8.4: Molecular Orbitals for Homonuclear Diatomics

While the specific forms of the molecular orbitals (their dependence on r and *z* in a cylindrical coordinate system) are different for each molecule, their dependence on the angle f as denoted by the quantum number l and their *g* or *u* behaviour with respect to inversion are completely determined by the symmetry of the system. These properties are common to all of the molecular orbitals for homonuclear diatomic molecules. In addition, the relative ordering of the orbital energies is the same for nearly all of the homonuclear diatomic molecules. Thus we may construct a molecular orbital energy level diagram, similar to the one used to build up the electronic configurations of the atoms in the periodic table. The molecular orbital energy level diagram (Figure 8.4.1) is as fundamental to the understanding of the electronic structure of diatomic molecules as the corresponding atomic orbital diagram is to the understanding of atoms.
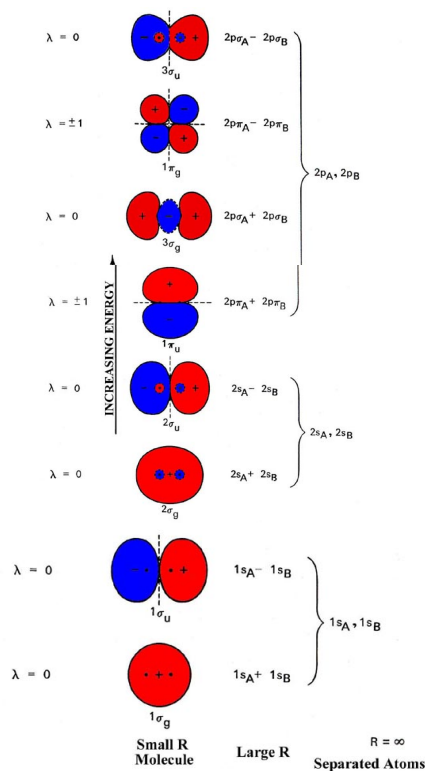

Figure 8.4.1: Molecular orbital energy level diagram for homonuclear diatomic molecules showing the correlation of the molecular orbitals with the atomic orbitals of the separated atoms. The schematic representation of the molecular orbitals is to illustrate their general forms and nodal properties (the nodes are indicated by dashed lines). Only one component of the degenerate 1pu and 1pg orbitals is shown. The second component is identical in form in each case but rotated 90° out of the plane. The ordering of the orbital energy levels shown in the figure holds generally for all homonuclear diatomic molecules with the exception of the levels for the 1pu and 3sg orbitals, whose relative order is reversed for the molecules after C_2.

Molecular orbitals exhibit the same general properties as atomic orbitals, including a nodal structure. The nodal properties of the orbitals are indicated inFigure 8.4.1. Notice that the nodal properties correctly reflect the *g* and *u* character of the orbitals. Inversion of a *g* orbital interchanges regions of like sign and the orbital is left unchanged. Inversion of a *u* orbital interchanges the positive regions with the negative regions and the orbital is changed in sign.

An orbital of a particular symmetry may appear more than once. When this occurs a number is added as a prefix to the symbol. Thus there are $1s_g$, $2s_g$, $3s_g$, etc. molecular orbitals just as there are 1*s*, 2*s*, 3*s*, etc. atomic orbitals. The numerical prefix is similar to the principal quantum number *n* in the atomic case. As *n* increases through a given symmetry set, for example, $1s_g$, $2s_g$, $3s_g$, the orbital energy increases, the orbital increases in size and consequently concentrates charge density further from the nuclei, and finally the number of nodes increases as *n* increases. All these properties are common to atomic orbitals as well.

We may obtain a qualitative understanding of the molecular orbital energy level diagram by considering the behaviour of the orbitals under certain limiting conditions. The molecular orbital must describe the motion of the electron for all values of the internuclear separation; from $R = ¥$ for the separated atoms, through $R = R_e$, the equilibrium state of the molecule, to $R = 0$, the united atom obtained when the two nuclei in the molecule coalesce (in a hypothetical reaction) to give a single nucleus. Hence a

molecular orbital must undergo a continuous change in form. At the limit of large R it must reduce to some combination of atomic orbitals giving the proper orbital description of the separated atoms and for $R = 0$ it must reduce to a single atomic orbital on the united nucleus.

