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FIGURE 1. The active molecular orbitals forming the chemical bond between two uranium atoms.
From the following article:
Quantum chemical calculations show that the uranium molecule U_2 has a quintuple bond
Laura Gagliardi and Björn O. Roos
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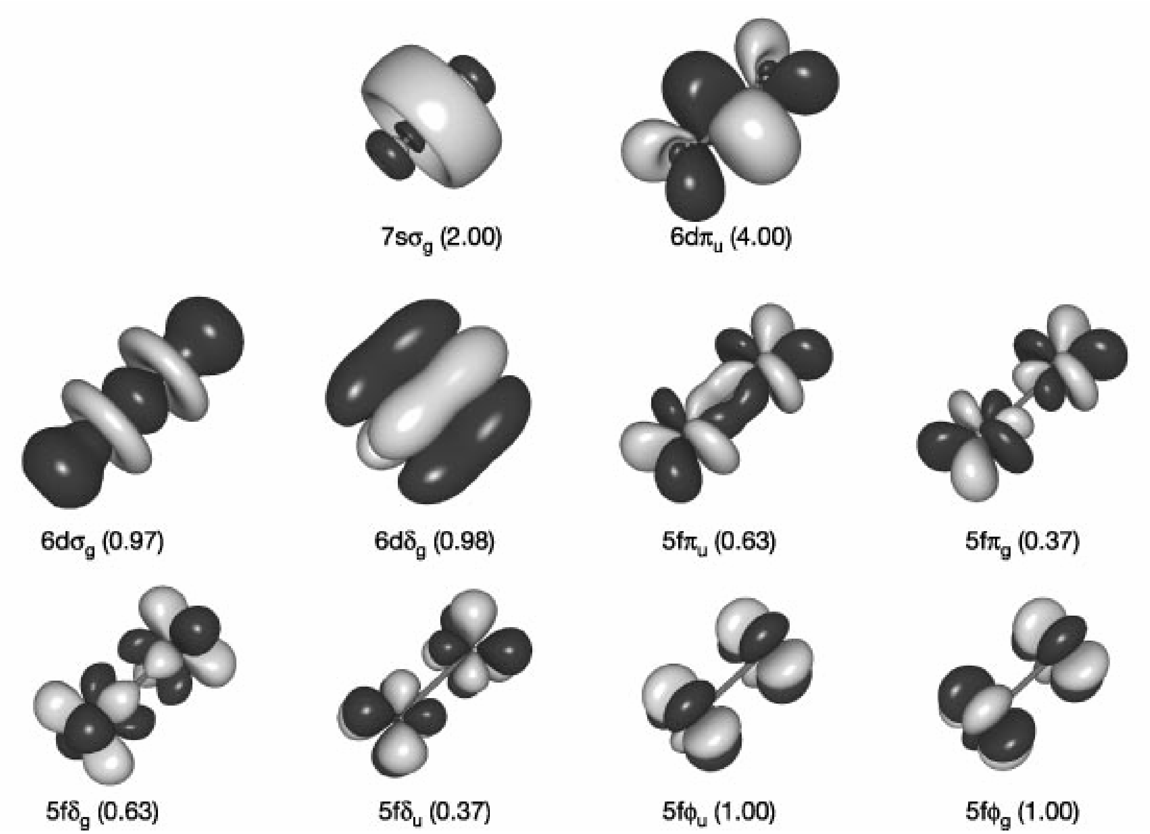

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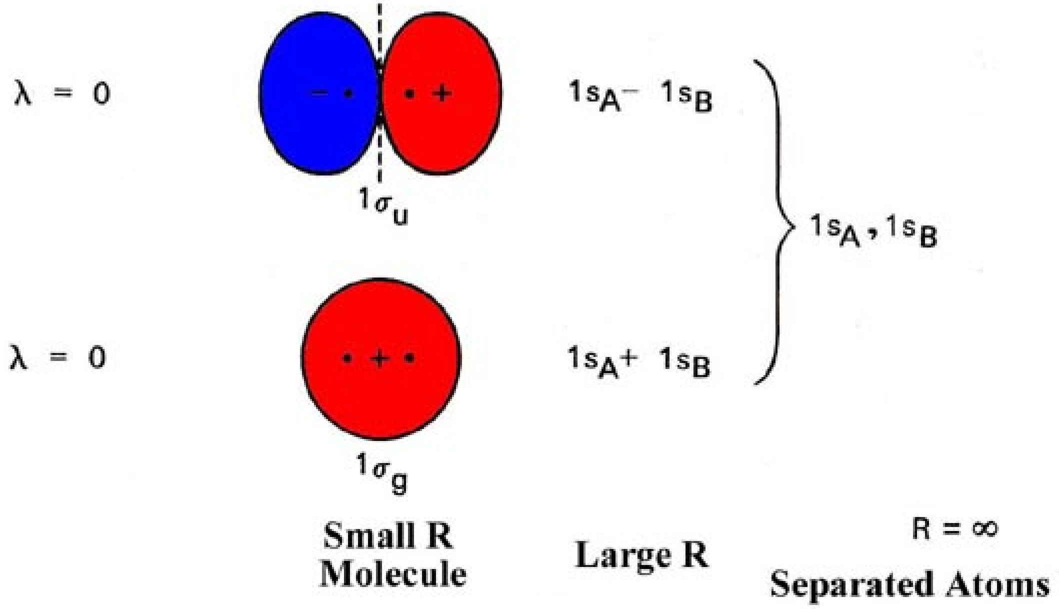
An Introduction to the Electronic Structure of Atoms and Molecules

Dr. Richard F.W. Bader

Molecular Orbitals for Homonuclear Diatomics

While the specific forms of the molecular orbitals (their dependence on ρ and *z* in a cylindrical coordinate system) are different for each molecule, their dependence on the angle ϕ as denoted by the quantum number λ 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 (Fig. 8-4) 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.



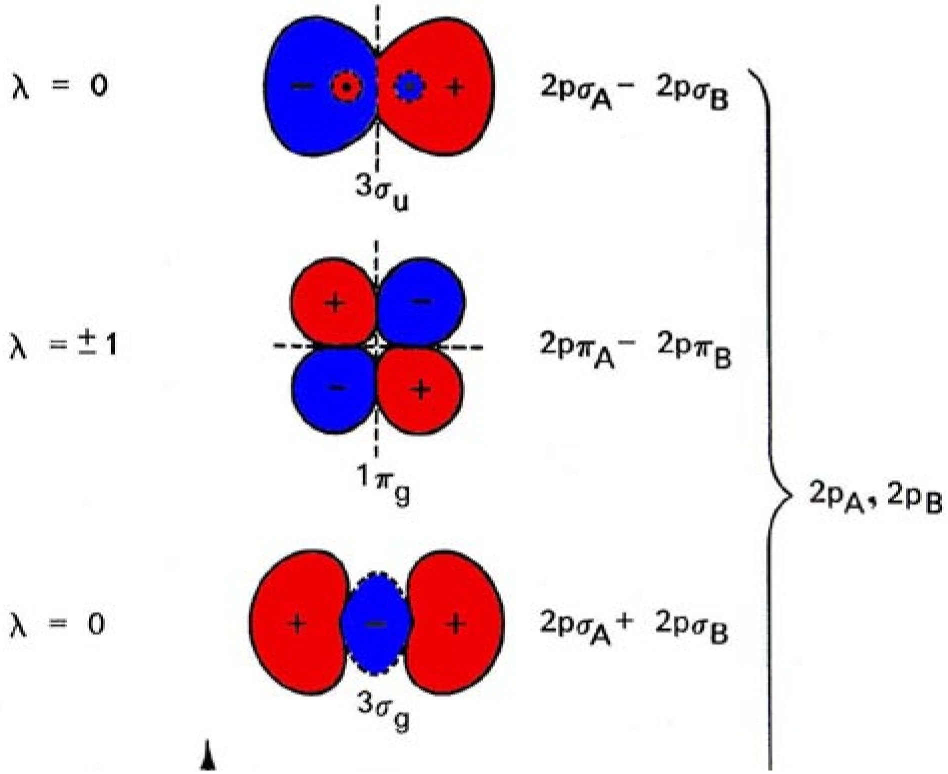
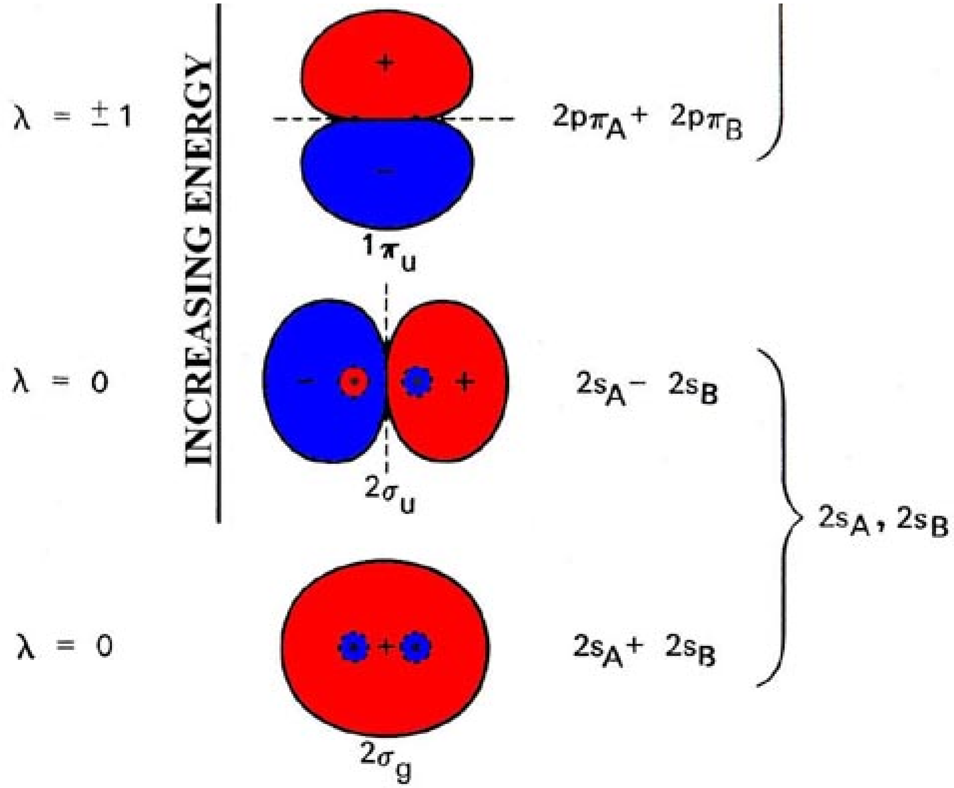


Fig. 8-4. Molecular orbital energy level diagram for homonuclear diatomic molecules



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 $1\pi_u$ and $1\pi_g$ 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 $1\pi_u$ and $3\sigma_g$ 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 in Fig. 8-4. 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 $1\sigma_g$, $2\sigma_g$, $3\sigma_g$, 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, $1\sigma_g$, $2\sigma_g$, $3\sigma_g$, 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 $R = \infty$ 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 $1\sigma_g$ 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 $1\sigma_g^2$. For large values of the internuclear separation, the hydrogen molecule dissociates into two hydrogen atoms. Thus the limiting form of the $1\sigma_g$ molecular orbital for an infinite separation between the nuclei should be a sum of 1*s* 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 $1\sigma_g$ orbital as

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

where ls_A is a 1*s* orbital centred on nucleus A, and ls_B is a l*s* orbital centred on nucleus B. This form for the $1\sigma_g$ orbital predicts the correct density distribution for the system at large values of R. Squaring the function $(\mathrm{ls}_\mathrm{A} + \mathrm{ls}_\mathrm{B})$ we obtain for the density

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

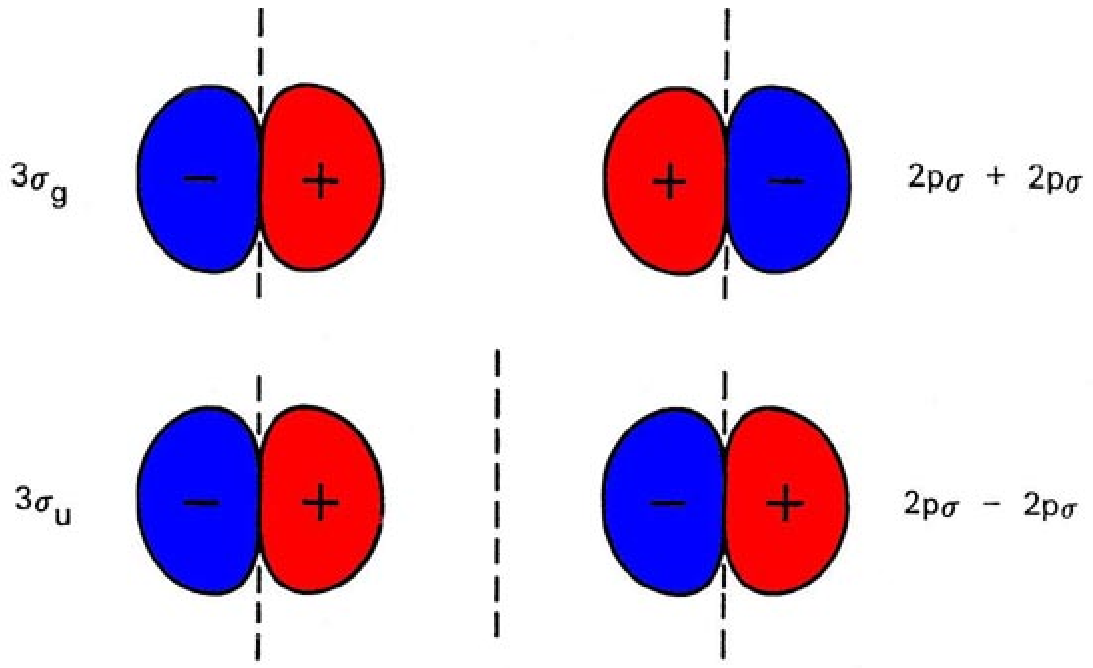
The first two terms denote that one electron is on atom A and one on atom B, both with 1s atomic density distributions. The cross term $2 \times \mathrm{ls}_\mathrm{A} \times \mathrm{ls}_\mathrm{B}$ obtained in the product is zero since the distance between the two nuclei is so great that the overlap of the orbitals vanishes. Notice as well that the function $(\mathrm{ls}_\mathrm{A} + \mathrm{ls}_\mathrm{B})$ has the same symmetry properties as does the $1\sigma_g$ 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 $1\sigma_g$ orbital for the ***molecule*** is said to ***correlate*** with the sum of 1*s* 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 $1\sigma_g$ orbital and the remaining two must, by the Pauli exclusion principle, be placed in the next vacant orbital of lowest energy, the$1\sigma_u$ orbital. The electronic configuration of He_2 is thus $1\sigma_g^2 1\sigma_u^2$. The $1\sigma_g$ orbital will correlate with the sum of the 1*s* orbitals for the separated helium atoms. Of the two electrons in the$1\sigma_g$ molecular orbital one will correlate with the 1*s* orbital on atom A and the other with the 1*s* orbital on atom B. Since each helium atom possesses two 1*s* electrons, the $1\sigma_u$ orbital must also correlate its electrons with 1*s* 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

$$1\sigma_u \rightarrow (1s_A - 1s_B)$$

The limiting density distribution obtained by squaring this function places one electron in a 1*s* atomic distribution on A, the other in a 1*s* atomic distribution on B. The sum of the limiting charge densities for the $1\sigma_g$ and $1\sigma_u$ molecular orbitals places two electrons in 1*s* 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 σ_g and π_u orbitals) or the difference (for σ_u and π_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 (Fig. 8-4) 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 2*p* atomic orbitals. The direction of approach of the two atoms defines a new axis of quantization for the atomic orbitals. The 2*p* orbital which lies along this axis is of σ symmetry while the remaining two 2*p* orbitals form a degenerate set of π symmetry with respect to this axis. The sum and difference of the 2*p*σ orbitals on each centre correlate with the $3\sigma_g$ and $3\sigma_u$ orbitals respectively, while the sum and the difference of the 2*p*π orbitals correlate with the π_u and π_g orbitals (Fig. 8-5).


$3\sigma_g$
−
+
+
−
$2p\sigma + 2p\sigma$
$3\sigma_u$
−
+
−
+
$2p\sigma - 2p\sigma$

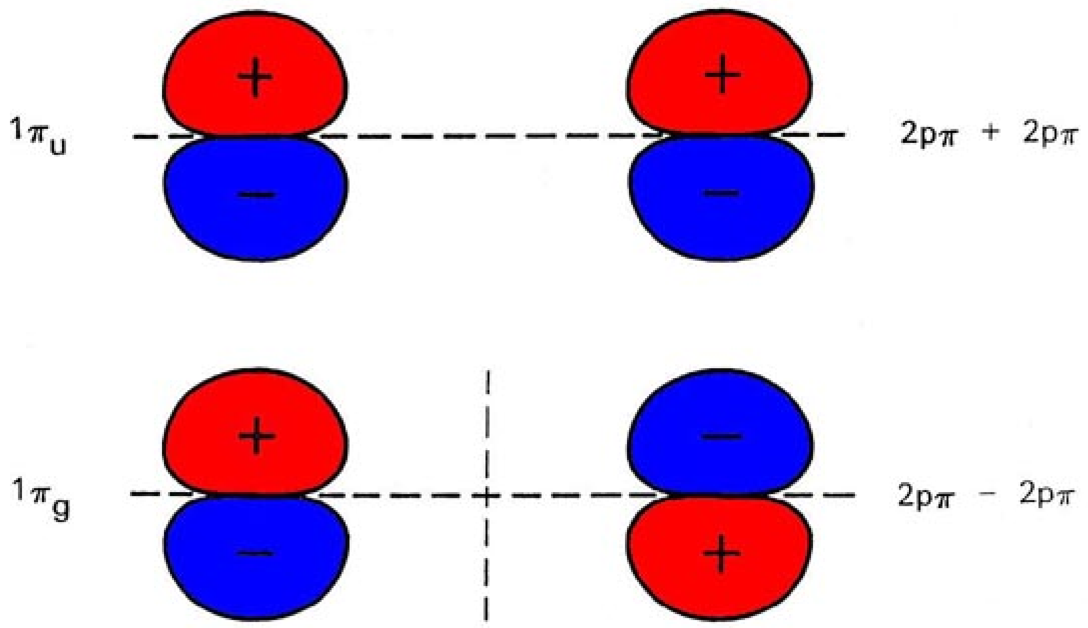


Fig. 8-5. The correlated separated atom forms of the $3\sigma_g$, $3\sigma_u$, $1\pi_u$ and $1\pi_g$ molecular orbitals. The nodal planes are indicated by dashed lines. Only one component of each π orbital is shown.

For large values of the internuclear distance, each molecular orbital is thus represented by a sum or a difference of atomic orbitals centred 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.

The correlation of the molecular orbitals with the appropriate atomic orbitals of the united atom is left as a problem for the reader (Problem 2).

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.

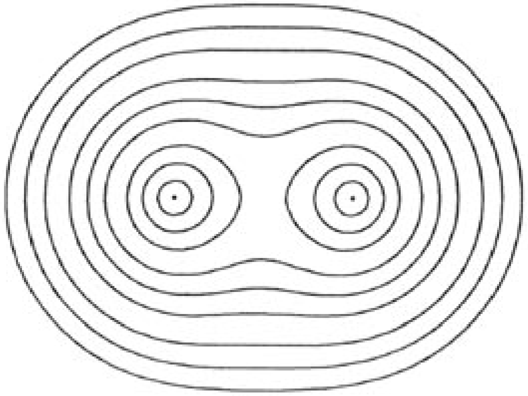
www.cartage.org.lb/.../Molecular/Molecular.htm

Hydrogen. The two electrons in the hydrogen molecule may both be accommodated in the $1\sigma_g$ orbital if their spins are paired and the molecular orbital configuration for H_2 is $1\sigma_g^2$. Since the $1\sigma_g$ orbital is the only occupied orbital in the ground state of H_2, the density distribution shown previously in Fig. 6-2 for H_2 is also the density distribution for the $1\sigma_g$ 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 $1\sigma_g$ charge density. Because it concentrates charge in the binding region and exerts an attractive force on the nuclei the $1\sigma_g$ orbital is classified as a ***bonding orbital***.

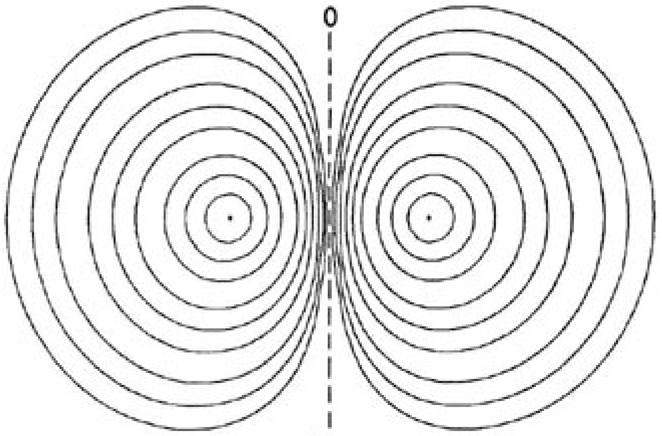
Excited electronic configurations for molecules may be described and predicted with the same ease within the framework of molecular orbital theory as are the excited configurations of atoms in the corresponding atomic orbital theory. For example, an electron in H_2 may be excited to any of the vacant 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 $1\sigma_g$ 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 $1\sigma_g^2\ 1\sigma_u^2$. A σ_u orbital, unlike a σ_g orbital, possesses a node in the plane midway between the nuclei and perpendicular to the bond axis. The $1\sigma_u$ orbital and all σ_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 (Fig. 8-6).

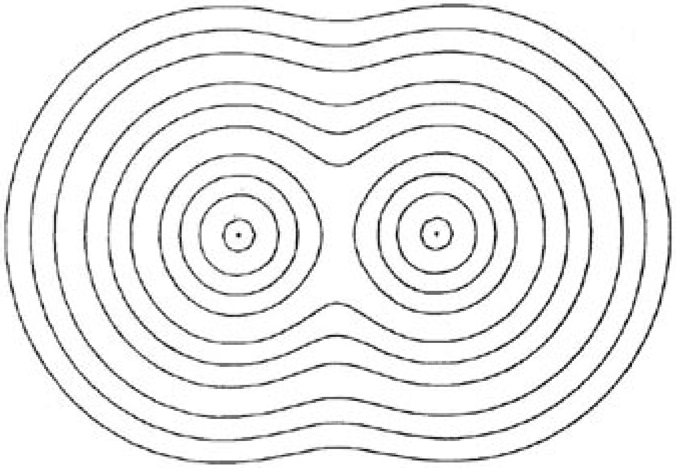
He_2



$1\sigma_g$



$1\sigma_u$



MOLECULAR CHARGE DENSITY

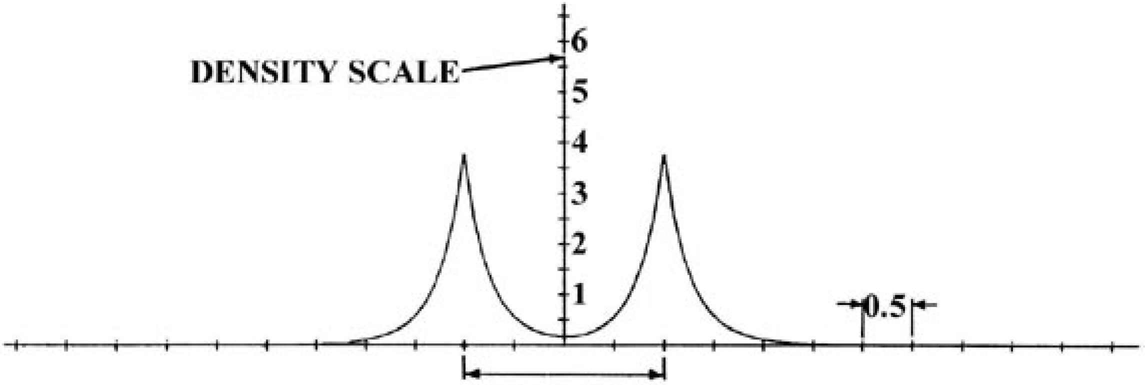


Fig. 8-6. Contour maps of the doubly-occupied $1\sigma_g$ and $1\sigma_u$ molecular orbital charge densities and of the total molecular charge distribution of He_2 at $R = 2.0$ au. A profile of the total charge distribution along the internuclear axis is also shown. Click here for contour values.

The σ_u orbitals are therefore classified as ***antibonding***. It is evident from the form of density distribution for the $1\sigma_u$ 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 σ_g and σ_u orbitals results in an unstable molecule. The attractive force exerted on the nuclei by the charge density in the σ_g orbitals is not sufficient to balance both the nuclear force of repulsion and the antibinding force exerted by the density in the σ_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 σ_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 $1\sigma_u$ antibonding orbital.

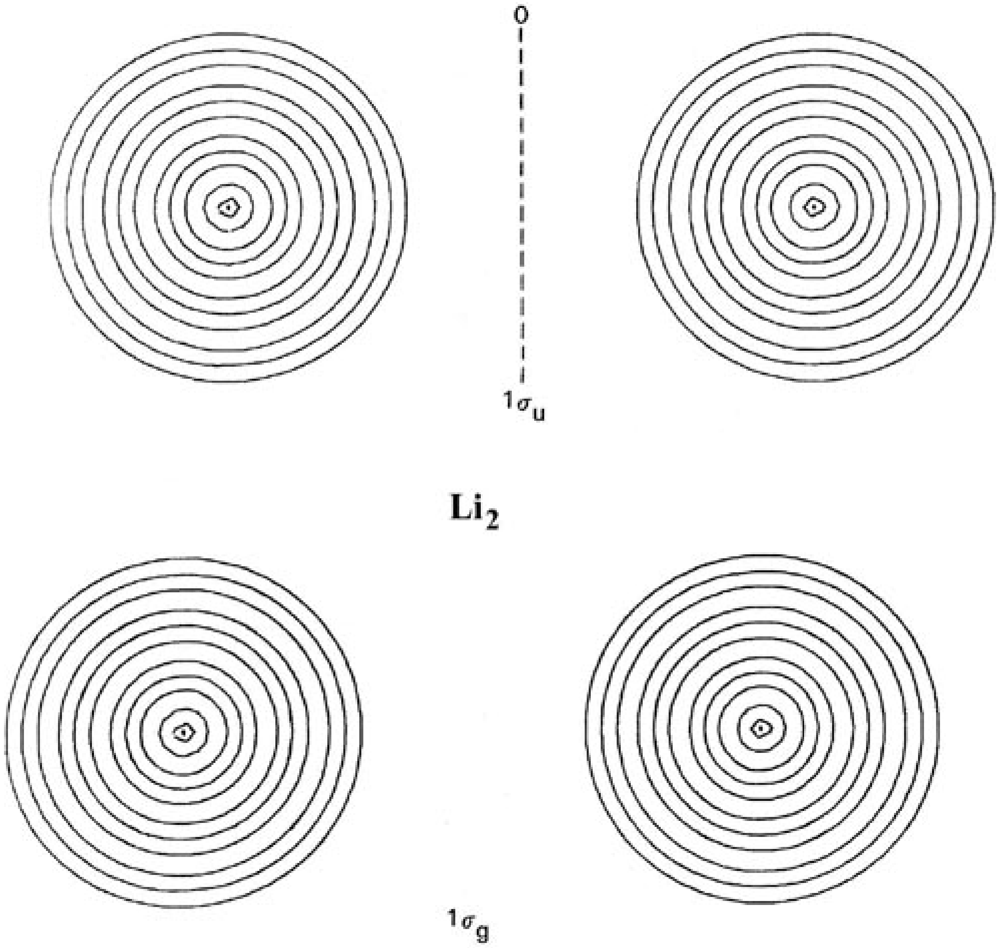
The total molecular charge distribution is obtained by summing the individual molecular orbital densities for single or double occupation numbers as determined by the electronic configuration of the molecule. Thus the total charge distribution for He_2 (Fig. 8-6) is given by the sum of the $1\sigma_g$ and $1\sigma_u$ orbital densities for double occupation of both orbitals. The adverse effect which the nodal property of the $1\sigma_u$ 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.

