

Name _____ Student Number _____

Final Exam

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. The exam is marked out of 200 points.

There are three parts to this exam. In part #1, questions are labelled by the mid-term they are most relevant to.

Part 1: 20 questions @ 8 points each.

Part 2: Pick 2 of 6 questions @ 20 points each.

Bonus: Pick 1 extra from the 5 questions in part 3 for up to 10 bonus marks. There are a few bonus marks sprinkled throughout Part #1 also.

Midterm #1 Grade: _____

Part 1 Midterm 1 Grade: _____

Midterm #2 Grade: _____

Part 1 Midterm 2 Grade: _____

Midterm #3 Grade: _____

Part 1 Midterm 3 Grade: _____

Midterm #4 Grade: _____

Part 1 Midterm 4 Grade: _____

Part 2 Final Exam Grade: _____

Total Final Exam Grade: _____

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	$1.05459 \times 10^{-34} \text{ J}\cdot\text{s}$
Speed of light in vacuum	c	$2.997925 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
Atomic mass unit	amu	$1.66056 \times 10^{-27} \text{ kg}$
Electron rest mass	m_e	$9.10953 \times 10^{-31} \text{ kg}$
Proton rest mass	m_p	$1.67265 \times 10^{-27} \text{ kg}$
Boltzmann constant	k_B	$1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ 0.69509 cm^{-1}
Molar gas constant	R	$8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Permittivity of a vacuum	ϵ_0	$8.854188 \times 10^{-12} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
	$4\pi\epsilon_0$	$1.112650 \times 10^{-10} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Midterm #1 Material

1. Consider a particle with unit mass and unit charge confined to a 3-dimensional box, with potential,

$$V_{\text{p-in-3D-box}}(x, y, z) = V_{\text{p-in-box}}(x) + V_{\text{p-in-box}}(y) + V_{\text{p-in-box}}(z)$$

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

We place this box in linearly polarized light, which induces a time-dependent potential with the form

$$V_{\text{light}}(x, y, z, t) = -2Vx \sin(\omega t - kz)$$

What is the time-dependent Schrödinger equation for this system, using atomic units (so $\hbar = 1$).

Bonus: (2 points) What would $V_{\text{light}}(x, y, z, t)$ be if the long-wavelength approximation was assumed to be true?

2. Consider a beam of electrons, accelerated through a potential of 100. Volts. What is the de Broglie wavelength of electrons in the beam?

The following text is used in problems #3 and #4.

The ground-state wavefunction and energy for the 1-dimensional harmonic oscillator can be written as:

$$\left(-\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} \alpha^2 x^2 \right) \psi_0(x) = E_0 \psi_0(x) \quad E_0 = \frac{1}{2} \hbar \omega \quad \psi_0(x) = \exp\left(-\frac{1}{2} \alpha x^2\right)$$

The water molecule has three vibrational modes, corresponding to the symmetric stretch, the asymmetric stretch, and the bending motion, and its Hamiltonian can be written as:

$$\hat{H}_{\text{vibration H}_2\text{O}} = -\frac{1}{2} \frac{d^2}{dx_{\text{sym}}^2} - \frac{1}{2} \frac{d^2}{dx_{\text{asym}}^2} - \frac{1}{2} \frac{d^2}{dx_{\text{bend}}^2} + \frac{1}{2} \alpha_{\text{sym}}^2 x_{\text{sym}}^2 + \frac{1}{2} \alpha_{\text{asym}}^2 x_{\text{asym}}^2 + \frac{1}{2} \alpha_{\text{bend}}^2 x_{\text{bend}}^2.$$

3. **What is the ground-state energy of the vibrational Hamiltonian of the water molecule?** Write the answer in terms of $\omega_{\text{sym}}, \omega_{\text{asym}}, \omega_{\text{bend}}$.

4. **What is the ground-state wavefunction of the vibrational Hamiltonian of the water molecule?** Write the answer in terms of $\alpha_{\text{sym}}, \alpha_{\text{asym}}, \alpha_{\text{bend}}$.

5. The infrared spectrum of $^1\text{H}^{35}\text{Cl}$ consists of an intense line at 2886 cm^{-1} . **What is the location of an analogous intense line in the spectrum of $^2\text{D}^{37}\text{Cl}$?** Please put your answer in the blank below for easy grading.

_____ cm^{-1}

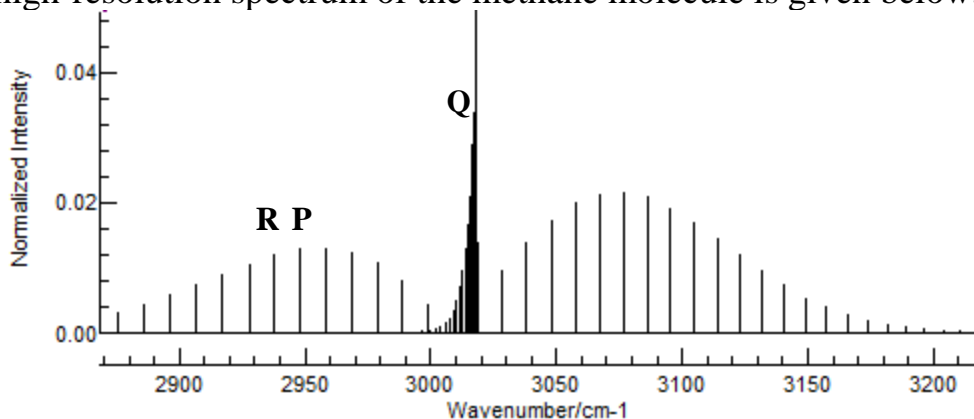
Midterm #2 Material

6. Write the electronic and nuclear Schrödinger equations for the N -electron P -atom molecule in SI units, showing the dependence on physical constants like the charge and mass of the electron.

electronic Schrödinger equation:

nuclear Schrödinger equation:

7. A high-resolution spectrum of the methane molecule is given below.



Three sets of lines are observed, which are called the P, Q, and R branch, respectively, corresponding to the dipole-allowed transitions for the rigid spherical top molecule, $\Delta J = 0, \pm 1$, $\Delta K = 0$. **The P-branch corresponds to which of the following transitions?** (Circle the answer.)

(A) $\Delta J = -1$

(B) $\Delta J = 0$

(C) $\Delta J = +1$

8. Consider a Nitrogen atom in its ground state, with $M_s = S = \frac{3}{2}$, where M_s is the spin angular momentum around the z axis. The Robertson-Schrödinger relation then allows us to state that for this state of the Nitrogen atom, in atomic units,

$$\langle \Psi | \hat{S}_x^2 | \Psi \rangle \langle \Psi | \hat{S}_y^2 | \Psi \rangle \geq \frac{9}{16}.$$

Show, mathematically, why this result is true. (That is, derive this result.)

9. The energy eigenvalues of a one-electron atom are

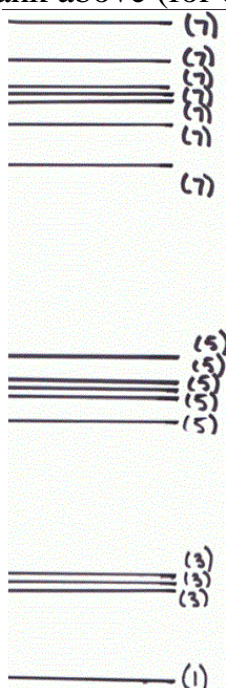
$$E_n = -\frac{m_e Z^2 e^4}{8\epsilon_0^2 h^2 n^2}$$

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?

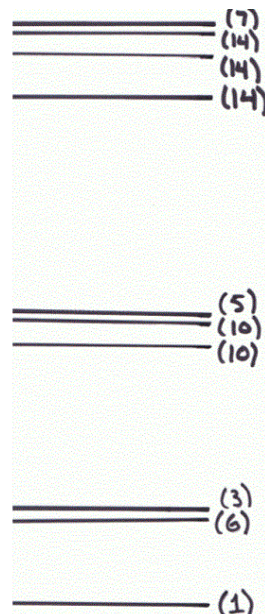
$$\langle \Psi_{n,\ell,m} | \nabla^2 | \Psi_{n,\ell,m} \rangle = \text{????}$$

10. _____ Which of the following energy-level diagrams corresponds to the rotational energy levels of a spherical top molecule? Put your answer in the blank above (for easy grading).

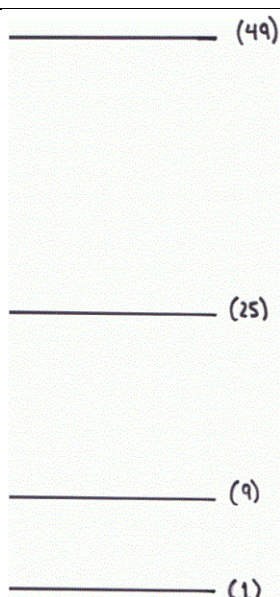
A



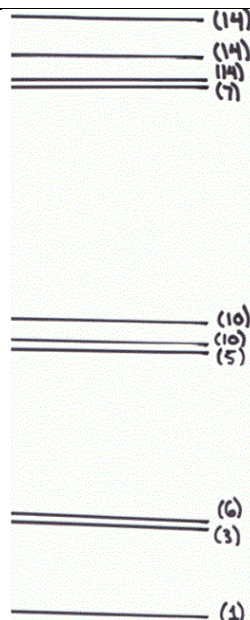
B



C



D



Bonus:

Which of these diagrams corresponds to prolate symmetric top _____?

Which of these diagrams corresponds to an oblate symmetric top _____?

Which of these diagrams corresponds to an asymmetric top _____?

Midterm #3 Material

11. _____ Assuming that Hund's rules apply, what is the ground-state term symbol for the Dysprosium atom, with electron configuration $[\text{Xe}]6s^2 4f^{10}$. Be sure to specify the appropriate value of the total angular momentum, J . Please list your answer above for easy grading.
12. What are the value(s) for the following quantum numbers for a state described by a 6H term symbol? 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)
13. What is the expression for the most probable distance to find an electron from the nucleus in the lowest-energy state of a one-electron atom with atomic number Z and angular momentum ℓ . (I.e., assume $\ell = n - 1$.)

The following information is relevant for problems 14 and 15.

