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Bonded-Atom Fragments for Describing Molecular Charge Densities

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For quantitative description of a molecular charge distribution it is convenient to dissect the molecule into well-defined atomic fragments. A general and natural choice is to share the charge density at each point among the several atoms in proportion to their free-atom densities at the corresponding distances from the nuclei. This prescription yields well-localized bonded-atom distributions each of which closely resembles the molecular density in its vicinity. Integration of the atomic deformation densities - bonded minus free atoms - defines net atomic charges and multipole moments which concisely summarize the molecular charge reorganization. They permit calculation of the external electrostatic potential and of the interaction energy between molecules or between parts of the same molecule. Sample results for several molecules indicate a high transferability of net atomic charges and moments.

Key words: Electron density - Bonded atoms - Populations - Dipole moments

1. Defining Atomic Fragments

Chemists have acquired, with experience, a reasonably serviceable notion of the charge distributions in the molecules they work with. In many instances a look at the structural formula of a molecule is enough to suggest which regions are electron-rich and so vulnerable to electrophilic attack and which are more likely to attract nucleophilic reagents. The theoretical underpinnings of these insights, however, have been slow to develop. Instructive quantum-mechanical calculations, both *ab initio* and semi-empirical, are available for a wide variety of small molecules; yet the electrostatic information that can be extracted from such studies is rarely presented in a usable form. Apart from a few expectation values that can be compared directly with experimental measurements, such as molecular dipole and quadrupole moments and the electric field gradients at selected nuclear positions, a detailed description of the theoretical charge distribution is usually lacking. If such a description *is* attempted this is likely to take the form of a listing of Mulliken atomic populations [1], sometimes accompanied by a warning that these indices have little quantitative significance [2, 3].

Central to any such population analysis is the idea, of unimpaired validity, that a good way to describe a molecule is to divide it into atoms and examine how these differ from the free atoms. An imposing variety of published schemes attest to the recurrent fascination of this theme and to the wealth of mathematical ingenuity it has inspired. But for a straightforward dissection of molecular charge, the partitioning procedure advanced by Politzer and Harris [4] has two compelling advantages over most of its rivals:

1) It makes the charge on each atom an unambiguous property of the molecular charge distribution, independent of the mathematical formalism used to derive this distribution;
2) When applied to the promolecule, made up of overlapping ground-state atoms prior to any charge migration between or within these atoms, it yields neutral atomic charges.

Politzer and his collaborators have applied this definition to a selection of linear molecules [5, 6] and have presented atomic charges that appear reasonable in magnitude, vary in a sensible manner among chemically similar molecules, and conform to accepted ideas about electronegativity differences between atoms and groups. They also tend to be smaller than values obtained by other methods [7].

Yet disconcerting shortcomings remain. The atomic fragments defined by Politzer and Harris [4] are bounded somewhat artificially by an array of partition planes. Bonded atoms with plane faces are conceptually foreign to quantum chemistry as well as mathematically awkward. While yielding acceptable atomic charges they are ill-suited to the definition of other properties that are needed for a more complete specification of the molecular charge distribution. For example, an apparent outward polarization of the bonded atoms in a series of diatomic molecules examined by Politzer [5] is undoubtedly in part an artifact of the partitioning procedure, which interchanges the mutually trespassing portions of overlapping atoms and so attributes spurious moments to the two atoms even in the promolecule. Moreover, it is unlikely that the proposed partitioning into atomic regions can be extended without ambiguity to non-linear molecules of arbitrary symmetry.

Fortunately, these disabilities can be remedied in a simple and natural fashion. In the promolecule the total density is a sum of well-defined contributions from all the constituent atoms. All we have to do is mimic this atomic composition of the promolecule density in apportioning the *actual* molecular density among the several atoms. Accordingly, we divide the molecular density *at each point* among the atoms of the molecule in proportion to their respective contributions to the promolecule density at that point. Like partners in a stockholders' corporation, each atom thus partakes of the local gain or loss in direct proportion to its share in the capital investment.

