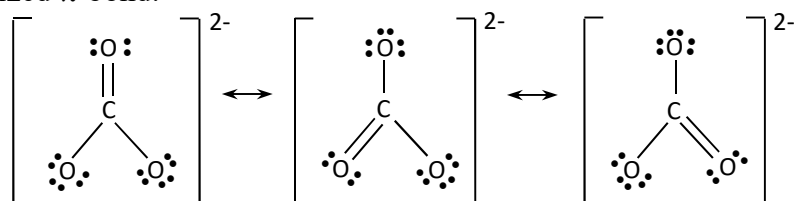


Chapter 26 Problems: Molecular Structure

1. Draw the Lewis dot resonance structures for the carbonate ion, CO_3^{2-} . Are the electrons delocalized? Give the average bond order for the bonds. The procedure for the determination of Lewis dot structures is:

(1). Place the nuclei to establish the expected connectivity. In polyatomics, the first listed non-hydrogen atom is assumed to be the central atom, unless otherwise stated. Alternatively, the atom with the smallest electronegativity is often the central atom. (2). Determine the total number of valence electrons. (3). Draw single bonds between the bonded pairs of atoms. (4). Fill in the remaining electrons as lone pairs without exceeding an octet on each heavy atom, or a duet on H or He. (5). If any atoms do not have a completed octet, move lone pairs to complete the octets by forming multiple bonds. (6). If several non-equivalent structures are possible, the predicted lowest energy structure is the structure that minimizes the total formal charges. (7). The bonding pattern that places the largest negative formal charges on the most electronegative atoms is the most important. (8). Use expanded octets on 3rd and 4th period elements only if necessary to accommodate the required total number of electrons. (9). Show the overall ionic charge in the final structures.

Answer: The C-atom is the central atom. The carbonate ion has $4 + 3(6) + 2 = 24$ valence electrons. The final two in the sum is added to account for the ionic charge. Following the procedure step 4, one of the atoms does not have a completed octet, which requires one double bond to resolve. Three equivalent structures result, differing only in the C-O pairs that are double bonded. The three resonance structures predict that the carbonate ion has a four-center delocalized π -bond.



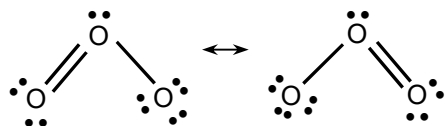
Focusing on the same particular C-O pair in each resonance structure, the total bonds between that particular pair in all the resonance structures is $2+1+1 = 4$. On average, over the three resonance structures, the qualitative bond order is $\frac{4}{3} = 1\frac{1}{3}$.

2. Draw the Lewis dot resonance structures for (a) ozone, (b) sulfur dioxide, and (c) nitrite ion, NO_2^- . Are the electrons delocalized? Give the average bond order for the bonds. The procedure for the determination of Lewis dot structures is summarized in the previous problem.

Answers: The plan is to note that ozone, sulfur dioxide, and nitrite ion are isoelectronic; each has 18 valence electrons. The Lewis dot resonance structures are the same for each.

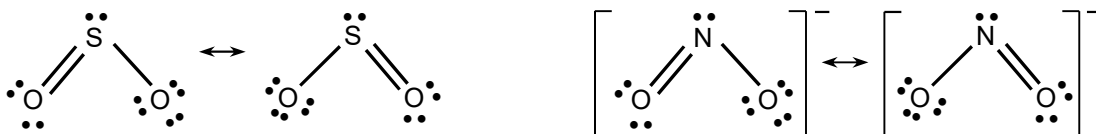
(a). Ozone has $3(6) = 18$ valence electrons. With single bonds only one atom does not have an octet, which requires one double bond to resolve. Two equivalent resonance structures result,

differing only in the O-O pairs that are double bonded. The two resonance structures predict that ozone has a three-center delocalized π -bond.



Focusing on the same particular O-O pair in each resonance structure, the total bonds between that particular pair in all the resonance structures is $2+1 = 3$. On average, over the two resonance structures, the qualitative bond order is $3/2 = 1\frac{1}{2}$.

(b) and (c). Sulfur dioxide and nitrite ion also have 18 valence electrons, giving delocalized three-center π -bonds with an average qualitative bond order of $1\frac{1}{2}$:



3. For the H_2^+ ion, show that for the bonding orbital $c_A = c_B$ using E_+ and for the anti-bonding orbitals $c_A = -c_B$ using E_- in the secular equations, Eq. 21.1.12.

Answer: The first of the two secular equations, Eqs. 21.1.12 (either one would do), is:

$$c_A(H_{AA} - E) + c_B(H_{AB} - ES) = 0$$

For a homonuclear molecule, $H_{AA} = H_{BB}$ and normalized atomic orbitals give $S_{AA} = S_{BB} = 1$.

(a). Substituting $E_+ = \frac{H_{AA} + H_{AB}}{1+S}$ into the secular equation gives:

$$c_A\left(H_{AA} - \frac{H_{AA} + H_{AB}}{1+S}\right) + c_B\left(H_{AB} - \frac{H_{AA} + H_{AB}}{1+S} S\right) = 0$$

Multiplying the last equation by $1+S$ gives:

$$c_A H_{AA}(1+S) - c_A H_{AA} - c_A H_{AB} + c_B H_{AB}(1+S) - c_B H_{AA}S - c_B H_{AB}S = 0$$

After cancelling common terms the result is:

$$c_A H_{AA}S - c_A H_{AB} + c_B H_{AB} - c_B H_{AA}S = 0$$

Collecting terms in c_A and c_B :

$$c_A (H_{AA}S - H_{AB}) + c_B (H_{AB} - H_{AA}S) = 0$$

which rearranges to give:

$$c_A (H_{AA}S - H_{AB}) = c_B (H_{AA}S - H_{AB})$$

The common term cancels to give: $c_A = c_B$

(b). Substituting $E_- = \frac{H_{AA} - H_{AB}}{1-S}$ into the secular equation gives:

$$c_A \left(H_{AA} - \frac{H_{AA} - H_{AB}}{1-S} \right) + c_B \left(H_{AB} - \frac{H_{AA} - H_{AB}}{1-S} S \right) = 0$$

Multiplying the last equation by $1+S$ gives:

$$c_A H_{AA}(1-S) - c_A H_{AA} + c_A H_{AB} + c_B H_{AB}(1-S) - c_B H_{AA}S + c_B H_{AB}S = 0$$

After cancelling common terms the result is:

$$-c_A H_{AA}S + c_A H_{AB} + c_B H_{AB} - c_B H_{AA}S = 0$$

Collecting terms in c_A and c_B :

$$c_A (-H_{AA}S + H_{AB}) + c_B (H_{AB} - H_{AA}S) = 0$$

which rearranges to give:

$$c_A (-H_{AA}S + H_{AB}) = c_B (H_{AA}S - H_{AB})$$

The common term cancels to give $c_A = -c_B$.

4. Show that the atomic integral for the H_2^+ molecule, $H_{AA} \equiv \int \Psi_A^* \hat{H} \Psi_A d\tau$, reduces to:

$$H_{AA} \cong E_A + \frac{e^2}{4\pi\epsilon_0 R}$$

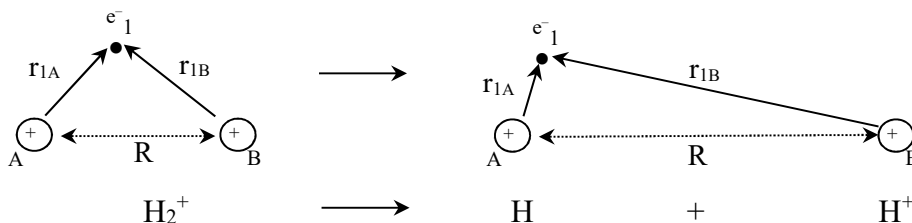
at large internuclear separation, Eq. 26.1.6. Then argue that at large R the atomic integral is approximately equal to the atomic energy of the H-atom. The bond dissociation at large R gives $H_2 \rightarrow H + H^+$.

Answer: The plan is to write the exact Hamiltonian for the H_2^+ ion and then determine the limit of the Hamiltonian for bond dissociation at large R .

The Schrödinger equation for H_2^+ is given by Eq. 26.1.1:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + \frac{e^2}{4\pi\epsilon_0} \left(-\frac{1}{r_{1A}} - \frac{1}{r_{1B}} + \frac{1}{R} \right) \Psi = E \Psi$$

Assume that the molecule dissociates at large R to give a H-atom on nucleus A and a H^+ ion on nucleus B:



In the limit of large R , the Coulomb attraction of the electron for nucleus B is negligible, $e^2/(4\pi\epsilon_0 r_{1B}) \rightarrow 0$. The remaining terms in the Hamiltonian are then the one-electron Hamiltonian for the H-atom on nucleus A, \mathcal{H}_A , and the nuclear-nuclear repulsion. The Hamiltonian acting on the one-electron H-atom orbital on nucleus A then simplifies to:

$$\mathcal{H}\Psi_A \cong \left(-\frac{\hbar^2}{2m} \nabla_1^2 \Psi - \frac{e^2}{4\pi\epsilon_0 r_{1A}} \right) \Psi_A + \frac{e^2}{4\pi\epsilon_0 R} \Psi_A = \mathcal{H}_A \Psi_A + \frac{e^2}{4\pi\epsilon_0 R} \Psi_A \cong E \Psi_A$$

The first term gives the one-electron atomic energy of the H-atom, $\mathcal{H}_A \Psi_A = E_A \Psi_A$:

$$E_A \Psi_A + \frac{e^2}{4\pi\epsilon_0 R} \Psi_A \cong E \Psi_A \quad \text{dividing by } \Psi \text{ gives: } \mathcal{H}\Psi_A \cong E_A + \frac{e^2}{4\pi\epsilon_0 R} \cong E$$

$$\text{Then } H_{AA} = \int \Psi_A^* \mathcal{H}\Psi_A \, d\tau \cong \int \Psi_A^* E \Psi_A \, d\tau \cong E_A + \frac{e^2}{4\pi\epsilon_0 R}$$

As $R \rightarrow \infty$, the nuclear-nuclear repulsion term becomes negligible and $H_{AA} \cong E_A$.

5. Determine the Pauling electronegativity of Br. The experimental bond dissociation energies are $D_o(\text{H-H}) = 432.0 \text{ kJ mol}^{-1}$, $D_o(\text{Br-Br}) = 190. \text{ kJ mol}^{-1}$, and $D_o(\text{H-Br}) = 363. \text{ kJ mol}^{-1}$. The electronegativity of H is 2.2.

Answer: The plan is to use the deviation from equal sharing, Eq. 26.3.13, with the bond energies converted to electron volts.

Given $1 \text{ eV} = 96.4853 \text{ kJ mol}^{-1}$, the experimental bond dissociation energies are $D_o(\text{H-H}) = 4.477 \text{ eV}$, $D_o(\text{Br-Br}) = 1.97 \text{ eV}$, and $D_o(\text{H-Br}) = 3.76 \text{ eV}$. The “*Energy Units Converter*” on the text Web page or companion CD is also useful for easy energy conversions. Using Eq. 26.3.13:

$$(\chi_{\text{Br}} - \chi_{\text{H}})^2 = (3.76 - [(4.477)(1.97)]^{1/2}) \text{ eV} = 0.790 \text{ eV}$$

Solving for the electronegativity of Br, taking the positive root: $\chi_{\text{Br}} = 2.2 + \sqrt{0.791} = 3.09$
The accepted value is 2.96, which is an average over several compounds.

6. Determine the Pauling electronegativity of Ge. The experimental bond dissociation energies are $D_o(\text{Ge-Ge}) = 272. \text{ kJ mol}^{-1}$, $D_o(\text{F-F}) = 154.8 \text{ kJ mol}^{-1}$, and $D_o(\text{Ge-F}) = 484. \text{ kJ mol}^{-1}$.^{1,2} The electronegativity of F is 3.98, in current revised scales.

Answer: The plan is to use the deviation from equal sharing, Eq. 26.3.13, with the bond energies converted to electron volts.

Given $1 \text{ eV} = 96.4853 \text{ kJ mol}^{-1}$, the experimental bond dissociation energies are $D_o(\text{Ge-Ge}) = 2.82 \text{ eV}$, $D_o(\text{F-F}) = 1.604 \text{ eV}$, and $D_o(\text{Ge-F}) = 5.02 \text{ eV}$. The “*Energy Units Converter*” on the course Web page or companion CD is useful for easy energy conversions. Using Eq. 26.3.13 gives:

$$(\chi_{\text{Ge}} - \chi_{\text{F}})^2 = (5.02 - [(2.82)(1.604)]^{1/2}) \text{ eV} = 2.89 \text{ eV}$$

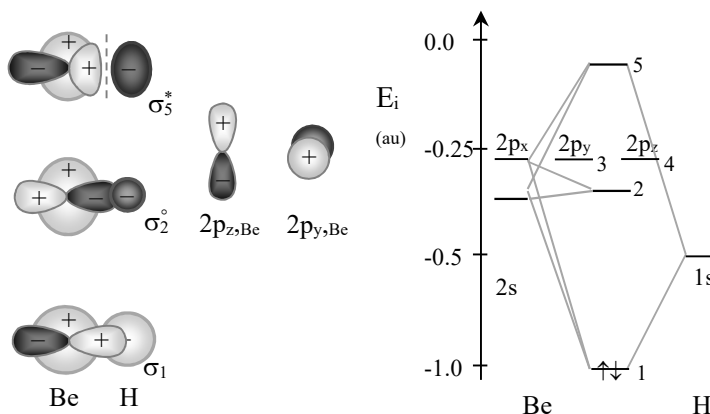
Solving for the electronegativity of Ge, taking the negative root: $\chi_{\text{Ge}} = 3.98 - \sqrt{2.89} = 2.28$
The negative root is used because the electronegativity of Ge is expected to be less than the electronegativity of F, based on the corresponding positions in the periodic table and the

direction of the dipole moment of GeF. The accepted value is 2.01, which is an average over several compounds. The experimental uncertainties for the D_o values for Ge_2 and GeF are $\sim 8\%$.

7. Sketch the qualitative molecular orbital diagram for BeH^+ . Calculate the qualitative bond order. Is the bond completely covalent, partially ionic, or strongly ionic?

Answer: The plan is to note the similarity of the molecular orbital diagram for BeH^+ with LiH . The ionic character of the bond is given by the difference in the electronegativities of Be and H.

The difference in electronegativity of Be and H is less than that for LiH , $\Delta\chi = \chi(\text{H}) - \chi(\text{Be}) = 0.63$. This decrease suggests that the bond between Be and H is less ionic than in LiH , which is $\sim 27\%$ ionic, Eq. 26.3.7. So the BeH bond is partially ionic. The decrease in $\Delta\chi$ also suggests that the $\text{Be}(2s)$ and $\text{H}(1s)$ are closer in energy than the $\text{Li}(2s)$ and $\text{H}(1s)$, giving greater covalent character. The valence atomic orbital ionization energies, Table 26.8.1, place the separated atom atomic orbital energies at $\text{Be}(2s)$ -9.30 eV, $\text{Be}(2p)$ -3.50 eV, and $\text{H}(1s)$ -13.6 eV. The orbitals are otherwise similar in character to LiH in relative order and symmetry, Figure 26.3.4. The x-axis is chosen as the internuclear axis. Combining four atomic orbitals on Be with one atomic orbital on H gives five final molecular orbitals. The valence atomic orbitals are $\text{Be}(2s)$, $\text{Be}(2p_x)$, $\text{Be}(2p_y)$, $\text{Be}(2p_z)$ and $\text{H}(1s)$. The $\text{Be}(2p_y)$ and $\text{Be}(2p_z)$ orbitals are non-interacting atomic non-bonding orbitals, because the overlap with $\text{H}(1s)$ is zero. The lowest energy molecular orbital has more $\text{Be}(2s)$ character than $\text{Be}(2p_x)$ because of better energy matching with $\text{H}(1s)$. The $\text{Be}(2s)$, $\text{Be}(2p_x)$, and $\text{H}(1s)$ create a bonding, non-bonding, anti-bonding triple. These three orbitals added to the $\text{Be}(2p_y)$ and $\text{Be}(2p_z)$ atomic non-bonding orbitals gives five total molecular orbitals:



BeH^+ has 2 valence electrons, filling only the lowest energy σ_1 orbital. The qualitative bond order is 1. While this problem was meant to be qualitative, you might try the CNDO level calculation at the experimental bond length of 1.342 Å, to verify your diagram.

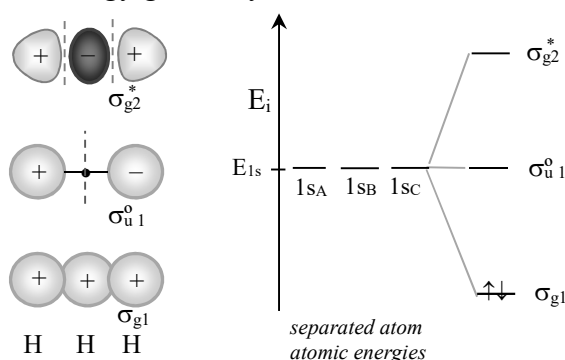
8. Sketch the qualitative molecular orbital diagram for linear H_3^+ . The H_3^+ ion is symmetrical about the center H-atom. Show that the odd number of atomic orbitals results in a bonding, non-bonding, anti-bonding trio of molecular orbitals. Calculate the qualitative bond order. Is the ion stable?

Answer: The plan is to note that since we are combining three atomic orbitals, three molecular orbitals result that must be symmetrical about the center H-atom.

