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and (3) when two methanol molecules are coordinated to a Cu^{2+} ion on the same side of a 6-ring window, the Cu^{2+} ion will be pulled away from the window to site II*, even if it were previously inside the window. A similar geometry of Cu^{2+}–methanol coordination has been reported in Cu^{2+}-doped zeolite rho.[21] The bulky size of the methanol molecule could be a determining factor to account for the fewer adsorbate molecules directly coordinated to the Cu^{2+} ion. From the symmetry, the Cu^{2+} ion at site II* with three framework oxygens and two methanol molecules directly coordinated would not exhibit axial symmetry. This is clearly evidenced by the ESR spectra (Figure 4).

Conclusions

ESR and ESEM results have revealed that, in hydrated CuH-SAPO-5, Cu^{2+} is located at site II*, a cation site inside a 12-ring channel but close to the center of a 6-ring window, directly coordinated to three water molecules in an octahedral geometry. Both the Cu^{2+} location and the ammonia interaction in the ammonia-adsorbed sample are similar to those in the hydrated CuH-SAPO-5. A nonaxially symmetric Cu^{2+} ESR signal is found for the methanol-adsorbed samples and the ESEM results show that two methanol molecules are directly coordinated with a Cu^{2+} ion and another methanol molecule directs its methyl group toward the Cu^{2+} ion. It is proposed that the Cu^{2+} ion at site II* directly coordinates with the two methanol molecules in the same 12-ring channel and indirectly coordinates with one methanol molecule in an adjacent 12-ring channel. This determination of the Cu^{2+} location and adsorbate interactions is potentially useful for understanding and controlling Cu^{2+}-catalyzed reactions in H-SAPO-5 molecular sieve.

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Atomic Size Dependence of Bader Electron Populations: Significance for Questions of Resonance Stabilization

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Abstract: Model calculations show that the location of the zero-flux surface depends on the size of atomic orbitals that make up the electronic distribution of molecules. As a result, Bader electron populations exaggerate electron densities at electronegative atoms. The resulting atomic charges are judged to be unreliable, especially as evidence against resonance in carboxylate anions and related species.

Introduction

Recently questions have been raised about the importance of resonance stabilization in accounting for the structures of amides and conjugated alkenes and for the acidity of carboxylic acids, carbonyl compounds, and alkenes.[1,2] The analysis is based in part on atomic charges calculated according to Bader's method for partitioning molecules into atoms.[3] This has raised objections, both experimental[4] and theoretical,[5,6] as well as a defense,[7] and experimental data claimed to support the analysis.[8] However, none of the objections focussed on the fundamental error of the analysis. It is the purpose of this paper to show that these atomic charges have a fatal flaw, since they depend strongly on atomic size.

To assign atomic charges by Bader's method, molecules are partitioned into atomic regions separated by zero-flux surfaces. Such a surface is defined by eq 1, where ρ is the total electron density and $\vec{n}$ is the normal to the surface.

$$\vec{\nabla}\rho\cdot\vec{n} = 0 \qquad (1)$$

It can be traced by finding the "critical point" along a bond, where the gradient of electron density is zero (eq 2), and then following paths of steepest descent from that point.

$$\vec{\nabla}\rho = \vec{0} \qquad (2)$$

The integrated electron density within a surface is then assigned to the atom within that surface. Therefore, the electron population assigned to an atom depends crucially on the location of the zero-flux surface.

Model Calculations

The influence of atomic size on the location of the zero-flux surface is most clearly seen by considering two *n*s atomic orbitals (AOs), ϕ_A and ϕ_B, of different effective nuclear charge Z_{eff} (Figure 1). Since both these AOs contain a factor $\exp(-Z_{eff}r/n)$, which falls off rapidly with increasing r, Z_{eff} measures not only electronegativity but also atomic size. In particular, AOs of greater Z_{eff} are smaller. It is easily shown that AO size affects the location of the critical point, independently of electronegativity.

