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Introduction

A modern chemist has access to good computational methods that generate numerically useful information on molecules, e.g., energy, geometry and vibrational frequencies. But we also have a collection of models based on orbital ideas incorporating concepts of symmetry, overlap and electronegativity. In this text we focus on the latter as these ideas have been a huge aid in understanding the connections between stoichiometry, geometry and electronic structure. The connections can be as simple as an electron count yielding user-friendly “rules.” Our problem here, the electronic structure of a cluster or a more extended structure of the type encountered in solid-state chemistry, requires the application of models beyond those reviewed in the Appendix. Models are like tools – they permit us to disassemble and assemble the electronic structure of molecules. For each problem we choose a model that will accomplish the task with minimum effort and maximum understanding. Just as one would not use a screwdriver to remove a hex nut, so too we cannot use highly localized models to usefully describe the electronic structures of many clusters and extended bonding systems. We must use a method that is capable of producing a sensible solution as well as one that is sufficiently versatile to treat both the bonding in small clusters and bulk materials.

The proven method we will use is one that generates solutions based on the orbitals and electrons that the atoms or molecular fragments bring to the problem. For molecules, it is the linear combination of atomic orbitals molecular orbital (LCAO-MO) method. Hence, as a prelude to subsequent chapters on clusters and extended structures, a qualitative review of the application of this model to simple molecules is presented. In all cases the intrinsically complex results are pruned to the essentials according to the guidance of several prize-winning chemists. In certain cases the ultimate simplification generates the familiar, easy-to-apply and handy electron-counting rules. We assume the reader has a strong background in the descriptive chemistry that is outlined in the Appendix. The Appendix or an inorganic text should be used as needed to refresh the memory of the chemical facts

as well as the popular localized descriptions of the bonding of simple molecules. If more is needed, general texts of inorganic or organometallic chemistry should be consulted.

1.1 Molecular orbitals without the nasty bits

The Appendix includes a few examples of non-cluster systems where the intrinsic limitations of the two-center–two-electron bond are revealed. By and large, however, the model is a good one. Many cluster systems demand a more flexible model to explain even less complex aspects like stoichiometry and geometry. The model that chemists have adopted is that of molecular orbitals with a Hoffmann-style approach, i.e., an approach in which the essence of the problem is identified with a small subset of molecular orbitals describing the system. This conceptual, essentially qualitative, approach has become the language of modern experimental chemistry. In the following, some of the essential aspects of the model are described utilizing experimental results of valence-level photoelectron spectroscopy for selected empirical support. In essence, the ionization energies of molecules are used in the same way as the ionization energies of atoms are used to justify the H atom model for the electronic structure of atoms.

In Section A1.3 the united atom model for H_2 is described. As a consequence, molecules may be viewed as “atoms” that contain multiple nuclei at different positions in space. Molecular orbitals (MOs) are thus “atomic orbitals” (AOs) distorted by a complex “nucleus.” These modified “atomic orbitals” can be correlated with the real atomic orbitals of the united atom as well as with linear combinations of the atomic orbitals of the separated atoms from which the molecule is constructed. Once one goes beyond simple diatomics, the united atom model rapidly loses its usefulness; however, the linear combination of atomic orbitals approach does not. It constitutes a productive approach to the generation of MOs. There are several good texts that present molecular orbital ideas for the experimental chemist, e.g., Albright, Burdett and Whangbo, and here a pragmatic approach to the utilization of MO models is presented. The examples and exercises given will produce sufficient familiarity that application of the approach to clusters and extended systems in successive chapters will produce understanding rather than confusion.

1.1.1 The H_2 model

Let's begin with H_2 . As shown in Figure 1.1, the combination of two H 1s orbitals yields two molecular orbitals – one bonding and one antibonding. For an electron in the bonding combination, additional electron density is placed between the nuclei (more than would be present if two non-bonding H atoms were placed at the

