An Orbital-Overlap Complement to Atomic Partial Charge
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Partial Charge and Reactivity

- Atomic partial charges obtained from computed wavefunctions are widely used for interpreting quantum chemistry simulations and chemical reactivities of molecules, solids, surfaces, and nanoparticles.
- In many cases partial charge alone gives an incomplete picture of reactivity.

1) PhN is a better nucleophile compared to PhO in Sn2 reactions with Mel, though PhO has a more negative charge on the nucleophilic atom.
2) The carbons of benzene and cyclobutadiene, or those of diamond, graphene, and C60, possess nearly identical partial charges and very different reactivities.
3) Many nucleophiles attack β-unsaturated ketones at the softer β carbon, not at the more positively charged carbonyl carbon.
4) Halide anions F, Cl, Br and I have identical charges but different nucleophilicities.
5) Carbons in aromatic benzene and anti-aromatic cyclobutadiene have nearly identical partial charges, but different reactivities.

Orbital Overlap Distance $D(r^2)$

- The Orbital Overlap Distance $D(r^2)$ is constructed from the Orbital Overlap Function $EDR(r,d)$.
- $EDR(r,d)$ quantifies the extent to which an electron at point $r$ in a calculated wave function overlaps over distance $r^2$.

$EDR(r,d) = \int d^3r \rho_1(r) \rho_2(r) \gamma(r) \rho(r)$

$\gamma(r) = \beta^{-1/2} \exp(-\beta r^2)$

$D(r) = \arg \max_{r} EDR(r,d)$

- Plots of $D(r^2)$ on density isosurfaces complements molecular electrostatic potentials.
- The atomic overlap distance $D_A$ is defined as the average overlap length of electrons assigned to atom A.

$D_A = \int d^3r \omega_1(r) D(r) \omega_2(r)$

where $\omega(r)$ is the Hirschfeld weight for atom A.

- $D_A$ complements computed Hirschfeld charges $Q_d$ by measuring the size of orbital lobes that best overlap with the wavefunction around an atom.
- Compact, chemically stable atoms tend to have overlap distances smaller than chemically soft, unstable atoms.

Combining Charge and Overlap Distance

- Combining atomic charges ($Q_d$) and overlap distances ($D_A$) captures trends in aromaticity, nucleophilicity, allotrope stability, and substituent effects.

Non-trivial Predictions for Nanomaterials

- Aromatic benzene, non-aromatic hexatriene, and anti-aromatic cyclobutadiene have nearly identical $Q_d$, their computed $D_A$ clearly distinguish the relatively unstable, weakly bound, diffuse carbons of cyclobutadiene.

Surface Overlap Distance

- Plots of overlap distance $D(r^2)$ on molecular surfaces like electron or spin density isosurfaces captures chemical hardness/softness, acid-base interactions, halogen bonding and other π-π interactions.
- Maximum surface value of $D(r^2)$ complements molecular electrostatic potential (ESP).

Capturing the Effects of Substituents

- Calculated in gas phase at B3LYP/6-31+(G,d,p) level.
- Relation is nearly linear within a substituent class, different substituents have different trends.
- More negative $Q_d$ give larger $D_A$, as only relatively diffuse orbitals are available to hold added electron density.
- Binding carbon to large, "puffy" bromine atoms makes its orbitals larger, giving a relatively large $D_A$, whereas compact fluorine atoms makes the carbon orbitals smaller, giving a relatively small $D_A$.

Atomic Overlap Distance and Aromaticity

- Calculated in gas phase at B3LYP/6-31+(G,d,p) level.
- The outer Au atoms have unusually small $D_{Au}$, while the central atom has an unusually large $D_{Au}$.
- Rationale for a big body of experimental and theoretical work on MAu$_n$ hexagons, in which the central atom is replaced with sproton M.

Selectivity in Protein-Ligand Interactions

- Why gold-specific protein GolB, shows higher selectivity for Au over Cu, though former has lower ESP?

References