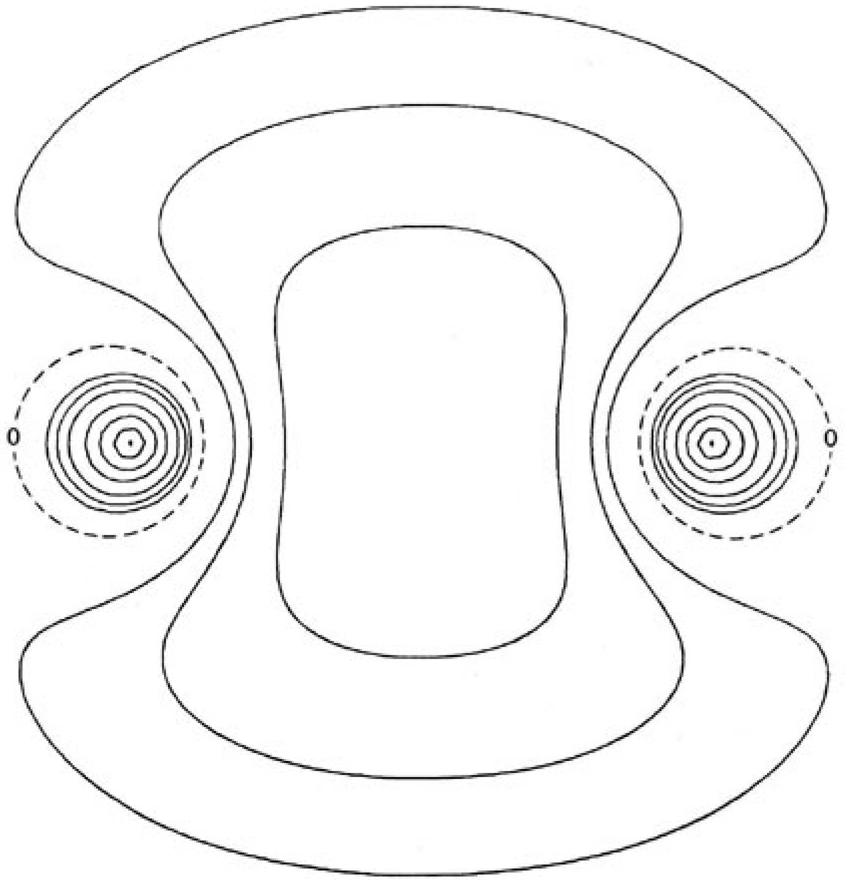
We should reconsider in the light of molecular orbital theory the stability of He_2^+ and the instability of the hydrogen molecule with parallel spins, cases discussed previously in terms of valence bond theory. He_2^+ will have the configuration $1\sigma_g^2\ 1\sigma_u^1$. Since the $1\sigma_u$ orbital 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 $1\sigma_g$ density predominate and He_2 is stable. The electron configuration of H_2 is $1\sigma_g^1()1\sigma_u^1()$ 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 $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$ marks the beginning of what can be called the second quantum shell in analogy with the atomic case. Since the $1\sigma_u$ antibonding orbital approximately cancels the binding obtained from the $1\sigma_g$ bonding orbital, the bonding in Li_2 can be described as arising from the single pair of electrons in the $2\sigma_g$ 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 (Fig. 8-7) bear out the prediction that a single electron pair bond is responsible for the binding in this molecule.

Fig. 8-7. Contour maps of the doubly-occupied $1\sigma_g$, $1\sigma_u$ and $2\sigma_g$ 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.





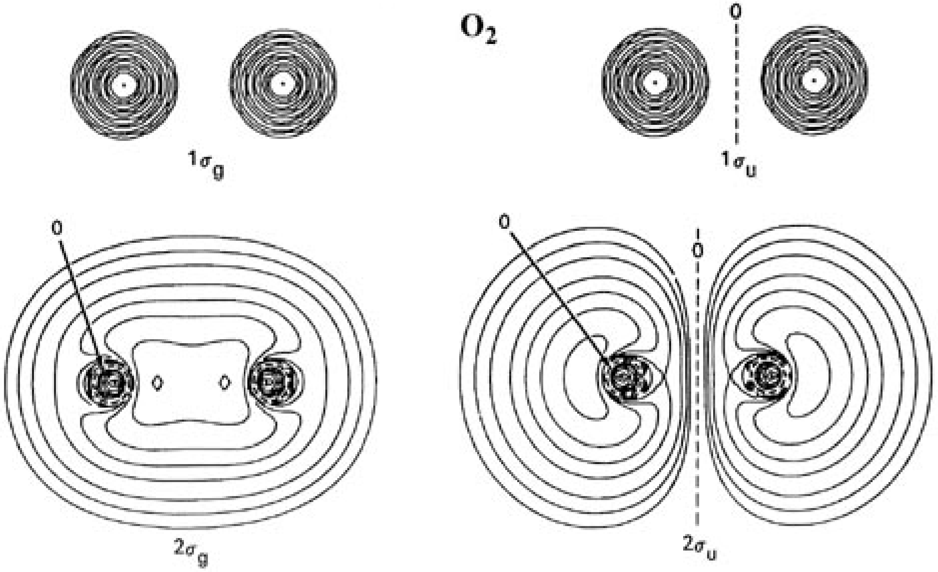
$2\sigma_g$

The $1\sigma_g$ and $1\sigma_u$ density distributions are both strongly localized in the regions of the nuclei with spherical contours characteristic of 1*s* atomic distributions. The addition of just the doubly-occupied $1\sigma_g$ and $1\sigma_u$ orbital densities in Li_2 will yield a distribution which resembles very closely and may be identified with the doubly-occupied 1*s* or inner shell atomic densities on each lithium nucleus. Only the charge density of the pair of valence electrons in the $2\sigma_g$ 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 1*s* electrons are bound very tightly to the nucleus as they experience almost the full nuclear charge and the effective radii of the 1*s* 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 $1\sigma_g$ and $1\sigma_u$ 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 $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2$ and the molecule is predicted to form a weakly bound van der Waals moecule.

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 $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$. The orbital densities are illustrated in Fig. 8-8.



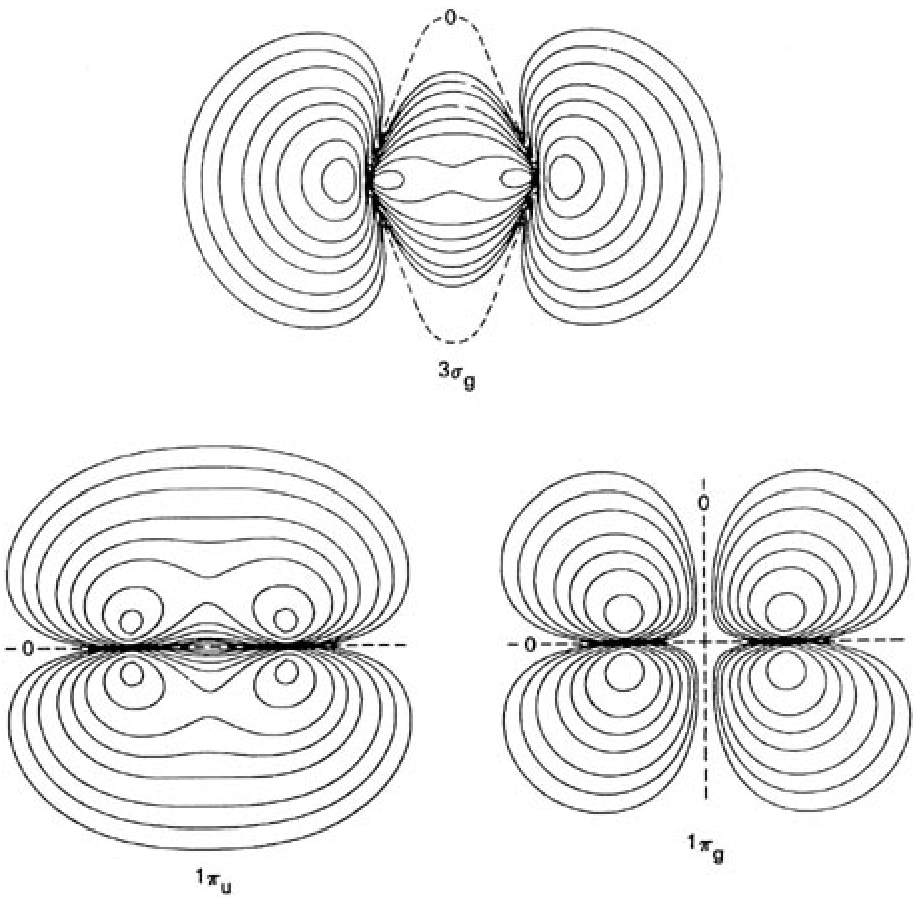


Fig. 8-8. Contour maps of the molecular orbital charge densities for O_2 at the equilibrium internuclear distance of 2.282 au. Only one component of the Iπ_g and 1π_u orbitals is shown. All the maps are for doubly-occupied orbitals with the exception of that for 1π_g for which each component of the doubly-degenerate orbital contains a single electron. The nodes are indicated by dashed lines. Click here for contour values.

The molecular orbitals of π symmetry are doubly degenerate and a filled set of π orbitals will contain four electrons. The node in a π_u orbital is in the plane which contains the internuclear axis and is not perpendicular to this axis as is the node in a σ_u orbital. (The nodal properties of the orbitals are indicated in Fig. 8-4.) The π_u orbital is therefore bonding. A π_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 π orbitals have just the opposite relationship to their *g* and *u* dependence as have the σ orbitals.

The $1\sigma_g$ and $1\sigma_u$ orbital densities have, as in the case of Li_2, degenerated into localized atomic distributions with the characteristics of 1*s* 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 $2\sigma_g$ and $2\sigma_u$orbital densities resemble the $1\sigma_g$ and $1\sigma_u$ valence density distributions of H_2 and He_2. A quantitative discussion of the relative binding abilities of the $2\sigma_g$, $3\sigma_g$ and 1π 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 π_g electrons could both occupy one of the π_g orbitals with paired spins or they could be assigned one to each of the π_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 π_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.

Molecular Orbitals for Heteronuclear Molecules

The molecular orbitals which describe the motion of a single electron in a molecule containing two unequal nuclear charges will not exhibit the *g* and *u* symmetry properties of the homonuclear diatomic case. The molecular orbitals in the heteronuclear case will in general be concentrated more around one nucleus than the other. The orbitals may still be classified as σ, π, δ, etc. because the molecular axis is still an axis of symmetry.

In simple numerical calculations the molecular orbitals are sometimes approximated by the sum and difference of single atomic orbitals on each centre, their limiting form. The molecular orbital is said to be approximated mathematically by a linear combination of atomic orbitals and the technique is known as the LCAO-MO method. It must be understood that the LCAO-MO method using a limited number of atomic orbitals provides only an approximation to the true molecular orbital. The concept of a molecular orbital is completely independent of the additional concept of approximating it in terms of atomic orbitals, except for the case of the separated atoms. However, by using a large number of atomic orbitals centred on each nucleus in the construction of a single molecular orbital sufficient mathematical flexibility can be achieved to approximate the exact form of the molecular orbital very closely.

While the LCAO approximation using a limited number of atomic orbitals is in general a poor one for quantitative purposes, it does provide a useful guide for the prediction of the qualitative features of the molecular orbital. There are two simple conditions which must be met if atomic orbitals on different centres are to interact significantly and form a ***molecular orbital which is delocalized over the whole molecule***. Both atomic orbitals must have approximately the same orbital energy and they must possess the same symmetry characteristics with respect to the internuclear axis. We shall consider the molecular orbitals in LiH, CH and HF to illustrate how molecular orbital theory describes the bonding in heteronuclear molecules, and to see how well the forms of the orbitals in these molecules can be rationalized in terms of the symmetry and energy criteria set out above.

The 1*s* and 2*s* atomic orbitals and the 2*p* orbital which is directed along the bond axis are all left unchanged by a rotation about the symmetry axis. They may therefore form molecular orbitals of σ symmetry in the diatomic hydride molecules. The 2*p* orbitals which are perpendicular to the bond axis will be of π symmetry and may form molecular orbitals with this same symmetry. The energies and symmetry properties of the relevant atomic orbitals and the electronic configurations of the atoms and molecules are given in Table 8-2.

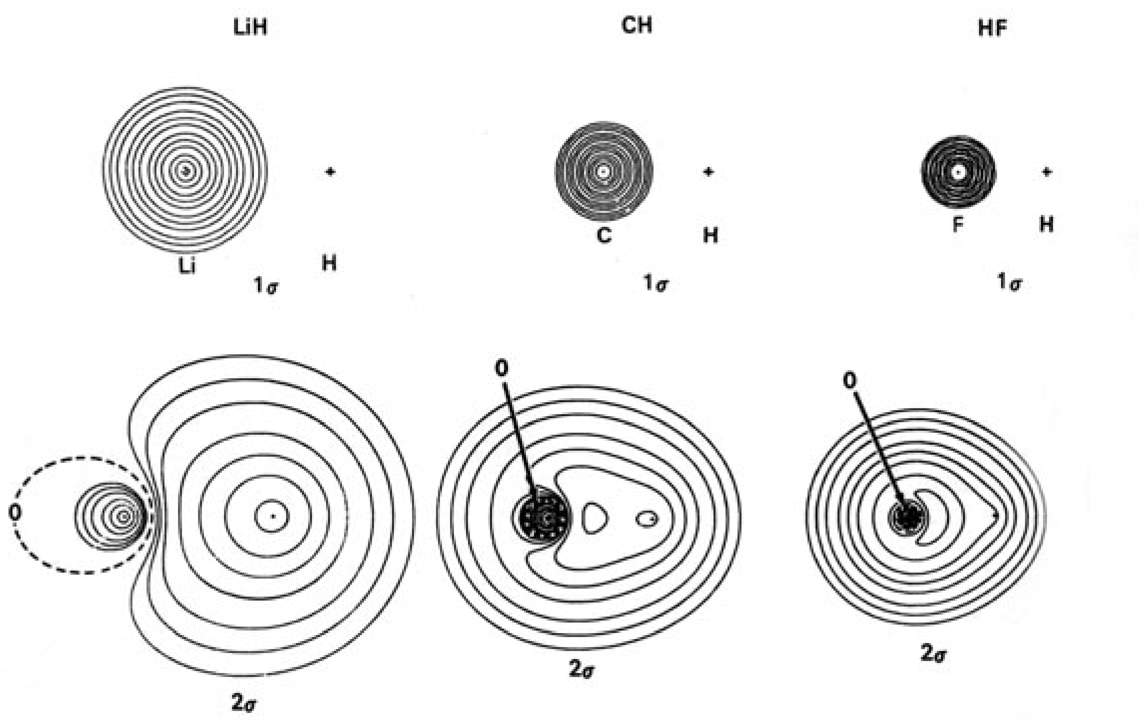
Table 8-2.
Atomic Orbital Energies and Symmetry Properties

	Energy (au)				Symmetry
	H	Li	C	F	
1*s*	-0.5	-2.48	-11.33	-26.38	σ
2*s*		-0.20	-0.71	-1.57	σ
2*p*			-0.43	-0.73	σ and π

Atomic Configurations	
Li	$1s^2 2s^1$
C	$1s^2 2s^2 2p^2$
F	$1s^2 2s^2 2p^5$

Molecular Configurations	
LiH	$1\sigma^2 2\sigma^2$
CH	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^1$
HF	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$

Density diagrams of the molecular orbitals for the LiH, CH, and HF molecules are illustrated in Fig. 8-9.



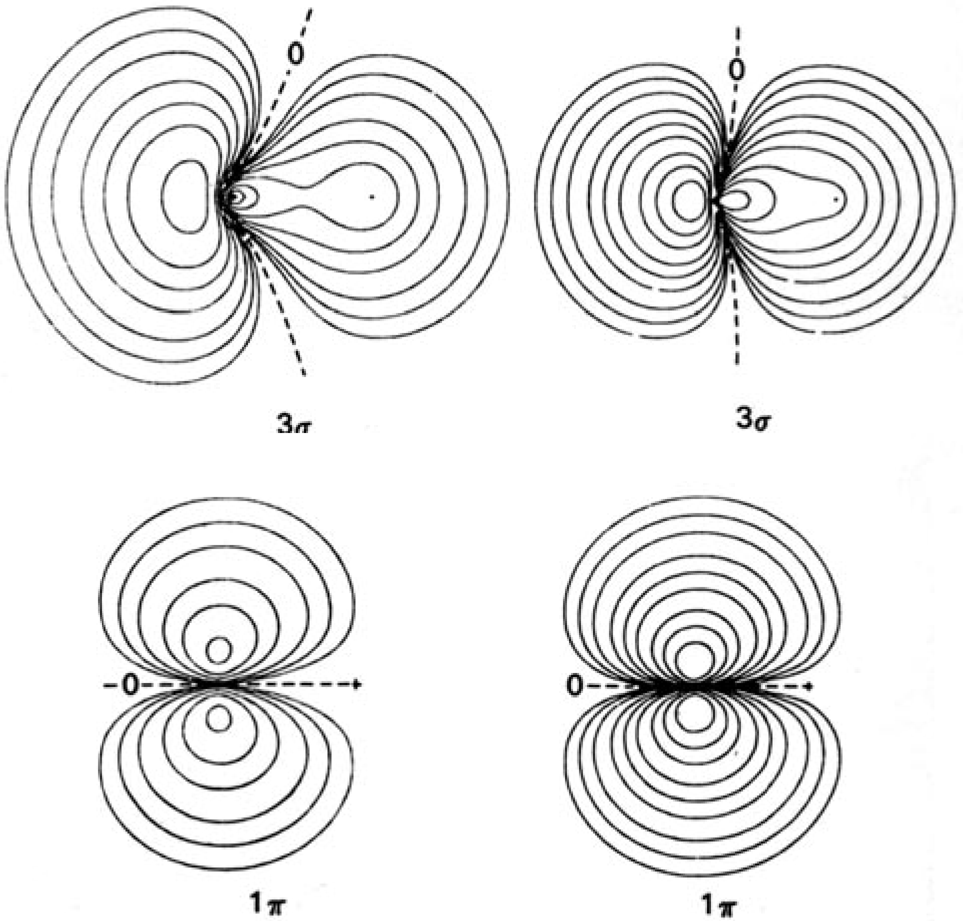


Fig. 8-9. Contour maps of the molecular orbital charge densities of the LiH, CH, HF diatomic hydrides. The nodes are indicated by dashed lines. Click here to see countour values.

The 1*s* orbital energies of Li, C and F all lie well below that of the H 1*s* orbital. The charge densities of these inner shell orbitals are tightly bound to their respective nuclei. They should not, therefore, be much affected by the field of the proton or interact significantly with the H 1*s* orbital. The molecular orbital of lowest energy in these molecules, the lσ molecular orbital, should be essentially nonbinding and resemble the doubly-occupied 1*s* atomic orbital on Li, C and F respectively. These predictions are borne out by the lσ orbital density distributions (Fig. 8-9). They consist of nearly spherical contours centred on the Li, C and F nuclei, the radius of the outer contour being less than the bond length in each case. The forces exerted on the proton by the lσ charge distributions are equivalent to placing two negative charges at the position of the heavy nucleus in each case. The charge density in the lσ molecular orbital simply screens two of the nuclear charges on the heavy nucleus from the proton. This same screening effect is obtained for the $1s^2$ charge distribution when the molecules dissociate into atoms. Thus the 1*s* atomic orbitals of Li, C and F are not much affected by the formation of the molecule and the lσ charge density is nonbinding as far as the proton is concerned. The lσ atomic-like distributions are slightly polarized. In LiH the lσ density is polarized away from the proton to a significant extent while in

CH and HF it is slightly polarized towards the proton. Thus the 1σ charge density exerts an antibinding force on the Li nucleus and a small binding force on the C and F nuclei.

The energies of the 2*s* atomic orbitals decrease (the electron is more tightly bound) from Li to F as expected on the basis of the increase in the effective nuclear charge from Li to F. The 2*s* orbital on Li is large and diffuse and will overlap extensively with the 1*s* orbital on H. However, the 2*s* electron on Li is considerably less tightly bound than is the 1*s* electron on H. Thus the charge density of the 2σ molecular orbital in LiH will be localized in the region of the proton corresponding to the transfer of the 2*s* electron on Li to the region of lower potential energy offered by the 1*s* orbital on H. This is approximately correct as shown by the almost complete concentration of the charge density in the region of the proton in the 2σ orbital density map for LiH. The small amount of density which does remain around the Li nucleus is polarized away from the proton. The 1σ and 2σ densities are polarized in a direction counter to the direction of charge transfer as required in ionic binding. The inwardly polarized accumulation of 2σ charge density centred on the proton binds both nuclei.

The 1σ molecular orbital in LiH is to a good approximation a polarized doubly-occupied 1*s* orbital on Li, and the 2σ molecular orbital is, to a somewhat poorer approximation, a doubly-occupied and polarized 1*s* orbital on H. Our previous discussion of the bonding in LiH indicated that the binding is ionic, corresponding to the description $Li^{+}(1s^{2})H^{-}(1s^{2})$. The molecular orbital description of an ***ionic bond*** is similar in that the molecular orbitals in the ionic extreme are localized in the regions of the individual nuclei, rather than being delocalized over both nuclei as they are for a covalent bond.

The matching of the 2*s* orbital energy with the H 1*s* orbital energy is closer in the case of C than it is for Li. Correspondingly, the 2σ charge density in CH is delocalized over both nuclei rather than concentrated in the region of just one nucleus as it is in the LiH molecule. There is a considerable buildup of charge density in the binding region which is shared by both nuclei. The 2σ charge density exerts a large binding force on both the H and C nuclei. This is the molecular orbital description of an interaction which is essentially covalent in character.

The 2*s* orbital energy of F is considerably lower than that of the H 1*s* orbital. The 2σ orbital charge density in HF, therefore, approximately resembles a localized 2*s* orbital on F. It is strongly polarized and distorted by the proton, but the amount of charge transferred to the region between the nuclei is not as large as in CH. The 2σ orbital in HF plays a less important role in binding the proton than it does in CH.

The 3σ molecular orbital in CH and HF will result primarily from the overlap of the 2*p*σ orbital on C and F, with the 1*s* orbital on H. The 2*p*-like character of the 3σ molecular orbital in both CH and HF is evident in the density diagrams (Fig. 8-9). In CH the 1*s* orbital of H interacts strongly with both the 2*s* and 2*p*σ orbitals on C. In terms of the forces exerted on the nuclei, the 2σ charge density is strongly binding for both C and H, while the 3σ charge density is only very weakly binding for H and is actually antibinding for the C. This antibinding effect is a result of the large accumulation of charge density in the region behind the C nucleus.

In HF, the H 1*s* orbital interacts only slightly with the 2*s* orbital on F, but it interacts very strongly with the 2*p*σ orbital in the formation of the 3σ molecular orbital. The 3σ charge density exerts a large binding force on the proton. Thus the proton is bound primarily by the 2σ charge density in CH and by the 3σ charge density in HF. The 3σ charge density in HF is primarily centred on the F nucleus and roughly resembles a 2*p*σ orbital. Although no density contours are actually centred on the proton, the proton is embedded well within the orbital density distribution. This is a molecular orbital description of a highly polar bond.

The 3σ orbital charge density exerts a force on the F and C nuclei in a direction away from the proton. The molecular orbitals which involve *p*σ orbitals are characteristically strongly polarized in a direction away from the bond in the region of the nucleus on which the *p* orbital is centred. Compare, for example, the 3σ orbitals of CH and HF with the $3\sigma_g$ molecular orbital of the homonuclear diatomic molecules.

When the C and H atoms are widely separated, we can consider the carbon atom to have one 2*p* electron in the 2*p*σ orbital which lies along the bond axis, and the second 2*p* electron in one of the 2*p*π orbitals which are perpendicular to the bond. The F atom has five 2*p* electrons and of these one may be placed in the 2*p*σ orbital; the remaining four 2*p* electrons will then completely occupy the 2*p*π orbitals. The singly-occupied 2*p*σ orbitals on F and C eventually interact with the singly-occupied 1*s* orbital on H to form the doubly-occupied 3σ molecular orbital in HF and CH. The remaining 2*p* electrons, those of π symmetry, will occupy the 1π molecular orbital. The H atom does not possess an orbital of π symmetry in its valence shell and the vacant 2*p*π orbital on H is too high in energy (-0.125 au) to interact significantly with the 2*p*π orbitals on C and F. Thus the 1π molecular orbital is atomic-like, centred on the F and C nuclei and is essentially nonbinding (Fig. 8-9). The 1π molecular orbital resembles a 2*p*π atomic orbital in each case, but one which is polarized in the direction of the proton.

The 1π orbitals of CH and HF illustrate an interesting and general result. In the formation of a bond between different atoms, the charge density in the σ orbitals is transferred from the least to the most electronegative atom. However, the charge density of π symmetry, if any is present, is invariably transferred, or at least polarized, in the opposite direction, towards the least electronegative atom. Although the amount of charge density transferred is less in the formation of the π orbitals than in the σ orbitals, one effect increases with the other. Thus the polarization is more pronounced in HF than in CH.

The three examples considered above demonstrate the essential points of a molecular orbital description of the complete range of chemical bonding. In the ionic extreme of LiH the charge density of the bonding molecular orbital is localized around the proton. In CH the valence charge density is more evenly shared by both nuclei and the bond is covalent. The motions of the electrons in HF are governed largely by the potential field of the F nucleus. This is evidenced by the appearance of the molecular orbital charge distributions. The proton is, however, encompassed by the valence charge density and the result is a polar bond.

http://www.chemistry.mcmaster.ca/esam/Chapter_8/section_6.html

Molecular Orbitals for Polyatomic Molecules

The concept of a molecular orbital is readily extended to provide a description of the electronic structure of a polyatomic molecule. Indeed molecular orbital theory forms the basis for most of the quantitative theoretical investigations of the properties of large molecules.

In general a molecular orbital in a polyatomic system extends over all the nuclei in a molecule and it is essential, if we are to understand and predict the spatial properties of the orbitals, that we make use of the symmetry properties possessed by the nuclear framework. An analysis of the molecular orbitals for the water molecule provides a good introduction to the way in which the symmetry of a molecule determines the forms of the molecular orbitals in a polyatomic system.

There are three symmetry operations which transform the nuclear framework of the water molecule into itself and hence leave the nuclear potential field in which the electrons move unchanged (Fig. 8-10).

