as well as the "inside" relaxation rate values confirm the existence of structure-forming effects in the system. This is not obvious, since in bulk solutions the structure-forming effects are due in part to stronger rearranged hydrogen bonds around the solute molecules, whereas in the AOT inverse micelles, the hydrogen bond rate (as given by the proton chemical shift[6]) is known to be lower than in pure water. Thus the other competitive molecular interactions must be seen as responsible for the observed structure-forming effects. The "outside" relaxation is induced when the water molecules are in the hydration shell of the SO_3^- groups, or hydrogen bonded to the ester groups, both close to the AOT polar head protons. τ_0 could then be seen as a lifetime for water in the AOT polar head hydration shell.

Conclusions

The molecular movements of water in reversed ionic micelles were clarified. The individual motions were shown to be very similar, even at very low water content, to those found in bulk concentrated ionic solutions. As in bulk water, the rotational and translational diffusions as well as the hydrogen exchanges could not be distinguished. The correlation time is then a mixture of various contributions of the same order of magnitude.

A qualitative picture of water–polar head interactions could be drawn. The amount of water molecules adsorbed on the polar heads is about four molecules per AOT molecule; the characteristic correlation time of the water–polar head interaction is in the 5×10^{-10} s range.

Besides, the experiment showed the need of an appropriate methodology to avoid misleading interpretations of NMR relaxation experiments in microheterogeneous systems where many nuclear interactions and movements occur simultaneously. However, this complexity can become a source of small-scale dynamical informations on these systems.

For further studies of water in reversed micelles, surfactants other than AOT should be used. The complexity of its polar head does not allow one to draw simple conclusions expandable to other surfactants, while its chemical instability and complex purification procedure can lead to experiments of low reliability and reproducibility.

Acknowledgment. The authors acknowledge several collegues for help or discussions. We primarily thank A. Lowenstein, J. Tabony, and one of the referees for constructive criticism of the interpretation, and M.-P. Pilêni and J.-F. Le Marêchal for help with the chemistry.

Appendix

To derive eq 9 to 11 in section b, we must integrate the dipolar spectral density for an isolated pair of protons over the core and shell distributions of protons. Because of the motion peculiarities in the shell (assumption f), the shell protons are confined on the surfaces of concentric spheres (of radii $R \geqslant R_2$), whereas the core protons diffuse inside a sphere (of radius R_1). The two-particle spectral density in this case, which can be found elsewhere,[15,16] is a series of Lorentzian functions:

$$J(\omega) = 1/R^6 \sum_{l,\ n=0}^{\infty}\sum A_{ln}\tau_{ln}/(1 + \omega^2\tau_{ln}^2) \tag{15}$$

where the A_{ln} are the reduced amplitudes:

$$A_{ln} = [(2l + 3)(l + 2)(l + 1)l^2]/[u_{ln}^2(u_{ln}^2 - l(l + 1))] \times (R_1/R)^{2l}/4\pi \tag{16}$$

$$A_{00} = 1/4\pi$$

and where the correlation times and the u_{ln} constants are given in eq 11 and 12.

For shell over core relaxation (J_1 in coefficients R_{11} and R_{12}), J must be integrated over R, with particle density N_2. Since R does not appear in the Lorentzian functions, the amplitudes integrations yield:

$$\int_{R_2}^{R_a} (A_{ln}/R^6)4\pi N_2R^2\,\mathrm{d}R = N_2/R_2^3B_{ln} \tag{17}$$

The explicit expression found for B_{ln} is given by eq 10.

For core over shell relaxation (J_2 in R_{21} and R_{22}), J must be multiplied by the number of core protons, $2NW$. The spectral density is then a function of R which labels the site distribution in the shell. Since the shell protons are aggregated into a single site (assumption j), the spectral density must be averaged over R. Finally the amplitudes averages give:

$$2NW\int_{R_2}^{R_a} (A_{ln}/R^6)4\pi N_2R^2\,\mathrm{d}R/37N = (2W/37)(N_2/R_2^3)B_{ln} \tag{18}$$

The $37N$ factor is the number of protons in the surfactant shell (there are 37 protons per AOT molecule and N is the aggregation number). The ratio of eq 17 and 18 yields $J_2(\omega)$ as given in expression 9.

