

Molecular Electronic Topology and Fragmentation Onset via Charge Partition Methods and Nuclear Fukui Functions: 1,1-Diamino-2,2-dinitroethylene

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Molecular partition methods

In the DMA method,¹⁻³ the molecular charge density is divided into a sum of products of atom-centered Gaussian basis functions, with coefficients determined from the one-electron density matrix. Any individual product of the atom-centered basis functions corresponds to a sum of multipole moments of ranks up to the degree of its polynomial. Therefore, the overlap of two s functions represents a pure charge (monopole), the product of an s with a p function describes a charge plus a dipole, the overlap of two p functions generates charge, dipole and quadrupole moments, and so on. If the orbitals are on different atoms, then each pair of Gaussian functions produces a finite multipole series at a point between the two atoms determined by the exponents of the involved Gaussian orbitals. These multipoles are described by a series on the nearest atom or another expansion site. DMA evaluates these exact representations and approximates each of them by a multipole expansion, usually centered on the atomic nuclei. This series rapidly converges due to the expansion on different points of the electron charge distribution. By combining the electron charge densities with the nuclei positive charge values, we obtain the molecular charge density.

The expansion terms of the DMA method have a clear-cut chemical interpretation. The monopole term represents charges localized on the atomic sites, with bonds between adjacent atoms usually having some degree of charge separation. Dipole vectors pictorially represent charge displacement in the form “- → +”, i.e., by a vector pointing from a negative charge “-” to a positive one “+” of same magnitude. Bond densities can produce significant site dipole moments depending on the different electronegativity values of adjacent atoms and the remaining molecular environment. Dipole moments

express atomic polarization, in general followed by charge separation in the opposite direction.^{4,5} An isolated atom would have a perfectly spherical electron cloud, thus no dipole vector.

The quadrupole moment is the first electrostatic moment to include contributions from the “out-of-plane density”, thereby it is associated with delocalized π electrons; the quadrupole moment can also have contributions from lone pair of electrons.² Since DMA provides an accurate description of the molecular charge density, the method can be used to study intermolecular interactions and to rationalize chemical bonding in different problems.^{4,8}

For dipole moments, a vector property, we report their magnitudes and draw the vectors whereas for quadrupole moments, a tensor, we present a number corresponding to the square root of the sum of all tensor components squared.

The DMA approach then provides an accurate description of the molecular charge density. The method can be considered in a certain sense a generalized population analysis without the drawbacks of the most popular ones.⁹ DMA is complete considering that “offers an exact representation of the potential outside the molecular charge distribution”.¹

In order to describe the nature of the bond strengths and provide quantitative information on impact sensitivity, we used a Coulombic bonding model based on the computed DMA charges.^{10,11} In this way, consider that: (i) bond strengths are dominated by Coulombic interactions between DMA charges and thus are ion-ion like; (ii) only nearest-neighbor atoms contribute to the bond strength; (iii) bond distances are similar. We followed a similar reasoning before to evaluate bond strengths on MoS₂ catalysts.⁸ Naturally, this Coulombic model could be improved in the context of DMA multipoles by including ion-dipole, dipole-dipole and even higher multipole terms. However, these contributions would be considerably smaller,¹² very complicated to calculate and would not change the reasoning given below.

In the DAM method,¹³ the partition of molecular density is done by assigning to each atomic fragment electron density

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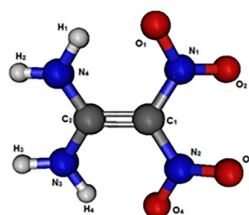
distributions centered on its nucleus plus the part of the closest two-center distributions. The atomic fragments are determined by a least deformation criterion.¹⁴ This criterion involves retaining as much as possible the sphericity of each atom fragment, characteristic of isolated atoms. The two-center distribution is partitioned according to the fast convergence of the multipolar expansion of the long-range potential of the molecular fragments towards the potential of the full (i.e., molecule) distribution.^{15,16} The method furnishes detailed pictures of the molecular electron density as regions of electron accumulation and depletion thereby reproducing the expected chemical concepts. This approach is similar to the electron density difference pictures in solid state,^{17,18} being a powerful method to interpret molecular phenomena.

Both partition methods have a sound physical and chemical basis. In this way, they provide a chemically motivated interpretative framework to examine molecular topological properties.

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Table S1. Computed nuclear Fukui vectors components and magnitude for each atomic site in atomic units



| Atom | Geometry | | | G_i | | | $ G_i $ | Φ_i | | | $ \Phi_i $ |
|------|----------|----------|----------|----------|----------|----------|---------|----------|----------|----------|------------|
| | x | y | z | x | y | z | | x | y | z | |
| C2 | 0.00000 | 0.00000 | 1.37023 | -0.00000 | -0.00000 | -0.02644 | 0.02644 | 0.00000 | 0.00000 | -0.05591 | 0.05591 |
| C1 | 0.00000 | 0.00000 | -0.05158 | -0.00000 | -0.00000 | -0.05375 | 0.05375 | 0.00000 | 0.00000 | 0.00341 | 0.00341 |
| N1 | -0.22591 | 1.19711 | -0.80276 | -0.00308 | 0.03936 | -0.05169 | 0.06504 | 0.00794 | -0.04755 | 0.03106 | 0.05735 |
| O1 | 0.00000 | 2.28940 | -0.24059 | -0.06104 | -0.29533 | -0.14211 | 0.33338 | 0.00304 | 0.01089 | 0.00957 | 0.01481 |
| N2 | 0.22591 | -1.19711 | -0.80276 | 0.00308 | -0.03936 | -0.05169 | 0.06504 | -0.00794 | 0.04755 | 0.03106 | 0.05735 |
| O4 | 0.00000 | -2.28940 | -0.24059 | 0.06104 | 0.29533 | -0.14211 | 0.33338 | -0.00304 | -0.01089 | 0.00957 | 0.01481 |
| O3 | 0.66699 | -1.12075 | -1.93269 | -0.13078 | -0.02448 | 0.30432 | 0.33213 | 0.00341 | 0.00302 | -0.01085 | 0.01177 |
| O2 | -0.66699 | 1.12075 | -1.93269 | 0.13078 | 0.02448 | 0.30432 | 0.33213 | -0.00341 | -0.00302 | -0.01085 | 0.01177 |
| N3 | -0.01898 | -1.14415 | 2.06568 | 0.02712 | 0.01819 | -0.00664 | 0.03332 | -0.00363 | -0.00127 | 0.00418 | 0.00568 |
| N4 | 0.01898 | 1.14415 | 2.06568 | -0.02712 | -0.01819 | -0.00664 | 0.03332 | 0.00363 | 0.00127 | 0.00418 | 0.00568 |
| H2 | -0.16352 | 1.13721 | 3.05272 | 0.00195 | -0.00022 | -0.04049 | 0.04054 | -0.00042 | -0.00156 | -0.00260 | 0.00306 |
| H1 | 0.05598 | 2.00720 | 1.53715 | -0.00019 | -0.00896 | -0.02330 | 0.02496 | -0.00171 | -0.00231 | -0.00511 | 0.00586 |
| H3 | 0.16352 | -1.13721 | 3.05272 | -0.00195 | 0.00022 | -0.04049 | 0.04054 | 0.00042 | 0.00156 | -0.00260 | 0.00306 |
| H4 | -0.05598 | -2.00720 | 1.53715 | 0.00019 | 0.00896 | -0.02330 | 0.02496 | 0.00171 | 0.00231 | -0.00511 | 0.00586 |