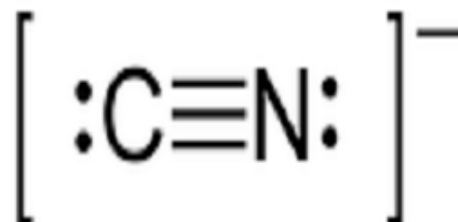
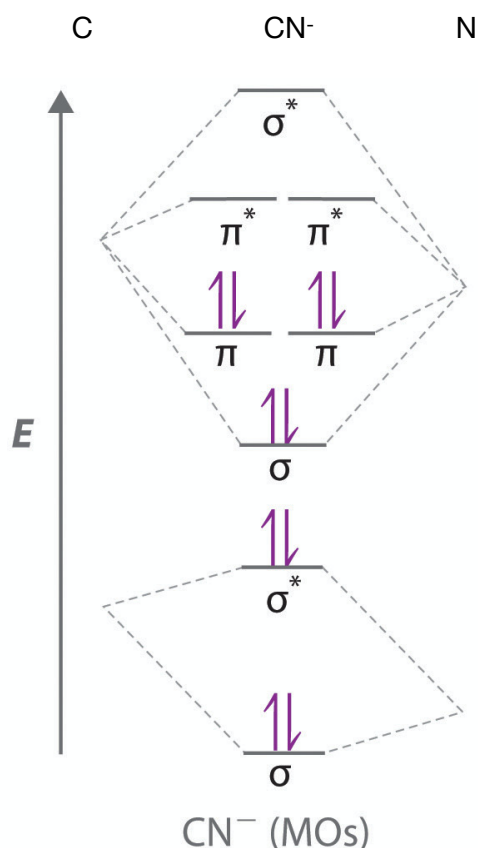


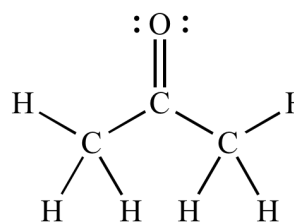
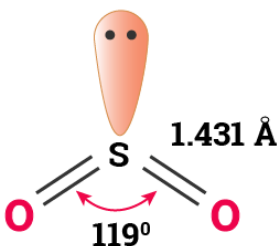
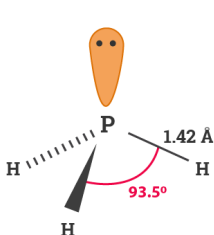
Using the correlation diagram for low-Z- second-row diatomic draw and label the correlation diagram for the diatomic ion CN^- . Note that this molecular ion involves a “normal” correlation diagram. (b) What is the bond order for this ion, and how does it compare with that for the neutral species CN ? (c) Draw the Lewis dot structure for CN^- .



$$BO_{\text{CN}^-} = \frac{1}{2}(6 - 0) = 3$$

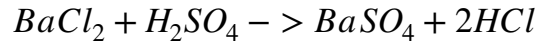
$$BO_{\text{CN}} = \frac{1}{2}(5 - 0) = 2.5 \quad BO_{\text{CN}^-} > BO_{\text{CN}}$$

Determine the hybridization state of the central atoms in the following molecules: (i) PH_3 ; (ii) CaCl_2 ; (iii) SO_2 ; (iv) acetone, $\text{C}_3\text{H}_6\text{O}$.



PH_3 is tetrahedral, so P is sp^3 hybridized. SO_2 is trigonal planar, so S is sp^2 hybridized. CaCl_2 is linear, so Ca is sp hybridized. There are three central atoms in acetone (all C's). Two of them are the same (the left and right carbons) and are sp^3 hybridized. The middle carbon is sp^2 hybridized, with its unhybridized p-orbital forming a π bond (a π MO) with oxygen's 2p orbitals.