Consider, for example, the limiting behaviour of the $1s_g$ orbital in the case of the hydrogen molecule. The most stable state of H_2 is obtained when both electrons are placed in this orbital with paired spins giving the electronic configuration $1s_g^2$. For large values of the internuclear separation, the hydrogen molecule dissociates into two hydrogen atoms. Thus the limiting form of the $1s_g$ molecular orbital for an infinite separation between the nuclei should be a sum of $1s$ orbitals, one centred on each of the nuclei. If we label the two nuclei as A and B we can express the limiting form of the $1s_g$ orbital as

$$1\sigma_g \rightarrow (1s_A + 1s_b)$$

where ls_A is a $1s$ orbital centered on nucleus A, and ls_B is a ls orbital centered on nucleus B. This form for the $1s_g$ orbital predicts the correct density distribution for the system at large values of R. Squaring the function $(1s_A + 1s_B)$ we obtain for the density

$$1s_A 1s_A + 1s_B 1s_B + 2 \times 1s_A 1s_B$$

The first two terms denote that one electron is on atom A and one on atom B, both with 1s atomic density distributions. The cross term $2 \times ls_A \times ls_B$ obtained in the product is zero since the distance between the two nuclei is so great that the overlap of the orbitals vanishes. Notice as well that the function $(ls_A + ls_B)$ has the same symmetry properties as does the $1s_g$ molecular orbital; it is symmetric with respect to both a rotation about the line joining the nuclei and to an inversion of the coordinates at the mid-point between the nuclei. The $1s_g$ orbital for the **molecule** is said to **correlate** with the sum of $1s$ orbitals, one on each nucleus, for the **separated atom case**.

Consider next the limiting case of the separated atoms for the helium molecule. Of the four electrons present in He_2 two are placed in the $1s_g$ orbital and the remaining two must, by the Pauli exclusion principle, be placed in the next vacant orbital of lowest energy, the $1s_u$ orbital. The electronic configuration of He_2 is thus $1s_g^2 1s_u^2$. The $1s_g$ orbital will correlate with the sum of the $1s$ orbitals for the separated helium atoms. Of the two electrons in the $1s_g$ molecular orbital one will correlate with the $1s$ orbital on atom A and the other with the $1s$ orbital on atom B. Since each helium atom possesses two $1s$ electrons, the $1s_u$ orbital must also correlate its electrons with $1s$ atomic functions on A and B. In addition, the correlated function in this case must be of u symmetry. A function with these properties is

$$1\sigma_g \rightarrow (1s_A - 1s_b)$$

The limiting density distribution obtained by squaring this function places one electron in a $1s$ atomic distribution on A, the other in a $1s$ atomic distribution on B. The sum of the limiting charge densities for the $1s_g$ and $1s_u$ molecular orbitals places two electrons in $1s$ atomic charge distributions on each atom, the proper description of two isolated helium atoms.

Every diatomic homonuclear molecular orbital may be correlated with either the sum (for s_g and p_u orbitals) or the difference (for s_u and p_g orbitals) of like orbitals on both separated atoms. By carrying out this correlation procedure for every orbital we may construct a molecular orbital correlation diagram (Figure 8.4.2) which relates each of the orbital energy levels in the molecule with the correlated energy levels in the separated atoms. It is important to note that the symmetry of each orbital is preserved in the construction of this diagram. Consider, for example the molecular orbitals which correlate with the $2p$ atomic orbitals. The direction of approach of the two atoms defines a new axis of quantization for the atomic orbitals. The $2p$ orbital which lies along this axis is of s symmetry while the remaining two $2p$ orbitals form a degenerate set of p symmetry with respect to this axis. The sum and difference of the $2ps$ orbitals on each center correlate with the $3s_g$ and $3s_u$ orbitals respectively, while the sum and the difference of the $2pp$ orbitals correlate with the p_u and p_g orbitals (Figure 8.4.2).
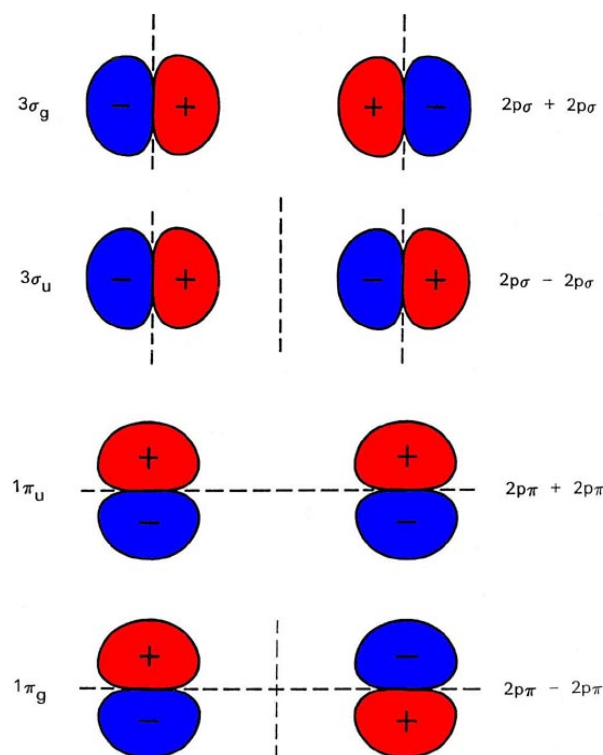
Figure 8.4.2: The correlated separated atom forms of the $3s_g$, $3s_u$, $1p_u$ and $1p_g$ molecular orbitals. The nodal planes are indicated by dashed lines. Only one component of each p orbital is shown.