For the 2-electron atom, we considered a wave function with the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2) \left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right)$$

where

$$\phi_{1s}(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}$$

We found that the energy of this wave function was given by the form,

$$\begin{aligned} E(\zeta) &\equiv \langle \Psi(\mathbf{r}_1, \mathbf{r}_2) | \hat{H} | \Psi(\mathbf{r}_1, \mathbf{r}_2) \rangle \\ &= -\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - Z) \end{aligned}$$

where the Hamiltonian of the 2-electron atom has the form

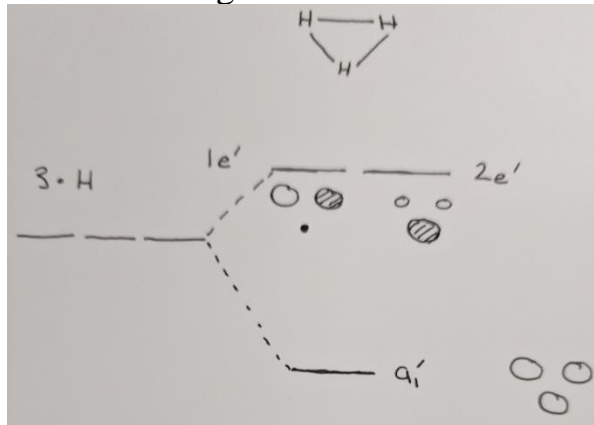
$$\hat{H} \equiv \frac{-\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

14. Suppose we approximate the energy of the Beryllium dication (Be^{+2}) by using first-order perturbation theory, where the electron-electron repulsion term in the Hamiltonian is treated as a perturbation. **What is the approximate energy?**

15. Suppose we approximate the energy of the Be^{+2} using the variational principle, using trial wave functions with the form given by in the problem statement. **What is the approximate energy?**

Midterm #4 Material

Consider the triangular/cyclic H_3^- molecular anion, neglecting the electron-electron repulsion. The molecular orbital diagram is



The wavefunctions for the 3 molecular orbitals are:

$$|\psi_{1a'_1}\rangle = \frac{1}{\sqrt{3}}|\psi_{1s}^A\rangle + \frac{1}{\sqrt{3}}|\psi_{1s}^B\rangle + \frac{1}{\sqrt{3}}|\psi_{1s}^C\rangle$$

$$|\psi_{1e'}\rangle = \frac{1}{\sqrt{2}}|\psi_{1s}^A\rangle - \frac{1}{\sqrt{2}}|\psi_{1s}^C\rangle$$

$$|\psi_{2e'}\rangle = \frac{1}{\sqrt{6}}|\psi_{1s}^A\rangle - \frac{2}{\sqrt{6}}|\psi_{1s}^B\rangle + \frac{1}{\sqrt{6}}|\psi_{1s}^C\rangle$$

Values of key integrals are:

$$\langle \psi_{1s}^{(A)} | -\frac{1}{2}\nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r}) | \psi_{1s}^{(A)} \rangle = -\frac{1}{2}$$

$$\langle \psi_{1s}^{(A)} | -\frac{1}{2}\nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r}) | \psi_{1s}^{(B)} \rangle = -\frac{1}{20}$$

all other integrals are zero

Here we have labeled the electron-nuclear potentials and the wavefunctions of the atoms with A, B, and C.

16. What is the Slater determinant for the ground state of cyclic H_3^- ? Write this out in “long” form, showing all the rows/columns of the matrix.

17. What is the ground-state energy of cyclic H_3^- , expressed in terms of the integrals given above, neglecting the electron-electron repulsion?

18. Label the following approximate (unnormalized) molecular orbitals using the $\sigma, \pi, \delta, u, g$, 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. **The last 4 are bonus (1/2 point each)**

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)

19. The equation for transition rates from an initial to a final state according to Fermi's Golden Rule is listed below.

$$W_{fi} = \frac{2\pi V^2 \left[g(\hbar\omega_{fi}) + g(\hbar\omega_{if}) \right]}{\hbar} \left| \langle \Phi_f | \mu_x | \Phi_i \rangle \right|^2$$

Explain the meaning/importance of each term in this expression.

Bonus: (2 points) What are the three main approximations that are used to derive Fermi's Golden Rule?

20. Listed below are formulas for the frequencies of the dipole-allowed (E1) transitions for the **(A)** one-electron atom **(B)** the one-dimensional-harmonic oscillator, and **(C)** rigid rotation of a diatomic molecule (with a dipole moment). The letter R is just a constant, which (obviously) has different interpretations in all three cases. **Label the formulas below correctly.**

_____ $\omega_{fi} = R$ (only one transition frequency)

_____ $\omega_{fi} = Rn$ $n = 1, 2, \dots$ (equally spaced transitions)

_____ $\omega_{fi} = R \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$ $n_1 = 1, 2, \dots$ $n_2 = 1, 2, \dots$ $n_1 > n_2$

Name _____ Student Number _____

Part 2.

Pick 2 of the following 6 questions. Pick an extra questions for bonus marks.

1. Valence Bond and Molecular Orbital Approaches are Equivalent.

- a. Write down a valence bond wavefunction for the hydrogen molecule in terms of the atomic $1s$ orbitals on the left- and the right-hydrogen atoms, $\phi_{1s}^{(l)}(\mathbf{r})$ and $\phi_{1s}^{(r)}(\mathbf{r})$, respectively. Clearly indicate the ionic and covalent terms.
- b. Write down an expression for the bonding and antibonding molecular orbitals in H_2 , in terms of the atomic $1s$ orbitals on the left- and the right-hydrogen atoms, $\phi_{1s}^{(l)}(\mathbf{r})$ and $\phi_{1s}^{(r)}(\mathbf{r})$, respectively.
- c. Write down an expression for the simplest molecular-orbital + configuration interaction wavefunction for H_2 , using your results from problem 1b.
- d. Show that the Valence-Bond wavefunction with covalent and ionic terms is equal to the molecular orbital wavefunction including configuration interaction.

2. Term symbols and atomic selection rules.

- a. Consider the ground state of the Phosphorous atom, with electron configuration $[Ne]3s^23p^3$. What is the ground-state term symbol for this atom? (You do not need to worry about the J quantum number.)
- b. What are *all* the term symbols associated with the excited state of the Phosphorous atom with configuration $[Ne]3s^23p^23d^1$.
- c. Assume that only electric-dipole-allowed transitions are observed (E1 selection rules). List the term symbols of the excited states in part b that are E1-allowed transitions from the ground state term symbol in part a.

3. Perturbation theory.

- Derive the expression for the first-order correction to the energy in time-independent perturbation theory, $\left(\frac{dE}{d\lambda}\right)_{\lambda=0}$.
- Derive the expression for the first-order correction to the wavefunction in time-independent perturbation theory, $\left(\frac{d\Psi}{d\lambda}\right)_{\lambda=0}$.
- Derive the expression for the second-order correction to the energy in time-independent perturbation theory, $\frac{1}{2}\left(\frac{d^2E}{d\lambda^2}\right)_{\lambda=0}$.

4. Properties of the 1-electron atom.

The following integral may be helpful to you.

$$\int_0^\infty r^n e^{-\beta r} dr = \frac{n!}{\beta^{n+1}}$$

- Compute the mean distance of an electron from the nucleus in the ground state of a one-electron atom with atomic number Z , $r_{\text{mean}} = \langle \psi_{1s} | r | \psi_{1s} \rangle$.
- Compute the rms distance of an electron from the nucleus in the ground state of a one-electron atom with atomic number Z , $r_{\text{rms}} = \sqrt{\langle \psi_{1s} | r^2 | \psi_{1s} \rangle}$.
- Recall that the Heisenberg uncertainty principle states that, for particles in one dimension,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

For particles in three dimensions, one has the principle,

$$\sigma_r \sigma_p \geq \frac{3\hbar}{2}$$

which can be derived from the uncertainty in the individual components of the position/momentum. **Verify, by explicit computation of σ_r and σ_p , that the Heisenberg uncertainty principle holds for the ground state of a one-electron atom.**

5. Spectroscopy of the 3-dimensional particle-in-a-box.

What is the formula for the transition frequencies, ω_{fi} , of the

(a) electric-dipole-allowed (E1) transitions and

(b) electric-quadrupole-allowed (E2) transitions

in the 3-dimensional particle in a box. Assume that the light propagates in the positive z direction, that the light is linearly polarized with its electric field oscillating in the x direction. The box is defined by the potential,

$$V(x, y, z) = \begin{cases} 0 & -\frac{1}{2}a_x < x < \frac{1}{2}a_x; \quad -\frac{1}{2}a_y < y < \frac{1}{2}a_y; \quad -\frac{1}{2}a_z < z < \frac{1}{2}a_z \\ +\infty & \text{otherwise} \end{cases}$$

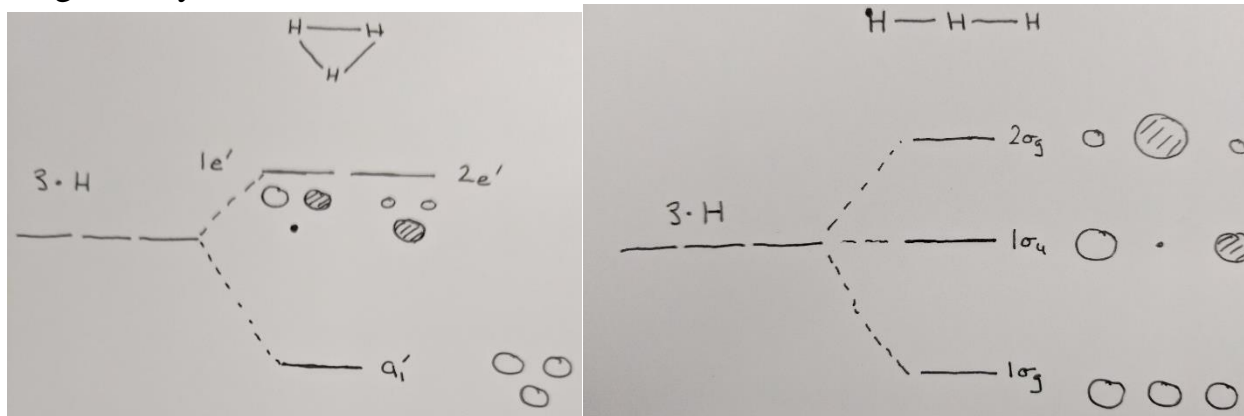
Recall the eigenfunctions for a particle in a box of width a centered at the origin are:

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right) & n = 1, 3, 5, \dots \\ \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) & n = 2, 4, 6, \dots \end{cases}$$

(c) The intensity of the electric-quadrupole-allowed transitions is observed to be much weaker than that of the electric-dipole-allowed transitions. Why?

6. H₃, revisited.

The molecular orbital diagrams for the H₃ molecule, in both its linear and cyclic geometry, are listed below.