The atomic orbitals are three H(1s) orbitals. The ion has two electrons. The symmetric combination of the three 1s-orbitals gives the most bonding orbital as: ○○○. The anti-bonding complement is generated by reversing the phase of the central orbital: ○●○. The trick to generate other possible molecular orbitals is to reverse the phase of an outer orbital: ○ · ●. However, this new orbital must be a non-bonding orbital, since neither ○●● nor ○○● are symmetrical about the center H-atom. For example, ○●● is anti-bonding on the left and bonding on the right. The molecular orbital diagram is shown below, with the two electrons in the bonding σ_{g1} orbital. The qualitative bond order is:

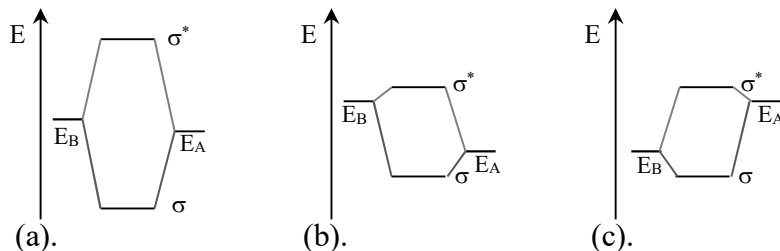
$$\text{qualitative BO} = (\text{bonding electrons} - \text{anti-bonding electrons})/2 = 1$$

Since we combined an odd number of atomic orbitals, an odd number of molecular orbitals necessarily result. Given the symmetry of the molecule, with one bonding and one-anti-bonding molecular orbital the intermediate molecular orbital must be intermediate in character. In this case the middle orbital is rigorously non-bonding. The ion is predicted to be stable, but not necessarily the lowest energy geometry.



9. Consider the bond between atoms A and B with bonding wave function:

$\Psi_1 = 0.800 \Psi_A + 0.360 \Psi_B$. (a). Calculate the % ionic character. (b). Choose the corresponding molecular energy diagram from below. (c). Find the corresponding anti-bonding orbital. Assume the atomic orbitals are normalized and the overlap integral is $S = 0.400$.



Answer: The plan to find the anti-bonding complement to the given bonding orbital is to use orthogonality and normalization.

(a). The % ionic character is given by Eq. 26.3.4:

$$\text{fraction ionic} = \frac{(0.800)^2 - (0.360)^2}{(0.800)^2 + (0.360)^2} = 0.663 \quad \text{or } 66.3\% \text{ ionic}$$

(b). Molecular orbital diagram (b) shows the atomic orbital for A as more electronegative than B, giving the bonding orbital with a larger coefficient for the A-atomic orbital than for the B-atomic orbital. Diagram (a) shows little ionic character, since the atomic orbitals are so similar in energy, so is not applicable.

(c). Assume the anti-bonding complement has coefficients $\Psi_2 = a \Psi_A + b \Psi_B$. Orthogonality gives the ratio of the orbital coefficients. Assuming the atomic orbitals are real, and normalized gives $\int \Psi_A^2 d\tau = \int \Psi_B^2 d\tau = 1$:

$$\begin{aligned} \int \Psi_1 \Psi_2 d\tau &= \int (0.800 \Psi_A + 0.360 \Psi_B) (a\Psi_A + b\Psi_B) d\tau = 0 \\ &= 0.800 a \int \Psi_A^2 d\tau + 0.360 b \int \Psi_B^2 d\tau + 0.800 b \int \Psi_A \Psi_B d\tau + 0.360 a \int \Psi_B \Psi_A d\tau \\ &= 0.800 a + 0.360 b + 0.800 b S + 0.360 a S = 0 \end{aligned}$$

The order of the orbitals doesn't matter, since they are just functions, giving $\int \Psi_A \Psi_B d\tau = \int \Psi_B \Psi_A d\tau = S$ from the definition of the overlap integral. Orthogonality then gives:

$$\begin{aligned} a(0.80 + 0.360 S) + b(0.360 + 0.80 S) &= 0 \\ a/b &= -(0.360 + 0.80 S) / (0.80 + 0.360 S) \quad \text{with } S = 0.400 \text{ given:} \\ a/b &= -0.7203 \end{aligned}$$

$$\text{giving: } a^2 = 0.5189 b^2 \quad \text{and} \quad ab = -0.7203 b^2$$

The normalization gives the final coefficients:

$$\begin{aligned} \int \Psi_2^2 d\tau &= \int (a\Psi_A + b\Psi_B)^2 d\tau = 1 \\ &= a^2 \int \Psi_A^2 d\tau + b^2 \int \Psi_B^2 d\tau + 2ab \int \Psi_A \Psi_B d\tau = 1 \\ &= a^2 + b^2 + 2abS = 1 \end{aligned}$$

Substituting in for a^2 and ab using the ratio from orthogonality gives:

$$\begin{aligned} 0.5189 b^2 + b^2 + 2(-0.7203)b^2(0.400) &= 1 \\ b^2 &= 1.0609 \quad \text{or } b = 1.0300 \quad \text{and } a = -0.7420 \end{aligned}$$

The final anti-bonding orbital is then $\Psi_2 = -0.742 \Psi_A + 1.030 \Psi_B$

10. Calculate the bond order and atom charges for BH at the CNDO level at the experimental bond length, 1.236 Å. Calculate the charges and bond order using the molecular orbital coefficients and the overlap integrals (in effect, verifying the listed bond order in the CNDO printout). [Use the online CNDO applet on the textbook Web site.]

Answer: The charge is zero with singlet spin multiplicity. The simplified listing is given below.

Atomic Coordinates (Å)				
Atom	x	y	z	
1 B	0.0	0.0	0.0	
2 H	1.236	0.0	0.0	

Coulombic repulsion integrals (bottom triangle) (a.u.)
and internuclear distances (top triangle) (a.u.) _____

Atoms:	1 B	2 H				
1 B	0.4723	2.3357				
2 H	0.3808	0.75				

Overlap Matrix						
	1 B2s	1 B2px	1 B2py	1 B2pz	2 H1s	
1 B2s	1.0	0.0	0.0	0.0	0.4984	
1 B2px	0.0	1.0	0.0	0.0	0.5241	
1 B2py	0.0	0.0	1.0	0.0	0.0	
1 B2pz	0.0	0.0	0.0	1.0	0.0	
2 H1s	0.4984	0.5241	0.0	0.0	1.0	

SCF eigenvalues (a.u.) and eigenvectors
(eigenvectors listed in columns)

E(i)	-0.8084	-0.4892	0.0817	0.0817	0.3019
vector	1	2	3	4	5
1 B2s	0.6739	-0.6534	0.0	0.0	-0.3449
1 B2px	0.3319	0.6848	0.0	0.0	-0.6487
1 B2py	0.0	0.0	0.0	1.0	0.0
1 B2pz	0.0	0.0	1.0	0.0	0.0
2 H1s	0.6601	0.3227	0.0	0.0	0.6784

Total Bond Order (Mulliken overlap population) _____

Atoms:	1 B	
2 H	1.389	

Electronic energy = -5.2668 a.u.
Total energy = -3.9824 a.u. includes nuclear-nuclear repulsion
Total bond dissociation energy, Do = 12.9941 eV = 1253.735 kJ/mol

Total atom electron densities and atomic charges

atom	density	charge
1 B	2.9204	0.08
2 H	1.0796	-0.08

The atomic orbitals on B in MO 1 and 2 are the 2s and 2p_x. Using Eq. 26.3.9, the orbital coefficients, and noting that there are two occupied molecular orbitals give the atom density on the B-atom as:

$$d_B = \sum_{j \text{ on B}} (n_1 c_{1j}^2 + n_2 c_{2j}^2) = 2(0.6739)^2 + 2(-0.6534)^2 + 2(0.3319)^2 + 2(0.6848)^2 = 2.9204$$

$$\begin{array}{cccccc} \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ n_1 (c_{1,B(2s)})^2 + n_2 (c_{2,B(2s)})^2 & + & n_1 (c_{1,B(2p_x)})^2 + n_2 (c_{2,B(2p_x)})^2 & & & \end{array}$$

The atomic charge, with three valence electrons for the B-atom: charge = 3 – 2.9204 = 0.0796. Alternately, the atom electron density on B is the sum of the diagonal population matrix elements for B. The charge on H is easier to calculate, and gives the same result.

The Mulliken overlap population is given by Eq. 26.3.10 for m molecular orbitals:

$$P_{BH} = \sum_{j \text{ on B}} \sum_{k \text{ on H}} \sum_{i=1,m} n_i c_{ij} c_{ik} S_{jk} \quad (\text{Mulliken})$$

$$= 4(0.674)(0.660)(0.498) + 4(-0.653)(0.323)(0.498) + 4(0.332)(0.660)(0.524) + 4(0.685)(0.323)(0.524)$$

$$= 2n_1 c_{1,B(2s)} c_{1,H(1s)} S_{2s,1s} + 2n_2 c_{2,B(2s)} c_{2,H(1s)} S_{2s,1s} + 2n_1 c_{1,B(2p_x)} c_{1,H(1s)} S_{2p_x,1s} + 2n_2 c_{2,B(2p_x)} c_{2,H(1s)} S_{2p_x,1s}$$

$$= 0.8868 - 0.4204 + 0.4592 + 0.4632 = 1.389$$

The results are within round-off error of the values given in the listing. The bond is 8% ionic. For comparison purposes, the Coulson bond order is given by the sum of the population matrix elements over the atomic orbitals on B and the atomic orbitals on H:

$$BO_{BH} = \sum_{j \text{ on B}} \sum_{k \text{ on H}} (\sum_{i=1,m} n_i c_{ij} c_{ik}) = \sum_{j \text{ on B}} \sum_{k \text{ on H}} p_{jk} \quad (\text{Coulson})$$

$$= 2(0.6739)(0.6601) + 2(-0.6534)(0.3227) + 2(0.3319)(0.6601) + 2(0.6848)(0.3227)$$

$$= n_1 c_{1,B(2s)} c_{1,H(1s)} + n_2 c_{2,B(2s)} c_{2,H(1s)} + n_1 c_{1,B(2p_x)} c_{1,H(1s)} + n_2 c_{2,B(2p_x)} c_{2,H(1s)}$$

$$= 0.8897 - 0.4217 + 0.4382 + 0.4420 = 0.4680 + 0.8802 = 1.348$$

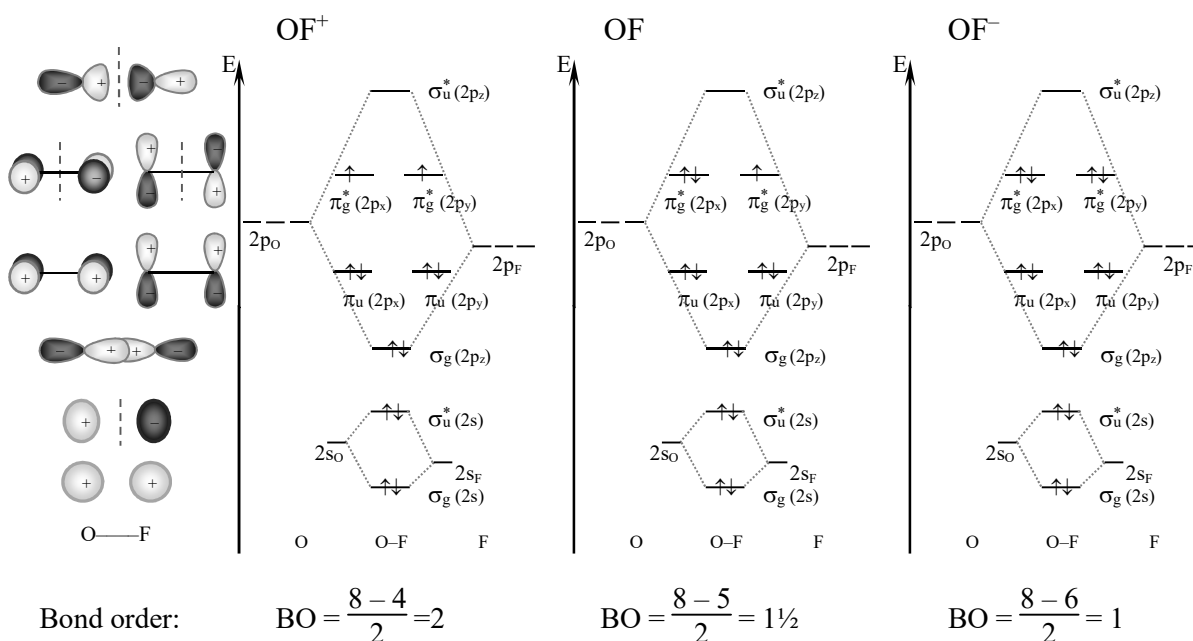
or taken directly from the population matrix listing: $BO_{BH} = 0.4679 + 0.8802 = 1.348$

You should locate the corresponding matrix elements in the CNDO listing for practice. The Coulson and Mulliken bond orders are usually quite similar. For comparison with more advanced methods, the atomic charge on B at the HF/6-31G** level is 0.126 and the Mulliken bond order is 0.927.

11. Using molecular orbital theory, decide if OF is more likely to form an OF^+ ion or an OF^- ion.

Answer: The plan is to assume the molecular orbital diagram is similar to O_2 . Note that O_2 and OF^+ are isoelectronic.

The OF molecule has $6+7 = 13$ valence electrons. The MOs fill with three electrons in the π_g^* orbitals. Removing an electron from OF to form OF^+ removes an anti-bonding electron, strengthening the bond. Adding an electron to OF to form OF^- adds an anti-bonding electron, weakening the bond. The required approach is to calculate the qualitative bond order, Eq. 26.4.1. As shown below, OF^+ has the largest bond order, giving the strongest bond, and is more likely to form from OF.

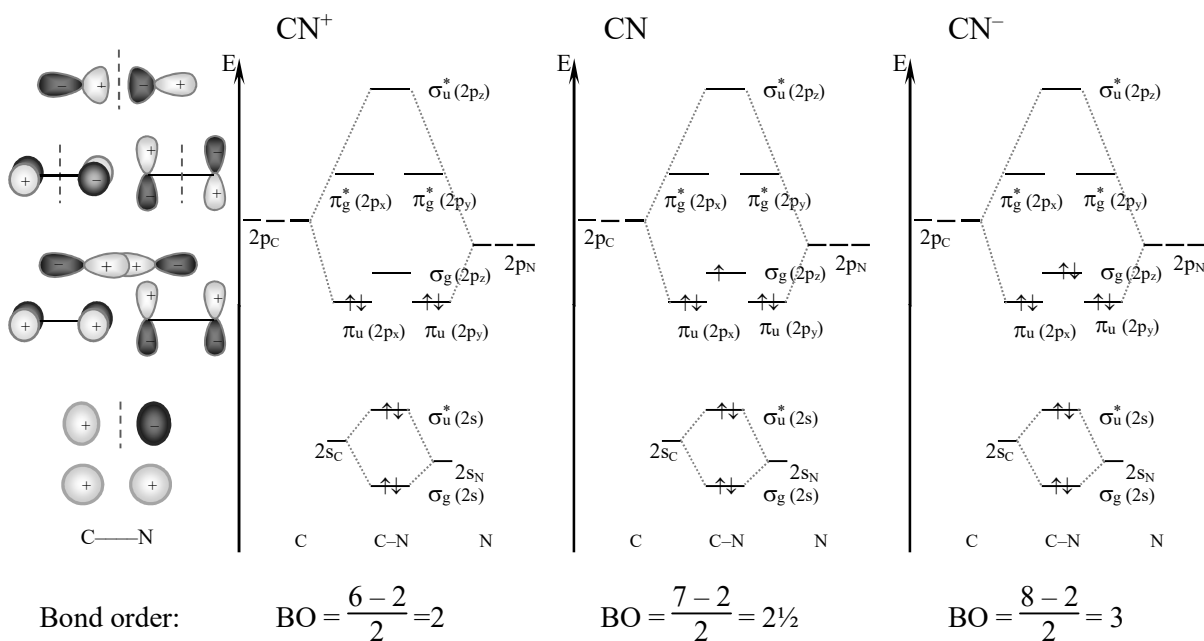


12. Using molecular orbital theory, which of CN , CN^+ , or CN^- has the strongest bond?

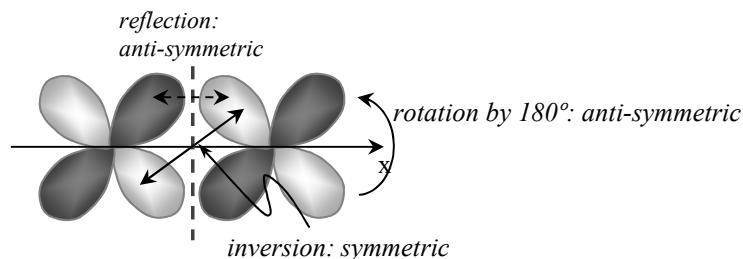
Answer: The plan is to note that the sum of the atomic numbers of CN is 13, which is less than the sum for N_2 of 14. The molecular orbital diagram is expected to have the same molecular orbital ordering as N_2 . The bond strengths are expected to correlate with the qualitative bond order.

There are 9 valence electrons. The MOs fill with one electron in the $\sigma_g(2p_z)$ -orbital. Removing an electron from CN to form CN^+ removes a bonding electron, weakening the bond. Adding an

electron to CN to form CN^- adds a bonding electron, strengthening the bond. The required approach is to calculate the qualitative bond order, Eq. 26.4.1. As shown below, CN^- has the largest bond order, giving the strongest bond. Note that CN^- is isoelectronic with N_2 .



13. What is the symmetry of the orbital formed from the side-on overlap of two d orbitals as shown below (σ, π , or δ ; bonding or anti-bonding; g or u)? The lobes of both orbitals lie in the plane of the paper. The x-axis is the internuclear axis.



Answer: The orbital changes sign under rotation by 180° , giving a π -orbital (see above). Reflection across the plane perpendicular to the internuclear axis and positioned midway between the nuclei gives a change in sign. The orbital is anti-symmetric with respect to reflection, giving an anti-bonding orbital. The reflection plane is coincident with the node that is perpendicular to the internuclear axis. Inversion through the center of mass gives the same orbital phase. The orbital is symmetric with respect to inversion, giving a “g” orbital. All together, the orbital is π_g^* .

