

## Chemical Bonding

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## An Orbital-Overlap Complement to Atomic Partial Charge

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**Abstract:** Atomic partial charges are widely used to predict reactivity. Partial charge alone is often insufficient: the carbons of benzene and cyclobutadiene, or those of diamond, graphene, and  $C_{60}$ , possess nearly identical partial charges and very different reactivities. Our atomic overlap distance complements computed partial charges 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. We show here how combining atomic charges and overlap distances captures trends in aromaticity, nucleophilicity, allotrope stability, and substituent effects. Applications to recent experiments in organic chemistry (counterintuitive Lewis base stabilization of alkenyl anions in anionic cyclization) and nanomaterials chemistry (facile doping of the central atom in  $Au_7$  hexagons) illustrate this combination's predictive power.

**P**artial charges obtained from computed wavefunctions are widely used for interpreting quantum chemistry simulations of molecules, solids, surfaces, and nanoparticles.<sup>[1]</sup> In many parts of chemistry, orbital-overlap-type effects are more important than partial charges, and partial charge alone gives an incomplete picture of reactivity. For example: a)  $PhS^-$  is a better nucleophile compared to  $PhO^-$  in  $S_N2$  reactions with MeI, though  $PhO^-$  has a more negative charge on the nucleophilic atom.<sup>[2]</sup> b) Deprotonated amides perform nucleophilic attack via the less negative nitrogen, rather than the more negative oxygen, in anionic cyclization of *o*-alkynyl benzamides.<sup>[3]</sup> c) Halide anions  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  have identical charges but different nucleophilicities. d) Many nucleophiles attack  $\alpha,\beta$ -unsaturated ketones at the softer  $\beta$  carbon, not at the more positively charged carbonyl carbon.<sup>[4]</sup> e) Allotropes diamond, graphene, and  $C_{60}$  have identical partial charges of zero but different heats of formation. f) Close-packed surfaces of different transition metals have similar partial charges near zero, but different chemisorption behavior. g) Carbons in aromatic benzene and anti-aromatic cyclobutadiene have nearly identical partial charges, but different reactivities. h) Adsorbates on metal surfaces can have similar partial atomic charges but different chemistry.<sup>[5]</sup>

There have been many efforts to quantify aspects of reactivity missing from partial atomic charges. Conceptual density functional theory (DFT) quantifies global properties.<sup>[6]</sup> Local information is provided by coordination num-

bers,<sup>[7]</sup> atomic radii<sup>[8]</sup> and kinetic energies,<sup>[9]</sup> Fukui functions,<sup>[10]</sup> the quantum theory of atoms-in-molecules (QTAIM),<sup>[11]</sup> local kinetic energies,<sup>[12]</sup> steric energies<sup>[13]</sup> and ionization potentials,<sup>[14]</sup> d-band filling,<sup>[15]</sup> the electron localization function,<sup>[16]</sup> and other tools<sup>[17]</sup> too numerous to list exhaustively. Many of these tools are arguably under-utilized by practicing chemists,<sup>[18]</sup> and few are as widely adopted as atomic partial charge. Building upon these powerful tools, in a way that is accessible to experimentalists, can help make quantum chemistry more useful.

We introduced the atomic overlap distance  $D_A$  as the average size of the molecular orbital lobes contributing to the wavefunction around atom A, i.e., the size of orbitals that best overlap with A.<sup>[19]</sup> Chemically hard, tightly bound atoms tend to have  $D_A$  smaller than softer, loosely bound atoms (Table 1).

**Table 1:**  $Q_C$  and  $D_C$  computed for representative carbons.

Molecule	$Q_C$ [e]	$D_C$ [bohr]
Isolated C atom (57) <sup>[a]</sup>	0	2.12
Methane (59)	−0.19	1.78
Methanol (66)	−0.05	1.68
Benzene (83)	−0.06	1.66
Cyclobutadiene (84)	−0.06	1.69
$CF_4$ (64)	+0.28	1.37

[a] Molecule numbers from Table S1-1.

