \psi_{2p_z}^{(r)}(\mathbf{r})$
	$\psi_{3d_{yz}}^{(l)}(\mathbf{r})-\psi_{3d_{yz}}^{(r)}(\mathbf{r})$ (bonus)
	$\psi_{3d_{yz}}^{(l)}(\mathbf{r}) + \psi_{3d_{yz}}^{(r)}(\mathbf{r})$ (bonus)
	$\psi_{3d_{xy}}^{(l)}(\mathbf{r}) - \psi_{3d_{xy}}^{(r)}(\mathbf{r})$ (bonus)
	$\psi_{3d_{xy}}^{(l)}(\mathbf{r})+\psi_{3d_{xy}}^{(r)}(\mathbf{r})$ (bonus)

9.	The ground-state term symbols for the ground state of the Nickel atom, [Ar]4s ² 3d ⁸ are ¹ S, ³ P, ¹ D, ³ F, ¹ G. What are the term symbols for the excited states of the Vanadium atom with electron configuration [Ar]4s ² 3d ² 4d ¹ ?
10,11.	The ground-state term symbol for the Holmium atom is ⁴ I. What are the possible values of the J quantum number of Holmium? Circle the J value that is predicted to be lowest in energy according to Hund's Rules.
12.	The ground-state term symbols for the $1s^22s^22p^13d^1$ configuration of the Carbon atom are 3P , 3D , 3F , 1P , 1D , 1F . List the terms in their Hund's Rule order.
	US: (8 pts) What would be the order of terms based on the Russell-Meggers and lnigg-Morgan Rules?