14. Calculate the bond order in linear BeH_2 in the CNDO approximation. Characterize the highest occupied molecular orbital (σ or π , bonding, non-bonding, or anti-bonding). The bond length is 1.330 \AA . Calculate the Mulliken bond order using the molecular orbital coefficients and the overlap integrals (in effect, verifying the listed bond order in the CNDO printout).

Chapter 26: Molecular Structure

Answer: The plan is to use the “*cndo*” applet, on the text book Web site and on the companion CD, to obtain the overlap matrix and the eigenvectors. The eigenvectors are the molecular orbital coefficients. The bond order is calculated using Eq. 26.3.10:

$$P_{ab} = \sum_j \sum_{\text{on a k on b}} \sum_{i=1}^m n_i 2c_{ij} c_{ik} S_{jk} \quad (\text{Mulliken})$$

for atoms a and b and MO i with n_i electrons. In this problem atom a is 1-Be and atom b is 2-H. The two Be-H bonds are equivalent, so either may be used.

The input was set-up as:

The screenshot shows the input parameters for the cndo applet:

- Atom 1: H
- Bond length: 1.33 Å
- Bond angle: 180 degrees
- Atom 2: Be
- Atom 3: H
- Bond length: 1.33 Å
- Charge: 0
- Multiplicity: singlet

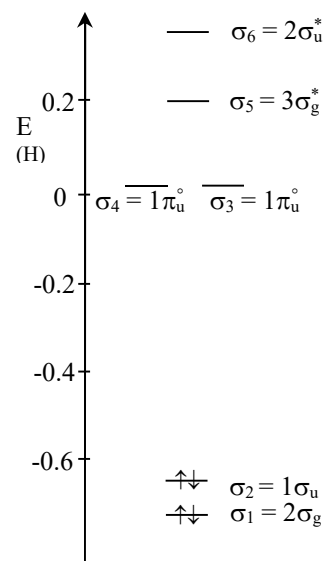
There are four valence electrons, filling through the second molecular orbital, giving the HOMO as σ -bonding. The Atomic Coordinates show that the x-axis is chosen as the intermolecular axis. Only the Be(2s) and Be(2p_x) contribute to the bonding with H(1s). Be(2p_y) and (2p_z) are atomic non-bonding. The overlap integrals, eigenvectors, and population analysis from the output are:

Overlap Matrix						
	1 Be2s	1 Be2px	1 Be2py	1 Be2pz	2 H1s	3 H1s
1 Be2s	1.0	0.0	0.0	0.0	0.4908	0.4908
1 Be2px	0.0	1.0	0.0	0.0	0.5593	-0.5593
1 Be2py	0.0	0.0	1.0	0.0	0.0	-0.0
1 Be2pz	0.0	0.0	0.0	1.0	0.0	0.0
2 H1s	0.4908	0.5593	0.0	0.0	1.0	0.046
3 H1s	0.4908	-0.5593	-0.0	0.0	0.046	1.0

SCF eigenvalues (a.u.) and eigenvectors (eigenvectors listed in columns)						
E(i) vector	-0.6963 1	-0.6594 2	0.0767 3	0.0767 4	0.2004 5	0.3277 6
atom:						
1 Be2s	0.6759	0.0	0.0	0.0	0.737	-0.0
1 Be2px	0.0	-0.6294	0.0	0.0	0.0	0.7771
1 Be2py	0.0	0.0	0.0	1.0	0.0	0.0
1 Be2pz	0.0	0.0	1.0	0.0	0.0	0.0
2 H1s	0.5212	-0.5495	0.0	0.0	-0.4779	-0.4451
3 H1s	0.5212	0.5495	0.0	0.0	-0.4779	0.4451

SCF Population matrix						
	1 Be2s	1 Be2px	1 Be2py	1 Be2pz	2 H1s	3 H1s
1 Be2s	0.9136	0.0	0.0	0.0	0.7045	0.7045
1 Be2px	0.0	0.7923	0.0	0.0	0.6917	-0.6917
1 Be2py	0.0	0.0	0.0	0.0	0.0	0.0
1 Be2pz	0.0	0.0	0.0	0.0	0.0	0.0
2 H1s	0.7045	0.6917	0.0	0.0	1.147	-0.0606
3 H1s	0.7045	-0.6917	0.0	0.0	-0.0606	1.147

Total Bond Order (Mulliken overlap population)		
Atoms:	1 Be	2 H
2 H	1.465	
3 H	1.465	-0.006



The molecular orbital energy diagram is shown at right, with the symmetry designations, for comparison with Figure 26.6.4. The Mulliken overlap population for the (1-Be)-(2-H) bond is:

$$\begin{aligned}
 P_{\text{BeH}} &= 4(0.6759)(0.5212)(0.4908) + 4(-0.6294)(-0.5495)(0.5593) && \text{(Mulliken)} \\
 &\quad \begin{array}{cccc} \uparrow & \uparrow & \uparrow & \uparrow \\ 2n_1 c_{1,\text{Be}(2s)} c_{1,\text{H}(1s)} S_{2s,1s} & & + & 2n_2 c_{2,\text{Be}(2p_x)} c_{2,\text{H}(1s)} S_{2p_x,1s} \\ \text{molecular orbital 1} & & & \text{molecular orbital 2} \end{array} \\
 &= 0.6916 - 0.7737 = 1.465
 \end{aligned}$$

as listed in the *cndo* printout. The Be(2p_x)-H(1s) term for molecular orbital 1 and the Be(2s)-H(1s) term for molecular orbital 2 vanish because of the zero coefficients for the corresponding Be atomic orbitals.

For comparison purposes, the Coulson bond order is given by the sum of the Population Matrix elements:

$$\begin{aligned}
 \text{BO}_{\text{BH}} &= \sum_{j \text{ on B}} \sum_{k \text{ on H}} \left(\sum_{i=1,m} n_i c_{ij} c_{ik} \right) && \text{(Coulson)} \\
 &= 2(0.6759)(0.5212) + 2(-0.6294)(-0.5495) \\
 &\quad \begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ n_1 c_{1,\text{B}(2s)} c_{1,\text{H}(1s)} & + & n_2 c_{2,\text{B}(2p_x)} c_{2,\text{H}(1s)} \end{array} \\
 &= 0.7046 + 0.6917 = 1.396
 \end{aligned}$$

The population matrix is also called the density matrix. You should locate the corresponding matrix elements in the CNDO listing for practice. The Coulson and Mulliken bond orders are usually quite similar. For comparison with more advanced methods, the atomic charge on Be at the HF/6-31G** level is 0.216 as compared to 0.294 at the CNDO level. The Mulliken bond order at HF/6-31G** is 0.988 and taking into account electron-electron correlation using B3LYP/6-311G** is 0.971.

15. Determine the bond order for the O-H bond in H₂O assuming a 90° bond angle and an O-H bond length of 0.96 Å, in the CNDO approximation. Calculate the bond order using the molecular orbital coefficients and the overlap integrals (in effect, verifying the listed bond order in the CNDO printout).

Answer: The plan is to use the “*cndo*” applet, on the text book Web site and on the companion CD, to obtain the overlap matrix and the eigenvectors. The eigenvectors are the molecular orbital coefficients. The bond order is calculated using Eq. 26.3.10. In this problem atom a is 1-O and atom b is 2-H. The two O-H bonds are equivalent, so either may be used.

The input was set up as:

Molecule (for triatomics select a third atom):

H

0.96 Å 90.0 degrees

O --- H

0.96 Å

Charge: 0 Multiplicity: singlet

The overlap matrix and eigenvectors were copied and pasted into a text document and then imported in Excel to make the calculation easier. The highlighted areas are the coefficients of interest:

A1	B	C	D	E	F	G	H	I	J	K
2		Overlap Matrix								
3		orbital	1-O2s	1-O2px	1-O2py	1-O2pz	2-H1s	3-H1s		
4		1-O2s	1	0	0	0	0.4777	0.4777		
5		1-O2px	0	1	0	0	0.382	0		
6		1-O2py	0	0	1	0	0	0.382		
7		1-O2pz	0	0	0	1	0	0		
8		2-H1s	0.4777	0.382	0	0	1	0.3331		
9		3-H1s	0.4777	0	0.382	0	0.3331	1		
10										
11		Eigenvalues and Eigenvectors			(Molecular Orbital Coefficients)					
12		E(i)	-1.498	-0.755	-0.7378	-0.657	0.319	0.3557		
13		vector	1	2	3	4	5	6		
14		1-O2s	0.8547	0	-0.3547	0	0	-0.3791		
15		1-O2px	0.0623	-0.5498	0.579	0	0.445	-0.4012		
16		1-O2py	0.0623	0.5498	0.579	0	-0.445	-0.4012		
17		1-O2pz	0	0	0	1	0	0		
18		2-H1s	0.3617	-0.4447	0.3192	0	-0.550	0.5169		
19		3-H1s	0.3617	0.4447	0.3192	0	0.550	0.5169		
20										
21	O-orbital	H-orbital	$c_{1,O}^*c_{1,H}$	$c_{2,O}^*c_{2,H}$	$c_{3,O}^*c_{3,H}$	$c_{4,O}^*c_{4,H}$		$\sum n_i^*c_{ij}^*c_{ik}$	$S_{i,k}$	$\sum n_i^*2^*c_{ij}^*c_{ik}^*S_{i,k}$
22	1-O2s	2-H1s	0.3091	0.0000	-0.1132	0.0000		0.3918	0.4777	0.3744
23	1-O2px	2-H1s	0.0225	0.2445	0.1848	0.0000		0.9037	0.3820	0.6904
24	1-O2py	2-H1s	0.0225	-0.2445	0.1848	0.0000		-0.0743	0.0000	0.0000
25										
26								TotalBO(O-H)=		1.0648

Since there are 6+1+1 valence electrons, the highest occupied molecular orbital is orbital 4. Therefore, for the sum, only orbitals 1-4 are required, each with $n_i = 2$. Cells I22:I24 are the sums over the molecular orbitals for each pair of atomic orbitals. For example, cell D22 is given by $c_{1,O2s} c_{1,H1s} = (0.8547)(0.3617) = D14*D18$ and the sum for the coefficients for the O 2s orbital with the H 1s orbital is given in cell I22= $\text{SUM}(D22:F22)*2$:

$$\begin{aligned}
 p_{O2s,H1s} &= \sum_{i=1}^4 2 c_{i,O2s} c_{i,H1s} \\
 &= 2(0.8547)(0.3617) + 2(0)(-0.4447) + 2(-0.3547)(0.3192) + 2(0)(0) = 0.3918
 \end{aligned}$$

where p is the population matrix entry. The population matrix is also called the density matrix. The O 2p_z orbital shows no interaction with the H 1s, so these sums are not calculated. These values are listed in the SCF Population matrix in the CNDO printout. Each sum is then multiplied by two and the corresponding overlap integral for the pair of orbitals and the overall sum gives the bond order:

$$\begin{aligned}
 P_{O,H} &= \sum_{j \text{ on O}} \sum_{k \text{ on H}} \sum_{i=1}^m n_i 2 c_{ij} c_{ik} S_{jk} = \sum_{j \text{ on a}} \sum_{k \text{ on b}} 2 p_{jk} S_{jk} \\
 &= 2p_{O2s,H1s} S_{O2s,H1s} + 2p_{O2px,H1s} S_{O2px,H1s} + 2p_{O2py,H1s} S_{O2py,H1s} + 2p_{O2pz,H1s} S_{O2pz,H1s} \\
 &= 2(0.3918)(0.4777) + 2(0.9037)(0.3820) + 2(-0.0743)(0.0) + 2(0)(0) = 1.065
 \end{aligned}$$

The bond orders at higher levels of approximation are: AM1 (0.967), PM3 (0.969), HF/6-31G** (0.892), and B3LYP/6-311G** (0.981). The larger value for the bond order is typical of the CNDO level. Because the bond order is not an experimentally measurable property, there is no method which is accepted as best for bond order estimations. Comparisons between molecules at the same level of approximation are useful for building chemical intuition.

16. Calculate the % ionic character in the lowest energy molecular orbital, for the valence electrons, of one of the O-H bonds in H₂O assuming a 90° bond angle and an O-H bond length of 0.96 Å, in the CNDO approximation (the same geometry as the previous problem).

Answer: The % ionic character from the CNDO calculation, considering only the H atom in the x-direction, is given by:

$$\% \text{ ionic character} = \frac{(0.8547)^2 + (0.0623)^2 - (0.3617)^2}{(0.8547)^2 + (0.0623)^2 + (0.3617)^2} = 69.8\%$$

The % ionic character is even higher at the AM1 level of approximation (see the following problem).

17. Characterize the highest occupied molecular orbital for H₂O as bonding, non-bonding, or anti-bonding. Is the orbital σ or π type, or is the orbital better characterized as purely atomic? Compare this result to the prediction from hybridization theory. You may use semi-empirical or HF/STO-3G methods.

Answer: The plan is to use any semi-empirical calculation to find the molecular orbital coefficients for the HOMO.

The CNDO level eigenvectors are given in Problem 12. Alternately at a better level of approximation, the MOPAC input file with the O atom at the origin is:

```
1SCF AM1 GEO-OK VECTORS
H2O 90 deg.

O
H 0.96 0 0.000 0 0.000 0 1 0 0
H 0.96 0 90.00 0 0.000 0 1 2 0
      ↑      ↑      ↑
      Don't optimize

atom 1 [atom 1 is at the origin]
atom 2 [the 2-1 distance is 0.96 Å]
atom 3 [the 3-1 distance is 0.96 Å, the 3-1-2 angle is 90°]
```

A portion of the MOPAC output file at the AM1 level is:

```
INTERATOMIC DISTANCES
      O 1      H 2      H 3
-----
O 1      .0000
H 2      .9600      .0000
H 3      .9600      1.3576      .0000

EIGENVECTORS
ROOT NO.      1      2      3      4      5      6
      -36.71064      -17.47187      -15.72093      -12.54516      4.80212      5.55102
S O 1      .88709      .00000      .38922      .00000      .24816      .00000
PX O 1      .11967      .55249      -.54759      .00000      .43107      .44131
PY O 1      .11967      -.55249      -.54759      .00000      .43107      -.44131
PZ O 1      .00000      .00000      .00000      1.00000      .00000      .00000
S H 2      .30367      .44131      -.35270      .00000      -.53234      -.55249
S H 3      .30367      -.44131      -.35270      .00000      -.53234      .55249
```

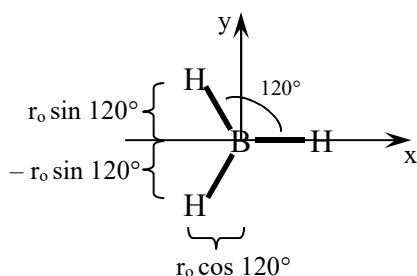
In either the CNDO or AM1 case, the highest occupied molecular orbital is orbital 4, since there are 6+1+1 valence electrons, requiring 4 orbitals. The molecular orbital coefficients on the H atoms are zero in the HOMO. Molecular orbital 4 is just an isolated $2p_z$ orbital on the O atom. The HOMO is then non-bonding. The HOMO can be considered as π -type since π -bonds would form perpendicular to the x-y plane of the molecule, if they were possible. Alternately, the HOMO can be described as an atomic non-bonding $2p_z$ orbital.

The prediction using hybridization is that there should be two equivalent lone pairs in sp^3 hybridized orbitals. The more accurate molecular orbital results give one lone pair as the HOMO, which is an atomic non-bonding $2p_z$ orbital. The other lone pair is approximately described as a core 2s orbital on oxygen, since the lowest energy molecular orbital is predominantly 2s in character with roughly 70% (CNDO) to 80% (AM1) ionic character. The % ionic character from the CNDO calculation is determined in the previous problem.

From an energetic perspective, the hybridization treatment is misleading. However, the electrostatic distribution is well approximated by both molecular orbital and hybridization approaches.

18. Using geometrical considerations, find the Cartesian coordinates for the planar molecule BH_3 . Place the B atom at the origin and use a bond length of 1.19 Å. Orient one of the H atoms along the x-axis. Obtain the overlap matrix and the molecular orbital coefficients using the version of the “*cndo*” applet that has Cartesian coordinate input, which is on the text book Web site and on the companion CD. Example input files are shown at the bottom of the applet. The first line of the input file is the number of atoms, the second line is a comment, and the remaining lines are the atom and the x, y, z coordinates. (a). Give the molecular orbital energy diagram and indicate the electron occupancy. (b). Draw orbital 3. (c). Write orbital 3 in terms of the molecular orbital coefficients and the atomic orbitals: $2s_B$, $2p_{x,B}$, $2p_{y,B}$, $2p_{z,B}$, $1s_{H2}$, $1s_{H3}$, and $1s_{H4}$, where the H atoms are atoms 2, 3, and 4. (d). Characterize orbital 3 as bonding, non-bonding, or anti-bonding. (e). Characterize the LUMO as bonding, non-bonding, or anti-bonding. (f). Show the lowest energy electronic transition on the energy level diagram. (g) Referring to the H atom along the x-axis, which atomic orbital on the central B atom has better overlap with the H atom 1s-atomic orbital?

