

1. (a) What is the difference in energy (in J) between a red photon at 650 nm and a blue photon at 480 nm? **Solution:**

$$\Delta E = \frac{hc}{480 \text{ nm}} - \frac{hc}{650 \text{ nm}} = \frac{(6.626 \cdot 10^{-34} \text{ J s})(2.998 \cdot 10^8 \text{ m s}^{-1})}{10^{-9} \text{ m/nm}} \left(\frac{1}{480} - \frac{1}{650} \right) = \boxed{1.08 \cdot 10^{-19} \text{ J}}$$

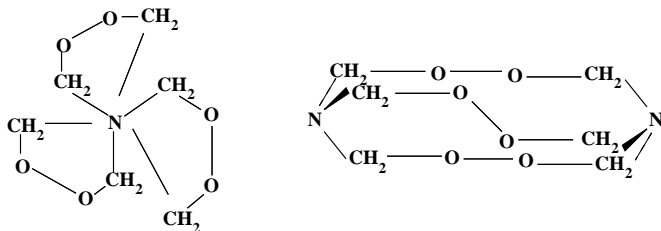
- (b) What is the transition energy ΔE in kJ/mol of the $n = 5 \rightarrow 4$ emission in Li^{2+} ? **Solution:**

$$\Delta E = -\frac{3^2}{2} \left(\frac{1}{5^2} - \frac{1}{4^2} \right) E_h = -0.101 E_h = \boxed{-266 \text{ kJ mol}^{-1}}$$

- (c) Write the expression for the *complex conjugate* of the $3p_{m_l=1}$ orbital wavefunction in B^{4+} . **Solution:**

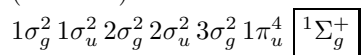
$$\begin{aligned} \psi_{3,1,1}^* &= \psi_{3,1,-1} = R_{3,1}(r) Y_1^{-1}(\theta, \phi) \\ &= \frac{4\sqrt{2}}{27\sqrt{3}} \left(\frac{5}{a_0} \right)^{3/2} \left(\frac{5r}{a_0} \right) \left(1 - \frac{5r}{6a_0} \right) e^{-5r/(3a_0)} \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi} \end{aligned}$$

- (d) Pretend you want to solve the vector model for ground state protactinium, with electron configuration $[\text{Rn}]7s^26d^15f^2$. Draw any **two** valid microstates (the diagrams with the little arrows) for this configuration, and write the M_L and M_S values. **Solution:** Many possible solutions, but for each of them: (i) we only need the 6d and 5f electrons; (ii) the maximum M_S is 3/2; (iii) the maximum M_L is 8.
- (e) If we count *all* of the spatial coordinates that describe one H_2O molecule,
- How many of these are translational coordinates? **Solution:** $\boxed{3}$
 - How many of these are rotational coordinates? **Solution:** non-linear, so $\boxed{3}$
 - How many of these are vibrational coordinates? **Solution:** non-linear, so $3N_{\text{atom}} - 6 = \boxed{3}$
 - How many of these are electronic coordinates? **Solution:** three coordinates for each of ten electrons, so $\boxed{30}$
- (f) Hexamethylene triperoxide diamine (HMTD) was one of the explosive compounds identified at a property in Escondido in November 2010, which led to the house being intentionally burned to the ground by authorities. Each atom is equivalent to the other atoms of same atomic number (so all six carbons are equivalent, both nitrogens, and so on). Assign HMTD to its point group, and identify the representation of the vibrational motion where the two nitrogens twist in opposite directions.



Solution: $\boxed{D_3}$ $\boxed{a_1}$

- (g) Write the MO configuration and term symbol for the ground state of O_2^{2+} . **Solution:** Same as for N_2 , except for possible switching of the $3\sigma_g$ and $1\pi_u$ when the O_2 bond gets stronger (CHECK).



