

8.E: Exercises

- (
a Give the molecular orbital electronic configurations of the N_2 and Ne_2 molecules.
)

(
b Does the difference in the number of occupied bonding and anti-bonding orbitals agree with the number of electron pair bonds which a Lewis structure would predict for these two molecules?
)
- Complete the correlation diagram ([Fig. 8-4](#)) for the homonuclear diatomic molecular orbitals by correlating each molecular orbital with an atomic orbital of the united atom. The symmetry and nodal property of each orbital must be conserved in the correlation. Starting with the molecular orbital of lowest energy each molecular orbital will in turn correlate with the atomic orbital of lowest energy which possesses the same symmetry. All atomic orbitals with even l values are of g symmetry and those with odd l values are of u symmetry.

The total and molecular orbital charge distributions of the bifluoride ion ($(\text{FHF})^-$) are shown in Fig. 8-12.

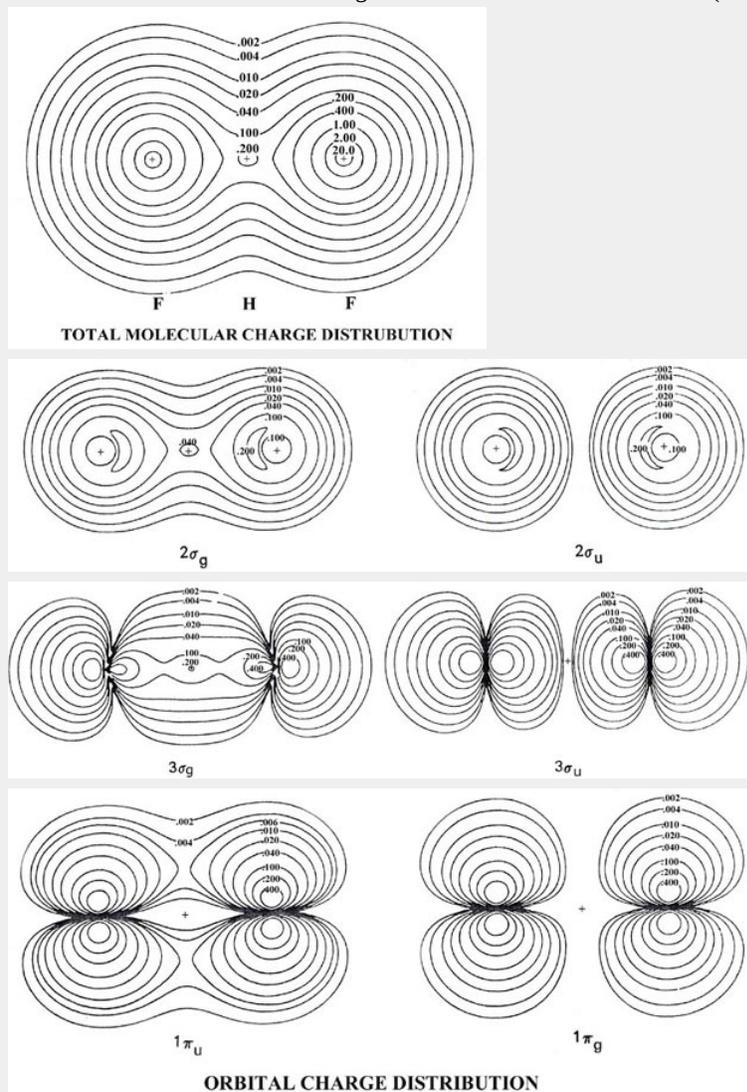


Fig. 8-12. Contour maps of the total molecular charge distribution and the molecular orbital densities for the $(\text{FHF})^-$ ion, which has the electronic configuration

$1s_g^2 1s_u^2 2s_g^2 2s_u^2 3s_g^2 1p_u^4 1p_g^4 3s_u^2$. Note that this electron configuration is formally identical to that for the unstable Ne_2 molecule. The binding properties of the orbitals in $(\text{FHF})^-$ are considerably altered from the homonuclear diatomic case by the presence of the proton, and the ion is a stable species. (The $1s_g$ and $1s_u$ densities are not shown.) ([Click here for enlarged picture.](#))

This negatively-charged molecule results from the reaction of a fluoride ion with a hydrogen fluoride molecule. The molecule has a linear, symmetric structure with the proton forming a bond between the fluorines. The molecular orbitals thus have the same symmetry classification (s or p and g or u) as do the orbitals for the homonuclear diatomic molecules.