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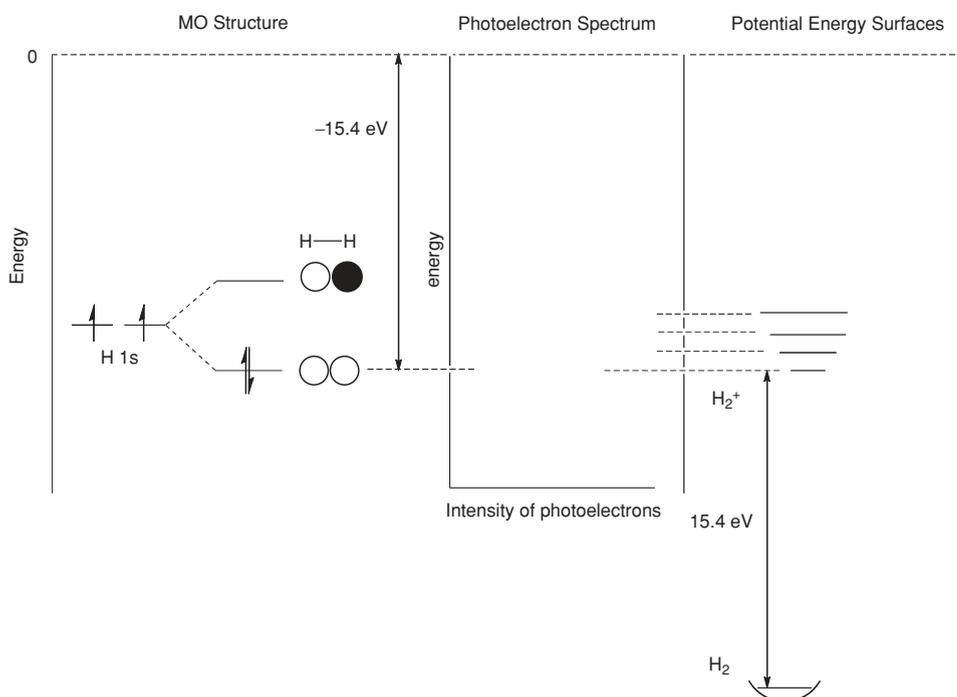


Figure 1.1

same positions). For an electron in the antibonding combination, electron density is removed from the region between the nuclei relative to two non-interacting H atoms separated by the same distance. In the former case, the nuclei are better shielded from each other and the electrons between the nuclei experience the attraction of two nuclei. This net attractive interaction is just balanced at the equilibrium internuclear distance of H₂ by electron–electron and nucleus–nucleus repulsions. The energy of the bonding MO is lower than that of the AOs for the non-interacting atoms. The opposite is true of the antibonding orbital. The ground state is represented by placing two electrons of opposite spin in the bonding MO. In this one-electron MO approach electrons are added after MO formation in the manner of the hydrogen atom model of heavier atoms.

Ionization of H₂ can be described as removing an electron from the bonding MO and Koopmans' theorem states that the ionization energy $IE = -\epsilon_{MO}$. The MO model suggests that $IE(H_2)$ should be larger than $IE(H) = 13.6$ eV. As shown by its photoelectron spectrum, $IE(H_2) = 15.4$ eV. The photoelectron spectrum gives us additional information about the nature of the occupied molecular orbital from the fine structure observed in the photoelectron band. This fine structure corresponds to vibrational excitation of the molecular ion H₂⁺ and reports on the role of the electron

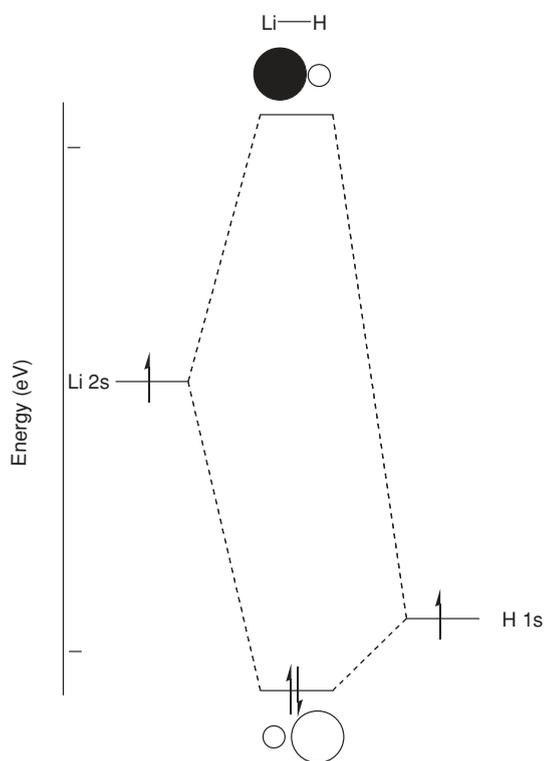


Figure 1.2

removed in the bonding of the molecule H_2 . The H–H stretching frequency in the molecule is 4820 cm^{-1} whereas in the molecular ion it is 2260 cm^{-1} . Removing the electron generates a more loosely bound ion; therefore the electron removed was a bonding electron and the MO from which it was removed is H–H bonding. The fact that a long vibrational progression is observed in the ion confirms that the structure (H–H distance) is considerably different in the ion vs. the molecule. The qualitative agreement of experiment and model suggest that even though MOs have no more real existence than AOs, they serve as a powerful tool for discussing electronic structure in meaningful terms.

