

## S. POPULATION ANALYSIS

On p. 569 the electronic density  $\rho$  is defined. If the wave function is a Slater determinant (p. 332) and assuming the double occupancy of orbitals  $\varphi_i$ , we have (see (11.5)):

$$\rho(\mathbf{r}) = 2[|\varphi_1(\mathbf{r})|^2 + |\varphi_2(\mathbf{r})|^2 + \cdots + |\varphi_{\frac{N}{2}}(\mathbf{r})|^2]. \quad (\text{S.1})$$

The density distribution  $\rho$  may be viewed as a cloud carrying a charge  $-Ne$  and eq. (S.1) says that the cloud is composed of individual clouds of molecular orbitals, each carrying two electrons. On the other hand in the LCAO approximation any molecular orbital is represented by the sum of atomic orbitals. If we insert the LCAO expansion into  $\rho$ , then  $\rho$  becomes the sum of the contributions, each being the product of two atomic orbitals. There is a temptation to go even further and to divide  $\rho$  somehow *into the contributions of particular atoms*, calculate the charge corresponding to such contributions and locate the (point) charge on the nucleus.<sup>1</sup> We might say therefore, what the “electron population” residing on the particular atoms is (hence the name: population analysis).

### Mulliken population analysis

Such tricks are of course possible, and one of them is called Mulliken population analysis. From (S.1), after using the LCAO expansion  $\varphi_i = \sum_r c_{ri} \chi_r$ , we have ( $S_{rs}$  stands for the overlap integrals between the atomic orbitals  $r$  and  $s$ , and  $c$  are the corresponding LCAO coefficients)

$$\begin{aligned} N &= \int \rho(\mathbf{r}) dV = 2 \sum_{i=1}^{N/2} \int |\varphi_i(\mathbf{r})|^2 dV = \sum_i \sum_{rs} 2c_{ri}^* c_{si} S_{rs} \\ &= \sum_{rs} P_{rs} S_{rs} = \text{Tr}(\mathbf{P}\mathbf{S}), \end{aligned} \quad (\text{S.2})$$

where  $\mathbf{P}$  is called the charge and bond-order matrix

$$P_{sr} = \sum_i 2c_{ri}^* c_{si}. \quad (\text{S.3})$$

The summation over  $r$  and  $s$  may be carried out, being careful from which atom  $A$  the particular atomic orbital comes (we assume that the AO's are centred on the nuclei). We get an equivalent formula ( $A$  and  $B$  denote atoms):

<sup>1</sup>This number need not be an integer.

$$N = \sum_A \sum_{r \in A} \sum_B \sum_{s \in B} P_{rs} S_{rs}.$$

Afterwards we may choose the following partitionings:

**Atomic partitioning:**

$$N = \sum_A q_A, \quad q_A = \sum_{r \in A} \left( \sum_B \sum_{s \in B} P_{rs} S_{rs} \right),$$

Mulliken  
charges

where  $q$  are called the *Mulliken charges*. They are often calculated in practical applications and serve to provide information on how much of the electronic density  $\rho$  is concentrated on atom  $A$ . Such a quantity is of interest because it may be directly linked to the reactivity of atom  $A$ , often identified with its ability to be attacked by nucleophilic or electrophilic agents.<sup>2</sup> Also, if we measure the dipole moment, we would like to know why this moment is large in a molecule. By performing Mulliken analysis, we might be able to identify those atoms that are responsible for this. This might be of value when interpreting experimental data.

**Atomic and bond partitioning:** The summation may also be performed in a slightly different way

$$N = \sum_A \sum_{r,s \in A} P_{rs} S_{rs} + \sum_{A < B} 2 \sum_{r \in A} \sum_{s \in B} P_{rs} S_{rs} = \sum_A \bar{q}_A + \sum_{A < B} \bar{q}_{AB}.$$

The first term represents the contributions  $\bar{q}_A$  of the atoms, the second pertains to the atomic pairs  $\bar{q}_{AB}$ .

