

Name _____ Student Number _____

Midterm #3

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There are nine questions (11 points each) on this midterm. There are three bonus questions. There is one “free point” since the exam is graded out of 100, but there is only the possibility of losing 99 points.

Key integrals and identities:

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

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

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

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

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

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

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

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

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

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

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

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

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

VALUES OF SOME PHYSICAL CONSTANTS

Constant	Symbol	Value
Avogadro's number	N_0	$6.02205 \times 10^{23} \text{ mol}^{-1}$
Proton charge	e	$1.60219 \times 10^{-19} \text{ C}$
Planck's constant	h	$6.62618 \times 10^{-34} \text{ J}\cdot\text{s}$
	\hbar	$1.05459 \times 10^{-34} \text{ J}\cdot\text{s}$
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Atomic mass unit	amu	$1.66056 \times 10^{-27} \text{ kg}$
Electron rest mass	m_e	$9.10953 \times 10^{-31} \text{ kg}$
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Boltzmann constant	k_B	$1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ 0.69509 cm^{-1}
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	$4\pi\epsilon_0$	$1.112650 \times 10^{-10} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
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	σ	$5.67032 \times 10^{-8} \text{ J}\cdot\text{m}^{-2}\cdot\text{K}^{-4}\cdot\text{s}^{-1}$

CONVERSION FACTORS FOR ENERGY UNITS

joule	$\text{kJ}\cdot\text{mol}^{-1}$	eV	au	cm^{-1}	Hz
1 joule = 1	6.022×10^{20}	6.242×10^{18}	2.2939×10^{17}	5.035×10^{22}	1.509×10^{13}
1 $\text{kJ}\cdot\text{mol}^{-1}$ = 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

Paul

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

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

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

$$\sin (\alpha \pm \beta) = \sin \alpha \cos \beta \pm \cos \alpha \sin \beta$$

$$\cos (\alpha \pm \beta) = \cos \alpha \cos \beta \mp \sin \alpha \sin \beta$$

$$e^{\pm i\theta} = \cos \theta \pm i \sin \theta$$

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$$

$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$$

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

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \dots$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \dots$$

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

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

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

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

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

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

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

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

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

1. Write the electronic and nuclear Schrödinger equations for the neutral hydrogen molecule in SI units, showing the dependence on physical constants like the charge and mass of the electron.

2. What is the expectation value of the r^{-1} for an eigenstate of the one-electron atom with atomic number Z ? That is, what is the value of the following integral?

$$\langle \Psi_{n,\ell,m} | r^{-1} | \Psi_{n,\ell,m} \rangle = \underline{\hspace{4cm}}$$

3. You are given an excited state of the Lithium atom, with electron configuration $1s^1 2s^1 2p^1$, and told that $L = 1$, $S = 3/2$, and $J = M_J = 5/2$. **Write a Slater determinant wavefunction for this state. Write the Slater determinant in the long form (as a matrix), showing the dependence on the spatial and spin coordinates of all 3 electrons.**

Problems 4 & 5: The ground-state term symbol for the Holmium atom, which has the electron configuration $[\text{Xe}]4f^{11}6s^2$, is 4I .

4. **What are the value(s) for the following quantum numbers for the ground-state term?** When the term symbol is not sufficient to fully specify the quantum number, please list all the possible values.

_____ L (total orbital angular momentum)

_____ M_L (orbital angular momentum around the z axis)

_____ S (total spin angular momentum)

_____ M_S (spin angular momentum around the z axis)

5. **What are the possible values of J for the ground state term of the Holmium atom? Circle the value of J that Hund's third rule predicts to be most stable.**

6. The term symbols corresponding to the ground-state of the Vanadium atom, with electron configuration $[\text{Ar}]4s^2 3d^3$, are listed below:

$$^2P, ^4P, ^2D, ^2D, ^2F, ^4F, ^2G, ^2H$$

Make a list of the electron configurations from lowest-energy to highest-energy, using Hund's rules. You do not need to specify the value of J .