Algebraically, we write the promolecule density at point r as

$$\rho^{\text{pro}}(r) = \sum_i \rho_i^{\text{at}}(r),$$

where the functions ρ_i^{at} are suitably positioned, spherically averaged ground-state atomic densities. For each atom we define a sharing function

$$w_i(r) = \rho_i^{\text{at}}(r)/\rho^{\text{pro}}(r),$$

that specifies its relative share in the promolecule density at r. The several functions $w_i(r)$ are all positive and their sum equals one everywhere. We now define the charge density of the bonded atom i as

$$\rho_i^{\text{b.a.}}(r) = w_i(r)\rho^{\text{mol}}(r), \tag{1}$$

where ρ^{mol} is the actual molecular density. In this way we obtain overlapping, continuous bonded-atom distributions that fully retain the two advantages, enumerated above, of the Politzer-Harris definition. The stockholder recipe is completely general, requires no arbitrary placing of boundary surfaces, and produces well-defined atomic fragments that differ from the free atoms only to the degree that the molecule itself differs from a superposition of free-atom densities.

From here we can proceed along either of two paths. We can subtract the density of the free atom from that of the bonded atom to obtain the *atomic deformation density*

$$\delta\rho_i(r) = \rho_i^{\text{b.a.}}(r) - \rho_i^{\text{at}}(r).$$

Alternatively, we can form the *molecular deformation density*, defined as the density difference between the molecule and the promolecule

$$\Delta\rho(r) = \rho^{\text{mol}}(r) - \rho^{\text{pro}}(r),$$

and apportion this to produce

$$\delta\rho_i(r) = w_i(r)\Delta\rho(r). \tag{2}$$

It is by virtue of our particular choice of sharing function w_i that these two routes lead to the same atomic deformation density $\delta\rho_i$.

By way of illustration, Fig. 1 shows the deformation density in the linear molecule HC≡C—C≡N, together with its separate atomic fragments. The atomic deformation densities are, as expected, well localized in space. They closely resemble the molecular deformation density in their respective neighborhoods, and density maxima in the bond regions are divided smoothly between the adjacent atoms. We note also that the molecular and the individual atomic deformation maps share coincident zero contours, as required by Eq. (2). Since the w_i all lie between 0 and 1, each atomic deformation function $\delta\rho_i$ has everywhere the same sign as $\Delta\rho$ and is smaller in magnitude.

2. Atomic Charges and Moments

The total electronic charge in our bonded atom is given by

$$Q_i = -\int \rho_i^{\text{b.a.}}(r)\,dv,$$

the negative sign, here and below, obeying the convention that electrons are negatively charged. Adding the nuclear charge Z_i gives the net atomic charge

$$q_i = Q_i + Z_i.$$

In practice, the integrand $\rho_i^{\text{b.a.}}$ varies too steeply for easy numerical integration; thus it is generally more convenient to integrate the atomic deformation density, which yields directly

$$q_i = -\int \delta\rho_i(r)\,dv. \tag{3}$$

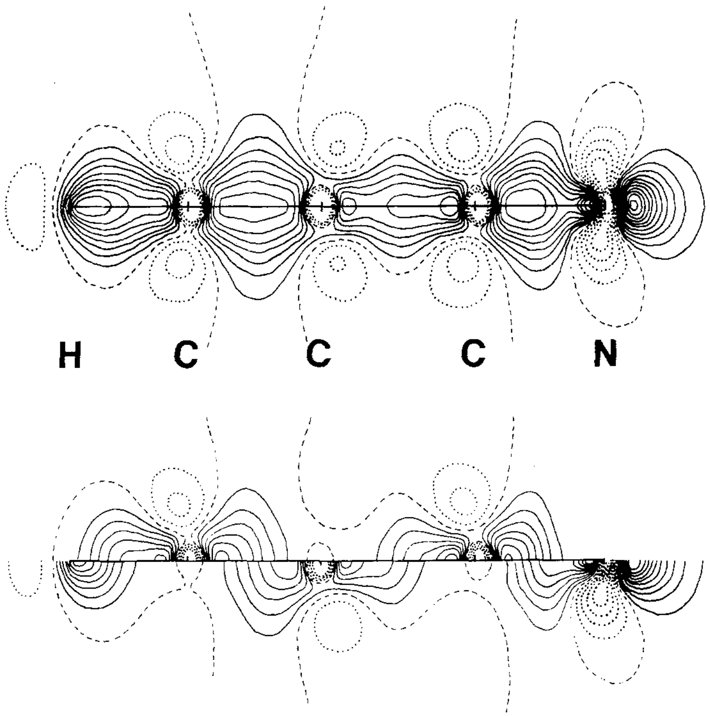

Fig. 1. Molecular deformation density $\Delta\rho$ (upper figure) in HC≡C–C≡N from Hartree-Fock wave function [8], resolved into atomic components $\delta\rho_i$ (lower figure: H, ≡C–, N below axis; two other C atoms above axis). Contour interval 0.1 eÅ^{-3}, zero contour broken, negative contours dotted. Inner contours around heavy nuclei have been omitted

