Name________________________________ Student Number______________________________

Midterm #2

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 ten questions (10 points each) on this midterm. There are two bonus questions.

Key integrals and identities:

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

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

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

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

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

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

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

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

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

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

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

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

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

VALUES OF SOME PHYSICAL CONSTANTS

Constant	*Symbol*	*Value*
Avogadro's number	N_0	$6.02205 \times 10^{23}\ \mathrm{mol^{-1}}$
Proton charge	e	$1.60219 \times 10^{-19}\ \mathrm{C}$
Planck's constant	h $\hbar$	$6.62618 \times 10^{-34}\ \mathrm{J \cdot s}$ $1.05459 \times 10^{-34}\ \mathrm{J \cdot s}$
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	$1.38066 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}$ $0.69509\ \mathrm{cm^{-1}}$
Molar gas constant	R	$8.31441\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
Permittivity of a vacuum	ε_0 $4\pi\varepsilon_0$	$8.854188 \times 10^{-12}\ \mathrm{C^2 \cdot s^2 \cdot kg^{-1} \cdot m^{-3}}$ $1.112650 \times 10^{-10}\ \mathrm{C^2 \cdot s^2 \cdot kg^{-1} \cdot m^{-3}}$
Rydberg constant (infinite nuclear mass)	R_∞	$2.179914 \times 10^{-23}\ \mathrm{J}$ $1.097373\ \mathrm{cm^{-1}}$
First Bohr radius	a_0	$5.29177 \times 10^{-11}\ \mathrm{m}$
Bohr magneton	μ_B	$9.27409 \times 10^{-24}\ \mathrm{J \cdot T^{-1}}$
Stefan-Boltzmann constant	σ	$5.67032 \times 10^{-8}\ \mathrm{J \cdot m^{-2} \cdot K^{-4} \cdot s^{-1}}$

CONVERSION FACTORS FOR ENERGY UNITS

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

Paul

SOME MATHEMATICAL FORMULAS

$$\sin\alpha \sin\beta = \tfrac{1}{2}\cos(\alpha-\beta) - \tfrac{1}{2}\cos(\alpha+\beta)$$
$$\cos\alpha \cos\beta = \tfrac{1}{2}\cos(\alpha-\beta) + \tfrac{1}{2}\cos(\alpha+\beta)$$
$$\sin\alpha \cos\beta = \tfrac{1}{2}\sin(\alpha+\beta) + \tfrac{1}{2}\sin(\alpha-\beta)$$
$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$
$$\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$
$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta$$
$$\cos\theta = \frac{e^{i\theta}+e^{-i\theta}}{2}$$
$$\sin\theta = \frac{e^{i\theta}-e^{-i\theta}}{2i}$$
$$f(x) = f(a) + f'(a)(x-a) + \frac{1}{2!}f''(a)(x-a)^2 + \frac{1}{3!}f'''(a)(x-a)^3 + \cdots$$
$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots$$
$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots$$
$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots$$
$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \cdots \qquad x^2 < 1$$
$$(1\pm x)^n = 1 \pm nx \pm \frac{n(n-1)}{2!}x^2 \pm \frac{n(n-1)(n-2)}{3!}x^3 \pm \cdots \qquad x^2 <$$
$$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}} \qquad (n \text{ positive integer})$$
$$\int_0^\infty e^{-ax^2}\,dx = \left(\frac{\pi}{4a}\right)^{1/2}$$
$$\int_0^\infty x^{2n}e^{-ax^2}\,dx = \frac{1\cdot3\cdot5\cdot\cdots\cdot(2n-1)}{2^{n+1}a^n}\left(\frac{\pi}{a}\right)^{1/2} \qquad (n \text{ positive integer})$$
$$\int_0^\infty x^{2n+1}e^{-ax^2}\,dx = \frac{n!}{2a^{n+1}} \qquad (n \text{ positive integer})$$
$$\int_0^a \sin\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = \int_0^a \cos\frac{n\pi x}{a}\cos\frac{m\pi x}{a}\,dx = \frac{a}{2}\delta_{nm}$$
$$\int_0^a \cos\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = 0 \qquad (m \text{ and } n \text{ integers})$$

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

1. **Write the Hamiltonian for a *P*-atom *N*-electron molecule in SI units, keeping track of physical constants like the charge and mass of the electron.**

2. **Referring to problem 1, write the electronic Schrödinger equation for the *P*-atom *N*-electron molecule in *atomic units*, assuming the Born-Oppenheimer approximation.**

3. **Referring to problems 1 and 2, write the nuclear Schrödinger equation for a *P*-atom molecule, assuming the Born-Oppenheimer approximation holds. You can use atomic units, but you don't have to do so.**

4. **For which of the following systems is the Born-Oppenheimer approximation most justified? In other words, neglecting all other effects, for which system do you expect corrections to the Born-Oppenheimer approximation will be least important. Please circle the correct answer.**

   (a) C_{60} (c) UF_6

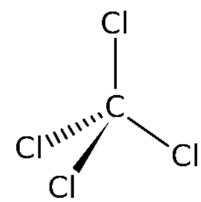
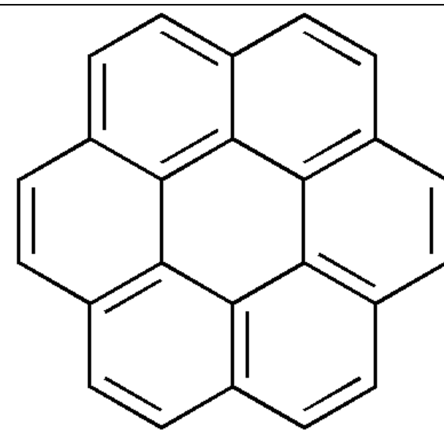
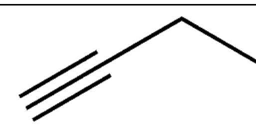
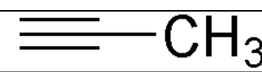
   (b) H_2 (d) Si_{60}