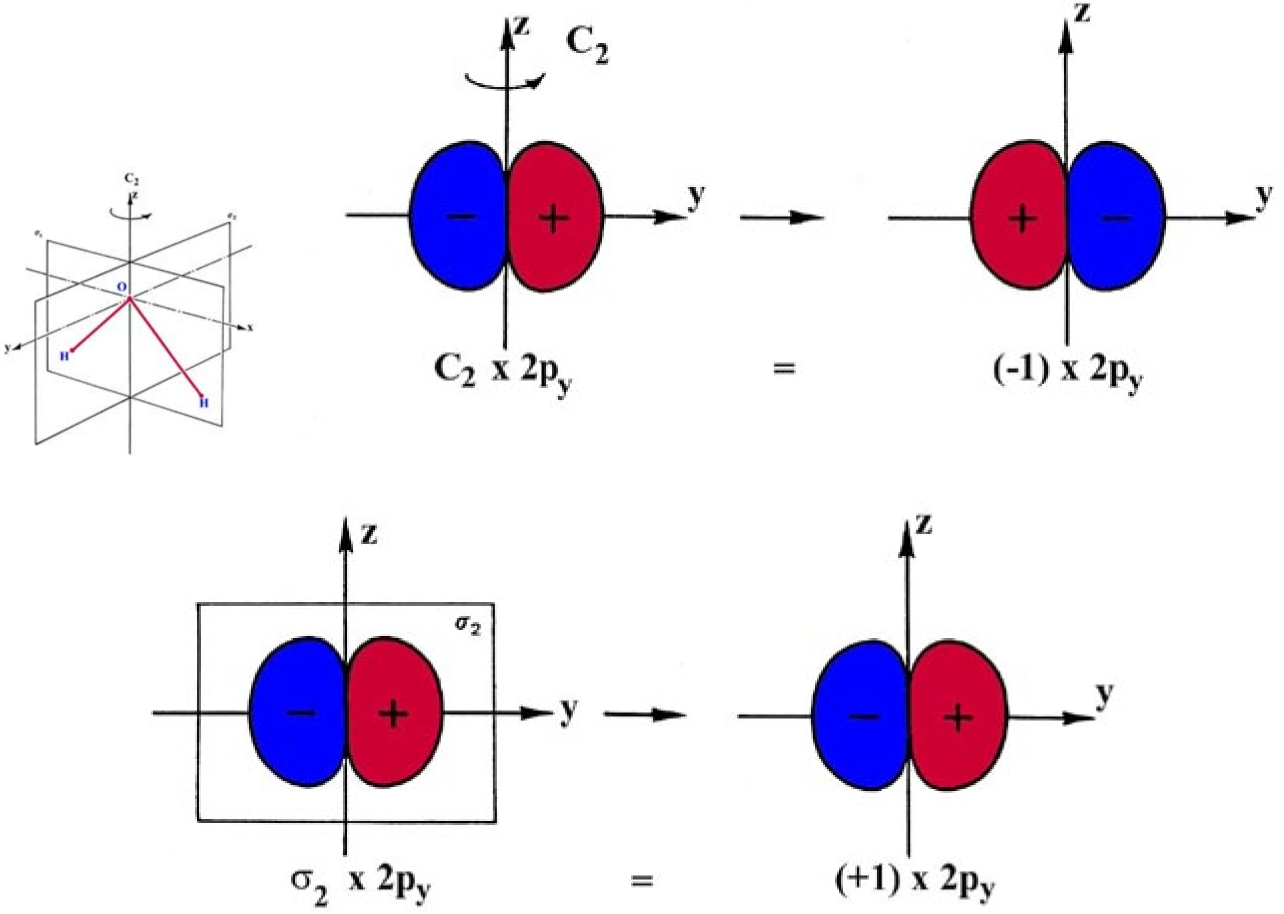


Fig. 8-10. Symmetry elements for H_2O. The bottom two diagrams illustrate the transformations of the $2p_y$ orbital on oxygen under the C_2 and σ_2 symmetry operations.

For each symmetry operation there is a corresponding symmetry ***element***. The symmetry elements for the water molecule are a two-fold axis of rotation C_2 and two planes of symmetry σ_1 and σ_2 (Fig. 8-10). A rotation of 180° about the C_2 axis leaves the oxygen nucleus unchanged and interchanges the two hydrogen nuclei. A reflection through the plane labelled σ_1 leaves all the nuclear positions unchanged while a reflection through σ_2 interchanges the two protons. The symmetry operations associated with the three symmetry elements either leave the nuclear positions unchanged or interchange symmetrically equivalent (and hence indistinguishable) nuclei. Every molecular orbital for the water molecule must, under the same symmetry operations, be left unchanged or undergo a change in sign.

Similarly we may use the symmetry transformation properties of the atomic orbitals on oxygen and hydrogen together with their relative orbital energy values to determine the primary atomic components of each molecular orbital in a simple LCAO approximation to the exact molecular orbitals. Only atomic orbitals which transform in the same way under the symmetry operations may be combined to form a molecular orbital of a given symmetry. The symmetry transformation properties of the atomic orbitals on oxygen and hydrogen are given in Table 8-3. A value of +1 or -1 opposite a given orbital in the table indicates that the orbital is unchanged or changed in sign respectively by a particular symmetry operation.

Table 8-3.
Symmetry Properties and Orbital Energies for the Water Molecule

Atomic Orbitals on Oxygen	Symmetry Behaviour Under			Symmetry Classification	Orbital Energy (au)
	σ_2	σ_1	σ_2		
1*s*	+1	+1	+1	a_1	-20.669
2s	+1	+1	+1	a_1	-1.244
$2p_z$	+1	+1	+1	a_1	-0.632
$2p_x$	-1	+1	-1	b_2	
$2p_y$	-1	-1	+1	b_1	
Atomic Orbitals on Hydrogen					
$(1s_1 + 1s_2)$	+1	+1	+1	a_1	-0.500
$(1s_1 - 1s_2)$	-1	+1	-1	b_2	

Molecular Orbital Energies for H_2O (au)

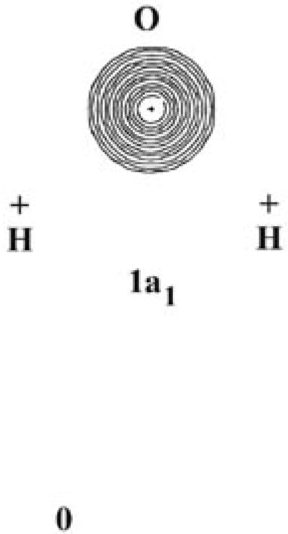
$1a_1$	$2a_1$	$1b_2$	$3a_1$	$1b_1$
-20.565	-1.339	-0.728	-0.595	-0.521

The 1*s*, 2*s* and $2p_z$ orbitals of oxygen are symmetric (i.e., unchanged) with respect to all three symmetry operations. They are given the symmetry classification a_1. The $2p_x$ orbital, since it possesses a node in the σ_2 plane (and hence is of different sign on each side of the plane) changes sign when reflected through the σ_2 plane or when rotated by 180° about the C_2 axis. It is classified as a b_2 orbital. The $2p_y$ orbital is antisymmetric with respect to the rotation operator and to a reflection through the σ_1 plane. It is labelled b_1.

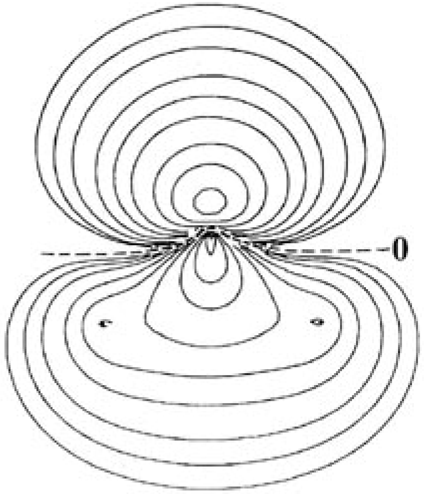
The hydrogen 1*s* orbitals when considered separately are neither unchanged nor changed in sign by the rotation operator or by a reflection through the σ_2 plane. Instead both these operations interchange these orbitals. The hydrogen orbitals are said to be symmetrically equivalent and when considered individually they do not reflect the symmetry properties of the molecule. However, the two linear combinations $(1s_1 + 1s_2)$ and $(1s_1 - 1s_2)$ do behave in the required manner. The former is symmetric under all three operations and is of a_1 symmetry while the latter is antisymmetric with respect to the rotation operator and to a reflection through the plane σ_2 and is of b_2 symmetry.

The molecular orbitals in the water molecule are classified as a_1, b_1 or b_2 orbitals, as determined by their symmetry properties. This labelling of the orbitals is analogous to the use of the σ–π and *g*-*u* classification in linear molecules. In addition to the symmetry properties of the atomic orbitals we must consider their relative energies to determine which orbitals will overlap significantly and form delocalized molecular orbitals.

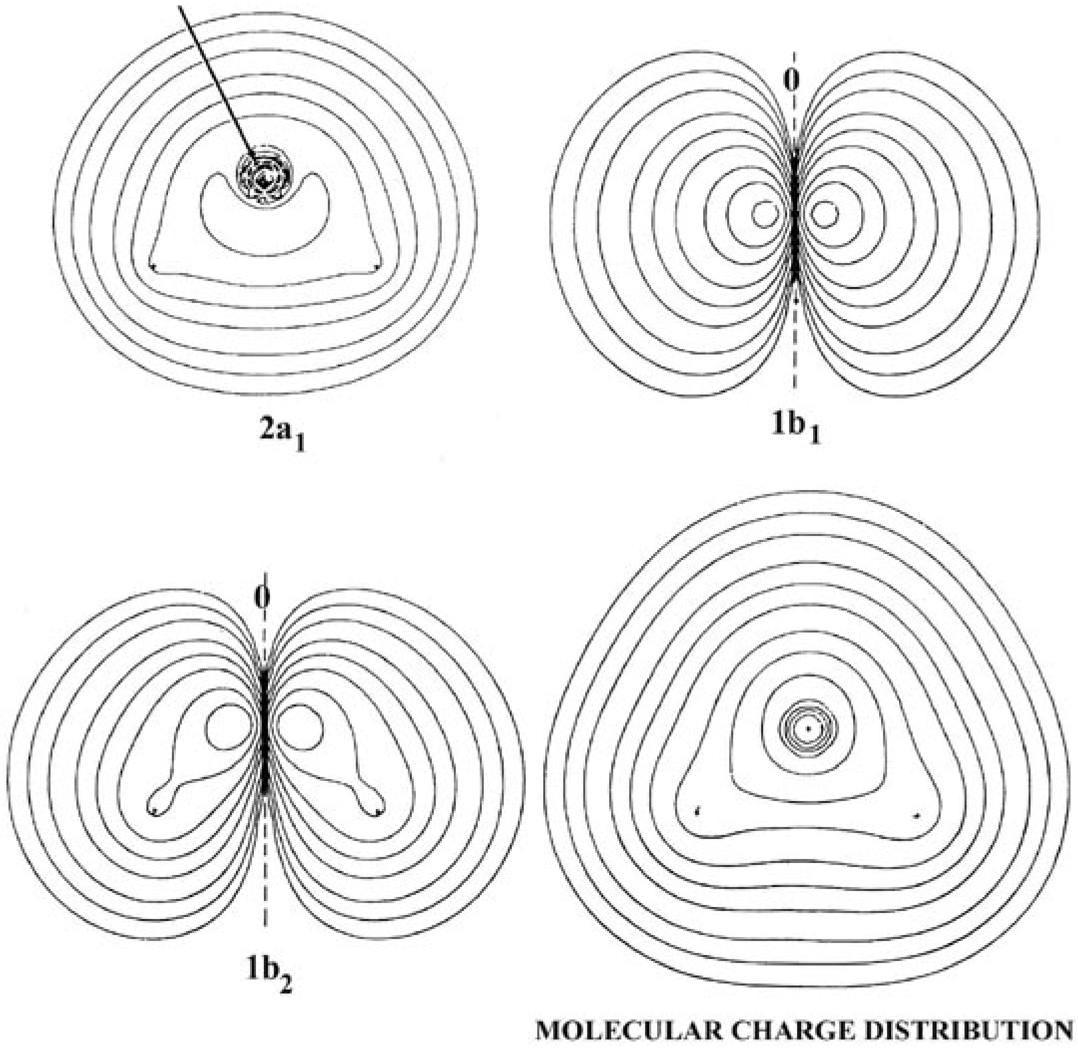
The 1*s* atomic orbital on oxygen possesses a much lower energy than any of the other orbitals of a_1 symmetry and should not interact significantly with them. The molecular orbital of lowest energy in H_2O should therefore correspond to an inner shell 1*s* atomic-like orbital centred on the oxygen. This is the first orbital of a_1 symmetry and it is labelled la$_1$. Reference to the forms of the charge density contours for the la, molecular orbital (Fig. 8-11) substantiates the above remarks regarding the properties of this orbital.



$1a_1$



$3a_1$



$2a_1$ $1b_1$ $1b_2$ MOLECULAR CHARGE DISTRIBUTION

Fig. 8-11. Contour maps of the molecular orbital charge densities for H_2O. The maps for the la_1, $2a_1$, $3a_1$and $1b_2$ orbitals (all doubly-occupied) are shown in the plane of the nuclei. The lb_1 orbital has a node in this plane and hence the contour map for the $1b_1$ orbital is shown in the plane perpendicular to the molecular plane. The total molecular charge density for H_2O is also illustrated. The density distributions were calculated from the wave function determined by R. M. Pitzer, S. Aung and S. I. Chan, J. Chem. Phys. *49*, 2071 (1968). Click here for contour values.

Notice that the orbital energy of the la_1 molecular orbital is very similar to that for the 1*s* atomic orbital on oxygen. The $1a_1$ orbital in H_2O is, therefore, similar to the lσ inner shell molecular orbitals of the diatomic hydrides.

The atomic orbital of next lowest energy in this system is the 2*s* orbital of a_1 symmetry on oxygen. We might anticipate that the extent to which this orbital will overlap with the $(1s_1 + 1s_2)$ combination of orbitals on the hydrogen atoms to form the $2a_1$ molecular orbital will be intermediate between that found for the 2σ molecular orbitals in the diatomic hydrides CH and HF (Fig. 8-9). The 2σ orbital in CH results from a strong mixing of the 2*s* orbital on carbon and the hydrogen 1*s* orbital. In HF the participation of the hydrogen orbital in the 2σ orbital is greatly reduced, a result of the lower energy of the 2*s* atomic orbital on fluorine as compared to that of the 2*s* orbital on carbon.

Aside from the presence of the second proton, the general form and nodal structure of the $2a_1$ density distribution in the water molecule is remarkably similar to the 2σ distributions in CH and HF, and particularly to the latter. The charge density accumulated on the bonded side of the oxygen nucleus in the $2a_1$ orbital is localized near this nucleus as the corresponding charge increase in the 2σ orbital of HF is localized near the fluorine. The charge density of the $2a_1$ molecular orbital accumulated in the region between the three nuclei will exert a force drawing all three nuclei together. The $2a_1$ orbital is a binding orbital.

Although the three 2*p* atomic orbitals are degenerate in the oxygen atom the presence of the two protons results in each 2*p* orbital experiencing a different potential field in the water molecule. The nonequivalence of the 2*p* orbitals in the water molecule is evidenced by all three possessing different symmetry properties. The three 2*p* orbitals will interact to different extents with the protons and their energies will differ.

The $2p_x$ orbital interacts most strongly with the protons and forms an orbital of b_2 symmetry by overlapping with the $(1s_1 - 1s_2)$ combination of 1*s* orbitals on the hydrogens. The charge density contours for the lb_2 orbital indicate that this simple LCAO description accounts for the principal features of this molecular orbital. The lb_2 orbital concentrates charge density along each O-H bond axis and draws the nuclei together. The charge density of the $1b_2$ orbital binds all three nuclei. In terms of the forces exerted on the nuclei the $2a_1$ and lb_2 molecular orbitals are about equally effective in binding the protons in the water molecule.

The $2p_z$ orbital may also overlap with the hydrogen 1*s* orbitals, the $(1s_1 + 1s_2)$ a_1 combination, and the result is the $3a_1$ molecular orbital. This orbital is concentrated along the *z*-axis and charge density is accumulated in both the bonded and nonbonded sides of the oxygen nucleus. It exerts a binding force on the protons and an antibinding force on the oxygen nucleus, a behaviour similar to that noted before for the 3σ orbitals in CH and HF.

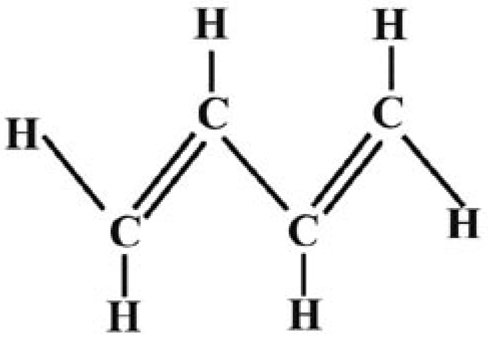
The $2p_y$ orbital is not of the correct symmetry to overlap with the hydrogen 1*s* orbitals. To a first approximation the $1b_1$ molecular orbital will be simply a $2p_y$ atomic orbital on the oxygen, perpendicular to the plane of the molecule. Reference to Fig. 8-11 indicates that the $1b_1$ orbital does resemble a 2*p* atomic orbital on oxygen but one which is polarized into the molecule by the field of the protons. The $1b_1$ molecular orbital of H_2O thus resembles a single component of the 1π molecular orbitals of the diatomic hydrides. The $1b_1$ and the 1π orbitals are essentially nonbinding. They exert a small binding force on the heavy nuclei because of the slight polarization. The force exerted on the protons by the pair of electrons in the $1b_1$ orbital is slightly less than that required to balance the force of repulsion exerted by two of the nuclear charges on the oxygen nucleus. The $1b_1$ and 1π electrons basically do no more than partially screen nuclear charge on the heavy nuclei from the protons.

In summary, the electronic configuration of the water molecule as determined by molecular orbital theory is

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$$

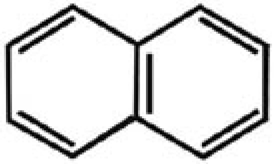
The la_1 orbital is a nonbinding inner shell orbital. The pair of electrons in the la_1 orbital simply screen two of the nuclear charges on the oxygen from the protons. The $2a_1$, $1b_2$ and $3a_1$ orbitals accumulate charge density in the region between the nuclei and the charge densities in these orbitals are responsible for binding the protons in the water molecule. Aside from being polarized by the presence of the protons, the lb_1 orbital is a non-interacting $2p_y$ orbital on the oxygen and is essentially nonbinding.

Before closing this introductory account of molecular orbital theory, brief mention should be made of the very particular success which the application of this theory has had in the understanding of the chemistry of a class of organic molecules called conjugated systems. Conjugated molecules are planar organic molecules consisting of a framework of carbon atoms joined in chains or rings by alternating single and double bonds. Some examples are



butadiene

benzene



naphthalene

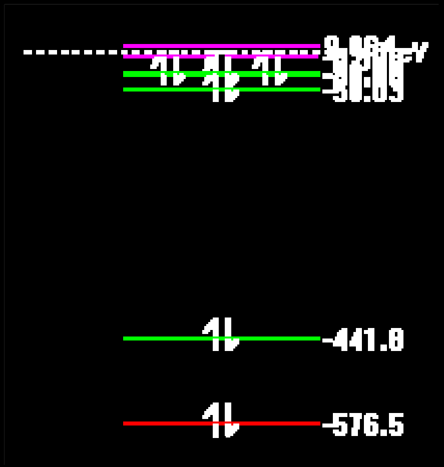
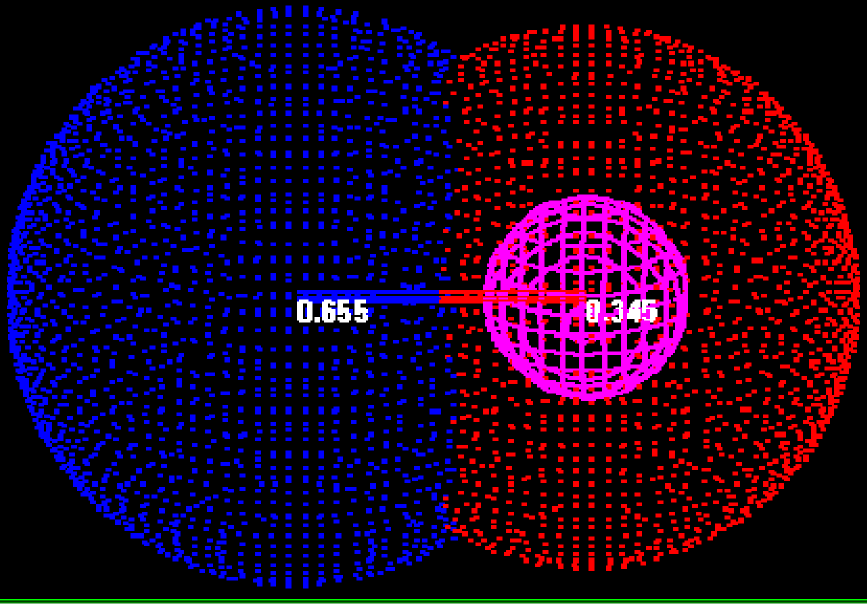
In the structural formulae for the cyclic molecules, e.g., benzene and naphthalene, it is usual not to label the positions of the carbon and hydrogen atoms by their symbols. A carbon atom joined to just two other carbon atoms is in addition bonded to a hydrogen atom, the C—H bond axis being projected out of the ring in the plane of the carbon framework and bisecting
the CCC bond angle.

The notion of these molecules possessing alternating single and double bonds is a result of our attempt to describe the bonding in terms of conventional chemical structures. In reality all six C—C bonds in benzene are identical and the C—C bonds in the other two examples possess properties intermediate between those for single and double bonds. In other words, the pairs of electrons forming the second or π bonds are not localized between specific carbon atoms but are delocalized over the whole network of carbon atoms, a situation ideally suited for a molecular orbital description.

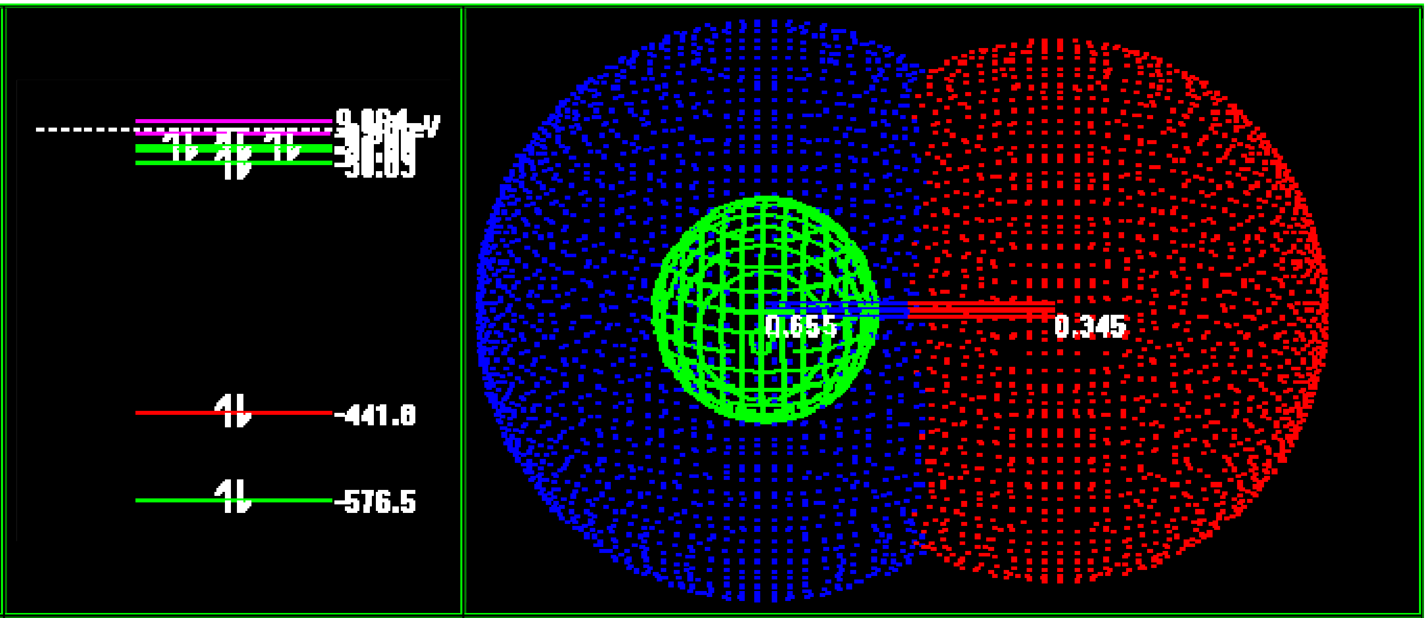
We may consider each carbon atom in a conjugated molecule to be sp^2 hybridized and bonded through these hybrid orbitals to three other atoms in the plane. This accounts for the bonding of the hydrogens and for the formation of the singly-bonded carbon network. The electrons forming these bonds are called σ electrons. The axis of the remaining $2p$ orbital on each carbon atom is directed perpendicular to the plane of the molecule and contains a single electron, called a π electron. A simple adaptation of molecular orbital theory, called Hückel theory, which takes the σ bonds for granted and approximates the molecular orbitals of the π electrons in terms of linear combinations of the $2p\pi$ atomic orbitals on each carbon atom, provides a remarkably good explanation of the properties of conjugated molecules. Hückel molecular orbital theory and its applications are treated in a number of books, some of which are referred to at the end of this chapter.