The reaction of BaCl_2 with H_2SO_4 gives BaSO_4 and HCl . Suppose we start with 3.9 g of BaCl_2 and 3.2 g of H_2SO_4 , and the reaction is allowed to go to completion. What is the amount of each compound that remains?



$$n_{\text{BaCl}_2} = m_{\text{BaCl}_2} \frac{1}{MW_{\text{BaCl}_2}} = 3.9\text{g} \frac{1\text{mol}}{208\text{g}} = 0.019\text{mol}$$

$$n_{\text{H}_2\text{SO}_4} = m_{\text{H}_2\text{SO}_4} \frac{1}{MW_{\text{H}_2\text{SO}_4}} = 3.2\text{g} \frac{1\text{mol}}{98\text{g}} = 0.033\text{mol}$$

So that BaCl_2 is limiting. Therefore, at completion there will be none of it.

$$n_{\text{H}_2\text{SO}_4} = 0.033\text{mol} - 0.019\text{mol} = 0.014\text{mol} \text{ remaining}$$

Consider the bond associated with the imaginary diatomic molecule LM, where the ionization energies of atoms L and M are 325 and 1510 kJ/mole, while the electron affinities are 45 and 300 kJ/mole. The equilibrium bond length is 1.64 Å. (a) Estimate the bond dissociation energy for molecule LM. (b) If its measured dipole moment is 7 D, what is the % ionic character of this bond?

$$EN_L \propto (IA_L + EA_L) = (325 + 45)\text{kJ/mole} = 370\text{kJ/mole}$$

$$EN_M \propto (IA_M + EA_M) = (1510 + 300)\text{kJ/mole} = 1810\text{kJ/mole} \quad \text{so M is more EN}$$

$$BE_{ML} = -V_{ML}(R_e) - [IE(L) - EA(M)] = -\frac{-e^2}{4\pi\epsilon_0(1.64 * 10^{-10}\text{m})} - [325\text{kJ/mole} - 300\text{kJ/mole}]$$

$$= -\frac{-(1.602 * 10^{-19}\text{C})^2}{4\pi * 8.85 * 10^{-12} \frac{\text{C}^2}{\text{J} * \text{m}} (1.64 * 10^{-10}\text{m})} \frac{1\text{kJ}}{1000\text{J}} \frac{6.022 * 10^{23}}{1\text{mol}} - [325\text{kJ/mole} - 300\text{kJ/mole}] = 822\text{kJ/mole}$$

$$\% \text{ ionic} = \frac{\mu_{\text{measured}}}{\mu_{\text{calculated}}} = \frac{7\text{D}}{1.602 * 10^{-19}\text{C} * 1.64 * 10^{-10}\text{m} \frac{1\text{D}}{3.33 * 10^{-30}\text{C} * \text{m}}} = \frac{7\text{D}}{7.9\text{D}} = 0.88$$

So 88% ionic character.

(a) Suppose we shine light of a certain frequency on a Li^{2+} ion whose electron is in its next-to-lowest ($n=2$) energy state, and we observe that the electron is ejected from the ion with a kinetic energy of 3.0 eV, i.e., the electron is not just freed from the Li nucleus but given enough extra energy to have it moving free with an extra 3.0 eV of kinetic energy. What was the frequency of the light?

$$E_p = h\nu = KE_e + \phi \quad \phi = BE_e = -\left(-\frac{Z^2}{n^2}R\right) = \frac{Z^2}{n^2}R = \frac{3^2}{2^2}(13.6\text{eV}) = 30.6\text{eV}$$

$$E_p = h\nu = KE_e + \phi = 3eV + 30.6eV = 33.6eV$$

$$\nu = \frac{33.6eV}{h} = \frac{33.6eV * 1.602 * 10^{-19} J/eV}{6.626 * 10^{-34} J * s} = 8.12 * 10^{15} s^{-1}$$

(b) Now consider another Li²⁺ ion whose electron is excited to one of the n=5 states. What are the emission frequencies observed?