7. List all the possible term symbols associated with the $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^1 4p^1$ electron configuration of the Scandium atom. You do not have to list the possible J values.
8. List all the possible term symbols associated with the ground state electron configuration of the Nitrogen atom, $1s^2 2s^2 2p^3$. You do not have to list the possible J values.

9. Suppose we did not know the wavefunction for the particle in a box,

$$V_{\text{p-in-box}}(x) = \begin{cases} +\infty & x < -1 \\ 0 & -1 \leq x \leq 1 \\ +\infty & x > 1 \end{cases}$$

with Hamiltonian (in atomic units)

$$\hat{H}_{\text{p-in-box}} = -\frac{1}{2} \frac{d^2}{dx^2} + V_{\text{p-in-box}}(x)$$

So instead we guessed a possible wavefunction form

$$\Psi(x) = x^4 + Ax^2 - (A+1)$$

(Notice that this wavefunction is not normalized.)

The energy determined by the variational principle in #9 is _____ the exact ground-state energy for the particle in a box with a parabolic bottom.

(a) above

(b) below

(c) equal to

Bonus (5 points)

Use the variational principle to determine an equation for the “best” value of A . (Warning, this is a somewhat involved bonus. Be sure to (a) clearly describe your strategy and (b) work on other problems first.)

Bonus: (5 points) In atomic units, the wavefunction of the hydrogenic atom with maximum allowed orbital angular momentum, $\ell = n - 1$, is

$$\Psi_{n,n-1,m}(r, \theta, \phi) = \sqrt{\frac{1}{2n[(2n-1)!]^3}} \left(\frac{2Z}{n}\right)^{n+\frac{1}{2}} r^{n-1} \exp\left(-\frac{Zr}{n}\right) Y_{n-1}^m(\theta, \phi)$$

On the last quiz we determined the expectation value of the distance of the electron from the nucleus

$$\langle \Psi_{n,\ell,m} | r | \Psi_{n,\ell,m} \rangle = \frac{n(2n+1)}{2Z}$$

What is the *most probable* distance to find an electron from the nucleus?

Bonus: (5 points) **What is the lowest-energy term symbol (including J) for the Neodymium cation, Nd^+ .** Nd^+ has the ground-state electron configuration $[\text{Xe}]4f^46s^1$? Assume that Hund's rules apply.

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

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

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

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

1. The **electronic and nuclear Schrödinger equations for the neutral hydrogen molecule in SI units, showing the dependence on physical constants like the charge and mass of the electron.**

In this case the atomic numbers of the two atoms are $Z_1 = Z_2 = 1$. And there are only two atoms and only two electrons. So the electronic Schrodinger equation is:

$$\left(\begin{aligned} & -\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_1}^2 - \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_2}^2 \\ & -\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{R}_1|} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_2 - \mathbf{R}_1|} \\ & -\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{R}_2|} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_2 - \mathbf{R}_2|} \\ & +\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{4\pi\epsilon_0 |\mathbf{R}_1 - \mathbf{R}_2|} \end{aligned} \right) \psi_e(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{R}_1, \mathbf{R}_2) = U(\mathbf{R}_1, \mathbf{R}_2) \psi_e(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{R}_1, \mathbf{R}_2)$$

and the nuclear Schrödinger equation is:

$$\left(-\frac{\hbar^2}{2M_H} \nabla_{\mathbf{R}_1}^2 - \frac{\hbar^2}{2M_H} \nabla_{\mathbf{R}_2}^2 + U(\mathbf{R}_1, \mathbf{R}_2) \right) \chi_n(\mathbf{R}_1, \mathbf{R}_2) = E \chi_n(\mathbf{R}_1, \mathbf{R}_2)$$

It would be OK to then separate out the translational/rotational components of the problem and then write something like:

$$\left(-\frac{\hbar^2}{2\mu_{H_2}} \nabla_{\mathbf{R}}^2 + U(R) \right) \chi_n(\mathbf{R}) = E \chi_n(\mathbf{R}) \quad \mu_{H_2} = \frac{1}{2} M_H \quad R = |\mathbf{R}_2 - \mathbf{R}_1|$$

or even:

$$\left(-\frac{\hbar^2}{2\mu_{H_2}} \left(\frac{1}{R^2} \frac{d}{dR} R^2 \frac{d}{dR} - \frac{\hat{L}^2}{R^2} \right) + U(R) \right) \chi_n(\mathbf{R}) = E \chi_n(\mathbf{R})$$

but this was not required for this problem.

