Population Analysis

A frequent object of quantum chemical studies, is the determination of the electronic configuration and net charge associated with each atom in a polyatomic molecule. Information concerning atomic charge distributions is important in rendering a chemical interpretation of the wave function, leading to a meaningful interpretation and an ability to draw analogies between different chemical phenomena.

From *ab initio* computations, a set of delocalized molecular orbitals is obtained. Many properties can be explained more vividly within the picture of localized (bond) orbitals. Moreover, chemists are interested in chemical properties, which are in the quantum mechanical sense *non-observables*, such as partial charges, bond orders, etc. The calculation of these properties poses the problem of how the calculated electron density should be "distributed within a molecule".

Natural Population Analysis (NPA)

Natural bond orbital (NBO) analysis originated as a technique for studying **hybridization, covalent and non-covalent effects** in polyatomic wave functions.[1] NBO analysis is based on a method for optimally transforming a given wave function into localized form, corresponding to the **one-center ("lone pairs") and two-center ("bonds") elements of the chemist's Lewis structure picture**. In NBO analysis, the input atomic orbital basis set is transformed, via natural atomic orbitals and hybrids into natural bond orbitals (See literature for more details of the localization procedure.):[2]

input basis set → **NAOs** → **NHOs** → **NBOs** → **NLMOs**.

These bond orbitals (NBOs) correspond to the widely-used Lewis picture, in which two-center bonds and lone pairs are localized (It is also possible to localize three-center bonds if required). The NBO for a localized σ bond φ_{AB} between the atoms A and B is formed from directed orthogonal hybrids h_A and h_B (natural hybrid orbitals):

$$\varphi_{AB} = c_A h_A + c_B h_B,$$

and the NHOs in turn are composed from a set of effective-shell atomic orbitals (NAOs), optimized for the chosen wave function.

The orthogonal localized NBOs **are maximally occupied (which can be less than 2)**. The energetically favored Lewis representation and non-covalent (Non-Lewis) effects can be numerically determined. The total energies are given by :

$$E = E(\text{Lewis}) + E(\text{Non-Lewis})$$

where the **non-covalent contributions are typically much less than 1%** of the E(Lewis):

$$E(\text{Non-Lewis}) < 1\%\ E(\text{Lewis}).$$

Therefore, the filled φ_{AB}-NBOs of the "natural Lewis structure" are well suited to describe the covalent effects within a molecule. The generation of bond orbitals also leads to orbitals that are unoccupied and that may be used to describe non-covalent effects (e.g. hyperconjugation). The most important orbitals of these are the antibonds φ^{*}_{AB}:

$$\varphi^{*}_{AB} = c_A h_A - c_B h_B.$$

The antibonding NBOs must not be confused with virtual MOs of the HF-SCF theory. The virtual MOs are strictly unoccupied and thus play no role in the wave function or any observable property, whereas **antibonds generally exhibit non-zero occupancies**, and their contributions lead to a definite energy reduction and change the form of the wave function.

The partly occupied orbitals (φ^{*}_{AB}) lead to differences from the ideal Lewis-picture and thus, to a small non-covalent correction in the model of localized covalent bonds. As pointed out before, the corrections to the Lewis-type picture are usually so small as to be well approximated by simple, second order perturbative expressions. By this perturbation approach, the donor-acceptor interaction involving a filled orbital φ (donor) and an unfilled antibonding orbital φ* (acceptor) can be quantitatively described (See Figure 6.1), the energy lowering is given by:

$$\Delta_{\varphi\varphi^*}E^{(2)} = -2\frac{\left(\left\langle \varphi \middle| \underline{F}\varphi^* \right\rangle\right)^2}{\varepsilon_{\varphi^*} - \varepsilon_{\varphi}}$$

Perturbative donor-acceptor interaction, involving a filled orbital φ and an unfilled orbital φ*, leading to an energy reduction in the resulting occupied orbital.

These non-covalent donor-acceptor interactions (delocalization effects) should not be confused with HOMO-LUMO interactions, nor should they be confused with "ionic resonance" since the quantity of charge, e, transferred, 10^{-3}e, is much less than required for formation of an ion pair. ***If electron density from a bonding orbital, or a lone pair, is donated into an antibonding orbital, it is referred to intramolecular donor-acceptor interaction (also hyperconjugation, anomeric effect etc.).***

The role of antibonds can be seen by generating localized molecular orbitals (**LMO**) from NBOs (bonding and antibonding) which, in turn, are occupied by **exactly two electrons**:

$$\varphi_{AB}^{LMO} = \varphi_{AB} + \lambda\varphi_{CD}^{*} + \ldots \ .$$

Here the small contributions of **the antibonds represent the delocalization of the bonding orbital**, φ_{AB}, from an idealized, strictly-localized Lewis-structure, over antibonding orbitals due to non-covalent, hyperconjungative interactions. Thus, the localized MOs offer a direct description of delocalization.