- (h) Estimate the $v = 1 \rightarrow 2$ transition energy of ${}^2D^{19}F$. **Solution:**

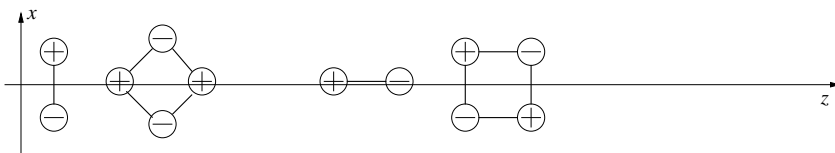
$$\begin{aligned} E &= \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 \\ \Delta E_{v=1 \rightarrow 2} &= \omega_e - \omega_e x_e (2.5^2 - 1.5^2) = \omega_e - 4\omega_e x_e \\ &= 2998.19 - 4(45.76) = \boxed{2815.15\text{cm}^{-1}}. \end{aligned}$$

- (i) What homonuclear diatomic molecule has a bond length of 2.56 \AA and an equilibrium rotational constant (for its most abundant isotope) of 0.0396 cm^{-1} ? **Solution:** For the homonuclear diatomic X_2 , the reduced mass μ is equal to $m_X^2/(2m_X) = m_X/2$.

$$\begin{aligned} B_e (\text{cm}^{-1}) &= \frac{\hbar}{4\pi c \mu R_e^2} = \frac{16.858}{\mu (\text{amu}) R_e (\text{\AA})^2} \\ \mu (\text{amu}) &= \frac{16.858}{B_e (\text{cm}^{-1}) R_e (\text{\AA})^2} = \frac{16.858}{(0.0396)(2.56)^2} = 64.96 \text{ amu} = \frac{1}{2} m_X \\ m_X &= 129.9 \text{ amu}. \end{aligned}$$

This is the atomic mass for ${}^{130}\text{Te}$, so the molecule is $\boxed{\text{Te}_2}$.

- (j) Using two point charges for a dipole, and four point charges for a quadrupole, draw an orientation in the xz plane of a dipole and a quadrupole such that the force of the interaction along z is exactly zero. **Solution:**



- (k) Calculate the *change* in energy when two tetrahedral Ar_4 clusters combine to form a cubic Ar_8 cluster, assuming that each nearest-neighbor interaction is $-\epsilon$. **Solution:** Each tetrahedral cluster has 6 interactions (the number of edges of a tetrahedron). The cubic cluster will have 12 (the number of edges of a cube). So – to a first approximation – there is no net change in the energy when the two Ar_4 clusters combine. Each atom interacts with three others before and after the process. $\boxed{\Delta E = 0}$.

- (l) The following equation is proposed as a model pair correlation function:

$$\mathcal{G}(R) \approx [1 - \cos(\pi R/R_0)] e^{-R/R_0}.$$

In what limit of R and in what way does this function have the wrong behavior? **Solution:** The function correctly goes to 0 at $R = 0$, and peaks at $R = R_0$. However, it converges to 0 as $R \rightarrow \infty$ when it should converge to 1.

Part 2: 180 points.

2. An electron has a normalized wavefunction

$$\begin{aligned} \psi(x) &= \sqrt{\frac{30}{a^5}} [(a/2)^2 - x^2] & -a/2 < x \leq a/2 \\ \psi(x) &= 0 & x \leq -a/2, x > a/2 \end{aligned}$$

which is not an eigenfunction of the kinetic energy operator. Find the expectation value of the kinetic energy in terms of the constant a . **Solution:** Because the function is not an eigenfunction of \hat{K} , we need to use the average value theorem. This means solving the integral over $\psi^* \hat{K} \psi$ over the interval $-a/2$ to $a/2$. Outside that interval, the wavefunction is zero and so is the value of the integral. If we slog forward, we find that we can solve the integral analytically:

$$\begin{aligned}
 \langle K \rangle &= \int_{-a/2}^{a/2} \psi^* \hat{K} \psi dx \\
 &= -\frac{\hbar^2}{2m_e} \left(\frac{30}{a^5} \right) \int_{-a/2}^{a/2} [(a/2)^2 - x^2] \left[\frac{\partial^2}{\partial x^2} ((a/2) - x^2) \right] dx \\
 &= -\frac{\hbar^2}{2m_e} \left(\frac{30}{a^5} \right) \int_{-a/2}^{a/2} [(a/2)^2 - x^2] [-2] dx \\
 &= \frac{\hbar^2}{m_e} \left(\frac{30}{a^5} \right) \int_{-a/2}^{a/2} [(a/2)^2 - x^2] dx \\
 &= \frac{\hbar^2}{m_e} \left(\frac{30}{a^5} \right) \left[(a/2)^2 x - \frac{x^3}{3} \right] \Big|_{-a/2}^{a/2} \\
 &= \frac{\hbar^2}{m_e} \left(\frac{30}{a^5} \right) \left[\frac{a^3}{8} - \frac{-a^3}{8} - \left(\frac{a^3}{24} - \frac{-a^3}{24} \right) \right] \\
 &= \frac{\hbar^2}{m_e} \left(\frac{30}{a^5} \right) \left(\frac{a^3}{6} \right) = \frac{5\hbar^2}{m_e a^2}.
 \end{aligned}$$