Registry No. AOT, 7732-18-5; H_2O, 577-11-7; D_2O, 7789-20-0.

On the Correspondence between Simple Orbital Concepts and Molecular Electron Distributions

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Abstract: It has been shown that definitions of atoms and their properties, bonds, and molecular structure can be obtained from a study of the molecular electron distribution. The charges on the atoms so defined are often close to "chemical intuition", but in some cases there are major differences. This paper clarifies the relationships between "chemical intuition" based on simple orbital arguments and the actual distribution of charge as described by its atomic charges and by the properties of critical points of the electron density (points where the gradient of the density vanishes). Equations are derived which show how changes and trends in critical point positions and properties can be understood in terms of perturbational molecular orbital (PMO) models. The relationship between PMO models and atomic charges is also quantified, and some previously published data are accounted for by using this relationship. Finally, the effects of the fluoro substituent on the ethyl, vinyl, and carbonyl groups are used to illustrate the general results.

The quantum theory of atoms in molecules developed over recent years by Bader and co-workers[1,2] yields definitions of atoms and bonds in molecules from an analysis of the topology, or qualitative form, of molecular electron distributions. The atoms

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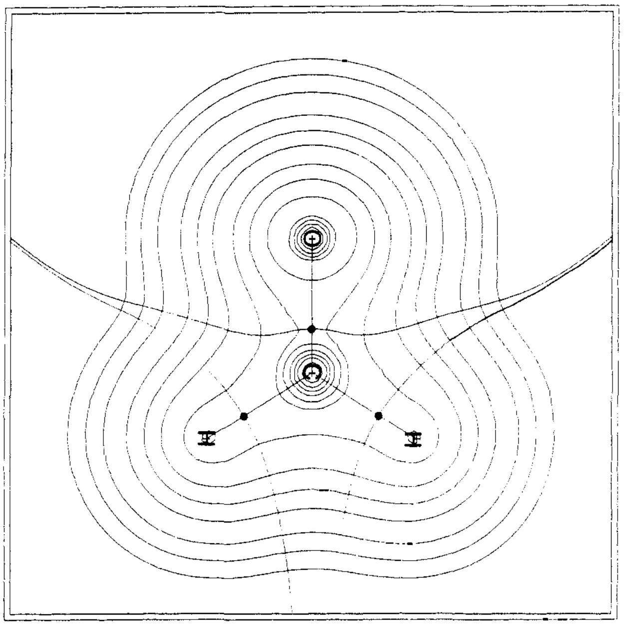

Figure 1. Contour plot of the electron density in the molecular plane of formaldehyde, from a 6-31G*/6-31G* calculation. The dots are the *bond points*, which mark the intersection of the *bond path* joining the nuclei with the *interatomic surface*, which separates the basins of the atoms.

so defined are unique in that they have well-defined quantum mechanical properties, which can be obtained from a variational principle.[1] It is observed[2] that between each and every nucleus customarily considered to be "bonded" in a molecule there is the three-dimensional equivalent of a "ridge" in the electron distribution, with the nuclei forming the peaks at each end of the ridge. The lowest point on this ridge is a saddle point and is called a "bond critical point" or "bond point" for short. Within the theory of atoms in molecules the presence of such a bond point, in a molecule close to an equilibrium geometry, *defines* the two atoms to be bonded.[3] The surface which separates the two atoms passes through this bond point, as shown in Figure 1 for the molecular plane of formaldehyde. The theory of atoms in molecules enables the characterization and analysis of molecular electron distributions from a firm theoretical base and in terms of the essential chemical concepts of atoms and bonds.

The atomic charges defined by the theory of atoms in molecules are expected to be of particular interest to chemists, and it has also been shown that the values of density related properties at bond points can summarize properties of that bond in a concise and chemically interesting manner.[4-6] In many cases the charges of the atoms defined from theory are similar to the ill-defined values which chemists customarily associate with atoms in the ubiquitous "ball-and-stick" representation of molecules. As an example, the charge on hydrogen is shown for the diatomic hydrides as the bonding partner X crosses the second and third periods in Figure 2.[7,8] The charge on the hydrogen changes essentially monotonically from almost −1 in the alkali metal hydrides to more than +0.7 in HF. In line with "intuition" based on electronegativity the second-row hydrides produce a more positive H than the third row except for the left hand side of the periodic table, where the difference between the periods is small.