Answer: The plan is to note that the bond angle in a symmetrical triatomic is 120° . If the B atom is at the origin and one H atom is along the x-axis at $(r_0, 0, 0)$, then the remaining two H atoms are at $(r_0 \cos 120^\circ, r_0 \sin 120^\circ, 0)$ and $(r_0 \cos 120^\circ, -r_0 \sin 120^\circ, 0)$:



The corresponding input file in XYZ format is:

4					<i>number of atoms</i>
BH3					<i>comment</i>
B	0.0	0.0	0.0		<i>Cartesian coordinates for each atom</i>
H	1.19	0.0	0.0		
H	-0.595	1.031	0.0		
H	-0.595	-1.031	0.0		

Notice that no information is given about the bonding partners, nor the types of bonds present, as would be required for a molecular mechanics input file. The results are:

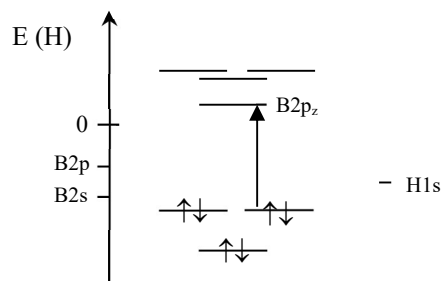
		Overlap Matrix							
		1 B2s	1 B2px	1 B2py	1 B2pz	2 H1s	3 H1s	4 H1s	
1	B2s	1.0	0.0	0.0	0.0	0.5198	0.5196	0.5196	
1	B2px	0.0	1.0	0.0	0.0	0.5366	-0.2681	-0.2681	
1	B2py	0.0	0.0	1.0	0.0	0.0	0.4646	-0.4646	
1	B2pz	0.0	0.0	0.0	1.0	0.0	0.0	0.0	
2	H1s	0.5198	0.5366	0.0	0.0	1.0	0.1209	0.1209	
3	H1s	0.5196	-0.2681	0.4646	0.0	0.1209	1.0	0.1208	
4	H1s	0.5196	-0.2681	-0.4646	0.0	0.1209	0.1208	1.0	

		SCF eigenvalues (a.u.) and eigenvectors (eigenvectors listed in columns)						
E (i)		-0.9874	-0.7035	-0.7035	0.0726	0.2625	0.3176	0.3176
vector		1	2	3	4	5	6	7
atom:								
1	B2s	0.7131	-0.0	-0.0003	0.0	-0.7011	0.0	0.001
1	B2px	0.0002	0.0	0.6679	0.0	0.001	0.0	0.7442
1	B2py	0.0	0.6679	-0.0	0.0	-0.0	0.7442	-0.0
1	B2pz	0.0	0.0	0.0	1.0	0.0	0.0	0.0
2	H1s	0.405	0.0	0.6075	0.0	0.4109	-0.0	-0.546
3	H1s	0.4047	0.5262	-0.304	0.0	0.4121	-0.4723	0.2721
4	H1s	0.4047	-0.5263	-0.3039	0.0	0.4121	0.4723	0.2721

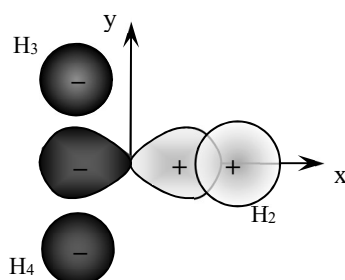
		Total Bond Order (Mulliken overlap population)			
Atoms:		1 B	2 H	3 H	
2	H	1.471			
3	H	1.471	-0.01		
4	H	1.471	-0.01	-0.01	

(a). Semi-empirical methods include only valence electrons, while *ab initio* include all electrons. The total number of valence electrons is $3+1+1+1 = 6$. Given double occupancy, the highest occupied molecular orbitals are 2 and 3. The HOMO is doubly degenerate in this molecule. The orbital energies are in Hartrees. The molecular orbital energy diagram and the electron occupancy are shown below. The energies of occupied atomic orbitals on B and H at the CNDO level are shown for comparison.

Chapter 26: Molecular Structure



(b). By convention, the positive lobe of the $2p_x$ orbital faces to the right along the positive x -direction. The overlap of the positive lobe of the $2p_x$ orbital with the $1s_{H,2}$ orbital is bonding, since both have positive phases. The overlap of the negative lobe of the $2p_x$ orbital with H atoms 3 and 4 is also bonding, because each orbital or lobe has negative phase. Orbital 3 has three direct bonding interactions:



The overlap matrix shows that the overlap integral for the $2p_x$ orbital with $1s_{H,2}$ is about twice that for $1s_{H,3}$ and $1s_{H,4}$. The $1s_{H,3}$ and $1s_{H,4}$ orbitals are shown smaller than the $1s_{H,2}$ because the corresponding molecular orbital coefficients for $1s_{H,3}$ and $1s_{H,4}$ are smaller (0.304). Each interaction is in the bonding plane, resulting in σ bonds to the three H atoms.

(c). Molecular orbital 3 is given by:

$$\Psi_3 = 0.668 2p_{x,B} + 0.608 1s_{H,2} - 0.304 1s_{H,3} - 0.304 1s_{H,4}$$

(d). Orbital 3 has three direct bonding interactions and no anti-bonding interactions making the orbital overall bonding.

(e). The LUMO is orbital 4, which is a pure B $2p_z$ orbital with zero coefficients on the three H atoms. No net overlap is possible between the $2p_z$ orbital and $1s$ orbitals that are in the nodal plane of the $2p_z$ orbital. The LUMO is non-bonding and can be considered as a π_{nb} orbital or just an atomic $2p_z$ orbital on the central B atom.

(f). The lowest energy electronic transition is shown on the energy level diagram. This transition is a sigma to non-bonding transition, $nb \leftarrow \sigma$, which is expected to have a strong transition dipole moment.

(g) The overlap integral of the B $2p_x$ orbital with $1s_{H,2}$ is larger, at 0.5366, than the B $2s$ orbital overlap with $1s_{H,2}$, which is 0.5198. The $2p_x$ orbital is better directed in space to overlap with H atom 1. However, the B $2p_z$ orbital is higher in energy than the $2s$, so energy matching with the $1s_H$ orbital is comparable.

19. Consider the B-H bond using the CNDO level calculation for BH_3 in the previous problem. Focus on the Mulliken overlap population between the B atom and H atom 2, which is along the

x-axis. Does the $2s_B-1s_{H,2}$ or the $2p_{x,B}-1s_{H,2}$ overlap make a stronger contribution to the bond strength?

Answer: The plan is to note that the overall bond strength includes contributions from both $2s_B-1s_{H,2}$ and the $2p_{x,B}-1s_{H,2}$ overlap. The total bond order is given by Eq. 26.3.10:

$$P_{ab} = \sum_{j \text{ on a}} \sum_{k \text{ on b}} \sum_{i=1}^m n_i 2c_{ij} c_{ik} S_{jk}$$

There are three filled molecular orbitals, $m = 3$. The specific terms for the $2s-1s_{H,2}$ and the $2p_x-1s_{H,2}$ coefficients must be evaluated.

The contribution of the $2s-1s_{H,2}$ overlap is:

$$2 p_{B2s,H1s} S_{B2s,H1s} = \sum_{i=1}^3 2 [2 c_{i,B2s} c_{i,H1s} S_{B2s,H1s}] \quad 1$$

The contribution of the $2p_x-1s_{H,2}$ overlap is:

$$2 p_{B2p_x,H1s} S_{B2p_x,H1s} = \sum_{i=1}^3 2 [2 c_{i,B2p_x} c_{i,H1s} S_{B2p_x,H1s}] \quad 2$$

From Eqs. 1 and 2 and the eigenvectors listed in the previous problem:

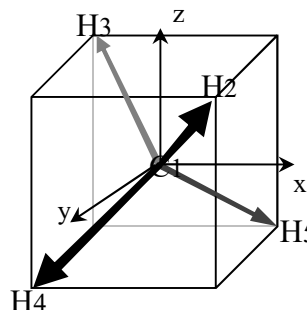
$$\begin{aligned} p_{B2s,H1s} S_{B2s,H1s} &= 2[2(0.7131)(0.4050) + 2(-0.0003)(0.6075)] 0.5198 \\ &= 2[0.5772(0.5198)] = 0.6002 \end{aligned}$$

$$\begin{aligned} p_{B2p_x,H1s} S_{B2p_x,H1s} &= 2[2(0.0002)(0.4050) + 2(0.6679)(0.6075)] 0.5366 \\ &= 2[0.8117(0.5366)] = 0.8710 \end{aligned}$$

The $2p_{x,B}-1s_{H,2}$ overlap has the stronger contribution. The total Mulliken bond order is then $0.6002 + 0.8710 = 1.4712$, which agrees with the CNDO printout. The overlap integral for $2p_{x,B}-1s_{H,2}$ is larger than $2s_B-1s_{H,2}$. However, the $2p_{x,B}$ orbital is higher in energy than the $2s_B$, so energy matching with the $1s_H$ orbital is comparable. In this particular case, the central atom orbital with the better overlap provides the stronger contribution to the bonding.

20. (a). Compare the molecular orbital and hybridization models of methane. (b). Find the C-H bond order and the charge on the C-atom in methane. Obtain the molecular orbital coefficients, atom electron distribution and bond order matrices using the version of the “*cnDO*” applet that has Cartesian coordinate input, which is on the text book Web site and on the companion CD. The atomic coordinates for methane with a C-H bond length of 1.084 Å are:

Atom	x	y	z
1 C	0.0	0.0	0.0
2 H	0.62565	0.62565	0.62565
3 H	-0.62565	-0.62565	0.62565
4 H	-0.62565	0.62565	-0.62565
5 H	0.62565	-0.62565	-0.62565



Chapter 26: Molecular Structure

Answer: The plan is to compare the CNDO results with the expected sp^3 hybridization.

The “*cn do*” applet input file for methane is:

```

5                                     number of atoms
CH4                                   comment
C   0.0   0.0   0.0                   x, y, z coordinates
H   0.62565   0.62565   0.62565
H  -0.62565  -0.62565   0.62565
H  -0.62565   0.62565  -0.62565
H   0.62565  -0.62565  -0.62565

```

The charge is zero and the multiplicity is singlet, all electrons are paired. The condensed “*cn do*” applet output is shown below:

SCF eigenvalues (a.u.) and eigenvectors (eigenvectors listed in columns)								
E(i) vector	-1.2755 1	-0.7268 2	-0.7268 3	-0.7268 4	0.3142 5	0.3334 6	0.3334 7	0.3334 8
atom:								
1 C2s	0.7261	0.0	0.0	0.0	-0.6876	-0.0	0.0	0.0
1 C2px	-0.0	0.2083	-0.1454	0.6596	0.0	0.5322	0.2732	-0.3774
1 C2py	-0.0	0.1873	0.6756	0.0898	-0.0	0.4659	-0.3139	0.4298
1 C2pz	-0.0	0.649	-0.1483	-0.2377	0.0	0.0015	0.572	0.4161
2 H1s	0.3438	0.5227	0.1911	0.2561	0.3631	-0.4995	-0.2655	-0.2341
3 H1s	0.3438	0.1268	-0.3395	-0.4939	0.3631	0.498	-0.3062	-0.1817
4 H1s	0.3438	-0.3352	0.485	-0.1662	0.3631	0.0339	0.5791	-0.1954
5 H1s	0.3438	-0.3142	-0.3366	0.404	0.3631	-0.0324	-0.0075	0.6113

SCF Population matrix									
	1 C2s	1 C2px	1 C2py	1 C2pz	2 H1s	3 H1s	4 H1s	5 H1s	
1 C2s	1.0545	0.0	0.0	-0.0	0.4993	0.4993	0.4993	0.4993	
1 C2px	0.0	0.9993	0.0	-0.0	0.5	-0.5	-0.5	0.5	
1 C2py	0.0	0.0	0.9993	0.0	0.5	-0.5	0.5	-0.5	
1 C2pz	-0.0	-0.0	0.0	0.9993	0.5	0.5	-0.5	-0.5	
2 H1s	0.4993	0.5	0.5	0.5	0.9869	-0.0138	-0.0138	-0.0138	
3 H1s	0.4993	-0.5	-0.5	0.5	-0.0138	0.9869	-0.0138	-0.0138	
4 H1s	0.4993	-0.5	0.5	-0.5	-0.0138	-0.0138	0.9869	-0.0138	
5 H1s	0.4993	0.5	-0.5	-0.5	-0.0138	-0.0138	-0.0138	0.9869	

Total Bond Order (Mulliken overlap population)				
Atoms:	1 C	2 H	3 H	4 H
2 H	1.371			
3 H	1.371	-0.005		
4 H	1.371	-0.005	-0.005	
5 H	1.371	-0.005	-0.005	-0.005

Total atom electron densities and atomic charges		
atom	density	charge
1 C	4.0524	-0.052
2 H	0.9869	0.013
3 H	0.9869	0.013
4 H	0.9869	0.013
5 H	0.9869	0.013

(a). Notice that the MOs involve C(2s) character or C(2p) character, but not both, in contradiction to hybridization arguments. The hybridization picture emerges when the average of MOs 1-4 is taken, giving s- and p-character. However, the CNDO s-character is greater than the canonical 25% expected for sp^3 hybridization. The hybridization has $(0.73)^2$ s-character. The SCF population matrix shows that the three p-orbital based bonding MOs, 2-4, are equivalent. Using MO 2 as representative gives $[(0.21)^2 + (0.19)^2 + (0.65)^2]$ p-character per MO. Taking MOs 1-4 into account corresponds to $s^{0.53}p^{1.51}$ overall hybridization. [Compare with the extended Hückel approach in Problem 39.]

(b). Using the total atom electron densities, the C-atom charge is -0.052. This small charge is consistent with the marginally larger electronegativity of carbon compared to hydrogen. Using the total bond order matrix, the bond order is 1.371. CNDO generally overestimates bond orders. However, bond order is an artificial, but useful, construct. Different calculation methods give strikingly different values for bond orders. No one method can be chosen as “best,” because the bond order between two atoms is not directly experimentally observable. Instead, we rely on correlations with bond strength properties to infer the bond order. Bond dissociation energy, bond force constant, and bond length are useful bond strength parameters.

21. Acrolein is the unsaturated aldehyde: $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{O}$. (a). Characterize the HOMO and LUMO of acrolein (σ or π , bonding, non-bonding, or anti-bonding). (b). Draw the molecular orbital energy diagram for the π -orbitals, only. (c) Find the charge on the O-atom of acrolein and the C-O and C-C bond orders. Base your answers on a molecular orbital calculation at the CNDO level. [You need not do any calculations by hand; just interpret the output of the MO program.] The input file for the “*cndo*” Web applet is given below in xyz format. The molecule is oriented in the x-y plane with the O-atom at the origin and the C=O bond along the x-axis.

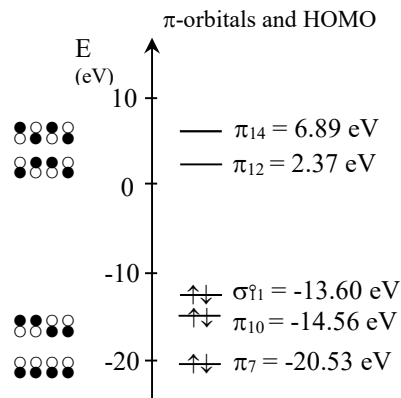
```

8
Acrolein
O      0      0      0
C    1.230    0      0
C    2.058    1.229  0
C    3.404    1.150  0
H    4.039    2.042  0
H    3.911    0.175  0
H    1.521    2.187  0
H    1.810   -0.961  0

```

Answer: The plan is to use the “*cndo*” applet, on the text book Web site and on the companion CD, to obtain the eigenvectors, the “Total Bond Order,” and “Total Atom Electron Densities.” (a). There are, in the order CHO, $3(4)+4(1)+(6) = 22$ valence electrons, giving the HOMO as orbital 11 and the LUMO as orbital 12. The π -orbitals are recognized by having only coefficients for the $2p_z$ -orbitals. Omitting the H-atom coefficients, the condensed output for the eigenvectors, including only the π -orbitals, the HOMO, and LUMO is:

SCF eigenvalues (a.u.) and eigenvectors (eigenvectors listed in columns)					
E(i) vector	7	10	11	12	14
atom:					
1 O2s	0.0	0.0	0.005	0.0	0.0
1 O2px	0.0	0.0	-0.012	0.0	0.0
1 O2py	0.0	0.0	-0.697	0.0	0.0
1 O2pz	0.508	-0.586	0.0	0.508	-0.376
2 C2s	0.0	0.0	0.040	0.0	0.0
2 C2px	0.0	0.0	0.034	0.0	0.0
2 C2py	0.0	0.0	0.325	0.0	0.0
2 C2pz	0.572	-0.304	0.0	-0.488	0.586
3 C2s	0.0	0.0	0.106	0.0	0.0
3 C2px	0.0	0.0	-0.141	0.0	0.0
3 C2py	0.0	0.0	-0.332	0.0	0.0
3 C2pz	0.520	0.485	0.0	-0.392	-0.583
4 C2s	0.0	0.0	0.001	0.0	0.0
4 C2px	0.0	0.0	0.051	0.0	0.0
4 C2py	0.0	0.0	0.119	0.0	0.0
4 C2pz	0.380	0.574	0.0	0.592	0.419



The HOMO is in the x-y plane, corresponding to a σ -type orbital. The biggest coefficient is on the O-atom. The moderate energy of the orbital and the large ionic character between the O-atom and the adjacent C-atom, $(0.697^2 - 0.325^2)/(0.697^2 + 0.325^2) \times 100\% = 64\%$, suggest non-bonding character. The HOMO of acrolein is predominantly a non-bonding $2p_y$ -orbital localized on the O-atom. The LUMO is an anti-bonding π -orbital, with two nodes: $\delta\delta\delta\delta$.

(b). The molecular orbital diagram for the π -orbitals and also including the HOMO is shown above. The MO energies are converted to eV, to provide a better feel for the energies and for comparison with subsequent problems.

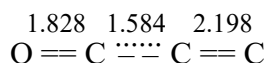
(c). The bond order and atom densities matrices are reproduced below. The charge on the O-atom is a modest -0.223.

