8.5: The Relative Binding Ability of Molecular Orbitals

We may determine the relative importance of each orbital density in the overall binding of the nuclei in a molecule through a comparison of the forces which the various molecular orbital charge distributions exert on the nuclei. In molecular orbital theory, the total charge density is given by the sum of the orbital charge densities. Thus the total force exerted on the nuclei by the electronic charge distribution will be equal to the sum of the forces exerted by the charge density in each of the molecular orbitals. It is of interest to compare the effectiveness of each orbital charge density in binding the nuclei with some standard case in which they all exhibit the same ability. The limiting forms of the molecular orbitals for the case of the separated atoms have this desired property. In addition, the properties of the separated atoms form a useful basis for the discussion of any molecular property from the point of view of determining the changes which have been brought about by the formation of the chemical bond.

Suppose we label the two nuclei of a homonuclear diatomic molecule as A and B and consider the forces exerted on the A nucleus by the pair of electrons in a molecular orbital when the orbital has assumed its limiting form for the separated atoms. At this limit, one electron correlates with an atomic orbital on nucleus A and the other with an identical orbital on nucleus B. The discussion of the forces exerted on the nuclei by such a limiting charge distribution is similar to the discussion given previously in Section 6 for the case of two separated hydrogen atoms. The charge density in the orbital on the A nucleus will not exert a force on that nucleus since an undistorted atomic orbital is centrosymmetric with respect to its nucleus. The charge density of the electron which correlates with the B nucleus will exert a force on the A nucleus equivalent to that obtained by concentrating the charge density to a point at the position of the B nucleus. The electron which correlates with the B nucleus will screen one of the nuclear charges of B from the A nucleus. Thus the force exerted on one of the nuclei by the pair of electrons in a molecular orbital for the limiting state of the separated atoms is equivalent to that obtained by placing one negative charge at the position of the second nucleus. ***Of the pair of electrons in a given homonuclear molecular orbital, only one is effective in binding either nucleus in the limit of the separated atoms***.

If there are a total of N electrons in the molecule, there will be $N/2$ occupied molecular orbitals since each molecular orbital contains a pair of electrons. Therefore, a total of $N/2$ electrons will correlate with each nucleus. The molecule dissociates into two neutral atoms each with a nuclear charge $Z = N/2$. Thus the $N/2$ electrons which correlate with each nucleus will exactly cancel the nuclear charge of both nuclei; the final force on the nuclei will be zero.

The limiting force exerted on the A nucleus by the pair of electrons in a molecular orbital is $(Z_A e^2/R^2)(-1)$, that is, ***the force is equivalent to placing one negative charge at the position of the B nucleus***. Thus we may express the total limiting force on nucleus A as the product of $(Z_A e^2/R^2)$ with the difference between the number of positive charges on the B nucleus (Z_B) and ***the number of electronic charges which are effective in exerting a force on the A nucleus***, ($N/2$):

$$F_A = \frac{Z_A e^2}{R^2}\left(Z_B - (N/2)\right)$$

The quantity $N/2$ is the ***charge equivalent*** of the electronic force, the number of charges which when placed at the position of one nucleus exerts the same force on the second nucleus as does the actual charge distribution. The zero force between the separated atoms may be viewed as a result of each electron screening one nuclear charge on one nucleus from the nuclear charge of the other atom.

As the atoms approach one another to form a chemical bond, the atomic distributions on each atom become increasingly distorted and charge density is transferred to the binding region between the nuclei. There is a net force of attraction on the nuclei. We may again express the electronic force on the A nucleus in terms of its charge equivalent by multiplying the electronic force of attraction by $R^2/Z_A e^2$. Because of the distortion of the atomic orbital densities and the formation of molecular orbitals concentrating charge density in the region between the nuclei, the charge density of more than just one electron in each molecular orbital is effective in binding the nuclei. Thus at intermediate R values the charge equivalent of the electronic force exceeds its limiting value of $N/2$ required to screen the nuclear charge and the result is a force of attraction drawing the nuclei together.

