Population Analysis

On p. 665, electronic density ρ is defined. If the wave function is a Slater determinant (p. 397) and assuming the double occupancy of orbitals φ_i, we have (see 11.7)

$$\rho\left(r\right) = 2\left[\left|\varphi_1\left(r\right)\right|^2 + \left|\varphi_2\left(r\right)\right|^2 + \ldots \left|\varphi_{\frac{N}{2}}\left(r\right)\right|^2\right]. \tag{S.1}$$

The density distribution ρ may be viewed as a cloud carrying a charge $-Ne$, and Eq. (S.1) says that the cloud is composed of the individual clouds of the molecular orbitals, each carrying two electrons. On the other hand, in the LCAO (Linear Combination of Atomic Orbitals) approximation, any molecular orbital is represented by a sum of atomic orbitals. If we insert the LCAO expansion into ρ, then ρ becomes a sum of the contributions, each being a product of two atomic orbitals. There is a temptation to go even further and to divide ρ somehow *into contributions of particular atoms*, calculate the charge corresponding to such contribution, and locate the (point) charge right on the nucleus.[1] We might ask, therefore, what the "*electron population*" residing on the particular atoms are (hence the name *population analysis*).

Mulliken Population Analysis

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

$$N = \int \rho\left(r\right) dV = 2\sum_{i=1}^{N/2} \int \left|\varphi_i\left(r\right)\right|^2 dV = \sum_i \sum_{rs} 2c_{ri}^* c_{si} S_{rs} = \sum_{rs} P_{rs} S_{rs} = \mathrm{Tr}(\boldsymbol{PS}), \tag{S.2}$$

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

$$P_{sr} = \sum_i 2c_{ri}^* c_{si}. \tag{S.3}$$

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[1] This number need not be an integer.

The summation r and s may be carried out with highlighting from which atom A the particular atomic orbital comes (we assume that the AO are centered on the nuclei). We get an equivalent formula (A ad B denote atoms):

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

Afterward we may choose the partitionings described next.

Atomic Partitioning

$$N = \sum_A q_A$$

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

where q are the so-called *Mulliken charges*. They are often computed in practical applications and serve to provide information on how much of the electronic density ρ is concentrated on atom A. Such a quantity is of interest because it may be directly linked to the reactivity of atom A, which is often identified with its ability to be attacked by a nucleophilic or an electrophilic agent.[2] Also, if somebody measures the dipole moments, then he would like to know why this moment in a molecule is particularly large. Performing Mulliken analysis, we are able to identify those atoms that are responsible for that. This might be of value when interpreting experimental data.

Atomic and Bond Partitioning

The same summation may 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, and the second term pertains to the atomic pairs $\bar{q}_{AB}$.

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

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[2] We have to remember that besides electrons, this atom has the nucleus. This has to be taken into account when calculating the atomic net charge.

The bond population $\bar{q}_{AB}$ may be treated as a measure of whether the bonding or antibonding character prevails in the $A - B$ atomic interaction.[3] If for two atoms, $\bar{q}_{AB} < 0$, then 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.

Example 1.   Hydrogen Molecule

Let us take the simplest example. First, let us consider the electronic ground state in the simplest molecular orbital approximation; i.e., the two electrons are described by the normalized orbital in the following form (a, b denote the $1s$ atomic orbitals centered on the corresponding nuclei; note that what we take is the famous bonding orbital):

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

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, $\mathbf{S} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}$, and therefore $\mathbf{PS} = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$. Thus, $\mathrm{Tr}\,(\mathbf{PS}) = 2 =$ 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 the electronic population greater than zero*; i.e., the atom-atom interaction is *bonding*.

Let us now consider H_2 with the two electrons occupying the normalized orbital of different character[4] $\varphi_2 = N_2(a - b)$, 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 $\mathbf{PS} = \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$ and $\mathrm{Tr}(\mathbf{PS}) = 2 =$ 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, q_{AB} tells us that this time, the atoms are interacting in the 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[5] S (and the overlap

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[3] P_{rs} is a sum (over the occupied orbitals) of products of the LCAO coefficients of two atoms in each of the occupied molecular orbitals. Equal signs of these coefficients (with $S_{rs} > 0$) means a *bonding* interaction (recall p. 439 and Appendix R available at booksite.elsevier.com/978-0-444-59436-5 on p. e135) and such a contribution increases P_{rs}. The opposite signs of the coefficients (with $S_{rs} > 0$) correspond 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*" have to be exchanged, but the effect remains the same. This means that the product $P_{rs}S_{rs}$ in all cases controls correctly the bonding $(P_{rs}S_{rs} > 0)$ or antibonding $(P_{rs}S_{rs} < 0)$ effects.

[4] The orbital is notorious for its antibonding character.

