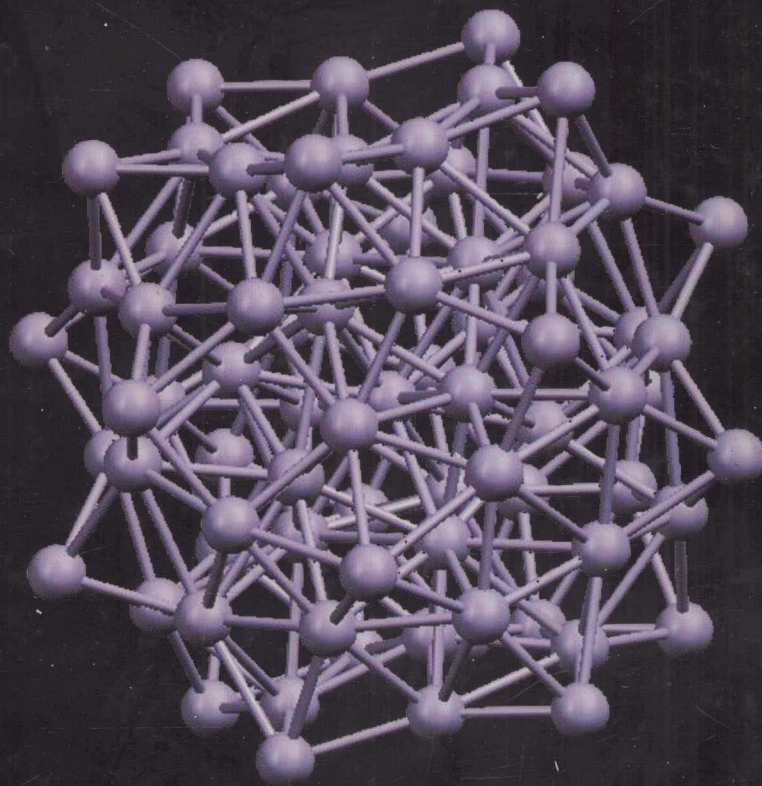


Molecular Clusters

A Bridge to Solid-State Chemistry

**Thomas P. Fehlner, Jean-François Halet,
and Jean-Yves Saillard**

CAMBRIDGE MOLECULAR SCIENCE



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MOLECULAR CLUSTERS

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Preface

Who, what, where, why, when and how – the elementary prescription for a news squib is also appropriate for a preface.

Who? The book is intended primarily as a text for advanced undergraduates and graduate students. It can also serve the needs of research workers in the wide area of nanochemistry, as molecular clusters and extended solid-state materials constitute the structural “bookends” of nanoparticles: species that are not large enough to be treated with solid-state concepts but too large to follow the simple rules of molecular clusters. Those interested in a wide-ranging introduction to models of electronic structure applicable to delocalized, three-dimensional systems will also find it useful.

What? This text circumscribes a non-traditional area of inorganic chemistry. The focus is on a class of compound that exhibits cluster bonding. Emphasis is on connections between the problems of small molecular clusters, where the vast majority of atoms are found at the surface, to large crystals, where most atoms are found in the bulk. A review of bonding in molecular compounds (Chapter 1) is followed by the fundamentals of cluster bonding in p-block clusters (Chapter 2) and transition-metal clusters (Chapter 3). After making connections with organometallic chemistry (Chapter 4), mixed p–d-block clusters are developed (Chapter 5). A bonding model for periodic extended structures (Chapter 6) is developed in the style of Chapter 1. Chapter 7 then illustrates some of the similarities and differences between the bonding of clusters and related solid-state structures. The finale (Chapter 8) abstracts a selection of recent research to illustrate real connections between clusters and solid-state systems.

Where? Time will tell where this text will fit in the curricula of relevant departments. Presently, there is no common course in chemistry that it could serve as a primary text. However, since the mid-1990s a first-year graduate course along the lines of the material contained within this text has been offered at Notre Dame.

Drafts of the present text have been used twice in Chem 616 “Solid-state and cluster chemistry” further developing the material herein.

Why? In inorganic texts solid-state chemistry appears ancillary to the main emphasis of molecular chemistry. The title of one first-year chemistry text proclaims chemistry a “molecular science.” Clusters fare less well. Service on standard inorganic exam committees reveals many teachers of inorganic chemistry who are uncomfortable with both solid-state and cluster chemistries. The conceptual barrier involves the delocalized bonding networks required for an understanding of electronic structure. This book attempts to smooth the transition between simple localized bonding models and the delocalized ones by using clusters to bridge molecular and solid-state chemistries. From the localized two-center bonds of three-connect clusters to the band structure of metals, cluster bonding provides a unifying paradigm.

When? Both solid-state chemistry and main-group cluster chemistry can be considered mature areas. Transition-metal cluster chemistry is of more recent origin; however, it too has been well defined in a number of edited works. There are texts on solid-state chemistry and one on cluster chemistry but there is no text that exploits connections between the two using simple models. Simplified models are the tools of the working chemist but the power of the simple models within an area also creates barriers to inter-area understanding. The time is right to show that the molecular and solid-state boundary conditions on clusters reveals the exciting problems of structure and properties that remain to be discovered in the region lying between small clusters and bulk materials – nanoparticles.