We compute  $D_A$  from the electron delocalization range function  $EDR(\mathbf{r};d)$ , which sums all occupied orbitals' overlap with a test 1s-type orbital centered at point  $\mathbf{r}$  and decaying over distance  $d$ .  $D_A$  is the atomic (Hirshfeld<sup>[20]</sup>) average of  $D(\mathbf{r}) = \text{argmax}_d EDR(\mathbf{r};d)$  (see the Supporting Information (SI)).  $Q_A$  is the corresponding Hirshfeld charge. Ref. [19] provides definitions, algorithmic details, and a few preliminary examples. Further details of our DFT calculations, and tests of method and basis dependence, are provided in the SI. The EDR and  $D(\mathbf{r})$  are available in the Gaussian 16 and NCIPLOT packages.<sup>[21]</sup>

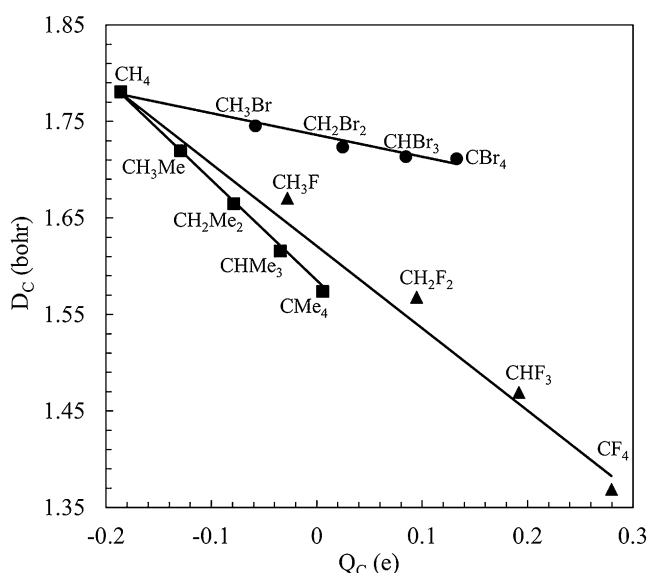
Applying the atomic overlap distance to the above examples shows how it functions as a partner to partial charge. a) The sulfur of  $PhS^-$  ( $Q_S = -0.56e$ , valence  $D_S = 2.02$  bohr, molecule **193**, Table S1) has overlap distance substantially larger than the oxygen of  $PhO^-$  **194** ( $Q_O = -0.82e$ , valence  $D_O = 1.36$  bohr), implying  $PhS^-$  is a better soft nucleophile despite its less negative charge.<sup>[22]</sup> b) The nitrogen of deprotonated *o*-phenyl alkynyl benzamide **195** ( $Q_N = -0.36e$ ,  $D_N = 1.20$  bohr) has overlap distance larger than the oxygen ( $Q_O = -0.48e$ ,  $D_O = 1.10$  bohr), matching experimental evidence that nitrogen is the preferred nucleophile despite its less negative charge.<sup>[3]</sup> c) Halides' valence  $D_{F(-)} = 1.2$ ,  $D_{Cl(-)} = 1.9$ ,  $D_{Br(-)} = 2.1$ ,  $D_{I(-)} = 2.4$  bohr distinguish species further down the periodic table. d) Butenone

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**196**  $\beta$  carbon ( $Q_{C\beta} = -0.07e$ ,  $D_{C\beta} = 1.30$  bohr) is less positively charged than the carbonyl carbon ( $Q_{CO} = 0.17e$ ,  $D_{CO} = 1.18$  bohr), however, the  $\beta$  carbon's larger overlap distance is consistent with improved orbital overlap with soft nucleophiles. e) Diamond **197**, graphene **198**, and  $C_{60}$  **199** have negligible atomic charges, whereas  $D_{\text{diamond}} = 1.54$  bohr,  $D_{\text{graphene}} = 1.58$  bohr,  $D_{C60} = 1.60$  bohr illustrate diamond's thermodynamic stability. f)  $Cu_{13}$ ,  $Ag_{13}$ ,  $Au_{13}$  icosahedra, minimal models for transition metal clusters & surfaces, have average atomic charge zero, whereas average valence  $D_{Cu} = 0.87$ ,  $D_{Ag} = 1.03$ ,  $D_{Au} = 1.09$  bohr highlight periodic trends. g) Table 1 shows that anti-aromatic cyclobutadiene **84** has  $Q_C$  comparable to aromatic benzene **83**, but slightly larger  $D_C$  consistent with its lower stability. Charged systems have similar trends: cyclopentadienyl cation **189** has  $D_C = 1.66$  bohr larger than cyclopropenyl cation **188** or cycloheptatrienyl cation **190** ( $D_C = 1.60$  bohr), cyclopentadienyl anion **33** has  $D_C = 1.70$  bohr smaller than cyclopropenyl **55** ( $D_C = 1.94$  bohr) or cycloheptatrienyl **56** ( $D_C = 1.73$  bohr).