We can compare that to $\pi^2 \hbar^2 / (2m_e a^2)$, which is the ground state ($n = 1$) kinetic energy of an electron in a one-dimensional box of length a . The system in our problem has a kinetic energy that differs by a factor of $5/(\pi^2/2) = 1.013$. The parabolic wavefunction in this problem is similar in shape to the half sine wave that is the correct $n = 1$ particle-in-a-box wavefunction, so it gives a similar average kinetic energy. The energy in this problem is a little higher, because the particle in a box gives the lowest possible kinetic energy for a system of length a , as per the variational principle described in Section ??.

- Write the explicit integral necessary to find the electron-electron repulsion energy in the triplet $1s2s$ excited state of atomic helium to first order in perturbation theory. **Solution:** For helium, $Z = 2$.

$$\begin{aligned}
 \Psi &= 1s(1)2s(2) - 2s(1)1s(2) \\
 1s(i) &= \sqrt{\frac{1}{4\pi}} 2 \left(\frac{2}{a_0} \right)^{3/2} e^{-2r_i/a_0} \\
 2s(i) &= \sqrt{\frac{1}{4\pi}} \frac{1}{\sqrt{2}} \left(\frac{2}{a_0} \right)^{3/2} \left(1 - \frac{r_i}{a_0} \right) e^{-r_i/a_0} \\
 \frac{1}{4\pi\epsilon_0} \left\langle \frac{e^2}{r_{12}} \right\rangle &= \frac{e^2}{4\pi\epsilon_0} \int_0^\infty \int_0^\pi \int_0^{2\pi} \int_0^\infty \int_0^\pi \int_0^{2\pi} |\Psi(1,2)|^2 \frac{1}{r_{12}} r_1^2 r_2^2 \sin\theta_1 \sin\theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2.
 \end{aligned}$$

- The table below lists orbital energies in E_h from a Hartree-Fock calculation on the N_2 molecule. The total Hartree-Fock energy of the molecule is $-108.983 E_h$.

(a) Assign each energy to the correct molecular orbital in the MO configuration.

-15.682	$1\sigma_g$
-15.678	$1\sigma_u$
-1.470	$2\sigma_g$
-0.777	$2\sigma_u$
-0.632	$3\sigma_g$
-0.612	$1\pi_u$
-0.612	$1\pi_u$

- (b) Calculate the total electron-electron *repulsion* energy in E_h . **Solution:** These are the orbital energies, and each orbital is occupied by two electrons. The sum of the orbital energies is $-35.463 E_h$, and we double this because there are two electrons in each orbital, obtaining $-70.926 E_h$. This sum contains each electron-electron interaction twice, so we subtract the total HF energy, $-108.983 E_h$, to get the repulsion energy:

$$-70.926 E_h - (-108.983 E_h) = \boxed{38.057 E_h}$$

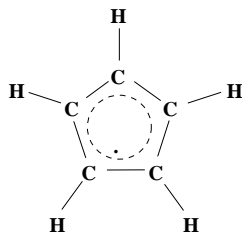
- (c) To estimate the strength of the electron-nuclear interaction, calculate the effective atomic number of an electron in the highest energy orbital. **Solution:** Since the $1\pi_u$ electrons correlate to the $2p$ atomic orbitals, we should set the principal quantum number equal to 2:

$$Z_{\text{eff}} = n\sqrt{-2E/E_h} = 2\sqrt{2 \cdot 0.612} = \boxed{2.21}$$

5. Construct a set of sp^3 hybrid orbitals from s , p_x , p_y , and p_z atomic orbitals such that one orbital has exactly 40% s character and the other three orbitals are all equivalent. **Solution:** There are infinite possibilities, but all must have a coefficient of magnitude $\sqrt{2/5}$ (giving 2/5 or 40% to the probability density) for the s contribution to the unique hybrid orbital, and $\sqrt{1/5}$ for each of the remaining equivalent orbitals. The simplest way – I think – to determine the p contributions is to align the unique orbital along the z axis (so omit p_x and p_z character), and put one of the remaining three equivalent orbitals in the xz plane (so the p_y character is zero). The last three hybrids equally divide the p_z character left over from the unique hybrid. The last two orbitals will equally divide the p_y character and the remaining p_x character.