http://www.uky.edu/~holler/orbitals/no/no.html

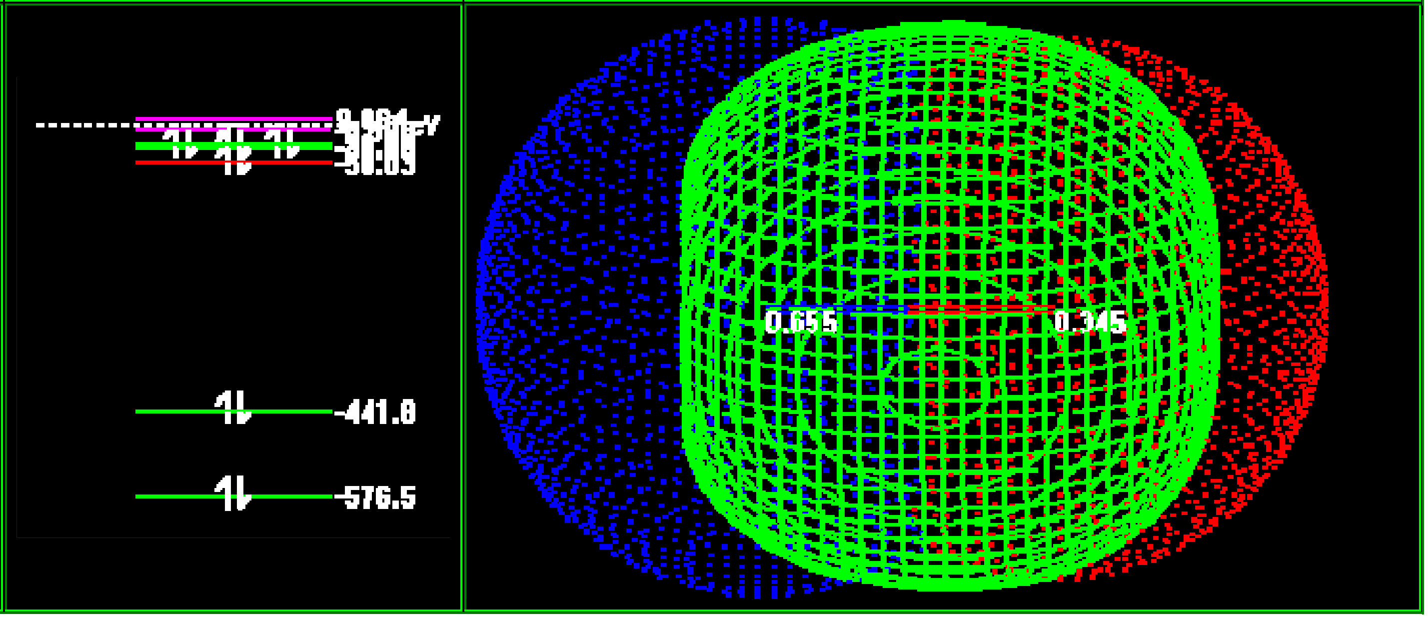
Molecular Orbitals of NO^+

Symbol	Energy Level Diagram	Molecular Orbital
σ_{1s}		

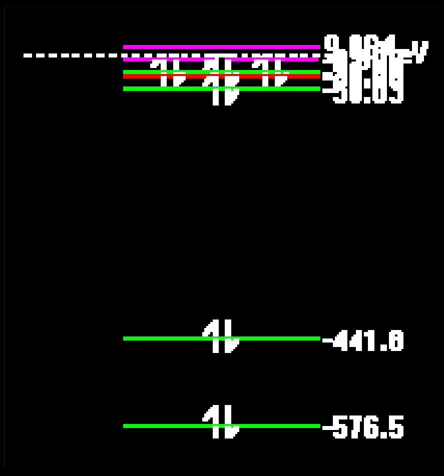
σ^*_{1s}

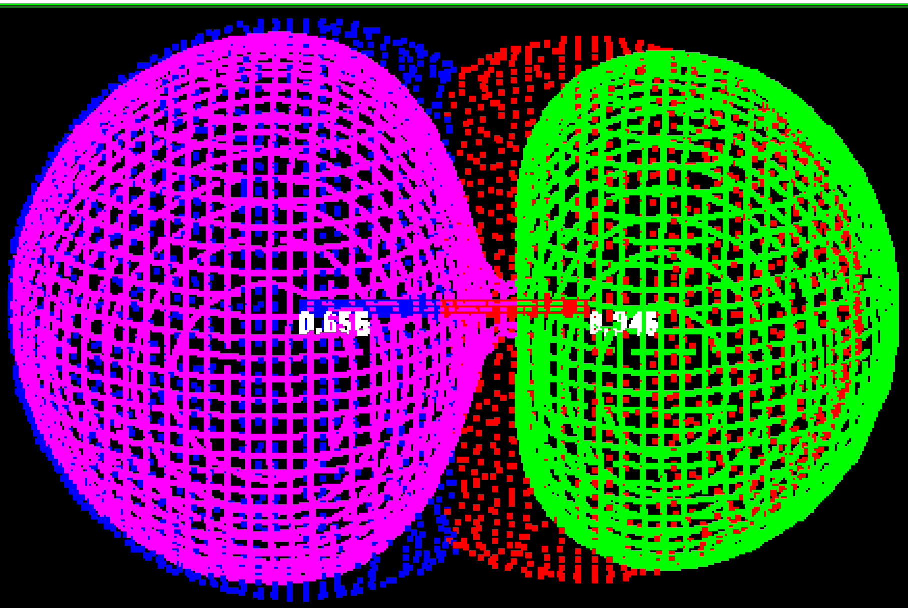


σ_{2s}

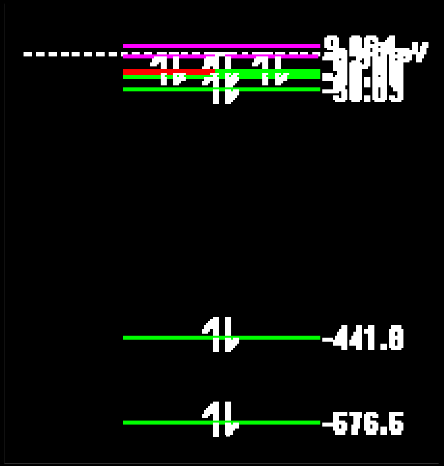


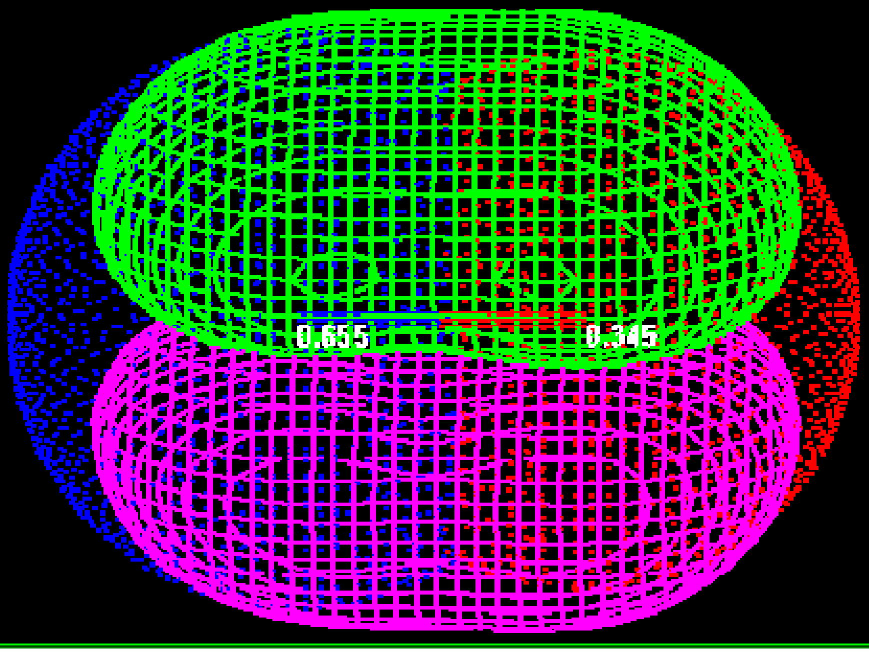
σ^*_{2s}



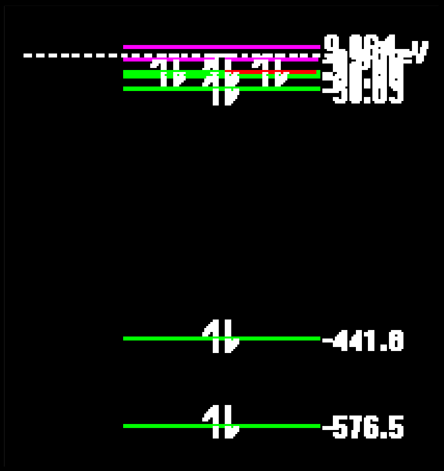


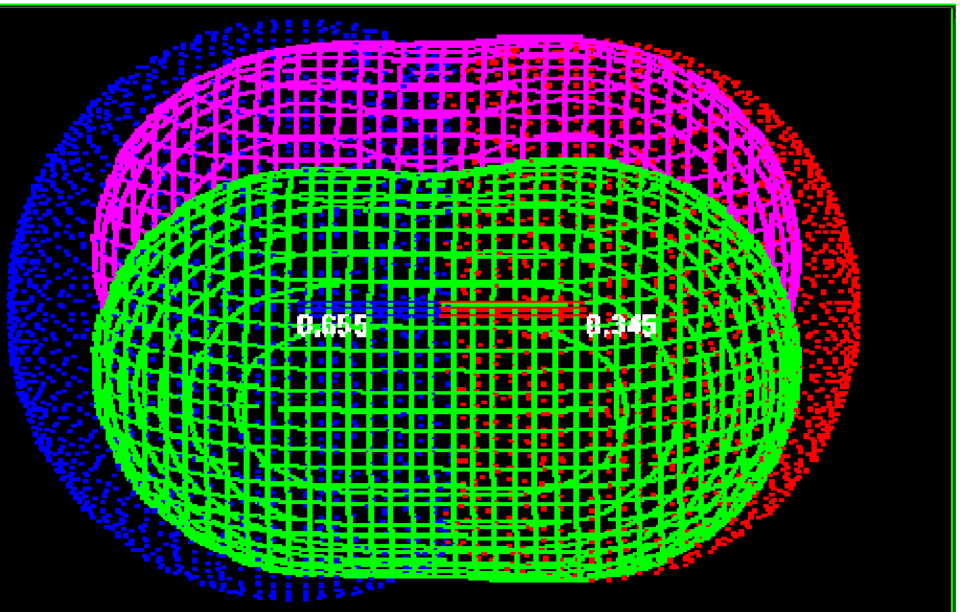
π_{2p_y}



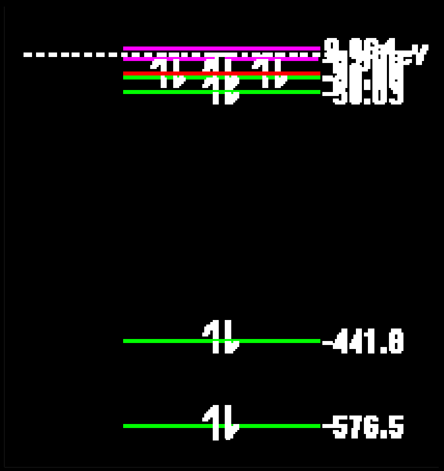


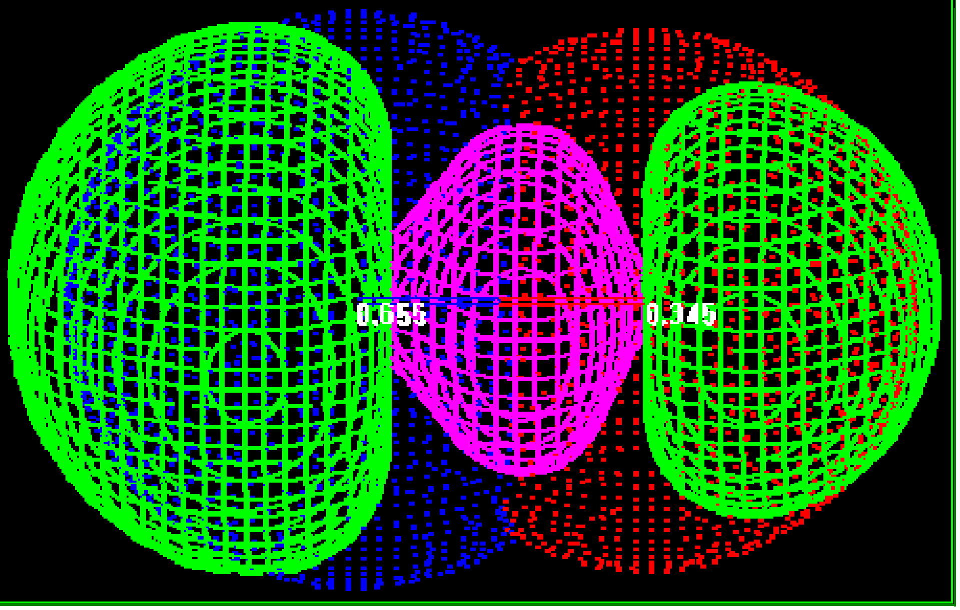
π_{2p_x}



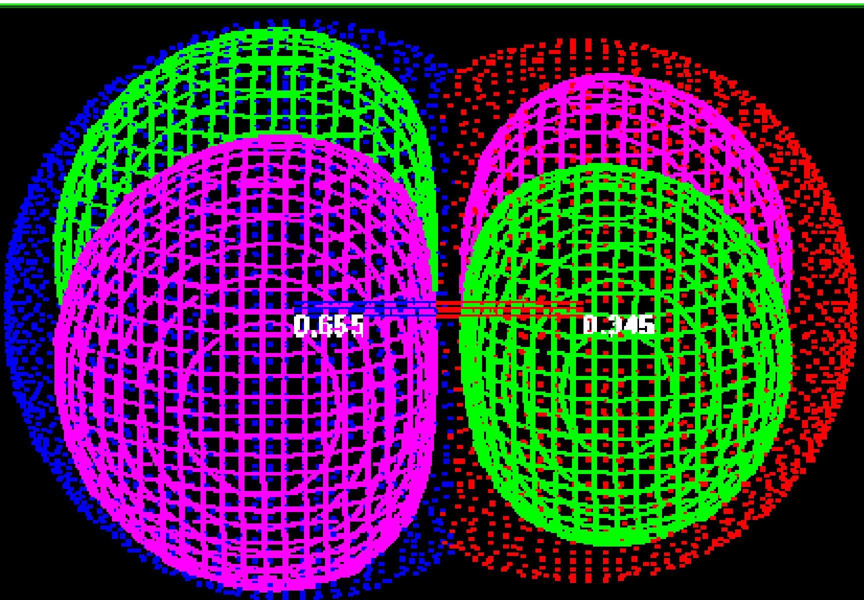


σ_{2p_z}

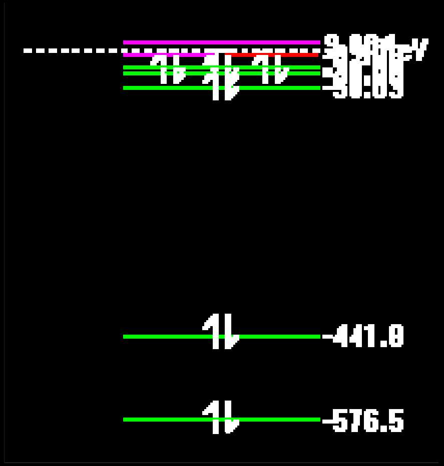


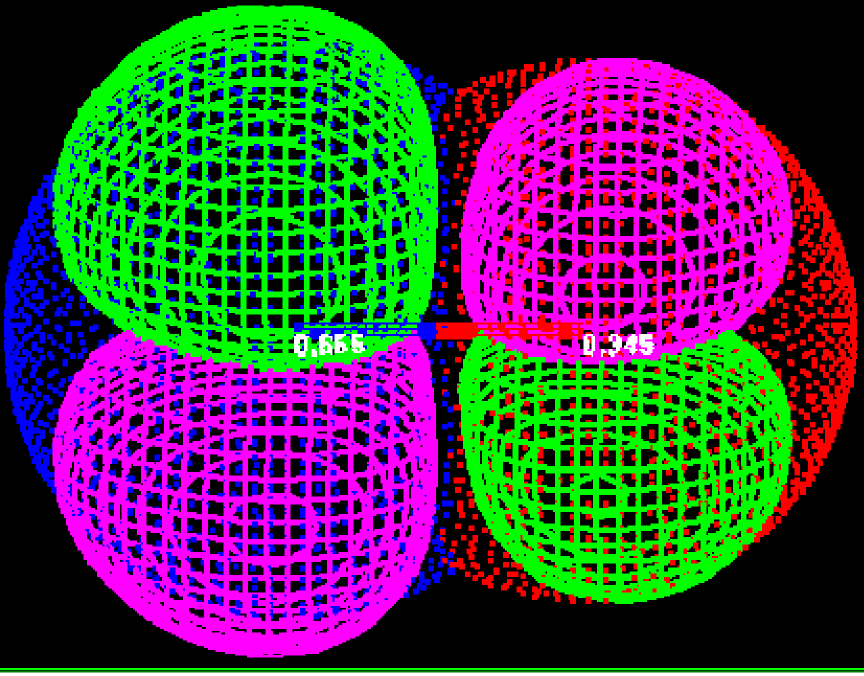


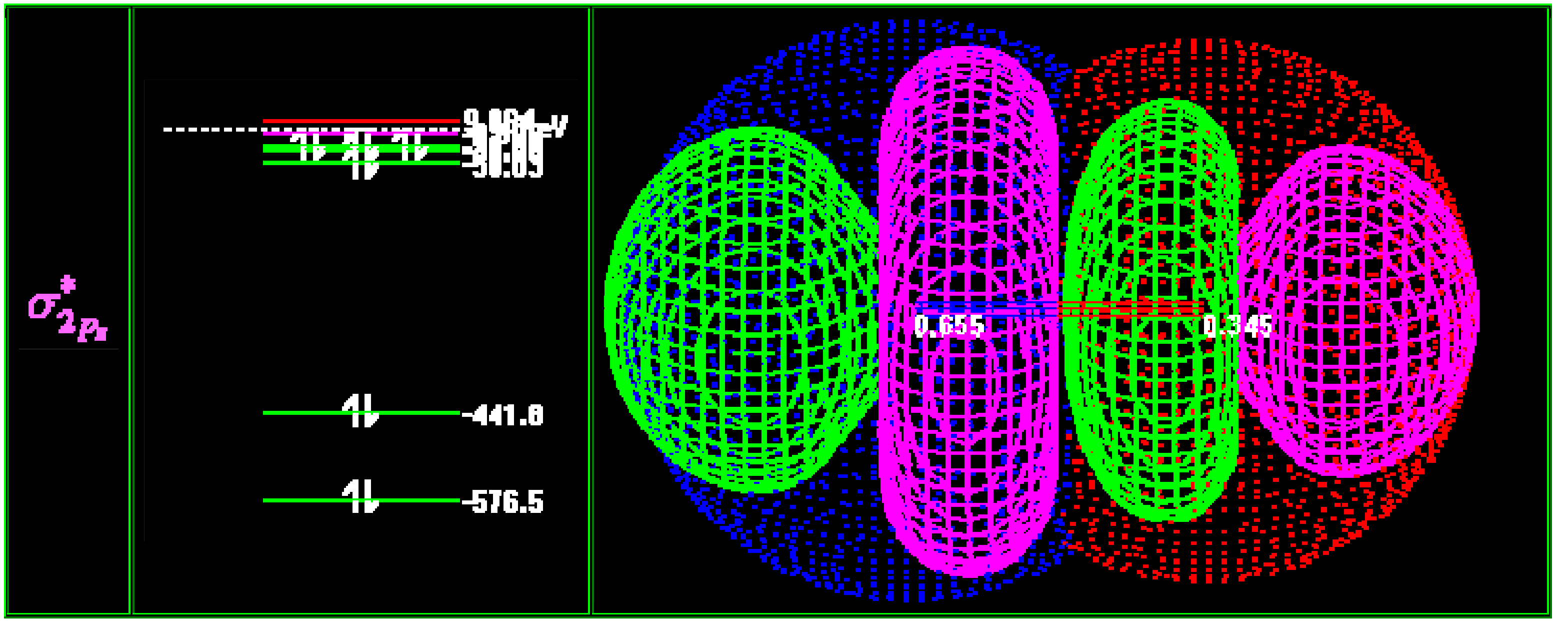
$\pi^*_{2p_x}$



$\pi^*_{2p_y}$



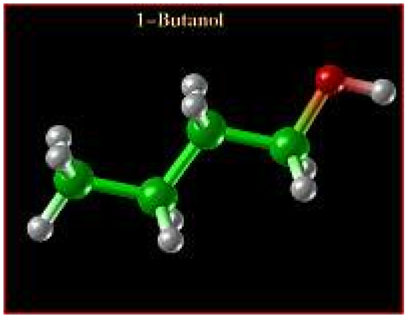
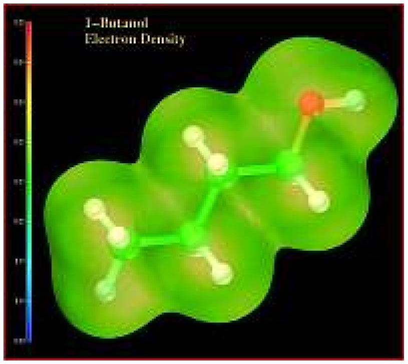
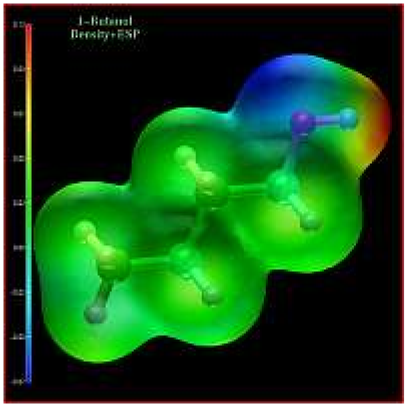
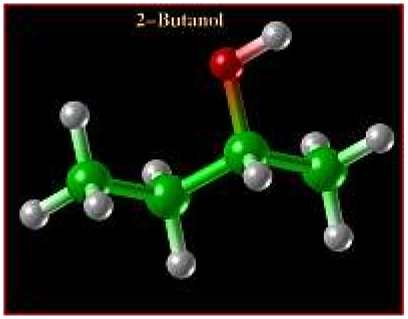
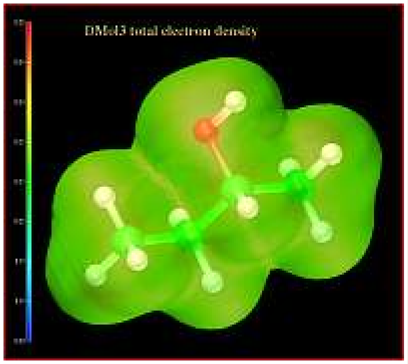
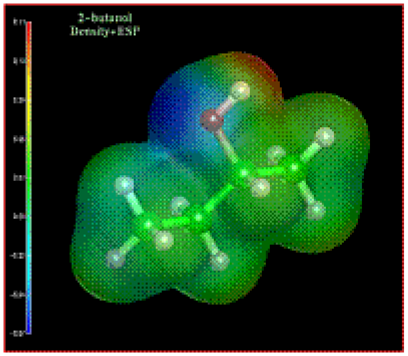


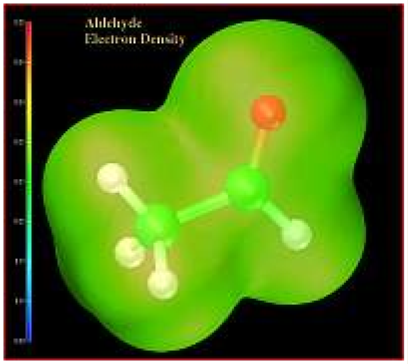
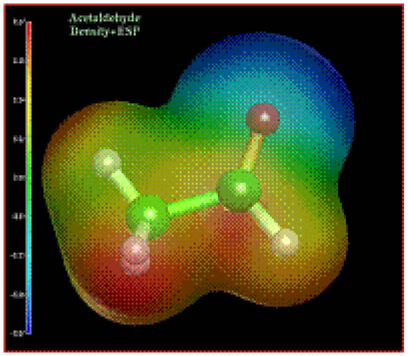
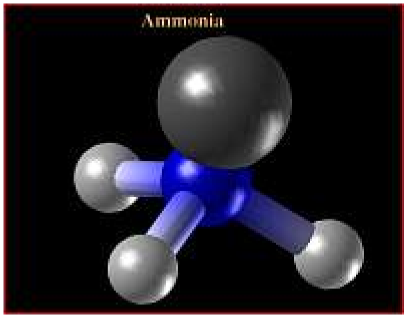
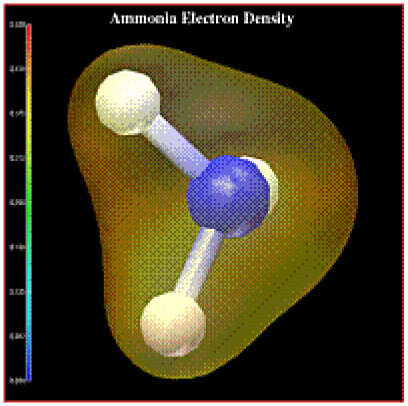
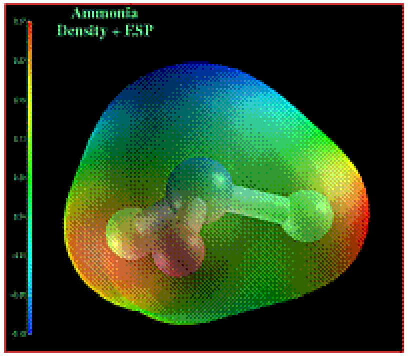
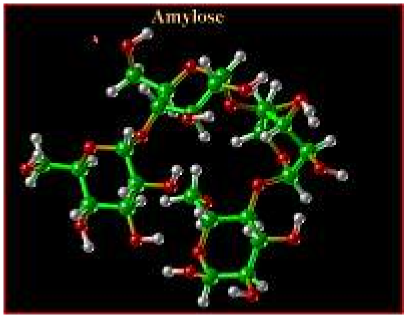
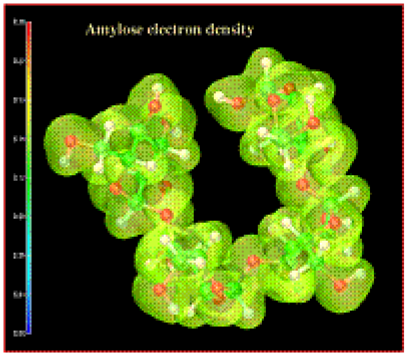
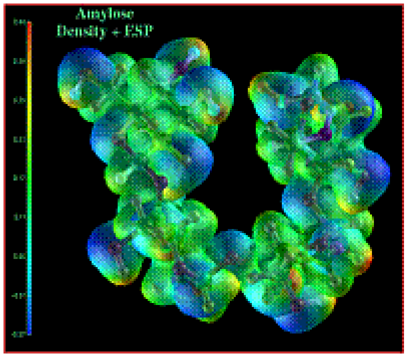

$\sigma^*_{2p_z}$
-441.8
-576.5
0.655
0.345

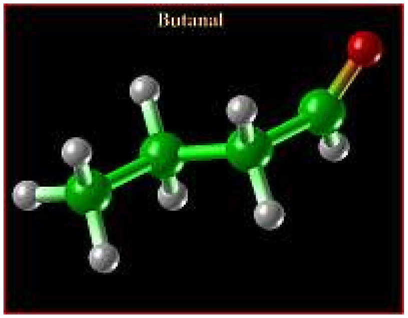
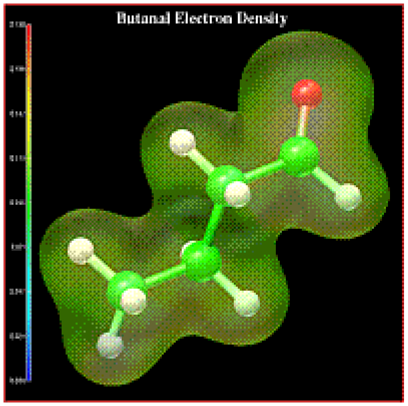
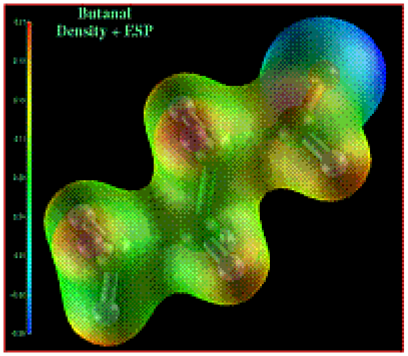
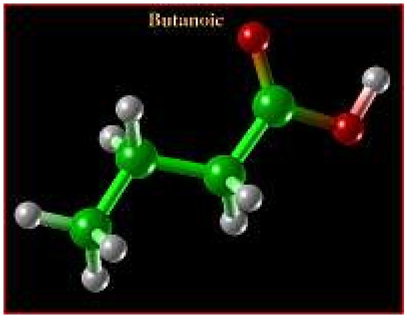
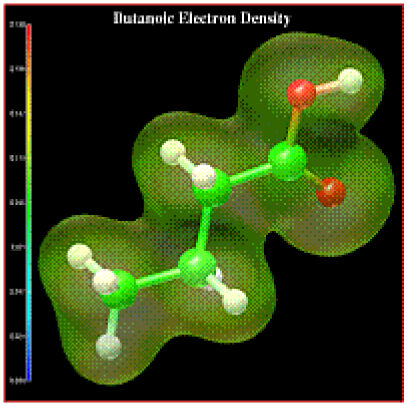
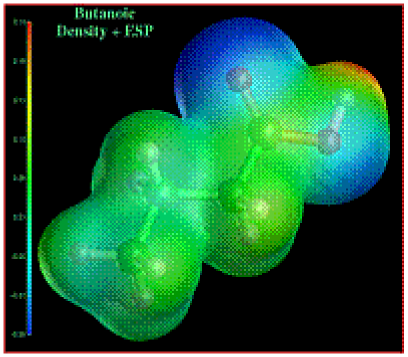
http://core.ecu.edu/phys/flurchickk/AtomicMolecularSystems/molecularStructures/molecularStructures.html