For large values of the internuclear distance, each molecular orbital is thus represented by a sum or a difference of atomic orbitals centered on the two interacting atoms. As the atoms approach one another the orbitals on each atom are distorted by polarization and overlap effects. In general, the limiting correlated forms of the molecular orbitals are ***not*** suitable descriptions of the molecular orbitals for finite internuclear separations.

We are now in a position to build up and determine the electronic configurations of the homonuclear diatomic molecules by adding electrons two at a time to the molecular orbitals with the spins of the electrons paired, always filling the orbitals of lowest energy first. We shall, at the same time, discuss the effectiveness of each orbital in binding the nuclei and make qualitative predictions regarding the stability of each molecular configuration.

Hydrogen. The two electrons in the hydrogen molecule may both be accommodated in the $1s_g$ orbital if their spins are paired and the molecular orbital configuration for H_2 is $1s_g{}^2$. Since the $1s_g$ orbital is the only occupied orbital in the ground state of H_2, the density distribution shown previously in Figure 8.4.2 for H_2 is also the density distribution for the $1s_g$ orbital when occupied by two electrons. The remarks made previously regarding the binding of the nuclei in H_2 by the molecular charge distribution apply directly to the properties of the $1s_g$ charge density. Because it concentrates charge in the binding region and exerts an attractive force on the nuclei the $1s_g$ orbital is classified as a ***bonding orbital***.

Excited electronic configurations for molecules may be described and predicted with the same ease within the framework of molecular orbital theory as are the excited configurations of atoms in the corresponding atomic orbital theory. For example, an electron in H_2 may be excited to any of the vacant orbitals of higher energy indicated in the energy level diagram. The excited molecule may return to its ground configuration with the emission of a photon. The energy of the photon will be given approximately by the difference in the energies of the excited orbital and the $1s_g$ ground state orbital. Thus molecules as well as atoms will exhibit a line spectrum. The electronic line spectrum obtained from a molecule is, however, complicated by the appearance of many accompanying side bands. These have their origin in changes in the vibrational energy of the molecule which accompany the change in electronic energy.

Helium. The electronic configuration of He_2 is $1s_g{}^2 1s_u{}^2$. A s_u orbital, unlike a s_g orbital, possesses a node in the plane midway between the nuclei and perpendicular to the bond axis. The $1s_u$ orbital and all s_u orbitals in general, because of this nodal property, cannot concentrate charge density in the binding region. It is instead concentrated in the antibinding region behind each nucleus (Figure 8.4.3).
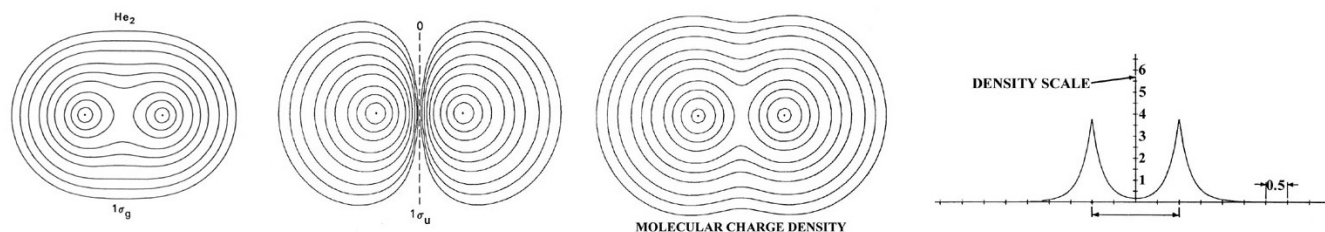
Figure 8.4.3: *Contour maps of the doubly-occupied* $1\sigma_g$ *and* $1\sigma_u$ *molecular orbital charge densities and of the total molecular charge distribution of* He_2 *at R = 2.0 au. A profile of the total charge distribution along the internuclear axis is also shown. Click here for contour values.*

