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Lewis–Langmuir Atomic Charges

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In spite of the very great advances made in computational quantum chemistry during the past 35 years, the majority of chemists rely primarily on Lewis dot structures for bonding insight and on formal charges and oxidation number for atomic charge information. The purpose of this communication is to call attention to a simple extension of the formal charge formula which provides a more realistic manifestation of bond polarity and significantly enhances its research utility. The concept of formal charge was introduced by Langmuir,[1] and the formula for computing it (on atom A) is very well-known:[2]

$$\text{(formal charge on A)} = \text{(group no. of A)} - \text{(no. of unshared electrons on A)} - \text{(no. of bonds connected to A)}$$

Oxidation number, the number of electrons added to or taken from an atom upon formation of fully ionic bonds, is calculated by the same formula, but assigns bonding electrons entirely to the more electronegative atoms.[2,3] Since formal charge is based on equal sharing of electrons between bonded atoms, a more natural balance between the covalent and ionic extremes can be achieved by a fractional electronegativity weighting that smoothly connects them (χ_A, χ_B, atomic electronegativity values for bond A–B):

$$\text{(Lewis–Langmuir charge on A)} = \text{(group no. of A)} - \text{(no. of unshared electrons on A)} - 2\sum_{B} \frac{\chi_A}{\chi_A + \chi_B} \quad (1)$$

For $\chi_A = \chi_B$, eq 1 returns to the familiar formal charge formula; for $\chi_A \gg \chi_B$, the sum over B equals 2, and the bonding electrons are both on A. The other oxidation number extreme occurs for $\chi_A \ll \chi_B$, in which case the sum over B is 0 and both bonding electrons are attached to atom B. Figure 1 plots the bond weighting function, $2\chi_A/(\chi_A + \chi_B)$, versus χ_A for bond A–B using typical values for χ_B. The extreme simplicity of eq 1 can make it a powerful aid to interpretation in organic and inorganic research.

Although Lewis, Langmuir, and others understood the polarity of bonds between nonidentical atoms,[1,4] Pauling's formulation of electronegativity and equation for percent ionic character were the first numerical expressions of this concept, and research developments of it were largely directed to bond energies rather than atomic charges.[4] However, an important paper by Waser[5] made use of percent ionic character to obtain electronegativity corrections to formal charges. Unfortunately, this approach has not been followed up or further improved due to the difficulty[4] in determining a general and accurate equation for percent ionic character. This problem is obviated in eq 1, where the electronegativity fraction is used as an interpolation scheme between no charge separation across the bond and complete charge separation. For N_2O, Waser[5] used the following Lewis structures with the first weighted twice the second and obtained the atomic charges shown on top of the atoms (right side, below).

$$:N{\equiv}N^{+}{-}O^{-}: \;\leftrightarrow\; :N^{-}{=}N^{+}{=}O: \qquad \begin{array}{ccc} -0.33 & +1.08 & -0.75 \\ N & N & O \\ -0.33 & +1.10 & -0.77 \end{array}$$

Equation 1 produces the values beneath the atoms. This example, and others like it,[6] show that eq 1 has the same conceptual basis as Pauling and Waser's original research.[4]