5. **For each of the systems listed below, list the type of special function(s) that appear in its eigenfunctions. The first one is done as an example.**

___D____ particle in a box	A. Associated Laguerre Polynomials.
________ harmonic oscillator	B. Hermite Polynomials
________ rigid rotor	C. Spherical Harmonics
________ 1-electron atom	D. Trigonometric functions like sine and cosine.

6. **Write a Slater determinant wavefunction (write out all the rows and columns) for the ground state of the Lithium atom, with electron configuration $1s^2 2s^1$.**

7. **Fill in the first column of the following table, labelling the following molecules as:**
   - **O** oblate symmetric top
   - **P** prolate symmetric top
   - **S** spherical top
   - **A** asymmetric top

Type of "top"	Name of Molecule	Structure of Molecule
	Carbon tetrachloride	
	Coronene	
	1-butyne	
	propyne	

8. **Match the following systems to the energy level diagrams on the next two pages.** Each line indicates an energy level, and the number in parenthesis next to the line indicates the degeneracy of that level. That is, the positions of the lines give the relative energies of the ground state (the first line) and a few excited states, and the number in parenthesis indicates the number of states with that energy.

_____ **One-Electron Atom**

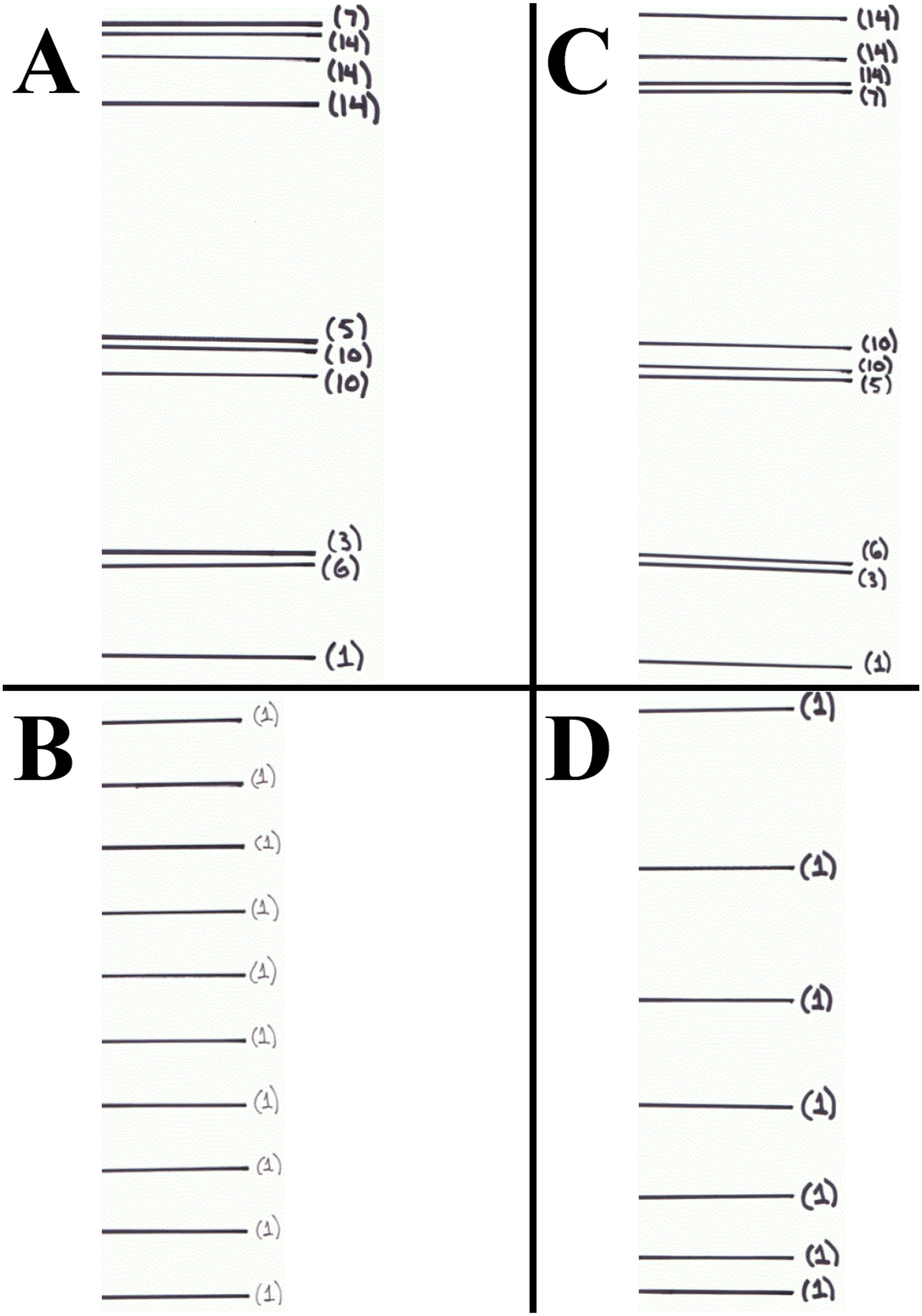
_____ **One-Dimensional Harmonic Oscillator**