To eliminate the influence of electronegativity so as to focus only on the size effect, we consider the hypothetical case of one electron in each AO, and without any bond between them. Then the electron density ρ is $\phi_A{}^2 + \phi_B{}^2$. Along the line A–B, eq 2 becomes eq 3.

$$\phi_A\frac{\partial\phi_A}{\partial r} = \phi_A\frac{\partial\phi_A}{\partial x} = \phi_B\frac{\partial\phi_B}{\partial(-x)} = \phi_B\frac{\partial\phi_B}{\partial r} \qquad (3)$$

Moreover, because of the factor $\exp(-Z_{eff}r/n)$ in ϕ, the values of $\phi(\partial\phi/\partial r)$ in eq 3 depend strongly on Z_{eff} and thus on atomic size. At large separations or large r, the value is larger for the AO of smaller Z_{eff}, since this is the more diffuse

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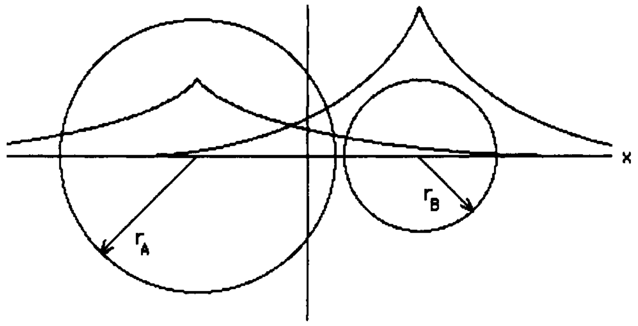

Figure 1. Two spherical atomic orbitals of different Z_{eff}. The orbital with the larger Z_{eff} is smaller, more concentrated, and with a faster falloff with r.

AO. However, at small separations or small r, $\phi(\partial\phi/\partial r)$ is larger for the AO of greater Z_{eff}, since this one is more concentrated near the nucleus. The distances and valence AO sizes (or Z_{eff}s) found in molecules correspond to this small-r condition. Therefore, at the midpoint between A and B (vertical line in Figure 1), the value of $\phi(\partial\phi/\partial r)$ is larger for the AO of greater Z_{eff}.

To satisfy eq 3, the critical point and the zero-flux surface must move away from the atom of greater Z_{eff}. This movement places the critical point even to the left of that point in Figure 1 where the exponentials intersect, which is where $\phi_A = \phi_B$. As a result the region of space assigned to the atom of greater Z_{eff} is increased. Even though that atom has the smaller AO, its volume is greater, so that additional electron density from the other AO is assigned to it.

It would be a fallacy to attribute this additional electron density to the greater electronegativity of the atom of greater Z_{eff}. The electron density ρ that was assumed is merely an artificial superposition of two electrons, one per atom, without any bond or any electron polarization from one atom to the other. In this hypothetical case the Bader method ought to divide both space and electron population nearly equally between the two atoms, but it does not. *The additional electron density transferred from one atom to the other is solely a consequence of orbital size* (and of how that size affects the location of the critical point or the zero-flux surface). Indeed, the position of the critical point would reverse at large separations and be located closer to the atom with the smaller AO.

This qualitative result has been recognized by Reed, Weinstock, and Weinhold.[9] They noted that the electron populations in the tails of a distribution are assigned so as to overestimate the density in the more contracted AO. In molecules with ionic bonds, such as Li^+F^-, this is the Li, but more commonly it is the more electronegative atom that is assigned the extra density. However, it is not clear whether this extra density is appreciable.

That this is not a trivial effect can be seen quantitatively with a model LCAO–MO. Any exact wave function obscures the effect of atomic size, since both electronegativity and atomic size contribute to the Bader charges. It is necessary to eliminate the effect of electronegativity and focus solely on the size effect. To do so, we need a hypothetical MO that localizes a known, and preferably equal, electron population on each atom. For definiteness we take a 1:1 combination of Slater sp hybrid AOs on carbon and oxygen, with the recommended[10a] Z_{eff}s, and at a C–O single-bond separation of 1.43 Å = 2.70 au (eq 4, where $r_A = [(x + 1.35)^2 + y^2$

$$\Psi = 2^{-1}(1 + S)^{-1/2}[(3.44^5/32\pi)^{1/2} \times (3^{-1/2}r_A + x + 1.35)\exp(-1.72r_A) + (4.5^5/32\pi)^{1/2}(3^{-1/2}r_B - x + 1.35)\exp(-2.25r_B)] \quad (4)$$

$+ z^2]^{1/2}$, $r_B = [(x - 1.35)^2 + y^2 + z^2]^{1/2}$, and $S = 0.565$).[11] This Ψ shows a critical point located 0.30 Å closer to the carbon than to the oxygen. (In contrast, the critical point would be 0.15 Å closer to oxygen than to carbon if the atoms were at a van der Waals separation of 2.9 Å.) By numerical integration[12] of ρ on a 0.04 au × 0.04 au grid, the zero-flux surface can be traced and the total electron density on each side calculated. For this 1:1 LCAO–MO the Bader populations are not equal but instead 0.30 on carbon and 0.70 on oxygen. Two electrons in such an LCAO–MO would then contribute +0.40 to the charge on carbon and −0.40 to the charge on oxygen. This is indeed a large effect!