Note: It may be confusing to some readers that the orthogonal hybrid orbitals, h_A and h_B, are used to describe the bonding between the atoms A and B, because the overlap integral of orthogonal functions is zero. However, here it can be argued that the energy lowering, ΔE, due to the interaction of h_A and h_B, can only come from an integral expression that includes a physical energy operator, $\underline{\mathbf{V}}$, not just an overlap integral, S_{AB}:

$$S_{AB} \ = \ \int \ h_A \, h_B \, d\tau \ = \ 0$$

$$\Delta E \ \sim \ \int \ h_A \, \underline{\mathbf{V}} \, h_B \, d\tau$$

$\underline{\mathbf{V}}$, in turn, comes from separating the Hamiltonian, $\underline{\mathbf{H}}$, into intra- and interatomic terms:

$$\underline{\mathbf{H}} = \underline{\mathbf{H}}^{(0)} + \underline{\mathbf{V}}$$

Applying perturbation theory means that the interatomic energy reduction, ΔE, should be evaluated with the eigenfunctions (h_A, h_B) of the unperturbed Hermitian, $\underline{H}^{(0)}$, and since $\underline{H}^{(0)}$ is Hermitian, these eigenfunctions are necessarily orthogonal:

$$\underline{H}^{(0)} = \underline{H}_A^{(0)} + \underline{H}_B^{(0)}$$

It is therefore fortunate that the operator $\underline{\mathbf{V}}$ is sandwiched between h_A, h_B, since otherwise the "interaction" is zero (as should be expected, since h_A, h_B are, by definition, eigenfunctions of the non-interacting $\underline{H}^{(0)}$, and hence best-possible, in the absence of a perturbation).
The "miracle" is that the physical matrix element:

$$\int h_A \; \mathbf{V} h_B \, d\tau$$

can often be well estimated by an overlap integral:

$$\int h_A' \, h_B' \, d\tau$$

of *non*-orthogonal hybrids:

$$\int h_A \underline{\mathbf{V}} h_B \, d\tau = k \int h_A' \, h_B' \, d\tau \quad \text{(Mulliken approximation)}$$

This simple idea allows us to "visualize" physical interactions in terms of "overlap strength", providing an useful learning-tool for describing bonding in overlap terms.
(Note: It would be a pity if this learning-tool were lost in the NBO framework, but fortunately it is not; the pre-NHO overlaps

$$\int h_A' \, h_B' \, d\tau$$

generally give an accurate visual guide as to what the physical matrix element

$$\int h_A \underline{\mathbf{V}} h_B \, d\tau$$

will be when calculated in all its gory detail.)

Comparison between NPA and Mulliken-Population Analyses

The orthogonal NAOs ($\left\{\phi_i^\alpha\right\}$, nuclear index $\alpha = 1 \ldots M$) provide the basis for an improved "natural population analysis", which corrects many of the deficiencies of the well-known Mulliken population analysis.[3,4] The natural population, q_i^α, of orbital, ϕ_i^α, on atom α, is simply the diagonal density matrix element in the NAO basis:

$$q_i^\alpha = \left\langle \phi_i^\alpha \middle| \underline{\Gamma} \phi_i^\alpha \right\rangle.$$

The one-particle density operator $\underline{\Gamma}$, which depends on the two orbital variables 1 and 1´ is given by:

$$\underline{\Gamma}(1|1') = N \int \Psi(1,2,\ldots N)\, \Psi^*(1',2,\ldots N)\ d\boldsymbol{x}_2 \ldots d\boldsymbol{x}_N\ .$$

These populations, q_i^α, automatically satisfy the Pauli principle ($0 \le q_i^\alpha \le 2$) and give atomic populations, q^α, when summing over all q_i^α:

$$q^\alpha = \sum_i q_i^\alpha\ ,$$

The total number of electrons N^{el} is then given by:

$$N^{el} = \sum_{\alpha=1}^{M} q^\alpha\ .$$

From these population values, the charge transfer, partial charges etc. can be derived.