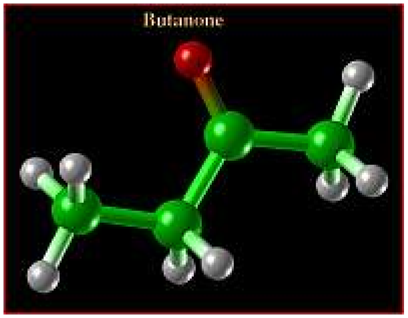
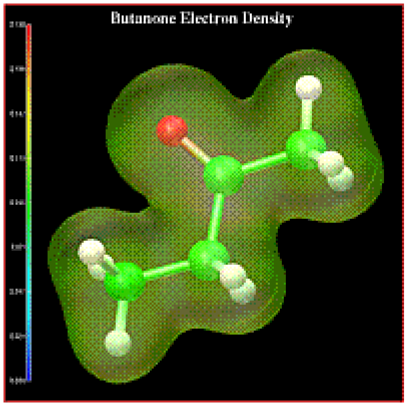
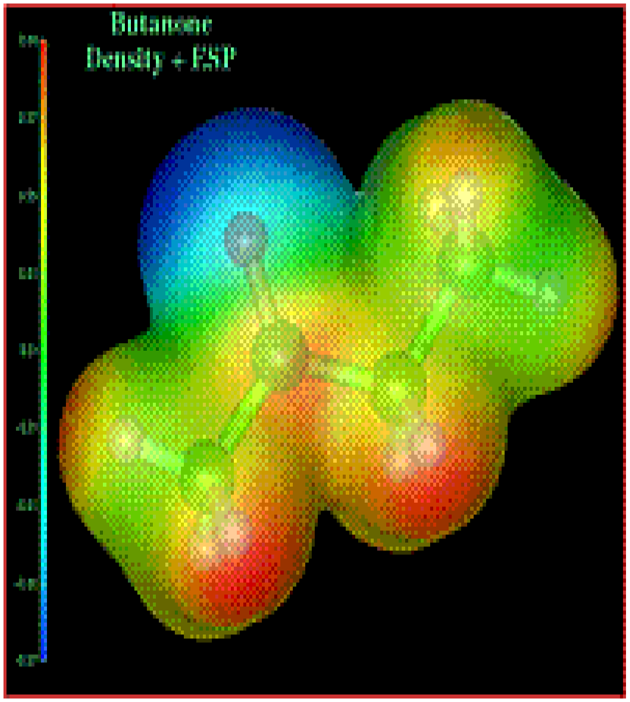
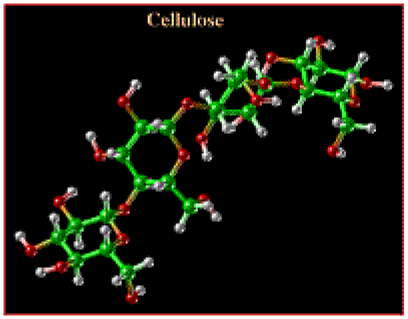
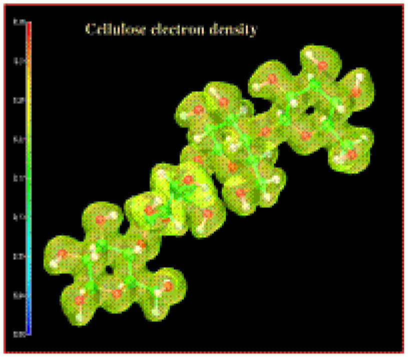
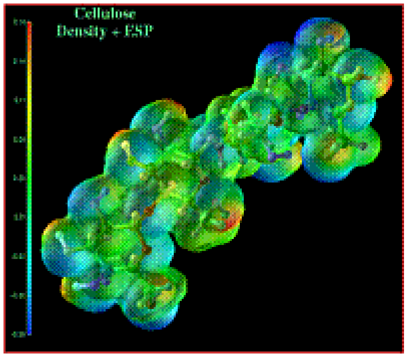
Molecular Structures and Charge Density

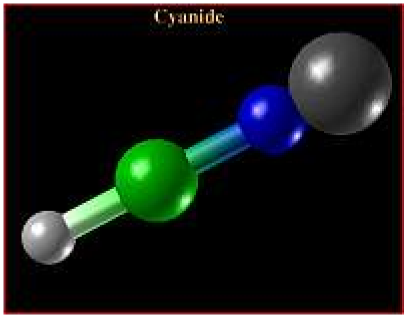
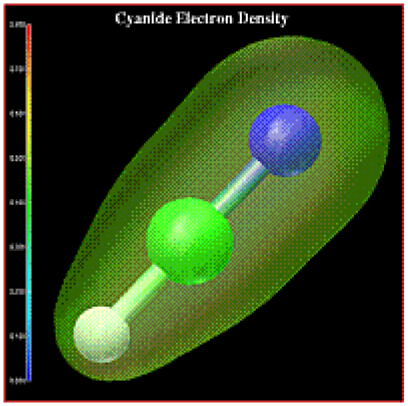
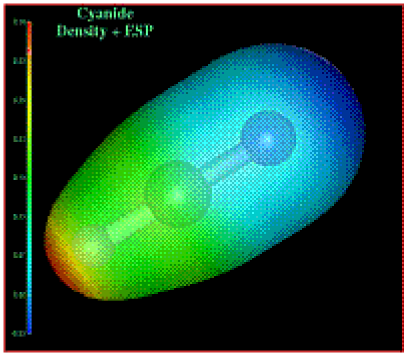
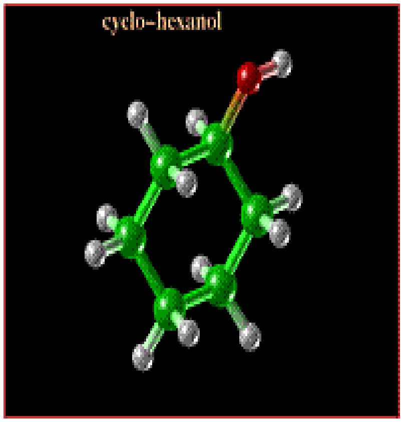
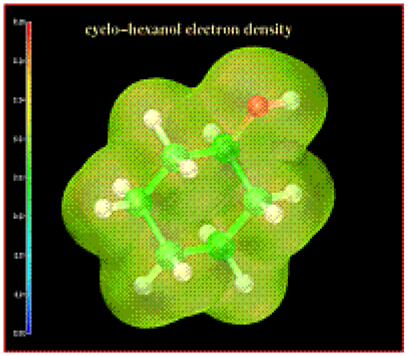
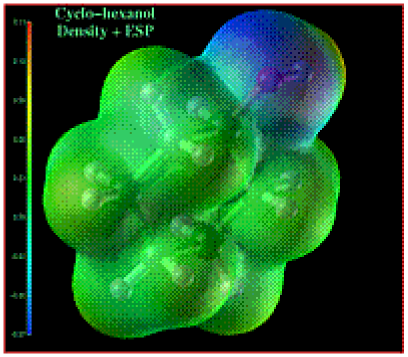
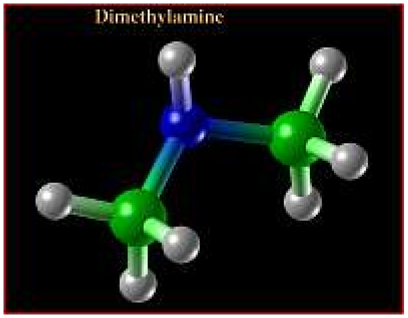
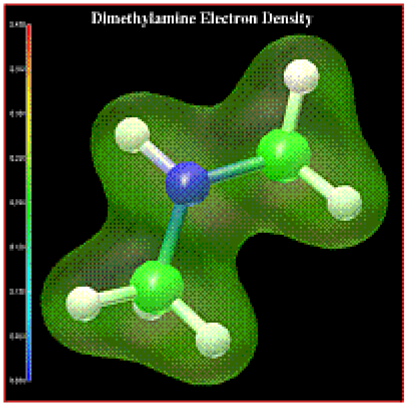
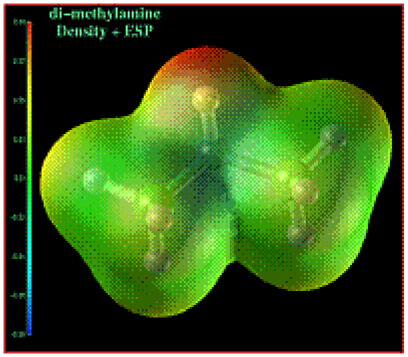
The structure, electron density and electrostatic potential for various molecules are shown below. The calculations for the energy optimized geometric structure, electron density and the electrostatic potential were done using DMOL^3 from Accelerys, Inc. The images were generated using AVS/Express and the STM modules. The images in the the third column are the **charge density**, (the electronic shape of the molecule) **colored by the data values of the electrostatic potential**. On some of the structures, there is a grey sphere, representing the non bonded pair of electrons.

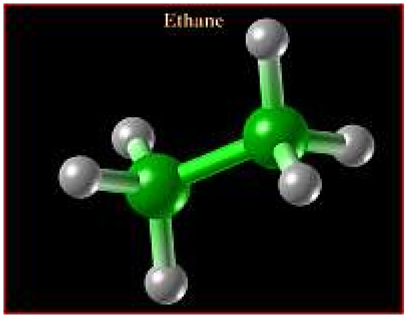
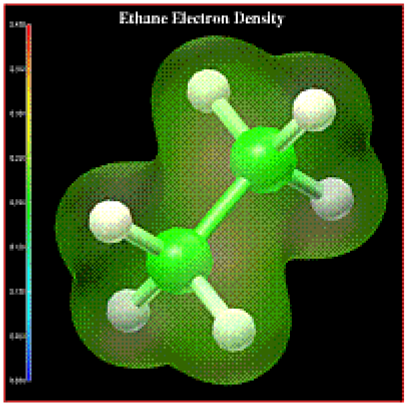
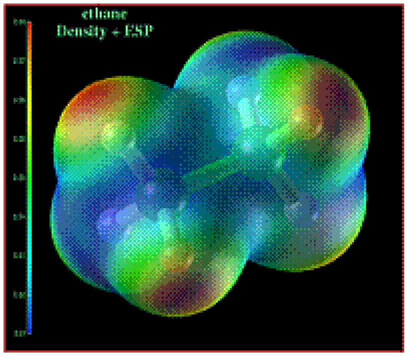
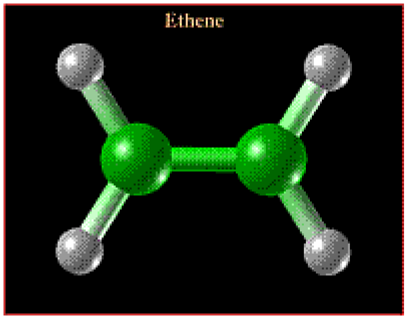
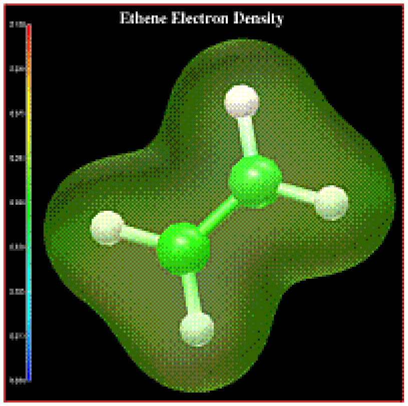
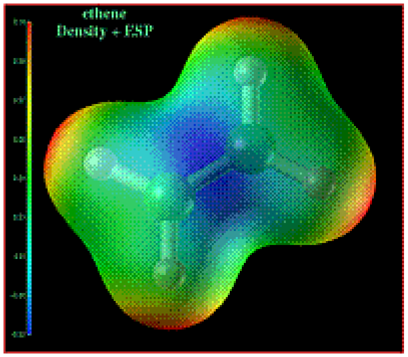
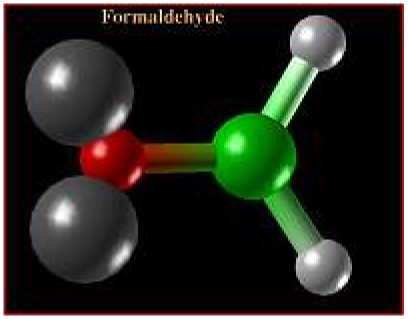
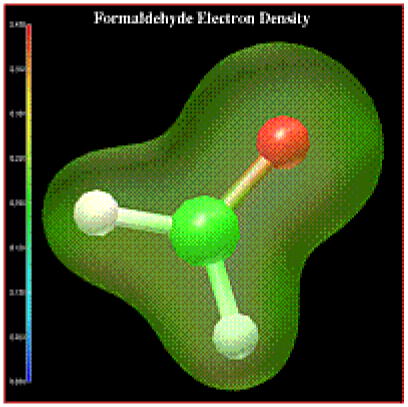
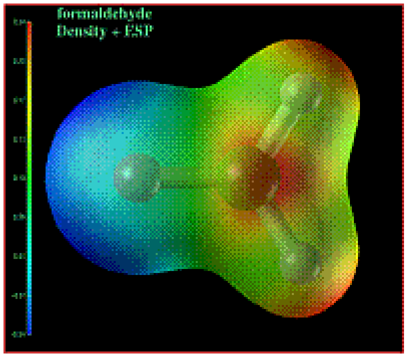
Chemical Species	Geometric Structure	Charge Density	Density plus Electrostatic Potential
1-butanol			
2-butanol			

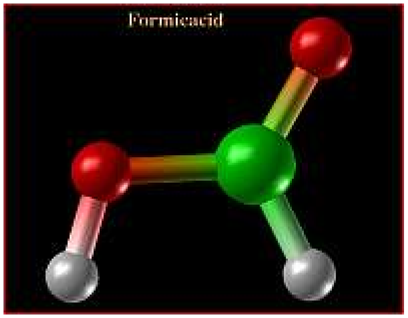
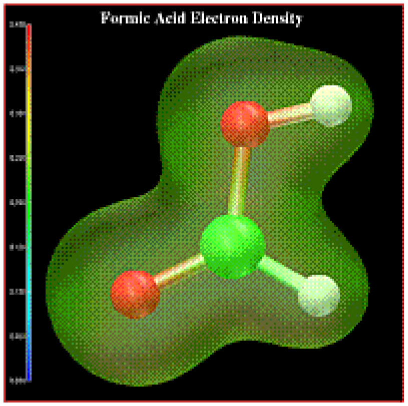
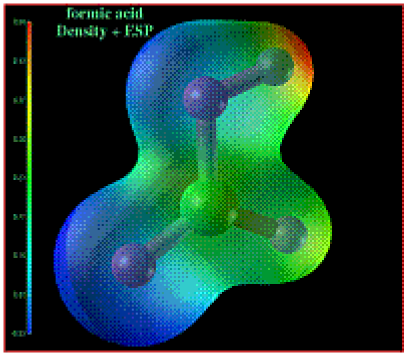
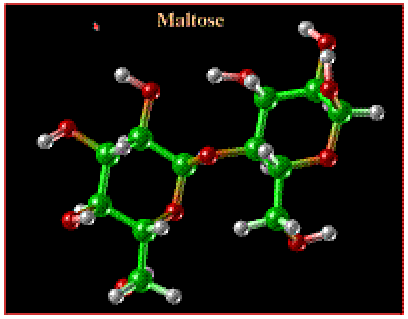
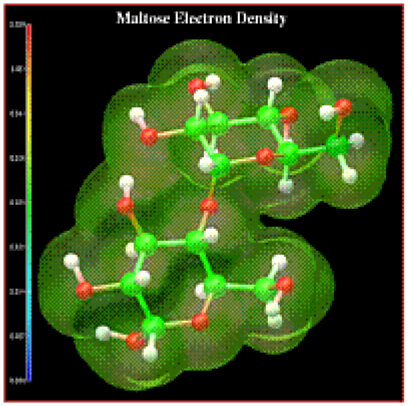
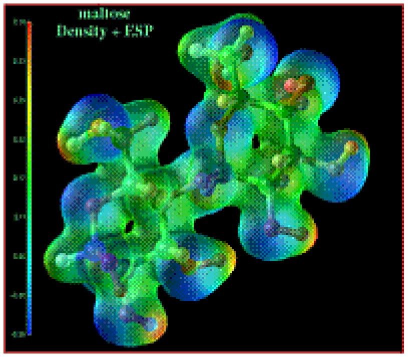
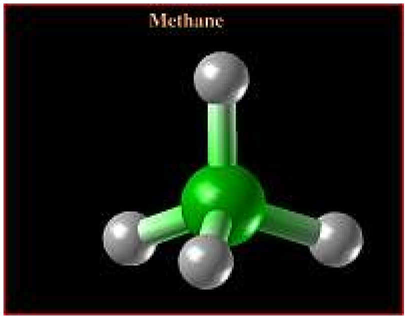
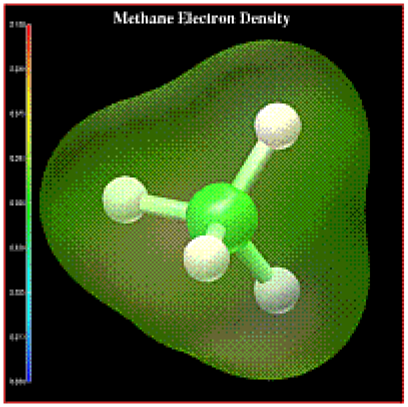
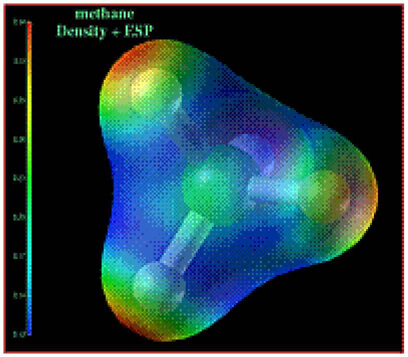
acetaldehyde			
ammonia			
amylose			

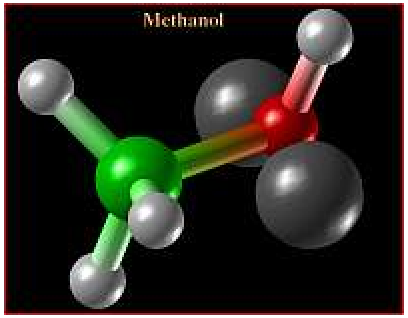
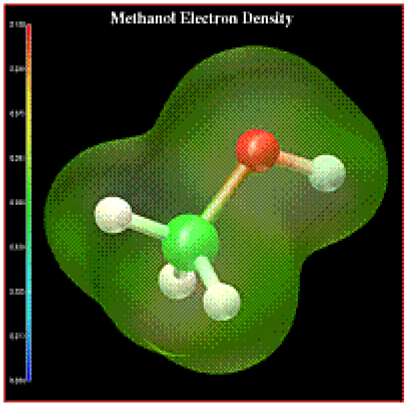
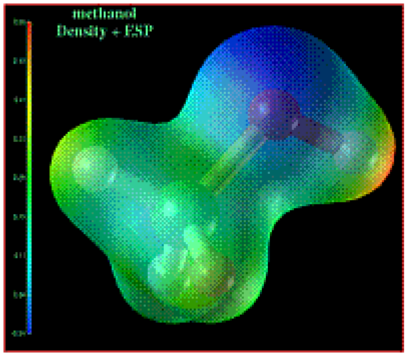
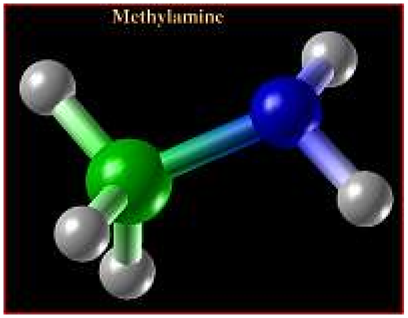
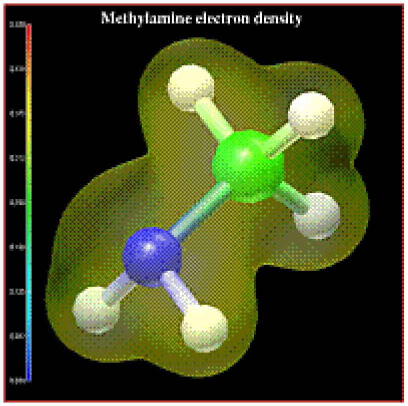
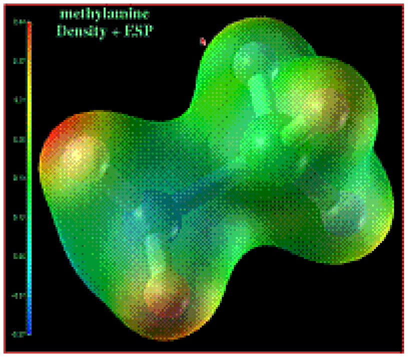
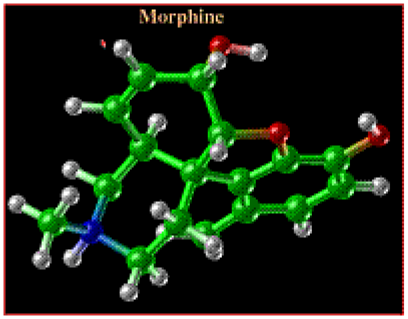
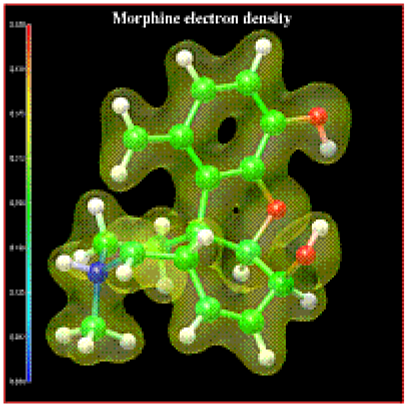
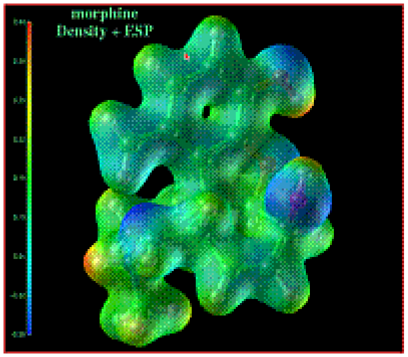
butanal			
butanoic			

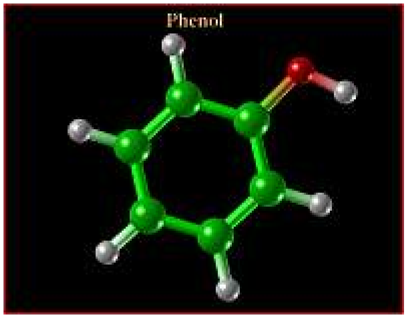
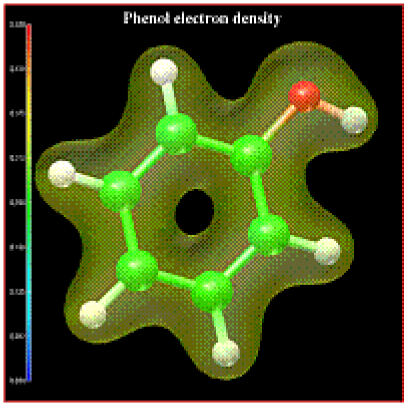
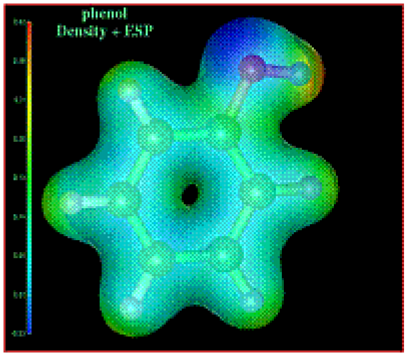
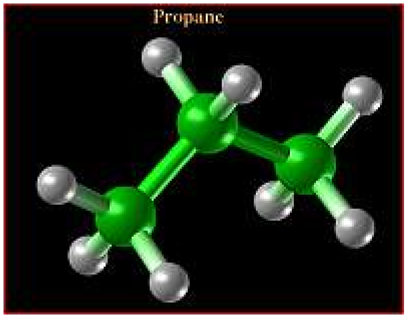
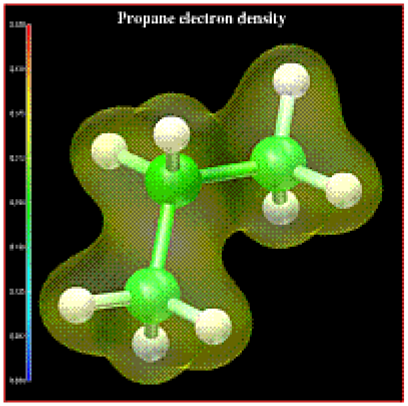
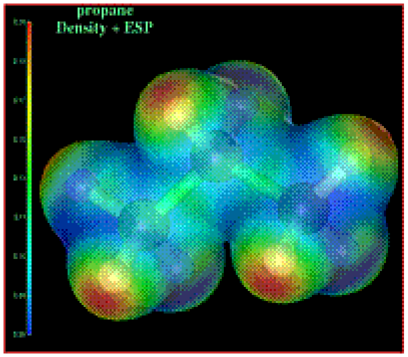
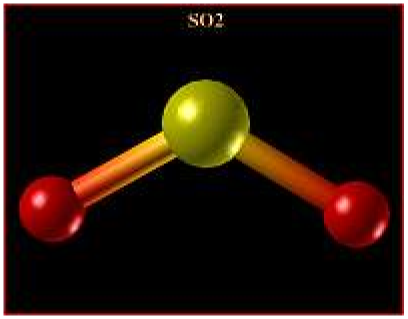
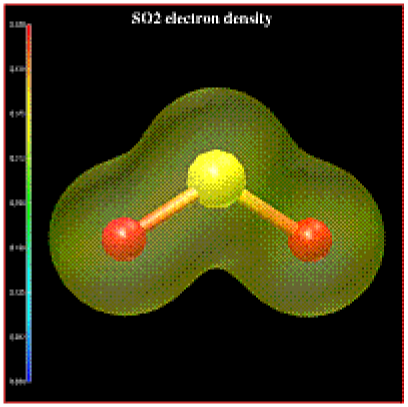
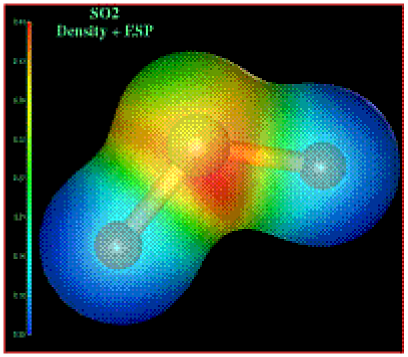
butanone	 Butanone	 Butanone Electron Density	 Butanone Density + ESP
cellulose	 Cellulose	 Cellulose electron density	 Cellulose Density + ESP

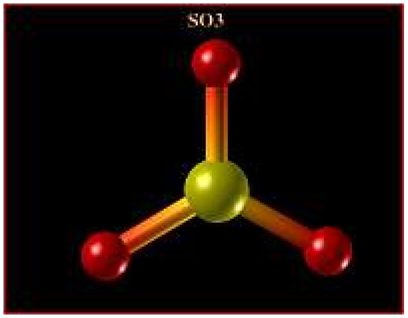
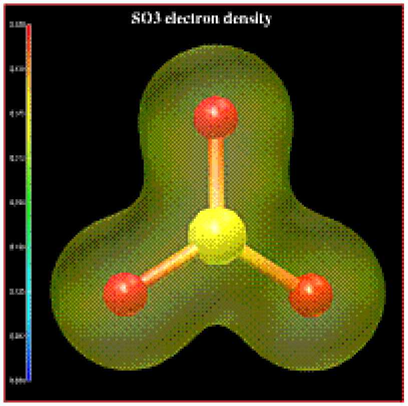
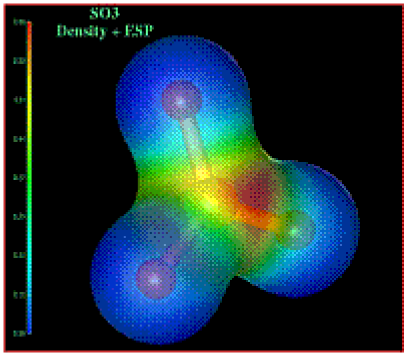
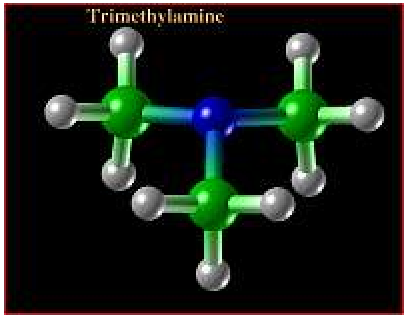
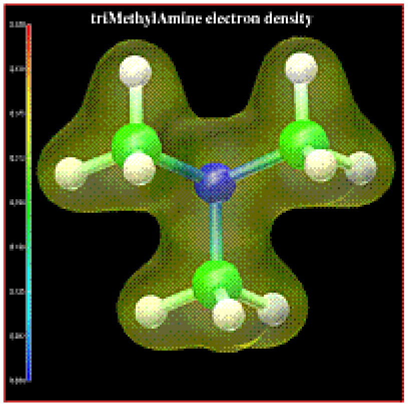
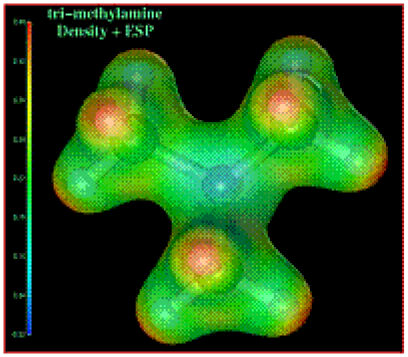
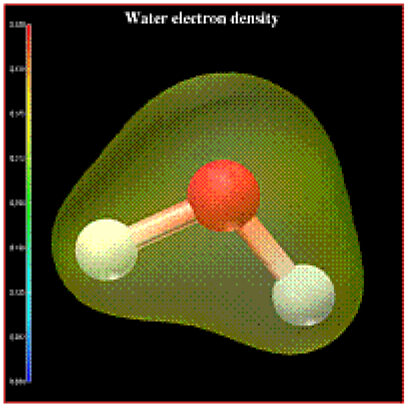
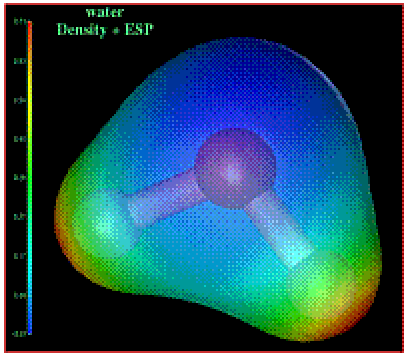
cyanide			
cyclohexanol			
dimethylamine			

ethane			
ethene			
formaldehyde			

formicacid			
maltose			
methane			

methanol			
methylamine			
morphine			

phenol			
propane			
SO_2			

SO_3			
trimethylamine			
water			

http://pubs.acs.org/cen/news/8251/8251notw1.html

December 20, 2004
Volume 82, Number 51 p. 10

Single N_2 Bonding Orbital Imaged

Femtosecond laser pulses are key to providing tomographic orbital image

IN ORBIT A new technique provides 3-D snapshots of molecular orbitals (HOMO of N_2 shown here) with femtosecond resolution.