$$\nu_{n=5 \rightarrow n=4}, \nu_{n=5 \rightarrow n=3}, \nu_{n=5 \rightarrow n=2}, \nu_{n=5 \rightarrow n=1}$$

$$\nu_{n=4 \rightarrow n=3}, \nu_{n=4 \rightarrow n=2}, \nu_{n=4 \rightarrow n=1}, \nu_{n=3 \rightarrow n=2}, \nu_{n=3 \rightarrow n=1}, \nu_{n=2 \rightarrow n=1}$$

For the one-dimensional harmonic oscillator, i.e., a point mass (m) bound to a spring and confined to move along the x-axis, the 2nd (next-to-lowest-energy) allowed state is given

by the wavefunction $\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$, with $\alpha = \frac{2\pi}{h}(km)^{1/2}$. Here k is the force constant of the spring, defining the restoring force -kx, with x the displacement of the spring from its equilibrium position, and of course h is Planck's constant.

(a) What are the units of the normalization constant $\left(\frac{4\alpha^3}{\pi}\right)^{1/4}$?

From b, $[\psi(x)] = m^{-1/2}$ so that $\left[\left(\frac{4\alpha^3}{\pi}\right)^{1/4} x\right] = [\psi(x)] = m^{-1/2}$

And therefore $\left[\left(\frac{4\alpha^3}{\pi}\right)^{1/4}\right] = m^{-3/2}$ (we saw on exam 2 that $[\alpha] = m^{-2}$)

(b) What are the units of the wavefunction?

$[\psi^2(x)dx] = \text{unitless}$, therefore, $[\psi^2(x)] = m^{-1}$ so that $[\psi(x)] = m^{-1/2}$

(c) What is the function of x that, when multiplied by dx, gives the probability of finding the particle with an x value between x and x+dx?

$\psi^2(x)$

(a) Using the fact that for the particle-in-a-box-system the energy is all kinetic energy

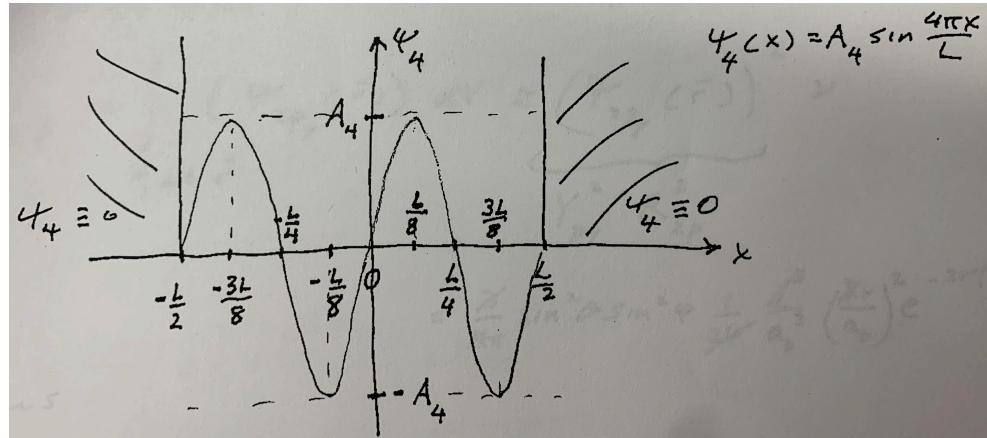
$(KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$, with v the velocity and p the linear momentum), calculate the

magnitude of the linear momentum p for the particle in its n=4 state. The box here is a one-dimensional box length L. What is the de Broglie wavelength associated with this momentum? HINT: Solve for the magnitude of the momentum in terms of h and L, not as a number.

$$E_{n=4} = \frac{h^2}{8mL^2}n^2 = \frac{16h^2}{8mL^2} = \frac{2h^2}{mL^2} = KE$$

$$KE = \frac{p^2}{2m} = \frac{2h^2}{mL^2} \quad p = \frac{2h}{L} \quad \lambda = \frac{h}{p} = \frac{h}{\frac{2h}{L}} = \frac{L}{2}$$