Because our definition, like that of Politzer and Harris [4], takes the promolecule as reference state, we expect the two recipes to yield rather similar atomic charges. This is tested in Table 1 for a selection of linear molecules analyzed by Politzer *et al.* [5, 6]. The two sets of values have been derived from the same wave functions [8]; thus the small differences in the listed charges q_i arise entirely from the difference between the two definitions, apart from negligible integration errors.

Among the regularities revealed by the tabulated charges is the near constancy of the charge difference across the C≡N bond, with $q_C - q_N$ ranging between 0.25 and 0.27 e in the three molecules HCN, HC≡C–C≡N, NC–CN. The C–H bond shows a more variable polarity, while the net charge on hydrogen remains close to the 0.1 e. Such trends are, of course, no more than tentative suggestions of what to look for in more extensive compilations as these become available.

We can now go on to derive additional properties of the bonded atoms, such as their dipole and quadrupole moments, etc. The *k* component (*k* = 1, 2, 3) of the dipole moment of atom *i* is

$$\mu_{i,k} = -\int x_k \delta\rho_i(r)\,dv, \qquad (4)$$

Table 1. Net charges q (e), dipole moments μ_z (eÅ), and second moments μ_{zz} and μ_{xx} (eÅ^2) of atomic deformation densities $\delta\rho_i$, derived by Eqs. (3, 4, 5). Molecular axis is z, positive to the right. Charges in parentheses are from Politzer *et al.* [5, 6]. Small charge imbalances reflect errors of numerical integration. The quadrupole moments in these axially symmetric molecules are given by $\Theta_{zz} = \mu_{zz} - \mu_{xx}$

HCN	H	C	N		
q	+0.133 (0.18)	+0.066 (0)	−0.201 (−0.18)		
μ_z	−0.104	−0.161	−0.045		
μ_{zz}	+0.089	+0.046	−0.134		
μ_{xx}	+0.096	+0.149	−0.037		
HCCCN	H	C	C	C	N
q	+0.124 (0.18)	−0.015 (−0.06)	−0.031 (−0.05)	+0.096 (0.09)	−0.176 (−0.16)
μ_z	−0.105	−0.167	+0.155	−0.127	−0.035
μ_{zz}	+0.082	+0.052	+0.005	−0.018	−0.101
μ_{xx}	+0.087	+0.079	+0.054	+0.117	−0.030
HCCH	H	C	C	H	
q	+0.094 (0.14)	−0.094 (−0.14)	−0.094	+0.094	
μ_z	−0.103	−0.159	+0.159	+0.103	
μ_{zz}	+0.079	+0.021	+0.021	+0.079	
μ_{xx}	+0.073	+0.038	+0.038	+0.073	
NCCN	N	C	C	N	
q	−0.126 (−0.10)	+0.126 (0.10)	+0.126	−0.126	
μ_z	+0.033	+0.143	−0.143	−0.033	
μ_{zz}	−0.104	+0.011	+0.011	−0.104	
μ_{xx}	−0.002	+0.164	+0.164	−0.002	
OCO	O	C	O		
q	−0.208 (−0.23)	+0.413 (0.46)	−0.208		
μ_z	+0.043	0	−0.043		
μ_{zz}	−0.006	−0.024	−0.006		
μ_{xx}	+0.001	+0.308	+0.001		

where x_k is the k component of the vector r measured from the atomic nucleus. We get formally the same result if we insert $\rho_i^{\text{b.a.}}$ rather than $\delta\rho_i$ in the integrand but, again, the deformation density is computationally more tractable.