We can use the hypothetical molecule LiH to gain an idea of how electronegativity enters into the MO model. In Figure 1.2 the calculated MOs of LiH are illustrated. Note that there are still two MOs as we have not included the 2p functions of Li for simplicity. One is bonding and filled and one is antibonding and empty. However, neither is symmetrical relative to the amplitude of the MO at the two different atomic centers. The bonding MO contains a higher proportion of H character, the more electronegative atom, whereas electropositive Li has a higher amplitude in the empty antibonding MO. The distribution of electron density in the molecule is

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given by the square of the absolute magnitude of the wave function (empty orbitals do not contribute). Hence, the H end of the molecule will be more electron rich than the Li end and the molecule will have a dipole moment. How much? Mulliken devised a simple measure of charge distribution by assigning charge to a given atom center according to its AO contributions to filled MOs. Called a Mulliken population analysis, it provides a relative measure of charge distribution. For LiH the Mulliken charges are 0.46 on Li and -0.46 on H; however, quantitative agreement with a measured dipole moment cannot be expected.

Suppose we consider the excitation of an electron from the bonding to the antibonding MO. The net result is to transfer electron density from the H end to the Li end of LiH thereby reducing the strength of the Li–H interaction. The effects of differing electronegativities in polyatomic molecules on MO characters are less easily anticipated; however, the changes result from the same factors illustrated by LiH.

Exercise 1.1. Sketch out the MO energies and wavefunction for the molecular ion $[\text{HeH}]^+$. Do you expect the H atom to have positive or negative character relative to He? Does the MO picture agree with your intuition?

Answer. The He 1s function is at lower energy than the H 1s function; hence, the qualitative MO diagram is that of Figure 1.2 with He in the position of H and H in the position of Li. In the ground state, H shares less of the bond pair than He and, hence, more of the positive charge of the molecule.

1.1.2 Extension of the H_2 model to p-block elements

H_2 only requires 1s functions for an MO description. Next we have to consider atoms with p functions as well. So let's look at B_2 . The results of a Fenske–Hall MO calculation on B_2 are shown in Figure 1.3 and Table 1.1. For clarity, the dashed correlation lines to each of the manifolds are only shown for one B atom each. Now, the MOs are represented by energies and linear combinations of the 2s and 2p functions of the two B atoms. The 2s and 2p functions are called the basis functions and the number of basis functions in any problem equals the number of MOs, i.e., here are four basis functions on each B atom so there are eight MOs. In the absence of any symmetry, each MO can contain a contribution from every basis function. But note that there are four MOs (counting from the lowest energy MO 3 and 5, each doubly degenerate) that contain only $2p_x$ and $2p_y$ functions (the z axis is the B–B axis). The reason is that functions with σ symmetry relative to the B–B axis (no change in sign on rotation about the B–B axis) are orthogonal to functions with π symmetry (one change in sign on 180° rotation about the B–B axis). As they do not mix, bonding MOs 3 and antibonding MOs 5 can be generated by a