		Total Bond Order (Mulliken overlap population)							
Atoms:	1 O	2 C	3 C	4 C	5 H	6 H	7 H	8 H	
2 C	1.828								
3 C	-0.016	1.584							
4 C	0.001	0.022	2.198						
5 H	-0.0	0.005	-0.006	1.359					
6 H	0.0	-0.01	-0.003	1.356	-0.023				
7 H	-0.003	-0.005	1.342	-0.004	-0.011	0.006			
8 H	-0.021	1.31	-0.022	-0.006	0.0	0.003	0.004		

Total atom electron densities and atomic charges

atom	density	charge
1 O	6.2225	-0.223
2 C	3.7646	0.235
3 C	4.0408	-0.041
4 C	3.9942	0.006
5 H	0.9842	0.016
6 H	0.9813	0.019
7 H	0.9722	0.028
8 H	1.0402	-0.04

The bond orders are diagrammed below, showing the four-center, delocalized nature of the bonding:



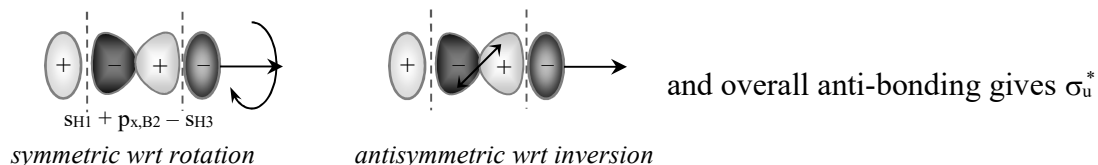
The bond orders from CNDO calculations are generally overestimated. For that reason, some authors prefer to use alternate bond order methods with *ab initio* calculations, instead. Every MO method has its strengths and weaknesses.

22. Consider the molecular orbital for linear BH_2 : $\Psi_{\text{MO}} = N(s_{\text{H1}} + p_{x,\text{B2}} - s_{\text{H3}})$ with N a normalization constant and the atom numbering $\text{H}_1 - \text{B}_2 - \text{H}_3 \rightarrow x$. The internuclear axis is the x-axis. (a). Determine the symmetry designation of the molecular orbital under the symmetry operations for a linear molecule (σ , π , g , u , and also overall bonding, non-bonding, anti-bonding). (b) Determine the symmetry designation of the molecular orbital under the symmetry operations appropriate to a bent molecule (a , b , 1 , 2 , and also overall bonding, non-bonding, anti-bonding, Figure 26.6.4).

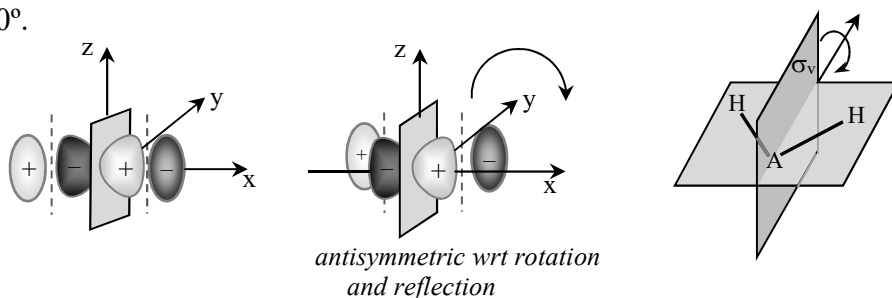
Answer: The plan is to draw the orbital to determine the symmetry with respect to rotation, reflection, and inversion. Refer to Figures 26.6.1 and 26.6.4.

The given orbital is the $2\sigma_u^*$ (b_2^*) orbital. The given orbital is the same as the most anti-bonding orbital for BeH_2 in Figures 26.6.1 and 26.6.4, except with the opposite overall sign. The reasoning follows.

Linear symmetry operations: The internuclear axis is the x-axis. Rotation around the internuclear axis of any angle retains the same phase, giving a σ -orbital. In other words, the orbital is symmetric with respect to rotation of arbitrary angle (wrt = with respect to). The center of mass is coincident with the B-atom nucleus. Inversion through the center of mass gives a change in sign. There are nodes on either side of the central atom, resulting in net anti-bonding character, giving the orbital as σ_u^* .



Bent symmetry operations: Picture the molecule as it bends in the x-y plane, as shown below. The rotation axis, or symmetry axis, is the y-axis for this original orientation. Rotation around the y-axis of 180° inverts the phase of the molecular orbital, giving a b-orbital. See the symmetry table in Figure 26.6.4. In other words, the orbital is antisymmetric with respect to rotation by 180° .



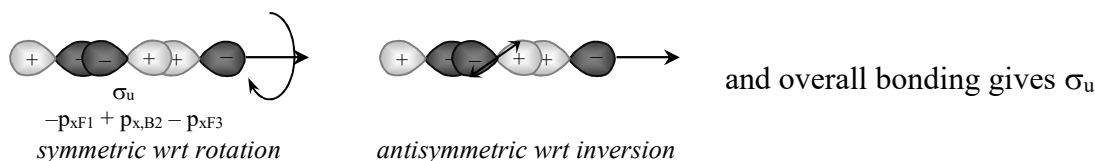
Reflection across the plane passing through the B-nucleus and bisecting the internuclear axes is antisymmetric, giving the final symmetry as b_2^* .

Molecules are assigned to symmetry groups on the basis of their symmetry operations. The symmetry group of a symmetrical bent molecule is called C_{2v} . The symmetry operations are rotation about the symmetry axis of 180° and reflection across the vertical plane that bisects the molecule. You might wonder about the inversion operation for a bent molecule. A C_{2v} molecule does not have an inversion center: the molecule is not centro-symmetric. An inversion operation does not apply to the C_{2v} case. The symmetry group for a symmetric linear triatomic is $D_{\infty h}$.

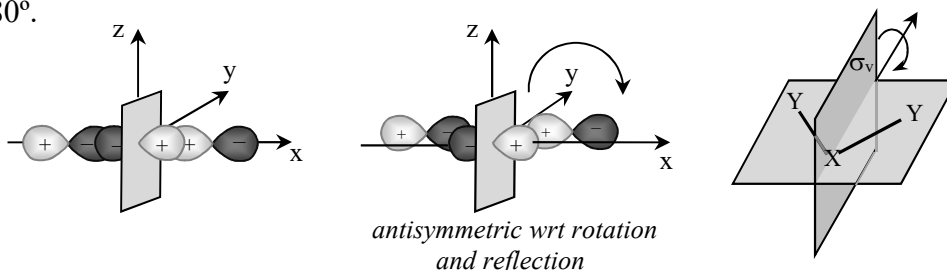
23. Consider the molecular orbital for linear BF_2 : $\Psi_{\text{MO}} = N(-p_{x,F1} + p_{x,B2} - p_{x,F3})$ with N a normalization constant and the atom numbering $\text{F}_1 - \text{B}_2 - \text{F}_3 \rightarrow x$. The internuclear axis is the x-axis. (a). Determine the symmetry designation of the molecular orbital under the symmetry operations for a linear molecule (σ , π , g , u , and also overall bonding, non-bonding, anti-bonding). (b) Determine the symmetry designation of the molecular orbital under the symmetry operations appropriate to a bent molecule (a , b , 1 , 2 , and also overall bonding, non-bonding, anti-bonding, Figure 26.6.4).

Answer: The plan is to draw the orbital to determine the symmetry with respect to rotation, reflection, and inversion. Refer to Figures 26.6.1 and 26.6.4.

The given orbital is the $3\sigma_u$ (b_2) orbital in Figures 26.6.7 and 26.6.8. The reasoning follows. *Linear symmetry operations:* The internuclear axis is the x-axis. Rotation around the internuclear axis of any angle retains the same phase, giving a σ -orbital. In other words, the orbital is symmetric with respect to rotation of arbitrary angle (wrt = with respect to). The center of mass is coincident with the B-atom nucleus. Inversion through the center of mass gives a change in sign. There are nodes on either side of the central atom, resulting in net anti-bonding character, giving the orbital as σ_u .



Bent symmetry operations: Picture the molecule as it bends in the x-y plane, as shown below. The rotation axis, or symmetry axis, is the y-axis for this original orientation. Rotation around the y-axis of 180° inverts the phase of the molecular orbital, giving a b-orbital. See the symmetry table in Figure 26.6.4. In other words, the orbital is antisymmetric with respect to rotation by 180° .



Reflection across the plane passing through the B-nucleus and bisecting the internuclear axes is antisymmetric, giving the final symmetry as b_2 .

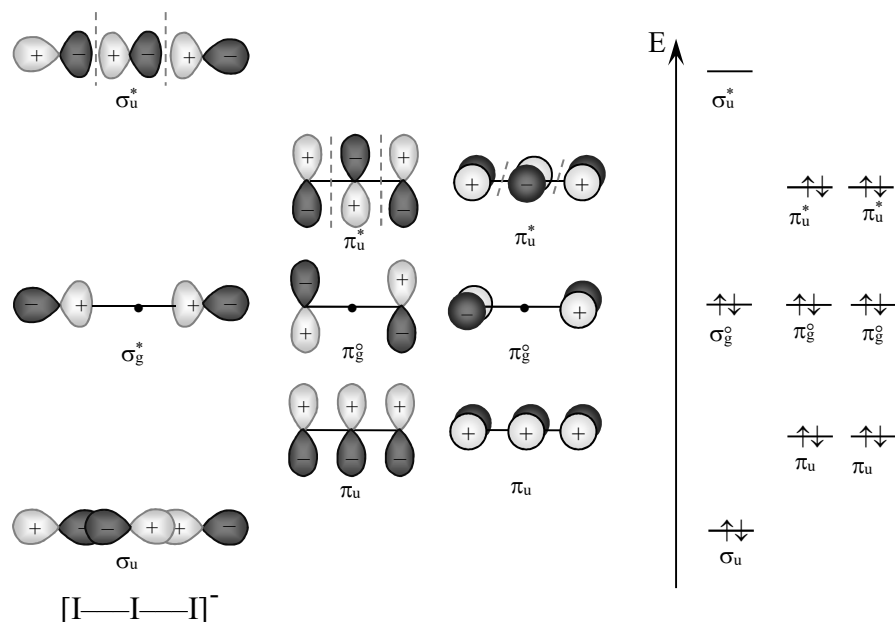
Molecules are assigned to symmetry groups on the basis of their symmetry operations. The symmetry group of a symmetrical bent molecule is called C_{2v} . The symmetry operations are rotation about the symmetry axis by 180° and reflection across the vertical plane that bisects the molecule. You might wonder about the inversion operation for a bent molecule. A C_{2v} molecule does not have an inversion center: the molecule is not centro-symmetric. An inversion operation does not apply to the C_{2v} case. The symmetry group for a symmetric linear triatomic is $D_{\infty h}$.

24. Sketch the qualitative molecular orbital diagram for I_3^- . The ion is linear and symmetric. Assume the valence 5s-orbitals are sufficiently lower in energy than the valence 5p-orbitals that the valence 5s-orbitals form an inner core set. Combine the valence p-orbitals to give the MO diagram. Characterize the molecular orbitals as σ or π , g or u. Characterize the molecular orbitals as overall bonding, non-bonding, or anti-bonding. Determine the electron filling and calculate the overall bond order. Characterize the bond order of each separate I-I bond. Halogens rarely form double bonds, especially as the atom radius increases. Does your MO diagram agree with this expectation? Determine the primary MOs that determine the bond order. Compare your MO

diagram to the MO diagram for $[\text{F}-\text{H}-\text{F}]^-$; explain the stability of I_3^- in terms of the pattern of MO formation.

Answer: The plan is to combine the $5p_x$, $5p_y$, and $5p_z$ -orbitals on each atom to give 12 molecular orbitals that follow the symmetry of the molecule; that is, have the same character, bonding or anti-bonding, on either side of the central I-atom.

The tri-iodide ion, I_3^- , is an electron excess ion. You can think of the ion as the complex between I^- and I_2 , both of which are closed shell. The $5s$ -orbitals on each atom give a completely filled, low energy, net non-bonding set of molecular orbitals: a bonding, non-bonding, and anti-bonding set: $\circ\circ\circ$, $\circ-\bullet$, and $\circ\bullet\circ$. As a consequence the $5s$ -orbitals do not contribute to the bonding and we omit these MOs from the diagram. Counting only p -electrons and including the negative charge gives $3(5) + 1 = 16$ electrons. We align the nuclei along the x -axis. The p_x -orbitals on each atom give a σ -set of molecular orbitals: a bonding, non-bonding, and anti-bonding set: $\circ\bullet\bullet\circ\circ$, $\bullet\circ-\bullet\circ$, and $\circ\bullet\circ\bullet\circ$. The most bonding π_u -orbital results from the constructive all-in-phase overlap of the p_z -orbitals, $\bullet\bullet\bullet\bullet$. The most anti-bonding π_u^* -orbital results from alternating phases for the p_z orbitals, $\bullet\bullet\bullet\bullet$.



Flipping the phase of the outer orbital gives a π_g^o non-bonding orbital along the z -axis. The p_y -orbitals overlap to give a corresponding π bonding, non-bonding, and anti-bonding set, which is perpendicular to the p_z -set. The eight pairs of electrons fill through the π -anti-bonding orbitals.

The overall bond order is $(6 - 4)/2 = 1$. The bond order of each separate $\text{I}-\text{I}$ bond is $1/2$. However, the net π -bond order is zero. There are as many π -bonding as π -anti-bonding electrons. Tri-iodide ion follows the expectation that halogens don't π -bond. The reason is that since the halogens are in group seven, the seven valence electrons are usually sufficient to fill the π -bonding and π -anti-bonding orbitals, giving a net π -bond order of zero. The primary MOs that determine the bond order are the σ -orbitals, just as in $[\text{F}-\text{H}-\text{F}]^-$, Figure 26.9.1. The stability of I_3^-

is determined by the ability to put electrons in a non-bonding σ -orbital, which while not adding to the stability does not detract from the stability.

Note that we could have simply used Figure 26.6.9, but building the molecular orbitals from scratch using only p-orbitals is instructive. The σ_g^o in this model will not end up being degenerate with the π_g^o non-bonding orbitals in careful calculations. However, because of the low energy of the 5s-orbital compared to the 5p-orbital for I-atoms, the σ_g^o orbital will remain rather non-bonding in character, instead of the predominately anti-bonding character of $5\sigma_g^*$ in carbon dioxide or linear ozone.

25. Bent's Rule states that an atom directs hybrids of greater p character toward more electronegative atoms.^{3,4} Consider linear HCN. The C atom sp hybrid that overlaps with the N is expected to have higher p character than the C atom hybrid that overlaps with the H. The hybrid orbital on C that overlaps with the orbital on N is given by $\Psi_{sp,1} = 0.698 s_C + 0.716 p_{x,C}$, which is a $sp^{1.05}$ hybrid. Find the second hybrid orbital on carbon, $\Psi_{sp,2}$, which also forms from the s orbital and the p_x orbital. Is the second hybrid $s^{1.05}p$?

Answer: The plan is to note that the set of hybrids for an atom are normalized and orthogonal:

$$\int \Psi_{sp,1}^* \Psi_{sp,1} d\tau = \int \Psi_{sp,2}^* \Psi_{sp,2} d\tau = 1 \quad \text{and} \quad \int \Psi_{sp,1}^* \Psi_{sp,2} d\tau = \int \Psi_{sp,2}^* \Psi_{sp,1} d\tau = 0 \quad 1$$

For hybrids, $\Psi_{sp,1} = c_{s,1} s + c_{p,1} p_x$ and $\Psi_{sp,2} = c_{s,2} s + c_{p,2} p_x$, normalization gives:

$$\int \Psi_{sp,2}^2 d\tau = \int (c_{s,2} s + c_{p,2} p_x)^2 d\tau = c_{s,2}^2 \int s^2 d\tau + c_{p,2}^2 \int p_x^2 d\tau + 2 c_{s,2} c_{p,2} \int s p_x d\tau = c_{s,2}^2 + c_{p,2}^2 = 1 \quad 2$$

because the atomic orbitals are normalized and orthogonal, $\int s^2 d\tau = 1$, $\int p_x^2 d\tau = 1$, $\int s p_x d\tau = 0$. Orthogonality requires:

$$\begin{aligned} \int \Psi_{sp,1} \Psi_{sp,2} d\tau &= \int (c_{s,1} s + c_{p,1} p_x) (c_{s,2} s + c_{p,2} p_x) d\tau \\ &= c_{s,1} c_{s,2} \int s^2 d\tau + c_{p,1} c_{p,2} \int p_x^2 d\tau + c_{s,1} c_{p,2} \int s p_x d\tau + c_{p,1} c_{s,2} \int p_x s d\tau \\ &= c_{s,1} c_{s,2} + c_{p,1} c_{p,2} = 0 \end{aligned} \quad 3$$

Solving Eq. 3 for $c_{p,2}$ gives:

$$c_{p,2} = -\frac{c_{s,1} c_{s,2}}{c_{p,1}} \quad 4$$

Substituting Eq. 4 into Eq. 2 and solving for $c_{s,2}$ gives:

$$c_{s,2}^2 = \frac{1}{1 + \frac{c_{s,1}^2}{c_{p,1}^2}} = \frac{c_{p,1}^2}{c_{s,1}^2 + c_{p,1}^2} \quad 5$$

Eq. 4 is then used to solve for $c_{p,2}$ or alternately, normality Eq. 2 gives: $c_{p,2}^2 = 1 - c_{s,2}^2$. From Eq. 5:

$$c_{s,2}^2 = \frac{c_{p,1}^2}{c_{s,1}^2 + c_{p,1}^2} = \frac{0.716^2}{0.698^2 + 0.716^2} = 0.512 \quad \text{or} \quad c_{s,2} = 0.716$$

and normality gives: $c_{p,2}^2 = 1 - c_{s,2}^2 = 1 - 0.512$ or $c_{p,2} = \sqrt{0.488} = \pm 0.698$

The negative root is necessary to fulfill orthogonality giving: $\Psi_{sp,2} = 0.716 s_C - 0.698 p_{x,C}$.

The corresponding s character in the hybrid is determined by the ratio of the squared coefficients:

$$\text{relative s-character} = c_{s,2}^2/c_{p,2}^2 = 0.512/0.488 = 1.05$$

which corresponds to $s^{1.05}p$ hybridization as expected.