The atomic moments μ_z listed in Table 1 seem to be more directly transferable than the net charges and are evidently strongly characteristic of the hybridization state of the bonded atom. Thus, we consistently have values near 0.10 eÅ for –H (the positive sense is –. . . +; 1 eÅ = 4.8 D), 0.15 eÅ for ≡C–, and –0.04 eÅ for ≡N, the negative sign here indicating that the nitrogen lone-pair moment slightly outweighs the opposite polarization of the bonding density (see Fig. 1).

The atomic charges q_i and dipole moments $\mu_{i,k}$ together determine the molecular dipole moment. With $X_{i,k}$ denoting the k coordinate of atom i relative to a chosen molecular origin, the molecular moment is given by

$$\mu_k = \sum_i X_{i,k} q_i + \sum_i \mu_{i,k}$$

and is thus made up of two kinds of terms. The first, involving the net atomic charges, arises from the interatomic charge migration and is related to the polarities of the several bonds. The second comprises the atomic moments, regarded here as reflecting an intra-atomic charge polarization. In HCN and HCCCN, as well as in the non-linear H_2CO (M. Eisenstein, unpublished calculations), this intra-atomic contribution to the molecular dipole moment is somewhat smaller than the interatomic and is in the same sense. This two-fold classification, though often overlooked, accords completely with well-established chemical thinking, which distinguishes between moment contributions from heteropolar bonding and those associated with non-spherical (e.g. lone-pair) distributions of the individual atoms. Even if we consider bond moments and atomic moments to represent no more than a mathematically useful decomposition of the over-all charge migration, the recognition that both contribute can save us from an unrewarding attempt to derive atomic charges from dipole moments alone. A qualitative but cogent exposition has been given by Coulson [9] in discussing the molecular moments of HCl, H_2O, NH_3, and CO, among others.

Proceeding further, we derive the symmetric second-moment tensor of the atomic deformation density, whose six independent components are

$$\mu_{i,kl} = -\int x_k x_l \delta\rho_i(r)\, dv. \tag{5}$$

These are related to the atomic quadrupole-moment tensor, with components given by

$$\Theta_{i,11} = \mu_{i,11} - \tfrac{1}{2}\mu_{i,22} - \tfrac{1}{2}\mu_{i,33}, \text{ etc.}$$

$$\Theta_{i,12} = \tfrac{3}{2}\mu_{i,12}, \text{ etc.}$$

Since the quadrupole moments may be derived from the second moments but not *vice versa*, we prefer to list the second moments in Table 1. For example, in the three cyano compounds listed both atoms of the C≡N group have negative quadrupole moments Θ_{zz}. But Table 1 shows that in the carbon atom this is due principally to a charge contraction towards the molecular axis, as evident in Fig. 1, while in nitrogen it arises from an expansion in the axial direction. (Because of the negative sign preceding the integral in Eq. (5) a positive diagonal second moment $\mu_{i,kk}$ implies a net contraction in the k direction.) Similarly, the uniformly small quadrupole moment of the bonded hydrogen atom provides scarcely a hint of its nearly isotropic contraction.

As these examples show, the intricate pattern of charge reorganization that attends the union of separate atoms in forming a molecule is compactly summarized by the charges and moments of the atomic deformation densities. While lacking some of the detail and almost all the subjective appeal of a contour diagram, such as Fig. 1, these numerical data offer a precision and a computational facility that no pictorial representation can match.

3. Derived Electrostatic Properties

One reason for our interest in the kind of data that are presented in Table 1 has been hinted at above: the search for regularities and trends that can help us to estimate the charge distributions in larger molecules from what we find in smaller molecules. A more immediate use is in the prediction of the properties and behavior of molecules in so far as these are governed by electrostatic effects. To illustrate this application, Fig. 2 shows the electrostatic potential around a molecule of HCN as derived from the data in Table 1, neglecting contributions from atomic multipoles higher than quadrupole. Such a calculation can be valid only in regions free of charge; hence the blank inner portion of the plot, defined roughly by the atomic van der Waals radii. For comparison, we also map the potential of a single point dipole, –0.682 eÅ = 3.27 D, and point quadrupole, 0.557 eÅ^2 = 2.68 buckinghams, at the molecular center of mass. The molecular quadrupole moment, like its atomic counterparts, may be deduced from the second moments of the molecular deformation density; these are given by the expression

$$\mu_{kl} = \sum_i (X_{i,k}X_{i,l}q_i + X_{i,k}\mu_{i,l} + X_{i,l}\mu_{i,k} + \mu_{i,kl}),$$

in which the atomic coordinates $X_{i,k}$ are measured from the center of mass of the molecule. Not surprisingly, the replacement of the individual atomic charges and moments by a single molecular interaction center is a good approximation far from the molecule but fails at distances comparable with the molecular dimensions (Fig. 2). An obvious corollary is that the larger the molecule the larger the region of space in which

