

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. The exam is marked out of 100 points.

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

19 questions @ 4 points each and 2 (pick of 3) problems @ 12 points each.
Some questions have bonus parts.

Key integrals and identities:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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	$6.62618 \times 10^{-34} \text{ J}\cdot\text{s}$ $1.05459 \times 10^{-34} \text{ J}\cdot\text{s}$
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 $4\pi\epsilon_0$	$8.854188 \times 10^{-12} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$ $1.112650 \times 10^{-10} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
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^{33}
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}
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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

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

$$\begin{aligned}\sin \alpha \sin \beta &= \frac{1}{2} \cos (\alpha - \beta) - \frac{1}{2} \cos (\alpha + \beta) \\ \cos \alpha \cos \beta &= \frac{1}{2} \cos (\alpha - \beta) + \frac{1}{2} \cos (\alpha + \beta) \\ \sin \alpha \cos \beta &= \frac{1}{2} \sin (\alpha + \beta) + \frac{1}{2} \sin (\alpha - \beta) \\ \sin (\alpha \pm \beta) &= \sin \alpha \cos \beta \pm \cos \alpha \sin \beta \\ \cos (\alpha \pm \beta) &= \cos \alpha \cos \beta \mp \sin \alpha \sin \beta\end{aligned}$$

$$\begin{aligned}e^{\pm i\theta} &= \cos \theta \pm i \sin \theta \\ \cos \theta &= \frac{e^{i\theta} + e^{-i\theta}}{2}\end{aligned}$$

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

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

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

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

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

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

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

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

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

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

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

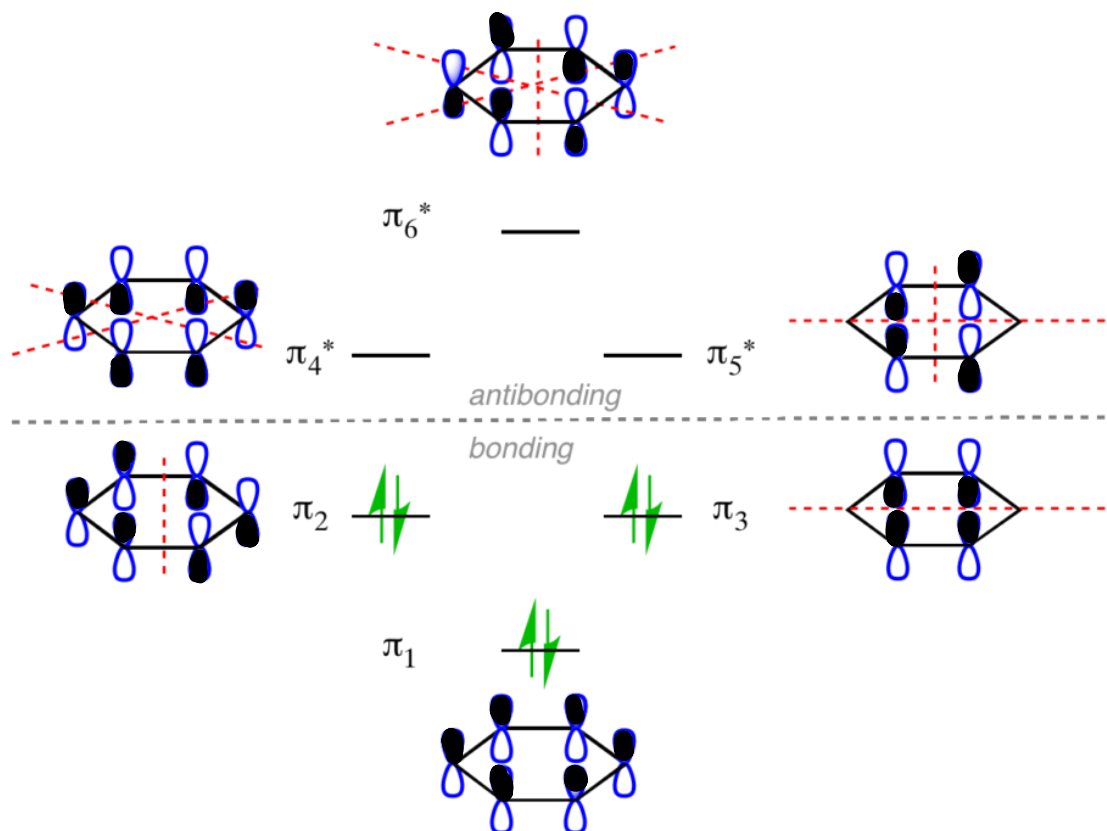
$$\int_0^a \sin \frac{m\pi x}{a} \sin \frac{n\pi x}{a} dx = \int_0^a \cos \frac{m\pi x}{a} \cos \frac{n\pi x}{a} dx = \frac{a}{2} \delta_{mn}$$

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

1. **Write the Hamiltonian for the N -electron P -atom molecule including the dependence on constants like $\hbar, e, \varepsilon_0, m_e, \dots$.**
2. **Write down a Slater determinant for the $1s^2 2s^2$ electron configuration of the Beryllium atom.** Show all rows and columns, and include the normalization factor.
3. **Write down Fermi's Golden Rule in a form suitable for dipole-allowed electronic transitions and explain the meaning of the terms within it.** You can earn **bonus** marks by doing an especially good job of explaining key terms.

4. The π -molecular orbital diagram of benzene is shown below. Starting from the ground state, an excitation of an electron from the π_3 orbital to which of the following orbitals is dipole allowed? (Circle all the answers that are appropriate.)

(a) π_4^* (b) π_5^* (c) π_6^* (d) none of these.



5. Which of the following effects is associated with the long-wavelength approximation being inaccurate? Circle all that apply.

(a) resonance Raman spectroscopy.
 (b) multi-photon processes, where the sum of the photons energies equals the energy of the transition.
 (c) electric quadrupole transitions are observed.
 (d) magnetic dipole transitions are observed.
 (e) light with energy that is slightly different from the transition energy can be absorbed.
 (f) transitions in which the spin of the electron changes are observed.

6,7. Write the electronic and nuclear Schrödinger equations for the H_3^+ molecule (hydrogen trimer cation). You can use atomic units. Label the 3 hydrogen atoms as A, B, and C.

8. What would be the ground state electronic wavefunction and energy for the H_3^+ molecule in the united atom limit in the absence of electron-electron repulsion?

9. What would be a ground state electronic wavefunction and energy for the H_3^+ molecule in the separated-atom limit. [There are several choices; you only need to list one.] (In the separated atom limit, *all* the atoms are infinitely far from each other.)

BONUS: What is the degeneracy of the ground state of H_3^+ in the separated atom limit.