_____ **One-Dimensional Particle in a Box with Infinite Sides**

_____ **Rigid Rotation of a Spherical Top Molecule**

_____ **Rigid Rotation of a Oblate Symmetric Top Molecule**

_____ **Rigid Rotation of a Prolate Symmetric Top Molecule**


A
(7)
(14)
(14)
(14)
(5)
(10)
(10)
(3)
(6)
(1)
C
(14)
(14)
(14)
(7)
(10)
(10)
(5)
(6)
(3)
(1)
B
(1)
(1)
(1)
(1)
(1)
(1)
(1)
(1)
(1)
(1)
D
(1)
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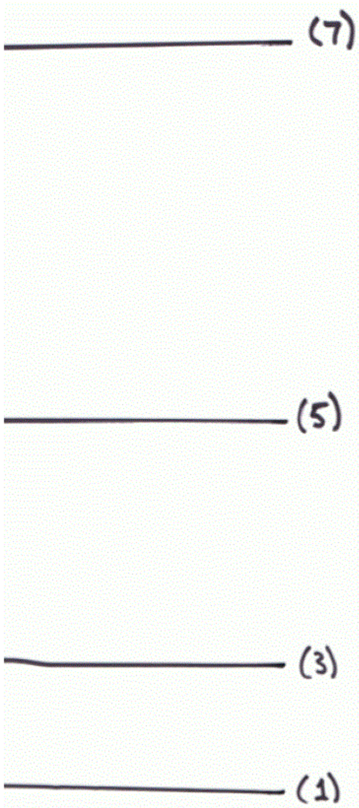
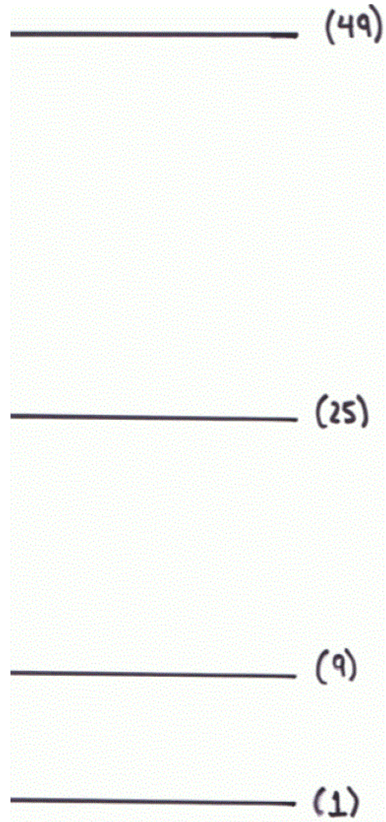
(1)
(1)
(1)
(1)
(1)

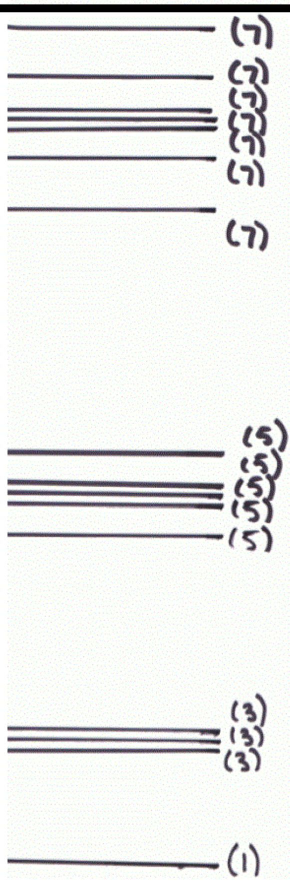
E



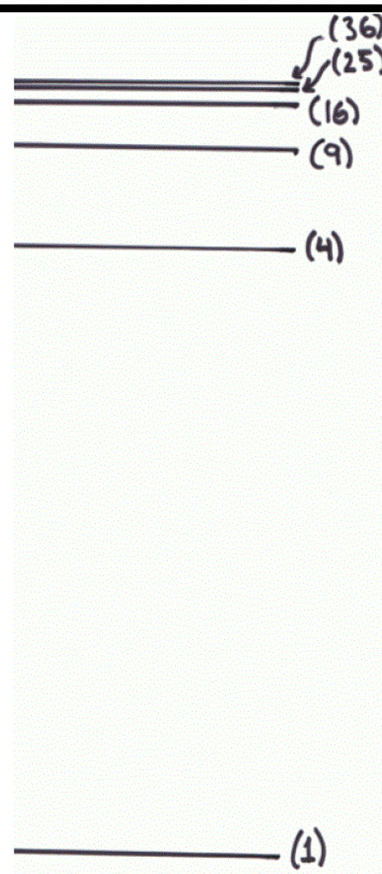
G



F



H



9. Fill in the blanks using names from the list of famous quantum mechanics listed below.

The atomic unit for energy is the ________________.

The atomic unit of length is the __________________.