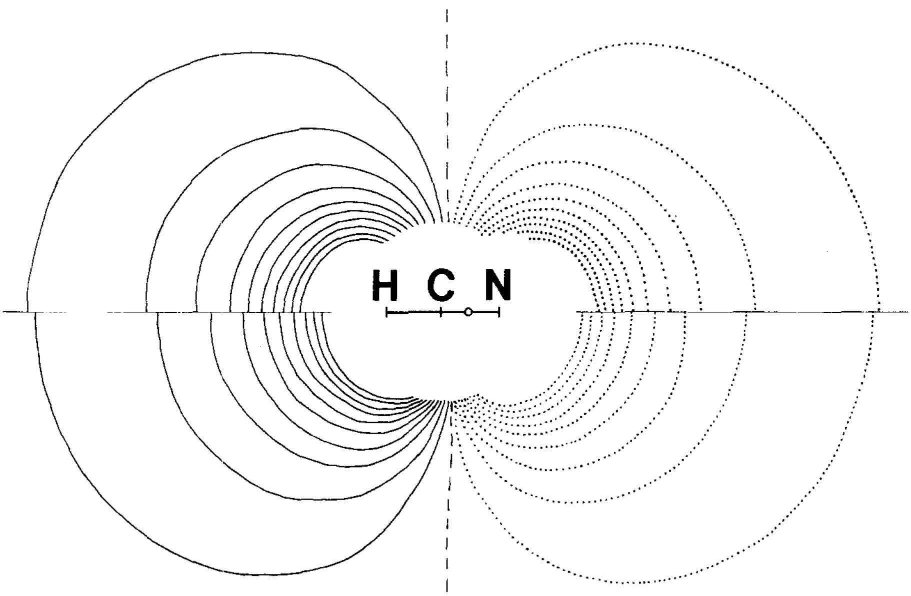

Fig. 2. Electrostatic potential around HCN molecule. Contour interval 0.01 e/Å = 0.144 V. Upper section: potential due to atomic charges and moments listed in Table 1. Lower section: potential due to point dipole and quadrupole at molecular center of mass (marked by small circle)

the potential can be estimated adequately only from an atomic-scale description of the charge distribution.

Fig. 3 plots the electrostatic interaction energy of a pair of HCN molecules, in parallel and in anti-parallel orientation, as a function of the vector separation of the two molecules. Treating the atoms as hard spheres with van der Waals radii of 1.1 Å for H, 1.7 Å for C, and 1.5 Å for N, we find two energy minima: –4.1 kcal/mole for the linear head-to-tail arrangement and –2.7 kcal/mole for side-to-side anti-parallel contact. While these numerical values neglect the mutual (static) polarization of the two molecules, dispersion forces, and the Pauli repulsion energy, the results illustrate a practical route to the qualitative prediction of stable configurations that play an undoubted role in crystallization and in chemical reactions. The same kind of calculation, applied to interactions between portions of the same molecule, can be of similar value in deriving the electrostatic component of intramolecular energy changes associated with conformational flexibility.