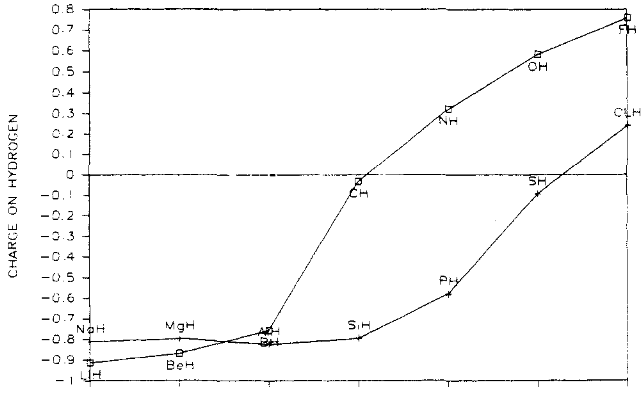

Figure 2. The charge on the hydrogen atom in diatomic hydrides HX. The values are calculated from near Hartree–Fock wave functions.[6]

Also in accord with electronegativity expectations, the atoms in CH are essentially neutral. Thus, the qualitative trends of the ab initio calculated atomic changes in diatomic hydrides are easily interpreted in terms of elementary chemical concepts and models.

There are also cases where the calculated atomic charges are surprising to many chemists. One example is the allyl cation. Resonance or simple π-orbital models of this ion suggest that each terminal carbon "atom" should have a charge of +0.5 electrons, where the "atomic charge" is here defined in terms of the Hückel density matrix. A published STO-3G wave function[9] yielded total (theoretical) atomic charges of −0.2 electrons on the terminal carbon atoms, +0.7 on the central carbon atom, and −0.1 on each of the hydrogens. The signs are the opposite of those expected from simple orbital models! Improvement of the basis set alters these numbers compared to STO-3G[10] but does not change the qualitative observation that the atomic charges are considerably different from the predictions of π orbital models. The cause of the discrepancy between "intuition" and calculations must lie elsewhere.

One of the main aims of the present paper is to uncover the roots of such discrepancies between chemical "intuition" and atomic or group charges as calculated from electron distributions. This is done by taking a close look at the relationships between chemical "intuition" based on perturbational molecular orbital (PMO) models[11] and the actual molecular charge distribution as described by the theory of atoms in molecules. The study provides a framework within which almost all the theoretical atomic charges published to date can be understood and within which qualitative orbital arguments can be tested against ab initio electron distributions. Atomic and critical properties in hydrocarbons are examined to illustrate the use of the approach, and the effects of the fluoro substituent on C—C, C=C, and C=O bonds are described to bring out other important aspects of the general relationships derived.

Hückel Theory and the Electron Distribution. The general problem is to describe the response of the charge density of a bond A–B between two groups A and B to perturbation. The perturbation may involve, for example, the alteration of a substituent in one of the groups A or B. The starting point is a description of the unperturbed A–B bond, and the goal is to estimate from Hückel theory-based models how the perturbation changes the electron distribution of the bond and how it alters the charges of A and B. Two important features of the approach are that the Hückel model is *required* to match the calculated density of the unperturbed bond and that the density in the bonding region is described by a Taylor series expansion about the bond point. Both

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(1) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1982**, *14*, 62–124.

(2) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 894–947.

(3) Bader, R. F. W.; Essen, H. *J. Chem. Phys.* **1984**, *80*, 1943–1960.

(4) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Krada, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061–5068.

(5) Cremer, D.; Kraka, E.; Slee, T. S.; Bader, R. F. W.; Lau, C. D. H.; Nguyen-Dang, T. T.; MacDougall, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 5069–5075.

(6) Cremer, D.; Kraka, E. *Croat. Chem.* **1984**, *57*, 1259–1281.

(7) Bader, R. F. W.; Beddall, P. M. *J. Am. Chem. Soc.* **1973**, *95*, 305–315.

(8) Bader, R. F. W.; Beddall, P. M. *Can. J. Chem.* **1974**, *52*, 2268–2282.

(9) Bader, R. F. W.; Tang, T.-H-.; Tal, Y.; Biegler-Konig, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 946–952.