The s_u orbitals are therefore classified as ***antibonding***. It is evident from the form of density distribution for the $1s_u$ orbital that the charge density in this orbital pulls the nuclei apart rather than drawing them together. Generally, the occupation of an equal number of s_g and s_u orbitals results in an unstable molecule. The attractive force exerted on the nuclei by the charge density in the s_g orbitals is not sufficient to balance both the nuclear force of repulsion and the antibinding force exerted by the density in the s_u orbitals. Thus molecular orbital theory ascribes the instability of He$_2$ to the equal occupation of bonding and antibonding orbitals. Notice that the Pauli exclusion principle is still the basic cause of the instability. If it were not for the Pauli principle, all four electrons could occupy a s_g-type orbital and concentrate their charge density in the region of low potential energy between the nuclei. It is the Pauli principle, and not a question of energetics, which forces the occupation of the $1s_u$ antibonding orbital.

The total molecular charge distribution is obtained by summing the individual molecular orbital densities for single or double occupation numbers as determined by the electronic configuration of the molecule. Thus the total charge distribution for He$_2$ (Figure 8.4.3) is given by the sum of the $1s_g$ and $1s_u$ orbital densities for double occupation of both orbitals. The adverse effect which the nodal property of the $1s_u$ orbital has on the stability of He$_2$ is very evident in the total charge distribution. Very little charge density is accumulated in the central portion of the binding region. The value of the charge density at the mid-point of the bond in He$_2$ is only 0.164 au compared to a value of 0.268 au for H$_2$.

We should reconsider in the light of molecular orbital theory the stability of He$_2^+$ and the instability of the hydrogen molecule with parallel spins, cases discussed previously in terms of valence bond theory. He$_2^+$ will have the configuration $1s_g^2\,1s_u^1$. Since the $1s_u$ orbital is only singly occupied in He$_2^+$, less charge density is accumulated in the antibinding regions than is accumulated in these same regions in the neutral molecule. Thus the binding forces of the doubly-occupied $1s_g$ density predominate and He$_2$ is stable. The electron configuration of H$_2$ is $1s_g^1()1s_u^1()$ when the electronic spins are parallel. The electrons must occupy separate orbitals because of the Pauli exclusion principle. With equal occupation of bonding and antibonding orbitals, the H$_2$ ()species is predicted to be unstable.

Lithium. The Li$_2$ molecule with the configuration $1s_g^2 1s_u^2 2s_g^2$ marks the beginning of what can be called the second quantum shell in analogy with the atomic case. Since the $1s_u$ antibonding orbital approximately cancels the binding obtained from the $1s_g$ bonding orbital, the bonding in Li$_2$ can be described as arising from the single pair of electrons in the $2s_g$ orbital. Valence bond theory, or a Lewis model for Li$_2$, also describes the bonding in Li$_2$ as resulting from a single electron pair bond. This is a general result. The number of bonds predicted in a simple Lewis structure is often found to equal the difference between the number of occupied bonding and antibonding orbitals of molecular orbital theory.