$$\begin{aligned} sp_a^3 &= \sqrt{\frac{2}{5}}(s) + (0)(p_x) + (0)(p_y) + \sqrt{\frac{3}{5}}(p_z) \\ sp_b^3 &= \sqrt{\frac{1}{5}}(s) + \sqrt{\frac{2}{3}}(p_x) + (0)(p_y) - \sqrt{\frac{2}{15}}(p_z) \\ sp_c^3 &= \sqrt{\frac{1}{5}}(s) - \sqrt{\frac{1}{6}}(p_x) + \sqrt{\frac{1}{2}}(p_y) - \sqrt{\frac{2}{15}}(p_z) \\ sp_d^3 &= \sqrt{\frac{1}{5}}(s) - \sqrt{\frac{1}{6}}(p_x) - \sqrt{\frac{1}{2}}(p_y) - \sqrt{\frac{2}{15}}(p_z) \end{aligned}$$

6. The cyclopentadienyl radical has the structure drawn below. All the carbons are equivalent and all the hydrogens are equivalent.



- (a) Find the point group for this molecule.
- (b) Show that the HOMO→LUMO transition (highest occupied to lowest unoccupied MO) in the π -bonding system of cyclopentadienyl must be allowed by electric dipole selection rules.

Solution: The point group is D_{5h} . There are five atomic p orbitals, which must combine to form five π MOs: the lowest energy will have no nodes (ignoring the node through the molecular plane), the second and third MOs form a degenerate pair with one node each, and the fourth and fifth form another degenerate pair with two nodes each. There also five electrons, which fill two of the lower energy orbitals but only half fill the third. The HOMO therefore has one node, while the LUMO has two nodes. For the function that introduces a node – a change in sign – perpendicular to the existing node, without changing the other symmetry properties of the π orbitals. That Γ_μ must have the same symmetry as the function x or y , and therefore corresponds to an electric dipole allowed transition.

7. For the ${}^7\Sigma_u^+$ state of N_2 in Fig. 6.7:

- (a) What is the spin S of this state? **Solution:** $2S + 1 = 7$ so $S = 3$.
- (b) What is the minimum number of unpaired electrons in this electronic state? **Solution:** To get a total spin of 3 from electrons with spins of $1/2$ each, there must be at least 6 unpaired electrons. (There could be more, in principle, because two unpaired electrons in different orbitals may have cancelling spins.)
- (c) What are the term symbols for the N atoms in the large- R limit? **Solution:** This state correlates with the ground states of the atoms, because it converges to the same energy at large R as the ground and lowest excited states. The ground state term of nitrogen is 4S .
- (d) What is the MO configuration for this state? **Solution:** To obtain a spin of 3, we need all six valence electrons to occupy separate orbitals:

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(3\sigma_g)^1(1\pi_g)^2(3\sigma_u)^1.$$

Each π MO is doubly degenerate, so we can put two electrons in $1\pi_u$, with one going in the π_x and one in the π_y orbital, for example.

8. The expectation value of x^2 of a particle with mass m in a harmonic oscillator potential is given by

$$\langle x^2 \rangle = \frac{\omega_e}{k} \left(v + \frac{1}{2} \right).$$

Use this to find an expression for $\langle p^2 \rangle$ in terms of m , ω_e , and v . **Solution:**

$$\begin{aligned} E &= \langle K + U \rangle = \langle K \rangle + \langle U \rangle \\ &= \left\langle \frac{p^2}{2m} \right\rangle + \left\langle \frac{1}{2} k x^2 \right\rangle = \frac{1}{2m} \langle p^2 \rangle + \frac{1}{2} k \langle x^2 \rangle \\ &= \frac{1}{2m} \langle p^2 \rangle + \frac{1}{2} k \frac{\omega_e}{k} \left(v + \frac{1}{2} \right) = \frac{1}{2m} \langle p^2 \rangle + \frac{1}{2} \omega_e \left(v + \frac{1}{2} \right) = \omega_e \left(v + \frac{1}{2} \right) \\ \frac{1}{2m} \langle p^2 \rangle &= \frac{1}{2} \omega_e \left(v + \frac{1}{2} \right) \\ \langle p^2 \rangle &= \frac{2m}{2} \omega_e \left(v + \frac{1}{2} \right) = m \omega_e \left(v + \frac{1}{2} \right). \end{aligned}$$