26. Give the hybridization, in the form sp^α , and show that the orbital is normalized for the hybrid orbital:

$$\Psi_{sp^\alpha,a} = 0.563 s + 0.826 p_x$$

Answer: The plan is to note that the corresponding p-character in the hybrid is determined by the ratio of the squared coefficients, $c_{p_x,a}^2/c_{s,a}^2$, with the hybrid represented as $\Psi_{sp^\alpha,i} = c_{s,i} s + c_{p_x,i} p_x$.

A few examples are useful at first.

An sp -hybridized orbital is $\Psi_{sp,a} = 1/\sqrt{2} (s + p_x)$ giving:

$$c_{p_x,a}^2/c_{s,a}^2 = 1$$

An sp^2 -hybridized orbital is $\Psi_{sp^2,a} = \frac{1}{\sqrt{3}} s + \frac{\sqrt{2}}{\sqrt{3}} p_x$ giving:

$$c_{p_x,a}^2/c_{s,a}^2 = 0.6666/0.3333 = 2$$

For the second sp^2 -hybrid $\Psi_{sp^2,b} = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y$, we need to sum over the p-coefficients:

$$\sum c_{p,b}^2/c_{s,b}^2 = (c_{p_x,b}^2 + c_{p_y,b}^2)/c_{s,b}^2 = [0.1667 + 0.5000]/0.3333 = 0.6667/0.3333 = 2$$

An sp^3 -hybridized orbital is $\Psi_{sp^3,a} = \frac{1}{2} (s + p_x + p_y + p_z)$ giving:

$$\sum c_{p,a}^2/c_{s,a}^2 = (c_{p_x,a}^2 + c_{p_y,a}^2 + c_{p_z,a}^2)/c_{s,a}^2 = [(1/2)^2 + (1/2)^2 + (1/2)^2]/(1/2)^2 = 0.75/0.25 = 3$$

The ratio for this problem is: $c_{p_x,a}^2/c_{s,a}^2 = (0.826)^2/(0.563)^2 = 2.15$

The hybridization is $sp^{2.15}$.

The normalization is:

$$\begin{aligned} \int \Psi_{sp^\alpha,a}^2 d\tau &= \int (0.563 s + 0.826 p_x)^2 d\tau \\ &= (0.563)^2 \int s^2 d\tau + (0.826)^2 \int p_x^2 d\tau + 2 (0.563) (0.826) \int s p_x d\tau \\ &= (0.563)^2 + (0.826)^2 = 1 \end{aligned}$$

where $\int s^2 d\tau = \int p_x^2 d\tau = 1$ and $\int s p_x d\tau = 0$ because the original atomic orbitals are orthonormal.

27. Calculate the bond angle in sp^3 hybridization.

Answer: The plan to follow Example 26.7.1.

The dot-product of two vectors is related to the angle between the two vectors by:

Chapter 26: Molecular Structure

$\vec{u} \cdot \vec{v} = |\vec{u}| |\vec{v}| \cos \theta$. The direction-vectors representing $\Psi_{sp^3,a}$ and $\Psi_{sp^3,b}$ are $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$, respectively. The lengths are equal: $|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}| = \sqrt{(\frac{1}{2})^2 + (\frac{1}{2})^2 + (\frac{1}{2})^2} = 0.8660$, and the dot-product is:

$$\begin{aligned} (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \cdot (-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}) &= |0.8660| |0.8660| \cos \theta \\ -0.25 + 0.25 - 0.25 &= 0.7500 \cos \theta \\ -0.25 &= 0.75 \cos \theta \end{aligned}$$

giving: $\cos \theta = -0.3333$ or 109.471° .

28. An sp^2 hybrid orbital oriented along the y-axis is given below. Find the two remaining sp^2 hybrids in the x-y plane. [Hint: Represent the hybrids $\Psi_{sp^2,i} = c_{s,i} s + c_{px,i} p_x + c_{py,i} p_y$. Solve for the ratio of the coefficients $r_{k,i} = c_{k,i}/c_{s,i}$ using orthogonality and then use normalization to find the final values.]

$$\Psi_{sp^2,1} = \frac{1}{\sqrt{3}} s + \frac{\sqrt{2}}{\sqrt{3}} p_y$$

Answer: The plan is to note that the set of hybrids for an atom are normalized and orthogonal:

$$\int \Psi_{sp^2,i}^* \Psi_{sp^2,i} d\tau = \int \Psi_{sp^2,i}^2 d\tau = 1 \quad \text{and} \quad \int \Psi_{sp^2,i}^* \Psi_{sp^2,j} d\tau = \int \Psi_{sp^2,i} \Psi_{sp^2,j} d\tau = 0 \quad 1$$

For the hybrids, $\Psi_{sp^2,i} = c_{s,i} s + c_{px,i} p_x + c_{py,i} p_y$, normalization gives:

$$\begin{aligned} \int \Psi_{sp^2,i}^2 d\tau &= \int (c_{s,i} s + c_{px,i} p_x + c_{py,i} p_y)^2 d\tau \\ &= c_{s,i}^2 \int s^2 d\tau + c_{px,i}^2 \int p_x^2 d\tau + c_{py,i}^2 \int p_y^2 d\tau + \\ &\quad 2 c_{s,i} c_{px,i} \int s p_x d\tau + 2 c_{s,i} c_{py,i} \int s p_y d\tau + 2 c_{px,i} c_{py,i} \int p_x p_y d\tau \\ &= c_{s,i}^2 + c_{px,i}^2 + c_{py,i}^2 = 1 \end{aligned} \quad 2$$

because the atomic orbitals are normalized and orthogonal, $\int s^2 d\tau = \int p_x^2 d\tau = \int p_y^2 d\tau = 1$ and $\int s p_x d\tau = \int s p_y d\tau = \int p_x p_y d\tau = 0$. Orthogonality requires for each pair of orbitals:

$$\begin{aligned} \int \Psi_{sp^2,i} \Psi_{sp^2,j} d\tau &= \int (c_{s,i} s + c_{px,i} p_x + c_{py,i} p_y) (c_{s,j} s + c_{px,j} p_x + c_{py,j} p_y) d\tau \\ &= c_{s,i} c_{s,j} \int s^2 d\tau + c_{px,i} c_{px,j} \int p_x^2 d\tau + c_{py,i} c_{py,j} \int p_y^2 d\tau + \\ &\quad c_{s,i} c_{px,j} \int s p_x d\tau + c_{s,i} c_{py,j} \int s p_y d\tau + c_{px,i} c_{s,j} \int s p_x d\tau + c_{px,i} c_{py,j} \int s p_y d\tau + \\ &\quad c_{py,i} c_{s,j} \int s p_y d\tau + c_{py,i} c_{px,j} \int p_x p_y d\tau \\ &= c_{s,i} c_{s,j} + c_{px,i} c_{px,j} + c_{py,i} c_{py,j} = 0 \end{aligned} \quad 3$$

The cross terms for different atomic orbitals vanish from orthogonality. Eq. 3 is most easily solved by finding the ratio of the coefficients. Defining the ratio as $r_{k,i} = c_{k,i}/c_{s,i}$ Eqs. 2 and 3 become:

$$c_{s,i}^2 (1 + r_{px,i}^2 + r_{py,i}^2) = 1 \quad 4$$

$$c_{s,i} c_{s,j} (1 + r_{px,i} r_{px,j} + r_{py,i} r_{py,j}) = 0 \quad 5$$

and then dividing Eq. 5 by $c_{s,i} c_{s,j}$ gives the orthogonality relationships as:

$$1 + r_{px,i} r_{px,j} + r_{py,i} r_{py,j} = 0 \quad 6$$

For the complete set of three hybrids:

$$\begin{aligned} 1 + r_{px,1} r_{px,2} + r_{py,1} r_{py,2} &= 0 \\ 1 + r_{px,1} r_{px,3} + r_{py,1} r_{py,3} &= 0 \\ 1 + r_{px,2} r_{px,3} + r_{py,2} r_{py,3} &= 0 \end{aligned} \quad 7$$

For the first hybrid as given in the problem statement:

$$r_{2px,1} = c_{2px,1}/c_{s,1} = 0 \quad \text{and} \quad r_{2py,1} = c_{2py,1}/c_{s,1} = \sqrt{2} \quad \text{giving:} \quad 8$$

$$1 + \sqrt{2} r_{py,2} = 0 \quad \text{or} \quad r_{py,2} = -1/\sqrt{2} \quad 9$$

$$1 + \sqrt{2} r_{py,3} = 0 \quad \text{or} \quad r_{py,3} = -1/\sqrt{2} \quad 10$$

$$1 + r_{px,2} r_{px,3} + r_{py,2} r_{py,3} = 1 + r_{px,2} r_{px,3} + \frac{1}{2} = r_{px,2} r_{px,3} + \frac{3}{2} = 0 \quad 11$$

From Eqs. 9 and 10, hybrid orbitals 2 and 3 have the same percentage s and p_y character, so they should also have equal p_x character. The hybrids are equivalent in the amount of p character and differ only in the orientation, which gives $r_{px,2} r_{px,3} = \pm r_{px,2}^2$ and then Eq. 11 can be solved for $r_{px,2}$:

$$r_{px,2} r_{px,3} + \frac{3}{2} = \pm r_{px,2}^2 + \frac{3}{2} = 0 \quad \text{or} \quad r_{px,2} = \frac{\sqrt{3}}{\sqrt{2}} \quad 12$$

Only the negative choice for $\pm r_{px,2}^2$ gives a valid solution, with the result that $r_{px,2}$ and $r_{px,3}$ are opposite in sign, $r_{px,3} = -r_{px,2} = -\sqrt{3}/\sqrt{2}$. The final coefficients are then obtained by normalization using Eq. 4:

$$c_{s,i}^2 + c_{px,i}^2 + c_{py,i}^2 = c_{s,i}^2 (1 + r_{px,i}^2 + r_{py,i}^2) = 1 \quad 13$$

for each hybrid:

$$\begin{aligned} c_{s,2}^2 (1 + r_{px,2}^2 + r_{py,2}^2) &= 1 & \text{giving} & \quad c_{s,2}^2 (1 + 3/2 + 1/2) = 1 \\ c_{s,3}^2 (1 + r_{px,3}^2 + r_{py,3}^2) &= 1 & \text{giving} & \quad c_{s,3}^2 (1 + 3/2 + 1/2) = 1 \quad \text{or} \quad c_{s,2} = c_{s,3} = 1/\sqrt{3} \end{aligned}$$

$$\text{Finally from the coefficient ratios: } c_{2px,2} = c_{s,2} r_{px,2} = \frac{1}{\sqrt{3}} \frac{\sqrt{3}}{\sqrt{2}} = \frac{1}{\sqrt{2}} \quad 14$$

$$c_{2py,2} = c_{s,2} r_{py,2} = -\frac{1}{\sqrt{3}} \frac{1}{\sqrt{2}} = -\frac{1}{\sqrt{6}} \quad 15$$

The final set of hybrids is:

$$\Psi_{sp^2,1} = \frac{1}{\sqrt{3}} s + \frac{\sqrt{2}}{\sqrt{3}} p_y \quad 16$$

$$\Psi_{sp^2,2} = \frac{1}{\sqrt{3}} s + \frac{1}{\sqrt{2}} p_x - \frac{1}{\sqrt{6}} p_y \quad 17$$

$$\Psi_{sp^2,3} = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{2}} p_x - \frac{1}{\sqrt{6}} p_y \quad 18$$

29. One model for $\text{Zn}(\text{CN})_4$ is to use sd^3 hybridization. Use VSEPR rules to determine the shape of $\text{Zn}(\text{CN})_4$. Which d-orbitals on Zn are used to form sd^3 hybrids.

Answer: The d-orbital based sd^3 hybridization is tetrahedral, just as in sp^3 hybridization. In other words, mixing four atomic orbitals on the central atom results in four hybrid atomic orbitals that are equivalent in energy, shape, and size. The orbitals differ only in direction. VSEPR rules give the relative orientation of the four hybrids that minimizes electron-electron repulsions as tetrahedral. The molecular geometry of $\text{Zn}(\text{CN})_4$ is then tetrahedral. The d-orbitals that combine to give sd^3 hybrids are the d_{xy} , d_{yz} , and d_{xz} orbitals.

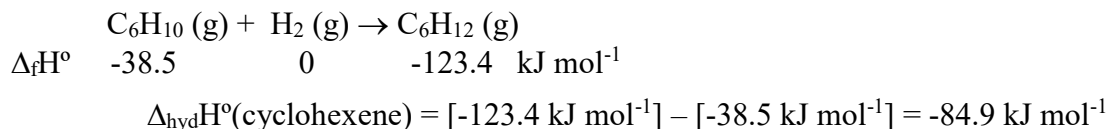
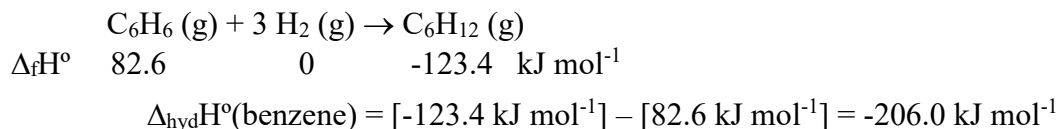
30. (a). Use the enthalpies of vaporization and formation in Tables 8.1.1 and 8.4.2 for benzene and cyclohexene to calculate the value of the Hückel $\text{C}(2p_z)\text{--}\text{C}(2p_z)$ resonance integral, β . (b). Repeat the calculation with 1,3-butadiene. Compare the two values for β .

Answer: Using historical values, the π -delocalization energy of benzene is given by comparison of enthalpy of hydrogenation of benzene to the hydrogenation of three moles of cyclohexene (Eq. 26.8.20):

$$\pi\text{-DE} = \underset{\text{benzene}}{[-206.0 \text{ kJ mol}^{-1}]} - \underset{-3(\text{cyclohexene})}{[3(-118.4 \text{ kJ mol}^{-1})]} = 149.2 \text{ kJ mol}^{-1} = |2\beta|$$

giving $\beta \cong -75 \text{ kJ mol}^{-1}$.

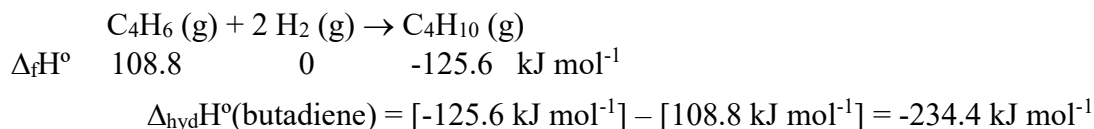
(a). Using Tables 8.1.1 and 8.4.2 at 298.15 K, the enthalpy of formation of gaseous cyclohexane is: $\Delta_f H^\circ(\text{g}) = \Delta_f H^\circ(\text{l}) + \Delta_{\text{vap}} H^\circ = -156.4 + 33.01 \text{ kJ mol}^{-1} = -123.4 \text{ kJ mol}^{-1}$. The current values for the enthalpies of formation of gaseous benzene and cyclohexene give the enthalpies of hydrogenation as:

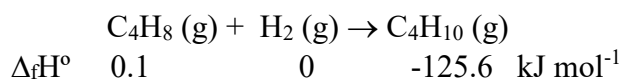


and the corresponding value of the π -delocalization energy and β as:

$$\pi\text{-DE} = [-206.0 \text{ kJ mol}^{-1}] - [3(-84.9 \text{ kJ mol}^{-1})] = 48.7 \text{ kJ mol}^{-1} \quad \text{and} \quad \beta \cong -24.4 \text{ kJ mol}^{-1}$$

(b). Using Table 8.4.2, at 298.15 K, the enthalpies of formation of gaseous 1,3-butadiene and 1-butene give the enthalpies of hydrogenation as:





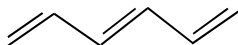
$$\Delta_{\text{hyd}} H^\circ(\text{butene}) = [-125.6 \text{ kJ mol}^{-1}] - [0.1 \text{ kJ mol}^{-1}] = -125.7 \text{ kJ mol}^{-1}$$

and the corresponding value of the π -delocalization energy and β as:

$$\pi\text{-DE} = [-234.4 \text{ kJ mol}^{-1}] - [2(-125.7 \text{ kJ mol}^{-1})] = 17.0 \text{ kJ mol}^{-1} \quad \text{and} \quad \beta \cong -8.5 \text{ kJ mol}^{-1}$$

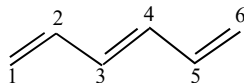
Both values for β are considerably smaller than the commonly quoted value. The discrepancy is in many ways immaterial, since more accurate methods are easily implemented. The usefulness of Hückel molecular orbital theory is to build chemical intuition.

31. Use Hückel molecular orbital theory to determine the molecular orbitals and energies for 1,3,5-hexatriene:



- Give the Hückel determinant in terms of x 's and 1's:
- Determine the energies and the orbital coefficients using a matrix diagonalization program. The "eigen" applet to diagonalize a matrix is available on the text book Web site or companion CD. MatLab or Mathematica are also useful.
- Sketch the orbitals with the appropriate phase for each p_z orbital.
- Give the number of nodes in each wave function. Classify each orbital as bonding or anti-bonding.
- Draw the energy level diagram. Give the electron filling.
- Calculate the π -bond order for each unique bond in the molecule (Eq. 26.8.6).
- Calculate the π -bond delocalization energy.
- Calculate the π -electron density on any two atoms of your choosing (Eq. 26.8.7).
- On the energy level in part (e), indicate the lowest energy electronic transition with a vertical arrow. Label the HOMO and LUMO.