Comparing NPA with the Mulliken population analysis (MPA), it can be shown:

- **Mulliken populations can have negative values, which do not posses any physical meaning;**
- **Mulliken populations are unduly sensitive to basis sets;**
- **Mulliken populations seem to give an unreasonable physical picture of charge distribution in compounds having significant ionic character.**

The NPA is a true alternative to conventional MPA (which uses a non-orthogonal basis). The population in NPA represent the occupancy of the AOs. As the AOs are orthogonal, all populations are always positive, and the sum gives exactly the total number of electrons. Moreover, the NPA seems to exhibit improved numerical stability and gives a better description of the electron distribution in compounds of high ionic character (no overestimation of the covalent character of a bond), such as those containing metals. Also, the basis set dependency is much smaller than for the MPA.

Bond Orders in the NBO-Program

NLMO Bond order (after Reed and Schleyer)

This type of bond order determination, introduced by Reed and Schleyer,[5,6] is based on the shared occupancies and hybrid overlaps of NAOs, which make up the NLMO. The LMOs can be analyzed by expressing the LMOs in terms of the basis set of natural atomic orbitals (NAOs) (A = number of basis functions):

$$\phi_i = \sum_{j=1}^{A} c_{ij}\chi_j^{NAO} \quad \text{with} \sum_{j=1}^{A} c_{kj}^2 = 1,$$

As the NAO basis is orthogonal, the normalization holds. For closed shell HF wave functions, each LMO is doubly occupied. The number of electrons, n_{iA}, "assigned" to atom A within a LMO i is obtained by summing over the squares of the coefficients from the NAOs on atom A:

$$n_{iA} = 2\sum_{j\in A} c_{ij}^2 \, .$$

Now, the number of covalently-shared electron pairs between atoms A and B is given by the minimum of n_{iA} and n_{iB}, yielding the bond index for the ith LMO b_{iAB}:

$$b_{iAB} = \min(n_{iA}, n_{iB})\, .$$

It is necessary to distinguish between bonding and antibonding interactions; this is done by examining the sign of the overlap integral, S_{iAB}, between the hybrid orbitals on atom A and B within the LMO:

$$S_{iAB} = \left\langle h_{iA}^{LMO} \middle| h_{iB}^{LMO} \right\rangle$$

with

$$h_{iA}^{LMO} = \left[\sum_{j\in A} c_{ij}^2\right]^{-1/2} \sum_{j\in A} c_{ij}\,\chi_j^{NONAO}\, .$$

The "non-orthogonal NAOs" (NONAO) differ from the NAOs through the omission of the NAO interatomic steps. Use of the NAOs, instead of the NONAOs would lead to zero overlap integrals, because the NAOs are orthogonal to each other. However to distinguish between bonding and antibonding interaction, the sign is required (the value is not of interest). The sign of the overlap yields the following bond index:

$$b_{iAB}^{\#} = \operatorname{sgn}(S_{iAB}) \min(n_{iA}, n_{iB}).$$

The bond order index, $b_{iAB}^{\#}$, varies linearly with the number of electrons covalently shared between a pair of atoms (A and B) and linearly with the polarity of the bond. In the LMO basis set, the density matrix is diagonal, so the sum of the bond order indices over all M occupied LMOs yields the total bond order:

$$BO_{AB} = \sum_{i=1}^{M} b_{iAB}^{\#}.$$

The total valency (sum of the total bond orders) of atom A is then found by summing over all atoms:

$$V_A = \sum_{B \neq A} BO_{AB}.$$

Within this procedure, LMOs found in the NPA/NBO analysis were applied. Similar results would be obtained from LMOs derived from other methods.

Bond index for an apolar and an ionic two-electron bond

a) **apolar two-electron bond**

For an apolar two-electron bond between two centers, A and B, we can write:

$$n_{iA} = 1.0 \text{ and } n_{iB} = 1.0,$$

thus the minimum is: $b_{iAB} = 1.0$.

b) **ionic two-electron bond**

In case of an ionic bond ($A^{-}B^{+}$), we can write:

$$n_{iA} = 2 \text{ and } n_{iB} = 0 \text{ with } b_{iAB} = 0.$$

The bond index, $b_{iAB} = 0.5$, corresponds to a 50% covalent and 50% ionic bond ($n_{iA} = 1.5$ and $n_{iB} = 0.5$).

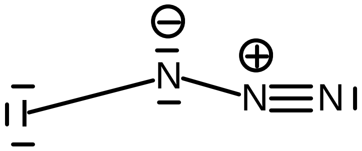
Calculated NLMO bond orders of iodine azide

Atom	N1	N2	N3	I
N1	0.00	2.39	-0.27	-0.06
N2	2.39	0.00	1.12	0.03
N3	-0.27	1.12	0.00	0.67
I4	-0.06	0.03	0.67	0.00

Sum of the NLMO bond orders (valency):

N1: 2.07; N2: 3.54; N3: 1.52; I4: 0.63

Best Lewis-picture according to NBO



Literature

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