When the distance between the nuclei is further decreased to its equilibrium value the force on the nuclei is again equal to zero. At this point, as when R equals infinity, the charge equivalent of the electronic force equals the nuclear charge. However, the state of electrostatic equilibrium in the molecule does not correspond to the charge density in each molecular orbital effectively screening one nuclear charge as it did in the separated atoms. Instead the charge equivalent of the density in each molecular orbital may be less than, equal to, or greater than the limiting value of unity observed for the separated atoms.

An orbital which concentrates charge density in the binding region will exert a force on the nuclei with a charge equivalent greater than unity. Such an orbital is called ***binding*** as it does more than simply screen one unit of positive charge on each nucleus. The charge equivalent of an orbital which concentrates density in the antibinding regions will be less than the separated atom value of unity. Such an orbital is termed ***antibinding*** as the charge density does not screen one unit of positive charge on each nucleus. When the charge equivalent of the force equals unity, it implies that the orbital charge density plays the same role in the molecule as in the separated atoms, that of screening one nuclear charge on B from nucleus A. An orbital with this property is termed ***nonbinding***.

Thus, by comparing the charge equivalent of the force exerted by the density in each molecular orbital with its separated atom value of unity, we may classify the orbitals as binding, antibinding or nonbinding:

Binding orbital	◆	charge equivalent > unity
Nonbinding orbital	◆	charge equivalent ~ unity
Antibinding orbital	◆	charge equivalent < unity

Table 8-1. Charge Equivalents of the Orbital Forces in Homonuclear Diatomic Molecules

Molecule	$1s_g$	$1s_u$	$2s_g$	$2s_u$	$1p_u$	$3s_g$	$1p_g$	Sum = Z_B	R_e (au)
He_2	1.78	-0.42						1.36*	(1.750)*
Li_2	0.70	0.68	1.62					3.00	5.051
Be_2	1.05	1.08	2.00	-0.40				3.68*	(3.500)*
B_2	0.98	0.98	2.32	-0.48	1.20			5.00	3.005
C_2	0.97	0.95	2.25	-0.43	1.13◆			6.00	2.348
N_2	1.15	1.08	2.67	-0.47	1.21◆	0.15		7.00	2.068
O_2	1.23	1.14	2.94	-0.52	1.30◆	0.18	0.43	8.00	2.282
F_2	1.24	1.12	2.45	-0.16	1.24◆	0.52	0.67◆	9.00	2.680

*He_2 and Be_2 form only weakly bound van der Waals molecules for relatively large internuclear seperations. The values of R quoted for these molecules are the internuclear distances used in the calculation of the charge equivalents listed in the table.

◆All of the values are quoted for double occupation of the orbitals for comparative purposes. The values marked by ◆are to be doubled to obtain the total electronic force as they refer to filled p orbitals.

The charge equivalents of the orbital forces for some homonuclear diatomic molecules are given in Table 8-1. Except for He_2 and Be_2 the sum of the charge equivalents equals the nuclear charge in each case as required for electrostatic equilibrium and the formation of a stable molecule. The charge equivalents of the orbital forces provide a quantitative measure of the role each orbital density plays in the binding of the nuclei in the molecule.

The $1s_g$ orbital in He_2 is binding. Of the two electronic charges in the $1s_g$ orbital, 1.78 of them are effective in binding the nuclei when R = 1.75 a_o as opposed to the one electronic charge which exerts a force when R = ¥. The $1s_u$ charge density, however, is strongly antibinding. The transfer of charge density to the antibinding regions in the formation of the $1s_u$ orbital in He_2 is so great that the charge equivalent is negative in sign. The antibinding nature of this orbital is very evident in the form of its charge distribution (Fig. 8-6). Not only does the charge density in this orbital no longer screen a positive charge on one nucleus from the other, it actually exerts a repulsive force on the nuclei, one which pulls the nuclei further apart from one another. The total eletronic force exerted on a nucleus in He_2 at R = 1.75 a_o is equivalent to placing (1.78 - 0.42) = 1.36 negative charges at the position of the second nucleus. Since the nuclear charge on helium is 2.00, a total of (2.00 - 1.36) = 0.64 positive charges on the second nucleus are left unscreened by the charge density. The net force on the nuclei is thus a repulsive one.