The integrals that you will need are:

$$\left\langle \psi_{1s}^{(A)} \left| -\frac{1}{2} \nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r}) \right| \psi_{1s}^{(A)} \right\rangle = -\frac{1}{2}$$

$$\left\langle \psi_{1s}^{(A)} \left| -\frac{1}{2} \nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r}) \right| \psi_{1s}^{(B)} \right\rangle = \begin{cases} -\frac{1}{20} & \text{A and B are bonded} \\ 0 & \text{otherwise} \end{cases}$$

all other integrals are zero

I will tell you that the molecular orbitals for linear H₃ are:

$$|\psi_{1\sigma_g}\rangle = \frac{1}{2} |\psi_{1s}^A\rangle + \frac{1}{\sqrt{2}} |\psi_{1s}^B\rangle + \frac{1}{2} |\psi_{1s}^C\rangle$$

$$|\psi_{1\sigma_u}\rangle = \frac{1}{\sqrt{2}} |\psi_{1s}^A\rangle - \frac{1}{\sqrt{2}} |\psi_{1s}^C\rangle$$

$$|\psi_{2\sigma_g}\rangle = \frac{1}{2} |\psi_{1s}^A\rangle - \frac{1}{\sqrt{2}} |\psi_{1s}^B\rangle + \frac{1}{2} |\psi_{1s}^C\rangle$$

(a) What is the energy of neutral linear H₃?

(b) What is the energy of neutral cyclic H₃?

(c) Suppose one changes one of the Hydrogen atoms for a Helium atom in linear H₃. This has the effect of changing one of the integrals above.

$$\left\langle \psi_{1s}^{(\text{He})} \left| -\frac{1}{2} \nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r}) \right| \psi_{1s}^{(\text{He})} \right\rangle = -\frac{9}{10}$$

(To a good approximation, none of the other integrals change.) **Is it better to add a Helium atom on the end of the linear molecule or at the middle of the linear molecule?**

Name _____ Student Number _____

Final Exam 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. The exam is marked out of 200 points.

There are three parts to this exam. In part #1, questions are labelled by the mid-term they are most relevant to.

Part 1: 20 questions @ 8 points each.

Part 2: Pick 2 of 6 questions @ 20 points each.

Bonus: Pick 1 extra from the 5 questions in part 3 for up to 10 bonus marks. There are a few bonus marks sprinkled throughout Part #1 also.

Midterm #1 Grade: _____

Part 1 Midterm 1 Grade: _____

Midterm #2 Grade: _____

Part 1 Midterm 2 Grade: _____

Midterm #3 Grade: _____

Part 1 Midterm 3 Grade: _____

Midterm #4 Grade: _____

Part 1 Midterm 4 Grade: _____

Part 2 Final Exam Grade: _____

Total Final Exam Grade: _____

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	$1.05459 \times 10^{-34} \text{ J}\cdot\text{s}$
Speed of light in vacuum	c	$2.997925 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
Atomic mass unit	amu	$1.66056 \times 10^{-27} \text{ kg}$
Electron rest mass	m_e	$9.10953 \times 10^{-31} \text{ kg}$
Proton rest mass	m_p	$1.67265 \times 10^{-27} \text{ kg}$
Boltzmann constant	k_B	$1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ 0.69509 cm^{-1}
Molar gas constant	R	$8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Permittivity of a vacuum	ϵ_0	$8.854188 \times 10^{-12} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
	$4\pi\epsilon_0$	$1.112650 \times 10^{-10} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$2 \quad \text{Joule} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2 = 1 \text{ Coulomb}\cdot\text{Volt}$$

Midterm #1 Material

1. Consider a particle with unit mass and unit charge confined to a 3-dimensional box, with potential,

$$V_{\text{p-in-3D-box}}(x, y, z) = V_{\text{p-in-box}}(x) + V_{\text{p-in-box}}(y) + V_{\text{p-in-box}}(z)$$

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

We place this box in linearly polarized light, which induces a time-dependent potential with the form

$$V_{\text{light}}(x, y, z, t) = -2Vx \sin(\omega t - kz)$$

What is the time-dependent Schrödinger equation for this system, using atomic units.

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2} + V_{\text{p-in-3D-box}}(x, y, z) + V_{\text{light}}(x, y, z, t) \right] \Psi(x, y, z, t) = i\hbar \frac{\partial \Psi(x, y, z, t)}{\partial t}$$

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{p-in-3D-box}}(x, y, z) + V_{\text{light}}(x, y, z, t) \right] \Psi(x, y, z, t) = i\hbar \frac{\partial \Psi(x, y, z, t)}{\partial t}$$

Bonus: (2 points) What would $V_{\text{light}}(x, y, z, t)$ be if the long-wavelength approximation was assumed to be true?

$$V_{\text{light}}^{\text{long wavelength approx.}}(x, y, z, t) = -2Vx \sin(\omega t)$$

2. 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 and Midterm #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

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

The kinetic energy can then be determined, and we use the conversion $1 \text{ C} \cdot \text{V} = 1 \text{ J}$. So

$$T = 1.609 \cdot 10^{-17} \text{ J} = \frac{p^2}{2m_e}$$

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

This gives that the momentum of the electron is

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

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

$$p = h/\lambda$$

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

The following text is used in problems #2 and #3.

The ground-state wavefunction and energy for the 1-dimensional harmonic oscillator can be written as:

$$\left(-\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}\alpha^2 x^2\right)\psi_0(x) = E_0\psi_0(x) \quad E_0 = \frac{1}{2}\hbar\omega \quad \psi_0(x) = \exp\left(-\frac{1}{2}\alpha x^2\right)$$

The water molecule has three vibrational modes, corresponding to the symmetric stretch, the asymmetric stretch, and the bending motion, and its Hamiltonian can be written as:

$$\hat{H}_{\text{vibration H}_2\text{O}} = -\frac{1}{2}\frac{d^2}{dx_{\text{sym}}^2} - \frac{1}{2}\frac{d^2}{dx_{\text{asym}}^2} - \frac{1}{2}\frac{d^2}{dx_{\text{bend}}^2} + \frac{1}{2}\alpha_{\text{sym}}^2 x_{\text{sym}}^2 + \frac{1}{2}\alpha_{\text{asym}}^2 x_{\text{asym}}^2 + \frac{1}{2}\alpha_{\text{bend}}^2 x_{\text{bend}}^2.$$

3. What is the ground-state energy of the vibrational Hamiltonian of the water molecule?

Write the answer in terms of $\omega_{\text{sym}}, \omega_{\text{asym}}, \omega_{\text{bend}}$.

$$E_0 = \frac{1}{2}\hbar(\omega_{\text{sym}} + \omega_{\text{asym}} + \omega_{\text{bend}})$$

4. What is the ground-state wavefunction of the vibrational Hamiltonian of the water molecule? Write the answer in terms of $\alpha_{\text{sym}}, \alpha_{\text{asym}}, \alpha_{\text{bend}}$.

$$\psi_0(x_{\text{sym}}, x_{\text{asym}}, x_{\text{bend}}) = \exp\left(-\frac{1}{2}\alpha_{\text{sym}}x_{\text{sym}}^2\right)\exp\left(-\frac{1}{2}\alpha_{\text{asym}}x_{\text{asym}}^2\right)\exp\left(-\frac{1}{2}\alpha_{\text{bend}}x_{\text{bend}}^2\right)$$

5. The infrared spectrum of $^1\text{H}^{35}\text{Cl}$ consists of an intense line at 2886 cm^{-1} . What is the location of an analogous intense line in the spectrum of $^2\text{D}^{37}\text{Cl}$? Please put your answer in the blank below for easy grading.

2066 cm^{-1}

There are several different ways to compute this. The easiest, I think, is to realize that the transition frequency is

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

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

and that the force constant is the same for both $^1\text{H}^{35}\text{Cl}$ and $^2\text{D}^{37}\text{Cl}$. So

$$\frac{\bar{\nu}_{^1\text{H}^{35}\text{Cl}}}{\bar{\nu}_{^2\text{D}^{37}\text{Cl}}} = \sqrt{\frac{\mu_{^2\text{D}^{37}\text{Cl}}}{\mu_{^1\text{H}^{35}\text{Cl}}}}$$

$$\bar{\nu}_{^2\text{D}^{37}\text{Cl}} = \bar{\nu}_{^1\text{H}^{35}\text{Cl}} \cdot \sqrt{\frac{\mu_{^1\text{H}^{35}\text{Cl}}}{\mu_{^2\text{D}^{37}\text{Cl}}}} = (2886\text{ cm}^{-1}) \cdot \sqrt{\frac{1 \cdot 35}{2 \cdot 37}} = (2886\text{ cm}^{-1}) \cdot \sqrt{\frac{35 \cdot 39}{36 \cdot 74}} = 2066\text{ cm}^{-1}$$

Midterm #2 Material

6. Write the electronic and nuclear Schrödinger equations for the N -electron P -atom molecule in SI units, showing the dependence on physical constants like the charge and mass of the electron.

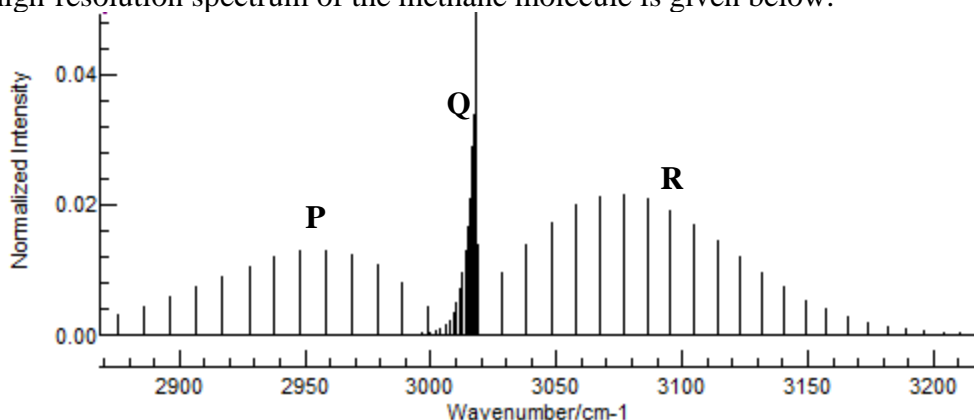
electronic Schrödinger equation:

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

nuclear Schrödinger equation:

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

7. A high-resolution spectrum of the methane molecule is given below.



Three sets of lines are observed, which are called the P, Q, and R branch, respectively, corresponding to the dipole-allowed transitions for the rigid spherical top molecule, $\Delta J = 0, \pm 1$, $\Delta K = 0$. **The P-branch corresponds to which of the following transitions?** (Circle the answer.)

(A) $\Delta J = -1$ _____

(B) $\Delta J = 0$

(C) $\Delta J = +1$

The $\Delta J = 0$ branch should be the branch that is in the middle (Q), because the $\Delta J = \pm 1$ spectral lines should be similar, and on either side, of that set of transitions. The main frequencies that we see are transitions from the ground vibrational state to the first excited vibrational state, with either $\Delta J = 1$ or (so that the molecule is rotating faster in the excited state, and the excitation energy is higher than it would be for at $\Delta J = 0$ transition, and the wavelength is shorter, so the frequency and wavenumber are larger. So $\Delta J = 1$ must correspond to the R branch and therefore, by process of elimination, $\Delta J = -1$ corresponds to the P branch.