(10) Slee, T. S.; MacDougall, P. J., submitted for publication.

(11) (a) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw Hill: New York, 1969. (b) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975. (c) Albright, T.; Whangbo, M. H.; Burdett, J. K. *Orbital Interactions in Chemistry*; Wiley: 1985.

Table I. Properties of Atoms and Bonds in Selected Organic Molecules[a]

bond (A-B)	ρ_c	λ_1	λ_2	λ_3	R(A)	R(B)	Q(A) [= $-Q$(B)]
H2CCH—H	0.286	-0.771	-0.763	0.465	1.293	0.741	-0.018
H3C—CH3	0.252	-0.477	-0.477	0.293	1.443	1.443	0.0
H2C=CH2	0.363	-0.815	-0.564	0.189	1.244	1.244	0.0
H2C=O	0.431	-1.275	-1.166	3.277	0.729	1.509	1.295
Me—H	0.277	-0.719	-0.719	0.457	1.288	0.760	0.008
Et—H	0.279	-0.725	-0.718	0.460	1.287	0.765	0.025
Me—CHCH2	0.266	-0.522	-0.508	0.296	1.391	1.448	0.052
MeCH=CH2	0.363	-0.816	-0.557	0.190	1.224	1.268	0.013
CH2CH—CHCH2	0.285	-0.584	-0.546	0.298	1.387	1.387	0.0
CH2CHCH=CH2	0.361	-0.812	-0.567	0.199	1.264	1.235	0.006

[a] All values are calculated at the 6-31G*/6-31G* level and are in au.

of these features reflect the pertubational nature of the approach.

In semiempirical theories such as the Hückel model a minimal basis set of atomic orbitals is assumed. If we invoke the zero differential overlap (ZDO) approximation then the density at any point in a bonding region is given by

$$\rho(x) = \sum_i q_i \cdot \rho_i(x) \tag{1}$$

where q_i is the population of the basis function, and $\rho_i(x)$ is the density of basis function ϕ_i with unit occupancy. Hückel theory avoids assigning explicit forms to the atomic orbitals, and so $\rho_i(x)$ is not precisely defined. This is not necessary, as the requirement that $\rho(x)$ as given by eq 1 match the ab initio density for the unperturbed molecule in the bonding region gives all the information that is needed. There is also an assumption implicit in Hückel theory and in other ZDO theories concerning the form of the atomic orbitals, which may be called the *localization assumption*: that each basis function is in some sense localized in a region around its center. This assumption will be built in to the analysis of the density at a number of points through the discussion and completes the information needed to educe the relationships between Hückel based models and changes in atomic and critical values.

If we perturb the system, then the density in a bond A–B will be altered, within ZDO models, by a superposition of three effects: (i) The bond lengths change. (ii) The populations of the basis functions change

$$q_i^0 \rightarrow q_i^0 + \delta q_i \tag{2}$$

(iii) The nature of the basis functions change

$$\rho_i(x) \rightarrow \rho_i(x) + \delta\rho_i(x) \tag{3}$$

Number (i) can either be estimated from PMO models or, as in the examples studied in the present paper, taken from the ab initio calculation to be analyzed. Number (ii) can be estimated from PMO models, at least qualitatively, and is the major concern of this study. The Hückel model applied to σ bonded systems[12] employs localized hybrid orbitals as a basis. The PMO method has recently been extended to this case by Herndon[13] and Dewar[14] and is the simplest orbital model of chemical changes to σ bonds. Although no particular orbital model is used in the current paper, the approach does have this σ PMO model in mind as a means of predicting changes to orbital populations. The use of hybrid orbitals means that we can employ the pairing theorem[11a] and its corollaries but also means that possible changes in participation of s and p orbitals in a given bond cannot be properly treated: factor (iii) above is neglected. Other simple orbital approaches[11c] focus on a basis set of spherical harmonic atomic orbitals, in which fixed hybridization is not assumed, but in which the pairing theorem is not used. In this case some of the results presented below must be modified slightly.