2. What is the expectation value of the r^{-1} for an eigenstate of the one-electron atom with atomic number Z ? That is, what is the value of the following integral?

$$\langle \Psi_{n,\ell,m} | r^{-1} | \Psi_{n,\ell,m} \rangle = \frac{-Z}{n^2}$$

Using the Hellmann-Feynman theorem for the one-electron atom,

$$\frac{\partial E_{n,l,m}}{\partial Z} = \left\langle \Psi_{n,l,m} \left| \frac{\partial \hat{H}}{\partial Z} \right| \Psi_{n,l,m} \right\rangle = \left\langle \Psi_{n,l,m} \left| \frac{\partial}{\partial Z} \left(\frac{-1}{2} \nabla^2 - \frac{Z}{r} \right) \right| \Psi_{n,l,m} \right\rangle = - \left\langle \Psi_{n,l,m} \left| \frac{1}{r} \right| \Psi_{n,l,m} \right\rangle$$

Then, using the equation for the energy of the one-electron atom,

$$\left\langle \Psi_{n,l,m} \left| \frac{1}{r} \right| \Psi_{n,l,m} \right\rangle = -\frac{\partial E_{nlm}}{\partial Z} = -\frac{\partial}{\partial Z} \left(\frac{-Z^2}{2n^2} \right) = \frac{Z}{n^2}$$

3. You are given an excited state of the Lithium atom, with electron configuration $1s^1 2s^1 2p^1$, and told that $L = 1$, $S = 3/2$, and $J = M_J = 5/2$. **Write a Slater determinant wavefunction for this state. Write the Slater determinant in the long form (as a matrix), showing the dependence on the spatial and spin coordinates of all 3 electrons.**

$$|\Psi_{1s2s2p}\rangle = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{1s}(\mathbf{r}_1)\alpha(1) & \psi_{2s}(\mathbf{r}_1)\alpha(1) & \psi_{2p_{+1}}(\mathbf{r}_1)\alpha(1) \\ \psi_{1s}(\mathbf{r}_2)\alpha(2) & \psi_{2s}(\mathbf{r}_2)\alpha(2) & \psi_{2p_{+1}}(\mathbf{r}_2)\alpha(2) \\ \psi_{1s}(\mathbf{r}_3)\alpha(3) & \psi_{2s}(\mathbf{r}_3)\alpha(3) & \psi_{2p_{+1}}(\mathbf{r}_3)\alpha(3) \end{vmatrix}$$

In choosing the right state, the key is the only way that I can have $M_J = 5/2$ is to have $M_S = 3/2$ and $M_L = +1$.

Problems 4 & 5: The ground-state term symbol for the Holmium atom, which has the electron configuration $[\text{Xe}]4f^{11}6s^2$, is 4I .

4. **What are the value(s) for the following quantum numbers for the ground-state term?**
When the term symbol is not sufficient to fully specify the quantum number, please list all the possible values.