In the computations leading to Fig. 3 it was found that the interaction of atomic point charges alone, neglecting the atomic dipole and quadrupole moments, accounted for a fairly constant fraction, between 1/3 and 1/2, of the total intermolecular energy at all separations. This observation, supported by similar experience with other highly polar

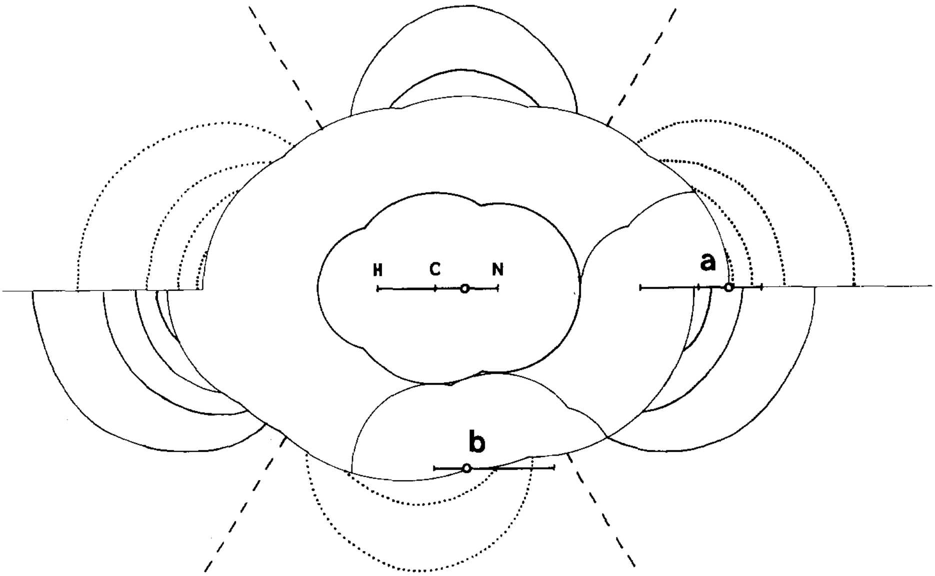

Fig. 3. Electrostatic energy of two HCN molecules as function of vector separation of their centers of mass (small circles). Inner excluded volume assumes hard-sphere radii of 1.1 Å for H, 1.7 Å for C, 1.5 Å for N. Contour interval 1 kcal/mole = 0.00301 e^2/Å. Two minimum-energy positions are shown at *a* (–4.1 kcal/mole) and *b* (–2.7 kcal/mole). Upper section: parallel molecules. Lower section: anti-parallel molecules.

molecules (HCCCN and H_2CO), suggests that a point-charge model, with suitably scaled-up atomic charges, might yield a fair approximation to intermolecular energies in some circumstances. The need for circumspection with such simplified models is emphasized, however, by the fact that with molecules lacking a dipole moment, such as HCCH, NCCN, and CO_2, the charge-charge terms provide a much smaller and less uniform fraction of the total energy of interaction between two molecules.

Evidently, quantitative information of the sort presented in Table 1 can be useful for estimating the electrostatic properties of molecules and for predicting many features of their physical and chemical behavior. As noted above, they may also serve for the correlation of properties of chemically related molecules and, in particular, for a quantitative examination of the degree of transferability of bond properties between molecules.

Yet the proposed method is obviously only one of many equally valid ways of expressing the same information. It should be superfluous to emphasize that, as there are no actual atoms in a molecule, any definition of atomic fragments must be essentially arbitrary. Thus we cannot canonize any single dissection scheme as more "correct" than any other. Nor should we expect that any one such procedure will prove superior *for all purposes* to its various alternatives. Were this so we should be deprived of valuable opportunities for enhanced understanding through alternative dissections of the same charge distribution, for example dividing a polar molecule both into atom-like and into ion-like pieces. However, the present recipe does offer certain virtues, some shared with various other schemes, that fit it for the specific uses suggested above. Being defined rigorously by the first-order charge density of the molecule, and of its component atoms, the bonded-atom fragments permit the unambiguous evaluation of all one-electron properties of the system, to an accuracy limited only by that of the charge density itself. Since these fragments are continuous but well localized in space, we expect their multipole expansions to converge smoothly. Because the atomic deformation densities vanish for the promolecule, they are particularly suited to describing those molecular properties, like the external Coulomb field, that arise entirely from the redistribution of charge on bonding. Finally, since the proposed decomposition can be applied with complete generality to any charge distribution, theoretical or experimental, linear or contorted, molecular or crystalline, neutral or charged, it permits the widest possible correlation of properties among species of unlimited chemical diversity. Whether or not these advantages outweigh others that may be claimed for alternative proposals, it is highly desirable that *some* unambiguous means be adopted for the reporting of quantitative charge-density information whenever this is produced by an accurate theoretical or experimental investigation.

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