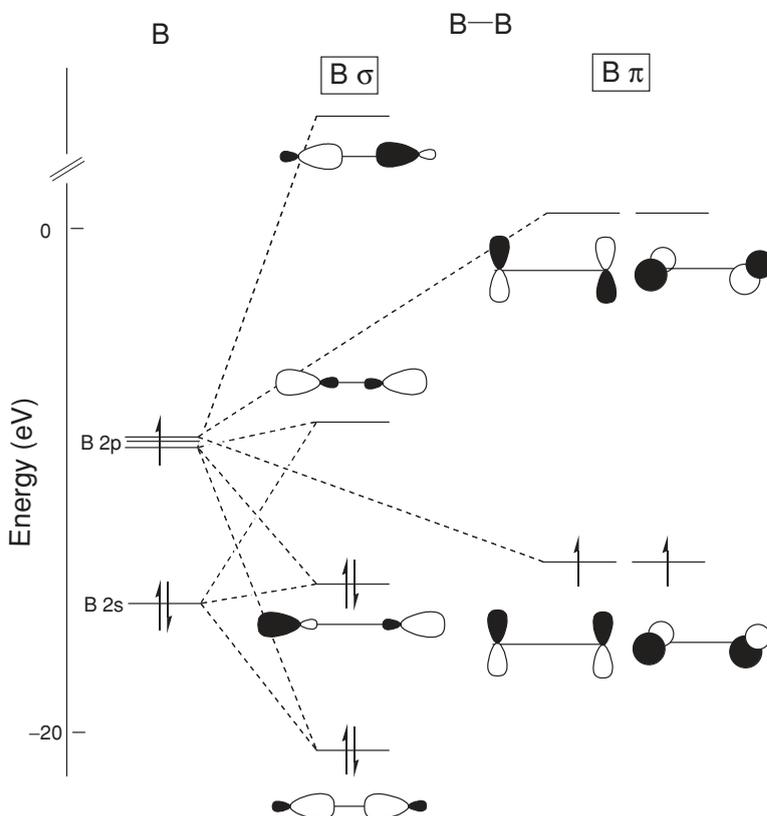


Figure 1.3

2×2 scheme just like the one used for H_2 above. Make yourself a little structure diagram with a coordinate system taking the molecular axis as the z axis. Then look at the table of eigenvectors (signs only) with AO %s for each eigenvector. Mark out the π MOs and draw MO pictures showing AO contributions to verify those in Figure 1.3. The eigenvectors give you the signs and the AO %s give the relative size of the AOs you draw. These are easy as each atom only contributes one AO.

The remaining four MOs, 1, 2, 4 and 6, formed from the $2s$ and $2p_z$ functions of σ symmetry require a 4×4 scheme. Take a closer look at these four orbitals and note in Table 1.1 that the lower ones have larger $2s$ character and the higher ones larger $2p$ character. Draw a picture of the lowest energy one. You should find it of predominantly $2s$ character and symmetric (no nodes). The $2s$ AO energy is lower than the $2p$ AO energy so the lowest energy orbital will be mainly of $2s$ character. Thus, the highest energy MO will have large $2p_z$ character. Check it the same way. It has a more complex $2s$ and $2p$ mixture so at the side add a $2s$ orbital to a $2p$ orbital and then subtract the two. What do you get? Yes, you get something that looks like

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Table 1.1. Eigenvalues and eigenvectors for B₂ from a Fenske–Hall calculation

MO ^a	1	2	3	4
Energies (eV)	−21.6	−13.3	−12.1	−12.1
1B 2s (%)	+(40)	−(25)	(0)	(0)
1B 2p _x (%)	(0)	(0)	+(50)	(0)
1B 2p _y (%)	(0)	(0)	(0)	+(50)
1B 2p _z (%)	+(11)	+(25)	(0)	(0)
2B 2s (%)	+(40)	+(25)	(0)	(0)
2B 2p _x (%)	(0)	(0)	+(50)	(0)
2B 2p _y (%)	(0)	(0)	(0)	+(50)
2B 2p _z (%)	−(11)	+(25)	(0)	(0)
MO ^a	5	6	7	8
Energies	−7.1	0.7	0.7	80
1B 2s (%)	+(10)	(0)	(0)	−(25)
1B 2p _x (%)	(0)	+(50)	(0)	(0)
1B 2p _y (%)	(0)	(0)	+(50)	(0)
1B 2p _z (%)	−(40)	(0)	(0)	−(25)
2B 2s (%)	+(10)	(0)	(0)	+(25)
2B 2p _x (%)	(0)	−(50)	(0)	(0)
2B 2p _y (%)	(0)	(0)	−(50)	(0)
2B 2p _z (%)	+(40)	(0)	(0)	−(25)

^a To simplify the table only the sign of the AO coefficients in the MOs are given along with the % characters in parentheses.

a hybridized orbital. But this happens automatically, when you turn the crank of the computer. It's not something you somehow should know. The highest energy MO is strongly B–B antibonding and has three nodes. Look at the remaining two MOs. They have one and two nodes, respectively, and the net bonding and antibonding characters are hard to judge from the drawings. Why? If the MO places electron density between the nuclei it has bonding character but if it places it outside it has antibonding character. Look at the σ MO with two nodes – this orbital places density both between the nuclei and outside. The photoelectron spectra discussed below show that this MO, when filled, is in fact nearly non-bonding in character. Note that in these rough drawings one only sketches out the major contributions plus the nodal and bonding/antibonding characters. One must pay attention to Table 1.1. Alternatively, plotting programs are available for precise MO drawings if desired.