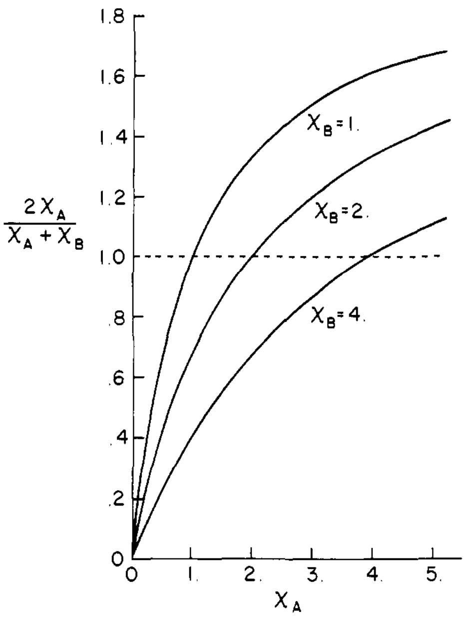

Figure 1. Bond weighting function, $2\chi_A/(\chi_A + \chi_B)$, versus χ_A with χ_B as a parameter for bond A–B. Curves for $\chi_B = 1$, 2, and 4 are shown. Note that $2\chi_A/(\chi_A + \chi_B) = 1$ is the condition for a pure covalent bond between atoms A and B and the crossing points for the $\chi_B = 1$, 2, and 4 curves correspond to the standard formal charge. The oxidation state corresponding to both electrons on atom B is at the origin, and the oxidation state for both electrons on atom A is the line $2\chi_A/(\chi_A + \chi_B) = 2$.

In order to test eq 1, we made 26 comparisons of trends and relative magnitudes in 17 molecules using Mulliken atomic charges[7] obtained from ab initio molecular orbital calculations with the 6-31G* basis set. Although numerous other methods of obtaining atomic charges from electronic wave functions have been proposed, and errors in the Mulliken prescription are well-known,[8] it is by far the most widely employed scheme and it gives a first evaluation of eq 1.[6] We have also employed Allred and Rochow[9] electronegativities although the choice of scale is not critical.[10] Lewis–Langmuir heavy atom charges are given in the form of ratios followed by the Mulliken charge ratio [in brackets]: FH/OH_2, $(-0.302/-0.456) = 0.66$ [0.60]; OH_2/NH_3, $(-0.456/-0.495) = 0.92$ [0.87]; NH_3/CH_4, $(-0.495/-0.255) = 1.94$ [1.51]; ClH/FH, $(-0.125/-0.301) = 0.41$ [0.47]; SH_2/OH_2, $(-0.103/-0.456) = 0.23$ [0.25]; PH_3/NH_3, $(0.100/-0.495) = -0.20$ [−0.04]; SiH_4/CH_4, $(0.467/-0.255) = -1.83$ [−0.83]; CH_4/C_2H_6, $(-0.255/-0.191) = 1.34$ [1.39]; C_2H_6/C_2H_4, $(-0.191/-0.128) = 1.49$ [1.35]; C_2H_4/C_3H_6, $(-0.128/-0.128) = 1.00$ [0.98]; C_2H_4/C_2H_2, $(-0.128/-0.064) = 2.00$ [1.28]. However, using eq 1 produces a common hydrogen charge for C_2H_6, C_2H_4, and C_2H_2, even though these are known to be increasingly positive. This is obviated by the common assumption that electronegativities increase with the percent s character on carbon in a C–H hybrid orbital,[11] $sp^3 \rightarrow sp^2 \rightarrow sp$. We assume a small increase[11] for each change in hybridization and obtain the carbon

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[2] Gillespie, R. J.; Humphreys, D. A.; Baird, N. C.; Robinson, E. A. *Chemistry*; Allyn and Bacon, Inc.: Toronto, 1986; Chapters 4 and 7.

[3] Carroll, J. A. *J. Chem. Ed.* **1986**, *63*, 28.

[4] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; Chapters 1 and 3.

[5] Waser, J. In *Structural Chemistry and Molecular Biology*; Rich, A., Davidson, N., Eds.; W. H. Freeman: San Francisco, 1968; pp 675–684.

[6] An extended comparison for other molecules (including those with nonzero formal charge) and for other atomic charge definitions is to be published separately.

[7] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343.

[8] Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985.

[9] Allred, A. L.; Rochow, E. C. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.

[10] A new definition of electronegativity, the average one-electron energy of valence-shell electrons in ground-state free atoms, which has recently been proposed (Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003), yields Lewis–Langmuir atomic charges very close to those obtained from the Allred and Rochow scale.

[11] Mulliken, R. S. *J. Phys. Chem.* **1937**, *41*, 318. Walsh, A. D. *Discuss. Faraday Soc.* **1947**, *2*, 18. A 1% increase was assumed for the values quoted, but changes 10 times greater do not significantly modify the overall agreement with Mulliken charge ratios.

