Higher orbitals

The H_2^+ molecule has additional orbitals. The Hamiltonian

$$H = -\frac{\hbar}{2m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{r_{AB}}$$

has cylindrical symmetry. Defining the molecular axis as the z-axis, transformation to spherical coordinates (or any coordinate system which includes the angle φ, such as elliptical or cylindrical) will make possible the separation of the equation in φ, which is

$$\frac{d^2\Phi(\varphi)}{d^2\varphi} = -\lambda^2\Phi, \quad \text{giving } \Phi(\varphi) = \frac{1}{\sqrt{2\pi}}e^{i\lambda\phi},$$

with $\lambda = 0, \pm1, \pm2, \cdots$. Another way to look at the situation is noting that the total orbital energy operator $\hat{L}^2$ does not commute with H, but $\hat{L}_z$ does. The eigenfunctions of H may therefore be chosen as eigenfunctions of $\hat{L}_z$ with the eigenvalue $\lambda\hbar$. The orbitals are classified according to λ, similar to the classification of atomic orbitals by their l value, and denoted by letters which are the Greek equivalents to the AO notations: an orbital with $\lambda = 0$ is called σ, $\lambda = \pm1$ gives a π orbital, $\lambda = \pm2$ corresponds to a δ orbital, etc. Note that only λ^2 will appear in the equation determining the energy, so that all orbitals (except σ) are doubly degenerate.

It is convenient to work with real, rather than complex, orbitals. We do the same in atoms, when we take real combinations of degenerate orbitals, e.g.

$$p_x = \frac{p_1 + p_{-1}}{\sqrt{2}}, \quad p_y = \frac{p_1 - p_{-1}}{i\sqrt{2}}.$$

For linear molecules, the + combination of ϕ_λ and $\phi_{-\lambda}$ gives a real orbital with a φ dependence of $\cos(\lambda\varphi)$, while the $-$ combination gives a φ factor of $\sin(\lambda\varphi)$.

The real form of the orbitals makes possible an understanding of their spatial shape. The orbital ϕ with a φ factor of $\sin(\lambda\varphi)$ will obviously vanish at all points satisfying $\sin(\lambda\varphi) = 0$, which happens for certain φ values. Each such φ value defines a plane which includes the molecular axis (the z axis), which is a nodal plane. The solutions of $\sin(\lambda\varphi) = 0$ are $\lambda\varphi = n\pi$, or $\varphi = n\pi/\lambda, n = 0, 1, \cdots$. It is easily seen that when n reaches λ we get nodal planes which have been counted before. Unique nodal planes are thus obtained for $n = 0, 1, \cdots, \lambda - 1$, and an orbital with the φ dependence $\sin(\lambda\varphi)$ will have λ nodal planes. Reversing the argument, the λ of an orbital (in its real form) is given by the number of nodal planes which include the molecular axis. The two H_2^+ orbitals discussed above have no such planes, and are therefore σ orbitals ($\lambda = 0$). Note that the second orbital ($1s_A - 1s_B$) has a nodal plane, but it does not include the molecular axis and is not counted for determining λ.

If the molecule has an inversion center, squares of orbitals are invariant under inversion, and the orbitals are invariant up to a possible minus sign (inversion is the transformation $x, y, z \to -x, -y, -z$; geometrically, a point (x, y, z) is connected to the origin and the vector is continued with the same length, giving the transformation of the original point). An orbital going to itself upon inversion is denoted by the subscript g, an orbital going to minus itself is u. The orbital $1s_A + 1s_B$ is $1\sigma_g$, and $1s_A - 1s_B$ is $1\sigma_u$. The 1 in both cases means this is the first orbital of the σ_g or σ_u symmetry.