It's tough to get electron orbitals to smile for a camera. But that hasn't stopped scientists from photographing them. Researchers in Canada have developed a technique for recording three-dimensional images of molecular orbitals. The procedure, which is based on ultrafast laser methods, may lead to new probes of chemical reaction dynamics and techniques for studying the motions of individual electrons.

Analytical methods such as X-ray diffraction and scanning tunneling microscopy are invaluable to scientists for their ability to probe electron density. The atomic structures of an enormous number of chemical systems have been determined by those techniques. Yet researchers would benefit from a procedure that's capable of probing individual electron orbitals with a resolution on the timescale of chemical reactions. Now they have one.

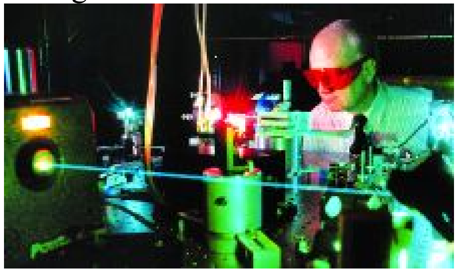
Scientists at the Canadian National Research Council (CNRC) in Ottawa have demonstrated a procedure in which femtosecond (10^{-15} second) laser pulses are used to construct a 3-D image of a single molecular orbital. The technique, which bears similarities to medical tomography, was used to image the highest occupied molecular orbital (HOMO) of a simple test system: dinitrogen [*Nature,* **432,** 867 (2004)].

The study was conducted by postdoctoral associate Jiro Itatani, staff member David M. Villeneuve, and group leader Paul B. Corkum, all of whom are at CNRC's Steacie Institute of Molecular Sciences, and their coworkers at other institutions in Canada and Japan.

Constructing an image of N_2's HOMO is a multistep process. First, the Ottawa group aligns the nitrogen molecules in a particular orientation by exposing them to a brief pulse of linearly polarized laser light. An instant later, the researchers deliver an intense femtosecond laser pulse to the gas molecules. Within the 10^{-15}-second period of the intense pulse, an electron in N_2's HOMO is forced away from the molecule and then driven to recollide with the molecule energetically. The collision angle between the electron and the molecule is fixed by controlling the angle between the two laser pulses.

The team members explain that the laser-molecule interactions produce a series of high-order harmonics--radiation with overtone frequencies that are multiples of the initial laser pulse. They note that the spectrum of overtones carries 2-D information about the electron orbital structure. So by varying the collision angle (via the alignment laser) and recording numerous overtone spectra, the group is able to use tomographic methods to construct a 3-D image of the HOMO.

Now that the group has shown that, in a simple molecule, the HOMO--the orbital directly involved in bonding--can be imaged with femtosecond resolution, more complex chemical systems may soon be within reach.
Henrik Stapelfeldt, an associate professor of chemistry at Aarhus University in Denmark, agrees. Commenting on the study in the same issue of *Nature*, Stapelfeldt notes that "in the near future, it should be possible to watch directly how electron clouds change during chemical reactions. This would be progress, indeed, and provide insight into one of the most fundamental steps in chemistry."



LIGHT BRIGHT CNRC's Villeneuve uses femtosecond laser methods to probe molecular processes.

http://www.nrc-cnrc.gc.ca/aboutUs/corporatereports/annual_report2005/electron_orbital_image_e.html

Remarkable First Image of an Electron Orbital

NRC molecular science researchers in Ottawa achieved a landmark in science in 2004-2005 when they captured the first picture of an electron orbital or cloud, the area in which an electron moves.

Electrons, and changes that happen to them in relation to other molecules, are the basis of all chemical reactions. Creating a 3D picture of an electron orbital is the first step towards creating images of how chemical bonds are broken and formed during reactions. This achievement has major implications for any industry where chemistry is involved, such as the design of new drugs. The ability to observe these changes is to observe the essence of chemistry.

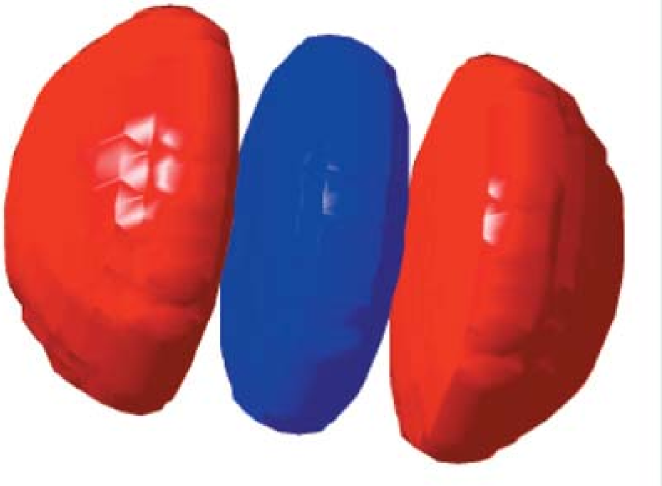
To be able to catch up with these electrons, you have to use a special kind of extremely fast and intense laser which produces laser pulses measured in femtoseconds. Using a femtosecond laser, the team fired a pulse into a vacuum chamber filled with nitrogen gas.

Just an instant earlier, another femtosecond laser had been fired to make sure all of the molecules in the gas were lined up in the same direction.

The team deliberately targeted one of the outermost and loosely bound electrons which, with the help of the laser, was temporarily dislodged from the parent nitrogen molecule. Temporary in this case means about 1.3 fs, after which the electron came hurtling back towards the parent molecule. During the process, the electron gains a tremendous amount of energy from the laser and when it collides it creates an intense emission of light in the extreme ultraviolet range, which the researchers have termed high harmonics. One member of the research team suggested that since the electron collision produced the emission, perhaps these high harmonics could give information about the shape of the orbital itself. In other words, if analyzed correctly; this spectrum would reveal the actual underlying shadow of the molecular orbital.

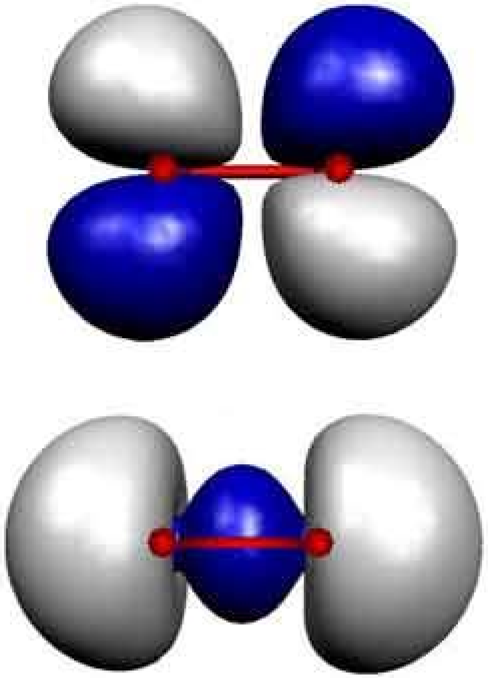
Because of Heisenberg's Uncertainty Principle, an electron in a molecule does not occupy a single point in space. It is spread out in a cloud. Imagine you have a car going around the race track and you take a picture every once in a while and you record the location of the car. Eventually you'll build up the shape the race track. The team was measuring the race track. But measuring an object from one angle does not reveal the true shape of the object. The team used a widely-used technique in medical imaging, known as tomography. By rotating the molecules in the vacuum chamber, they were able to build up a three-dimensional picture of the molecular orbital.

Creating a 3D picture of an electron orbital is the first step towards creating images of how chemical bonds are broken and formed during reactions. This achievement has major implications for any industry where chemistry is involved, such as the design of new drugs. The ability to observe these changes is to observe the essence of chemistry. The team accomplished this feat through the creative combination of a widely-used medical imaging technique known as tomography and an extremely fast and intense femtosecond laser which was used to temporarily dislodge an electron from its parent molecule.



http://focus.aps.org/story/v14/st12

Cloud Watchers



A. Alnaser/Kansas State Univ.

Orderly orbitals. A new technique gives a general picture of the electron clouds, or orbitals, of a molecule based on data from blasting the molecule apart with a laser pulse. The results correspond to these theoretically calculated orbitals for O_2 (top) and N_2.

Researchers have demonstrated a new method of observing the electron "clouds" surrounding simple molecules. Using laser pulses, they split molecules of oxygen and nitrogen into pairs of ions, then reconstructed the shapes of the molecules' original electron clouds, or "orbitals," based on the ions' paths. The results, published in the 10 September *PRL*, confirm the theoretical prediction that the likelihood of a molecule breaking up in an electric field depends on the shapes of its orbitals. The technique may help researchers probe reactions that occur in laser fusion systems, in the sun's corona, and between biological molecules.

If molecules drift into a strong electromagnetic field, such as exists on the surface of the sun, they can't help but ionize. Researchers can study this process in the lab using ultrashort laser pulses. The laser's strong electric field forces a pair of electrons from a two-atom molecule, leaving two lone ions behind. Recent experiments suggested that molecules such as O_2 and S_2 tend to resist ionization compared with molecules such as N_2--which was puzzling because the bonds that hold all three molecules together are about the same strength. The explanation seemed to be found in the orbitals various shapes: some orbital shapes align the electrons more readily with the laser's electric field, which makes them more susceptible to ionization.

Lewis Cocke's optical physics group at Kansas State University in Manhattan decided to test the idea with a new technique that the team believes is more direct than other methods of visualizing orbitals. They sprayed oxygen and nitrogen molecules across the path of a laser tuned to emit pulses eight femtoseconds long and 15 microjoules in energy--just enough to split a single molecule. A nearby detector plate collected the ions and recorded their positions. The researchers then reconstructed the orientation of the original molecule with respect to the laser's electric field.

The team then constructed a map for each molecule. For each orientation angle they placed a point on the graph whose distance from the center corresponded to the probability of breaking up the molecule. Nitrogen, for example, ionized most easily when the laser's electric field was aligned with the molecule's long axis, and only rarely when the alignment differed. Nitrogen's map looks like a long ellipse oriented horizontally, at zero degrees. That pattern matches the general shape of nitrogen's outer orbital, known from separate calculations: it's concentrated mainly along the line connecting the two atoms. Oxygen molecules, on the other hand, were more likely to break up when the electric field and molecular axis were offset by 45 degrees, corresponding to the four-leaf-clover shape of the molecule's outer orbital.

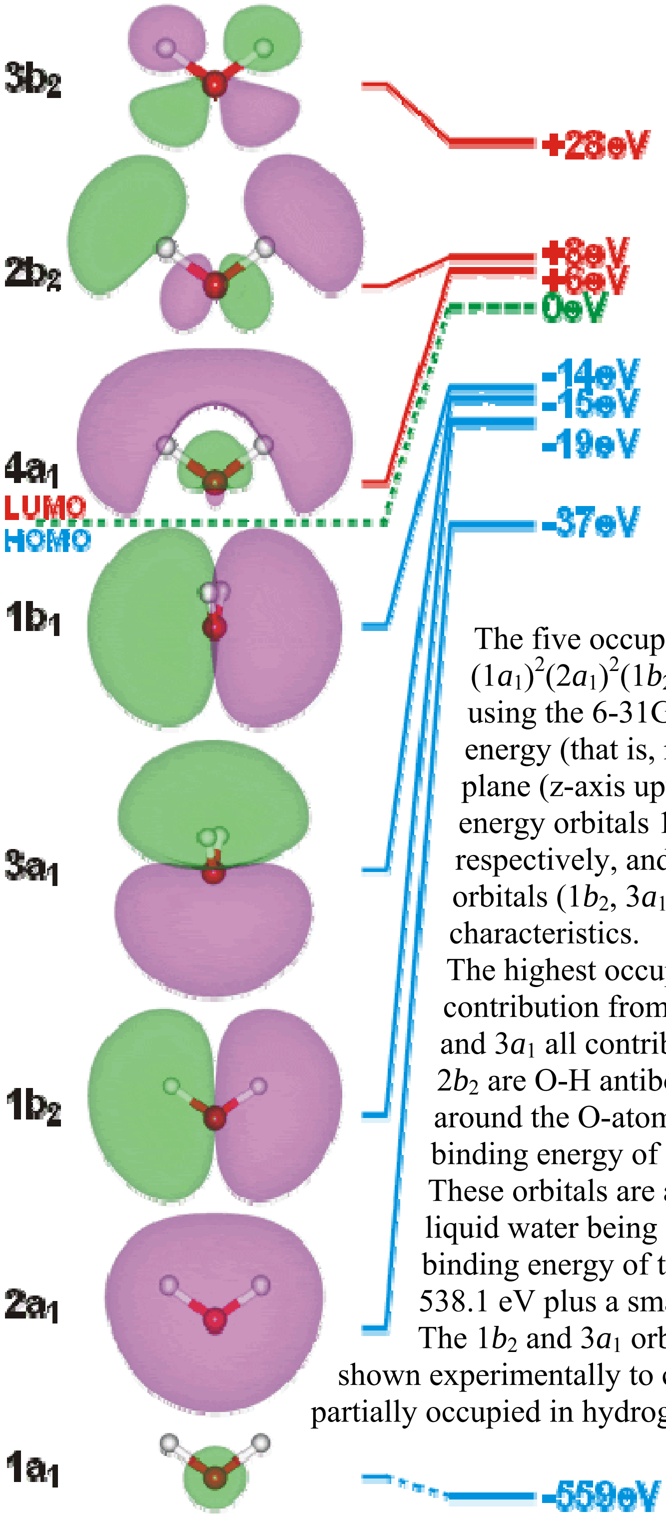
The agreement between ionization data and the orbital shapes confirms recent theories on nitrogen and oxygen, says team member Ali Alnaser. He says the method could be used to study the orbitals and ionization of more complicated molecules, such as CO_2 or C_2H_2. He also envisions learning about the electronic structure of more complex biological molecules with more elaborate experiments.

"It is a beautiful illustration of the influence of molecular symmetry," says chemist Henrik Stapelfeldt of the University of Aarhus in Denmark. "The resemblance of the measured angular distributions of the recoiling ions to the well known molecular orbitals of the valence electrons is striking."

--JR Minkel JR Minkel is a freelance science writer in New York City. **Effects Of Molecular Structure on Ion Disintegration Patterns In Ionization of O_2 and N_2 by Short Laser Pulses** A. S. Alnaser, S. Voss, X. -M. Tong, C. M. Maharjan, P. Ranitovic, B. Ulrich, T. Osipov, B. Shan, Z. Chang, and C. L. Cocke Phys. Rev. Lett. **93**, 113003
(issue of 10 September 2004)

RHF mos for water, **www.lsbu.ac.uk/water/h2oorb.html**
symmetry, ground config, etc.

Molecular Orbitals for Water (H_2O)

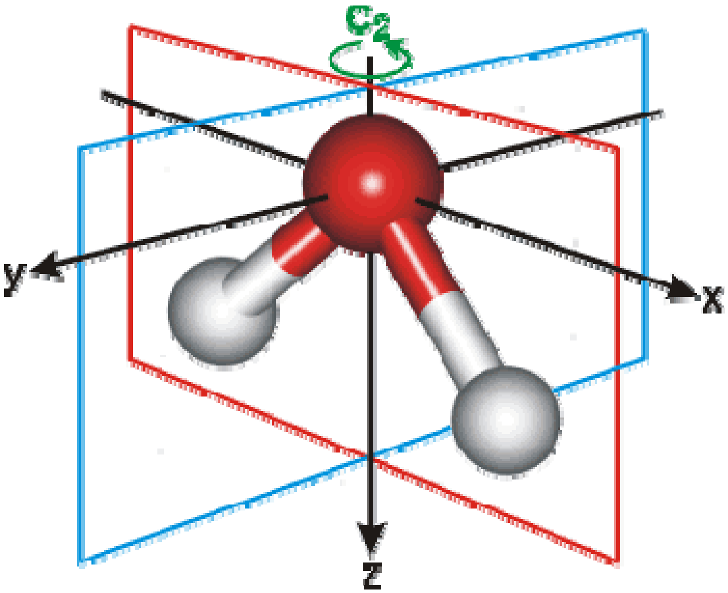


The five occupied and the lowest three unoccupied molecular orbitals of the isolated molecule $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ were calculated using the Restricted Hartree-Fock wave function (RHF) using the 6-31G** basis set (experimental data is given in [1289]). They are set out with the lowest energy (that is, most negative energy) molecular orbitals at the bottom. They are all given in the xz plane (z-axis upwards) except $1b_1$ and $3a_1$, which are in the yz plane (z-axis upwards).[a] The two lowest energy orbitals $1a_1$ and $2a_1$ are contributed from the 1s and 2s (mostly) orbitals of the oxygen atom, respectively, and are consequentially approximately spherical. The three highest energy occupied orbitals ($1b_2$, $3a_1$, $1b_1$) are orthogonal around the oxygen atom and without obvious sp^3 hybridization characteristics.

The highest occupied molecular orbital (HOMO), $1b_1$, is predominantly p_z^2 in character with no contribution from the hydrogen 1s orbital and mainly contributes to the "lone pair" effects. The $2a_1$, $1b_2$ and $3a_1$ all contribute to the O-H bonds. The two lowest unoccupied molecular orbitals $4a_1$ (LUMO) and $2b_2$ are O-H antibonding orbitals, seen in X-ray spectroscopy. They have greatest electron densities around the O-atom whereas orbital $3b_2$ has greatest electron density around the H-atoms. The experimental binding energy of the $1a_1$ orbital in the gas phase is 539.9 eV [1227].

These orbitals are appreciably changed in ice and water; the experimental electron binding energies in liquid water being $2a_1$ 30.90 eV, $1b_2$ 17.34 eV, $3a_1$ 13.50 eV, $1b_1$ 11.16 eV [877]. The experimental binding energy of the $1a_1$ orbital in the liquid phase consists of a broad energy distribution centered about 538.1 eV plus a smaller contribution at 536.6 eV within the tetrahedrally hydrogen bonded bulk [1227]. The $1b_2$ and $3a_1$ orbitals are largely responsible for the donation of hydrogen bonding with the $3a_1$ orbital shown experimentally to contribute the most [411]. Also, the $4a_1$ and $2b_2$ antibonding orbitals are reported to be partially occupied in hydrogen bond formation, receiving electron density from donor $1b_1$ orbitals [814].

Footnote



[a] The nomenclature is based upon the symmetry of the orbitals. The figure right shows the planes of symmetry (xz and yz) and the two-fold axis of rotation (C_2, z-axis).

If the orbitals are unchanged (that is, symmetric) with respect to the planes of symmetry (xz and yz) and the two-fold axis of rotation (C_2) then they are denoted as 'a_1' orbitals and numbered from the lowest energy (*i.e.* $1a_1$ is the lowest energy a_1 orbital). If the sign of the orbital changes with respect to 180° rotation about C_2 and reflection through the xz plane it is $b_{1,}$ whereas if the sign of the orbital changes with respect to 180° rotation about C_2 and reflection through the yz plane it is b_2. An a_2 orbital has no change in sign with respect to 180° rotation about C_2 but changes sign on reflection through both xz and yz planes (for example, the 9th lowest unoccupied molecular orbital for H_2O). [Back]

ionization of water Dyson orbitals:
www-rcf.usc.edu/~krylov/research/dyson/

molecular states of ion and neutral

Dyson orbitals for ionization from the ground and electronically excited states in EOM-CCSD formalism

To model angular distributions of photoelectrons, we implemented the calculation of Dyson orbitals using EOM-EE/IP/EA-CCSD.

For the Hartree-Fock wave functions and within Koopmans' approximation of the ionized states, the Dyson orbitals are just the canonical HF orbitals. For general correlated wave functions, Dyson orbitals represent the overlap between an N electron molecular wavefunction and the N-1/N+1 electron wavefunction of the corresponding cation/anion:

$$\Psi^{\mathrm{Dyson}}(\vec{r}_1) = \int \Psi^{N}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)\, \Psi^{N-1}(\vec{r}_2, \ldots, \vec{r}_N)\, d\vec{r}_2 \ldots d\vec{r}_N$$

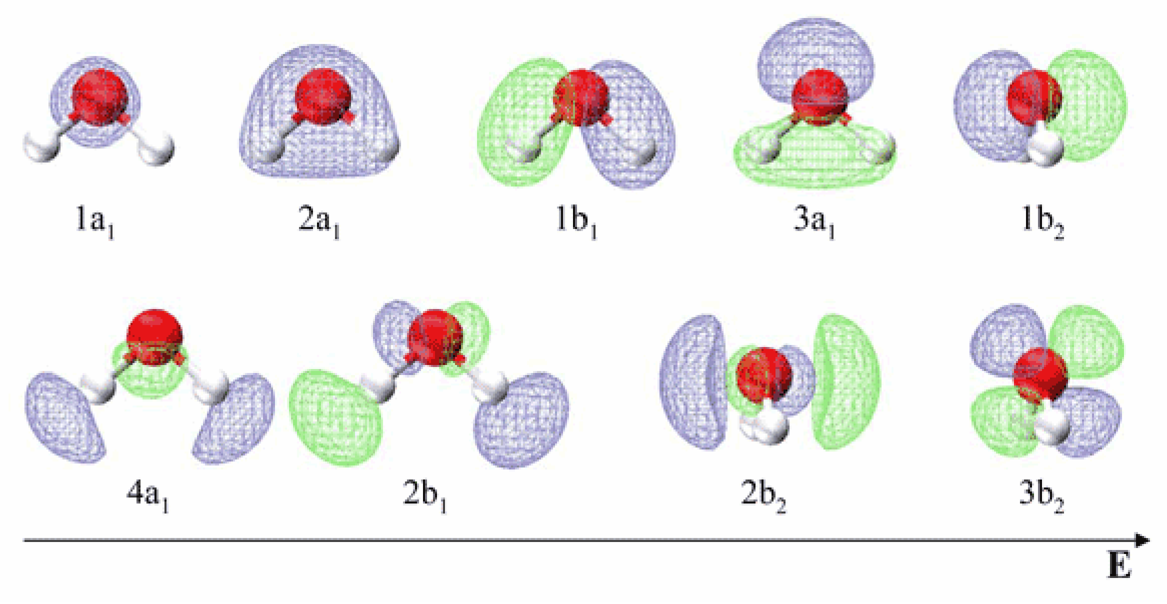
The probability of an electron being ejected in a certain direction (photoelectron angular distribution) is given by the ionization dipole moment:

$$I(\theta, \varphi) \propto \int_r \Psi^{N}\, \vec{\mu}\, \Psi^{N-1}\, \Psi^{\mathrm{el}}\, r^2 \sin\theta\, dr\, d\theta\, d\varphi = \int_r \Psi^{\mathrm{Dyson}}\, \vec{\mu}\, \Psi^{\mathrm{el}}\, r^2 \sin\theta\, dr\, d\theta\, d\varphi$$

Ψ^{el} is the wavefunction of the outgoing electron, and its angular momentum can be described by spherical harmonics $Y_{l,m}(\theta, \varphi)$:

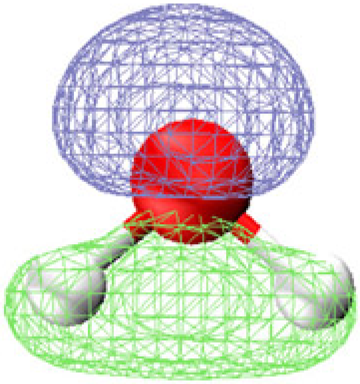
$$\Psi^{\mathrm{el}} = \sum_{l,m,k} e^{ikr} Y_{l,m}(\theta, \varphi)$$

Dyson orbitals can be thought of as the wavefunction of the leaving electron (before ionization), analogous to the Koopmans' picture, which is quite transparent from the equations above. Thus, for the ground-state ionization, the Dyson orbital is usually well approximated by the molecular orbital (MO) of the ionized electron. For example, the calculated Dyson orbital for ionization of water in its ground state has 99.7% $3a_1$ MO contribution.

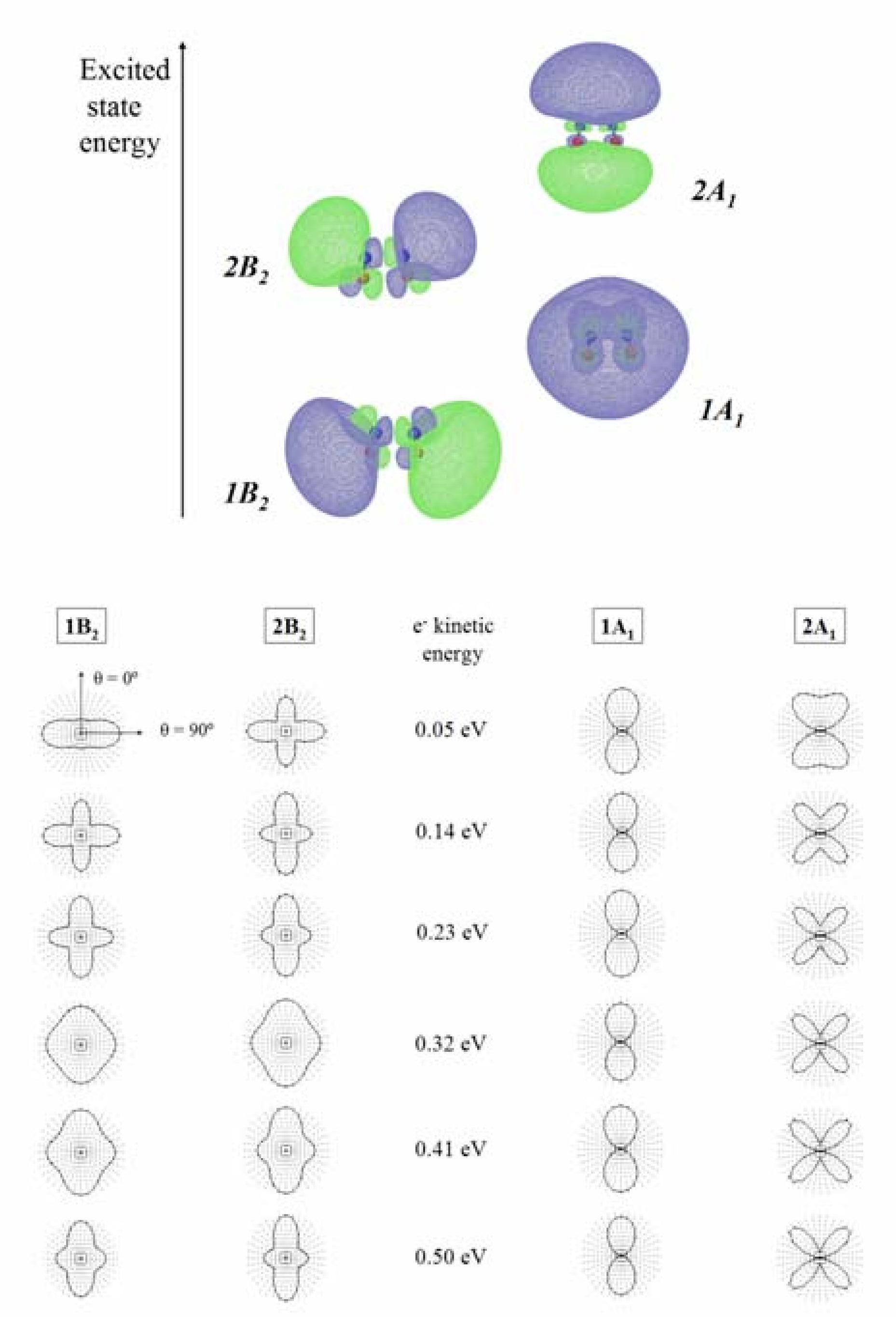


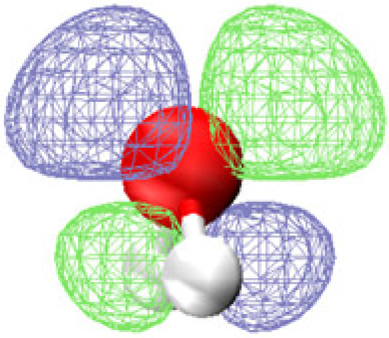
Occupied (top) and selected virtual (bottom) HF molecular orbitals of water

For the ionization from electronically excited states, the shape of the Dyson orbital is less intuitive. For the ionization of water $1B_2$ excited state ($1b_2$ to $4a_1$ electron excitation) to the ground state ($1A_1$) of the cation ($3a_1$ MO ionized), the Dyson orbital consists in a combination of virtual and occupied b_2 orbitals: 85.5% $3b_2$ + 0.3% $2b_2$ + 11.3% $1b_2$.