8. Consider a Nitrogen atom in its ground state, with $M_s = S = \frac{3}{2}$, where M_s is the spin angular momentum around the z axis. The Robertson-Schrödinger relation then allows us to state that for this state of the Nitrogen atom, in atomic units,

$$\langle \Psi | \hat{S}_x^2 | \Psi \rangle \langle \Psi | \hat{S}_y^2 | \Psi \rangle \geq \frac{9}{16}.$$

Show, mathematically, why this result is true. (That is, derive this result.)

The average spin about the x or y axis for the atom in an eigenstate of \hat{S}_z is zero. So we have that

$$\sigma_{S_x}^2 = \langle \Psi | \hat{S}_x^2 | \Psi \rangle - \left(\langle \Psi | \hat{S}_x | \Psi \rangle \right)^2 = \langle \Psi | \hat{S}_x^2 | \Psi \rangle$$

$$\sigma_{S_y}^2 = \langle \Psi | \hat{S}_y^2 | \Psi \rangle - \left(\langle \Psi | \hat{S}_y | \Psi \rangle \right)^2 = \langle \Psi | \hat{S}_y^2 | \Psi \rangle$$

The Heisenberg Uncertainty principle then states that:

$$\sigma_{S_x} \sigma_{S_y} \geq \frac{1}{2} \hbar \left| \langle \Psi | [\hat{S}_x, \hat{S}_y] | \Psi \rangle \right| = \frac{1}{2} \hbar \left| \langle \Psi | \hbar \hat{S}_z | \Psi \rangle \right|$$

$$\sigma_{S_x}^2 \sigma_{S_y}^2 \geq \frac{1}{4} \hbar^4 \left| \langle \Psi | \hat{S}_z | \Psi \rangle \right|^2 = \frac{1}{4} \hbar^4 \left| \frac{3}{2} \hbar \right|^2 = \frac{9}{16} \hbar^6$$

So

$$\langle \Psi | \hat{S}_x^2 | \Psi \rangle \langle \Psi | \hat{S}_y^2 | \Psi \rangle \geq \frac{9}{16} \text{ a.u. .}$$

9. The energy eigenvalues of a one-electron atom are

$$E_n = -\frac{m_e Z^2 e^4}{8 \epsilon_0^2 \hbar^2 n^2}$$

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?

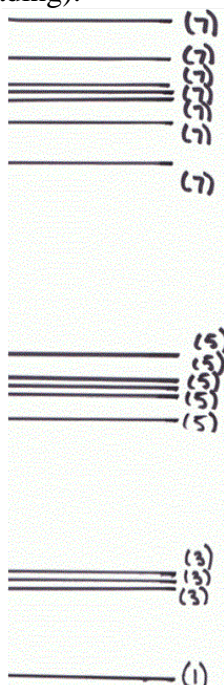
$$\langle \Psi_{n,\ell,m} | \nabla^2 | \Psi_{n,\ell,m} \rangle = \text{?????}$$

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

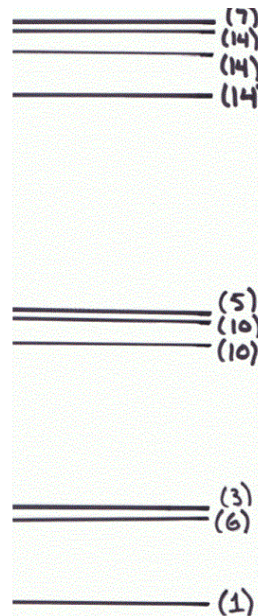
$$\begin{aligned}
 \frac{\partial E}{\partial m_e} &= \left\langle \Psi_{n,\ell,m} \left| \frac{\partial \hat{H}}{\partial m_e} \right| \Psi_{n,\ell,m} \right\rangle = \left\langle \Psi_{n,\ell,m} \left| \frac{\partial \left[\frac{-\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right]}{\partial m_e} \right| \Psi_{n,\ell,m} \right\rangle = \left\langle \Psi_{n,\ell,m} \left| \frac{\hbar^2}{2m_e^2} \nabla^2 \right| \Psi_{n,\ell,m} \right\rangle \\
 -\frac{Z^2 e^4}{8\epsilon_0^2 \hbar^2 n^2} &= \left\langle \Psi_{n,\ell,m} \left| \frac{\hbar^2}{2m_e^2} \nabla^2 \right| \Psi_{n,\ell,m} \right\rangle \\
 -\frac{2m_e^2 Z^2 e^4}{8\hbar^2 \epsilon_0^2 \hbar^2 n^2} &= \left\langle \Psi_{n,\ell,m} \left| \nabla^2 \right| \Psi_{n,\ell,m} \right\rangle \\
 -\frac{m_e^2 Z^2 e^4}{4\left(\frac{\hbar}{2\pi}\right)^2 \epsilon_0^2 \hbar^2 n^2} &= \left\langle \Psi_{n,\ell,m} \left| \nabla^2 \right| \Psi_{n,\ell,m} \right\rangle \\
 -\frac{m_e^2 \pi^2 Z^2 e^4}{\epsilon_0^2 \hbar^4 n^2} &= \left\langle \Psi_{n,\ell,m} \left| \nabla^2 \right| \Psi_{n,\ell,m} \right\rangle
 \end{aligned}$$

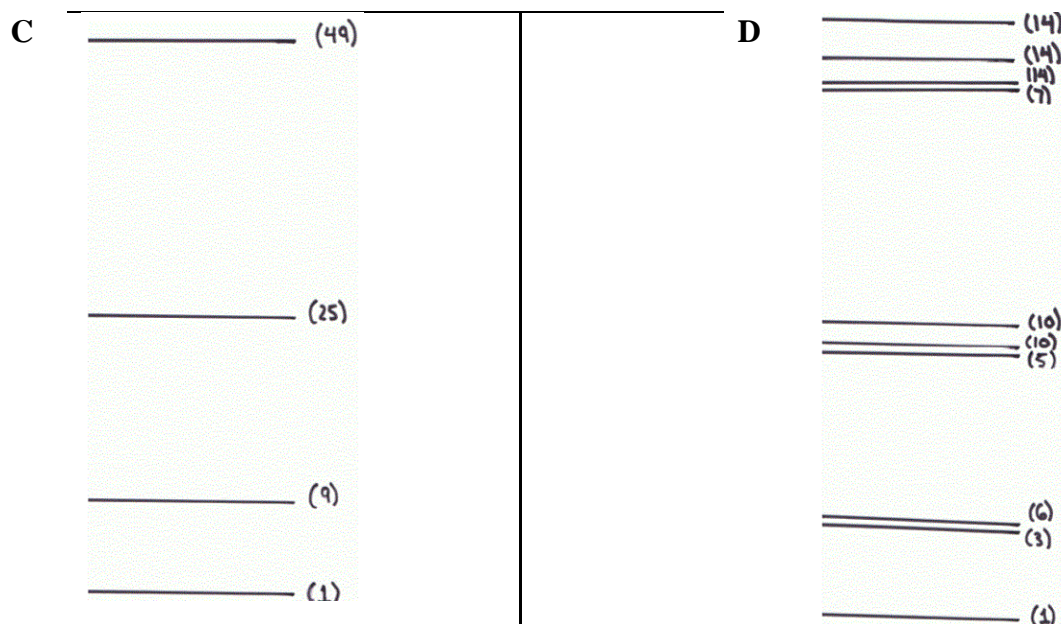
10. C Which of the following energy-level diagrams corresponds to the rotational energy levels of a spherical top molecule? Put your answer in the blank above (for easy grading).

A



B





Bonus:

Which of these diagrams corresponds to prolate symmetric top D?

Which of these diagrams corresponds to an oblate symmetric top B?

Which of these diagrams corresponds to an asymmetric top A?

Midterm #3 Material

11. 5I_8 Assuming that Hund's rules apply, what is the ground-state term symbol for the Dysprosium atom, with electron configuration $[\text{Xe}]6s^24f^{10}$. Be sure to specify the appropriate value of the total angular momentum, J . Please list your answer above for easy grading.

The ground state L and S here will be the same as that for the $[\text{Xe}]6s^24f^4$ configuration. Choose a Slater determinant that maximizes M_S (first) and M_L (second) to find the maximum possible L and S . This determinant will be $\begin{vmatrix} \cdots & \phi_{f_3}^\uparrow & \phi_{f_2}^\uparrow & \phi_{f_1}^\uparrow & \phi_{f_0}^\uparrow \end{vmatrix}$ so there is a state with $S = 2$ and $L = 6$. This corresponds to a 5I term. The shell is more than half-filled so we choose the largest possible value of J which is 8.

12. What are the value(s) for the following quantum numbers for a state described by a 6H term symbol? When the term symbol is not sufficient to fully specify the quantum number, please list all the possible values.

5 L (total orbital angular momentum)

5,4,3,2,1,0,-1,-2,-3,-4,-5 M_L (orbital angular momentum around the z axis)

5/2 S (total spin angular momentum)

5/2,3/2,1/2,-1/2,-3/2,-5/2 M_S (spin angular momentum around the z axis)

13. What is the expression for the most probable **distance to find an electron from the nucleus**

in the lowest-energy state of a one-electron atom with atomic number Z and angular momentum ℓ . (I.e., assume $\ell = n - 1$.)

The wavefunction for the lowest-energy state of a given angular momentum is, up to a normalization constant,

$$\psi_{n,n-1,m}(r, \theta, \phi) = A r^{n-1} \exp\left(-\frac{Z}{n} r\right) Y_{n-1}^m(\theta, \phi)$$

We don't care about the normalization factor or the spherical harmonic, as we only want to know the radial distance from the origin. So we make the probability of seeing an electron a set distance away,

$$P_{n,n-1,m}(r) = 4\pi r^2 \left| \psi_{n,n-1,m} \right|^2 \propto r^2 r^{2n-2} \exp\left(-\frac{2Z}{n} r\right)$$

Then we differentiate this function to find the maximum,

$$\begin{aligned} 0 &= \frac{\partial P_{n,n-1,m}(r)}{\partial r} = 2nr^{2n-1} \exp\left(-\frac{2Z}{n} r\right) + r^{2n} \left(-\frac{2Z}{n}\right) \exp\left(-\frac{2Z}{n} r\right) \\ 0 &= 2n - \frac{2Z}{n} r \\ r &= \frac{n^2}{Z} \end{aligned}$$

The following information is relevant for problems 14 and 15.