9. Based on the parameters below, estimate in **kJ/mol** the total intermolecular potential energy for attraction between HI and CO at a separation of 4.0 Å and at 298 K:

	ΔE (eV)	μ (D)	α (Å ³)
HI	7.72	0.45	5.44
CO	8.07	0.11	1.95

Solution: Let's approximate the ΔE for both molecules as 7.9 eV. The individual contributions are

$$\begin{aligned}
 \langle u_{2-2} \rangle_{N,\theta,\phi} &= -\frac{2\mu_A^2\mu_B^2}{(4\pi\epsilon_0)^2 3k_B T R^6} \\
 &= -\frac{2(0.45 \text{ D})^2(0.11 \text{ D})^2(3.3356 \cdot 10^{-30} \text{ C m/D})^4}{(1.113 \cdot 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})^2(1.381 \cdot 10^{-23} \text{ J K}^{-1})(298 \text{ K})(4.0 \cdot 10^{-10} \text{ m})^6} \\
 &= -2.91 \cdot 10^{-24} \text{ J} = -0.0018 \text{ kJ mol}^{-1} \\
 u_{2-2^*}(R) &= -\frac{4\mu_A^2\alpha}{(4\pi\epsilon_0)R^6} \\
 &= -\frac{4(0.45 \text{ D})^2(3.3356 \cdot 10^{-30} \text{ C m/D})^2(1.95 \cdot 10^{-30} \text{ m}^3)}{(1.113 \cdot 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})(4.0 \cdot 10^{-10} \text{ m})^6} \\
 &= -3.85 \cdot 10^{-23} \text{ J} = -0.023 \text{ kJ mol}^{-1} \\
 u_{2-2^*}(R) &= -\frac{4\mu_A^2\alpha}{(4\pi\epsilon_0)R^6} \\
 &= -\frac{4(0.11 \text{ D})^2(3.3356 \cdot 10^{-30} \text{ C m/D})^2(5.44 \cdot 10^{-30} \text{ m}^3)}{(1.113 \cdot 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})(4.0 \cdot 10^{-10} \text{ m})^6} \\
 &= -6.43 \cdot 10^{-24} \text{ J} = -0.0039 \text{ kJ mol}^{-1} \\
 u_{\text{disp}} &\approx -\frac{\alpha^2 \Delta E}{8R^6} \\
 &= -\frac{(5.44 \cdot 10^{-30} \text{ m}^3)(1.95 \cdot 10^{-30} \text{ m}^3)(7.9 \text{ eV})(1.602 \cdot 10^{-19} \text{ J/eV})}{8(4.0 \cdot 10^{-10} \text{ m})^6} \\
 &= -4.10 \cdot 10^{-22} \text{ J} = -0.25 \text{ kJ mol}^{-1}.
 \end{aligned}$$

Adding these together gives a total of $\boxed{-0.28 \text{ kJ mol}^{-1}}$, dominated by the dispersion term.

10. Benzene crystallizes at 1 atm. and 278.5 K to an orthorhombic lattice with lattice constants $a = 7.49 \text{ Å}$, $b = 9.71 \text{ Å}$, and $c = 7.07 \text{ Å}$. The density of the unit cell is 0.606 amu/Å^3 . If we put one molecule at each lattice point, where in the unit cell will we find the molecules? **Solution:** The mass of one benzene molecule is about 78 amu, and the volume of the unit cell is $abc = 514 \text{ Å}^3$. The number of molecules per unit cell is therefore

$$\left(\frac{1 \text{ molecule}}{78 \text{ amu}} \right) \left(\frac{0.606 \text{ amu}}{1 \text{ Å}^3} \right) \left(\frac{514 \text{ Å}^3}{\text{unit cell}} \right) = 4 \frac{\text{molecules}}{\text{unit cell}}$$

We can put one benzene at each corner of the unit cell, but this contributes only one molecule to the unit cell overall. We have to account for three more. Because the unit cell has six faces, and any molecule located at one of the faces lies half in our unit cell, we can obtain three more molecules by placing them at the faces. This is not a face-centered lattice (there is no face-centered orthorhombic Bravais lattice) because the benzenes in the middle of each face are not oriented the same way as the benzenes at the corners. For the center of each face to be a lattice point, the molecules at that site would have to be indistinguishable from those at the corners. Instead, this

is a primitive lattice with a basis of four molecules. The original structure was determined in Ref. [?].