Dyson orbital for the transition between the ground state H_2O ($1A_1$) to ground state H_2O^+ ($1A_1$)





Dyson orbital for the transition between the excited state H_2O ($1B_2$) and ground state H_2O^+ ($1A_1$)

We have used this approach to aid in the interpretation of the experimental results for the photodissociation of the $(NO)_2$ species. Shown below are the calculated photoelectron angular distributions for four different excited states and the corresponding Dyson orbitals. Comparison with experimental data suggests that the B_2 state is the one leading to the dissociation of the dimer, although the shapes of the calculated photoelectron angular distributions vary drastically with the kinetic energy of the electron.

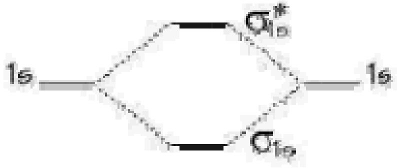
Dyson orbitals and calculated photoelectron angular distributions for several excited states in the NO dimer

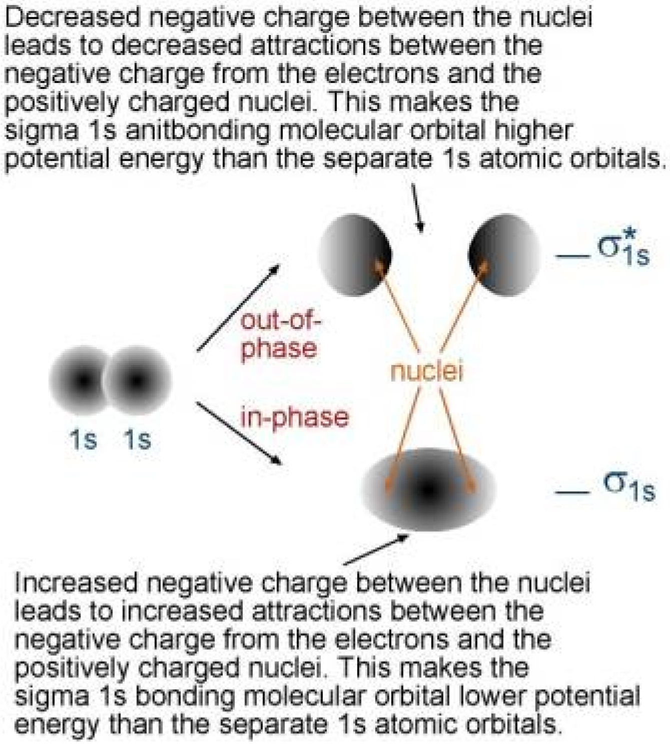
Related Publications

59. C.M. Oana and A.I. Krylov
Dyson orbitals for ionization from the ground and electronically excited states within equation-of-motion coupled-cluster formalism: Theory, implementation, and examples
J. Chem. Phys. **127**, 234106 (2007) Abstract PDF (873 kB)

applications of mos to visualizing conjugation and reactions www.chemcomp.com/journal/molorbs.htm

The following diagram shows the bonding and antibonding molecular orbitals formed from the interaction of two 1s atomic orbitals.



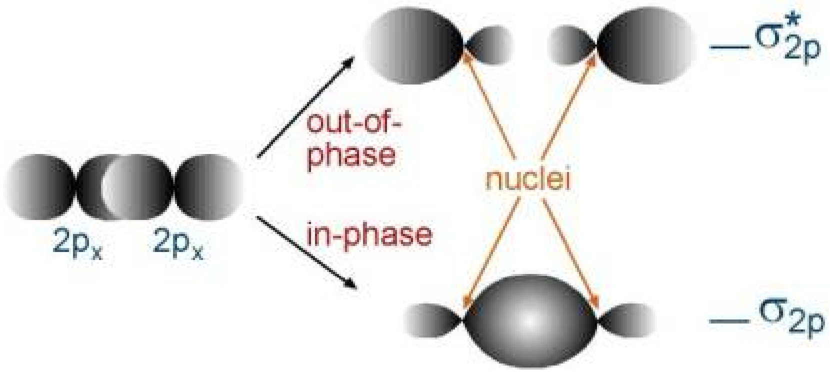

Decreased negative charge between the nuclei leads to decreased attractions between the negative charge from the electrons and the positively charged nuclei. This makes the sigma 1s anitbonding molecular orbital higher potential energy than the separate 1s atomic orbitals.

Increased negative charge between the nuclei leads to increased attractions between the negative charge from the electrons and the positively charged nuclei. This makes the sigma 1s bonding molecular orbital lower potential energy than the separate 1s atomic orbitals.

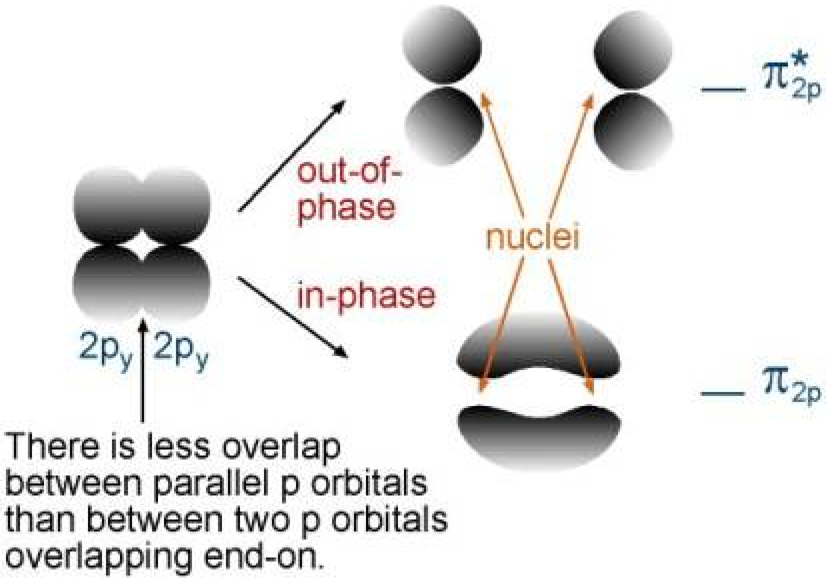
When two larger atoms atoms combine to form a diatomic molecule (like O_2, F_2, or Ne_2), more atomic orbitals interact. The LCAO approximation assumes that only the atomic orbitals of *about* the same energy interact. For O_2, F_2, or Ne_2, the orbital energies are different enough so only orbitals of the *same* energy interact to a significant degree.

Like for hydrogen, the 1s from one atom overlaps the 1s from the other atom to form a σ_{1s} bonding molecular orbital and a σ^*_{1s} antibonding molecular orbital. The shapes would be similar to those formed from the 1s orbitals for hydrogen. The 2s atomic orbital from one atom overlaps the 2s from the other atom to form a σ_{2s} bonding molecular orbital and a σ^*_{2s} antibonding molecular orbital. The shapes of these molecular orbitals would be similar to those for the σ_{1s} and σ^*_{1s} molecular orbitals. Both σ_{2s} and σ^*_{2s} molecular orbitals are higher energy and larger than the σ_{1s} and σ^*_{1s} molecular orbitals.

The p atomic orbitals of the two atoms can interact in two different ways, parallel or end-on. The molecular orbitals are different for each type of interaction. The end-on interaction between two $2p_x$ atomic orbitals yields sigma molecular orbitals, which are symmetrical about the axis of the bond.



The two $2p_y$ atomic orbitals overlap in parallel and form two pi molecular orbitals. Pi molecular orbitals are asymmetrical about the axis of the bond.

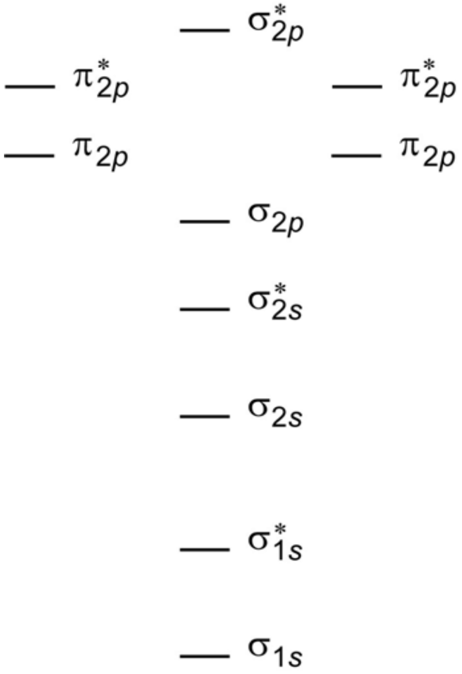


The $2p_z$-$2p_z$ overlap generates another pair of π_{2p} and π^*_{2p} molecular orbitals. The $2p_z$-$2p_z$ overlap is similar to the The $2p_y$-$2p_y$ overlap. To visualize this overlap, picture all of the orbitals in the image above rotated 90 degrees so the axes that run through the atomic and molecular orbitals are perpendicular to the screen (paper). The molecular orbitals formed have the same potential energies as the molecular orbitals formed from the $2p_y$-$2p_y$ overlap.

There is less overlap for the parallel atomic orbitals. When the interaction is in-phase, less overlap leads to less electron charge enhancement between the nuclei. This leads to less electron charge between the nuclei for the pi bonding molecular orbital than for the sigma bonding molecular orbital. Less electron character between the nuclei means less plus-minus attraction, less stabilization, and higher potential energy for the pi bonding molecular orbital compared to the sigma bonding molecular orbital.

When the interaction is out-of-phase, less overlap leads to less shift of electron charge from between the nuclei. This leads to more electron charge between the nuclei for the pi antibonding molecular orbital than for the sigma antibonding molecular orbital. More electron charge between the nuclei means more plus-minus attraction and lower potential energy for the pi antibonding molecular orbital compared to the sigma antibonding molecular orbital.

The expected molecular orbital diagram from the overlap of 1s, 2s and 2p atomic orbitals is as follows. We will use this diagram to describe O_2, F_2, Ne_2, CO, and NO.



We use the following procedure when drawing molecular orbital diagrams.

- Determine the number of electrons in the molecule. We get the number of electrons per atom from their atomic number on the periodic table. (Remember to determine the total number of electrons, not just the valence electrons.)
- Fill the molecular orbitals from bottom to top until all the electrons are added. Describe the electrons with arrows. Put two arrows in each molecular orbital, with the first arrow pointing up and the second pointing down.
- Orbitals of equal energy are half filled with parallel spin before they begin to pair up.

We describe the stability of the molecule with bond order.

bond order = 1/2 (#e- in bonding MO's - #e- in antibonding MO's)

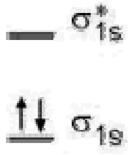
We use bond orders to predict the stability of molecules.

- If the bond order for a molecule is equal to zero, the molecule is unstable.
- A bond order of greater than zero suggests a stable molecule.
- The higher the bond order is, the more stable the bond.

We can use the molecular orbital diagram to predict whether the molecule is paramagnetic or diamagnetic. If all the electrons are paired, the molecule is diamagnetic. If one or more electrons are unpaired, the molecule is paramagnetic.

EXAMPLES:

1. The molecular orbital diagram for a diatomic hydrogen molecule, H_2, is



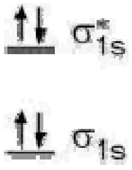
The bond order is 1. Bond Order = 1/2(2 - 0) = 1

- The bond order above zero suggests that H_2 is stable.
- Because there are no unpaired electrons, H_2 is diamagnetic.

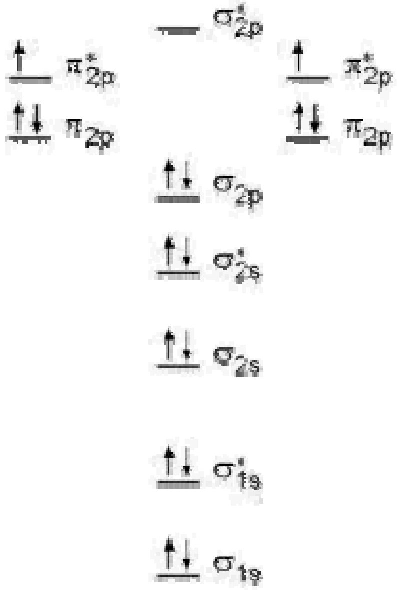
2. The molecular orbital diagram for a diatomic helium molecule, He_2, shows the following.

The bond order is 0 for He_2. Bond Order = 1/2(2 - 2) = 0

- The zero bond order for He_2 suggests that He_2 is unstable.
- If He_2 did form, it would be diamagnetic.



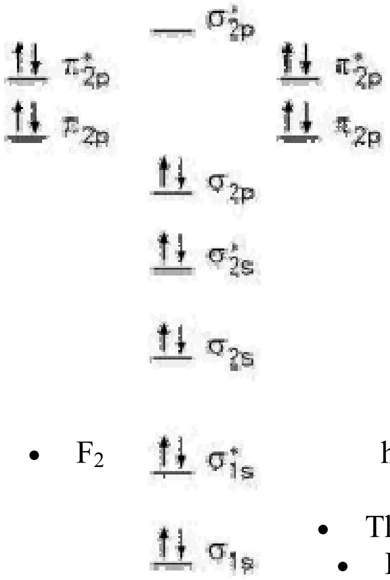
3. The molecular orbital diagram for a diatomic oxygen molecule, O_2, is



- O_2 has a bond order of 2. Bond Order = 1/2(10 - 6) = 2

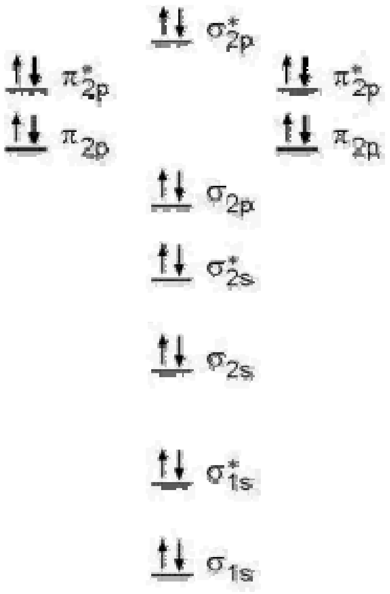
- The bond order of two suggests that the oxygen molecule is stable.
- The two unpaired electrons show that O_2 is paramagnetic.

4. The molecular orbital diagram for a diatomic fluorine molecule, F_2, is



- F_2 has a bond order of 1. Bond Order = 1/2(10 - 8) = 1
  - The bond order of one suggests that the fluorine molecule is stable.
  - Because all of the electrons are paired, F_2 is diamagnetic.

5. The molecular orbital diagram for a diatomic neon molecule, Ne_2, is



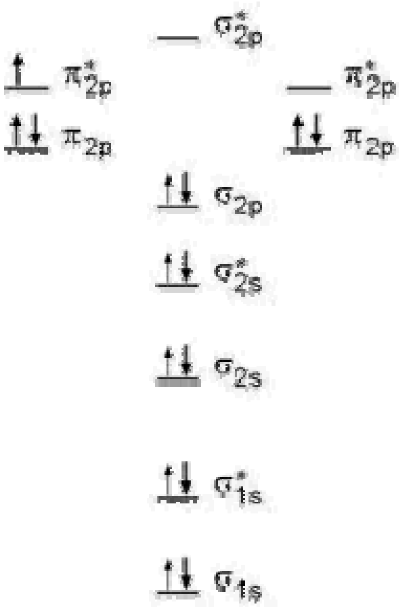
- Ne_2 has a bond order of 0. Bond Order = 1/2(10 - 10) = 0

- The zero bond order for Ne_2 suggests that Ne_2 is unstable.
- If Ne_2 did form, it would be diamagnetic.

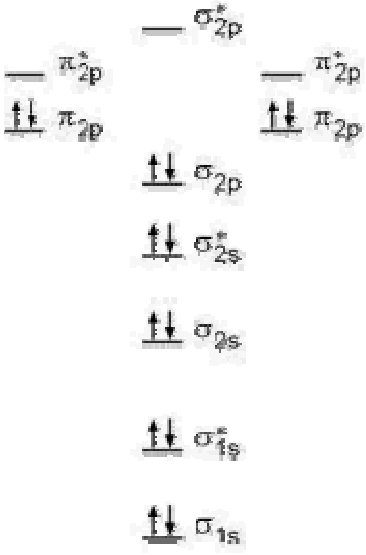
We can describe diatomic molecules composed of atoms of different elements in a similar way. The bond between the carbon and oxygen in carbon monoxide is very strong despite what looks like a strange and perhaps unstable Lewis Structure.

$:\mathrm{C}\equiv\mathrm{O}:$

The plus formal charge on the more electronegative oxygen and the minus formal charge on the less electronegative carbon would suggest instability. The molecular orbital diagram predicts CO to be very stable with a bond order of three.



We predict the nitrogen monoxide molecule to be unstable according to the Lewis approach to bonding.



The unpaired electron and the lack of an octet of electrons around nitrogen would suggest an unstable molecule. NO is actually quite stable. The molecular orbital diagram predicts this by showing the molecule to have a bond order of 2.5.

applications of mos to visualizing conjugation and reactions
www.chemcomp.com/journal/molorbs.htm

Definition

A Molecular Orbital (MO) is a composite of weighted Atomic Orbitals (AO's) which collectively define the shape and spatial density of the electrons in a molecular species [Szabo 1989]. In most quantum chemistry calculations, the starting point is a collection of atoms which each possess one or more atomic orbital functions:

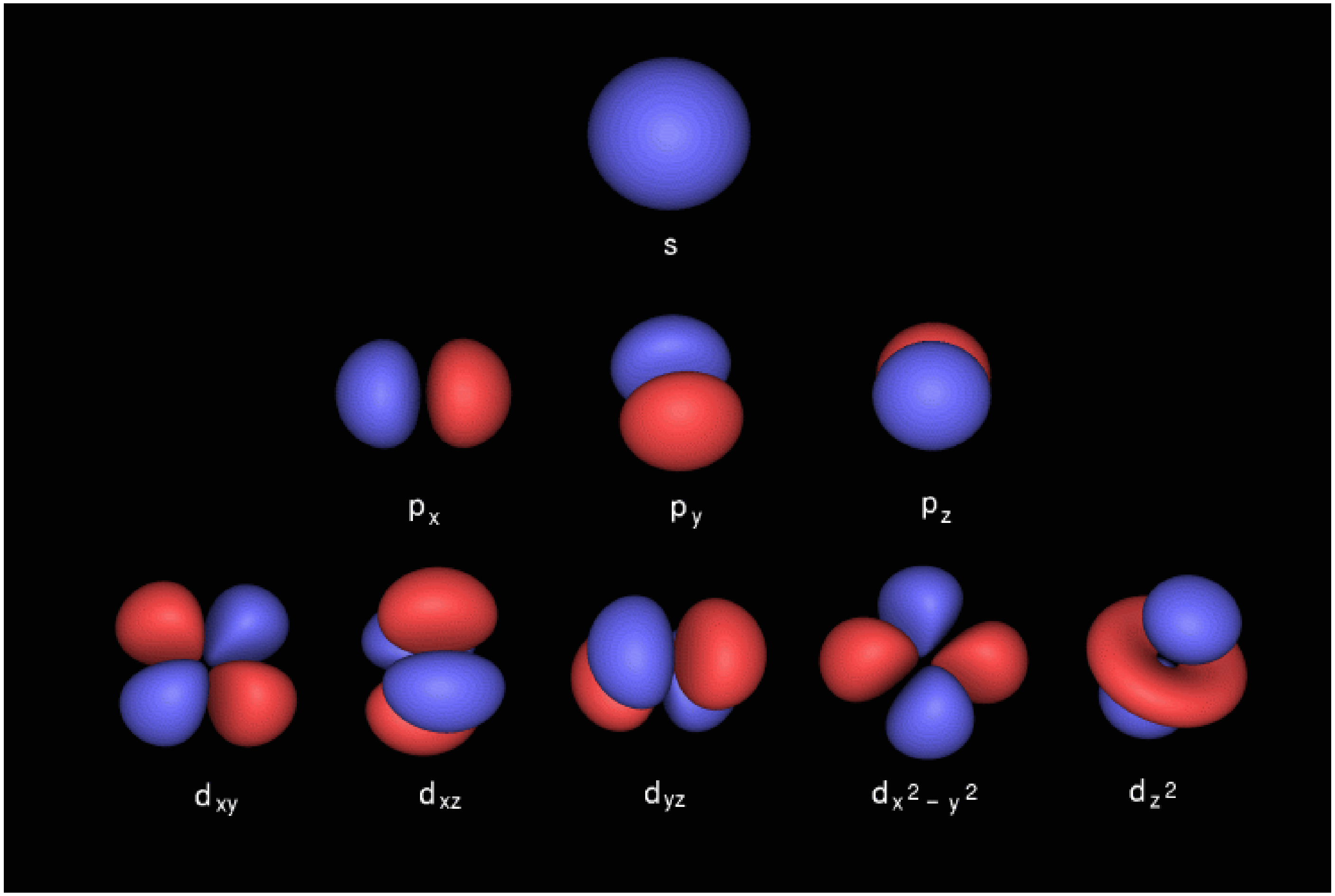


Figure 1: Atomic orbitals

In the simplistic model, hydrogen is generally described as having just one atomic orbital of interest, `1s`. Second row atoms include the spherical inner 1s shell, and four atomic orbitals for the valence shell: 2s and $2p_x$, $2p_y$, $2p_z$. Third row atoms add d-orbitals into the mix, and so on.

The actual atomic orbitals which are used depends on the basis set and varies somewhat; for instance *semi-empirical* methods such as those used by MOPAC, which is the main topic of this article, only include parameterized atomic orbitals for the valence shell (e.g. carbon has just 2s, $2p_x$, $2p_y$, $2p_z$). High level basis sets used with *ab initio* methods often add atomic orbitals which are not highly populated (e.g. `2s` and `2p` orbitals on hydrogen, d-orbitals on carbon, etc.)

The Linear Combination of Atomic Orbitals (LCAO) method treats the overall wavefunction as a series of weightings of atomic orbitals. The methods used to compute the wavefunction are beyond the scope of this article, but the immediate output from all of the quantum chemistry calculations based on the Hartree-Fock/Self Consistent Field method consist of two matrices: eigenvectors and eigenvalues.

The eigenvectors are expressed as a square matrix where the dimensionality is equal to the total number of atomic orbitals which were fed into the calculation at the beginning. The rows correspond to atomic orbitals and the columns to molecular orbitals:

$$\begin{array}{ccccccc}
 & & \multicolumn{5}{c}{\text{M.O.}} \\
 & & \mathbf{1} & \mathbf{2} & \mathbf{3} & .. & \mathbf{N} \\
 & \mathbf{1} & c_{11} & c_{12} & c_{13} & .. & c_{1N} \\
 & \mathbf{2} & c_{21} & c_{22} & c_{23} & .. & c_{2N} \\
\text{A.O.} & \mathbf{3} & c_{31} & c_{32} & c_{33} & .. & c_{3N} \\
 & .. & .. & .. & .. & .. & .. \\
 & \mathbf{N} & c_{N1} & c_{N2} & c_{N3} & .. & c_{NN}
\end{array}$$

The eigenvectors are sometimes referred to as the *wavefunction*. If one were to take column #1, it would be appropriate to say that the first molecular orbital is:

$$\psi(1) = c_{11}\phi(1) + c_{21}\phi(2) + c_{31}\phi(3) + .. + c_{N1}\phi(N)$$

where *psi* is the spatial form of the molecular orbital, and *phi* is a function that describes the particular atomic orbital. Hence the total density of the orbital at a point in space is the sum of those of the constituent atomic orbitals at that point, multiplied by the weighting coefficient taken from the eigenvector matrix.

The eigenvalues are represented as a diagonal matrix, where each element on the diagonal line (e_{ii}) is the energy of the corresponding orbital (column) *i* in the eigenvector matrix.

$$\begin{array}{cccccc}
 & \mathbf{1} & \mathbf{2} & \mathbf{3} & .. & \mathbf{N} \\
\mathbf{1} & e_{11} & & & & \\
\mathbf{2} & & e_{22} & & & \\
\mathbf{3} & & & e_{33} & & \\
.. & & & & .. & \\
\mathbf{N} & & & & & e_{NN}
\end{array}$$

The columns of the eigenvectors table are always ordered by the corresponding eigenvalues, so that MO#1 is the lowest in energy, increasing therefrom. Chemistry texts often plot the energy levels and electron occupancies of the molecular orbitals; the former is the value of e_{ii}.

The ordering by energy makes it straightforward to populate the electron occupancy of the molecular orbitals: if there are M electrons in a closed-shell system, then the first M/2 molecular orbitals are occupied, with two electrons each. The last of these to be filled is referred to as the Highest Occupied Molecular Orbital (HOMO). The molecular orbitals which are not filled are sometimes referred to as "virtual orbitals". The first of these is referred to as the Lowest Unoccupied Molecular Orbital (LUMO), and is the same as HOMO+1.

Basis Functions

Each of the atomic orbitals is represented by a mathematical expression which describes its intensity at all points in 3-dimensions. For purposes of graphically plotting the shapes of the molecular orbitals, these functions must be known, in addition to the wavefunction. There are several related ways to represent atomic orbitals, all of which are approximations to the orbitals shown in Figure 1.

The most conceptually simple manner in which the individual atomic orbitals are reasonably described is in terms of Slater functions, which have the general formula:

$$\phi(i) = N x^{a} y^{b} z^{c} e^{-\zeta r}$$

where a, b, c and zeta are parameters for the orbital, and N is a derived constant. The Cartesian terms arise from *a*, *b* and *c* when they are nonzero, which are the angular momentum numbers for the particular axis/axes. For the spherically symmetric s-orbitals these are 0, which makes the equation somewhat simpler, $\phi(i) = N e^{-\zeta r}$. The Cartesian variables (x, y, z) are the displacements from the center of the atomic orbital (the center being the position of the atom) and r is the magnitude of distance from the center. p-orbitals are described where just one of a, b or c is equal to 1, depending on whether it is p_x, p_y or p_z.

Ab initio methods generally cannot use Slater functions directly, because it is necessary to evaluate a vast number of 3D spatial integrals during the calculation. In order to make integral calculation feasible, a series of contracted Gaussian-type functions (where the exponential term is e^{-kr2}) are used instead. *Semi-empirical* methods exist mainly for the purpose of circumventing the need to evaluate these integrals and rely instead of parameterization. For determining the molecular orbitals of results from *ab initio* packages, it is more appropriate to use the Gaussian approximations, which may be obtained from the chosen basis set. Because this article is concerned with the results from the *semi-empirical* program MOPAC, it is appropriate to consider the atomic orbitals as Slater functions. For each orbital only one scaling constant is required, zeta.