For the 2-electron atom, we considered a wave function with the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2) \left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right)$$

where

$$\phi_{1s}(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}$$

We found that the energy of this wave function was given by the form,

$$\begin{aligned} E(\zeta) &\equiv \langle \Psi(\mathbf{r}_1, \mathbf{r}_2) | \hat{H} | \Psi(\mathbf{r}_1, \mathbf{r}_2) \rangle \\ &= -\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - Z) \end{aligned}$$

where the Hamiltonian of the 2-electron atom has the form

$$\hat{H} \equiv \frac{-\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

14. Suppose we approximate the energy of the Beryllium dication (Be^{+2}) by using first-order perturbation theory, where the electron-electron repulsion term in the Hamiltonian is treated as a perturbation. **What is the approximate energy?**

In this case we evaluate the energy *without* using an effective nuclear charge, but just using the hydrogenic orbitals, with $Z = 4$. So

$$E(Z = 4) \equiv -Z^2 + \frac{5}{8}Z = -16 + \frac{5}{2} = -13.5 \text{ Hartree}$$

15. Suppose we approximate the energy of the Be^{+2} using the variational principle, using trial wave functions with the form given by in the problem statement. **What is the approximate energy?**

To use the variational principle, we minimize the energy with respect to the effective nuclear charge, ζ . So we solve for the optimal effective nuclear charge:

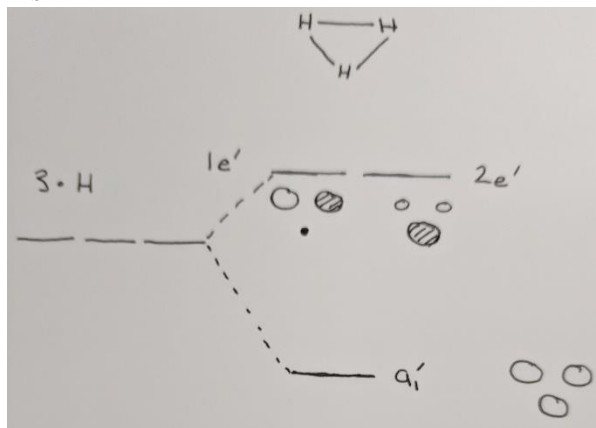
$$\begin{aligned} 0 &= \frac{\partial E(\zeta)}{\partial \zeta} = \frac{\partial \left(-\zeta^2 + \frac{5}{8}\zeta + 2\zeta^2 - 2\zeta Z \right)}{\partial \zeta} \\ &= -2\zeta + \frac{5}{8} + 4\zeta - 2Z \\ 2Z - \frac{5}{8} &= 2\zeta \\ \zeta &= Z - \frac{5}{16} = 4 - \frac{5}{16} = 3.6875 \end{aligned}$$

and then substitute back into the energy expression,

$$\begin{aligned} E(Z) &= -\left(Z - \frac{5}{16}\right)^2 + \frac{5}{8}\left(Z - \frac{5}{16}\right) + 2\left(Z - \frac{5}{16}\right)\left(Z - \frac{5}{16} - Z\right) \\ E(3) &= -\left(4 - \frac{5}{16}\right)^2 + \frac{5}{8}\left(4 - \frac{5}{16}\right) - \frac{5}{8}\left(4 - \frac{5}{16}\right) \\ &= -\left(4 - \frac{5}{16}\right)^2 = -(3.6875)^2 \\ &= -13.598 \text{ Hartree} \end{aligned}$$

Midterm #4 Material

Consider the triangular/cyclic H_3^- molecular anion, neglecting the electron-electron repulsion. The molecular orbital diagram is



The wavefunctions for the 3 molecular orbitals are:

$$|\psi_{1a_1'}\rangle = \frac{1}{\sqrt{3}}|\psi_{1s}^A\rangle + \frac{1}{\sqrt{3}}|\psi_{1s}^B\rangle + \frac{1}{\sqrt{3}}|\psi_{1s}^C\rangle$$

$$|\psi_{1e'}\rangle = \frac{1}{\sqrt{2}}|\psi_{1s}^A\rangle - \frac{1}{\sqrt{2}}|\psi_{1s}^C\rangle$$

$$|\psi_{2e'}\rangle = \frac{1}{\sqrt{6}}|\psi_{1s}^A\rangle - \frac{2}{\sqrt{6}}|\psi_{1s}^B\rangle + \frac{1}{\sqrt{6}}|\psi_{1s}^C\rangle$$

Values of key integrals are:

$$\langle\psi_{1s}^{(A)}|-\frac{1}{2}\nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r})|\psi_{1s}^{(A)}\rangle = -\frac{1}{2}$$

$$\langle\psi_{1s}^{(A)}|-\frac{1}{2}\nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r})|\psi_{1s}^{(B)}\rangle = -\frac{1}{20}$$

all other integrals are zero

Here we have labeled the electron-nuclear potentials and the wavefunctions of the atoms with A, B, and C.

16. What is the Slater determinant for the ground state of cyclic H_3^- ? Write this out in “long” form, showing all the rows/columns of the matrix.

$$|\Psi_{\text{H}_3^-}\rangle = \sqrt{\frac{1}{4!}} \begin{vmatrix} \psi_{1a_1'}(\mathbf{r}_1)\alpha(1) & \psi_{1a_1'}(\mathbf{r}_1)\beta(1) & \psi_{1e'}(\mathbf{r}_1)\alpha(1) & \psi_{2e'}(\mathbf{r}_1)\alpha(1) \\ \psi_{1a_1'}(\mathbf{r}_2)\alpha(2) & \psi_{1a_1'}(\mathbf{r}_2)\beta(2) & \psi_{1e'}(\mathbf{r}_2)\alpha(2) & \psi_{2e'}(\mathbf{r}_2)\alpha(2) \\ \psi_{1a_1'}(\mathbf{r}_3)\alpha(3) & \psi_{1a_1'}(\mathbf{r}_3)\beta(3) & \psi_{1e'}(\mathbf{r}_3)\alpha(3) & \psi_{2e'}(\mathbf{r}_3)\alpha(3) \\ \psi_{1a_1'}(\mathbf{r}_4)\alpha(4) & \psi_{1a_1'}(\mathbf{r}_4)\beta(4) & \psi_{1e'}(\mathbf{r}_4)\alpha(4) & \psi_{2e'}(\mathbf{r}_4)\alpha(4) \end{vmatrix}$$

17. What is the ground-state energy of cyclic H_3^- , expressed in terms of the integrals given above, neglecting the electron-electron repulsion?

The energy is the sum of the occupied orbital energies. We can evaluate these directly as:

$$\langle\psi_{\text{MO}}|-\frac{1}{2}\nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r})|\psi_{\text{MO}}\rangle$$

Using the equations for the molecular orbitals given above. This is the most straightforward way to do this problem. Below I will show how to do it in this way.

But there is a *much* easier way: notice that the e' orbital must be “1/2 as much above” the

energy of the isolated hydrogen atom as the $1a_1'$ orbital is below the energy of the isolated hydrogen atom.

To show something more sophisticated, however, remember that the molecular orbitals are eigenvalues of the Hamiltonian, with elements

$$\begin{bmatrix} \langle \psi_{1s}^{(A)} | \hat{h} | \psi_{1s}^{(A)} \rangle & \langle \psi_{1s}^{(A)} | \hat{h} | \psi_{1s}^{(B)} \rangle & \langle \psi_{1s}^{(A)} | \hat{h} | \psi_{1s}^{(C)} \rangle \\ \langle \psi_{1s}^{(B)} | \hat{h} | \psi_{1s}^{(A)} \rangle & \langle \psi_{1s}^{(B)} | \hat{h} | \psi_{1s}^{(B)} \rangle & \langle \psi_{1s}^{(B)} | \hat{h} | \psi_{1s}^{(C)} \rangle \\ \langle \psi_{1s}^{(C)} | \hat{h} | \psi_{1s}^{(A)} \rangle & \langle \psi_{1s}^{(C)} | \hat{h} | \psi_{1s}^{(B)} \rangle & \langle \psi_{1s}^{(C)} | \hat{h} | \psi_{1s}^{(C)} \rangle \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \frac{-1}{20} & \frac{-1}{20} \\ \frac{-1}{20} & -\frac{1}{2} & \frac{-1}{20} \\ \frac{-1}{20} & \frac{-1}{20} & -\frac{1}{2} \end{bmatrix}$$

The sum of the eigenvalues does not change, i.e., the e' orbital is half as much about $-1/2$ as the a_1' orbital is below it. So the eigenvalues must be of the form:

$$\mathcal{E}_{1a_1'} = -\frac{1}{2} - a$$

$$\mathcal{E}_{1e'} = \mathcal{E}_{2e'} = -\frac{1}{2} + \frac{1}{2}a$$

We can determine a this using any of the known eigenvalues. The easiest is the $1e'$ orbital, which has the energy,

$$\begin{aligned} & \begin{bmatrix} \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & \frac{-1}{20} & \frac{-1}{20} \\ \frac{-1}{20} & -\frac{1}{2} & \frac{-1}{20} \\ \frac{-1}{20} & \frac{-1}{20} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{bmatrix} \\ &= \frac{1}{2} \begin{bmatrix} 1 & 0 & -1 \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & \frac{-1}{20} & \frac{-1}{20} \\ \frac{-1}{20} & -\frac{1}{2} & \frac{-1}{20} \\ \frac{-1}{20} & \frac{-1}{20} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} \\ &= \frac{1}{2} \left(\begin{bmatrix} 1 & 0 & -1 \end{bmatrix} \begin{bmatrix} -\frac{1}{2} + \frac{1}{20} \\ 0 \\ -\frac{1}{20} + \frac{1}{2} \end{bmatrix} \right) \\ &= \frac{1}{2} \left(2 \cdot \left(-\frac{1}{2} + \frac{1}{20} \right) \right) \\ &= -0.45 \end{aligned}$$

And so $a = 0.1$. We have then that $E_{1a_1'} = -0.6$ and $E_{1e'} - E_{2e'} = -0.45$. There are two electrons in the lowest orbital and one electron in each of the higher orbitals. So the total energy is

$$E = 2(-0.6) + (-0.45) + (-0.45) = -2.1$$

18. Label the following approximate (unnormalized) molecular orbitals using the $\sigma, \pi, \delta, u, g$, 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.

The last 4 are bonus (1/2 point each)

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^+	$\psi_{3d_{z^2}}^{(l)}(\mathbf{r}) - \psi_{3d_{z^2}}^{(r)}(\mathbf{r})$
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)
δ_g^-	$\psi_{3d_{xy}}^{(l)}(\mathbf{r}) + \psi_{3d_{xy}}^{(r)}(\mathbf{r})$ (bonus)

19. The equation for transition rates from an initial to a final state according to Fermi's Golden Rule is listed below.

$$W_{fi} = \frac{2\pi V^2 \left[g(\hbar\omega_{fi}) + g(\hbar\omega_{if}) \right]}{\hbar} \left| \langle \Phi_f | \mu_x | \Phi_i \rangle \right|^2$$

Explain the meaning/importance of each term in this expression.

The V is the amplitude of the electric field, or the intensity of the radiation. The stronger the field the higher the rate of transitions.

The fact $g(\hbar\omega_{fi})$ and $g(\hbar\omega_{if})$ enter the expression symmetrically means that absorption of radiation by a lower-energy state to form a higher-energy state and stimulated emission of radiation from a higher-energy state to a lower-energy state occur at the same rate. The term $g(\hbar\omega_{fi})$ is the density-of-states of photons with energy $\hbar\omega_{fi}$. If the photons do not have the correct energy to perform the transition, then no transition occurs (in the weak-field approximation).