The $1s_g$ and $1s_u$ molecular orbitals are inner shell orbitals in the remaining molecules, Li_2 to F_2. An idealized inner shell molecular orbital has a charge equivalent of unity, the same as the separated atom value. Each electron should be localized in an atomic-like distribution and screen one nuclear charge. This is illustrated by the $1s_g$ and $1s_u$ charge density maps for the O_2 molecule (Fig. 8-8).

The charge equivalents of the $1s_g$ and $1s_u$ orbital densities for Li_2 (Fig. 8-7) are significantly less than unity. While these orbitals are not as contracted around the nuclei in Li_2 as they are in O_2 (the nuclear charge for lithium is three compared to eight for oxygen), they are still atomic-like with no effective overlap between the two centres. The charge equivalents are less than the screening value of unity because each of the atomic-like distributions is polarized into the antibinding region and exerts an antibinding force on the nucleus on which it is centred. The charge equivalents for the $1s_g$ and $1s_u$ density distributions in the remaining molecules are close to unity indicating that they are essentially nonbinding inner shell orbitals. The slight binding character of the $1s_g$ charge density in O_2 and F_2 is the result of small inward polarizations of the atomic-like distributions.

The $2s_g$ molecular charge density is binding in every molecule. A comparison of the charge equivalents shows that the $2s_g$ charge density is the most binding of all the molecular orbitals in this series of molecules. The charge equivalent of the force exerted by the $2s_g$ density in O_2 is almost three times greater than it is for the separated oxygen atoms. This is a result of the large amount of charge density accumulated in the binding region by this orbital (Fig. 8-8).

The $2s_u$ orbital is uniformly strongly antibinding. The extreme concentration of charge density in the antibinding regions observed for the $2s_u$ orbital is typified by the $2s_u$ density plot for O_2 (Fig. 8-8). It is obvious that the density in this orbital, as that in the $1s_u$ orbital of He_2 will pull the nuclei away from one another rather than bind them together. Notice that Be_2 is analogous to He_2 except that the $2s_g$ and $2s_u$ orbitals rather than the $1s_g$and $1s_u$ orbital densities are involved. In Be_2 the $1s_g$ and $1s_u$densities are nonbinding and together simply screen two nuclear charges on each atom. The $2s_g$ density exerts a binding force equivalent to one electronic charge in excess of the simple screening effect. The $2s_u$ orbital density, however, leaves a single nuclear charge unscreened which cancels the net attractive force of the $2s_g$ density and in addition exerts an antibinding force equivalent to increasing the nuclear charge by 0.40 units. The beryllium molecule is therefore unstable at this value of R.

The $1p_u$ orbital density is binding in each case, but only weakly so. The charge density of a p_u molecular orbital is concentrated around the internuclear axis rather than along it as in a s_g molecular orbital. Consequently the $1p_u$ density distributions exert only weak binding forces on the nuclei. In fact, the inner shell $1s_g$ charge density in F_2 exerts as large a binding force on the nuclei as does a pair of electrons in the$1p_u$ orbital.

The charge equivalent of the $3s_g$ orbital density is less than unity in the three cases where it is occupied. Thus it is an antibinding orbital even though it is of s_g symmetry. The charge density contours for this orbital in O_2 (Fig. 8-8) show that charge density is accumulated in the region between the nuclei as expected for an orbital of s_g symmetry. However, the $3s_g$ orbital correlates with a 2*p*s atomic orbital on each nucleus. The strong participation of the 2*p*s orbitals in the molecular orbital is evidenced by the node at each nucleus and by the concentration of charge density on both sides of each nucleus. The concentration of charge in the antibinding regions nullifies the binding effect arising from the accumulation of charge density in the region between the nuclei. The net result is an attractive force considerably less than that required to screen one positive charge on each nucleus.

The $1p_g$ orbital density is only weakly antibinding just as the $1p_u$ density is only weakly binding. The formation of the $1p_g$ orbital results in the removal of charge density from the binding region, not from along the internuclear axis but instead from regions around the axis. Notice that unlike the $2s_u$ orbital densities, the $1p_g$ charge density is antibinding only in the sense that it does not screen its share of nuclear charge, not because it exerts a force which draws the nuclei apart.

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