The forms of the orbital density distributions for Li$_2$ (Figure 8.4.4) bear out the prediction that a single electron pair bond is responsible for the binding in this molecule.
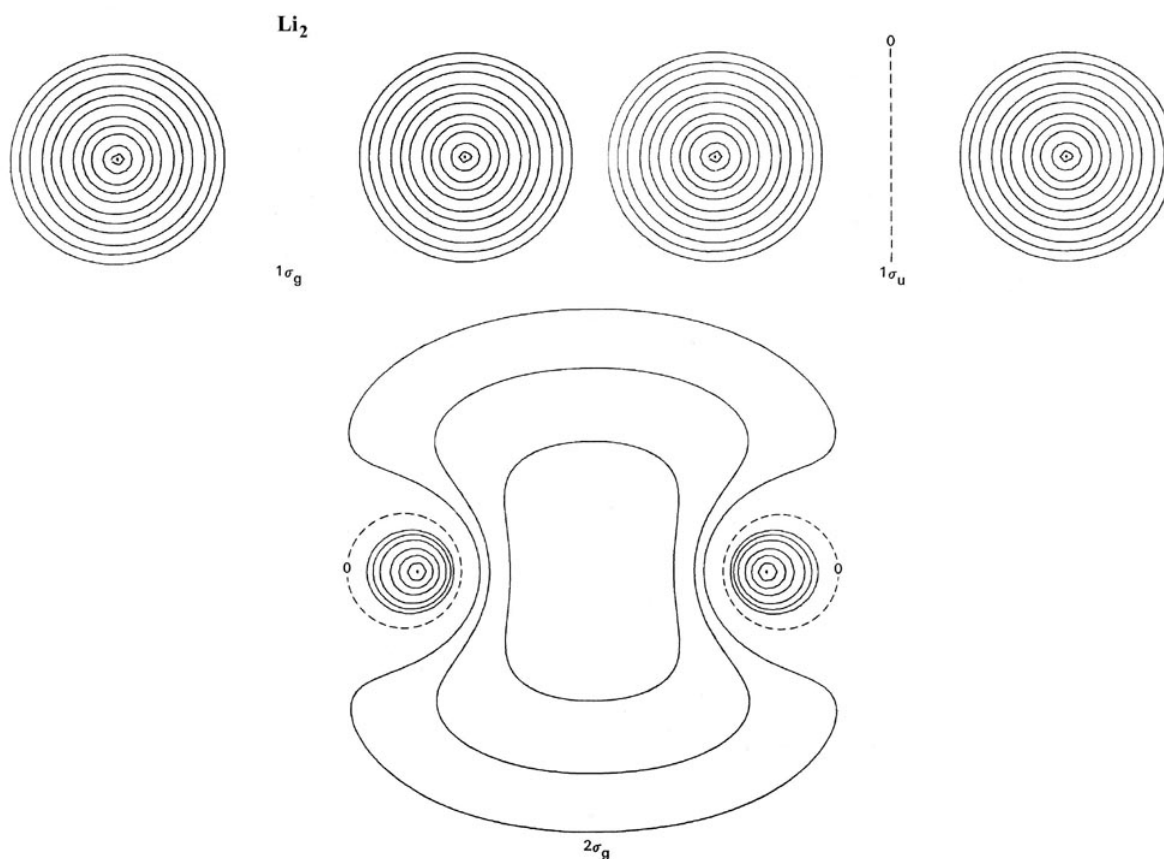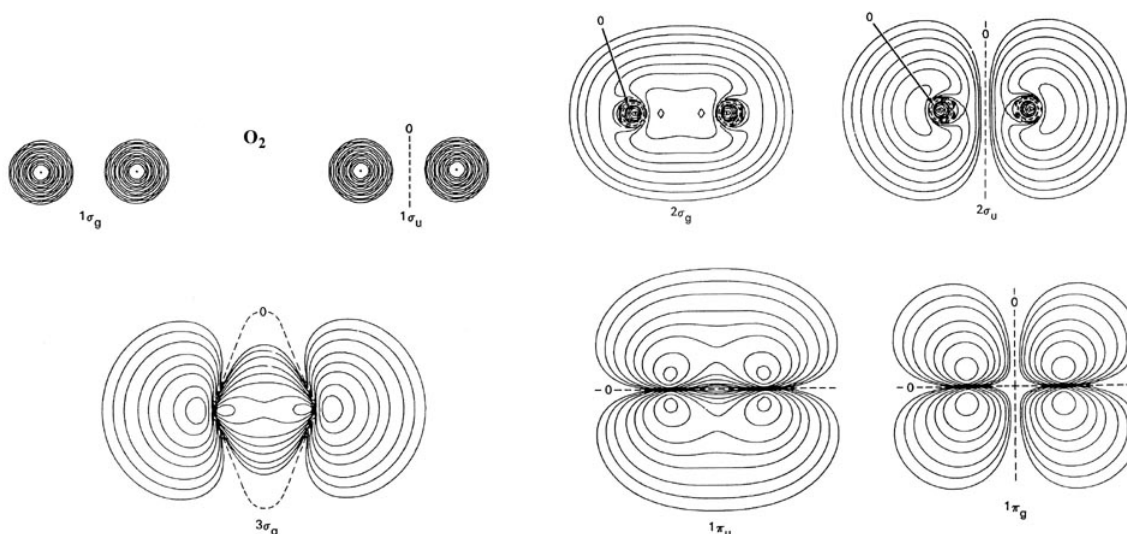
Figure 8.4.4: Contour maps of the doubly-occupied $1s_g$, $1s_u$ and $2s_g$ molecular orbital charge densities for Li_2 at $R = 5.051$ au, the equilibrium internuclear separation. Click here for contour values. The total molecular charge distribution for Li_2 is shown in Fig. 7-3.