The force constant for $^1\text{H}^{35}\text{Cl}$ (note the isotope labels) is 517 N/m. Recall that $1 \text{ N} = \text{kg}\cdot\text{m}\cdot\text{s}^{-2}$.

10. What is the wavenumber, $\bar{\nu} = 1/\lambda$, associated with lowest-energy vibrational transition (to two significant figures)?

- | | | |
|---------------------------|----------------------------|----------------------------|
| (a) 100 cm^{-1} | (d) 1000 cm^{-1} | (g) 3000 cm^{-1} |
| (b) 200 cm^{-1} | (e) 2000 cm^{-1} | (h) 5000 cm^{-1} |
| (c) 500 cm^{-1} | (f) 2500 cm^{-1} | (i) none of the above |

11. The wavenumber, $\bar{\nu} = 1/\lambda$, associated with the first vibrational transition in $^3\text{H}^{37}\text{Cl}$ is _____ times the wavenumber associated with the corresponding vibrational transition in $^1\text{H}^{35}\text{Cl}$ (to within the significant figures shown)?

- | | | |
|-------------------|---------|---------|
| (a) 1 (unchanged) | (d) 0.6 | (g) 1.7 |
| (b) 0.3 | (e) 0.7 | (h) 2 |
| (c) 0.5 | (f) 1.4 | (i) 3 |

12. What is the momentum of a photon with wavelength 600 nm?

13. Some physicists think that the universe has 10 spatial dimensions. **How many quantum numbers would be required to specify the state of four (noninteracting) electrons bound in an 10-dimensional harmonic potential?**

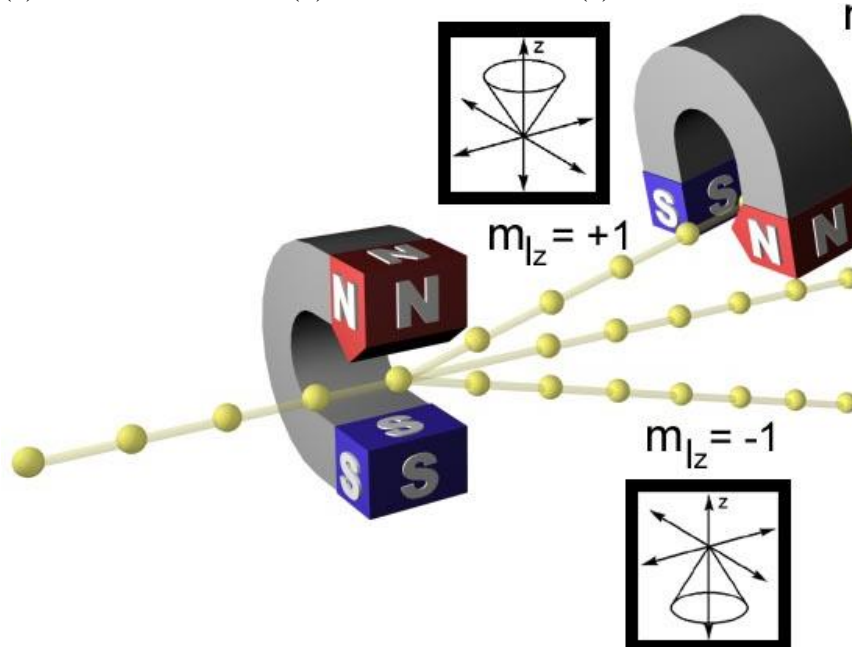
14. The ground-state term symbol for the Promethium atom is ^6H . The electron configuration of Promethium is $[\text{Xe}]6s^24f^5$ **What are the possible values of the J quantum number of Promethium? Circle the J value that is predicted to be lowest in energy according to Hund's Rules.**

15. Which of the following expressions are equal to $-i\hbar\hat{L}_y$? Circle all that apply.

- (a) $[\hat{L}_z, \hat{S}_x]$
- (b) $[\hat{L}_x, \hat{L}_z]$
- (c) $[\hat{L}_y, \hat{L}_z]$
- (d) $[\hat{L}_y, \hat{L}_x]$
- (e) $[\hat{J}_x, \hat{L}_z]$
- (f) $[\hat{L}_z, \hat{J}_x]$
- (g) $[\hat{J}_x, \hat{J}_z] + [\hat{S}_z, \hat{S}_x]$
- (h) $[\hat{J}_x, \hat{J}_z] + [\hat{L}_z, \hat{L}_x]$

16. In the following Stern-Gerlach experiment, how many beams (corresponding to the different possible M_J values) do you expect to see emerge from the right-most magnet, which is assumed to be perpendicular to the first (left-most magnet)? The atom that passes through the apparatus is in the 1P state.

- (a) one
- (b) two
- (c) three
- (d) six
- (e) nine



17. As we discussed earlier in the course, sometimes the simple one-dimensional particle-in-a-box model can be improved by adding harmonic confinement of electrons in the other dimensions. Consider an electron described by the following Hamiltonian (in atomic units):

$$\hat{H} \equiv -\frac{1}{2} \nabla_1^2 + V_{\text{p-in-box}}(x_1) + y_1^2 + z_1^2$$

where the box-length is 6 atomic units,

$$V_{\text{p-in-box}}(x) = \begin{cases} 0 & 0 \leq x \leq 6 \text{ a.u.} \\ +\infty & \text{otherwise} \end{cases}$$

All the constants are given in atomic units ($\hbar = m_e = 1$). Recall that the Hamiltonian and wavefunctions for the harmonic oscillator are:

$$\begin{aligned} \hat{H}_{\text{harmonic-oscillator}} &= -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \\ \psi_0(x) &= \left(\frac{k\mu}{\pi^2 \hbar^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k\mu}{4\hbar^2}} \right)} \\ \psi_1(x) &= \left(\frac{k\mu}{\pi^2 \hbar^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k\mu}{4\hbar^2}} \right)} \left(2x \left(\frac{k\mu}{4\hbar^2} \right)^{1/4} \right) \end{aligned}$$

What is the ground-state energy and wavefunction for the system with Hamiltonian

$$\hat{H} \equiv -\frac{1}{2} \nabla_1^2 + V_{\text{p-in-box}}(x_1) + y_1^2 + z_1^2 ?$$

Note: Writing the mathematical form of the particle in the box wavefunction is expected in this problem. Use atomic units to compute your answer.

18. A muon has the same spin and charge as an electron, but weights 207 times more. Suppose that the Born-Oppenheimer approximation is more-or-less valid anyway. **What would be the ground-state energy and wavefunction for a system consisting of the (a) the neon nucleus ($Z=10$) and (b) one muon?**

19. **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.