In a one-electron model the electrons are added after the MOs are formed. Thus, the eight MOs of B₂ provide a qualitative description of any diatomic molecule with s and p valence functions only. Electrons are added using the same rules we

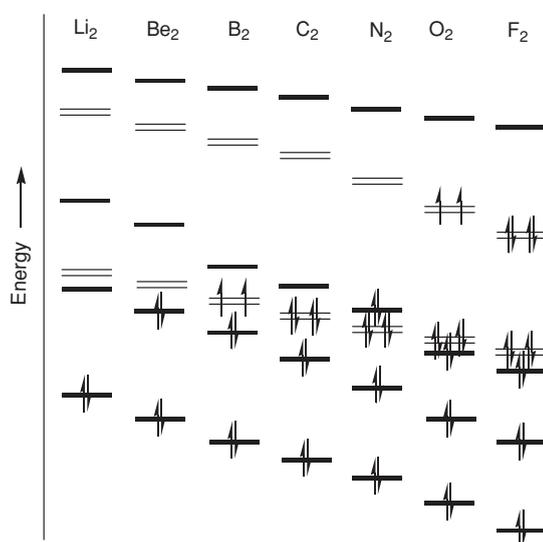


Figure 1.4

use for filling AOs of atoms. However, the placement of the σ and π manifolds relative to each other will depend on the relative 2s and 2p energies which, in turn, depend on the atom identities. For a given electron count, the measured multiplicity of the ground state provides information on the relative energy ordering. Figure 1.4 presents the accepted MO level diagrams of the first row diatomics and one sees, for example, that the paramagnetism of O_2 , which is a problem for the two-center–two-electron bond model, can now be explained. The model also explains nicely why $IE(O_2) < IE(N_2)$ even though the electronegativity of $O > N$.

The next step is to look at heterodiatomics, e.g., CO. One expects the same number and type of MOs as found with the homonuclear molecules and the number and symmetry types of basis functions are the same. However, the energies and compositions are distorted by the differing electronegativities of the two atoms just as they were for H_2 vs. LiH above. In Figure 1.5 the MO diagrams of N_2 and CO are compared as are the photoelectron spectra. The spectra clearly show that the highest occupied MOs (HOMOs) are nearly non-bonding. Both are sharp bands (little change in inter-nuclear distance on ionization) and the vibrational frequencies in the ion states are nearly the same as those in the molecules; 2191 vs. 2345 cm^{-1} for N_2 and 2200 vs. 2157 cm^{-1} for CO. Perhaps this is a problem for the reader as in the Appendix we describe these molecules as triply bonded and a triple bond is often represented by one filled σ -bonding orbital and two filled π -bonding orbitals. In the MO description the filled π -bonding MOs are obvious; however, the σ -bonding orbital is not. If it's not the highest lying filled σ MO where is it? In the MO model the σ bonding character is spread over all three filled σ orbitals!

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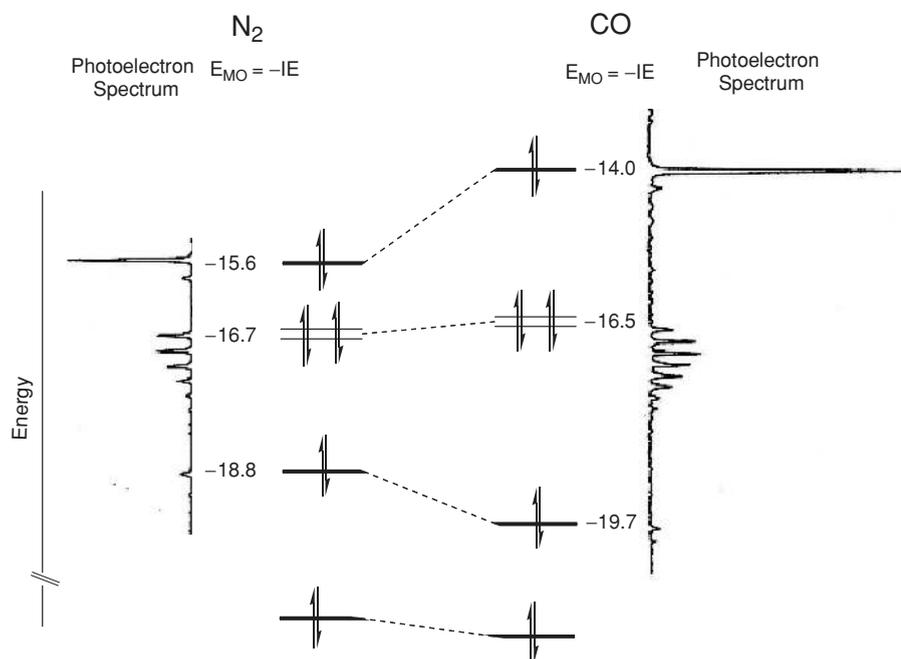