The latter populations are large and positive for those pairs of atoms for which chemists assign chemical bonds.

The bond population  $\bar{q}_{AB}$  may be treated as a measure of whether in the  $A - B$  atomic interaction, bonding or antibonding character prevails.<sup>3</sup> If, for two atoms,  $\bar{q}_{AB} < 0$ , we may say that they are not bound by any chemical bond, if  $\bar{q}_{AB}$  is large, then we may treat it as an indication that these two atoms are bound by a chemical bond or bonds.

<sup>2</sup>We have to remember that, besides electrons, this atom has a nucleus. This has to be taken into account when calculating the atomic net charge.

<sup>3</sup> $P_{rs}$  is the sum (over the occupied orbitals) of the products of the LCAO coefficients of two atoms in each of the occupied molecular orbitals. The equal signs of these coefficients (with  $S_{rs} > 0$ ) means a *bonding* interaction (recall Chapter 8 and Appendix R on p. 1009) and such a contribution increases  $P_{rs}$ . The opposite signs of the coefficients (with  $S_{rs} > 0$ ) corresponds to the antibonding interactions and in such a case the corresponding contribution decreases  $P_{rs}$ . If  $S_{rs} < 0$ , then the words “bonding” and “antibonding” above have to be exchanged, but the effect remains the same. This means that the product  $P_{rs} S_{rs}$  in all cases correctly controls the bonding ( $P_{rs} S_{rs} > 0$ ) or antibonding ( $P_{rs} S_{rs} < 0$ ) effects.

**Example 1. The hydrogen molecule.** Let us take the simplest example. First, let us consider the electronic ground-state in the simplest molecular orbital approximation, i.e. two electrons are described by the normalized orbital in the form ( $a, b$  denote the  $1s$  atomic orbitals centred on the corresponding nuclei; note that this is the famous bonding orbital)

$$\varphi_1 = N_1(a + b),$$

where  $N_1 = (2 + 2S)^{-\frac{1}{2}}$ , and  $S \equiv (a|b)$ . Then,

$$P_{sr} = \sum_i 2c_{ri}^* c_{si} = 2c_{r1}^* c_{s1} = (1 + S)^{-1},$$

independent of the indices  $r$  and  $s$ . Of course,

$$S = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}, \quad \text{and therefore} \quad PS = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}.$$

Thus,  $\text{Tr}(PS) = 2 =$  the number of electrons  $= P_{11}S_{11} + P_{22}S_{22} + 2P_{12}S_{12} = q_A + q_B + q_{AB}$ , with  $q_A = q_B = (1 + S)^{-1}$ , and  $q_{AB} = \frac{2S}{1+S} > 0$ . Thus we immediately see that the HH bond has an electronic population greater than zero, i.e. the atom–atom interaction is *bonding*.

Let us now consider  $H_2$  with two electrons occupying the normalized orbital of a different character<sup>4</sup>  $\varphi_2 = N_2(a - b)$ , with  $N_2 = (2 - 2S)^{-\frac{1}{2}}$ , then

$$P_{sr} = \sum_i 2c_{ri}^* c_{si} = 2c_{r2}^* c_{s2} = (1 - S)^{-1}$$

for  $(r, s) = (1, 1)$  and  $(r, s) = (2, 2)$  while  $P_{rs} = -(1 - S)^{-1}$  for  $(r, s) = (1, 2)$  and  $(r, s) = (2, 1)$ .

Now, let us calculate

$$PS = \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

and  $\text{Tr}(PS) = 2 =$  the number of electrons  $= P_{11}S_{11} + P_{22}S_{22} + 2P_{12}S_{12} = q_A + q_B + q_{AB}$ , but now  $q_A = q_B = (1 - S)^{-1}$  and  $q_{AB} = -\frac{2S}{1-S} < 0$ . Thus, a glance at  $q_{AB}$  tells us that this time the atoms are interacting in an antibonding way.