Orbital Symmetry Label	Molecular Orbital
	$\psi_{3d_{xz}}^{(l)}(\mathbf{r}) + \psi_{3d_{xz}}^{(r)}(\mathbf{r})$
	$\psi_{2p_z}^{(l)}(\mathbf{r}) - \psi_{2p_z}^{(r)}(\mathbf{r})$

Pick 2 of the following 3 problems. (12 points each)

If you work all 3 problems, the last counts as a 6-point bonus.

- 1. The electron configuration for the ground state of the Copper atom is $[\text{Ar}]4s^13d^{10}$. What are the term symbols for the excited state of the Copper atom with electron configuration $[\text{Ar}]4s^13d^94p^1$? Circle the term symbols that have a dipole-allowed transition to the ground state of the Copper atom.**

2. Recall that the Hamiltonian and wavefunctions for an electron bound in a harmonic well are, in atomic units:

$$\hat{H}_{\text{harmonic-oscillator}} = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$$

$$\psi_0(x) = \left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}} \right)}$$

$$\psi_1(x) = \left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}} \right)} \left(2x \left(\frac{k}{4} \right)^{1/4} \right)$$

Consider now an electron bound in the following well, where there is an additional (small) quartic term,

$$\hat{H}_{\text{ho+quartic}} = -\frac{1}{2} \frac{d^2}{dx^2} + 2x^2 + \frac{1}{10} x^4$$

Give an upper and lower bound to the energy for the Hamiltonian on the previous line.

BONUS (up to 12 points): Use the variational principle to provide a more accurate estimation of the energy for the quartic-perturbed harmonic oscillator. You may not be able to work out all the math, but go as far as you can.

3. The Morse potential is often used as an approximate model for the vibrations of diatomic molecules. In convenient units where $\frac{\hbar^2}{2m} = 1$, the time-independent Schrödinger equation for a Morse oscillator can be written as

$$\left(-\frac{d^2}{dx^2} + \lambda^2 (e^{-2x} - 2e^{-x}) \right) \psi_n(x) = E_n \psi_n(x)$$

The first two eigenfunctions of the Morse oscillator are given by the following expressions (which are not normalized)

$$\psi_0(x) = \exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right)$$

$$\psi_1(x) = \exp\left(-\left(\lambda - \frac{3}{2}\right)x - \lambda e^{-x}\right) (2\lambda - 2 - 2\lambda e^{-x})$$

What is the ground-state energy for the Morse oscillator?

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SOME MATHEMATICAL FORMULAS

Paul

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1. Write the Hamiltonian for the N -electron P -atom molecule including the dependence on constants like $\hbar, e, \epsilon_0, m_e, \dots$.

$$\hat{H}_{\text{molecule}} = \sum_{i=1}^N -\frac{\hbar^2}{2} \nabla_i^2 + \sum_{\alpha=1}^P -\frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 + \sum_{\alpha=2}^P \sum_{\beta=1}^{\alpha-1} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 |\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} + \sum_{i=2}^P \sum_{j=1}^{i-1} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\alpha=1}^P \sum_{i=1}^N \frac{-Z_{\alpha} e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_{\alpha}|}$$

2. Write down a Slater determinant for the $1s^2 2s^2$ electron configuration of the Beryllium atom. Show all rows and columns, and include the normalization factor.

$$\frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_{1s}(\mathbf{r}_1)\alpha(1) & \psi_{1s}(\mathbf{r}_1)\beta(1) & \psi_{2s}(\mathbf{r}_1)\alpha(1) & \psi_{2s}(\mathbf{r}_1)\beta(1) \\ \psi_{1s}(\mathbf{r}_2)\alpha(2) & \psi_{1s}(\mathbf{r}_2)\beta(2) & \psi_{2s}(\mathbf{r}_2)\alpha(2) & \psi_{2s}(\mathbf{r}_2)\beta(2) \\ \psi_{1s}(\mathbf{r}_3)\alpha(3) & \psi_{1s}(\mathbf{r}_3)\beta(3) & \psi_{2s}(\mathbf{r}_3)\alpha(3) & \psi_{2s}(\mathbf{r}_3)\beta(3) \\ \psi_{1s}(\mathbf{r}_4)\alpha(4) & \psi_{1s}(\mathbf{r}_4)\beta(4) & \psi_{2s}(\mathbf{r}_4)\alpha(4) & \psi_{2s}(\mathbf{r}_4)\beta(4) \end{vmatrix}$$

3. Write down Fermi's Golden Rule and explain the meaning of the terms within it. You can earn bonus marks by doing an especially good job of explaining key terms.