Answer: The atom numbering is arbitrary. The atom assignments chosen are:



(1). The Hückel determinant in terms of x 's and 1's is:

$$\begin{array}{c} \text{Atom} \\ \begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \\ \begin{pmatrix} -x & 1 & 0 & 0 & 0 & 0 \\ 1 & -x & 1 & 0 & 0 & 0 \\ 0 & 1 & -x & 1 & 0 & 0 \\ 0 & 0 & 1 & -x & 1 & 0 \\ 0 & 0 & 0 & 1 & -x & 1 \\ 0 & 0 & 0 & 0 & 1 & -x \end{pmatrix} & = 0 & E_i = \alpha + x_i \beta \quad \text{with } x_i \text{ the eigenvalues} \end{array} \end{array}$$

Chapter 26: Molecular Structure

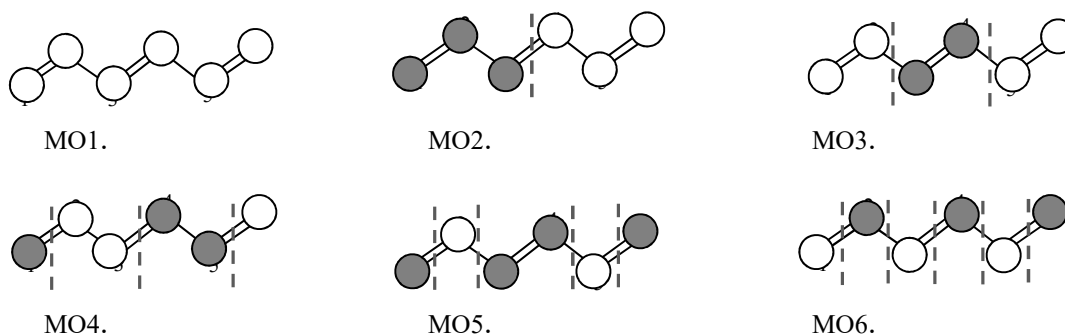
(2). The energies and the orbital coefficients using a matrix diagonalization program are:

```

Eigenvector 1: Eigenvalue=1.80194
0.231921
0.417907
0.521121
0.521121
0.417907
0.231921
-----
Eigenvector 2: Eigenvalue=1.24698
-0.417907
-0.521121
-0.231921
0.231921
0.521121
0.417907
-----
Eigenvector 3: Eigenvalue=0.445042
0.521121
0.231921
-0.417907
-0.417907
0.231921
0.521121
-----
Eigenvector 4: Eigenvalue=-0.445042
-0.521121
0.231921
0.417907
-0.417907
-0.231921
0.521121
-----
Eigenvector 5: Eigenvalue=-1.24698
-0.417907
0.521121
-0.231921
-0.231921
0.521121
-0.417907
-----
Eigenvector 6: Eigenvalue=-1.80194
0.231921
-0.417907
0.521121
-0.521121
0.417907
-0.231921

```

(3). Sketches of the orbitals with the appropriate phase for each p orbital are:

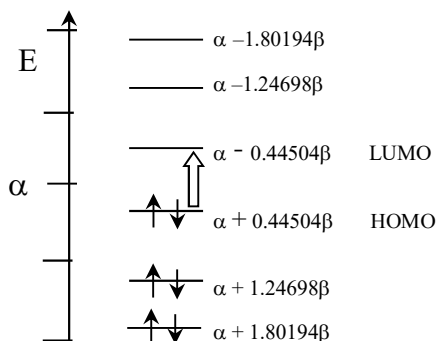


(4). The nodes in the wavefunctions are shown by dotted lines in the sketches, above. The number of nodes in each wave function and the overall bonding or anti-bonding character are:

MO1: 0 nodes-bonding; MO2: 1 node-bonding; MO3: 2 nodes-three bonding interactions and two anti-bonding interactions, so net bonding; MO4: 3 nodes-two bonding interactions

and three anti-bonding interactions, so net anti-bonding; MO5: 4-anti-bonding; MO6: 5 nodes-completely anti-bonding

(5). The energy level diagram, electron filling, HOMO, LUMO, and lowest energy electronic transition are:



(6). The π -bond order for each unique bond in the molecule is: $P_{ij} = \sum_k n_k c_{ki} c_{kj}$

$$P_{12} = 2(0.231921)(0.417907) + 2(-0.417907)(-0.521121) + 2(0.521121)(0.231921) = 0.871$$

$$P_{23} = 2(0.417907)(0.521121) + 2(-0.521121)(-0.231921) + 2(0.231921)(-0.417907) = 0.483$$

$$P_{34} = 2(0.521121)(0.521121) + 2(-0.231921)(0.231921) + 2(-0.417907)(-0.417907) = 0.785$$

The total π -bond order is $2(0.871) + 2(0.483) + 0.785 = 3.493$ showing the effect of conjugation.

(7). The total π -bond energy is:

$$E_{\text{tot}} = 2(\alpha + 1.80194\beta) + 2(\alpha + 1.24698\beta) + 2(\alpha + 0.445042\beta) = 6\alpha + 6.9879\beta$$

As the localized reference, each isolated double bond with two electrons has an energy of $E = 2\alpha + 2\beta$. There are three isolated double bond equivalents, so the localized reference energy is $3(2\alpha + 2\beta)$, giving the pi bond delocalization energy as:

$$\pi\text{DE} = (6\alpha + 6.9879\beta) - (6\alpha + 6\beta) = 0.9879\beta.$$

The α part always cancels out.

(8). The π -electron density on each unique atom is: $d_i = \sum_k n_k c_{ki}^2$

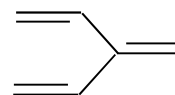
$$d_1 = 2(0.231921)^2 + 2(-0.417907)^2 + 2(0.521121)^2 = 1$$

$$d_2 = 2(0.417907)^2 + 2(-0.521121)^2 + 2(0.231921)^2 = 1$$

$$d_3 = 2(0.521121)^2 + 2(-0.231921)^2 + 2(-0.417907)^2 = 1$$

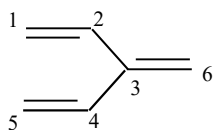
(9). The HOMO, LUMO, and lowest energy electronic transition are shown in the energy level diagram in part (5).

32. Answer the questions listed in Problem 31 for 3-vinyl-1,3-butadiene:



Chapter 26: Molecular Structure

Answer: The atom numbering is arbitrary. The atom assignments chosen are:



(1). The Hückel determinant in terms of x 's and 1's is:

Atom	1	2	3	4	5	6	
1	$-x$	1	0	0	0	0	$= 0$
2	1	$-x$	1	0	0	0	
3	0	1	$-x$	1	0	1	
4	0	0	1	$-x$	1	0	
5	0	0	0	1	$-x$	0	
6	0	0	1	0	0	$-x$	

$E_i = \alpha + x_i \beta$ with x_i the eigenvalues

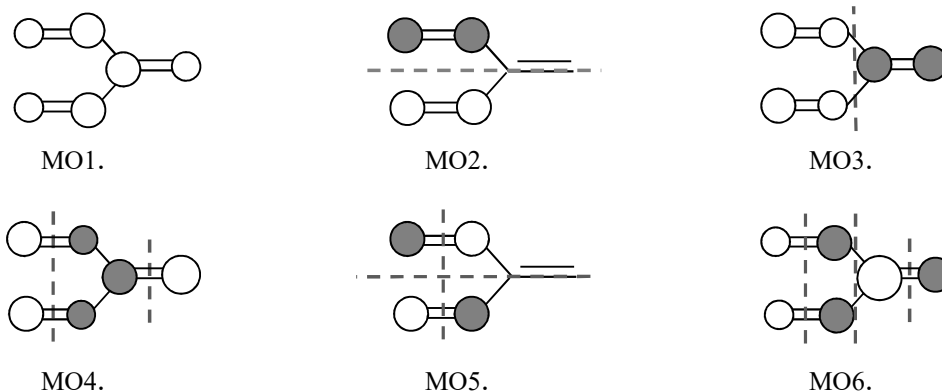
(2). The energies and the orbital coefficients using a matrix diagonalization program are:

```

Eigenvector 1: Eigenvalue=1.93185
0.22985
0.444037
0.627963
0.444037
0.22985
0.325058
-----
Eigenvector 2: Eigenvalue=1
-0.5
-0.5
0
0.5
0.5
0
-----
Eigenvector 3: Eigenvalue=0.517638
0.444037
0.22985
-0.325058
0.22985
0.444037
-0.627963
-----
Eigenvector 4: Eigenvalue=-0.517638
0.444037
-0.22985
-0.325058
-0.22985
0.444037
0.627963
-----
Eigenvector 5: Eigenvalue=-1
-0.5
0.5
0
-0.5
0.5
0
-----
Eigenvector 6: Eigenvalue=-1.93185
0.22985
-0.444037
0.627963
-0.444037
0.22985
-0.325058

```

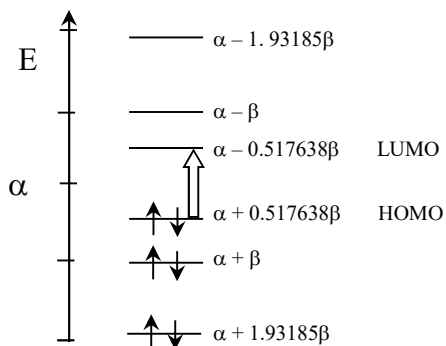
(3). Sketches of the orbitals with the appropriate phase for each p orbital are:



(4). The nodes in the wavefunctions are shown by dotted lines in the sketches, above. The number of nodes in each wave function and the overall bonding or anti-bonding character are:

See diagrams above for the nodes: MO1: 0 nodes-bonding; MO2: 1 node-two bonding interactions and no anti-bonding interactions, so net bonding; MO3: 1 node-three bonding interactions and two anti-bonding interactions, so net bonding; MO4: 2 nodes-two bonding interactions and three anti-bonding interactions, so net anti-bonding; MO5: 2 nodes-anti-bonding; MO6: 3 nodes-completely anti-bonding

(5). The energy level diagram, electron filling, HOMO, LUMO, and lowest energy electronic transition are:



(6). The π -bond order for each unique bond in the molecule is: $P_{ij} = \sum_k n_k c_{ki} c_{kj}$

$$P_{12} = 2(0.22985)(0.444037) + 2(-0.50000)(-0.50000) + 2(0.444037)(0.22985) = 0.908$$

$$P_{23} = 2(0.444037)(0.627962) + 2(-0.50000)(0) + 2(0.22985)(-0.325058) = 0.408$$

$$P_{36} = 2(0.627962)(0.325058) + 2(0)(0) + 2(-0.325058)(-0.627963) = 0.816$$

The total π -bond order is $2(0.907) + 2(0.354) + 0.816 = 3.338$ showing the effect of conjugation.

(7). The total π -bond energy is:

$$E_{\text{tot}} = 2(\alpha + 1.93185\beta) + 2(\alpha + 1.00000\beta) + 2(\alpha + 0.517638\beta) = 6\alpha + 6.8990\beta$$

Chapter 26: Molecular Structure

As the localized reference, each isolated double bond with two electrons has an energy of $E = 2\alpha + 2\beta$. There are three isolated double bond equivalents, so the localized reference energy is $3(2\alpha + 2\beta)$, giving the pi bond delocalization energy as:

$$\pi DE = (6\alpha + 6.8990\beta) - (6\alpha + 6\beta) = 0.8990 \beta.$$

The α part always cancels out.

(8). The π -electron density on each unique atom is: $d_i = \sum_k n_k c_{ki}^2$

$$d_1 = 2(0.22985)^2 + 2(-0.50000)^2 + 2(0.444037)^2 = 1$$

$$d_2 = 2(0.444037)^2 + 2(-0.50000)^2 + 2(0.22985)^2 = 1$$

$$d_3 = 2(0.627963)^2 + 2(0)^2 + 2(-0.325058)^2 = 1$$

$$d_6 = 2(0.325058)^2 + 2(0)^2 + 2(-0.627963)^2 = 1$$

(9). The HOMO, LUMO, and lowest energy electronic transition are shown in the energy level diagram in part (5).

33. Heteroatoms are introduced into the HMO matrix using two parameters, h and k . The diagonal element is the Coulomb integral, which for carbon is α . The off-diagonal elements are the resonance integrals, which for directly bonded carbon atoms are β . The diagonal element for a heteroatom is changed to $\alpha + h\beta$ and the off-diagonal element for directly bonded atoms is changed to $k\beta$. A table of h and k is given below.

Table P26.1: Hückel Parameters for Heteroatoms.

Atom	Bond Type	π electrons for atom	h	k
C	-C=C-	1	0	1
N	-C=N- (pyridine)	1	0.5	1.0
N	=C-N< (pyrrole)	2	1.5	0.8
N	-N=N- (azo)	1	1.0	1.0
O	-C=O (carbonyl)	1	1.0	1.0
O	=C-O- (furan)	2	2.0	0.8
F	=C-F	2	3.0	0.7
Cl	=C-Cl	2	2.0	0.4
Br	=C-Br	2	1.5	0.3
S	=C-S- (thiophene)	2	1.5	0.8

For example, acrolein, $C_A=C_B-C_C=O_D$, has four total π -electrons and the lower diagonal elements of the Hückel matrix in the form of Eq. 26.8.16 is:

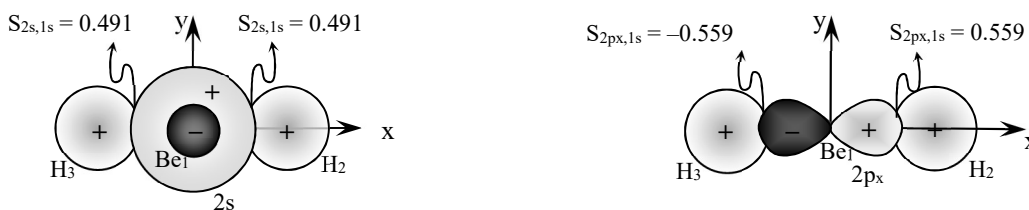
$$\begin{bmatrix} 0 & & & \\ 1 & 0 & & \\ 0 & 1 & 0 & \\ 0 & 0 & 1 & 1 \end{bmatrix}$$

For acrolein:

- Give the Hückel determinant in terms of x 's and 1 's:
- Determine the energies and the orbital coefficients using a matrix diagonalization program. The "eigen" applet to diagonalize a matrix is available on the text book Web site or companion CD. MatLab or Mathematica are also useful.
- Sketch the orbitals with the appropriate phase for each p_z orbital.
- Give the number of nodes in each wave function. Classify each orbital as bonding or anti-bonding.
- Draw the energy level diagram. Give the electron filling.
- Calculate the π -bond order for each unique bond in the molecule (Eq. 26.8.6).
- Calculate the π -bond delocalization energy.
- Calculate the π -electron density on any two atoms of your choosing (Eq. 26.8.7).
- On the energy level in part (e), indicate the lowest energy electronic transition with a vertical arrow. Label the HOMO and LUMO.

34. Use Hückel molecular orbital theory and the parameters in Table P26.1 to determine the HOMO for vinyl fluoride, $\text{CH}_2=\text{CH-F}$. Draw the molecular orbital diagram and show the electron filling. Characterize the HOMO as σ or π , bonding, non-bonding, or anti-bonding. Does the HOMO have predominant character on any one particular atom?

35. Characterize the highest occupied molecular orbital in linear BeH_2 . Use extended Hückel theory. Draw the molecular orbital energy diagram and sketch the molecular orbitals. Orient the molecule along the x -axis. Number the Be as atom 1 and the two hydrogens as 2 and 3. The bond length in BeH_2 is 1.330 \AA giving the $\text{Be}(2s)\text{-H}(1s)$ overlap integrals of 0.491 and the $\text{Be}(2p_x)\text{-H}(1s)$ overlap as 0.559 . Notice the change in sign for the $\text{H}(1s)_3\text{-Be}(2p_x)$ overlap:



Answer: The plan is to use the "Secular" equation applet on the text Web site or companion CD. The VOIEs are $\text{Be}(2s) -32.3 \text{ eV}$, $\text{O}(2p_x, 2p_y, 2p_z) -15.9 \text{ eV}$, and $\text{H}(1s) -13.6$. Once the overlap integrals are specified, the resonance integrals are completely determined using Eq. 26.8.22.

For example, the resonance integral for $\text{H}(1s)\text{-Be}(2p_x)$ is given using $K = 1.75$ as:

$$\text{H}(1s)_2\text{-Be}(2p_x)_1: \quad H_{1s,2p_x} = K S_{ij} \frac{(H_{ii} + H_{jj})}{2} = 1.75(0.559) \frac{(-6.00 + (-13.60))}{2} \text{ eV} = -9.59 \text{ eV}$$

However, for this problem, we'll cheat and click on the "Generate H" button to have the applet fill in the Hamiltonian matrix automatically, based on the orbital labels. The $\text{Be}(2p_y)$ and $\text{Be}(2p_z)$ orbitals are non-bonding, because the overlap integral with the H-atoms is zero by symmetry. At

Chapter 26: Molecular Structure

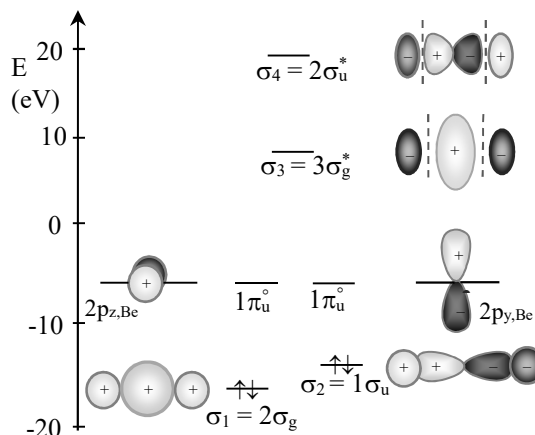
this low level of approximation, the energies of the $2p_y$ and $2p_z$ are unaffected by the electrons in the σ -molecular orbitals. Because the $\text{Be}(2p_y)$ and $\text{Be}(2p_z)$ -orbitals are non-interacting, we don't need to include them in the secular equations. The input is set-up as follows, using the overlap integrals given in the problem:

1			
0	1		
0.491	0.559	1	
$S =$	0.491	-0.559	0
Atom:			
Label:	Be	Be	H
	2s	2px	1s

-9.3			
0	-6		
$H =$	-9.83841	-9.58685	-13.6
	-9.83841	9.58685	0
			-13.6

The output and corresponding molecular orbital energy diagram are:

Eigenvalues and eigenvectors (eigenvectors listed in columns)				
E(i)	-15.350	-14.242	8.416	19.208
vector	1	2	3	4
atom:				
Be2s	0.474	0.0	0.744	0.0
Be2px	0.0	-0.269	-0.0	-0.752
H1s	0.623	-0.681	-0.472	0.466
H1s	0.623	0.681	-0.472	-0.466



With four valence electrons, the HOMO is orbital 2, which is a σ -bonding orbital ($1\sigma_u$) constructed from the overlap of the $\text{H}(1s)$ and $\text{Be}(2p_x)$ orbitals. We added in the non-bonding $2p_y$ and $2p_z$ orbitals on Be to complete the energy level diagram; their energies are given by the unperturbed VOIEs, -6.00 eV. The symmetry designations correspond to Figure 26.6.1. The overall signs of orbitals 2 and 3 are opposite to Figure 26.6.1. However, the change in overall sign of a molecular orbital is immaterial; Ψ^2 and $(-\Psi)^2$ give the same electron distribution. Compare this calculation with Problem 11, which is at the CNDO level.