(b) Draw a picture (labeling axis, zeros, maxima, etc.) of the $n=4$ wavefunction for this particle in a box and compare its wavelength with the de Broglie wavelength you calculated from the momentum of the particle in this state.



$$\lambda = \frac{L}{2} = \lambda_{deBroglie}$$

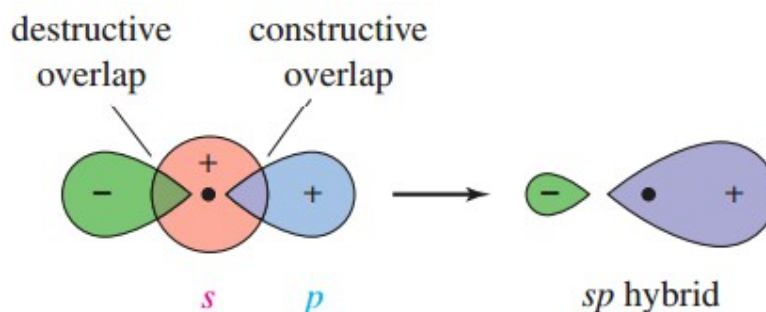
Consider the lowest state of the H_2^+ molecule, whose wavefunction can be approximated well by the following linear combination of 1s orbitals for the H-atom:

$\psi_1(\vec{r}) = \psi_{g,1s}(\vec{r}) \propto (1_{s_A}(\vec{r}) + 1_{s_B}(\vec{r}))$. Here A and B refer to the proton positions on the left and right sides of the molecule. Suppose the distance between the two nuclei is $3a_0$, where a_0 is the Bohr radius. Draw a picture showing how the value of the wavefunction varies along the internuclear axis.



The wavefunction is positive

Sketch the sp -hybrid orbital defined by $sp(\vec{r}) = \left(\frac{1}{\sqrt{2}}\right)(2s(\vec{r}) + 2p_z(\vec{r}))$.



In class we considered the position of the electron in H_2^+ to be midway between the protons, and showed that the total force on each proton acted to push the proton towards the other proton. Suppose the electron were position instead a distance $\frac{R_{AB}}{2}$ on one side of one of the nuclei (R_{AB} is the distance between the two protons). Calculate the net force acting on each proton. Would you consider this electron to lie within the “bonding region” of the molecule?



For the force on proton A (H_A), both forces act in the same direction (the electron attracts proton A to the left, and proton B repels proton A to the left), so the forces are added:

$$F_A = F_{Ae} + F_{AB} = \frac{(e)(e)}{4\pi\epsilon_0\left(\frac{R_{AB}}{2}\right)^2} + \frac{(e)(e)}{4\pi\epsilon_0(R_{AB}^2)} = \frac{e^2}{\pi\epsilon_0 R_{AB}^2} + \frac{e^2}{4\pi\epsilon_0 R_{AB}^2} = \frac{5e^2}{4\pi\epsilon_0 R_{AB}^2}$$

This force acts to the left, pulling proton A away from proton B.

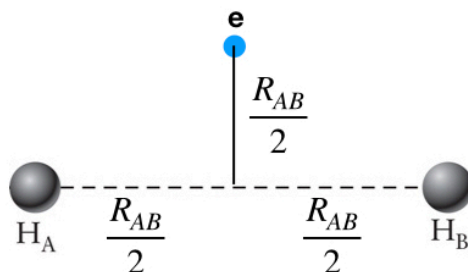
For the force on proton B (H_B), the forces act in opposite directions (the electron attracts proton B to the left, and proton A repels proton B to the right), so the forces are subtracted:

$$F_B = F_{Be} + F_{BA} = \frac{(e)(-e)}{4\pi\epsilon_0\left(\frac{3R_{AB}}{2}\right)^2} + \frac{(e)(e)}{4\pi\epsilon_0 R_{AB}^2} = \frac{-e^2}{9\pi\epsilon_0 R_{AB}^2} + \frac{e^2}{4\pi\epsilon_0 R_{AB}^2} = \frac{5e^2}{36\pi\epsilon_0 R_{AB}^2}$$

This force acts to the right, pushing proton B away from proton A.