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

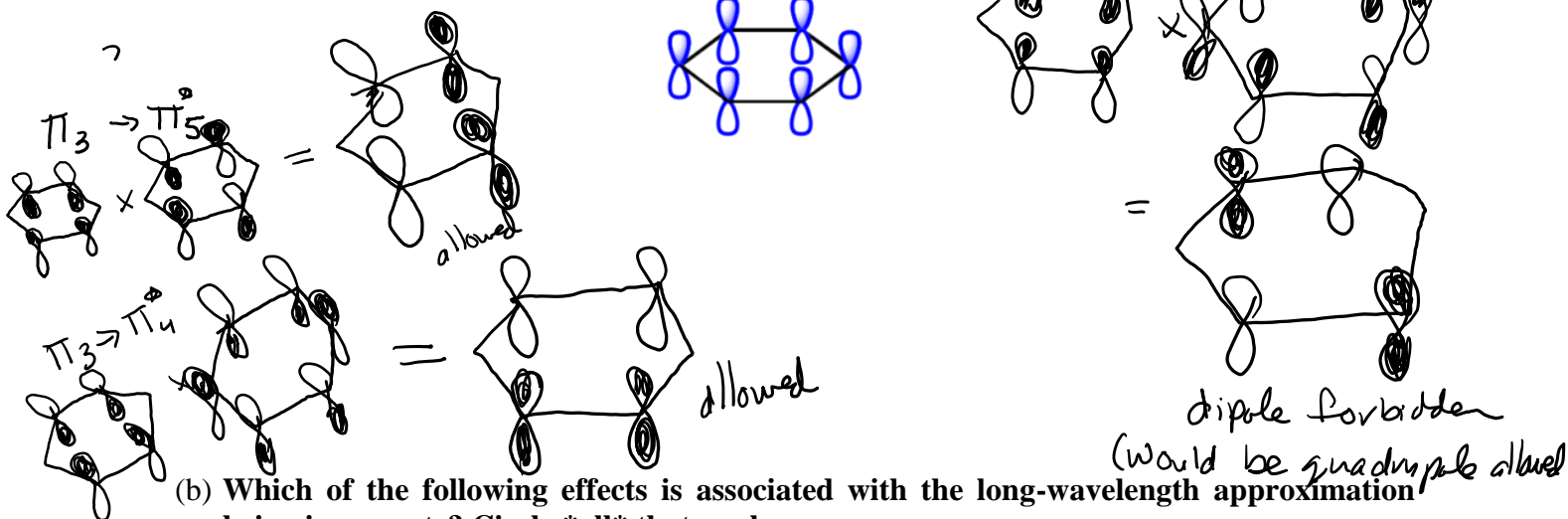
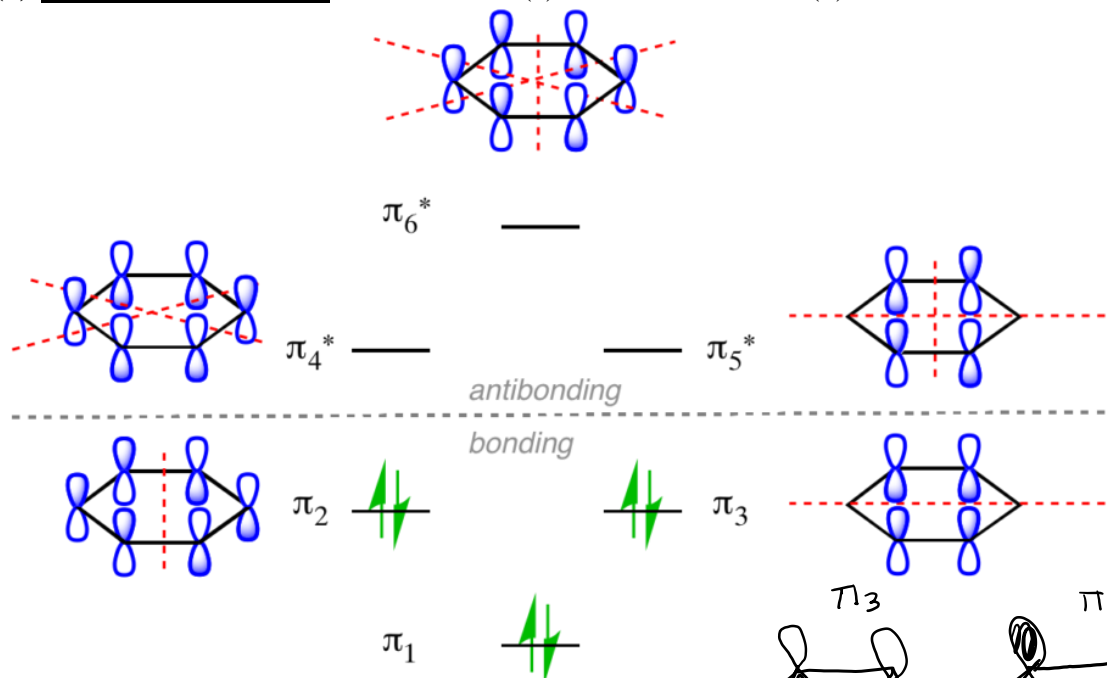
The V is the amplitude of the electric field, or the intensity of the radiation. The stronger the field the higher the rate of transitions.

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.

4. The π -molecular orbital diagram of benzene is shown below. Starting from the ground state, an excitation of an electron from the π_3 orbital to which of the following orbitals is dipole allowed? (Circle all the answers that are appropriate.)

(a) π_4^* (b) π_5^* (c) π_6^* (d) none of these.



- (a) resonance Raman spectroscopy.
 (b) multi-photon processes, where the sum of the photons energies equals the energy of the transition.
 (c) **electric quadrupole transitions are observed.**
 (d) **magnetic dipole transitions are observed.**
 (e) light with energy that is slightly different from the transition energy can be absorbed.
 (f) transitions in which the spin of the electron changes are observed.

6,7. Write the electronic and nuclear Schrödinger equations for the H_3^+ molecule (hydrogen trimer cation). You can use atomic units. Label the 3 hydrogen atoms as A, B, and C.

electronic:

$$\left(\begin{aligned} & -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ & + \frac{1}{|\mathbf{R}_A - \mathbf{R}_B|} + \frac{1}{|\mathbf{R}_A - \mathbf{R}_C|} + \frac{1}{|\mathbf{R}_B - \mathbf{R}_C|} \\ & - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_C|} \\ & - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_C|} \end{aligned} \right) \psi_e(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{R}_A, \mathbf{R}_B, \mathbf{R}_C) = U(\mathbf{R}_A, \mathbf{R}_B, \mathbf{R}_C) \psi_e(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{R}_A, \mathbf{R}_B, \mathbf{R}_C)$$

nuclear:

$$\left(-\frac{1}{2m_H} \nabla_A^2 - \frac{1}{2m_H} \nabla_B^2 - \frac{1}{2m_H} \nabla_C^2 + U(\mathbf{R}_A, \mathbf{R}_B, \mathbf{R}_C) \right) \chi_n(\mathbf{R}_A, \mathbf{R}_B, \mathbf{R}_C) = E_{\text{molecule}} \chi_n(\mathbf{R}_A, \mathbf{R}_B, \mathbf{R}_C)$$

8. What would be the ground-state electronic wavefunction and energy for the H_3^+ molecule in the united atom limit in the absence of electron-electron repulsion?

In the united atom limit, this is like a Lithium atom. The energy of the 2-electron Lithium atom *without* electron-electron repulsion is just twice the energy of the 1-electron Lithium atom. And the wavefunction is the (Slater determinant) of the Lithium 1s orbitals. So

$$E = (2 \text{ electrons}) \left(-\frac{(Z=3)^2}{2(n=1)^2} \right) = -9 \text{ a.u.}$$

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

9. What would be the ground-state electronic wavefunction and energy for the H_3^+ molecule in the separated-atom limit. (In the separated atom limit, *all* the atoms are infinitely far from each other.)

In the separated-atom limit, the ground-state energy is the sum of the hydrogenic energies

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

and the ground-state wavefunction will be some linear combination of the isolated hydrogenic orbitals. The most trivial of these linear combinations just puts one electron on one atom and the other on a different atom. But there are other choices. Two choices would be:

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^A(\mathbf{r}_1) \alpha(1) & \phi_{1s}^B(\mathbf{r}_1) \beta(1) \\ \phi_{1s}^A(\mathbf{r}_2) \alpha(2) & \phi_{1s}^B(\mathbf{r}_2) \beta(2) \end{vmatrix} \text{ and } \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^A(\mathbf{r}_1) \alpha(1) & (\phi_{1s}^B(\mathbf{r}_1) \pm \phi_{1s}^C(\mathbf{r}_1)) \alpha(1) \\ \phi_{1s}^A(\mathbf{r}_2) \alpha(2) & (\phi_{1s}^B(\mathbf{r}_2) \pm \phi_{1s}^C(\mathbf{r}_2)) \alpha(2) \end{vmatrix}$$

BONUS: What is the degeneracy of the ground state of H_3^+ in the separated atom limit.