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and hydrogen charge ratios, respectively: CH_4/C_2H_6, $(-0.255/-0.191) = 1.34$ [1.39], $(0.064/0.064) = 1.00$ [1.04]; C_2H_6/C_2H_4, $(-0.191/-0.138) = 1.38$ [1.35], $(0.064/0.069) = 0.93$ [0.90]; C_2H_4/C_3H_6, $(-0.138/-0.138) = 1.00$ [0.98], $(0.069/0.069) = 1.00$ [0.98]; C_2H_4/C_2H_2, $(-0.138/-0.074) = 1.87$ [1.28], $(0.069/0.074) = 0.93$ [0.64]. Hydrogens are getting more positive, as required, and the matching to Mulliken ratios is improved for both carbon and hydrogen. This example shows how the simplicity of eq 1 can be employed to separate different effects influencing atomic charge and help identify their origin. Lewis–Langmuir/Mulliken charge ratios for F and Cl each in two different environments show notable commonality: FH, $(-0.302/-0.517) = 0.58$; F_3Cl, $(-0.183/-0.308) = 0.59$; ClH, $(-0.125/-0.242) = 0.52$; ClF_3, $(0.546/1.34) = 0.41$. Separation of charge between atoms in functional groups, e.g., CO and CN, is also an important test, and the ratio of charge shifts, Lewis–Langmuir/Mulliken, for H_2CO, $(-0.333 - 0.205)/(-0.416 - 0.135) = 0.98$, and HCN, $(-0.307 - 0.243)/(-0.379 - 0.066) = 1.24$, shows a similarity in these two charge definitions. Likewise, the corresponding ratio of the large charge shift on H when it changes its attachment from the most electropositive to the most electronegative element, LiH → FH, is $(-0.388 - 0.302)/(-0.177 - 0.517) = 0.99$. Overall, these examples demonstrate a parallelism between Lewis–Langmuir and Mulliken charges.

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Synthesis and Characterization of the "Chiral Wall" Porphyrin: A Chemically Robust Ligand for Metal-Catalyzed Asymmetric Epoxidations

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One of the most important problems in modern organic synthesis is the development of new methods for the enantioselective transformation of prochiral substrates into optically active products. In general, one of the most appealing solutions to this problem is chiral catalysis. Recent years have seen a tremendous growth in the number of practical asymmetric catalysts and some, in particular the Sharpless catalyst for the asymmetric epoxidation of allylic alcohols,[1] are commonly employed in the synthesis of optically active natural products. As part of a program aimed at developing a new family of rationally designed asymmetric catalysts, we have embarked on the construction of optically active tetraarylporphyrin macrocycles. In this report, we describe the synthesis of 5α,10β,15α,20β-tetrakis[(*R*)-1,1′-binaphth-2-yl]porphyrin ($TBNPH_2$; **1**). Since metalloporphyrins catalyze a number of interesting reactions,[2] porphyrin **1** is a potential general chiral ligand for several enantioselective metal-mediated transformations.

Our approach to $TBNPH_2$ took advantage of the accessibility of optically pure (*R*)-binaphthaldehyde (**2**) by the elegant route of Meyers.[3] Condensation of this aldehyde with pyrrole was effected in methylene chloride at room temperature in the presence of a catalytic amount of BF_3–etherate (Lindsey conditions,[4] Figure 1). Following oxidation of the resultant tetrapyrrole with *p*-chloranil, the crude $TBNPH_2$ was purified by chromatography on a florisil flash column in 9% isolated yield.