A similar analysis for polyatomic molecules gives more subtle and more interesting results.

### Other population analyses

Partitioning of the electron cloud of  $N$  electrons according to Mulliken population analysis represents only one of possible choices. For a positively definite matrix<sup>5</sup>  $S$  (and the overlap matrix is always positively definite) we may introduce the powers

<sup>4</sup>We do not want to suggest anything, but this orbital is notorious for antibonding character.

<sup>5</sup>I.e. all the eigenvalues positive.

of the matrix<sup>6</sup>  $S^x$ , where  $x$  is an arbitrary real number (in a way shown in Appendix J on p. 977), and we have  $S^{1-x}S^x = S$ . Then we may write<sup>7</sup>

$$N = \text{Tr}(PS) = \text{Tr}(S^xPS^{1-x}). \quad (\text{S.4})$$

Now, we may take any  $x$  and for this value construct the corresponding partition of  $N$  electronic charges into atoms. If  $x = 0$  or  $1$ , then we have a Mulliken population analysis, if  $x = \frac{1}{2}$  then we have what is called the *Löwdin population analysis*, etc.

Löwdin  
population  
analysis

### Multipole representation

Imagine a charge distribution  $\rho(\mathbf{r})$ . Let us choose a Cartesian coordinate system. We may calculate the Cartesian moments of the distribution:  $\int \rho(\mathbf{r}) dV$ , i.e. the total charge, then  $\int x\rho(\mathbf{r}) dV$ ,  $\int y\rho(\mathbf{r}) dV$ ,  $\int z\rho(\mathbf{r}) dV$ , i.e. the components of the dipole moment,  $\int x^2\rho(\mathbf{r}) dV$ ,  $\int y^2\rho(\mathbf{r}) dV$ ,  $\int z^2\rho(\mathbf{r}) dV$ ,  $\int xy\rho(\mathbf{r}) dV$ ,  $\int xz\rho(\mathbf{r}) dV$ ,  $\int yz\rho(\mathbf{r}) dV$  – the components of the quadrupole moment, etc. The moments mean a complete description of  $\rho(\mathbf{r})$  as concerns its interaction with another (distant) charge distribution. The higher the powers of  $x, y, z$  (i.e. the higher the moment) the more important distant parts of  $\rho(\mathbf{r})$  are. If  $\rho(\mathbf{r})$  extends to infinity (and for atoms and molecules it does), higher order moments tend to infinity. This means trouble when the consecutive interactions of the multipole moments are calculated (multipole expansion, Appendix X) and indeed, the multipole expansion “explodes”, i.e. diverges.<sup>8</sup> This would not happen if the interacting charge distributions could be enclosed in two spheres.

There is also another problem: where to locate the origin of the coordinate system, with respect to which the moments are calculated? The answer is: *anywhere*. Wherever such an origin is located it is OK from the point of view of mathematics. However, such choices may differ enormously from the practical point of view. For example, let us imagine a spherically symmetric charge distribution. If the origin is located at its centre (as “most people would do”), then we have a quite simple description of  $\rho(\mathbf{r})$  by using the moments, namely, the only non-zero moment is the charge, i.e.  $\int \rho(\mathbf{r}) dV$ . If, however, the origin is located off centre, all the moments would be non-zero. They are all needed to calculate accurately the interaction of the charge distribution (with anything). As we can see, it is definitely better to locate the origin at the centre of  $\rho(\mathbf{r})$ .

Well, and what if the charge distribution  $\rho(\mathbf{r})$  were divided into segments and each segment represented by a set of multipoles? It would be all right, although, in view of the above example, it would be better to locate the corresponding origins at the centre of the segments. It is clear that, in particular, it would be OK if the segments were very small, e.g., the cloud was cut into tiny cubes and we consider

<sup>6</sup>They are symmetric matrices as well.