There are 3 spatial orbitals. You can doubly occupy any of them (3 choices), but due to electron-electron repulsion this is higher in energy than singly-occupying them. Alternatively, you can singly occupy two of them; in that case there are 3 choices (of which orbital to not occupy) and 4 choices (2 choices of spin for each occupied orbital) of how to occupy the singly-occupied orbitals. So there is 12-fold degeneracy. The singlet and triplet are degenerate in the separated-atom limit.

The force constant for $^1\text{H}^{35}\text{Cl}$ (note the isotope labels) is 480 N/m. Recall that $1 \text{ N} = \text{kg}\cdot\text{m}\cdot\text{s}^{-2}$.

10. What is the wavenumber, $\bar{\nu} = 1/\lambda$, associated with lowest-energy vibrational transition?

- (a) 100 cm^{-1} (d) 1000 cm^{-1} (g) **3000 cm^{-1}**
 (b) 200 cm^{-1} (e) 2000 cm^{-1} (h) 5000 cm^{-1}
 (c) 500 cm^{-1} (f) 2500 cm^{-1} (i) none of the above

The energy levels of the harmonic oscillator are

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) = \sqrt{\frac{k}{\mu}}\left(n + \frac{1}{2}\right)$$

$$E_{n+1} - E_{n-1} = \hbar\omega = \hbar\sqrt{\frac{k}{\mu}}$$

$$\Delta E = h\nu = \frac{hc}{\lambda} = \hbar\sqrt{\frac{k}{\mu}} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

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

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = \frac{1}{2.998 \cdot 10^{10} \frac{\text{cm}}{\text{s}}}\sqrt{\frac{517 \frac{\text{kg}}{\text{s}^2}}{\left(\frac{1.35}{36} \text{ u}\right)\left(1.66 \cdot 10^{-27} \frac{\text{kg}}{\text{u}}\right)}} = 3005 \text{ cm}^{-1}$$

11. The wavenumber, $\bar{\nu} = 1/\lambda$, associated with the first vibrational transition in $^3\text{H}^{37}\text{Cl}$ is _____ times the wavenumber associated with the corresponding vibrational transition in $^1\text{H}^{35}\text{Cl}$ (to within the significant figures shown)?

- (a) 1 (unchanged) (d) 0.6 (g) **1.7**
 (b) 0.3 (e) 0.7 (h) 2
 (c) 0.5 (f) 1.4 (i) 3

It's clear from #10 that $\bar{\nu}(\mu) \propto \mu^{-1/2}$ so $\bar{\nu}_{^3\text{H}^{37}\text{Cl}} = \bar{\nu}_{^1\text{H}^{35}\text{Cl}} \sqrt{\frac{\mu_{^1\text{H}^{35}\text{Cl}}}{\mu_{^3\text{H}^{37}\text{Cl}}}} = \sqrt{\frac{37 \cdot 3}{37 + 3} \cdot \frac{35 \cdot 1}{35 + 1}} = 1.689 \cdot \bar{\nu}_{^1\text{H}^{35}\text{Cl}}$

12. What is the momentum of a photon with wavelength 662 nm?

$$p = \frac{h}{\lambda} = \frac{6.626 \cdot 10^{-34} \frac{\text{kg}\cdot\text{m}^2}{\text{s}}}{662 \cdot 10^{-9} \text{ m}} = 1.00 \cdot 10^{-27} \frac{\text{kg}\cdot\text{m}}{\text{s}}$$

13. Some physicists think that the universe has 10 spatial dimensions. **How many quantum numbers would be required to specify the state of four (noninteracting) electrons bound in an 10-dimensional harmonic potential?**

There are 4 electrons times 10 dimensions so 40-fold degeneracy (plus spin for 80-fold degen.).

15. The ground-state term symbol for the Promethium atom is ^6H . The electron configuration of Promethium is $[\text{Xe}]6s^2 4f^5$ **What are the possible values of the J quantum number of Promethium? Circle the J value that is predicted to be lowest in energy according to Hund's Rules.**

This is $S = 5/2$ and $L = 5$. So the possible J values are

$J =$ **5/2**, 7/2, 9/2, 11/2, 13/2, and 15/2. Since the shell is less than half-filled the lowest energy is the lowest J, 5/2.

15. Which of the following expressions are equal to $-i\hbar\hat{L}_y$? Circle all that apply.

(a) $[\hat{L}_z, \hat{S}_x] = 0$

(b) $[\hat{L}_x, \hat{L}_z] = -[\hat{L}_z, \hat{L}_x] = -i\hbar\hat{L}_y$

(c) $[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$

(d) $[\hat{L}_y, \hat{L}_x] = -i\hbar\hat{L}_z$

(e) $[\hat{J}_x, \hat{L}_z] = [\hat{L}_x + \hat{S}_x, \hat{L}_z] = [\hat{L}_x, \hat{L}_z] + [\hat{S}_x, \hat{L}_z] = -i\hbar\hat{L}_y + 0$

(f) $[\hat{L}_z, \hat{J}_x] = -[\hat{J}_x, \hat{L}_z] = +i\hbar\hat{L}_y$

(g) $[\hat{J}_x, \hat{J}_z] + [\hat{S}_z, \hat{S}_x] = -i\hbar\hat{J}_y + i\hbar\hat{S}_y = -i\hbar(\hat{L}_y + \hat{S}_y) + i\hbar\hat{S}_y = -i\hbar\hat{L}_y$

(h) $[\hat{J}_x, \hat{J}_z] + [\hat{L}_z, \hat{L}_x] = -i\hbar\hat{J}_y + i\hbar\hat{L}_y = -i\hbar(\hat{L}_y + \hat{S}_y) + i\hbar\hat{L}_y = -i\hbar\hat{S}_y$

16. In the following Stern-Gerlach experiment, how many spots (corresponding to the different possible M_J values) do you expect to see on the screen?

