10.7: Mulliken Populations

Mulliken populations (R.S. Mulliken, J. Chem. Phys. 23, 1833, 1841, 23389, 2343 (1955)) can be used to characterize the electronic charge distribution in a molecule and the bonding, antibonding, or nonbonding nature of the molecular orbitals for particular pairs of atoms. To develop the idea of these populations, consider a real, normalized molecular orbital composed from two normalized atomic orbitals.

$$\psi_i = c_{ij}\phi_j + c_{ik}\phi_k \tag{10.7.1}$$

The charge distribution is described as a probability density by the square of this wavefunction.

$$\psi_i^2 = c_{ij}^2\phi_j^2 + c_{ik}^2\phi_k^2 + 2c_{ik}\phi_i\phi_j \tag{10.7.2}$$

Integrating over all the electronic coordinates and using the fact that the molecular orbital and atomic orbitals are normalized produces

$$1 = c_{ij}^2 + c_{ik}^2 + 2C_{ij}c_{ik}S_{jk} \tag{10.7.3}$$

where S_{jk} is the overlap integral involving the two atomic orbitals.

Mulliken's interpretation of this result is that one electron in molecular orbital ψ_t contributes c_{ij}^2 to the electronic charge in atomic orbital φ_j, c_{ik}^2 to the electronic charge in atomic orbital φ_k, and $2c_{ij}c_{ik}S_{jk}$ to the electronic charge in the overlap region between the two atomic orbitals. He therefore called c_{ij}^2 and c_{ik}^2, the *atomic-orbital populations*, and $2c_{ij}c_{ik}S_{jk}$, the *overlap population*. The overlap population is >0 for a bonding molecular orbital, <0 for an antibonding molecular orbital, and 0 for a nonbonding molecular orbital.

It is convenient to tabulate these populations in matrix form for each molecular orbital. Such a matrix is called the *Mulliken population matrix*. If there are two electrons in the molecular orbital, then these populations are doubled. Each column and each row in a population matrix is corresponds to an atomic orbital, and the diagonal elements give the atomic-orbital populations, and the off-diagonal elements give the overlap populations. For our example, Equation 10.7.1, the population matrix is

$$P_i = \begin{pmatrix} c_{ij}^2 & 2c_{ij}c_{ik}S_{jk} \\ 2c_{ij}c_{ik}S_{jk} & c_{ik}^2 \end{pmatrix} \tag{10.7.4}$$

Since there is one population matrix for each molecular orbital, it generally is difficult to deal with all the information in the population matrices. Forming the *net population matrix* decreases the amount of data. The net population matrix is the sum of all the population matrices for the occupied orbitals.

$$NP = \sum_{i=occupied} P_i \tag{10.7.5}$$

The net population matrix gives the atomic-orbital populations and overlap populations resulting from all the electrons in all the molecular orbitals. The diagonal elements give the total charge in each atomic orbital, and the off-diagonal elements give the total overlap population, which characterizes the total contribution of the two atomic orbitals to the bond between the two atoms.

The *gross population matrix* condenses the data in a different way. The net population matrix combines the contributions from all the occupied molecular orbitals. The gross population matrix combines the overlap populations with the atomic orbital populations for each molecular orbital. The columns of the gross population matrix correspond to the molecular orbitals, and the rows correspond to the atomic orbitals. A matrix element specifies the amount of charge, including the overlap contribution, that a particular molecular orbital contributes to a particular atomic orbital. Values for the matrix elements are obtained by dividing each overlap population in half and adding each half to the atomic-orbital populations of the participating atomic orbitals. The matrix elements provide the gross charge that a molecular orbital contributes to the atomic orbital. *Gross* means that overlap contributions are included. The gross population matrix therefore also is called the *charge matrix for the molecular orbitals*. An element of the gross population matrix (in the jth row and ith column) is given by

$$GP_{ji} = Pi_{jj} + \frac{1}{2}\sum_{k\neq j} Pi_{jk} \tag{10.7.6}$$

where P_i is the population matrix for the ith molecular orbital, Pi_{jj} is the atomic-orbital population and the Pi_{jk} is the overlap population for atomic orbitals j and k in the ith molecular orbital.

Further condensation of the data can be obtained by considering atomic and overlap populations by atoms rather than by atomic orbitals. The resulting matrix is called the *reduced-population matrix*. The reduced population is obtained from the net population matrix by adding the atomic orbital populations and the overlap populations of all the atomic orbitals of the same atom. The rows and columns of the reduced population matrix correspond to the atoms.

Atomic-orbital charges are obtained by adding the elements in the rows of the gross population matrix for the occupied molecular orbitals. Atomic charges are obtained from the atomic orbital charges by adding the atomic-orbital charges on the same atom. Finally, the net charge on an atom is obtained by subtracting the atomic charge from the nuclear charge adjusted for complete shielding by the 1s electrons.

Exercise 10.7.1

Using your results from Exercise $10.7.29$ for HF, determine the Mulliken population matrix for each molecular orbital, the net population matrix, the charge matrix for the molecular orbitals, the reduced population matrix, the atomic orbital charges, the atomic charges, the net charge on each atom, and the dipole moment. Note: The bond length for HF is 91.7 pm and the experimental value for the dipole moment is $6.37 \times 10^{-30}\ C \cdot m$.