36. Calculate the Be-H bond order in BeH_2 using the results in the previous problem, at the extended Hückel level of approximation.

Answer: The plan is to note that since BeH_2 is symmetrical, both Be-H bonds are equivalent. Use the $\text{Be}_1\text{-H}_2$ bond. The bond order is given by Eq. 26.3.10. The answer is compared to Problem 11%%%.

Using Eq. 26.3.10, there are only two occupied molecular orbitals and each orbital only involves one orbital on the central Be -atom:

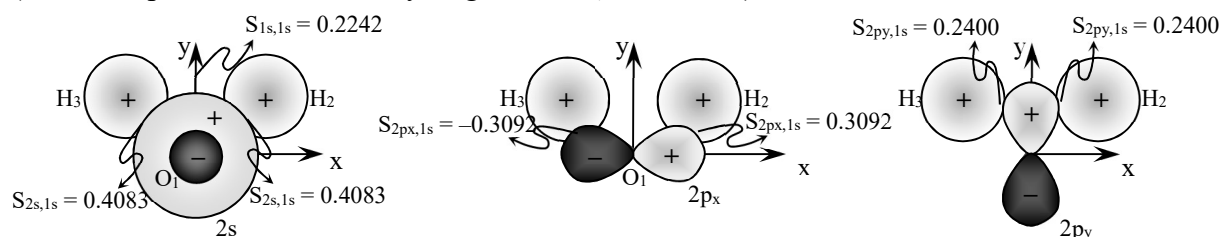
$$\begin{aligned}
 P_{12} &= \sum_{j \text{ on a}} \sum_{k \text{ on b}} \sum_{i=1}^m n_i 2c_{ij} c_{ik} S_{jk} \\
 &= 4 c_{1,2s\text{Be}} c_{1,1s\text{H}} S_{2s\text{Be},1s\text{H}} + 4 c_{2,2p_x\text{Be}} c_{2,1s\text{H}} S_{2p_x\text{Be},1s\text{H}} \\
 &\quad \text{MO 1} \qquad \qquad \qquad \text{MO 2} \\
 &= 4(0.4737)(0.6228)(0.4908) + 4(-0.2688)(-0.68811)(0.5593) \\
 &= 0.5792 + 0.4138 = 0.9930
 \end{aligned}$$

The extended Hückel Mulliken bond order of 0.9930 is significantly smaller than the CNDO bond order of 1.465 from Problem 11. However, the bond order at HF/6-31G** is 0.988 and at B3LYP/6-311G** is 0.971, giving reasonable agreement between the extended Hückel method and the more advanced methods. However, little should be inferred about the accuracy of the extended Hückel method from this rather fortuitous agreement. For extended Hückel calculations the bond order is often approximated, instead, by the Coulson bond order, which is given by:

$$\begin{aligned}
 \text{BO}_{12} &= \sum_{j \text{ on a}} \sum_{k \text{ on b}} \sum_{i=1}^m n_i c_{ij} c_{ik} \\
 &= 2 c_{1,2s\text{Be}} c_{1,1s\text{H}} + 2 c_{2,2p_x\text{Be}} c_{2,1s\text{H}} \\
 &\quad \text{MO 1} \qquad \qquad \qquad \text{MO 2} \\
 &= 2(0.4737)(0.6228) + 2(-0.2688)(-0.68811) \\
 &= 0.5900 + 0.3699 = 0.9599
 \end{aligned}$$

The Mulliken overlap population of 0.993 and the Coulson estimate of the bond order both agree with the semi-empirical MNDO bond order of 0.911. While very approximate, the extended Hückel method is easy to apply and tenable for very large systems. Every approximation method has its strengths and weaknesses.

37. Use extended Hückel theory to find the molecular orbital energy diagram for water. Number the oxygen as atom 1 and the two hydrogens as 2 and 3. Orient the molecule in the x-y plane. The overlap integrals for a bond angle and 105° and bond lengths of 0.962 \AA are shown below (the overlap between the two hydrogens is $S_{1s,1s} = 0.2242$):



Answer: The plan is to use the “*Secular*” equation applet on the text Web site or companion CD. The VOIEs are O(2s) -32.3 eV, O(2p_x, 2p_y, 2p_z) -15.9 eV, and H(1s) -13.6. Once the overlap integrals are specified, the resonance integrals are completely determined using Eq. 26.8.22.

For example, the resonance integral for H(1s)₂-O(2p_x) is given using $K = 1.75$ as:

$$\text{H}(1s)_2\text{-O}(2p_x)_1: \quad H_{1s,2p_x} = K S_{ij} \frac{(H_{ii} + H_{jj})}{2} = 1.75(0.3092) \frac{(-15.9 + (-13.6))}{2} \text{ eV} = -7.98 \text{ eV}$$

Chapter 26: Molecular Structure

However, for this problem, we'll cheat and click on the "Generate H" button to have the applet fill in the Hamiltonian matrix automatically, based on the orbital labels. The $O(2p_z)$ orbital is non-bonding, because the overlap integral with the H-atoms is zero by symmetry. At this low level of approximation, the energy of the $2p_z$ is unaffected by the presence of the electrons in the σ -molecular orbitals. Because the $O(2p_z)$ orbital is non-interacting, we don't need to include the $2p_z$ in the secular equations. The input is set-up as follows, using the overlap integrals given in the problem:

$S =$

1				
0	1			
0	0	1		
0.4083	0.3092	0.2400	1	
0.4083	-0.3092	0.2400	2242	1

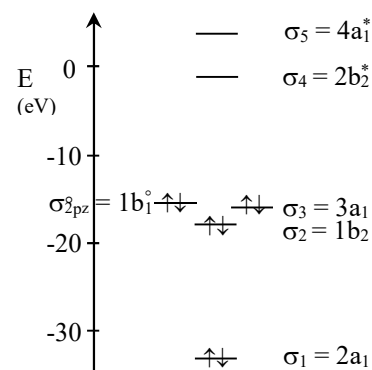
Atom: 1 1 1 2 3
 Label: O O O H H
 2s 2px 2py 1s 1s

$H =$

-32.3				
0	-15.9			
0	0	-15.9		
-16.3983	-7.98122	-6.19499	-13.6	
-16.3983	7.981224	-6.19499	-5.33596	-13.6

In terms of looking up the VOIEs, the distinction between $2p_x$, $2p_y$, and $2p_z$ is immaterial. The x, y, and z subscripts are just used to label the output, to make the results easier to read. The results are listed below with the molecular orbital diagram:

Eigenvalues and eigenvectors (eigenvectors listed in columns)					
E (i)	-33.0869	-17.9708	-16.6346	-0.3806	3.0583
vector	1	2	3	4	5
atom:					
1 O2s	0.9816	-0.0	0.1952	0.0	0.5312
1 O2px	-0.0	0.856	-0.0	0.5825	0.0
1 O2py	-0.0272	-0.0	-0.9546	-0.0	0.389
2 H1s	0.1337	0.3656	-0.1592	-0.5748	-0.5322
3 H1s	0.1337	-0.3656	-0.1592	0.5748	-0.5322



In the MO diagram, we added in the $2p_z$ non-bonding orbital at -15.9 eV, between σ_3 and σ_4 . With eight valence electrons, the HOMO is the $O(2p_z)$ non-bonding orbital. The correspondence of the MOs with the symmetry designations are given in the plot for comparison with Figure 26.6.4. The switch in order of the anti-bonding orbitals is seen in other semi-empirical and HF calculations, depending on bond length and angle. CNDO calculations are more realistic than extended Hückel calculations, but the extended Hückel result is easy to calculate and determines the proper molecular orbital ordering and nodal patterns for this case. Several improvements in the extended Hückel approach are also in common use. We hope that you find the extended Hückel method informative about the inner workings of molecular orbital calculations.

38. Calculate the O-H bond order in water from the extended Hückel calculation in the previous problem.

Answer: Use the O₁-H₂ bond. The bond order is given by Eq. 26.3.10:

$$\begin{aligned}
 P_{12} &= \sum_{j \text{ on a}} \sum_{k \text{ on b}} \sum_{i=1}^m n_i 2c_{ij} c_{ik} S_{jk} \\
 &= 4 c_{1,2sO} c_{1,1sH} S_{2sO,1sH} + 4 c_{1,2pyO} c_{1,1sH} S_{2py,1sH} + 4 c_{2,2pxO} c_{2,1sH} S_{2pxO,1sH} \\
 &\quad + 4 c_{3,2sO} c_{3,1sH} S_{2sO,1sH} + 4 c_{3,2spy} c_{3,1sH} S_{2py,1sH} \\
 &= 4(0.982)(0.134)(0.408) + 4(-0.027)(0.134)(0.240) + 4(0.856)(0.366)(0.309) \\
 &\quad + 4(0.195)(-0.159)(0.408) + 4(-0.955)(-0.159)(0.240) \\
 &= 0.2148 - 0.0035 + 0.3872 - 0.0506 + 0.1458 = 0.6937
 \end{aligned}$$

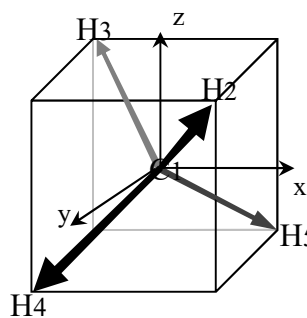
The extended Hückel bond order of 0.694 is significantly smaller than the CNDO bond order of 1.085. For extended Hückel calculations the bond order is often approximated, instead, by the Coulson bond order:

$$\begin{aligned}
 BO_{12} &= \sum_{j \text{ on a}} \sum_{k \text{ on b}} \sum_{i=1}^m n_i c_{ij} c_{ik} \\
 &= 2 c_{1,2sO} c_{1,1sH} + 2 c_{1,2pyO} c_{1,1sH} + 2 c_{2,2pxO} c_{2,1sH} + 2 c_{3,2sO} c_{3,1sH} + 2 c_{3,2spy} c_{3,1sH} \\
 &= 2(0.982)(0.134) + 2(-0.027)(0.134) + 2(0.856)(0.366) \\
 &\quad + 2(0.195)(-0.159) + 2(-0.955)(-0.159) \\
 &= 0.2632 - 0.0072 + 0.6266 - 0.0620 + 0.3037 = 1.1243
 \end{aligned}$$

This case is unusual; Mulliken and Coulson bond orders are usually similar. For comparison, the HF/6-31G** Mulliken bond order is 0.881 and the B3LYP/6-311G** bond order is 0.967.

39. Calculate the charge on the C-atom in methane. Use the extended Hückel method. The atomic coordinates for methane with a C-H bond length of 1.084 Å are:

Atom	x	y	z
1 C	0.0	0.0	0.0
2 H	0.62565	0.62565	0.62565
3 H	-0.62565	-0.62565	0.62565
4 H	-0.62565	0.62565	-0.62565
5 H	0.62565	-0.62565	-0.62565



For this orientation, the overlap matrix is:

	1 C2s	1 C2p _x	1 C2p _y	1 C2p _z	2 H1s	3 H1s	4 H1s	5 H1s
1 C2s	1.0	0.0	0.0	0.0	0.5224	0.5224	0.5224	0.5224
1 C2p _x	0.0	1.0	0.0	0.0	0.2832	-0.2832	-0.2832	0.2832
1 C2p _y	0.0	0.0	1.0	0.0	0.2832	-0.2832	0.2832	-0.2832
1 C2p _z	0.0	0.0	0.0	1.0	0.2832	0.2832	-0.2832	-0.2832
2 H1s	0.5224	0.2832	0.2832	0.2832	1.0	0.1877	0.1877	0.1877
3 H1s	0.5224	-0.2832	-0.2832	0.2832	0.1877	1.0	0.1877	0.1877
4 H1s	0.5224	-0.2832	0.2832	-0.2832	0.1877	0.1877	1.0	0.1877
5 H1s	0.5224	0.2832	-0.2832	-0.2832	0.1877	0.1877	0.1877	1.0

Answer: The plan is to use the “*Secular*” applet and Eqs. 26.3.9.

The hydrogen atoms are placed at the opposing corners of a cube that has faces oriented perpendicular to the axes. To quickly determine the overlap integrals as listed, we used the atomic coordinates as input for the “*cndo*” applet. The “*cndo*” applet lists overlap integrals. Yes, we know that using a more advanced level of approximation to get the overlap integrals for a lower-level extended Hückel calculation is cheating, but the instructional value of the extended Hückel calculation is undiminished. Notice that the C(2s)-H(1s) overlaps are all identical, as expected, while the C(2p)-H(1s) differ only in sign. Adjacent pairs of H-atoms have a significant overlap, 0.1877, as expected from VSEPR theory. Entering these overlap integrals into the “*Secular*” applet gives:

Using the Generate H option, the Hamiltonian matrix is:

The final output is:

Eigenvalues and eigenvectors (eigenvectors listed in columns)								
E(i) vector	-23.2715 1	-14.9487 2	-14.9487 3	-14.9487 4	6.44 5	6.44 6	6.44 7	35.4649 8
atom:								
C2s	0.8444	0.0	0.0	-0.0	0.0	-0.0	0.0	0.7746
C2px	-0.0	-0.0623	0.6373	0.0684	-0.5167	0.0307	0.4336	0.0
C2py	-0.0	-0.6387	-0.0561	-0.0595	0.2014	-0.58	0.2811	-0.0
C2pz	-0.0	0.053	0.0736	-0.6375	0.3852	0.3444	0.4347	0.0
H1s	0.2678	-0.385	0.389	-0.3734	-0.0381	0.1119	-0.6277	-0.3162
H1s	0.2678	0.4479	-0.3015	-0.384	-0.3826	-0.4881	0.1529	-0.3162
H1s	0.2678	-0.3739	-0.4556	0.3027	-0.1819	0.5216	0.3207	-0.3162
H1s	0.2678	0.3109	0.3681	0.4547	0.6026	-0.1454	0.1541	-0.3162

Notice that the MOs involve C(2s) character or C(2p) character, but not both, in contradiction to hybridization arguments. The hybridization picture emerges when the average of MOs 1-4 is

taken, giving s- and p-character. However, the s-character is greater than the canonical 25% expected for sp^3 hybridization. The hybridization has $(0.84)^2$ s-character and approximately $3(0.64)^2$ p-character for $s^{0.71}p^{1.23}$ overall.

The atom electron density for atom-a is calculated as the sum over all atomic orbitals j on atom-a and the sum over all molecular orbitals i :

$$d_a = \sum_{j \text{ on } a} \sum_{i=1}^m n_i c_{ij}^2 \quad j = \text{all atomic orbitals on atom-a} \quad (9)$$

With 8 valence electrons, the HOMO is orbital 4. The atom electron density on the C-atom is:

$$\begin{aligned} d_C &= 2(0.8444)^2 && \text{contribution from } C(2s) \\ &+ 2(-0.0623)^2 + 2(0.6373)^2 + 2(0.0684)^2 && \text{contribution from } C(2p_x) \\ &+ 2(-0.6387)^2 + 2(-0.0561)^2 + 2(-0.0595)^2 && \text{contribution from } C(2p_y) \\ &+ 2(0.0530)^2 + 2(0.0736)^2 + 2(-0.6375)^2 && \text{contribution from } C(2p_z) \\ &= 3.9137 \end{aligned}$$

The contributions from the $C(2p_x)$, $C(2p_y)$, and $C(2p_z)$ are identical, as expected by symmetry. Since carbon has four valence electrons, the charge on the C-atom is $4 - 3.9137 = +0.0862$. For comparison, the charge at the CNDO level is -0.052 . The charge on an atom is an artificial, but useful, construct. Different calculation methods give strikingly different values for the charges on atoms. No one method can be chosen as “best,” because the charge on an atom is not experimentally observable.

The bond length chosen for this example is the HF/6-31G(d) minimized structure.

40. Place the following electronic structure methods in order of typical energy accuracy: HF, CNDO, MNDO, AM1, PM3, CISD or CCSD, CISDT or CCSDT, CCSD(T), LSDA, B3LYP.

Answer: The general order is: advanced correlated better than density functional better than Hartree Fock better than semi empirical better than Extended Hückel better than Hückel. However, for some circumstances this ordering is arguable (open shell transition states). For the specific methods, in the following list when there is a tie, the more general method is ranked higher than the more specific method:

CNDO, MNDO, AM1~PM3, HF, LSDA, B3LYP~CISD/CCSD, CCSD(T), CISDT/CCSDT

The assumption is that correlation consistent basis sets are used (i.e. 6-311G** or cc-pVTZ). Many might question the indicated rough tie between B3LYP and CISD/CCSD, but in support, B3LYP methods are run with more complete basis sets than CCSD in comparable time. Note that CCSD(T) isn't listed in Figure 26.2.2 because with two electrons triple excitations aren't possible.

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