Again, it would be a fallacy to attribute to electronegativity differences the charges we have calculated. The Z_{eff}s have been invoked only for their influence on AO size, not for their influence on electron-density redistribution. Instead, the LCAO–MO was chosen to be a 1:1 linear combination, with no electron polarization toward the more electronegative oxygen. If Bader charges were reliable, they should be zero or negligible for this MO, but they are not. *The apparent charges arise solely as an artifact of AO size* (and of how that size affects the location of the zero-flux surface).

Moreover, the calculated charges of ±0.40 are nearly as large as the Bader charges of +0.61 and −0.66 on CH_2 and OH, respectively, calculated for ethanol.[2] Without the artifact of size, the charges on CH_2 and OH might be only +0.21 and −0.26, corresponding to an exaggeration by as much as 3-fold. Unfortunately, it is not possible to be so specific, since the effects of size and electronegativity cannot be separated in a real molecule, especially a polyatomic one. Nevertheless, a *major* basis for the Bader charges is certainly the disparity in AO sizes, rather than solely the difference in electronegativity between carbon and oxygen.

Although this LCAO–MO is oversimplified, it correctly demonstrates the effect of atomic size. It is true that a proper LCAO–MO would weight more heavily the more electronegative atom. Larger basis sets would allow for additional AOs on each atom. In a real molecule other MOs would also be involved. With configuration interaction the MOs lose their integrity. Therefore, the charges calculated from this simple MO are only approximate. Nevertheless, the result is purely a consequence of how the electron density falls off with distance from an atom of greater or lesser electronegativity. Therefore, the qualitative conclusion from this model calculation must still hold even for an accurate ab initio calculation: Because the electron density near the more electronegative atom is more concentrated, the zero-flux surface moves away, so that a greater volume is assigned to that atom and the Bader population on that atom is exaggerated.

Discussion

The calculations above show that the greater Bader population on an electronegative atom arises not only because of electronegativity differences but also because the location of the zero-flux surface depends on atomic sizes, which ought to be irrelevant. Unfortunately, it is not possible in real molecules to separate the two effects. Both contribute, so that is is certainly not justified to assume that only electronegativity determines Bader populations. The calculations above show that a major contributor to charge separation is the effect of AO size.

Some relationships among electronegativity, atomic size, and the location of the zero-flux surface have been recognized. It is immediately obvious from MO calculations that the critical point moves away from an electronegative atom, so that the volume assigned to an atom increases with its electronegativity.[13] Specifically, it was found that the (finite) volume assignable to a carbon atom increases substantially on changing the nominal hybridization from sp³ to sp² to sp or on converting from hydrocarbon to carbocation.[14] It is commonly assumed that the position of the critical point depends primarily or exclusively on

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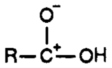
the relative electronegativities of the substituents.[15] However, the above calculations show that the position of the critical point also depends strongly on AO sizes, separate from electronegativity. An undesirable consequence of this dependence, which has not previously been recognized, is that additional electron density is assigned to electronegative atoms, whose charges are therefore exaggerated.

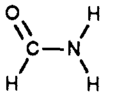
This dependence of Bader populations on atomic size invalidates some objections to resonance. It has been claimed[2] that the acidity of carboxylic acids, relative to alcohols, does not arise from carboxylate resonance (**1**) but from carbonyl polarization that is already present in the acid (**2**). Part of the evidence was that

1



2

the atomic charges, calculated from 6–31+G* electron densities in **2** (R = H), are large (+2.06 at CH and −1.39 at carbonyl O), and they change only to +2.00 and −1.50, respectively, upon deprotonation. Similarly, the 6–31G** atomic charges in formamide (**3**) are −1.476 at N, +1.980 at C, and −1.392 at O, changing to −1.222, +1.758, and −1.343, respectively, in conformation **4** with the nitrogen lone pair in the molecular plane.[1a]



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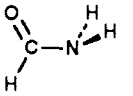