_____ **6** _____ L (total orbital angular momentum)

_____ **-6,-5,-4,-3,-2,-1,0,1,2,3,4,5,6** _____ M_L (orbital angular momentum around the Z axis)

_____ **3/2** _____ S (total spin angular momentum)

_____ **-3/2, -1/2, 1/2, 3/2** _____ M_S (spin angular momentum around the Z axis)

5. **What are the possible values of J for the ground state term of the Holmium atom? Circle the value of J that Hund's third rule predicts to be most stable.**

The values range for $J_{\max} = L + S = 6 + \frac{3}{2} = \frac{15}{2}$ to $J_{\min} = |L - S| = |6 - \frac{3}{2}| = \frac{9}{2}$. So the possible choices are (in Hund's-rule-order): $J = \boxed{\frac{15}{2}}, \frac{13}{2}, \frac{11}{2}, \frac{9}{2}$

6. The term symbols corresponding to the ground-state of the Vanadium atom, with electron configuration $[\text{Ar}]4s^2 3d^3$, are listed below:

$$^2P, ^4P, ^2D, ^2D, ^2F, ^4F, ^2G, ^2H$$

Make a list of the electron configurations from lowest-energy to highest-energy, using Hund's rules. You do not need to specify the value of J .

$$^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D, ^2P$$

7. List all the possible term symbols associated with the $1s^2 2s^2 2p^6 3s^2 3p^4 4s^1 3d^1 4p^1$ electron configuration of the Scandium atom. You do not have to list the possible J values.

There are 3 unpaired electrons so the choices of $M_S = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ and the possible spin-multiplicities of each term (because all the unpaired orbitals are inequivalent) are quadruplet and doublet. Similarly, the possible values of the orbital angular momentum are $|\ell_{3d} + \ell_{4p}| \dots |\ell_{3d} - \ell_{4p}| = 3, 2, 1$ (where the 4s electron cannot contribute). So the possible terms are:

$${}^4F, {}^2F, {}^4D, {}^2D, {}^4P, {}^2P$$

This could also have been done by first forming the term symbols of the $3d^1 4p^1$ configuration and then coupling that to the $4s^1$ configuration.

8. List all the possible term symbols associated with the ground state electron configuration of the Nitrogen atom, $1s^2 2s^2 2p^3$. You do not have to list the possible J values.

I have filled out the microstate table below, keeping in mind that I can always generate the portions with $M_L < 0$ by changing $m_l \rightarrow -m_l$ and the portions with $M_S < 0$ by changing $m_s \rightarrow -m_s$.

	$M_L = 2$	$M_L = 1$	$M_L = 0$
$M_S = 3/2$			$ \phi_{2p+1}\alpha \ \phi_{2p_0}\alpha \ \phi_{2p-1}\alpha $
$M_S = 1/2$	$ \phi_{2p+1}\alpha \ \phi_{2p+1}\beta \ \phi_{2p_0}\alpha $	$ \phi_{2p+1}\alpha \ \phi_{2p_0}\alpha \ \phi_{2p_0}\beta $ $ \phi_{2p+1}\alpha \ \phi_{2p+1}\beta \ \phi_{2p-1}\alpha $	$ \phi_{2p+1}\beta \ \phi_{2p_0}\alpha \ \phi_{2p-1}\alpha $ $ \phi_{2p+1}\alpha \ \phi_{2p_0}\beta \ \phi_{2p-1}\alpha $ $ \phi_{2p+1}\alpha \ \phi_{2p_0}\alpha \ \phi_{2p-1}\beta $

This gives me the terms: 2D , 2P , 4S .

9. Suppose we did not know the wavefunction for the particle in a box,

$$V_{\text{p-in-box}}(x) = \begin{cases} +\infty & x < -1 \\ 0 & -1 \leq x \leq 1 \\ +\infty & x > 1 \end{cases}$$

with Hamiltonian (in atomic units)

$$\hat{H}_{\text{p-in-box}} = -\frac{1}{2} \frac{d^2}{dx^2} + V_{\text{p-in-box}}(x)$$

So instead we guessed a possible wavefunction form

$$\Psi(x) = x^4 + Ax^2 - (A+1)$$

(Notice that this wavefunction is not normalized.)

The energy determined by the variational principle in #9 is _____ the exact ground-state energy for the particle in a box with a parabolic bottom.

(a) above

(b) below

(c) equal to

Bonus (5 points)

Use the variational principle to determine an equation for the “best” value of A.