The Densities of Reference Bonds. The crucial step in relating the changes in Hückel electronic structure to changes in the properties of critical points (and thus to changes in atomic properties) is to describe the charge density of the unperturbed bond by a truncated Taylor series expansion about the bond point.[15] This enables us to predict how a bond will respond to perturbation from a knowledge of the *critical values* of a reference bond only: i.e., the position of the bond point (x_c), the value of the density at the bond point (ρ_c), and the eigenvales of the Hessian matrix (i.e., the principal curvatures of the density at the bond point), λ_i, i = 1, 2, 3. One principal curvature (λ_3) is positive and is directed along the bond path. The other two (λ_1, λ_2) are perpendicular to the bond path and are negative. The critical values are exactly the information used to classify critical points by their topological character[2] and can be obtained for the unperturbed bond from a single SCF calculation and from application of an interactive program, EXTREME, part of the PROAIMS package available from this laboratory.[16]

All SCF calculations carried out for this paper employed the GAUSSIAN 80 program[17] with default convergence criteria, by using the 6-31G* basis set and gradient geometry optimization again by using default convergence criteria. All integrations over atomic basins were carried out by using the PROAIMS package, and are expected to be accurate to 0.005 electrons.[15]

The reference bonds to be studied in this paper are the C—C bond in ethane, the C=C bond in ethene, and the C=O bond in formaldehyde. A knowledge of the critical values of these bonds enables us to make predictions concerning the density of the CC bonds in any substituted ethane or ethene molecule and the CO bond in any carbonyl compound. The critical values of these reference bonds (computed at the 6-31G*/6-31G* level) along with the CH bond in ethene are presented in Table I, and the density along the internuclear axis is plotted in Figure 3 for each of the bonds, together with the quadratic Taylor series approximation. These data show the marked differences between the bond types: differences that have a large influence on how the bonds respond to perturbations. The highly asymmetric nature of the polar CO bond means that the quadratic Taylor series approximation does not work nearly as well as for the symmetrical CC bonds. The bond point is pushed right up against the core of the carbon atom, which rises sharply to the left of the figure, while the valence density of the oxygen rises more gently to the right.

We now have all the information needed to show how changes in the density predicted by simple orbital models should alter the critical and atomic values of actual electron densities.

Interpretation and Understanding of Atomic and Critical Properties. The equations which describe the effects of perturbations on critical and atomic properties are grouped together in Table II. Their detailed derivations are presented in the Appendix, while the current section is content to give first a brief qualitative justification for the results and then a discussion of their interpretation, by using some simple examples.

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(12) Sandorfy, C. *Can. J. Chem.* **1955**, *33*, 1337–1351.

(13) Herndon, W. C. *Tetrahedron Lett.* **1979**, 3801–3804. Herndon, W. C. *J. Chem. Ed.* **1979**, 448–451.

(14) Dewar, M. J. S. *Bull. Soc. Chim. Belg.* **1979**, *88*, 955–967. Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669–682.

(15) Slee, T. S. *J. Am. Chem. Soc.* **1986**, *108*, 606–612.

(16) Biegler-Konig, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *13*, 317–328.

(17) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topio, S.; Kahn, L. R.; Pople, J. A. *Carnegie*-Mellon University, GAUSSYIAN 80.