Both forces act to push the two protons apart, so we call this an **anti-bonding electron**.

In class we considered the position of the electron in H_2^+ to be midway between the protons, along their line of centers, and showed that the total force on each proton acted to push the proton towards the other proton. Suppose the electron were position instead along the perpendicular bisector of the line between the protons, lying a distance $\frac{R_{AB}}{2}$ above that line. (R_{AB} is the distance between the two protons). Calculate the component of the net force acting on each proton, along the line of centers. Would you consider this electron to lie within the “bonding region” of the molecule?



For the force on proton A (H_A), the forces act in opposite directions (the electron attracts proton A to the right, and proton B repels proton A to the left), so the forces are subtracted: But, we have to be careful here to only calculate the component of the force along the bonding axis (we will call this the z-axis).

$$F_{A_z} = F_{Ae_z} - F_{AB_z}$$

$$F_{AB_z} = F_{AB} = \frac{(e)(e)}{4\pi\epsilon_0 R_{AB}^2} = \frac{e^2}{4\pi\epsilon_0 R_{AB}^2} \text{ to the left.}$$

To calculate the z-component of F_{Ae} we need to properly handle the geometry of the problem: namely, that the distance between A and e is $\frac{2^{1/2}R_{AB}}{2} = \frac{R_{AB}}{2^{1/2}}$, and that the z-component of the force is the force multiplied by $\cos(\theta) = \cos(45) = \frac{1}{2} = \frac{1}{2^{1/2}}$.

$$F_{Ae_z} = F_{Ae} \cos(\theta) = \frac{(e)(e)}{4\pi\epsilon_0 \left(\frac{R_{AB}}{2^{1/2}}\right)^2} \cos(45) = \frac{e^2}{2\pi\epsilon_0 R_{AB}^2} \frac{1}{2^{1/2}} = \frac{e^2}{2^{3/2}\pi\epsilon_0 R_{AB}^2} \text{ to the right.}$$

$$F_{A_z} = F_{Ae_z} - F_{AB_z} = \frac{e^2}{2^{3/2}\pi\epsilon_0 R_{AB}^2} - \frac{e^2}{4\pi\epsilon_0 R_{AB}^2} = \frac{1}{4}(2^{1/2} - 1) \frac{e^2}{\pi\epsilon_0 R_{AB}^2} > 0, \text{ so to the right.}$$

This force acts to pull proton A to the right. By symmetry F_A equals F_B with opposite sign, but let's calculate it to verify:

$$F_{B_z} = F_{Be_z} - F_{BA_z}$$

$$F_{BA_z} = F_{BA} = \frac{(e)(e)}{4\pi\epsilon_0 R_{AB}^2} = \frac{e^2}{4\pi\epsilon_0 R_{AB}^2} \text{ to the right.}$$

From above (the geometry is identical):

$$F_{Be_z} = F_{Be} \cos(\theta) = \frac{(e)(e)}{4\pi\epsilon_0 \left(\frac{R_{AB}}{2^{1/2}}\right)^2} \cos(45) = \frac{e^2}{2\pi\epsilon_0 R_{AB}^2} \frac{1}{2^{1/2}} = \frac{e^2}{2^{3/2}\pi\epsilon_0 R_{AB}^2} \text{ to the left.}$$

$$F_{B_z} = F_{Be_z} - F_{BA_z} = \frac{e^2}{2^{3/2}\pi\epsilon_0 R_{AB}^2} - \frac{e^2}{4\pi\epsilon_0 R_{AB}^2} = \frac{1}{4}(2^{1/2} - 1) \frac{e^2}{\pi\epsilon_0 R_{AB}^2} > 0, \text{ so to the left.}$$

This force acts to pull proton B to the left,

Both forces act to pull the two protons together, so we call this a **bonding electron**.