Schrödinger	Fock	Born	Mulliken
Heisenberg	De Broglie	Bohr	Hellmann
Planck	Curie	Compton	Feynman
Hartree	Pauling	Einstein	Franck

10. The energy eigenvalues and eigenfunctions of a one-electron atom are

$$E_n = -\frac{m_e Z^2 e^4}{8\varepsilon_0^2 h^2 n^2}$$

$$\Psi_{n,\ell,m}(r,\theta,\phi) = -\sqrt{\frac{(n-\ell-1)!}{2n\left[(n+\ell)!\right]^3}}\left(\frac{2Z}{na_0}\right)^{\ell+\frac{3}{2}} r^{\ell}\exp\left(-\frac{Zr}{na_0}\right)L_{n-\ell-1}^{2\ell+1}\left(\frac{2Zr}{na_0}\right)Y_{\ell}^{m}(\theta,\phi)$$

Using the Hellmann-Feynman theorem, what is the expectation value of the Laplacian for the one-electron atom? That is, what is the value of the following integral?

$$\left\langle \Psi_{n,\ell,m} \middle| \nabla^2 \middle| \Psi_{n,\ell,m} \right\rangle = ??????$$

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

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

What is the expectation value of the distance of the electron from the nucleus?

$$\left\langle \Psi_{n,\ell,m}\middle| r \middle| \Psi_{n,\ell,m}\right\rangle = ??????$$

[Hint: it is easiest to use the same strategy we used to derive the Hellmann-Feynman theorem.]

Bonus: (5 points) The infrared spectrum of $^{75}Br^{19}F$ consists of an intense line at 380 cm^{-1}. **Calculate the force constant of $^{75}Br^{19}F$.**

Name______________________________ Student Number____________________________

Midterm #2 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:

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

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

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

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

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

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

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VALUES OF SOME PHYSICAL CONSTANTS

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

Paul

SOME MATHEMATICAL FORMULAS

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$$\cos\alpha\cos\beta = \tfrac{1}{2}\cos(\alpha-\beta) + \tfrac{1}{2}\cos(\alpha+\beta)$$
$$\sin\alpha\cos\beta = \tfrac{1}{2}\sin(\alpha+\beta) + \tfrac{1}{2}\sin(\alpha-\beta)$$
$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$
$$\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$
$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta$$
$$\cos\theta = \frac{e^{i\theta}+e^{-i\theta}}{2}$$
$$\sin\theta = \frac{e^{i\theta}-e^{-i\theta}}{2i}$$
$$f(x) = f(a) + f'(a)(x-a) + \frac{1}{2!}f''(a)(x-a)^2 + \frac{1}{3!}f'''(a)(x-a)^3 + \cdots$$
$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots$$
$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots$$
$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots$$
$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \cdots \qquad x^2 < 1$$
$$(1 \pm x)^n = 1 \pm nx \pm \frac{n(n-1)}{2!}x^2 \pm \frac{n(n-1)(n-2)}{3!}x^3 \pm \cdots \qquad x^2 <$$
$$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}} \qquad (n \text{ positive integer})$$
$$\int_0^\infty e^{-ax^2}\,dx = \left(\frac{\pi}{4a}\right)^{1/2}$$
$$\int_0^\infty x^{2n}e^{-ax^2}\,dx = \frac{1\cdot 3\cdot 5\cdot\cdots\cdot(2n-1)}{2^{n+1}a^n}\left(\frac{\pi}{a}\right)^{1/2} \qquad (n \text{ positive integer})$$
$$\int_0^\infty x^{2n+1}e^{-ax^2}\,dx = \frac{n!}{2a^{n+1}} \qquad (n \text{ positive integer})$$
$$\int_0^a \sin\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = \int_0^a \cos\frac{n\pi x}{a}\cos\frac{m\pi x}{a}\,dx = \frac{a}{2}\delta_{nm}$$
$$\int_0^a \cos\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = 0 \qquad (m \text{ and } n \text{ integers})$$

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

1. **Write the Hamiltonian for a *P*-atom *N*-electron molecule in SI units, keeping track of physical constants like the charge and mass of the electron.**

$$\underbrace{\sum_{\alpha=1}^{P}\frac{-\hbar^2}{2M_\alpha}\nabla_\alpha^2}_{\text{nuclear kinetic energy}} + \underbrace{\sum_{i=1}^{N}-\frac{\hbar^2}{2m_e}\nabla_i^2}_{\text{electronic kinetic energy}} + \underbrace{\sum_{\alpha=1}^{P}\sum_{i=1}^{N}\frac{-Z_\alpha e^2}{4\pi\varepsilon_0\left|\mathbf{r}_i-\mathbf{R}_\alpha\right|}}_{\text{electron-nuclear attraction potential}} + \underbrace{\sum_{\alpha=1}^{P}\sum_{\beta=\alpha+1}^{P}\frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0\left|\mathbf{R}_\alpha-\mathbf{R}_\beta\right|}}_{\text{nuclear-nuclear repulsion potential}} + \underbrace{\sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{e^2}{4\pi\varepsilon_0\left|\mathbf{r}_i-\mathbf{r}_j\right|}}_{\text{electron-electron repulsion potential}}$$