So far we constructed molecular orbitals from the atomic $1s$ orbitals. MOs may similarly be constructed from higher AOs. The $2s$ AOs will give

$$2\sigma_g \approx 2s_A + 2s_B, \quad 2\sigma_u \approx 2s_A - 2s_B.$$

Here, as for $1s$, the $+$ combination will be bonding, while the $-$ combination will have a nodal plane between the atoms and will be antibonding. The case of $2p$ orbitals is more complicated. The $2p_x, 2p_y,$ and $2p_z$ orbitals are equivalent in the atom. In the molecule, the z direction is where the other nucleus lies, and it differs from the other two directions. The $2p_z$ orbitals form two σ MOs,

$$3\sigma_g \approx 2p_{zA} - 2p_{zB}, \quad 3\sigma_u \approx 2p_{zA} + 2p_{zB},$$

with the first bonding and the second antibonding. Note that the shape of the atomic $2p$ dictates signs opposite to that of the s orbitals. The combinations of $2p_x$ and $2p_y$ orbitals have nodal planes which include the molecular (z) axis, the yz plane for $2p_x$ and xz for $2p_y$. The MOs obtained from them will therefore have π symmetry. These MOs will be

$$1\pi_u \approx 2p_{xA} + 2p_{xB}, \quad 1\pi_g \approx 2p_{xA} - 2p_{xB},$$

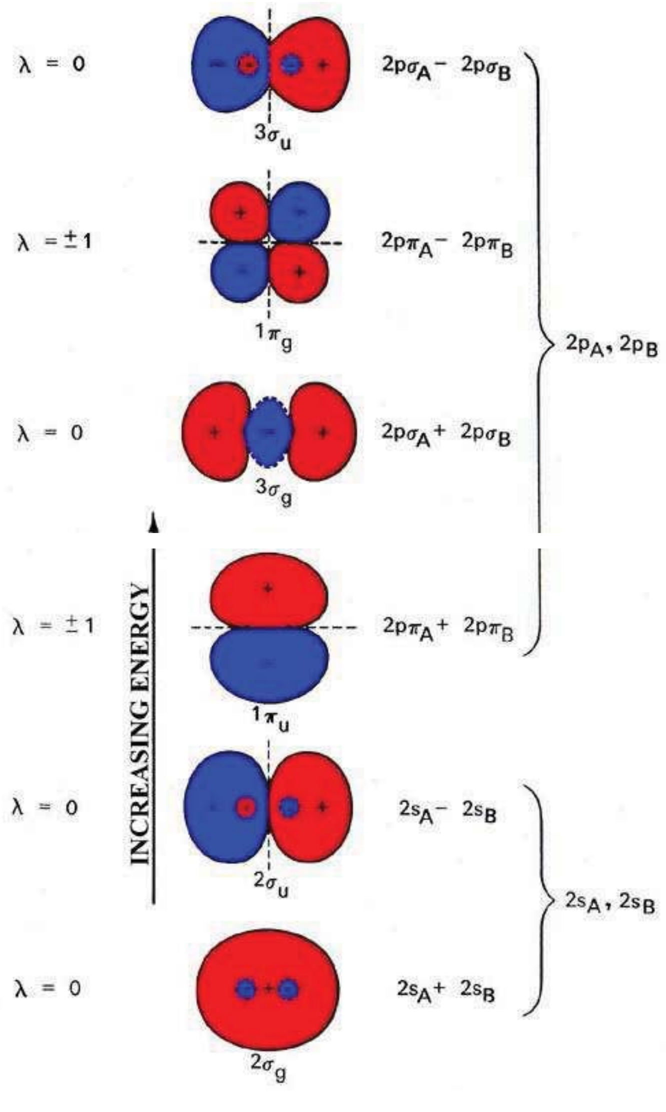
$$1\pi_u \approx 2p_{yA} + 2p_{yB}, \quad 1\pi_g \approx 2p_{yA} - 2p_{yB}.$$

Note that each MO appears twice. As discussed above, all orbitals with $\lambda > 0$ are doubly degenerate. The $1\pi_u$ orbitals have the positive lobes of the AOs next to each other, and similarly for the negative lobes; they are therefore bonding. The $1\pi_g$ orbitals, on the other hand, have the positive lobe of one

AO next to the negative lobe of the other; they will therefore have a nodal plane between the atoms and will be antibonding. The bonding orbitals obtained from the 2p AOs will have lower energy than the antibonding MOs. The ordering in these groups is less obvious. In most (but not all) cases, the π orbitals lie below the σ ones, so the order is

$$1\pi_u < 3\sigma_g << 1\pi_g < 3\sigma_u,$$

but the order within the first two or last two may change sometimes.



