A clean and simple approach to wave function interpretation

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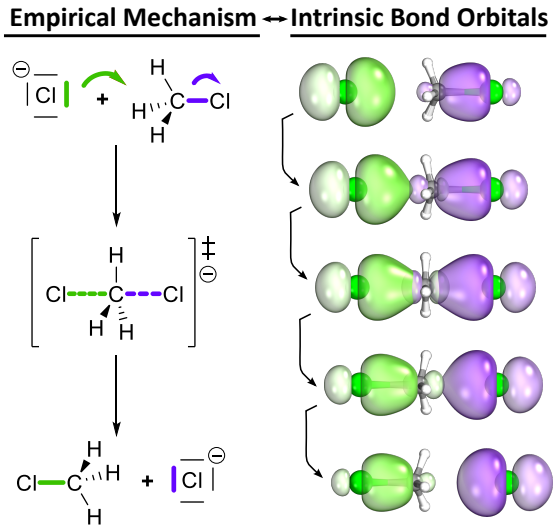
Quantum chemistry allows accurate quantitative calculations of almost any molecular system; however, the obtained wave function expansions are complex and often hard to interpret directly. This difficulty is partly caused by the computational basis sets, which have little correspondence to the classical atomic orbitals (e.g., 1s-2pz for carbon), on which most of chemical thinking is based. We here show that the intuitive chemical picture can be restored via the simple and essentially non-empirical intrinsic atomic orbitals (IAOs)[1], a set of orbitals of the same size and shape as a minimal basis, but perturbed so it exactly spans the occupied space of a given Kohn-Sham wave function.

We show that partial charges and bond orders derived from IAOs correspond closely to chemical intuition. Furthermore, by combining the IAOs with a Pipek-Mezey-inspired orbital localization[1], the occupied orbitals can unitarily transformed into a bond orbital representation (IBOs), in which core orbitals, lone pairs, 2-center bonds, and multi-center bonds are directly seen—not only in simple cases, but also in metal complexes or catalytic reactions. This exact re-expression of a large-basis determinant wave function reveals a classical bonding picture entirely within the framework of first-principles molecular orbital theory—even "curly arrow"-reaction mechanisms can be directly followed[2]. The IBO methodology may thus be a valuable addition to the established techniques of Natural Bond Orbitals (NBOs) and Energy Decomposition Analysis (EDA).

1. G. Knizia, *"Intrinsic Atomic Orbitals: An Unbiased Bridge between Quantum Theory and Chemical Concepts"* J. Chem. Theory Comput. 9, pp 4834–4843 (2013), dx.doi.org/10.1021/ct400687b
2. G. Knizia, J.E.M.N. Klein, *"Electron flow in reaction mechanisms—revealed from first principles"* Angew. Chem. Int. Ed. accepted (2015), dx.doi.org/10.1002/anie.201410637R1

Reaction mechanisms from first principles: IBOs are defined with a continuous localization criterion and can be easily followed across reaction paths[2]. This provides a direct connection from first-principles quantum chemistry to curly-arrow reaction mechanisms.

The used IboView program is freely available under www.iboview.org.



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