Figure 1 shows trends in  $Q_C$  and  $D_C$  of  $CH_nR_{4-n}$ . Figures S3–S5 show similar trends for anions, cations, and radicals. More negative  $Q_C$  give larger  $D_C$ , as only relatively diffuse orbitals are available to hold added electron density.



**Figure 1.** Partial charge  $Q_C$  and overlap distance  $D_C$  of the central carbon in  $CH_nR_{4-n}$ ,  $R = \text{Me, F, Br}$ .

Whereas the relation is nearly linear within a substituent class, different substituents have different trends. For example,  $CHBr_3$  **62** has  $D_C$  larger than  $CH_2F_2$  **130** despite nearly identical  $Q_C$ , consistent with bromine's leaving group ability. Other situations where  $D_C$  distinguishes carbons with similar charge but different chemistry include the  $D_C > 2$  bohr of isolated atoms (**149**, **57**, **1**), the large  $D_C = 1.72$  bohr of reactive carbonium  $CH_5^+$  **166**, and the  $C=N$  carbons of acetonitrile **77** and methyl isocyanide **108**, whose modest differences in  $Q_C$  0.08e vs.  $-0.11e$  and large differences in  $D_C$  1.62 bohr vs. 1.90 bohr highlight isocyanide reactivity.

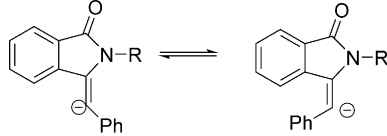
Combining atomic charge and overlap distance captures substituent effects in monosubstituted benzenes (Table S2). Experimental substituent effects are distilled in Hammett's  $\sigma_m$  and  $\sigma_p$  parameters.<sup>[23]</sup> We fit  $\sigma_m$  and  $\sigma_p$  to the *meta* and *para*  $Q_C$  and  $D_C$  of 33 monosubstituted benzenes (Figure S7):

$$\sigma = \alpha Q_C + \beta D_C + \gamma \quad (1)$$

The fit reproduces experiment, with  $R^2 = 0.96$ , standard error 0.075;  $\alpha = 21/e$ ,  $\beta = 79/\text{bohr}$ ,  $\gamma = 134$ ; standard error in parameters  $\alpha = 1/e$ ,  $\beta = 8/\text{bohr}$ ,  $\gamma = 13$ . Fitting  $Q_C$  alone ( $\beta = 0$ ) degrades the fit to  $R^2 = 0.88$ , standard error 0.12;  $\alpha = 29/e$ ,  $\gamma = 1.7$ , standard error in parameters  $\alpha = 1/e$ ,  $\gamma = 0.08$ .  $Q_C$  captures broad outlines of substituent effects, and  $D_C$  adds useful details.

We close with two applications of the atomic overlap distance to problems we have recently studied: one organic reaction, and one problem in nanoparticle chemistry. In both, the atomic overlap distance provides nontrivial and never before reported predictions for reactivity. Table 2 shows the

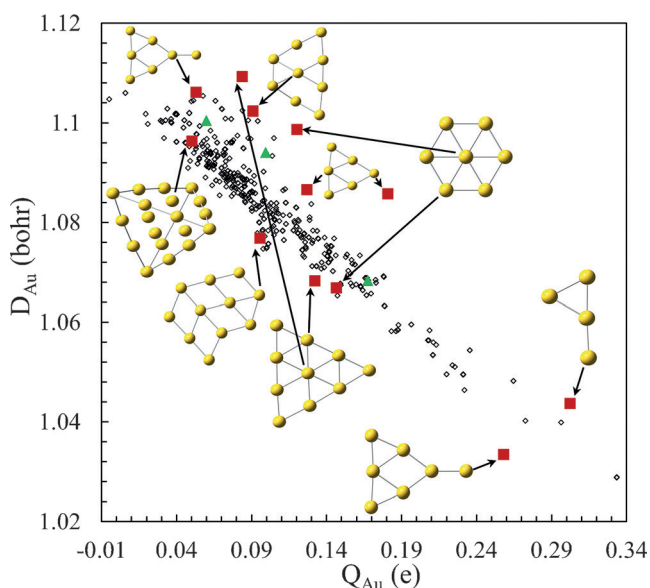
**Table 2:** Z:E tautomerization of an alkenyl anion intermediate implicated in aromatic alkynols and alkynyl amine cyclization selectivity. Tautomerization equilibrium constants  $K_{eq}$  predicted for anionic intermediate and protonated product.<sup>[a]</sup>

R		
	Z-5-exo	E-5-exo
<hr/>		
	$K_{eq}$ , anionic intermediate	$K_{eq}$ , protonated product
<hr/>		
$CH_3$	48 (36)	14
$CH_2CH_2NEt_2$	47 (58)	5
$CH_2F$	74 (97)	5
$CH_2tBu$	250 (880)	42
$CHF_2$	470 (1800)	240

[a] Results in parenthesis are computed without continuum solvation.