2. **Referring to problem 1, write the electronic Schrödinger equation for the *P*-atom *N*-electron molecule in *__atomic units__*, assuming the Born-Oppenheimer approximation.**

$$\left(\sum_{i=1}^{N}-\frac{1}{2}\nabla_i^2+\sum_{\alpha=1}^{P}\sum_{i=1}^{N}\frac{-Z_\alpha}{\left|\mathbf{r}_i-\mathbf{R}_\alpha\right|}+\sum_{\alpha=1}^{P}\sum_{\beta=\alpha+1}^{P}\frac{Z_\alpha Z_\beta}{\left|\mathbf{R}_\alpha-\mathbf{R}_\beta\right|}+\sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}\right)\psi_e\left(\{\mathbf{r}_i\}_{i=1}^{N}\middle|\{\mathbf{R}_\alpha\}_{\alpha=1}^{P}\right)$$
$$=U\left(\{\mathbf{R}_\alpha\}_{\alpha=1}^{P}\right)\psi_e\left(\{\mathbf{r}_i\}_{i=1}^{N}\middle|\{\mathbf{R}_\alpha\}_{\alpha=1}^{P}\right)$$

3. **Referring to problems 1 and 2, write the nuclear Schrödinger equation for a *P*-atom molecule, assuming the Born-Oppenheimer approximation holds. You can use atomic units, but you don't have to do so.**

$$\left(\sum_{\alpha=1}^{P}-\frac{\hbar^2}{2M_\alpha}\nabla_i^2+U\left(\{\mathbf{R}_\alpha\}_{\alpha=1}^{P}\right)\right)\chi_n\left(\{\mathbf{R}_\alpha\}_{\alpha=1}^{P}\right)=E\chi_n\left(\{\mathbf{R}_\alpha\}_{\alpha=1}^{P}\right)$$

4. **For which of the following systems is the Born-Oppenheimer approximation most justified? In other words, neglecting all other effects, for which system do you expect corrections to the Born-Oppenheimer approximation will be least important. __Please circle the correct answer.__**

(a) C_{60} (c) UF_6

(b) H_2 **(d)** Si_{60}

The corrections will be less depending on the weight of the lightest atom in the molecule. So the Born-Oppenheimer approximation is least accurate for H_2, then C_{60}, then UF_6 (because of the Fluorine atoms), and finally most accurate for Si_{60}.

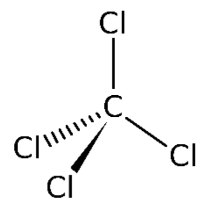
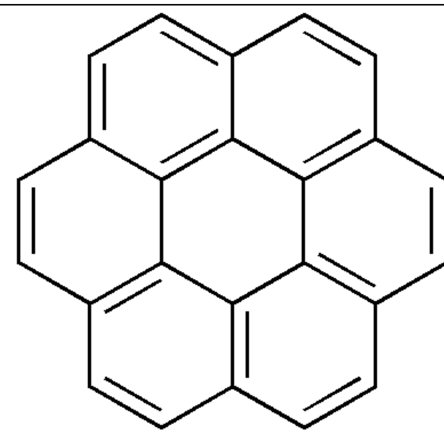
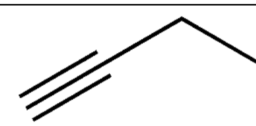
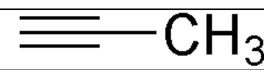
5. **For each of the systems listed below, list the type of special function(s) that appear in its eigenfunctions. The first one is done as an example.**

___D____ particle in a box	A. Associated Laguerre Polynomials.
____**B**____ harmonic oscillator	B. Hermite Polynomials
_____**C**___ rigid rotor	C. Spherical Harmonics
______**A**__ 1-electron atom	D. Trigonometric functions like sine and cosine.

6. **Write a Slater determinant wavefunction (write out all the rows and columns) for the ground state of the Lithium atom, with electron configuration $1s^2 2s^1$.**

$$\left|\Psi_{\text{Li}}\right\rangle=\frac{1}{\sqrt{3!}}\begin{vmatrix}\psi_{1s}(\mathbf{r}_1)\alpha(1) & \psi_{1s}(\mathbf{r}_1)\beta(1) & \psi_{2s}(\mathbf{r}_1)\alpha(1)\\ \psi_{1s}(\mathbf{r}_2)\alpha(2) & \psi_{1s}(\mathbf{r}_2)\beta(2) & \psi_{2s}(\mathbf{r}_2)\alpha(2)\\ \psi_{1s}(\mathbf{r}_3)\alpha(3) & \psi_{1s}(\mathbf{r}_3)\beta(3) & \psi_{2s}(\mathbf{r}_3)\alpha(3)\end{vmatrix}$$

7. **Fill in the first column of the following table, labelling the following molecules as:**
   - **O** oblate symmetric top
   - **P** prolate symmetric top
   - **S** spherical top
   - **A** asymmetric top

Type of "top"	Name of Molecule	Structure of Molecule
S	**Carbon tetrachloride**	
O	**Coronene**	
A	**1-butyne**	
P	**propyne**	

7. **Match the following systems to the energy level diagrams on the next two pages.** Each line indicates an energy level, and the number in parenthesis next to the line indicates the degeneracy of that level. That is, the positions of the lines give the relative energies of the ground state (the first line) and a few excited states, and the number in parenthesis indicates the number of states with that energy.