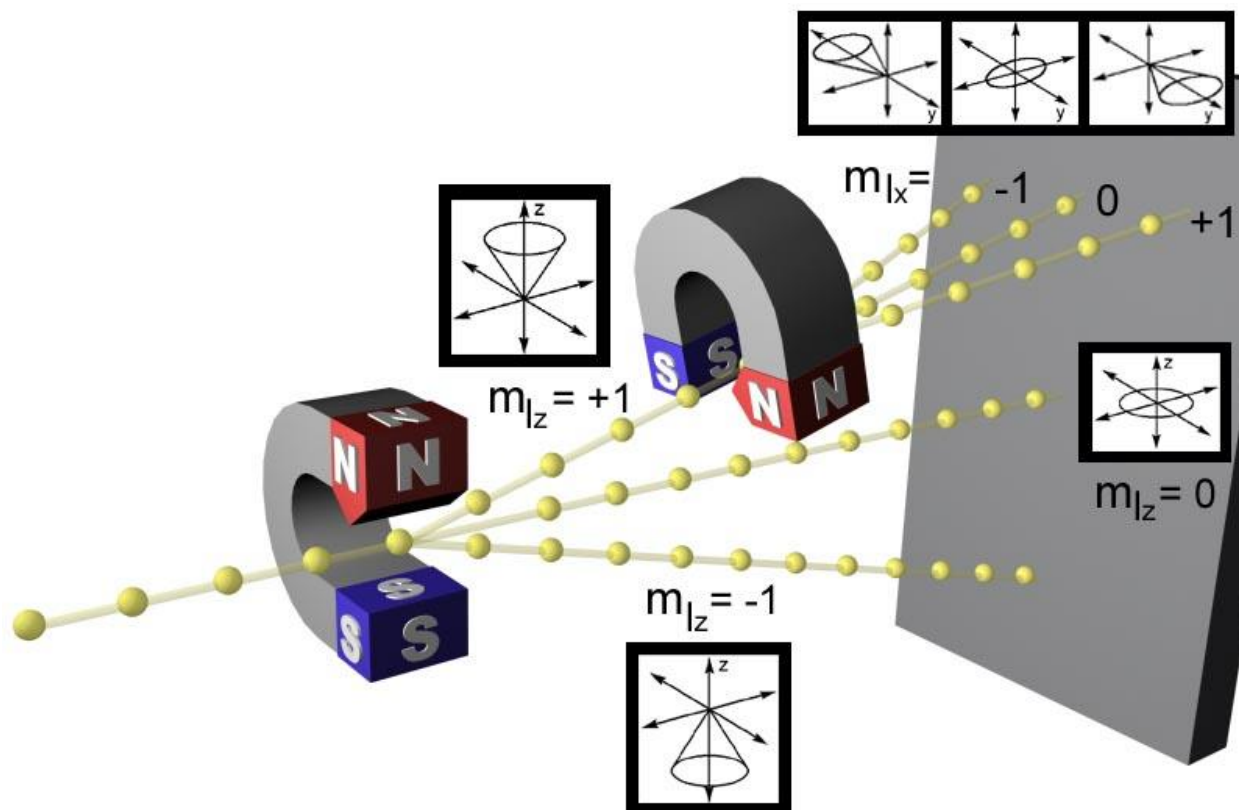
(a) one

(b) two

(c) three

(d) six

(e) nine



17. As we discussed earlier in the course, sometimes the simple one-dimensional particle-in-a-box model can be improved by adding harmonic confinement of electrons in the other dimensions. Consider an electron described by the following Hamiltonian (in atomic units):

$$\hat{H} \equiv -\frac{1}{2} \nabla_1^2 + V_{\text{p-in-box}}(x_1) + y_1^2 + z_1^2$$

where the box-length is 6 atomic units,

$$V_{\text{p-in-box}}(x) = \begin{cases} 0 & 0 \leq x \leq 6 \text{ a.u.} \\ +\infty & \text{otherwise} \end{cases}$$

All the constants are given in atomic units ($\hbar = m_e = 1$). Recall that the Hamiltonian and wavefunctions for the harmonic oscillator are:

$$\begin{aligned} \hat{H}_{\text{harmonic-oscillator}} &= -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \\ \psi_0(x) &= \left(\frac{k\mu}{\pi^2 \hbar^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k\mu}{4\hbar^2}} \right)} \\ \psi_1(x) &= \left(\frac{k\mu}{\pi^2 \hbar^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k\mu}{4\hbar^2}} \right)} \left(2x \left(\frac{k\mu}{4\hbar^2} \right)^{1/4} \right) \end{aligned}$$

What is the ground-state energy and wavefunction for the system with Hamiltonian

$$\hat{H} \equiv -\frac{1}{2} \nabla_1^2 + V_{\text{p-in-box}}(x_1) + y_1^2 + z_1^2 ?$$

This is a sum of exactly-solvable Hamiltonians, so the wavefunction is the product of the wavefunctions of each term in the sum,

$$\begin{aligned} \psi &= \left(\sqrt{\frac{2}{(6 \text{ a.u.})}} \sin\left(\frac{\pi x}{6 \text{ a.u.}}\right) \right) \left(\left(\frac{(2)(1)}{\pi^2 (1)^2} \right)^{1/8} e^{-\left(y^2 \sqrt{\frac{2}{4}} \right)} \left(\frac{(2)(1)}{\pi^2 (1)^2} \right)^{1/8} e^{-\left(z^2 \sqrt{\frac{2}{4}} \right)} \right) \\ &= \left(\frac{1}{3} \right)^{1/2} \left(\frac{2}{\pi^2} \right)^{1/4} \sin\left(\frac{\pi x}{6}\right) \exp\left(-\frac{y^2 + z^2}{\sqrt{2}}\right) \end{aligned}$$

and the energy is the sum of the energies of the terms in the sum,

$$\begin{aligned} E_{n_x, n_y, n_z} &= \frac{\hbar^2 n_x^2}{8m_e a^2} + \hbar \omega \left(n_y + \frac{1}{2} \right) + \hbar \omega \left(n_z + \frac{1}{2} \right) \\ &= \frac{(2\pi)^2 \hbar^2 n_x^2}{8m_e (6 \text{ a.u.})^2} + \hbar \sqrt{\frac{k}{m_e}} (n_x + n_y + 1) \\ &= \frac{(2\pi)^2 n_x^2}{288} + \sqrt{2} (n_x + n_y + 1) \end{aligned}$$

In the last line I introduced atomic units. The ground state is

$$E_{g.s.} = E_{100} = \frac{(2\pi)^2}{288} + \sqrt{2} (1) = 1.55 \text{ a.u.}$$

18. A muon has the same spin and charge as an electron, but weights 207 times more. Suppose that the Born-Oppenheimer approximation is more-or-less valid anyway. **What would be the ground-state energy and wavefunction for a system consisting of the (a) the neon nucleus ($Z=10$) and (b) one muon?**

The Schrodinger equation, in atomic units, is

$$\left(-\frac{1}{2(207)}\nabla^2 - \frac{10}{r}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Multiply both sides by 207, which gives a form that looks like a hydrogen atom, but with atomic charge of 2070,

$$\left(-\frac{1}{2}\nabla^2 - \frac{2070}{r}\right)\psi(\mathbf{r}) = (207 \cdot E)\psi(\mathbf{r})$$

The ground-state wavefunction then looks like the hydrogenic wavefunction with nuclear charge 2070,

$$\psi_{g.s.} = \sqrt{\frac{2070^3}{\pi}} e^{-2070r}$$


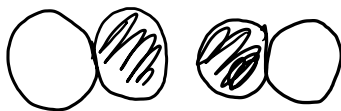
The eigenenergies are then

$$207E_n = \frac{-(2070)^2}{2n^2}$$

and the ground-state energy is:

$$E_{g.s.} = -10350 \text{ a.u.}$$

19. **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.