We first need to determine the function:

$$E(A) = \frac{\langle \Psi | \hat{H}_{\text{para-box}} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int_{-1}^1 (x^4 + Ax^2 - (A+1)) \left[\frac{-1}{2} \frac{d^2}{dx^2} - x^2 \right] (x^4 + Ax^2 - (A+1)) dx}{\int_{-1}^1 (x^4 + Ax^2 - (A+1))^2 dx}$$

It is a bit easier to do the integral if we note that the integrand is even, so the integral from -1 to 0 is the same as the integral from 0 to +1. So we can write:

$$\begin{aligned} E(A) &= \frac{2 \int_0^1 (x^4 + Ax^2 - (A+1)) \left[\frac{-1}{2} \frac{d^2}{dx^2} \right] (x^4 + Ax^2 - (A+1)) dx}{2 \int_0^1 (x^4 + Ax^2 - (A+1))^2 dx} \\ &= \frac{- \int_0^1 (x^4 + Ax^2 - (A+1)) \left[\frac{1}{2} \frac{d^2}{dx^2} \right] (x^4 + Ax^2 - (A+1)) dx}{\int_0^1 x^8 + A^2 x^4 + (A+1)^2 + Ax^6 - (A+1)x^4 - (A^2 + A)x^2 dx} \\ &= \frac{- \int_0^1 \int_0^1 (x^4 + Ax^2 - (A+1)) [6x^2 + A] dx}{\int_0^1 x^8 + Ax^6 + (A^2 - A - 1)x^4 - (A^2 + A)x^2 + (A+1)^2 dx} \\ &= \frac{- \int_0^1 6x^6 + 7Ax^4 + (A^2 - 6A - 6)x^2 - (A^2 + A) dx}{\frac{1}{9} + \frac{1}{7}A + \frac{1}{5}(A^2 - A - 1) - \frac{1}{3}(A^2 + A) + (A+1)^2} \\ &= \frac{- \left(\frac{6}{7} + \frac{7}{5}A + \left(\frac{1}{3}A^2 - 2A - 2 \right) - (A^2 + A) \right)}{\left(\frac{1}{9} - \frac{1}{5} + 1 \right) + \left(\frac{1}{7} - \frac{1}{5} - \frac{1}{3} + 2 \right)A + \left(\frac{1}{5} - \frac{1}{3} + 1 \right)A^2} \\ &= - \frac{\left(\frac{6}{7} - 2 \right) + \left(\frac{7}{5} - 2 - 1 \right)A + \left(\frac{1}{3} - 1 \right)A^2}{\frac{41}{45} + \frac{169}{105}A + \left(\frac{13}{15} \right)A^2} \\ &= \frac{\frac{8}{7} + \frac{8}{5}A + \frac{2}{3}A^2}{\frac{41}{45} + \frac{169}{105}A + \left(\frac{13}{15} \right)A^2} \end{aligned}$$

There are a couple ways we can proceed. We can integrate these forms explicitly (they are just polynomials) and then take the derivative of the energy with respect to A and B. Alternatively, we can use a Hellmann-Feynman like trick and differentiate under the integral sign.

In the end, to process the ratio, it is useful to recall that:

$$\begin{aligned}
0 &= \frac{\partial E}{\partial A} = \frac{\frac{\partial [\text{numerator}]}{\partial A}}{[\text{denominator}]} - \frac{[\text{numerator}] \frac{\partial [\text{denominator}]}{\partial A}}{[\text{denominator}]^2} \\
0 &= [\text{denominator}] \frac{\partial [\text{numerator}]}{\partial A} - [\text{numerator}] \frac{\partial [\text{denominator}]}{\partial A} \\
0 &= \frac{\partial E}{\partial B} = \frac{\frac{\partial [\text{numerator}]}{\partial B}}{[\text{denominator}]} - \frac{[\text{numerator}] \frac{\partial [\text{denominator}]}{\partial B}}{[\text{denominator}]^2} \\
0 &= [\text{denominator}] \frac{\partial [\text{numerator}]}{\partial B} - [\text{numerator}] \frac{\partial [\text{denominator}]}{\partial B}
\end{aligned}$$