Finally, $\left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2$ provides dipole (E1) selection rules: if the final state isn't such that a oscillating dipole field can induces transitions from the initial state, then no transition occurs.

Bonus: (2 points) What are the three main approximations that are used to derive Fermi's Golden Rule?

long wavelength approximation; weak field approximation; long time approximation.

20. Listed below are formulas for the frequencies of the dipole-allowed (E1) transitions for the (A) one-electron atom (B) the one-dimensional-harmonic oscillator, and (C) rigid rotation of a diatomic molecule (with a dipole moment). The letter R is just a constant, which (obviously) has different interpretations in all three cases. **Label the formulas below correctly.**

_____ **B** _____ $\omega_{fi} = R$ (only one transition frequency)

_____ **C** _____ $\omega_{fi} = Rn$ $n = 1, 2, \dots$ (equally spaced transitions)

_____ **A** _____ $\omega_{fi} = R \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$ $n_1 = 1, 2, \dots$ $n_2 = 1, 2, \dots$ $n_1 > n_2$

Name _____ Student Number _____

Part 2.**Pick 2 of the following 6 questions. Pick an extra questions for bonus marks.****1. Valence Bond and Molecular Orbital Approaches are Equivalent.**

- a. Write down a valence bond wavefunction for the hydrogen molecule in terms of the atomic 1s orbitals on the left- and the right-hydrogen atoms, $\phi_{1s}^{(l)}(\mathbf{r})$ and $\phi_{1s}^{(r)}(\mathbf{r})$, respectively. Clearly indicate the ionic and covalent terms.

$$\Psi^{VB+ionic} \propto \left(c_{\text{cov}} \left(\psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1) \psi_{1s}^{(l)}(\mathbf{r}_2) \right) + c_{\text{ionic}} \left(\psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) \right) \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

- b. Write down an expression for the bonding and antibonding molecular orbitals in H_2 , in terms of the atomic 1s orbitals on the left- and the right-hydrogen atoms, $\phi_{1s}^{(l)}(\mathbf{r})$ and $\phi_{1s}^{(r)}(\mathbf{r})$, respectively.

$$\phi_{\sigma_g}(\mathbf{r}) = \phi_{\text{bond}}(\mathbf{r}) \propto \psi_{1s}^{(l)}(\mathbf{r}_1) + \psi_{1s}^{(r)}(\mathbf{r}_1)$$

$$\phi_{\sigma_u}(\mathbf{r}) = \phi_{\text{antibond}}(\mathbf{r}) \propto \psi_{1s}^{(l)}(\mathbf{r}_1) - \psi_{1s}^{(r)}(\mathbf{r}_1)$$

- c. Write down an expression for the simplest molecular-orbital + configuration interaction wavefunction for H_2 , using your results from problem 1b.

$$\begin{aligned} \Psi^{MO+CI} &\propto \left(c_{\text{bond}} \phi_{\sigma_g}(\mathbf{r}_1) \phi_{\sigma_g}(\mathbf{r}_2) + c_{\text{antibond}} \phi_{\sigma_u}(\mathbf{r}_1) \phi_{\sigma_u}(\mathbf{r}_2) \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \\ &= \left(c_{\text{bond}} \left(\psi_{1s}^{(l)}(\mathbf{r}_1) + \psi_{1s}^{(r)}(\mathbf{r}_1) \right) \left(\psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_2) \right) + c_{\text{antibond}} \left(\psi_{1s}^{(l)}(\mathbf{r}_1) - \psi_{1s}^{(r)}(\mathbf{r}_1) \right) \left(\psi_{1s}^{(l)}(\mathbf{r}_2) - \psi_{1s}^{(r)}(\mathbf{r}_2) \right) \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \end{aligned}$$

- d. Show that the Valence-Bond wavefunction with covalent and ionic terms is equal to the molecular orbital wavefunction including configuration interaction.

$$\begin{aligned}
\Psi^{MO+CI} &\propto \left(c_{\text{bond}} \left(\psi_{1s}^{(l)}(\mathbf{r}_1) + \psi_{1s}^{(r)}(\mathbf{r}_1) \right) \left(\psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_2) \right) \right. \\
&\quad \left. + c_{\text{antibond}} \left(\psi_{1s}^{(l)}(\mathbf{r}_1) - \psi_{1s}^{(r)}(\mathbf{r}_1) \right) \left(\psi_{1s}^{(l)}(\mathbf{r}_2) - \psi_{1s}^{(r)}(\mathbf{r}_2) \right) \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \\
&= \left(c_{\text{bond}} \begin{pmatrix} \psi_{1s}^{(l)}(\mathbf{r}_1)\psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1)\psi_{1s}^{(r)}(\mathbf{r}_2) \\ + \psi_{1s}^{(l)}(\mathbf{r}_1)\psi_{1s}^{(r)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1)\psi_{1s}^{(l)}(\mathbf{r}_2) \end{pmatrix} \right. \\
&\quad \left. + c_{\text{antibond}} \begin{pmatrix} \psi_{1s}^{(l)}(\mathbf{r}_1)\psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1)\psi_{1s}^{(r)}(\mathbf{r}_2) \\ - \psi_{1s}^{(l)}(\mathbf{r}_1)\psi_{1s}^{(r)}(\mathbf{r}_2) - \psi_{1s}^{(r)}(\mathbf{r}_1)\psi_{1s}^{(l)}(\mathbf{r}_2) \end{pmatrix} \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \\
&= \left((c_{\text{bond}} + c_{\text{antibond}}) \left(\psi_{1s}^{(l)}(\mathbf{r}_1)\psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1)\psi_{1s}^{(r)}(\mathbf{r}_2) \right) \right. \\
&\quad \left. + (c_{\text{bond}} - c_{\text{antibond}}) \left(\psi_{1s}^{(l)}(\mathbf{r}_1)\psi_{1s}^{(r)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1)\psi_{1s}^{(l)}(\mathbf{r}_2) \right) \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \\
&\propto \Psi^{VB+ionic}
\end{aligned}$$

Moreover,

$$c_{\text{ion}} = c_{\text{bond}} + c_{\text{antibond}}$$

$$c_{\text{cov}} = c_{\text{bond}} - c_{\text{antibond}}$$

2. Term symbols and atomic selection rules.

- a. Consider the ground state of the Phosphorous atom, with electron configuration $[\text{Ne}]3s^23p^3$. **What is the ground-state term symbol for this atom? (You do not need to worry about the J quantum number.)**

The maximum M_S and M_L that can be achieved is associated with the determinant $|\cdots \phi_{3p_0}^\uparrow \phi_{3p_{+1}}^\uparrow \phi_{3p_{-1}}^\uparrow|$

. So we have $S = 3/2$ and $L = 0$. The state is then 4S .

- b. What are *all* the term symbols associated with the excited state of the Phosphorous atom with configuration $[\text{Ne}]3s^23p^23d^1$.

We start with the configurations associated with the p^2 configuration and then couple to the remaining d electron with $L = 2$; $S = 1/2$. For the p^2 configuration, we have

	$M_L=2$	$M_L=1$	$M_L=0$
$M_S=1$		$ \cdots p_{+1}^\uparrow p_0^\uparrow $	$ \cdots p_{+1}^\uparrow p_{-1}^\uparrow $
$M_S=0$	$ \cdots p_{+1}^\uparrow p_{+1}^\downarrow $	$ \cdots p_{+1}^\uparrow p_0^\downarrow $ $ \cdots p_{+1}^\downarrow p_0^\uparrow $	$ \cdots p_{+1}^\uparrow p_{-1}^\downarrow $ $ \cdots p_{+1}^\downarrow p_{-1}^\uparrow $ $ \cdots p_0^\uparrow p_0^\downarrow $

corresponding to the terms 1D , 3P , and 3S . These states then are coupled to the spin and angular momentum of the d^1 configuration,

$$^1D \rightarrow ^2S, ^2P, ^2D, ^2F, ^2G$$

$$^1S \rightarrow ^2D$$

$$^3P \rightarrow ^2S, ^2P, ^2D, ^2F; ^4S, ^4P, ^4D, ^4F$$

This is the full list of term symbols: $2(^2S), 2(^2P), 3(^2D), 2(^2F), ^2G, ^4S, ^4P, ^4D, ^4F$.

- c. Assume that only electric-dipole-allowed transitions are observed (E1 selection rules). **List the term symbols of the excited states in part b that are E1-allowed transitions from the ground state term symbol in part a.**

The selection rules are that the spin cannot change and the angular momentum must change by 1. So the only E1 allowed transition is to the 4P state.

3. Perturbation theory.

- a. Derive the expression for the first-order correction to the energy in time-independent perturbation theory, $\left(\frac{dE}{d\lambda}\right)_{\lambda=0}$.
- b. Derive the expression for the first-order correction to the wavefunction in time-independent perturbation theory, $\left(\frac{d\Psi}{d\lambda}\right)_{\lambda=0}$.
- c. Derive the expression for the second-order correction to the energy in time-independent perturbation theory, $\frac{1}{2}\left(\frac{d^2E}{d\lambda^2}\right)_{\lambda=0}$.

4. Properties of the 1-electron atom.

The following integral may be helpful to you.

$$\int_0^{\infty} r^n e^{-\beta r} dr = \frac{n!}{\beta^{n+1}}$$

- a. Compute the mean distance of an electron from the nucleus in the ground state of a one-electron atom with atomic number Z , $r_{\text{mean}} = \langle \psi_{1s} | r | \psi_{1s} \rangle$.

$$\begin{aligned} r_{\text{mean}} = \langle r \rangle &= \langle \phi_{1s} | r | \phi_{1s} \rangle = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr} \right)^* r \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr} \right) r^2 \sin \theta d\phi d\theta dr \\ &= (4\pi) \left(\frac{Z^3}{\pi} \right) \int_0^{\infty} e^{-2Zr} r^3 dr \\ &= (4Z^3) \left(\frac{3!}{(2Z)^4} \right) = 4Z^3 \left(\frac{6}{16Z^4} \right) \\ &= \frac{3}{2Z} \text{ Bohr} \end{aligned}$$

If you forgot the normalization constant, you could also evaluate the normalization constant by solving

$$\begin{aligned} 1 &= \langle \phi_{1s} | \phi_{1s} \rangle = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} (Ae^{-Zr})^* (Ae^{-Zr}) r^2 \sin \theta d\phi d\theta dr \\ 1 &= (4\pi) A^2 \int_0^{\infty} e^{-2Zr} r^2 dr \\ 1 &= (4\pi) A^2 \left(\frac{2!}{(2Z)^3} \right) = A^2 \left(\frac{\pi}{Z^3} \right) \\ A &= \sqrt{\frac{Z^3}{\pi}} \end{aligned}$$

- b. Compute the rms distance of an electron from the nucleus in the ground state of a one-electron atom with atomic number Z , $r_{\text{rms}} = \sqrt{\langle \psi_{1s} | r^2 | \psi_{1s} \rangle}$.

$$\begin{aligned} r_{\text{rms}} &= \sqrt{\langle r^2 \rangle} = \sqrt{\langle \phi_{1s} | r^2 | \phi_{1s} \rangle} = \sqrt{\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr} \right)^* r^2 \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr} \right) r^2 \sin \theta d\phi d\theta dr} \\ &= \sqrt{(4\pi) \left(\frac{Z^3}{\pi} \right) \int_0^{\infty} e^{-2Zr} r^4 dr} \\ &= \sqrt{(4Z^3) \left(\frac{4!}{(2Z)^5} \right)} = \sqrt{4Z^3 \left(\frac{24}{32Z^5} \right)} = \sqrt{\frac{3}{Z^2}} \\ &= \frac{\sqrt{3}}{Z} \text{ Bohr} \end{aligned}$$

- c. Recall that the Heisenberg uncertainty principle states that, for particles in one dimension,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

For particles in three dimensions, one has the principle,

$$\sigma_r \sigma_p \geq \frac{3\hbar}{2}$$

which can be derived from the uncertainty in the individual components of the position/momentum. **Verify, by explicit computation of σ_r and σ_p , that the**

Heisenberg uncertainty principle holds for the ground state of a one-electron atom.