Orbital Symmetry Label	Molecular Orbital
π_g^+	$\psi_{3d_{xz}}^{(l)}(\mathbf{r}) + \psi_{3d_{xz}}^{(r)}(\mathbf{r})$ 
σ_g^+	$\psi_{2p_z}^{(l)}(\mathbf{r}) - \psi_{2p_z}^{(r)}(\mathbf{r})$ 

Pick 2 of the following 3 problems. (12 points each)

If you work all 3 problems, the last counts as a 6-point bonus.

1. The electron configuration for the ground state of the Copper atom is $[\text{Ar}]4s^13d^{10}$. What are the term symbols for the excited state of the Copper atom with electron configuration $[\text{Ar}]4s^13d^94p^1$? Circle the term symbols that have a dipole-allowed transition to the ground state of the Copper atom.

The ground state term symbol for the Copper atom with electron configuration $[\text{Ar}]4s^13d^{10}$ is 2S ($S=1/2$, $L=0$). For the copper atom in this excited state, we will work in order. We first form the states corresponding to the $4s^13d^9$ configuration. Since there is only one hole in the d shell, this is equivalent to the $4s^13d^1$ configuration. That is, we are coupling states with $S=1/2$, $L=0$ and $S=1/2$, $L=2$. The resulting state has $L=2$ and $S=\{0,1\}$.

Next we couple the $4s^13d^1$ electrons to the $4p^1$ electron. We have

$$S_1 = \{0, 1\}; S_2 = \{\frac{1}{2}\} \rightarrow S_{\text{final}} = \{\frac{1}{2}, \frac{1}{2}, \frac{3}{2}\}$$

$$L_1 = \{2\}; L_2 = \{1\} \rightarrow L_{\text{final}} = \{1, 2, 3\}$$

So the terms (keeping in mind that there are multiple terms with the same label) are

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

E1-allowed
transitions
to the ground
state

For the allowed transition, the excited state must be a doublet (spin cannot change) and since $L=0$ to $L'=0$ transitions are not allowed, the excited state must have $L=1$. So the allowed transitions come from the 2P terms. (The excitation is from a d to a p orbital, and so the angular momentum of the excited electron changes by one unit, and is allowed.)

2. Recall that the Hamiltonian and wavefunctions for an electron bound in a harmonic well are, in atomic units:

$$\hat{H}_{\text{harmonic-oscillator}} = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$$

$$\psi_0(x) = \left(\frac{k}{\pi^2}\right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)}$$

$$\psi_1(x) = \left(\frac{k}{\pi^2}\right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \left(2x \left(\frac{k}{4}\right)^{1/4}\right)$$

Consider now an electron bound in the following well, where there is an additional (small) quartic term,

$$\hat{H}_{\text{ho+quartic}} = -\frac{1}{2} \frac{d^2}{dx^2} + 2x^2 + \frac{1}{10} x^4$$

Give an upper and lower bound to the energy for the Hamiltonian on the previous line.

The force constant for this Hamiltonian is 4. Since the quartic potential is nonnegative, totally neglecting the potential gives a lower bound on the energy. That is, a lower bound on the energy can be deduced from the harmonic oscillator, which is

$$E_{\text{lower}} = E_{\text{harmonic oscillator}} = \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2}\right) = \sqrt{\frac{4}{1}} \left(\frac{1}{2}\right) = 1 \text{ a.u.}$$

As an upper bound, we can evaluate the energy of the system guessing that its wavefunction was the harmonic-oscillator wavefunction. Since this is not the right wavefunction, the variational principle tells us this will be an upper bound. So

$$\begin{aligned} E_{\text{upper}} &= \int_{-\infty}^{\infty} \left(\frac{4}{\pi^2}\right)^{1/8} e^{-x^2} \left[-\frac{1}{2} \frac{d^2}{dx^2} + 2x^2 + \frac{1}{10} x^4\right] \left(\frac{4}{\pi^2}\right)^{1/8} e^{-x^2} dx \\ &= 1 + \int_{-\infty}^{\infty} \left(\frac{4}{\pi^2}\right)^{1/8} e^{-x^2} \left[\frac{1}{10} x^4\right] \left(\frac{4}{\pi^2}\right)^{1/8} e^{-x^2} dx \\ &= 1 + \left(\frac{4}{\pi^2}\right)^{1/4} \left(\frac{1}{10}\right) \int_{-\infty}^{\infty} x^4 e^{-2x^2} dx \\ &= 1 + \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{1}{10}\right) \int_{-\infty}^{\infty} x^4 e^{-2x^2} dx \end{aligned}$$

In the second line we used the fact that we know that the expectation value of the energy for the Harmonic Oscillator Hamiltonian (which is the first two terms of the Hamiltonian given here) is 1 a.u.. Evaluating the integral, I get,

$$E_{\text{upper}} = 1 + \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{1}{10}\right) \left[2 \cdot \frac{1 \cdot 3}{8 \cdot 2^2}\right] \sqrt{\frac{\pi}{2}} = 1 + \frac{6}{320} = 1.01875 \text{ a.u.}$$

BONUS (up to 12 points): Use the variational principle to provide a more accurate estimation of the energy for the quartic-perturbed harmonic oscillator. You may not be able to work out all the math, but go as far as you can.