_H____ **One-Electron Atom**

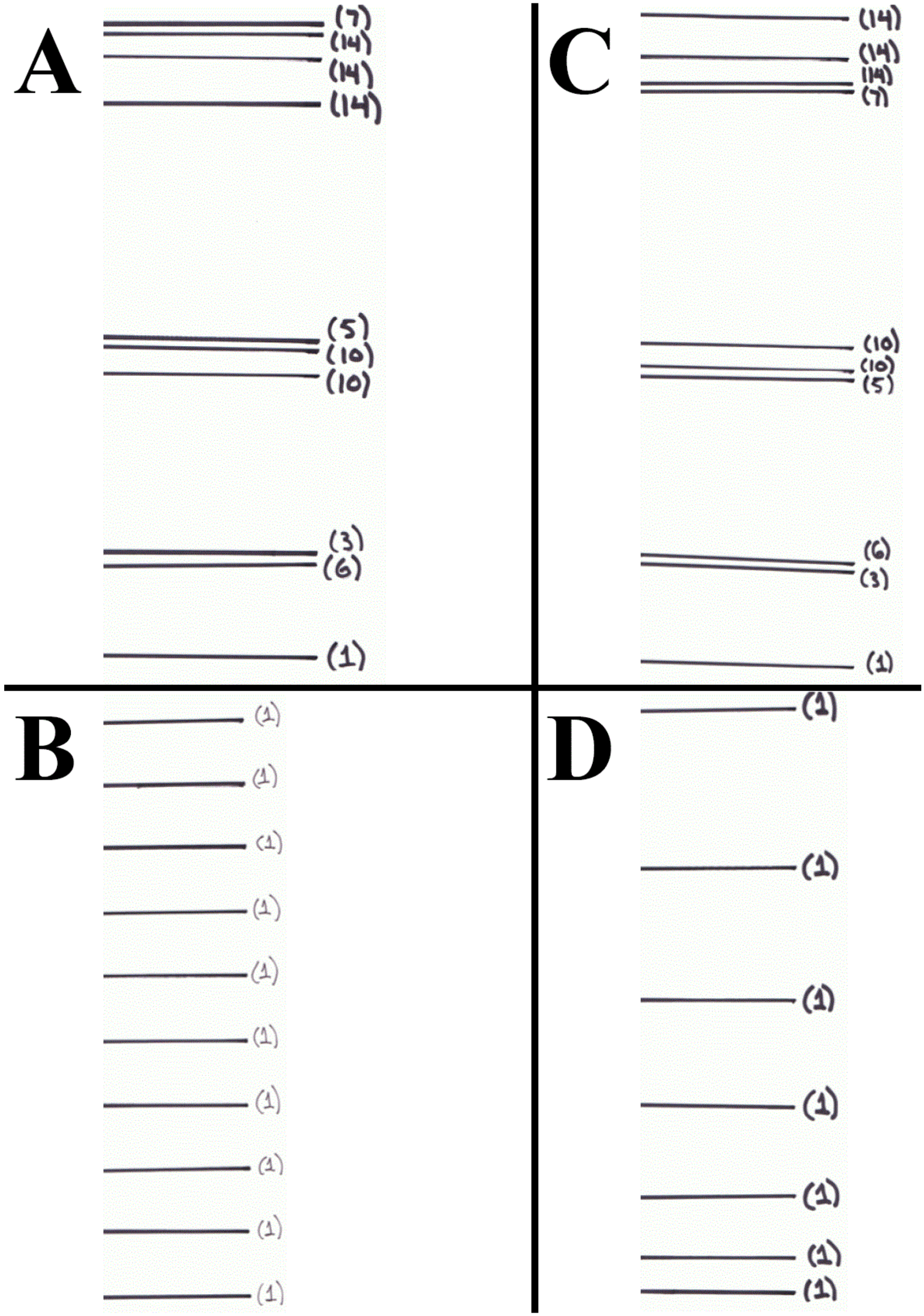
_B____ **One-Dimensional Harmonic Oscillator**