Utility

There are many properties of molecular species that can be computed if the wavefunction is known (e.g. electron density, atomic partial charges, dipole moment, oscillator strengths, etc.). This article is concerned specifically with the graphical evaluation of the frontier molecular orbitals - the HOMO and LUMO - which provide qualitative information to the trained chemist regarding the highest energy electron orbital, and the lowest energy available un-filled orbital.

A number of reactions can be rationalized by examining the distribution of the frontier molecular orbitals, both with regard to mechanism (such as Diels-Alder reactions and sigmatropic rearrangements), and preferential reaction sites when examination of steric constraints does not provide the answer. Analysis of the molecular orbitals also reveals the extent of conjugation, and elucidates the nature of extended pi-systems in particular. Electron-rich and electron-poor species tend to reveal the localization or delocalization of the partial or full charge by the shape of the HOMO or LUMO.

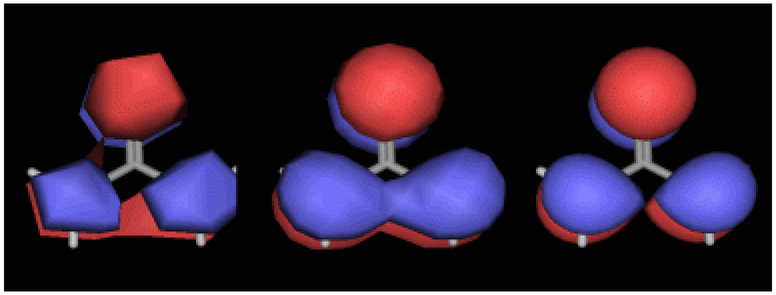
Methodology

In the MOE 2004.03 release, all of the wavefunction information is derived from results extracted from MOPAC. This popular *semi-empirical* computational package can be readily coaxed into yielding the following information, upon completing a geometry optimization:

- Eigenvectors (molecular orbitals in terms of atomic orbital coefficients)
- Eigenvalues (molecular orbital energy levels)
- Number of filled molecular orbitals (½ # electrons)
- Atomic orbital information (corresponding atom center, symmetry symbol, zeta value)
- Atom coordinates

The above information is sufficient to compute the intensity of any orbital at any region in space. For the purpose of creating a visual representation, a grid-based sampling is taken. The intervals and extents are arbitrary; a granularity of 1 Å in all directions leads to a visual representation which is hardly ideal, but still is sufficient for discerning general shape. Granularities of ½ Å and ¼ Å produce incrementally better views, but at a cost: 8 and 64 times as many sampling points, respectively. The extents can comfortably be selected at 3 Å further than the farthest atoms (+ and -) on each axis.

Figure 2: Granularity vs Quality



Note that the orbital is numerically represented as positive (blue) and negative (red) intensity values. This distinction has only relative meaning; the two signs are out of phase within the context of the molecular orbital, but in comparing two different molecular orbitals, there is no absolute significance - red and blue can be switched, as long as this is done within the entire context. The same applies to the atomic orbitals from which they are assembled.

For each of the sampling points, the following parameters are known: position in space (x, y, z) and molecular orbital (j). The intensity of the orbital at the position is therefore:

$$\text{intensity} = \sum_{i=1}^{N} c_{ij}\, \phi(i)$$

where N is the number of atomic orbitals, i is the iterator over the atomic orbitals, c_{ij} is the coefficient obtained from the eigenvectors matrix (row = atomic orbital, column = molecular orbital), and *phi*(i) is the basis function for atomic orbital i.

As previously mentioned, the basis functions for the atomic orbitals used here are the Slater functions, which are generalized for most of the orbitals as:

$$\phi(i) = N\, x^{a}\, y^{b}\, z^{c}\, e^{-\zeta r}$$

Where N is given as $k\frac{(2\zeta)^{n+\frac{1}{2}}}{(2n)!\sqrt{\pi}}$, n is the principal quantum number (1, 2, ...), k is a constant depending on the general symmetry type: 1 for s, sqrt(3) for p, sqrt(15) for d.

The values used for x, y and z are normalized to refer to position relative to the atom upon which the basis function is centered. r is calculated as the magnitude of the (x,y,z) vector.

For MOPAC, the value of zeta is the same for any atom type/symmetry block (s,p,d); zeta is parameterized because MOPAC is a *semi-empirical* method, and the parameterization is furthermore specific to the choice of Hamiltonian (e.g. AM1, PM3, MNDO, etc.), so care must be taken to ensure that the values of zeta used correspond to the method.

s-orbitals are spherically symmetric, as their cartesian components are zero (a = b = c = 0), therefore the equation becomes:

$$\phi(i) = N\, e^{-\zeta r}$$

p-orbitals have just one of the Cartesian modifiers defined (maximum angular momentum is 1, which is assigned to *a*, *b* or *c*):

$$\phi(i) = N\, x\, e^{-\zeta r}$$
$$\phi(i) = N\, y\, e^{-\zeta r}$$
$$\phi(i) = N\, z\, e^{-\zeta r}$$

d-orbitals have a total angular momentum of 2, which is expressed in the following ways:

$$\phi(i) = N\, x\, y\, e^{-\zeta r}$$
$$\phi(i) = N\, x\, z\, e^{-\zeta r}$$
$$\phi(i) = N\, y\, z\, e^{-\zeta r}$$
$$\phi(i) = N\, ½\, (x^2 - y^2)\, e^{-\zeta r}$$
$$\phi(i) = N\, \mathrm{sqrt}(\frac{1}{12})\, (2\, z^2 - x^2 - y^2)\, e^{-\zeta r}$$

Display

Once the grid points have been sampled for each of the molecular orbitals of interest, the last calculation to be done is the formation of a viewable surface. The grid is logically divided into two parts, the positive and negative values of the orbital intensity being treated separately before eventually being recombined.

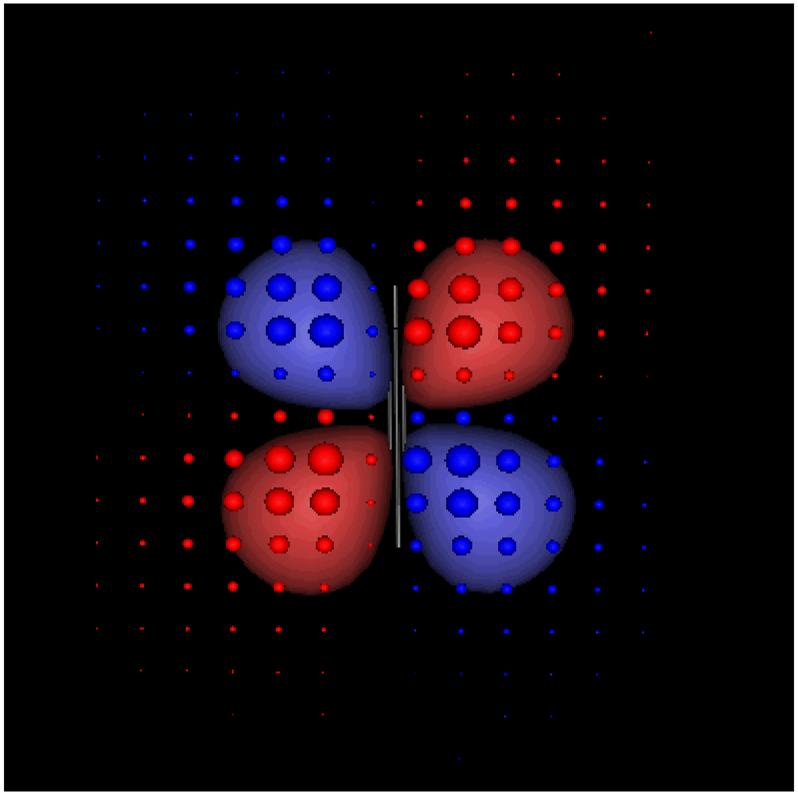


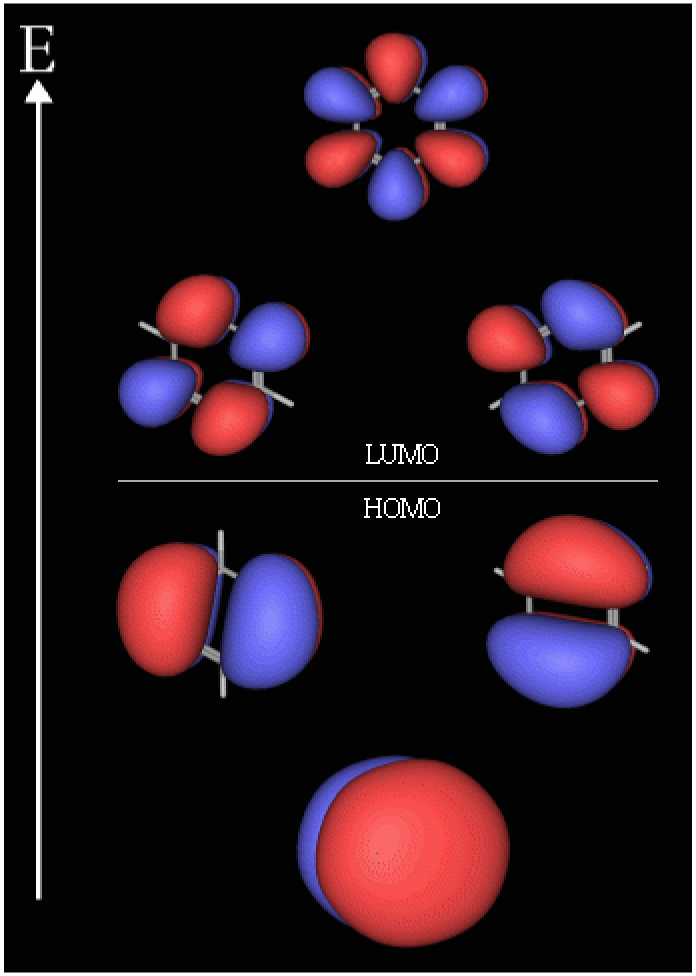
Figure 3: Grid points and surface cutoff

The two surfaces are formed by taking a cutoff point, which is some fraction of the maximum extent; interpolated grid points with a value equal to this cutoff are considered to be the surface (points with a greater value are within the surface, lesser are without). The choice of cutoff is generally arbitrary; if it were too small the orbitals would engulf the molecule and little information could be discerned; if it were too high, then important features of the electron distribution (such as continuity over multiple atoms) might not be seen.

Results

Benzene

The pi-orbitals of benzene which make up the aromatic core of the molecule is a popular textbook demonstration, as shown in the diagram below. The 6 orbitals which make up the aromatic system are shown ranked in order of their respective energies. The lower three orbitals are occupied, the higher three are vacant.



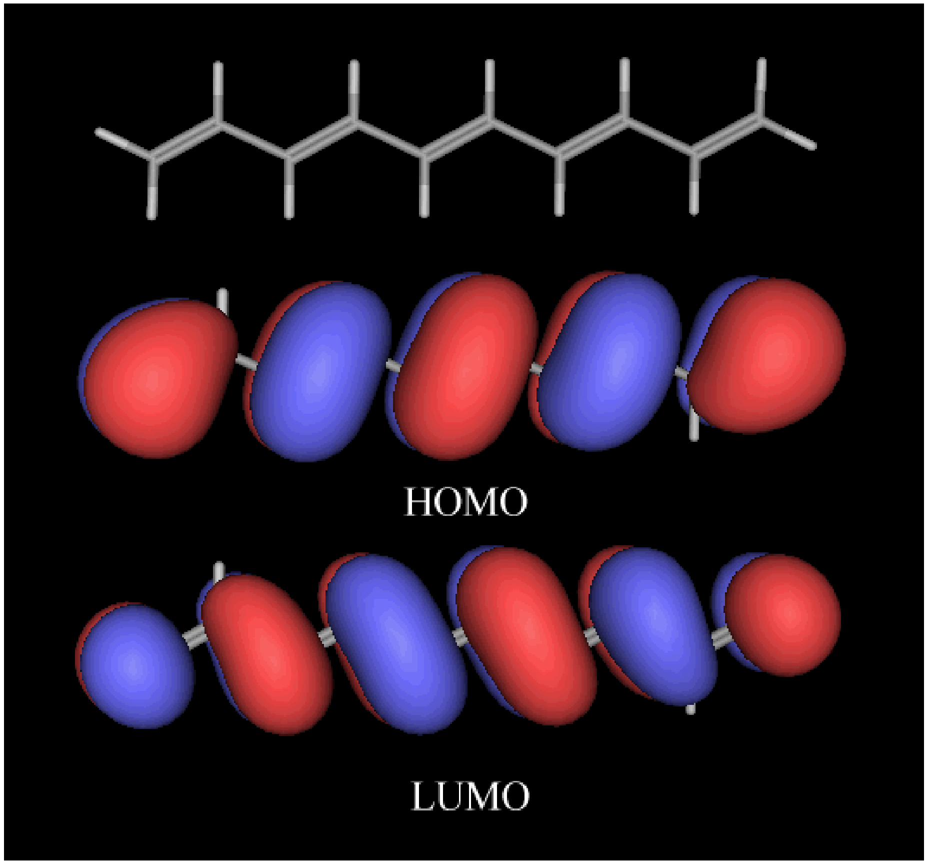
The lowest energy orbital attributed entirely to the aromatic ring current has just one node, and has the same overall symmetry as a single atomic p-orbital.

The two HOMO orbitals are degenerate, and are complementary. It can be seen that they have the same symmetry, and operate over the same region of space; the distributions are respectively out of phase by 90° about the z-axis. These orbitals have two node-planes, which is a qualitative rationalization for their higher energy relative to the lower orbital of p-type symmetry.

The two LUMO orbitals are also degenerate and complementary, and feature a larger number of nodes than the HOMO orbitals. The highest energy orbital making up the aromatic system has more nodes still.

Conjugated Oligomers

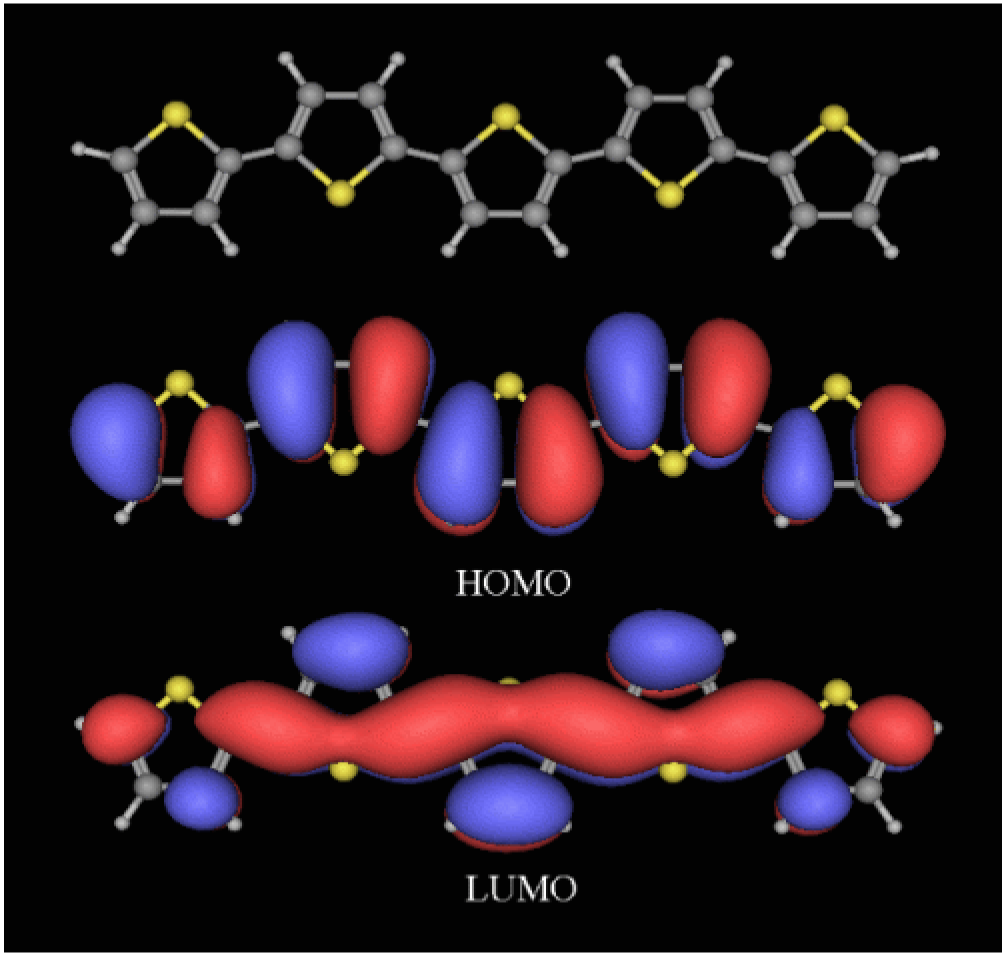
Molecular orbital representations are particularly good for showing the nature of conjugated systems. For instance in this oligomer of acetylene (dec-1,3,5,7,9-pentaene):



It can clearly be seen that the HOMO molecular orbital is an even, alternating-phase contribution from each of the pi double bonds. While this is suggestive of strong conjugation, examination of the LUMO supports this idea further. The LUMO is suggestive of a diradical state - that is, the species which would be formed if one were to alternate all of the C=C double bonds to their neighboring C-C single bonds, and place an unpaired electron at either end to make up the difference.

It might be expected that if the polyacetylene chain were extended further, the energy gap between the HOMO and LUMO would converge sufficiently that the "diradical" state would have significant thermal population at room temperature - and so the material would become a conductor.

Consider the more functionally rich 2,4-thiophene oligomer:

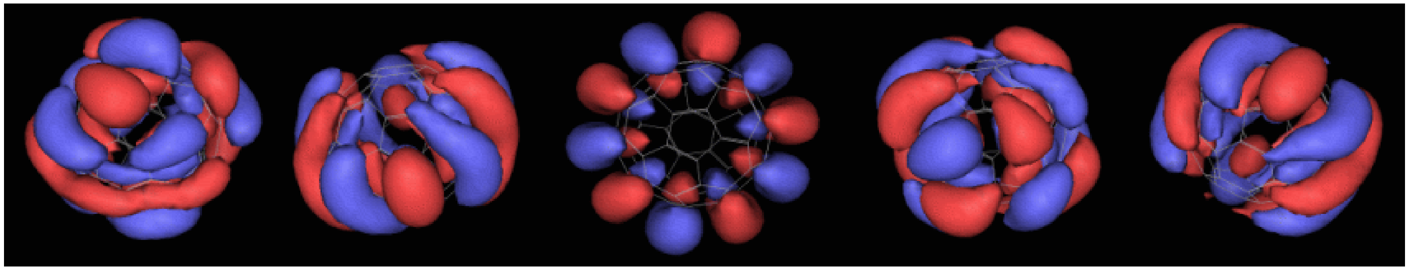


As with the alkene example, the HOMO

distribution suggests that the double bonds are conjugated. The distribution of the LUMO has a similar implication, that the excited diradical state, if it were readily accessible, would provide a clear path for electrons to flow. [MacDiarmid 2001]

C_{60}

Buckminsterfullerene molecular orbitals are interesting because of their very high symmetry. [Newton 1986] The following image shows the 5 degenerate HOMO's of C_{60}:

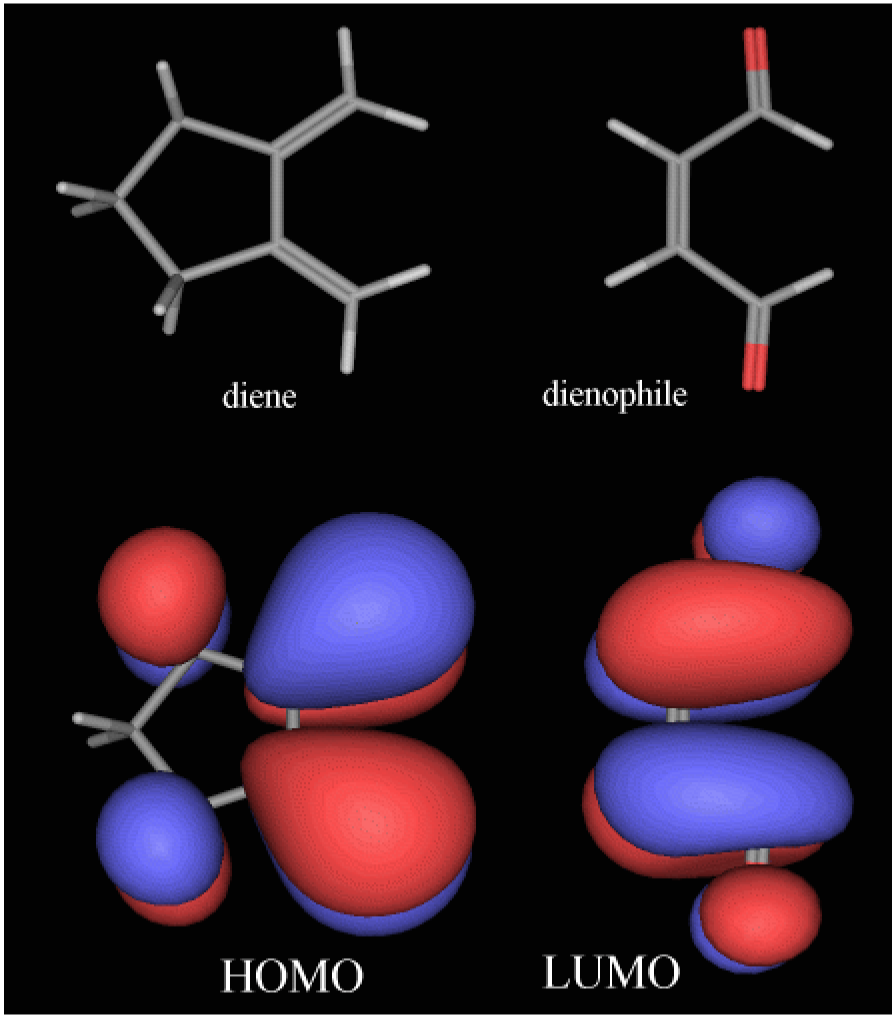


Although it is not immediately obvious from the diagram, all five of these orbital distributions are complementary and have the same symmetry. Visual analysis of the molecular orbitals allows concepts of structural symmetry to be extended to frontier electron symmetry.

Diels-Alder

Perhaps one of the best illustrations of a reaction in organic chemistry which is controlled by the interaction of frontier molecular orbitals is the Diels-Alder [Diels 1928]. The reaction can be written in the classical manner using 3 arrows to show the movement of bonds from the starting materials to the product, but this figurative interpretation does not explain the stereospecificity of the reaction, nor does it provide much insight as to why the reaction proceeds in a concerted manner.

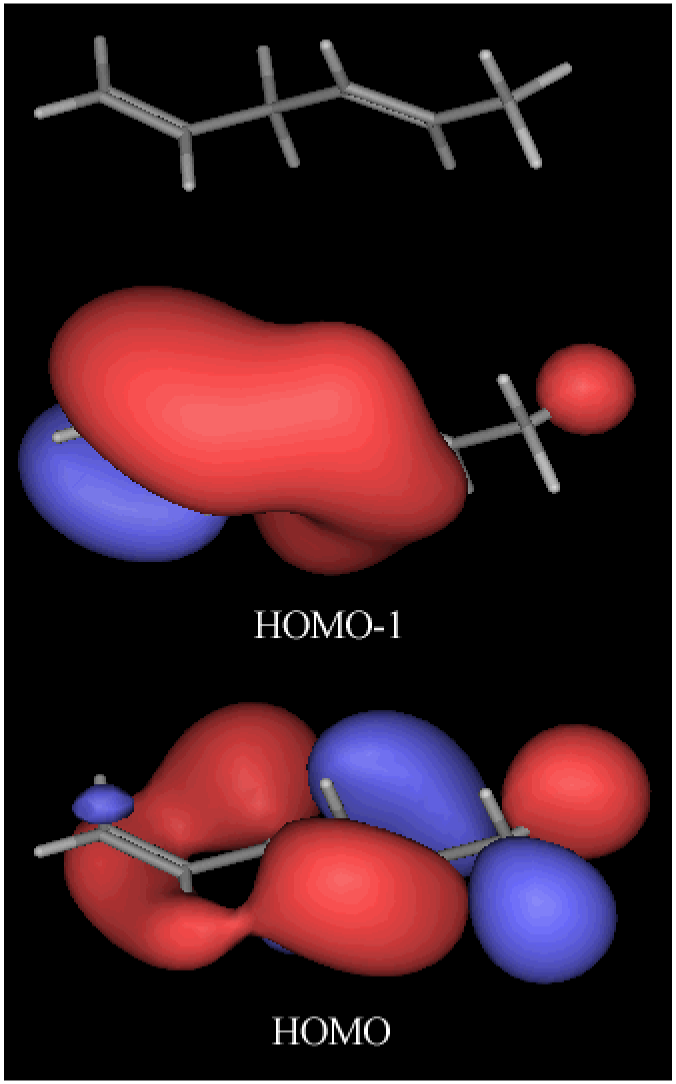
The interacting orbitals are from the electron-rich HOMO of the diene, which is spread out over the conjugated double bonds, and the electron-vacant LUMO of the dienophile, as shown below:



From a molecular orbital point of view, either of these two reaction orientations is favorable: the shape and symmetry of the diene HOMO and the dienophile LUMO are ideally matched for maximum in-phase overlap.

Bromination

In some cases it is actually possible to predict reactivity by examining the molecular orbitals, rather than just rationalizing existing results. In this case, the reaction of 1,4-hexadiene with bromine is considered:



The example has been chosen because there are two alkene functional groups, one of them terminal, the other not. The alkenes are separated by a methylene group and are hence not in a pi-conjugated system.

The reaction of this substrate with exactly one equivalent of molecular bromine, or some other small electrophile, presents a choice of two double bonds to attack. Steric factors are unlikely to be significant for this case, and the predominant choice of reacting bond can be expected to be electronic.

The diagram above shows both the HOMO and HOMO-1; two occupied frontier orbitals are necessary in this case because the alkene functional groups are not conjugated, and there is to a large extent a localization of the pi-type wavefunction on individual double bonds (which is the opposite of what was observed for the model conjugated conductors described earlier).

As it happens, the HOMO-1, which is lower in energy than the HOMO, features a large contribution from the terminal alkene pi-system; the HOMO itself features the pi-system of the non-terminal alkene functional group.

A strongly electrophilic reagent such as bromine reacts readily with unsaturated electron rich pi-bonds, and given a choice, it should react preferentially with the highest energy such bond, which is the non-terminal alkene. This prediction is consistent with general observations regarding kinetics of alkene halogenation. [Nelson 2000]

Summary

Molecular orbitals, when viewed in a qualitative graphical representation, can provide insight into the nature of reactivity, and some of the structural and physical properties of molecules. Well known concepts such as conjugation, aromaticity and lone pairs are well illustrated by molecular orbitals.

References

[MOPAC]	The Molecular Orbital PACkage version 7 is generally available as public domain source, and compiled binaries are provided with the Molecular Operating Environment, for all supported platforms. Principle author J.J.P. Stewart.
[Szabo 1989]	Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, A. Szabo, N.S. Ostlund, McGraw Hill (1989).
[MacDiarmid 2001]	A.G. MacDiarmid, Rev. Mod. Phys. 73, 701 (2001).
[Newton 1986]	M.D. Newton, R.E. Stanton, J. Am. Chem. Soc. **108**, 2469 (1986); H.P. Lothi, F.J. Alml, J. Chem. Phys. Lett. **135**, 357 (1987); M. Ozaki, Takahashi, A. Chem. Phys. Lett. **127**, 242 (1986).

[Diels 1928] O. Diels and K. Alder, Ann. **460**, 98 (1928); **470**, 62 (1929) Ber. 62, 2081 (1929).

[Nelson 2000] D. Nelson and T. Perng, *The Use of Relative Magnitudes of Steric Effects to Explore Reactions of Molecular Halogens With Representative Acyclic Alkenes*, Proceedings of the Oklahoma Academy of Science, **80**, 141 (2000).