For the bonus, I want to use the variational principle to refine the variational bound from perturbation theory. That is, I will allow the width of the Gaussian to change. This is a bit more involved, but all the integrals can be done using the formulas on the sheet. Alternatively, I can be clever and do some of the integrals directly. Using the Hellmann-Feynman theorem and the fact the ground-state energy of the electron in one-dimensional harmonic confinement in atomic units is $E(k) = \frac{1}{2}\sqrt{k}$, I have:

$$\begin{aligned}\frac{\partial E}{\partial k} &= \int_{-\infty}^{\infty} \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) \frac{\partial H}{\partial k} \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) dx \\ \frac{\partial \frac{1}{2}\sqrt{k}}{\partial k} &= \int_{-\infty}^{\infty} \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) \frac{1}{2} x^2 \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) dx \\ \frac{1}{2\sqrt{k}} &= \int_{-\infty}^{\infty} \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) x^2 \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) dx\end{aligned}$$

If you multiply this expression by $\frac{1}{2}k$, you have:

$$\begin{aligned}\frac{\sqrt{k}}{4} &= \int_{-\infty}^{\infty} \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) \frac{1}{2} k x^2 \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) dx \\ &= \text{potential energy}\end{aligned}$$

Since kinetic energy plus potential energy is the total energy, one has

$$\begin{aligned}\text{kinetic energy} &= \frac{1}{2}\sqrt{k} - \frac{1}{4}\sqrt{k} = \frac{1}{4}\sqrt{k} \\ &= \int_{-\infty}^{\infty} \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) \left[-\frac{1}{2} \frac{d^2}{dx^2} \right] \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) dx\end{aligned}$$

Finally, we need to evaluate the integral associated with the quartic term. It is

$$\begin{aligned}\int_{-\infty}^{\infty} \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) x^{10} \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}}\right)} \right) dx &= \left(\frac{k}{\pi^2} \right)^{1/4} \int_{-\infty}^{\infty} x^4 e^{-\sqrt{k}x^2} dx \\ &= \left(\frac{k}{\pi^2} \right)^{1/4} \left(\frac{\pi}{\sqrt{k}} \right)^{1/2} \left(\frac{3}{(2\sqrt{k})^2} \right) \\ &= \frac{3}{4k}\end{aligned}$$

Putting it all together, the energy expression we need to evaluate is:

$$\begin{aligned}
E(k) &= \int_{-\infty}^{\infty} \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}} \right)} \right) \left(-\frac{1}{2} \frac{d^2}{dx^2} + 2x^2 + \frac{1}{10} x^4 \right) \left(\left(\frac{k}{\pi^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k}{4}} \right)} \right) dx \\
&= \frac{1}{4} \sqrt{k} + 2 \cdot \frac{1}{2\sqrt{k}} + \frac{1}{10} \frac{3}{4k} \\
&= \frac{1}{4} k^{1/2} + k^{-1/2} + \frac{3}{40} k^{-1}
\end{aligned}$$

Taking the derivative of the energy at setting it equal to zero gives,

$$0 = \frac{1}{8} k^{-1/2} - \frac{1}{2} k^{-3/2} - \frac{3}{40} k^{-2}$$

Multiply both sides by $40k^2$; this gives

$$0 = 5k^{3/2} - 20k^{1/2} - 3$$

This is a cubic equation for \sqrt{k} . This can be solved analytically (painful!) but the roots are:

$$\sqrt{k} = -1.920, -0.151, 2.071. \text{ Only positive values are sensible, so we have } k = (2.071)^2 = 4.29$$

This makes sense as we expect a force constant slightly greater than before (when it was $k = 4$), since the electrons are a bit more confined.

The energy is then evaluated by substituting this result back into the equation for the energy,

$$E(k = 4.29) = \frac{1}{4} \sqrt{4.29} + \frac{1}{\sqrt{4.29}} + \frac{3}{40 \cdot 4.29} = 1.0181 \text{ a.u.}$$

This is only slightly better than our previous result.

3. The Morse potential is often used as an approximate model for the vibrations of diatomic molecules. In convenient units where $\frac{\hbar^2}{2m} = 1$, the time-independent Schrödinger equation for a Morse oscillator can be written as

$$\left(-\frac{d^2}{dx^2} + \lambda^2 (e^{-2x} - 2e^{-x}) \right) \psi_n(x) = E_n \psi_n(x)$$

The first two eigenfunctions of the Morse oscillator are given by the following expressions (which are not normalized)

$$\psi_0(x) = \exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right)$$

$$\psi_1(x) = \exp\left(-\left(\lambda - \frac{3}{2}\right)x - \lambda e^{-x}\right) (2\lambda - 2 - 2\lambda e^{-x})$$

What is the ground-state energy for the Morse oscillator?

This requires applying the Hamiltonian to the ground-state wavefunction of the Morse oscillator and finding the eigenvalue. It's a straightforward but tedious exercise:

$$\begin{aligned} \frac{d}{dx} \left[\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \right] &= \exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \cdot \frac{d}{dx} \left[-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x} \right] \\ &= \exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \cdot \left[-\left(\lambda - \frac{1}{2}\right) + \lambda e^{-x} \right] \\ \frac{d^2}{dx^2} \left[\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \right] &= \frac{d}{dx} \left(\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \cdot \left[-\left(\lambda - \frac{1}{2}\right) + \lambda e^{-x} \right] \right) \\ &= \exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \cdot \left[-\left(\lambda - \frac{1}{2}\right) + \lambda e^{-x} \right]^2 \\ &\quad + \exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \cdot \frac{d}{dx} \left[-\left(\lambda - \frac{1}{2}\right) + \lambda e^{-x} \right] \\ &= \left(\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \right) \cdot \left[\left[-\left(\lambda - \frac{1}{2}\right) + \lambda e^{-x} \right]^2 - \lambda e^{-x} \right] \\ &= \left(\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \right) \cdot \left(\left(\lambda - \frac{1}{2}\right)^2 - 2\lambda \left(\lambda - \frac{1}{2}\right) e^{-x} + \lambda^2 e^{-2x} - \lambda e^{-x} \right) \\ &= \left(\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \right) \cdot \left(\left(\lambda - \frac{1}{2}\right)^2 - 2\lambda^2 e^{-x} + \lambda^2 e^{-2x} \right) \\ &= \left(\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \right) \cdot \left(\left(\lambda - \frac{1}{2}\right)^2 + \lambda^2 (e^{-2x} - 2e^{-x}) \right) \\ \left(-\frac{d^2}{dx^2} + \lambda^2 (e^{-2x} - 2e^{-x}) \right) \left[\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \right] &= -\left(\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \right) \cdot \left(\left(\lambda - \frac{1}{2}\right)^2 + \lambda^2 (e^{-2x} - 2e^{-x}) \right) \\ &\quad + \left[\lambda^2 (e^{-2x} - 2e^{-x}) \right] \left(\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \right) \\ &= -\left(\lambda - \frac{1}{2}\right)^2 \left(\exp\left(-\left(\lambda - \frac{1}{2}\right)x - \lambda e^{-x}\right) \right) \end{aligned}$$

So the ground-state energy of the Morse oscillator is $E = -\left(\lambda - \frac{1}{2}\right)^2$.