Table I. Catalytic Asymmetric Epoxidation of Olefins with MnTBNPCl[a]

substrate	enantiomeric excess, %	catalytic efficiency[d]
styrene[b]	20	240
p-chlorostyrene	20	160
2-vinylnaphthalene	20	220
trans-β-methylstyrene	15	190
cis-β-methylstyrene[c]	40	200

[a] Epoxidations were performed following Meunier conditions (hypochlorite as oxidant in a two-phase system, 0.03 mol % catalyst).[10] Chemical yields were calculated by GC analysis. The epoxides were purified by flash chromatography on silica (CH_2Cl_2) and the degree of asymmetric induction was determined by NMR with the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(**III**).[9] [b] Phenylacetaldehyde, a common side product of porphyrin-catalyzed styrene epoxidations, was not observed. [c] Analysis of the product by ^1H NMR showed a small amount of optically active *trans*-epoxide in addition to *cis*-epoxide (7:1 cis:trans). [d] Number of turnovers in 15 min.

The purified material was free of other atropisomers[5] as determined by 1-D and 2-D COSY NMR analyses (Figure 2).[6] The COSY spectrum (data not shown) allowed the unambiguous assignment of *all* resonances in the aromatic region to a single binaphthyl (δ 8.28–6.44, 13 protons). This indicated that the compound was either the $\alpha,\beta,\alpha,\beta$ or the $\alpha,\alpha,\alpha,\alpha$ atropisomer, since only those two possibilities have four identical binaphthyls. Proof that this was indeed the $\alpha,\beta,\alpha,\beta$ form came from the observation of two singlet β-pyrrolic resonances (δ 8.58, 8.36; 4 protons each)—the spectrum of the $\alpha,\alpha,\alpha,\alpha$ compound would have exhibited two doublets. The remaining atropisomers eluted as an inseparable mixture. Yields of recovered material suggest that the desired $\alpha,\beta,\alpha,\beta$ isomer constitutes approximately 40% of the porphyrin product. The porphyrin was readily metallated[7] by standard procedures (Figure 1).

Each identical face of the porphyrin possesses C_2 symmetry. We predicted that a prochiral alkene substrate would prefer to orient one of its enantiofaces toward the active metal center due to nonbonded steric interactions between the olefin substituents and the chiral binaphthyl "walls".

The results of preliminary investigations into the properties of Mn^{III}TBNPCl as an epoxidation catalyst are shown in Table I. Extremely high catalytic efficiency and moderate enantioselectivites for a variety of unfunctionalized olefin substrates were observed. The enantiomeric excesses (ee's) compare favorably with the state-of-the-art for asymmetric epoxidation of unfunctionalized alkenes. For example, Groves and Myers employed a chiral binaphthoic acid derivatized porphyrin as a catalyst for oxygen atom transfer from iodosylbenzene to alkenes. They obtained enantioselectivities ranging from 20 to 51%.[8] A

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[2] See for example: Callot, H. J.; Metz, F.; Piechoki, C. *Tetrahedron* **1982**, 2365–2369 (cyclopropanation of alkenes). Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462–8470 (hydroxylation of alkanes). Aoyama, Y.; Tanaka, Y.; Yoshida, Y.; Toi, H.; Ogoshi, H. *J. Organomet. Chem.* **1987**, *329*, 251–266 (aldol condensation).

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[5] Four atropisomers are possible depending on which face of the porphyrin plane the second naphthalene of each binaphthyl is situated. Only the desired $\alpha,\beta,\alpha,\beta$ has two identical faces—a crucial point since the reaction may occur on either face of the macrocycle. Our choice of Lindsey's mild thermodynamic cyclization conditions was based on the idea that the $\alpha,\beta,\alpha,\beta$ suffers the least steric interaction between neighboring binaphthyls and would be formed in greater than statistical proportions.

[6] Independent confirmation that this compound is a single atropisomer was generously provided by Prof. W. H. Pirkle (University of Illinois) through analysis on chiral HPLC columns.

[7] Additional characterization data: FAB mass spectrum of $TBNPH_2$ (**1**) gave m/z = 1319.5 and MnTBNPCl (**3**) gave m/z = 1373 (loss of Cl). Visible spectra: λ_{max} = 433 nm for **1** and λ_{max} = 479 nm for **3**.