4

Resonance would require a partial positive charge on N, not a large negative one. Moreover, the greater electron population on N in **3** than in **4** was taken as further evidence against resonance stabilization in amides. Similarly, the negative charge on N in vinylamine, $CH_2{=}CH{-}NH_2$, is 1.338, and this decreases to 1.237, rather than increasing, when the NH_2 is twisted to prevent any possible resonance.[1c] Comparable results have also been obtained for esters and their enolate anions[1b] and for nitramide.[16]

Nevertheless, the calculations above indicate how these charges can be rationalized without rejecting resonance. The calculated charges of +2.06 and −1.39 in formic acid (**2**, R = H) arise not only from electronegativity differences but also from a size effect, which transfers extra electron density from carbon to oxygen. Certainly there is some polarization of the carbonyl, but its true extent cannot be determined. It is not justified to use these exaggerated charges to assess the involvement of resonance. Likewise the large negative charge at N of **3** is an overestimate and cannot be used to reject the involvement of resonance in amides.

Similarly, the *changes* of atomic charge on deprotonation of carboxylic acid **2** or on rotation of formamide **3** or vinylamine cannot be used to reject resonance. The negative charge of 1.39 at carbonyl oxygen increases only to 1.50 upon deprotonation, not only because it is already so large, but also because the oxygen AOs in the anion are more diffuse than in the acid. As a result the zero-flux surface moves away, and this reduces the exaggeration of electron density assigned to oxygen. Likewise, the apparently greater electron population at nitrogen in planar **3** relative to twisted **4** is indeed due to the difference in hybridization,[1a] but the change arises because the more diffuse AO of the sp^3 nitrogen of **4** permits the zero-flux surface to move closer, so that it is assigned a reduced electron population. The Bader charges in **4** are lower because the disparity in AO sizes between carbon and nitrogen is reduced. The same argument applies to vinylamine.

It might be hoped that the exaggeration of charges might cancel in comparisons of similar molecules. However, the cases above show that the exaggeration is not uniform, so that there is a systematic error that precludes such comparison. Since Z_{eff} of an oxygen or nitrogen AO decreases as p character or overall negative charge increases, so does the effective AO size increase, thereby reducing the disparity in atomic sizes between oxygen or nitrogen and the neighboring atom. The exaggeration of charge is thus reduced in the carboxylate anion and in the nonplanar amide or vinylamine. Similarly, the apparent invariance of the −0.23 charge on nitrogen in NH_3 and NH_4^+,[17] despite the net positive charge on the latter, is due to the contraction of the nitrogen AOs in the ion and a greater exaggeration of its electron polarization.

The magnitude of Bader charges is a further clue that they have been overestimated. This is not merely prejudice arising from familiarity with historical Mulliken charges, since there is an independent way to demonstrate a contradiction. In particular, it is quite unreasonable that the additional electron density on an electronegative atom can exceed the additional nuclear charge that confers that electronegativity. This is a corollary of Sanderson's principle of electronegativity equalization.[18] For example, the electron population on nitrogen in formimidate anion, $HCONH^-$, is 8.48.[1d] On replacing the nitrogen by oxygen, as in the isoelectronic formic acid, HCOOH, the electron population increases to 9.29, since the additional nuclear charge attracts additional electron density. The increase is only 0.81, properly less than the unit additional positive charge. In contrast, the electron population of 6.19 at the β carbon of the enolate of acetaldehyde, H_2CCHO^-, becomes 8.39 at nitrogen in the isoelectronic formamide, H_2NCHO. The increase of 2.20 overcompensates the extra unit positive charge and more than equalizes the increased electronegativity. The calculations above suggest that a substantial portion of these high electron populations arises not from electronegativity differences but merely from an atomic-size effect, which assigns extra volume and extra electron density to the smaller atom.

Conclusions

The calculations above show that the Bader population on an electronegative atom is exaggerated. The extra electron density arises not only because of electronegativity differences but also because the location of the zero-flux surface depends on atomic size. Since the latter ought to be irrelevant, we conclude that Bader populations are unreliable for answering questions of molecular electronic structure. Unless this size effect can be removed, the atomic charges are quite unreliable. In particular, they cannot be used as evidence against resonance.

It is useless to recommend that atomic charges be abandoned, since chemists adhere to such simple parameters. Yet they are always arbitrary, since they are not well-defined. Although the total electron density ρ is a quantum-mechanical observable, atomic charges are not, since it is arbitrary how the electron density is apportioned to atoms. This has long been recognized for Mulliken populations.[9,10b] Bader[3] has shown that the zero-flux surfaces are natural boundaries, with many useful properties. It is sensible to try to use them to define atomic charges. Unfortunately, this leads to artifacts due to atomic-size dependence.