We know that the average position of an electron in the hydrogen atom is the center of the atom which is $\mathbf{r} = 0$. So, using the result from 5b,

$$\sigma_r^2 = \langle \mathbf{r} \cdot \mathbf{r} \rangle - \langle \mathbf{r} \rangle^2 = \langle r^2 \rangle - \langle \mathbf{r} \rangle^2 = \frac{3}{Z^2} - 0$$

$$\sigma_r = \frac{\sqrt{3}}{Z}$$

Similarly, we know that the average momentum of the electrons is zero. So we have

$$\sigma_p^2 = \langle \mathbf{p} \cdot \mathbf{p} \rangle - \langle \mathbf{p} \rangle^2 = \langle p^2 \rangle - 0$$

The easiest way to evaluate the integral we need to do is to note that it is related to the kinetic energy, which in turn can be computed from the difference between the total energy and the potential energy. I.e.,

$$\langle p^2 \rangle = 2m \left\langle \frac{p^2}{2m} \right\rangle = 2mT = 2m(E - V)$$

For the electron in atomic units, $m = 1$. The energy is known, and the potential energy is given by an integral not unlike those we have already performed. So

$$\begin{aligned} \langle p^2 \rangle &= 2(E - V) = 2 \left(\frac{-Z^2}{2n^2} - \left\langle \phi_{1s} \left| \frac{-Z}{r} \right| \phi_{1s} \right\rangle \right) \\ &= 2 \left(\int_0^\infty \int_0^\pi \int_0^{2\pi} \left(\frac{Z^3}{\pi} \right) e^{-2Zr} \left(\frac{Z}{r} \right) r^2 \sin \theta d\phi d\theta dr - \frac{Z^2}{2(1)^2} \right) \\ &= 2 \left(4\pi \left(\frac{Z^3}{\pi} \right) (Z) \int_0^\infty r e^{-2Zr} dr - \frac{Z^2}{2(1)^2} \right) \\ &= 2 \left(4Z^4 \left(\frac{1!}{(2Z)^2} \right) - \frac{Z^2}{2(1)^2} \right) \\ &= 2 \left(Z^2 - \frac{Z^2}{2} \right) \\ &= Z^2 \end{aligned}$$

So now we have

$$\sigma_p = \sqrt{Z^2} = Z$$

Multiplying the two forms together, we have

$$\sigma_{\mathbf{p}}\sigma_{\mathbf{r}} = Z\left(\frac{\sqrt{3}}{Z}\right) = \sqrt{3} \geq \frac{3}{2}\hbar = \frac{3}{2}$$

where at the very end we have used the fact that $\hbar = 1$ in atomic units.

5. Spectroscopy of the 3-dimensional particle-in-a-box.

What is the formula for the transition frequencies, ω_{fi} , of the

(a) electric-dipole-allowed (E1) transitions and

(b) electric-quadrupole-allowed (E2) transitions

in the 3-dimensional particle in a box. Assume that the light propagates in the positive z direction, that the light is linearly polarized with its electric field oscillating in the x direction. The box is defined by the potential,

$$V(x, y, z) = \begin{cases} 0 & -\frac{1}{2}a_x < x < \frac{1}{2}a_x; \quad -\frac{1}{2}a_y < y < \frac{1}{2}a_y; \quad -\frac{1}{2}a_z < z < \frac{1}{2}a_z \\ +\infty & \text{otherwise} \end{cases}$$

Recall the eigenfunctions for a particle in a box of width a centered at the origin are:

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right) & n = 1, 3, 5, \dots \\ \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) & n = 2, 4, 6, \dots \end{cases}$$

(c) The intensity of the electric-quadrupole-allowed transitions is observed to be much weaker than that of the electric-dipole-allowed transitions. Why?

(a) The eigenfunctions and eigenvalues of the particle in a box are:

$$\psi_{n_x n_y n_z}(x, y, z) = \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2} \right)$$

where we have used the solutions for the 1-dimensional particle in a box. The transition from state (n_x, n_y, n_z) to state (n'_x, n'_y, n'_z) is dipole allowed if

$$\begin{aligned} 0 \neq \langle \psi_{n'_x n'_y n'_z} | x | \psi_{n_x n_y n_z} \rangle &= \int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} \int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} \psi_{n'_x n'_y n'_z}(x, y, z) x \psi_{n_x n_y n_z}(x, y, z) dz dy dx \\ &= \frac{8}{a_x a_y a_z} \int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} x \psi_{n_x}(x) \psi_{n'_x}(x) dx \int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \psi_{n_y}(y) \psi_{n'_y}(y) dy \int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} \psi_{n_z}(z) \psi_{n'_z}(z) dz \\ &= \frac{8}{a_x a_y a_z} \underbrace{\left[\int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} x \psi_{n_x}(x) \psi_{n'_x}(x) dx \right]}_{\substack{f(x)=x \text{ is an odd function} \\ \psi_{n_x}(x) \text{ is odd if } n_x \text{ is even} \\ \text{and even if } n_x \text{ is odd.}}} \underbrace{\left[\int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \psi_{n_y}(y) \psi_{n'_y}(y) dy \right]}_{\substack{\text{zero unless } n_y = n'_y \text{ because eigenvectors} \\ \text{are orthogonal}}} \underbrace{\left[\int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} \psi_{n_z}(z) \psi_{n'_z}(z) dz \right]}_{\substack{\text{zero unless } n_z = n'_z \text{ because eigenvectors} \\ \text{are orthogonal}}} \\ &= \frac{8}{a_x a_y a_z} (\text{zero unless } n_x + n'_x \text{ is odd}) (\text{zero unless } n_y = n'_y) (\text{zero unless } n_z = n'_z) \end{aligned}$$

This allows us to write the energy of the allowed transitions as:

$$\begin{aligned}
E_{n'_x n'_y n'_z} - E_{n_x n_y n_z} &= \frac{h^2}{8m} \left(\frac{n'^2_x}{a_x^2} + \frac{n'^2_y}{a_y^2} + \frac{n'^2_z}{a_z^2} \right) - \frac{h^2}{8m} \left(\frac{n^2_x}{a_x^2} + \frac{n^2_y}{a_y^2} + \frac{n^2_z}{a_z^2} \right) \\
&= \frac{h^2}{8ma_x^2} \left((n'_x)^2 - n_x^2 \right) & n'_x = n_x + 1, n_x + 3, \dots \\
&= \frac{h^2}{8ma_x^2} \left((n_x + k)^2 - n_x^2 \right) & k = 1, 3, 5, \dots \\
&= \frac{h^2}{8ma_x^2} (2kn_x + k^2) & k = 1, 3, 5, \dots; n_x = 1, 2, 3, \dots
\end{aligned}$$

The frequencies of the allowed transitions are:

$$\begin{aligned}
\omega_{fi} &= \frac{E_{n'_x n'_y n'_z} - E_{n_x n_y n_z}}{\hbar} \\
&= \frac{h^2}{\hbar 8ma_x^2} (2kn_x + k^2) & k = 1, 3, 5, \dots; n_x = 1, 2, 3, \dots \\
&= \frac{2\pi h}{8ma_x^2} (2kn_x + k^2) & k = 1, 3, 5, \dots; n_x = 1, 2, 3, \dots
\end{aligned}$$

(b) The transition from state (n_x, n_y, n_z) to state (n'_x, n'_y, n'_z) is quadrupole allowed if

$$\begin{aligned}
0 &\neq \langle \psi_{n'_x n'_y n'_z} | xz | \psi_{n_x n_y n_z} \rangle = \int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} \int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} \psi_{n'_x n'_y n'_z}(x, y, z) xz \psi_{n_x n_y n_z}(x, y, z) dz dy dx \\
&= \frac{8}{a_x a_y a_z} \int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} \int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} xz \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z) \psi_{n'_x}(x) \psi_{n'_y}(y) \psi_{n'_z}(z) dz dy dx \\
&= \frac{8}{a_x a_y a_z} \underbrace{\left[\int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} x \psi_{n_x}(x) \psi_{n'_x}(x) dx \right]}_{\substack{f(x)=x \text{ is an odd function} \\ \psi_{n_x}(x) \text{ is odd if } n_x \text{ is even} \\ \text{and even if } n_x \text{ is odd.}}} \underbrace{\left[\int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \psi_{n_y}(y) \psi_{n'_y}(y) dy \right]}_{\substack{\text{zero unless } n_y = n'_y \text{ because eigenvectors} \\ \text{are orthogonal}}} \underbrace{\left[\int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} z \psi_{n_z}(z) \psi_{n'_z}(z) dz \right]}_{\substack{f(z)=z \text{ is an odd function} \\ \psi_{n_z}(z) \text{ is odd if } n_z \text{ is even} \\ \text{and even if } n_z \text{ is odd.}}} \\
&= \frac{8}{a_x a_y a_z} (\text{zero unless } n_x + n'_x \text{ is odd}) (\text{zero unless } n_y = n'_y) (\text{zero unless } n_z + n'_z \text{ is odd})
\end{aligned}$$

and so

$$\begin{aligned}
E_{n'_x n'_y n'_z} - E_{n_x n_y n_z} &= \frac{h^2}{8m} \left(\frac{n'^2_x}{a_x^2} + \frac{n'^2_y}{a_y^2} + \frac{n'^2_z}{a_z^2} \right) - \frac{h^2}{8m} \left(\frac{n^2_x}{a_x^2} + \frac{n^2_y}{a_y^2} + \frac{n^2_z}{a_z^2} \right) \\
&= \frac{h^2}{8m} \left(\frac{(n_x + k_x)^2 - n_x^2}{a_x^2} + \frac{(n_z + k_z)^2 - n_z^2}{a_z^2} \right) & k_x, k_z = 1, 3, 5, \dots \\
&= \frac{h^2}{8m} \left(\frac{2n_x k_x + k_x^2}{a_x^2} + \frac{2n_z k_z + k_z^2}{a_z^2} \right) & k_x, k_z = 1, 3, 5, \dots \\
& & n_x, n_z = 1, 2, 3, \dots
\end{aligned}$$