How? The text is representative, not comprehensive, and we attempt to balance simplification and detail. Additional sources are gathered at the end of each chapter but this list is far from complete. Literature is cited when it is felt the reader might benefit from following the original arguments or when a more comprehensive monograph provides access to the details of a given topic or area. For non-chemists the Appendix contains an outline of the fundamental concepts of chemistry prerequisite to the body of the text. With the exception of Chapter 8, each chapter includes worked exercises and homework problems at the end of the chapter. A number of problems are drawn from the research literature to illustrate the approach advocated. They are challenging by design and a few of the solutions are not published.

Caveats. Those familiar with cluster chemistry will mark the absence of cluster synthesis, framework dynamics and reactivity. Considerable information exists and these topics for selected cluster types are well developed in cluster reviews and edited volumes. However, our focus on electronic structure is deliberate. We wished to compare and contrast geometric and electronic structure across the large sweep of element composition and cluster size up to and including bulk materials. To keep the book of manageable size relative to a typical one-semester advanced course yet

still bridge the disparate areas encompassed in “cluster chemistry” we chose a focus consistent with our scope. The approach is unabashedly qualitative but we hope the reader finds the material an *hors d'oeuvre* leading to more satisfying *entrées* in the literature of the many broad topics touched upon.

Thank yous. First, we owe an intellectual debt to the masters of both cluster and solid-state chemistries from whom the models presented arose. Some are acknowledged by name in the text where appropriate. Many others, unacknowledged, created and described the magnificent bodies of chemistry, experimental and theoretical, which constitute the foundations of this work. That is the nature of science – most of us are ants piling our grains of chemistry so that those with longer sight can see even farther.

One of us (TF) held a Leverhulme Visiting Professorship at the University of Bath in the spring of 2004 during which the writing of this book was begun. Dr. Andrew S. Weller made this happen. Many thanks to Andy and his department for both a productive and pleasant sojourn in England. We are also grateful to the CNRS and the NSF for the support of our independent research as well as a joint project of cooperative research which facilitated our writing efforts. Our thanks go to Nancy Fehlner who read the entire manuscript in its final form as well as Dr. Mouna Ben Yahia who kindly performed some theoretical calculations to check qualitative (sometimes not) ideas we had in mind. Still, it is highly unlikely we have produced an error-free book – entropy rules – and the errors that remain are ours.

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1

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

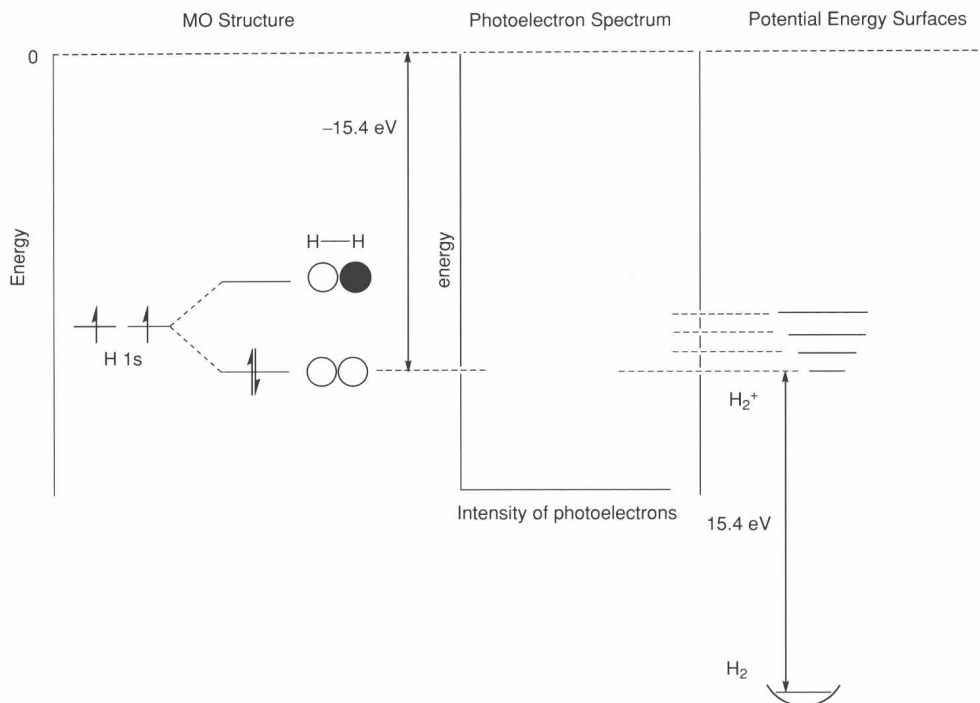


Figure 1.1

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 H_2 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 H_2 can be described as removing an electron from the bonding MO and Koopmans' theorem states that the ionization energy $\text{IE} = -\epsilon_{\text{MO}}$. The MO model suggests that $\text{IE}(\text{H}_2)$ should be larger than $\text{IE}(\text{H}) = 13.6 \text{ eV}$. As shown by its photoelectron spectrum, $\text{IE}(\text{H}_2) = 15.4 \text{ eV}$. 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 H_2^+ and reports on the role of the electron