It remains to be seen whether newer methods for assigning atomic charges might be more useful. Among these are the natural population analysis,[9] charges derived to fit the calculated molecular electrostatic potential,[19] and charges obtained from generalized atomic polar tensors.[20] Comparisons of the various methods are informative,[6,21] but all show that Bader charges are usually much larger than those calculated by other methods.

At this time we decline to judge whether resonance is important for carboxylates and related species. Our results do not justify

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any conclusion except the one that some previous objections to resonance are unfounded. Thus we insist that the argument not be based on arbitrary assignments of atomic charges but rather on the more reliable energies and geometries. Among the meaningful questions to be answered are: If there *is* resonance in allyl anion, why is the barrier to C–C rotation so much lower than that in allyl cation? If there *is* resonance in amides, why is the C–O bond not lengthened, relative to a twisted amide? If there is *no* resonance in amides, why is there so large a barrier to rotation about the C–N bond?

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Experimental and Theoretical Study of Near-Infrared Absorbing Naphthoquinone Methide Dyes with a Nonplanar Geometry

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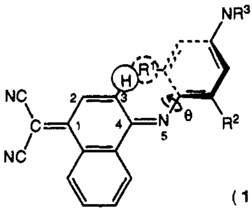
Abstract: The bathochromic shift of the near-infrared absorption spectra of naphthoquinone methide dyes has been observed as a function of increased steric hindrance between the quinone imine and aniline segments. This novel shift that results from the loss of planarity has been examined by means of semiempirical INDO/S and AM1 models. Based on the configuration interaction (CI) analysis, the observed transitions in both the near-infrared and UV regions have been assigned. The introduction of an acetylamino group at the 2-position of aniline ring has caused a bathochromic shift with a remarkable increase in molecular extinction coefficient. In order to interpret these results, both an electronic factor and a steric effect have been analyzed. This interesting color–structure relationship of a nonplanar chromophoric system has been elucidated.

I. Introduction

Conventionally, color chemistry has been primarily concerned with the study of organic compounds which absorb ultraviolet and/or visible light, and thousands of colored molecules have so far been identified. In recent years, there has been a demand for dyes with specific and optimized properties, particularly with respect to a near-infrared absorption (beyond ca. 700 nm). Near-infrared absorbing dyes ("deep-colored" compounds) have attracted considerable attention because of various new applications including diode-laser optical storage media,[1] photosemiconductor layers in laser printers,[2] laser filters,[3] and photochemotherapeutic agents.[4] Despite extensive efforts to prepare highly conjugated compounds suitable for these applications, dyes with such light absorption properties are still rather rare. We have previously reported the syntheses of new deep-colored naphthoquinone methide dyes, 4-(4-dialkylaminophenylimino)-1,4-dihydronaphthylidenemalononitrile (**1**), by condensing 1-naphthylmalononitrile[5] with 4-dialkylaminoaniline in the presence of an oxidizing agent under alkaline conditions.[6] These compounds, which are far less conjugated than has traditionally been considered necessary for the attainment of the bathochromic shift, in fact, absorb near-infrared light at 722–761 nm (ϵ_{max} 24 200 – 30 800 dm^3 mol^{-1} cm^{-1}) in CHCl$_3$. These compounds also have good film properties for use as diode-laser optical storage media.

Fundamental studies of this unusual chromophoric system might therefore be useful in elucidating the basic structural features that contribute to a large bathochromic shift. The longest wavelength absorption (band I) for this dye is mainly considered to result from an intramolecular charge transfer corresponding to a migration of an electron from the aniline ring to the quinone imine segment which includes the dicyanomethylene group. As shown in Scheme I, however, the coplanarity between the two segments is disturbed by an intramolecular overcrowding of the molecule. In fact, X-ray analysis of acetylamino derivative (**1d**)[7] indicated that the plane formed by the C$_2$=C$_3$—C$_4$=N$_5$ portion of the quinone imine segment is tilted out of the aniline segment by 42.60°. It is a remarkable feature of these dyes that they can absorb near-infrared light despite such large steric strain. Moreover, the introduction of an acetylamino group at the 2-position in the aniline ring (compound **1d**) results in hydrogen bond formation with the nitrogen atom at the 5-position. The hydrogen bonding enables a bathochromic shift with a large increase in the molecular extinction coefficient compared to the dye (**1a**) (see Table I). The near-

Scheme I



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