Figure 1.5

In contrast to the nice, neat two-center–two-electron bond model, it is not so easy to determine the overall bonding character from MO orbital drawings alone. We need another measure. This comes from the Mulliken overlap population which is a numerical indicator of bonding (positive) and antibonding (negative) character between a pair of atoms within a molecule. For N_2 in an approximate calculation the overall overlap populations are +0.68 for the three σ filled MOs and +0.54 each for the π MOs. If one considers each π interaction of bond order one then the overall bond order is clearly three.

1.1.3 Importance of frontier orbitals

One more elementary MO concept needs to be mentioned. Fukui shared in a Nobel award for his effective use of the frontier orbitals of a molecule (the highest occupied MO, HOMO, and lowest unoccupied MO, LUMO) to correlate and predict chemical behavior. Good Lewis bases are expected to have high lying HOMOs and good Lewis acids are expected to have low lying LUMOs. For CO the HOMO is a σ orbital, C–O non-bonding, with the highest amplitude on C, which is the more electropositive atom. This justifies carbon-bound CO when found as a ligand to a transition metal such as Fe (see Appendix): a fact that is counterintuitive based on a

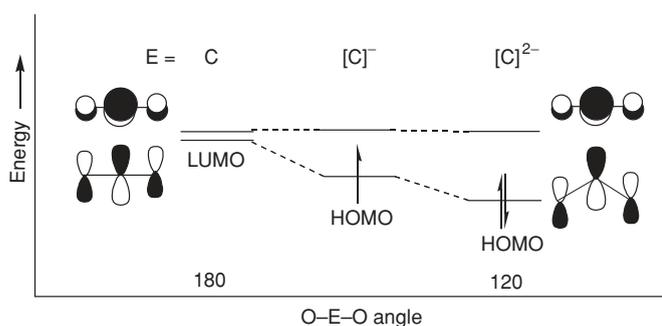


Figure 1.6

simple interpretation of the effect of electronegativities on charge distribution. The LUMO of CO has π symmetry and is CO antibonding but it, too, has its highest amplitude on C. To act as a Lewis acid when bound through the C atom, CO must interact with a metal center that has filled orbitals with π symmetry relative to the M–C axis. The later transition metals, such as Fe, possess the requisite filled orbitals. Thus, the primary CO donor interaction to the metal is buttressed by secondary π back donation to the CO ligand leading to a robust Fe–CO bond. Note that depopulation of the non-bonding σ MO of CO combined with population of the antibonding π MOs of CO leads to a net weakening of C–O bonding on coordination. In fact, the CO frequency decreases on binding to a transition metal Lewis acid, e.g., Fe, whereas it remains about the same if bound to a Lewis acid incapable of acting as a π acceptor, e.g., BH_3 .

Walsh showed that the properties of the HOMO could be used to rationalize the shapes of polyatomic molecules. A good example is the O–E–O series of triatomic molecules, E = C, N and O. In Figure 1.6 the HOMO energy is plotted as a function of the O–E–O angle. It correlates with one component of the degenerate LUMO of CO_2 and decreases in energy because of the increasing O–O bonding interaction as the angle decreases. Consideration of the properties of a single MO neatly correlates with the observed O–E–O angles of 180° , 134° and 117° , respectively, for E = C, $[\text{C}]^-$ and $[\text{C}]^{2-}$ isoelectronic with the known series E = C, N and O. The importance of HOMO/LUMO properties provides a gratifying simplification of the MO approach.

1.1.4 Polyatomic molecules

An excursion into polyatomic molecules is next. An informative series from the point of view of two-center bonds is CH_4 , NH_3 , OH_2 , FH, Ne. In Figure 1.7 a representation of the photoelectron spectroscopic bands (IEs) illustrate how the