

Natural Bond Orbital (NBO) Analysis: Formaldehyde example

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Description: Students learn how to execute NBO calculations, interpret the output by extracting various chemical data such as natural charges, bond types and order (Lewis structure), hybridization, and how to visualize natural bond orbitals. Students will compare NBO and Mulliken charges and their basis set dependence. Students will use Mulliken and NBO atomic charges to compute dipole moments and compare them with proper dipole moments computed using the original densities.

Suggested level: Beginning graduate.

Learning objectives: Learn how to derive bonding picture from quantum chemical calculations. By visualizing the shape of NBOs and MOs, students can compare localized (NBO-based) versus delocalized (canonical MO) representation of the electronic density. By comparing dipole moments computed using point charges with the dipole moments computed using the original density, students will learn the limitations of point charges.

I. WAVE FUNCTIONS, DENSITIES, AND PROPERTIES

Electron density is a compact quantity that can be computed for any many-electron wave function:

$$\rho(1) = \int \Psi^*(1, 2, \dots, N) \Psi(1, 2, \dots, N) d2 \dots dN \quad (1)$$

$$\rho(1) = \sum_{pq} \gamma_{pq}^{MO} \phi_p(1) \phi_q(1) = \sum_{\mu\nu} \gamma_{\mu\nu}^{AO} \xi_\mu(1) \xi_\nu(1) \quad (2)$$

where N is the number of electrons. The matrices γ contain the coefficients representing the density in the basis of molecular (ϕ_p) or atomic (ξ_μ) orbitals (MOs and AOs, respectively). The density matrix contains all the information needed to compute properties derived from one-electron operators. For example, the expectation value of the dipole moment operator simply is:

$$\langle \mu \rangle = Tr[\mu \gamma] = \sum_{pq} \mu_{pq} \gamma_{qp} \quad (3)$$

From the wave function normalization condition, it follows that:

$$Tr[\gamma^{MO}] = Tr[\gamma^{AO} S] = N \quad (4)$$

where $S_{\mu\nu} = \langle \xi_\mu | \xi_\nu \rangle$. By considering γ in the basis of AOs, one can *interpret* traces of γ corresponding to a particular atom (e.g., atom A) as the number of electrons belonging to that atom (N_A):

$$N_A = \sum_{p \in A} [\gamma^{AO} S]_{pp} \quad (5)$$

Similarly, one can interpret the density from the AB block as the number of electrons contributing to the bonding between A and B . This is the essence of various density-based population analysis schemes.

The most basic scheme is the so called Mulliken charges and bond orders where equations like (5) are used.

Natural Bond Orbital (NBO) analysis employs a more sophisticated scheme that uses the concept of natural orbitals and occupation-based symmetric orthogonalization that leads to more robust results. The net result of NBO analysis is that the total density is broken into localized contributions associated with individual atoms giving rise to natural charges and further into 1-center (lone pairs) and two-center (bonds) pieces. This leads to a straightforward determination of Lewis structures. NBO also allows one to determine hybridization of the AOs contributing to a particular bond. For more details, see the NBO paper and NBO and *Q-Chem* user manuals.

Although such schemes are extremely useful for deriving chemical insight, one should remember that neither atomic charges nor bond orders are observables from the quantum mechanical point of view.

II. NBO ANALYSIS OF FORMALDEHYDE

Use the ω B97X-D/6-31G* optimized structure of formaldehyde from the “*Introduction to IQmol: Exploring potential energy surfaces*” lab (refer to the *IQmol* tutorial how to build and optimize structures). At this geometry, perform NBO calculations using the density computed at the Hartree-Fock level of theory with the 6-31G* and 6-31+G* basis sets. Answer the questions below:

- Write down natural charges for each atom and compare them with Mulliken’s net atomic charges. Compare partial charges on C, O, and H in each calculation. Do the charges agree with relative electronegativities?
- Why do the charges change with the basis set? Compare the basis set dependence of Mulliken’s and NBO charges. Without doing calculations, predict how Mulliken charges in 6-31++G* basis will compare with the Mulliken charges in the 6-31G* and 6-31+G* bases.
- Write down the natural electronic configuration for each atom using the computed natural populations of core, valence, and Rydberg orbitals.
- Based on the NBO analysis, specify bond type, bond order, hybridization and write down the natural Lewis structure of formaldehyde. Do the predicted Lewis structures agree with your chemical intuition? Are they basis set dependent? Quantify, how well the density can be mapped into a Lewis structure.
- Using Mulliken’s and NBO natural atomic charges, compute the dipole moment of formaldehyde for each basis set. Compare this dipole moment with the proper dipole moment calculated by *Q-Chem* using Eq. (3).

- Explain the trend in the proper dipole moment (computed as expectation value). Do the changes in Mulliken charges (and the associated dipole moments) agree with the trend in the true dipole moment? What about NBO charges/dipole moments? Explain the difference between the three dipole moments. What did you learn from the observed discrepancy?

Advanced question: Visualize the NBOs and compare them with MOs from the “*Bonding and molecular orbitals*” lab.

Hint: To visualize NBOs, you should generate cube files (see *Q-Chem* user manual). Once you have cube files on your computer, they can be opened and viewed in *IQmol*.

¹ E.D. Glendening, J.K. Badenhop, A.E. Reed, J.E. Carpenter, J.A. Bohmann, C.M. Morales, and F. Weinhold, NBO 5.0., Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001.