So we have:

$$0 = \left[\frac{41}{45} + \frac{169}{105} A + \left(\frac{13}{15} \right) A^2 \right] \left[\frac{4}{3} A + \frac{8}{5} \right] - \left[\frac{8}{7} + \frac{8}{5} A + \frac{2}{3} A^2 \right] \left[\frac{26}{15} A + \frac{169}{105} \right]$$

This is a cubic equation for A . We could solve it using the cubic formula or numerically. Once we solved it, we would substitute the value of A into $E(A)$ to get the energy.

Bonus: (5 points) In atomic units, the wavefunction of the hydrogenic atom with maximum allowed orbital angular momentum, $\ell = n - 1$, is

$$\Psi_{n,n-1,m}(r, \theta, \phi) = \sqrt{\frac{1}{2n[(2n-1)!]^3}} \left(\frac{2Z}{n}\right)^{n+\frac{1}{2}} r^{n-1} \exp\left(-\frac{Zr}{n}\right) Y_{n-1}^m(\theta, \phi)$$

On the last quiz we determined the expectation value of the distance of the electron from the nucleus

$$\langle \Psi_{n,\ell,m} | r | \Psi_{n,\ell,m} \rangle = \frac{n(2n+1)}{2Z}$$

What is the *most probable* distance to find an electron from the nucleus?

This problem is from MacQuarrie. Let us rewrite the wavefunction in a simpler form, namely as:

$$\Psi_{n,n-1,m}(\mathbf{r}) = A_n r^{n-1} \exp\left(-\frac{Zr}{n}\right)$$

where A_n is a normalization constant that does not depend on the distance. The probability of observing an electron a set distance, r , from the nucleus is equal to the surface area of the sphere with radius r , ($4\pi r^2$) times the wavefunction squared. So the probability of observing an electron a set distance from the nucleus is

$$\begin{aligned} p(r) &= 4\pi r^2 \left(A_n r^{n-1} \exp\left(-\frac{Zr}{n}\right) \right)^2 \\ &= \left(A_n^2 4\pi \right) r^{2n} \exp\left(\frac{-2Zr}{n}\right) \end{aligned}$$

and the most probable distance is the maximum of this function, which can be found by locating where its derivative is zero, namely,

$$\begin{aligned} 0 &= \frac{dp(r)}{dr} = \left(4\pi A_n^2 \right) \left[(2n) r^{2n-1} \exp\left(\frac{-2Zr}{n}\right) + r^{2n} \left(\frac{-2Z}{n} \right) \exp\left(\frac{-2Zr}{n}\right) \right] \\ 0 &= (2n) + r \left(\frac{-2Z}{n} \right) \\ r &= \frac{n^2}{Z} \end{aligned}$$

Bonus: (5 points) **What is the lowest-energy term symbol (including J) for the Neodymium cation, Nd^+ , with electron configuration $[\text{Xe}]4f^4 6s^1$?** Assume that Hund's rules apply.

We want to find a Slater determinant with the maximum number of unpaired electrons and the maximum orbital angular momentum. The biggest M_L and M_S we can make is associated with the determinant: $[\text{Xe}] \quad 6s^{\uparrow} \quad 4f_{+3}^{\uparrow} \quad 4f_{+2}^{\uparrow} \quad 4f_{+1}^{\uparrow} \quad 4f_0^{\uparrow}]$. This determinant has $M_L = L = 6$ (I) and $M_S = S = 5/2$. So it corresponds to the ^{11}I term. The system is less than half-filled, so we expect that the minimal value of $J_{\min} = |L - S| = \left| 6 - \frac{5}{2} \right| = \frac{7}{2}$ will be most stable. So the ground-state term is

$$\boxed{^{11}I_{\frac{7}{2}}}$$