<sup>7</sup>We easily check that  $\text{Tr}(ABC) = \text{Tr}(CAB)$ . Indeed,  $\text{Tr}(ABC) = \sum_{i,k,l} A_{ik}B_{kl}C_{li}$ , while  $\text{Tr}(CAB) = \sum_{i,k,l} C_{ik}A_{kl}B_{li}$ . Changing summation indices  $k \rightarrow i, l \rightarrow k, i \rightarrow l$  in the last formula, we obtain  $\text{Tr}(ABC)$ .

<sup>8</sup>Although the first terms (i.e. before the “explosion”) may give accurate results.

every cube's content as a separate cloud.<sup>9</sup> But, well... , what are the multipoles for? Indeed, it would be sufficient to take only the charges of the cubes, because they approximate the original charge distribution. In this situation higher multipoles would certainly be irrelevant! Thus we have two extreme cases:

- a single origin and an infinite number of multipoles,
- or an infinite number of centres and monopoles (charges) only.

We see that when the origins are located on atoms, we have an intermediary situation and it might be sufficient to have a few multipoles per atom.<sup>10</sup> This is what the concept of what is called the *cumulative multipole moments* is all about (Camm<sup>11</sup>). Besides the isotropic atomic charges  $q_a = M_a^{(000)}$  calculated in an arbitrary population analysis, we have, in addition, higher multipoles  $M_a^{(klm)}$  (atomic dipoles, quadrupoles, octupoles, etc.) representing the anisotropy of the atomic charge distribution (i.e. they describe the deviations of the atomic charge distributions from the spherical)

cumulative  
multipole  
moments

$$M_a^{(klm)} = Z_a x_a^k y_a^l z_a^m - \sum_{r \in a} \sum_s D_{sr} (r | x^k y^l z^m | s) \\ - \sum_{k' \leq k} \sum_{l' \leq l} \sum_{m' \leq m,} \sum_{(k', l', m') \neq (k, l, m)} \binom{k}{k'} \binom{l}{l'} \binom{m}{m'} \\ \times x_a^{k-k'} y_a^{l-l'} z_a^{m-m'} \cdot M_a^{k'l'm'},$$

where  $M_a^{(klm)}$  is the multipole moment of the “ $klm$ ” order with respect to the Cartesian coordinates  $x, y, z$  located on atom  $a$ ,  $M_a^{(000)}$  stands for the atomic charge, e.g., from the Mulliken population analysis,  $Z_a$  is the nuclear charge of the atom  $a$ ,  $(r | x^k y^l z^m | s)$  stands for the one-electron integral of the corresponding multipole moment, and  $D_{sr} \chi_r^* \chi_s$  represents the electronic density contribution related to AO's:  $\chi_s$  and  $\chi_r$  and calculated by any method (LCAO MO SCF, CI, MP2, DFT, etc.). We may also use multipole moments expressed by spherical harmonic functions as proposed by Stone.<sup>12</sup>

<sup>9</sup>The clouds might eventually overlap.

<sup>10</sup>If the clouds overlapped, the description of each centre by an infinite number of multipoles would lead to a redundancy (“overcompleteness”). I do not know of any trouble of that kind, but in my opinion trouble would come if the number of origins were large. This is in full analogy with the overcompleteness of the LCAO expansion. These two examples differ by a secondary feature: in the LCAO, instead of moments, we have the s, p, d, ... orbitals, i.e. some moments multiplied by exponential functions.

<sup>11</sup>W.A. Sokalski and R. Poirier, *Chem. Phys. Lett.* 98 (1983) 86; W.A. Sokalski, A. Sawaryn, *J. Chem. Phys.* 87 (1987) 526.

<sup>12</sup>A.J. Stone, *Chem. Phys. Lett.* 83 (1981) 233; A.J. Stone, M. Alderton, *Mol. Phys.* 56 (1985) 1047.