This Week's Citation Classic®

With increasing availability of good all-electron linear combination of atomic orbital-molecular orbital (LCAO-MO) wave functions for molecules, a systematic procedure for obtaining maximum insight from such data became desirable. An analysis in quantitative form was given in terms of breakdowns of the electronic population into partial and total "gross atomic populations" or into partial and total "net atomic populations" together with "overlap populations." Gross atomic populations distribute the electrons almost perfectly among the various AOs of the various atoms in the molecule. [The *SCI®* indicates that this paper has been cited in over 2,060 publications since 1955.]

Robert S. Mulliken
Department of Chemistry
University of Chicago
Chicago, IL 60637

July 30, 1985

Historically, there have been two main approaches to a quantum-mechanical description of chemical bonding in a molecule. One, popularized especially by Linus Pauling,[1] shows how the molecule could be built up from atoms connected by valence bonds. The structure of each atom is described in terms of electrons in atomic orbitals (AOs) together with a suitable arrangement of electron spins. An atomic orbital is a one-electron orbital wave function.

A different approach describes the electrons in a molecule as occupying wave functions called molecular orbitals (MOs), where each MO may be spread over two or more atoms and may help to hold them together. It is usually convenient to approximate an MO by a linear combination of AOs (LCAO-MO). For greater accuracy, the AOs should be somewhat modified as compared with those in free atoms; or also, smaller amounts of additional AOs may be included in the LCAO expression.

My 1954-1955 work included three additional papers on what I called "population analysis" of LCAO-MO wave functions.[2-4] When a chemist looks at such a wave function, he or she may wonder if it is possible to divide the LCAO expressions so that the total electron population is divided into populations in particular AOs or on particular atoms. I found that this can be done in a way that, although not quite right, is very instructive.

The procedure can be illustrated by the simple case of a diatomic molecule containing a population of N electrons in one MO. Let the MO be written in a normalized LCAO form, $\phi = a\phi_A + b\phi_B$, where ϕ_A and ϕ_B are AOs of atoms A and B. The population distribution in the MO can then be obtained as N times the square of the LCAO expression for ϕ. This is $Na^2\phi_A^2 + Nb^2\phi_B^2 + 2Nab\phi_A\phi_B$. I have called Na^2 the net electron population in ϕ_A on A, Nb^2 that in ϕ_B on B, and $2Nab$ the overlap population, since $\phi_A\phi_B$ occupies the region of overlap of the two atoms.

A chemist may now want numbers for the total or "gross" populations on each atom. The gross population on A or B certainly includes the respective net population. But for each atom one must also include a part of the overlap population. The simplest procedure is to divide the latter into two parts allocated one to A and the other to B. Arguing from the fact that the overlap population 2Nab depends symmetrically on atoms A and B, even when a and b are unequal, I assigned just half of it, i.e., Nab, to each atom. Adding this to the net population of either atom, a gross population, N(A) or N(B), is obtained. Note that N(A) + N(B) = N. The procedure is easily generalized to polyatomic molecules and in other ways, for example, to specify numbers of σ and π electrons in a molecule.

As indicated by the *Science Citation Index®*, my procedure for obtaining a population analysis for atoms in molecules described by LCAO-MO wave functions has been very popular. This is in spite of the fact, which I have pointed out more than once, that the numbers it gives have only a somewhat approximate meaning and in some special cases border on nonsense. But fortunately such cases are rare. And even though the method is faulty, it has the insidious appeal of always giving definite numbers.

1. **Pauling L.** *The nature of the chemical bond and the structure of molecules and crystals.*
   Ithaca, NY: Cornell University Press, 1939. 429 p. [See also: **Pauling L.** Citation Classic.
   Current Contents/Engineering, Technology & Applied Sciences 16(4):16, 28 January 1985 and
   CC/Physical, Chemical & Earth Sciences 25(4):16, 28 January 1985.]
2. **Mulliken R S.** Electronic population analysis on LCAO-MO molecular wave functions. II. Overlap populations, bond
   orders, and covalent bond energies. *J. Chem. Phys.* 23:1841-6, 1955. (Cited 805 times.)
3. ------------. Electronic population analysis on LCAO-MO molecular wave functions. III. Effects of hybridization on
   overlap and gross AO populations. *J. Chem. Phys.* 23:2338-42, 1955. (Cited 440 times.)
4. ------------. Electronic population analysis on LCAO-MO molecular wave functions. IV. Bonding and antibonding in
   LCAO and valence-bond theories. *J. Chem. Phys.* 23:2343-6, 1955. (Cited 480 times.)