*o*-alkynyl benzamide cyclization of example (b). Z-5-*exo* vs. E-5-*exo* selectivity is predicted to depend on the depicted alkenyl anion intermediate.<sup>[24]</sup> Whereas the anionic carbon has  $Q_C = -0.30$ ,  $D_C = 1.70$  bohr nearly identical in Z and E forms, the  $R = CH_3$  group's  $D_H$  increases 1.94 bohr (Z) to 1.99 bohr (E). The atomic overlap distance predicts that R group C–H bonds are just the right size, and at just the right distance, to stabilize the E carbanion. This extension of  $R = NH_2$  stabilization<sup>[24b]</sup> is consistent with computed C–H bond lengths and orders (see the SI) and with the Z products seen experimentally without a stabilizing R.<sup>[3a]</sup> Simulations predict that C–H bond polarization ( $R = CHF_2$ ) further stabilizes E intermediate.  $R = CH_2CH_2NEt_2$  group's experimentally demonstrated unusual selectivity to E-5-*exo* cyclization<sup>[24c]</sup> is rationalized as stabilization of the E anion by the R group's many polarized C–H bonds (Figure S8). Though details are sensitive to simulation conditions, this explanation for how a Lewis base stabilizes an adjacent carbanion is nontrivial.

Figure 2 shows the atomic overlap distance's nontrivial predictions for nanomaterials chemistry, illustrated by the site-dependent reactivity of experimentally demonstrated<sup>[25]</sup> Au<sub>7</sub><sup>+</sup> hexagons. Gold clusters' catalytic activity<sup>[26]</sup> is a sensitive



**Figure 2.** Partial charge  $Q_{\text{Au}}$  vs. overlap distance  $D_{\text{Au}}$  in 60 cationic gold clusters. Structures of interesting outliers are included.

function of geometry.<sup>[27]</sup> Partial charge alone provides limited insight into the most reactive parts of a cluster.<sup>[28]</sup> Figure 2 plots  $Q_{\text{Au}}$  vs. valence  $D_{\text{Au}}$  for 60 clusters Au<sub>3</sub><sup>+</sup>–Au<sub>20</sub><sup>+</sup>.<sup>[25]</sup> Small  $D_{\text{Au}}$  occurs for stable Au<sub>19</sub><sup>+</sup> and Au<sub>20</sub><sup>+</sup>.<sup>[27e]</sup> Aromatic<sup>[27c]</sup> Au<sub>5</sub>Zn<sup>+</sup> (triangles) has small  $D_{\text{Au}}$  given the small cluster size. Hexagonal Au<sub>7</sub><sup>+</sup> (top right) has small  $D_{\text{Au}}$  in the outer ring and unusually large  $D_{\text{Au}}$  for the central atom. Planar Au<sub>9</sub><sup>+</sup> and Au<sub>10</sub><sup>+</sup> show similar trends. This predicted reactivity of the central atom rationalizes previous evidence for facile doping of this atom. Experiments confirm this structure for TiAu<sub>6</sub><sup>–</sup>, VAu<sub>6</sub><sup>–</sup>, CrAu<sub>6</sub><sup>–</sup>,<sup>[27b]</sup> and YAu<sub>6</sub>.<sup>[29]</sup> Simulations predict this is a low-energy structure for MAu<sub>6</sub><sup>0/–</sup> (M = Ni, Pd,<sup>[30]</sup> Mg,<sup>[31]</sup> V,<sup>[30c,32]</sup> Sc, Ti, Cr,<sup>[30c]</sup> and Mn<sup>[30c,33]</sup>) and MAu<sub>6</sub><sup>+</sup> (M = Ti, V, Cr, Mn, Fe<sup>[34]</sup>). Figure S9 confirms that CO adsorbs strongly to the central Au.

To summarize, the atomic overlap distance complements atomic partial charges, and their combination provides a more complete picture of site-dependent reactivity.

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## Conflict of interest

The authors declare no conflict of interest.

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