The scheme above produces a series of molecular orbitals for diatomic homonuclear (=same atoms) molecules. In order of increasing energy, with a star marking antibonding orbitals, the series is

$$1\sigma_g, 1\sigma_u^*, 2\sigma_g, 2\sigma_u^*, 1\pi_u, 3\sigma_g, 1\pi_g^*, 3\sigma_u^*.$$

The structure and bonding of diatomic homonuclear molecules can be understood by filling the orbitals from the bottom up and counting the bonding and nonbonding electrons. The bond order n is defined as the number of electrons in bonding orbitals minus their number in nonbonding orbitals, divided by 2. It corresponds to the traditional chemical idea of bond type (single, double, etc.) and gives a semiquantitative measure of the bond strength, as measured by R_e, the equilibrium internuclear distance, and D_e, the dissociation energy. Obviously, smaller R_e and larger D_e indicate a stronger bond.

	config.	n	D_e(eV)	R_e(Å)
H_2^+	$1\sigma_g$	0.5	2.79	1.06
H_2	$1\sigma_g^2$	1	4.75	0.741
He_2^+	$1\sigma_g^2 1\sigma_u$	0.5	2.5	1.08
He_2	$1\sigma_g^2 1\sigma_u^2$	0	0.0009	3.0
Li_2	$\cdots 2\sigma_g^2$	1	1.07	2.67
Be_2	$\cdots 2\sigma_g^2 2\sigma_u^2$	0	0.10	2.45
B_2	$\cdots 1\pi_u^2$	1	3.1	1.59
C_2	$\cdots 1\pi_u^4$	2	6.3	1.24
N_2^+	$\cdots 1\pi_u^4 3\sigma_g$	2.5	8.85	1.12
N_2	$\cdots 1\pi_u^4 3\sigma_g^2$	3	9.91	1.10
O_2^+	$\cdots 1\pi_u^4 3\sigma_g^2 1\pi_g$	2.5	6.78	1.12
O_2	$\cdots 1\pi_u^4 3\sigma_g^2 1\pi_g^2$	2	5.21	1.21
F_2	$\cdots 1\pi_u^4 3\sigma_g^2 1\pi_g^4$	1	1.66	1.41
Ne_2	$\cdots 1\pi_u^4 3\sigma_g^2 1\pi_g^4 3\sigma_u^2$	0	0.0036	3.1

The table shows these trends in diatomic homonuclear molecules. There are a few exceptions. Thus, Li_2^+, with a bond order of 0.5, has a stronger bond (D_0=1.44 eV) than Li_2 with a bond order

1. More accurate calculations give the correct results, but the highly qualitative treatment above gives very good predictions in almost all cases. It also explains why the oxygen molecule is paramagnetic. The ground state has a π_g^2 open shell, which gives rise to triplet and singlet states, with the triplet lower by Hund's rules. The tiny binding energies of the rare gas molecules are due to van der Waals interactions. The small D_e of Be_2, which has a bond order 0, is caused by the closeness of the $2p$ LUMO to the $2s$ HOMO, which allows some hybridization.

The MO picture gives a simple understanding of excited states too. Let us take He_2 as an example. The ground state is bound only by van der Waals interaction, which is very weak. Exciting an electron gives the $1\sigma_g^2 1\sigma_u 2\sigma_g$ configuration. This configuration has a bond order of 1, and gives rise to triplet and singlet states, with binding energy of about 2.5 eV.