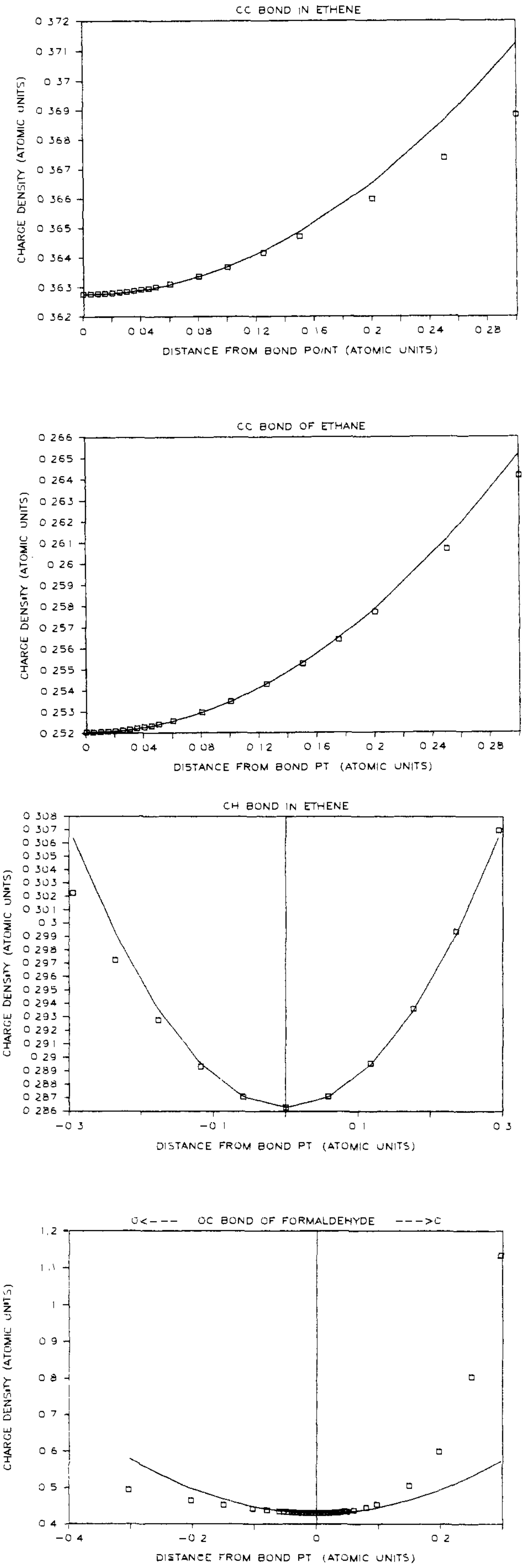

Figure 3. The charge density along the bond path in reference bonds. The computed charge density is marked by open squares, the quadratic Taylor series approximation by a the continuous line.

Table II. Relationships between Simple Orbital Models and the Charge Density. See the Text for Explanation of Symbols, Derivations and Discussion

bond pt. position	$\delta x_c = (q_t\lambda_t - q_s\lambda_s)\delta R/2\lambda_3 - (\delta q_s\rho'_s + \delta q_t\rho'_t)/\lambda_3$	IA
	$\delta x_c = \rho'_t(\delta q_s - \delta q_t)/\lambda_3$ (symmetrical bonds)	IB
radius of atom A	$\delta r_B(A) = q_t\lambda_t\delta R/\lambda_3 - (\delta q_s\rho'_s + \delta q_t\rho'_t)/\lambda_3$	IIA
	$\delta r_B(A) = \delta R/2 + \rho'_t(\delta q_s - \delta q_t)/\lambda_3$ (symmetrical bonds)	IIB
density at bond pt.	$\delta\rho_c = \delta q_s\rho_s^0 + \delta q_t\rho_t^0 - q_t\rho'_t\delta R$	IIIA
	$\delta\rho_c = (\delta q_s + \delta q_t)\rho_c^0/2 - \rho'_t\delta R$ (symmetrical bonds)	IIIB
atomic population	$\delta N(A) = \sum_i n_i(A)\delta q_i - \sum_{B\rightarrow A} N(S)(\delta q_s\rho'_s + \delta q_t\rho'_t)/\lambda_3$	IVA
	$\delta N(A) = \sum_i n_i(A)\delta q_i - \sum_{B\rightarrow A} N(S)\rho'_t(\delta q_s - \delta q_t)/\lambda_3$ (symmetrical bonds)	IVB
	$\delta N(A) = \sum_i n_i(A)\delta q_i + \sum_{B\rightarrow A} N(S)\delta x_c$	IVC

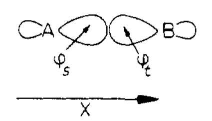

Figure 4. Simple hybrid orbital representation of a σ bond, showing the orientation used in the text.

The position of the bond point (x_c) and the density at the bond point (ρ_c) in unstrained bonds are only affected *directly* by the σ density. Changes to the π density only affect them in as much as they alter the σ distribution or the bond length. Choosing hybrid orbitals ϕ_s and ϕ_t as a basis for the representations of a σ bond is very simple and is given in Figure 4.