_D____ **One-Dimensional Particle in a Box with Infinite Sides**

_G____ **Rigid Rotation of a Spherical Top Molecule**

_A____ **Rigid Rotation of a Oblate Symmetric Top Molecule**

_C____ **Rigid Rotation of a Prolate Symmetric Top Molecule**


A
(7)
(14)
(14)
(14)
(5)
(10)
(10)
(3)
(6)
(1)
C
(14)
(14)
(14)
(7)
(10)
(10)
(5)
(6)
(3)
(1)
B
(1)
(1)
(1)
(1)
(1)
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D
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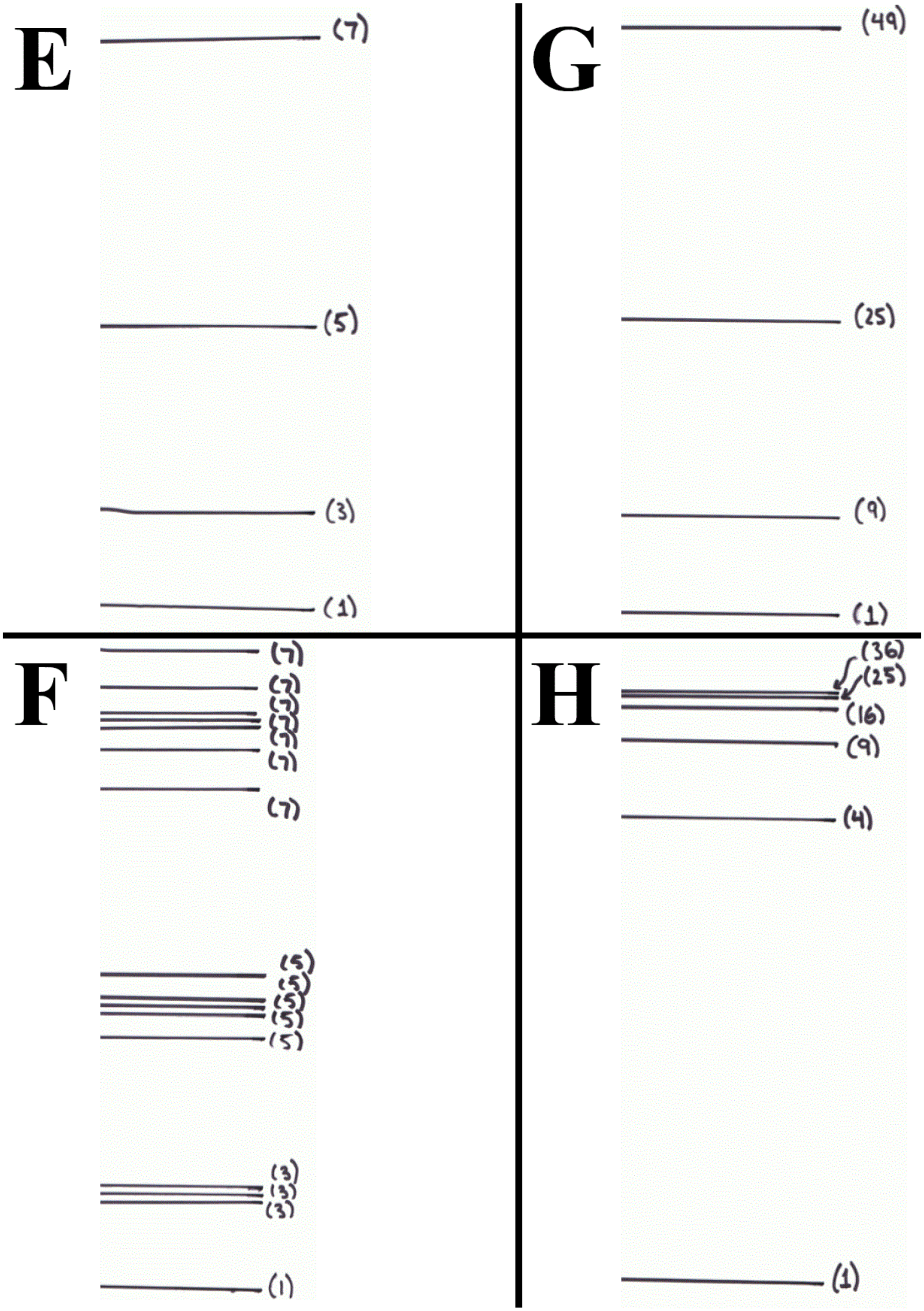
(1)
(1)


E
(7)
(5)
(3)
(1)
G
(49)
(25)
(9)
(1)
F
(7)
(7)
(7)
(7)
(7)
(7)
(7)
(5)
(5)
(5)
(5)
(5)
(3)
(3)
(3)
(1)
H
(36)
(25)
(16)
(9)
(4)
(1)

9. Fill in the blanks using names from the list of famous quantum mechanics listed below.

The atomic unit for energy is the ___Hartree____________.

The atomic unit of length is the ____Bohr_____________.

Schrödinger	Fock	Born	Mulliken
Heisenberg	De Broglie	Bohr	Hellmann
Planck	Curie	Compton	Feynman
Hartree	Pauling	Einstein	Franck

10. The energy eigenvalues and eigenfunctions of a one-electron atom are

$$E_n = -\frac{m_e Z^2 e^4}{8\varepsilon_0^2 h^2 n^2}$$

$$\Psi_{n,\ell,m}(r,\theta,\phi) = -\sqrt{\frac{(n-\ell-1)!}{2n\left[(n+\ell)!\right]^3}}\left(\frac{2Z}{na_0}\right)^{\ell+\frac{3}{2}} r^{\ell} \exp\left(-\frac{Zr}{na_0}\right) L_{n-\ell-1}^{2\ell+1}\left(\frac{2Zr}{na_0}\right) Y_\ell^m(\theta,\phi)$$

Using the Hellmann-Feynman theorem, what is the expectation value of the Laplacian for the one-electron atom? That is, what is the value of the following integral?

$$\left\langle \Psi_{n,\ell,m} \middle| \nabla^2 \middle| \Psi_{n,\ell,m} \right\rangle = ??????$$

We write the Hellmann-Feynman theorem for differentiation with respect to the mass of the electron as

$$\frac{\partial E}{\partial m_e} = \left\langle \Psi_{n,\ell,m} \middle| \frac{\partial \hat{H}}{\partial m_e} \middle| \Psi_{n,\ell,m} \right\rangle = \left\langle \Psi_{n,\ell,m} \middle| \frac{\partial\left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]}{\partial m_e} \middle| \Psi_{n,\ell,m} \right\rangle = \left\langle \Psi_{n,\ell,m} \middle| \frac{\hbar^2}{2m_e^2}\nabla^2 \middle| \Psi_{n,\ell,m} \right\rangle$$

$$-\frac{Z^2 e^4}{8\varepsilon_0^2 h^2 n^2} = \left\langle \Psi_{n,\ell,m} \middle| \frac{\hbar^2}{2m_e^2}\nabla^2 \middle| \Psi_{n,\ell,m} \right\rangle$$

$$-\frac{2m_e^2 Z^2 e^4}{8\hbar^2 \varepsilon_0^2 h^2 n^2} = \left\langle \Psi_{n,\ell,m} \middle| \nabla^2 \middle| \Psi_{n,\ell,m} \right\rangle$$

$$-\frac{m_e^2 Z^2 e^4}{4\left(\frac{h}{2\pi}\right)^2 \varepsilon_0^2 h^2 n^2} = \left\langle \Psi_{n,\ell,m} \middle| \nabla^2 \middle| \Psi_{n,\ell,m} \right\rangle$$

$$-\frac{m_e^2 \pi^2 Z^2 e^4}{\varepsilon_0^2 h^4 n^2} = \left\langle \Psi_{n,\ell,m} \middle| \nabla^2 \middle| \Psi_{n,\ell,m} \right\rangle$$

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

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

What is the expectation value of the distance of the electron from the nucleus?

$$\left\langle \Psi_{n,\ell,m}\middle| r \middle| \Psi_{n,\ell,m}\right\rangle = ??????$$

[Hint: it is easiest to use the same strategy we used to derive the Hellmann-Feynman theorem.]