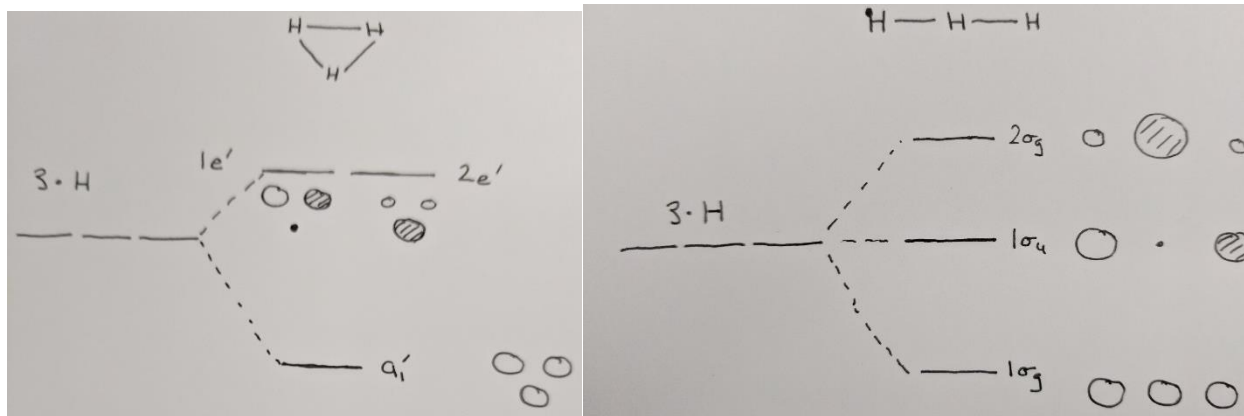
and finally

$$\omega_{fi} = \frac{2\pi\hbar}{8m} \left(\frac{2n_x k_x + k_x^2}{a_x^2} + \frac{2n_z k_z + k_z^2}{a_z^2} \right) \quad \begin{array}{l} k_x, k_z = 1, 3, 5, \dots \\ n_x, n_z = 1, 2, 3, \dots \end{array}$$

(c) Quadrupole transitions are only allowed when the long-wavelength approximation is imperfect, and they occur at a rate approximately λ^{-2} smaller than dipole-allowed transitions. For all typical transitions, this will be true. For example, a typical “particle-in-a-box” system with absorbance frequencies in the visible region (wavelength in the hundreds of nanometers) has a size of at most a few nanometers (hundreds of times smaller than the typical wavelength).

6. H₃, revisited.

The molecular orbital diagrams for the H₃ molecule, in both its linear and cyclic geometry, are listed below.



The integrals that you will need are:

$$\left\langle \psi_{1s}^{(A)} \left| -\frac{1}{2} \nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r}) \right| \psi_{1s}^{(A)} \right\rangle = -\frac{1}{2}$$

$$\left\langle \psi_{1s}^{(A)} \left| -\frac{1}{2} \nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r}) \right| \psi_{1s}^{(B)} \right\rangle = \begin{cases} -\frac{1}{20} \\ 0 \end{cases}$$

A and B are bonded
otherwise

all other integrals are zero

I will tell you that the molecular orbitals for linear H₃ are:

$$\left| \psi_{1\sigma_g} \right\rangle = \frac{1}{2} \left| \psi_{1s}^A \right\rangle + \frac{1}{\sqrt{2}} \left| \psi_{1s}^B \right\rangle + \frac{1}{2} \left| \psi_{1s}^C \right\rangle$$

$$\left| \psi_{1\sigma_u} \right\rangle = \frac{1}{\sqrt{2}} \left| \psi_{1s}^A \right\rangle - \frac{1}{\sqrt{2}} \left| \psi_{1s}^C \right\rangle$$

$$\left| \psi_{2\sigma_g} \right\rangle = \frac{1}{2} \left| \psi_{1s}^A \right\rangle - \frac{1}{\sqrt{2}} \left| \psi_{1s}^B \right\rangle + \frac{1}{2} \left| \psi_{1s}^C \right\rangle$$

(a) What is the energy of neutral linear H₃?

(b) What is the energy of neutral cyclic H₃?

(c) Suppose one changes one of the Hydrogen atoms for a Helium atom in linear H₃. This has the effect of changing one of the integrals above.

$$\left\langle \psi_{1s}^{(\text{He})} \left| -\frac{1}{2} \nabla^2 + v_A(\mathbf{r}) + v_B(\mathbf{r}) + v_C(\mathbf{r}) \right| \psi_{1s}^{(\text{He})} \right\rangle = -\frac{9}{10}$$

(To a good approximation, none of the other integrals change.) **Is it better to add a Helium atom on the end of the linear molecule or at the middle of the linear molecule?**

(a) The eigenvalues of the linear problem will be split equally “above” and “below” the Hydrogenic energy of -1/2. That is, $E_{1\sigma_g} = -\frac{1}{2} - a$, $E_{1\sigma_u} = -\frac{1}{2}$, $E_{2\sigma_g} = -\frac{1}{2} + a$. The Hamiltonian matrix has the form,

$$\mathbf{H} = \begin{bmatrix} -\frac{1}{2} & -\frac{1}{20} & 0 \\ -\frac{1}{20} & -\frac{1}{2} & -\frac{1}{20} \\ 0 & -\frac{1}{20} & -\frac{1}{2} \end{bmatrix}$$

And we can evaluate a by looking at either of the two states. Choosing the ground state I have

$$\begin{aligned}\varepsilon_{1\sigma_g} &\equiv \mathbf{c}^T \mathbf{H} \mathbf{c} = \begin{bmatrix} \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & -\frac{1}{20} & 0 \\ -\frac{1}{20} & -\frac{1}{2} & -\frac{1}{20} \\ 0 & -\frac{1}{20} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} \frac{1}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{bmatrix} \\ &= \begin{bmatrix} \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{bmatrix} \begin{bmatrix} -\frac{1}{4} - \frac{1}{20\sqrt{2}} \\ -\frac{1}{40} - \frac{1}{2\sqrt{2}} - \frac{1}{40} \\ -\frac{1}{20\sqrt{2}} - \frac{1}{4} \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{bmatrix} \begin{bmatrix} -.2854 \\ -.4036 \\ -.2854 \end{bmatrix} = -.5708\end{aligned}$$

There are two electrons in this orbital and 1 in the nonbonding orbital. So the total energy is:

$$2\varepsilon_{1\sigma_g} + 1\varepsilon_{1\sigma_u} = 2(-.5708) + 1(-.5) = -1.6416$$

(b) From problem 17, the energy of the neutral (now only 3 electrons) is

$$E = 2(-.6) + (-.45) = -1.65$$

It is curious that in fact, experimentally, the linear molecule is more stable. That is already a sign that the approximations in this problem are too strong.

(c) There are several ways to do this. One is to evaluate the eigenvalues of the different Hamiltonians,

$$\begin{aligned}H_{\text{He-on-end}} &= \mathbf{H} = \begin{bmatrix} -\frac{9}{10} & -\frac{1}{20} & 0 \\ -\frac{1}{20} & -\frac{1}{2} & -\frac{1}{20} \\ 0 & -\frac{1}{20} & -\frac{1}{2} \end{bmatrix} \rightarrow -2.906 \\ H_{\text{He-in-middle}} &= \mathbf{H} = \begin{bmatrix} -\frac{1}{2} & -\frac{1}{20} & 0 \\ -\frac{1}{20} & -\frac{9}{10} & -\frac{1}{20} \\ 0 & -\frac{1}{20} & -\frac{1}{2} \end{bmatrix} \rightarrow -2.824\end{aligned}$$

This is difficult to do other than numerically (which is what I did above). However, you can also use perturbation theory. In that case, you just have to evaluate the change in the orbital energies due to changing the Hamiltonian, assuming that the orbitals do not change. That can also be done, and it is quite easy if one writes the problem as:

$$\begin{aligned}\varepsilon &= \mathbf{c}^T \mathbf{H}_{\text{He}} \mathbf{c} = \mathbf{c}^T (\mathbf{H}_0 + \mathbf{V}) \mathbf{c} = \mathbf{c}^T \mathbf{H}_0 \mathbf{c} + \mathbf{c}^T \mathbf{V} \mathbf{c} \\ \varepsilon &= \varepsilon_0 + \mathbf{c}^T \begin{bmatrix} -\frac{4}{10} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \mathbf{c} && (\text{He on end}) \\ \varepsilon &= \varepsilon_0 + \mathbf{c}^T \begin{bmatrix} 0 & 0 & 0 \\ 0 & -\frac{4}{10} & 0 \\ 0 & 0 & 0 \end{bmatrix} \mathbf{c} && (\text{He in middle})\end{aligned}$$

Using this, I have (remember that there are now 4 electrons!) for the He-on-end case:

$$\begin{aligned}
 E_{\text{He-on-end}} &= 2\left(\varepsilon_{1\sigma_g}^{\text{H}_3} + \left(-\frac{4}{10}\right)\left(\frac{1}{2}\right)^2\right) + 2\left(\varepsilon_{1\sigma_u}^{\text{H}_3} + \left(-\frac{4}{10}\right)\left(\frac{1}{2}\right)\right) \\
 &= 2\left(-.5708 - \frac{1}{10}\right) + 2\left(-.5 - .2\right) \\
 &= -2.7416
 \end{aligned}$$

$$\begin{aligned}
 E_{\text{He-in-middle}} &= 2\left(\varepsilon_{1\sigma_g}^{\text{H}_3} + \left(-\frac{4}{10}\right)\left(\frac{1}{\sqrt{2}}\right)^2\right) + 2\left(\varepsilon_{1\sigma_u}^{\text{H}_3} + \left(-\frac{4}{10}\right) \cdot 0^2\right) \\
 &= 2\left(-.5708 - .2\right) + 2\left(-.5\right) \\
 &= -2.5416
 \end{aligned}$$

While the energies are not at all accurate, the trend (adding the He on the end is better than adding it in the middle) is clear. This, in fact, could have been deduced from the picture of the orbitals: the unoccupied orbital is mostly in the middle, and He stabilizes the site it sits on. Stabilizing the *unoccupied* orbital is not the effect one wants: one wants to stabilize the occupied orbital, which means it is most favorable to add the Helium atom on the ends of the molecule.