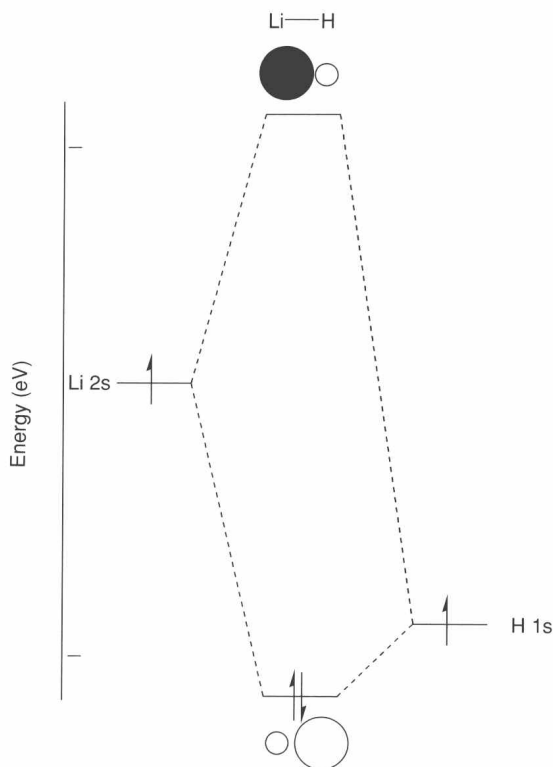


Figure 1.2

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

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

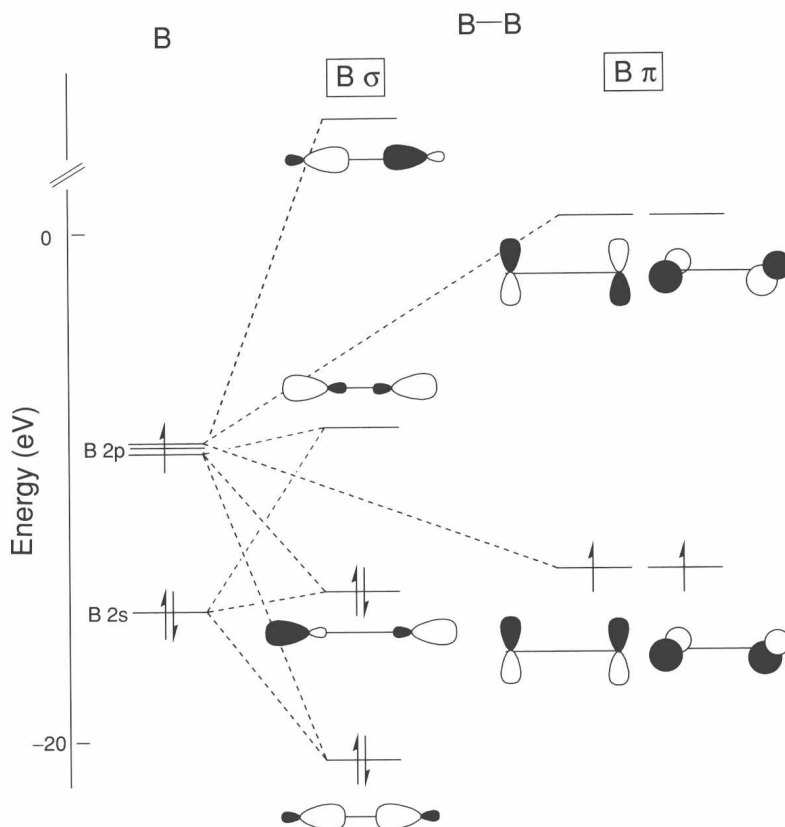


Figure 1.3

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

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

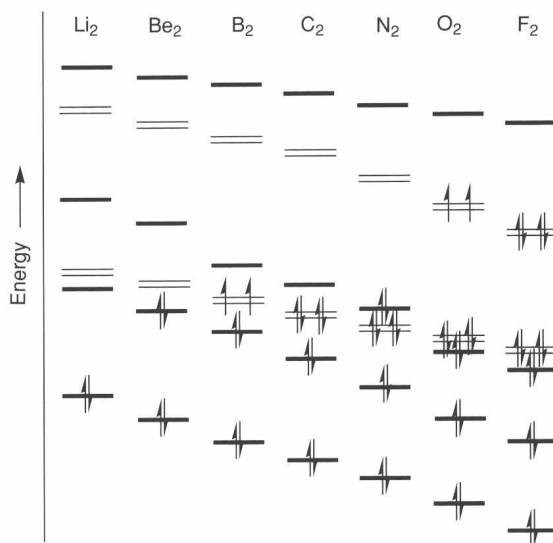


Figure 1.4

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!