Let us rewrite the wavefunction in a simpler form, namely as:

$$\Psi_{n,n-1,m}(\mathbf{r}) = A_n Z^{n+\frac{1}{2}}\exp\left(-\tfrac{Zr}{n}\right)$$

where A_n is a normalization constant that does not depend on the atomic number, Z. The normalization integral is:

$$1 = \int\left(A_n Z^{n+\frac{1}{2}}\exp\left(-\tfrac{Zr}{n}\right)\right)^2 d\mathbf{r} = A_n^2\int Z^{2n+1}\exp\left(-\tfrac{2Zr}{n}\right)d\mathbf{r}$$

Differentiate both sides of this expression with respect to Z. Then I have:

$$\frac{\partial(1)}{\partial Z} = \frac{\partial}{\partial Z}A_n^2\int Z^{2n+1}\exp\left(-\tfrac{2Zr}{n}\right)d\mathbf{r}$$

$$0 = A_n^2\int(2n+1)Z^{2n}\exp\left(-\tfrac{2Zr}{n}\right) + Z^{2n+1}\left(-\tfrac{2r}{n}\right)\exp\left(\tfrac{-2Zr}{n}\right)d\mathbf{r}$$

In the second line we pulled the differentiation inside the integral and differentiated the integrand. The second term is closely related to the expectation value of r; the first term is closely related to the normalization integral for the wavefunction. Using these insights and simplifying the expression above, we have:

$$A_n^2\int Z^{2n+1}\left(\tfrac{2r}{n}\right)\exp\left(\tfrac{-2Zr}{n}\right)d\mathbf{r} = A_n^2\int(2n+1)Z^{2n}\exp\left(-\tfrac{2Zr}{n}\right)d\mathbf{r}$$

$$\tfrac{2}{n}\left[A_n^2\int r\cdot Z^{2n+1}\exp\left(\tfrac{-2Zr}{n}\right)d\mathbf{r}\right] = (2n+1)A_n^2\int Z^{2n}\exp\left(-\tfrac{2Zr}{n}\right)d\mathbf{r}$$

$$\tfrac{2}{n}\left[\int r\cdot\left(A_n Z^{n+\frac{1}{2}}\exp\left(\tfrac{-Zr}{n}\right)\right)^2 d\mathbf{r}\right] = (2n+1)A_n^2\int\frac{Z^{2n+1}}{Z}\exp\left(-\tfrac{2Zr}{n}\right)d\mathbf{r}$$

$$\tfrac{2}{n}\left\langle\Psi_{n,n-1,m}\middle|r\middle|\Psi_{n,n-1,m}\right\rangle = \left(\frac{2n+1}{Z}\right)A_n^2\int Z^{2n+1}\exp\left(-\tfrac{2Zr}{n}\right)d\mathbf{r}$$

$$\tfrac{2}{n}\left\langle\Psi_{n,n-1,m}\middle|r\middle|\Psi_{n,n-1,m}\right\rangle = \frac{2n+1}{Z}$$

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

Bonus: (5 points) The infrared spectrum of $^{75}Br^{19}F$ consists of an intense line at 380 cm^{-1}. **Calculate the force constant of $^{75}Br^{19}F$.**

This is example 5-3 in MacQuarrie's book. We know that the energy levels of the harmonic oscillator are

$$E_k = \tfrac{1}{2}\hbar\omega(2k+1) \qquad\qquad k = 0,1,2,\ldots$$

and that the angular frequency is related to the force constant and reduced mass by

$$\omega = \sqrt{\frac{k}{\mu}}$$

The transition energy in question will be between the ground and first-excited states (k = 0 and k = 1), so

$$\Delta E = \hbar\omega = \hbar\sqrt{\frac{k}{\mu}} = \underbrace{h\nu = \frac{hc}{\lambda}}_{\text{using } c=\lambda\nu} = \underset{\text{using } \bar{\nu}=\frac{1}{\lambda}}{hc\bar{\nu}}$$

So

$$\hbar\sqrt{\frac{k}{\mu}} = hc\bar{\nu}$$

$$\sqrt{\frac{k}{\mu}} = 2\pi c\bar{\nu}$$

$$k = \mu\left(2\pi c\bar{\nu}\right)^2$$

$$= \left(\frac{75\cdot 19}{75+19}\right)\left(1.66\cdot 10^{-27}\ \tfrac{\text{kg}}{u}\right)\left[\left(2\pi\right)\left(3.00\cdot 10^{10}\ \tfrac{\text{cm}}{\text{s}}\right)\left(380\ \text{cm}^{-1}\right)\right]^2$$

$$= 129\,\tfrac{\text{kg}}{\text{s}^2} = 120\ \tfrac{\text{N}}{\text{m}}$$