The $1s_g$ and $1s_u$ density distributions are both strongly localized in the regions of the nuclei with spherical contours characteristic of $1s$ atomic distributions. The addition of just the doubly-occupied $1s_g$ and $1s_u$ orbital densities in Li_2 will yield a distribution which resembles very closely and may be identified with the doubly-occupied $1s$ or inner shell atomic densities on each lithium nucleus. Only the charge density of the pair of valence electrons in the $2s_g$ orbital is delocalized over the whole of the molecule and accumulated to any extent in the binding region.

Thus there are cases where the molecular orbitals even at the equilibrium bond length resemble closely their limiting atomic forms. This occurs for inner shell molecular orbitals which correlate with the inner shell atomic orbitals on the separated atoms. Inner shell $1s$ electrons are bound very tightly to the nucleus as they experience almost the full nuclear charge and the effective radii of the $1s$ density distributions are less than the molecular bond lengths. Because of their tight binding and restricted extension in space, the inner electrons do not participate to any large extent in the binding of a molecule. Thus with the exception of H_2 and He_2 and their molecular ions, the $1s_g$ and $1s_u$ molecular orbitals degenerate into non-overlapping atomic-like orbitals centred on the two nuclei and are classed as nonbonding orbitals.

Beryllium. The configuration of Be_2 is $1s_g^2 1s_u^2 2s_g^2 2s_u^2$ and the molecule is predicted to form a weakly bound van der Waals molecule like the helium dimer.

Oxygen. Since the method of determining electronic configurations is clear from the above examples, we shall consider just one more molecule in detail, the oxygen molecule. Filling the orbitals in order of increasing energy the sixteen electrons of O_2 are described by the configuration $1s_g^2 1s_u^2 2s_g^2 2s_u^2 3s_g^2 1p_u^4 1p_g^2$. The orbital densities are illustrated in Figure 8.4.5.

Figure **8.4.5***: Contour maps of the molecular orbital charge densities for O_2 at the equilibrium internuclear distance of 2.282 au. Only one component of the Ipg and 1pu orbitals is shown. All the maps are for doubly-occupied orbitals with the exception of that for 1pg for which each component of the doubly-degenerate orbital contains a single electron. The nodes are indicated by dashed lines. Click here for contour values.*

The molecular orbitals of p symmetry are doubly degenerate and a filled set of p orbitals will contain four electrons. The node in a p_u orbital is in the plane which contains the internuclear axis and is not perpendicular to this axis as is the node in a $s_u$orbital. (The nodal properties of the orbitals are indicated in Figure 8.4.5) The p_u orbital is therefore bonding. A p_g orbital, on the other hand, is antibonding because it has, in addition to the node in the plane of the bond axis, another at the bond mid-point perpendicular to the axis. The bonding and antibonding characters of the p orbitals have just the opposite relationship to their *g* and *u* dependence as have the s orbitals.

The $1s_g$ and $1s_u$ orbital densities have, as in the case of Li$_2$, degenerated into localized atomic distributions with the characteristics of 1s core densities and are nonbonding. The valence electrons of O_2 are contained in the remaining orbitals, a feature reflected in the extent to which their density distributions are delocalized over the entire molecule. Aside from the inner nodes encircling the nuclei, the $2s_g$ and $2s_u$orbital densities resemble the $1s_g$ and $1s_u$ valence density distributions of H_2 and He_2. A quantitative discussion of the relative binding abilities of the $2s_g$, $3s_g$ and 1p orbital densities is presented in the following section.

One interesting feature of the electronic configuration of O_2 is that its outer orbital is not fully occupied. The two p_g electrons could both occupy one of the p_g orbitals with paired spins or they could be assigned one to each of the p_g orbitals and have parallel spins. Hund's principle applies to molecules as well as to atoms and the configuration with single occupation of both p_g orbitals with parallel spins is thus predicted to be the most stable. This prediction of molecular orbital theory regarding the electronic structure of O_2 has an interesting consequence. The oxygen molecule should be magnetic because of the resultant spin angular momentum possessed by the electrons. The magnetism of O_2 can be demonstrated experimentally in many ways, one of the simplest being the observation that liquid oxygen is attracted to the poles of a strong magnet.