Give a qualitative comparison of the forms and binding properties of the molecular orbitals for $(\text{FHF})^-$ with those for the (homonuclear diatomic molecule F_2). (The molecular orbitals for F_2 are very similar to those shown in Fig. 8-8 for O_2 . The $3s_u$ orbital is not occupied in the ground state of F_2 .) The $1s_g$ and $1s_u$ molecular orbital densities for $(\text{FHF})^-$ are not illustrated since they, like the corresponding orbitals in the homonuclear diatomics, are simply inner shell 1s atomic-like distributions centred on the fluorine atom.

(Account for the general forms and the primary atomic orbital components of the molecular orbitals in $(\text{FHF})^-$ in terms of the simple LCAO approximation using symmetry properties and the relative energies of the orbitals on H and F.)

4. The CO_2 molecule is another linear symmetric triatomic molecule possessing the same symmetry properties as do the homonuclear diatomic molecules. The molecular orbitals will be of s or p and g or u symmetry. From a knowledge of the symmetries of the $1s$, $2s$ and $2p$ atomic orbitals and their relative energies as given for C and O in Fig. 5-3 predict the electronic configuration of the CO_2 molecule in terms of molecular orbitals.
5. The CO molecule is isoelectronic with the N_2 molecule and can be thought of as being derived from N_2 by transferring one proton from one N nucleus to the other. The molecular orbitals of CO will be of s or p symmetry but will not exhibit any g or u dependence since the centre of symmetry has been lost. Derive the electronic configuration of CO by considering how each molecular orbital of N_2 will be changed as one N nuclear charge is increased by one unit and the other is decreased by one unit. As a hint, the $1s_g$ orbital of N_2 will become the $1s$ orbital of CO. Reference to Fig. 5-3 shows the $1s$ orbital of O to be considerably more stable than the $1s$ orbital of C. Thus the $1s_g$ orbital of N_2 which is concentrated equally in $1s$ -like atomic orbitals on both N nuclei, becomes a $1s$ -like atomic orbital on O. Similarly the $1s_u$ orbital of N_2 becomes a $1s$ -like orbital on C.
6. Using the $1s$, $2s$, $2p_s$ and $2p_p$ atomic orbitals on C and the $1s$ orbital on H discuss the simple LCAO forms expected for the molecular orbitals of the linear form of methylene, CH_2 . One can consider this problem from the point of view of how the molecular orbitals of CH given in the text would change if a second proton was brought up to the nonbonded side of the C atom.
7. Construct a correlation diagram for the HF molecule which relates the molecular orbitals with the orbitals of the separated atoms. Arrange the atomic orbitals of H and F on the right hand side of the diagram in order of increasing energy. The energies of the $1s$, $2s$, $3s$, and $1p$ molecular orbitals in the HF molecule are -26.29 au, -1.60 au, -0.77 au and -0.65 au respectively. Is the energy of the $1s$ orbital on F much affected by the formation of the chemical bond with H?
8. Construct a correlation diagram for the CO molecule which relates the molecular orbitals with those of the separated atoms. Arrange the atomic orbitals of both C and O on the right hand side of the diagram in the order of increasing energy. Only atomic orbitals of the same symmetry can interact to form a molecular orbital and the resulting molecular orbital will have this same symmetry. The energies of the molecular orbitals in CO in au are $1s(-20.67)$, $2s(-11.37)$, $3s(-1.53)$, $4s(-0.81)$, $5s(-0.56)$, $1p(-0.65)$. Recall that the $2p$ atomic orbitals on C and O may form molecular orbitals of both s and p symmetry.
9. The correlation diagram in Problem 7 correlates the separated atom orbitals for $R = \infty$ with the molecular orbitals at R_e , the equilibrium internuclear distance in the molecule. Continue the correlation of the orbitals to the limiting case of $R = 0$, the united atom. When the distance between the F nucleus and the proton is decreased to zero the result is a neon nucleus and a neon atom. The electronic energy of each molecular orbital should correlate smoothly with an atomic energy level of the united atom, the symmetry again being conserved. For example, the $1s$ molecular orbital will correlate with the $1s$ atomic orbital of the Ne atom. Do the spacings between the energy levels for HF resemble those for the united or separated atoms more closely? That is, is the electronic structure of the HF best compared to that of the Ne atom or to that of perturbed energy levels of the F and H atoms?

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