[5] That is, all the eigenvalues are positive.

matrix is always positively definite), we may introduce the powers of the matrix[6] S^x, where x is an arbitrary real number (in a way shown in see Appendix J available at booksite.elsevier.com/978-0-444-59436-5 on p. e98), and we have $S^{1-x}S^x = S$. Then, we may write[7]

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

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 one has the Mulliken population analysis, if $x = \frac{1}{2}$ then we have the so-called *Löwdin population analysis*, etc.

Multipole Representation

Imagine a charge distribution $\rho(r)$. Let us choose a Cartesian coordinate system. We may compute the Cartesian moments of the distribution as follows: $\int \rho(r)dV$ (i.e., the total charge); $\int x\rho(r)dV$, $\int y\rho(r)dV$, $\int z\rho(r)dV$ (i.e., the components of the dipole moment); $\int x^2\rho(r)dV$, $\int y^2\rho(r)dV$, $\int z^2\rho(r)dV$, $\int xy\rho(r)dV$, $\int xz\rho(r)dV$, $\int yz\rho(r)dV$ - (the components of the quadrupole moment), etc. The moments mean a complete description of $\rho(r)$ as it 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 are the distant parts of $\rho(r)$. If $\rho(r)$ 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 computed (multipole expansion, see Appendix X available at booksite.elsevier.com/978-0-444-59436-5) and indeed, the multipole expansion "*explodes*" (i.e., diverges).[8] This would not happen if the interacting charge distributions did not overlap.

There is also another problem: where should one locate the origin of the coordinate system, with respect to which the moments are calculated? The answer is: *anywhere*. Wherever such origin is located, it is all right from the point of view of mathematics. However, such choices may differ enormously from the practical point of view. For instance, let us imagine a spherically symmetric charge distribution. If the origin is located in its center (as "*most people would do*"), then one has a very simple description of $\rho(r)$ by using the moments–namely, the only nonzero moment is the charge; i.e., $\int \rho(r)dV$. If, however, the origin was located off center, then all the moments would be nonzero. All they are needed to calculate accurately the interaction (with something) of such simple object as a sphere. As we can see, it is definitely better to locate the origin in the center of $\rho(r)$.

But what if the charge distribution $\rho(r)$ were divided into segments and each segment represented by a set of the multipoles? It would be better, though, in view of the above example, to locate the corresponding origins in the centers of the segments. It is clear that in particular,

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[6] They are symmetric matrices as well.

[7] 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 $k \to i, l \to k, i \to l$ in the last formula, we obtain $\text{Tr}(ABC)$.

[8] Note, however, that the first terms (i.e., before the "*explosion*") may give accurate results.

it would be all right if the segments were very small; e.g., the cloud is cut into tiny cubes and one considers every cube's content as a separate cloud.[9] But, then, what are the multipoles for? Indeed, it would be sufficient to take the charges of the cubes only, because they approximate the original charge distribution. In this situation, higher multipoles would certainly be irrelevant. Thus, we now discuss two extreme cases:

- A single origin and an infinite number of multipoles
- An infinite number of centers and the monopoles (charges) only

It is seen 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.[10] This is what the concept of the so-called cumulative atomic multipole moments is all about (CAMM[11]). Besides the isotropic atomic charges $q_a = M_a^{(000)}$ computed in an arbitrary population analysis, we also have 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 spherical ones):

$$
M_a^{(klm)} = Z_a x_a^k y_a^l z_a^m - \sum_{r \in a} \sum_s D_{sr} \left(r | x^k y^l z^m | s \right)
$$

$$
- \sum_{\substack{k' \leq k \ \ l' \leq l \ \ m' \leq m, \\ (k'l'm') \neq (klm)}} \binom{k}{k'} \binom{l}{l'} \binom{m}{m'}
$$

$$
\times x_a^{k-k'} y_a^{l-l'} z_a^{m-m'} \cdot M_a^{k'l'm'},
$$

where $M_a^{(klm)}$ is the multipole moment of the klm order with respect to the Cartesian coordinates x, y, and z located on atom a ($M_a^{(000)}$ standing for atomic charge; e.g., from the Mulliken population analysis); Z_a denotes the nuclear charge of the atom a; $\left(r | x^k y^l z^m | s \right)$ 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 AOs: χ_s and χ_r and calculated by any method (LCAO MO SCF, CI, MP2, DFT, etc.). We may also use the multipole moments expressed by the spherical harmonic functions as proposed by Stone.[12]

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[9] The clouds might eventually overlap.

[10] If the clouds overlap, the description of each center by an infinite number of multipoles would lead to a redundancy ("*overcompleteness*"). I do not know about any trouble of that kind, but in my opinion, there would be difficulties if the numbers of the origins were large. This is fully analogous to 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.

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

[12] A.J. Stone, *Chem. Phys. Lett.*, *83*, 233 (1981); A.J. Stone and M. Alderton, *Mol. Phys.*, *56*, 1047 (1985).