The density of the unperturbed bond is given, at the bond point x_c^0, by the sum of the densities of the orbitals

$$\rho_c^0 = q_s\rho_s^0 + q_t\rho_t^0 \tag{4}$$

where ρ_s^0 is the density of the basis function ϕ_s with unit occupancy at x_c^0. As was pointed out above, a knowledge of the total density of the reference bond is assumed. The general perturbation to be applied is one where the nuclear positions change by δR_A and δR_B and the populations of the basis functions are changed by δq_s and δq_t. The expression for the modified density then becomes

$$\rho(x) = (q_s + \delta q_s)\rho_s(x - \delta R_A) + (q_t + \delta q_t)\rho_t(x - \delta R_B) \tag{5}$$

The change in position of the bond point can be derived from eq 5 by using a Taylor series expansion about x_c^0 to describe ρ_s and ρ_t, treating the changes δq and δR to first order only and then requiring that the gradient of ρ vanish to find the new critical point. The result, relative to the mid-point of the bond, is eq IA of Table II. In this equation, the gradients of the orbital densitis are ρ'_s, and ρ'_t, while the orbital second derivatives along the bond path are λ_s and λ_t. The neglect of second-order terms separates the bond length and orbital population effects. Equation IIA expresses the shift in bond point with the nucleus of atom A as origin and differs from IA only in the bond length contribution. The simple correspondence of these equations to chemical ideas is discussed below: for the moment it is worth noting that the bond point position moves in response to the (weighted) difference between the orbital population changes and so describes the polarity of the bond.

The new values of ρ_c can also be found from eq 5 if the density in the valence region is approximated by a constant: the result is equation IIIA of Table II. Again, the restriction to first order in the assumed small quantities δq and δR leads to a simple equation with distinct contributions from orbital population and bond length changes. The density responds to the (weighted) sum of orbital populations rather than the difference and decreases with a simple bond stretch.

The CC bonds of both ethane and ethene are symmetrical about the bond point and the populations of the atomic orbitals are unity, so that the curvatures λ_s and λ_t are both $\lambda_3/2$, and $\rho'_s = \rho'_t$. For these important cases simplifications of eq IA–IIIA occur, which are equations IB, IIB, and IIIb in Table II.

Also in Table II are results relating orbital models and bond point properties to the change in atomic population, $\delta N(A)$. These equations (IVA–IVC) are also to first order and so are again a sum of two separate contributions, but in this case the first contribution refers to changes that take place inside the basin of the unperturbed atom (the *basin* term) and the second to changes that arise from the change in volume of the atom as the bond points move (the *surface* term). A change in population of any basis function with density in the basin of atom A will contribute to the basin term of that atom, and the first term in eq IV thus involves a sum over *all* basis functions. The shift in bond point that is involved here turns out to be relative to the bond midpoint as origin (see eq IVC), as explained in the Appendix. This gives the correct result that a simple stretch of a symmetrical bond produces no net change in the population of either half of the molecule by using equation IVC

$$\delta N(\mathrm{A}) = \sum_{i \text{ on B}} -q_i n_i(S)\delta R + N(S)\delta R/2 = -[N(S)/2]\delta R + N(S)\delta R/2 = 0 \quad (6)$$

Equations IV make it clear that the changes in atomic charges are *not* the same things as the changes in the atomic orbital populations of simple orbital models, but that the two are closely related, so that changes in atomic charges can be interpreted in terms of orbital models. The truncation errors for the equations of Table II, which may be thought to be important, are also discussed in the Appendix, and it is shown that they can be neglected.

I will now look in more detail at the interpretation of critical and atomic properties in terms of orbital models by using eq I–IV of Table II. Referring to Figure 4 we see that atom or group B is at positive x with respect to A. In accord with the localization assumption, I will require ρ'_s to be negative and ρ'_t positive, and this allows us to make qualitative conclusions concerning the response of the bond to a simple change. Consider a perturbation in which q_s is increased by δq and q_t is decreased by the same amount, with the bond length kept constant. This corresponds to a polarization of the bond. The bond point will, by eq IA, be moved toward the positive end of the bond dipole, i.e., toward atom B. The distance through which it is moved, for a given type of bond, is a measure of the polarity of that bond. The density at the bond point as given by eq IIIA responds to the (weighted) sum of the orbital population changes and so will change very little in response to a simple polarization of the bond. In symmetrical bonds no change at all in ρ_c is predicted. Finally, eq IV shows that the bond point shift will produce a surface contribution which increases the population of group A. Employing the localization assumption, we can assert that $n_s(\mathrm{A})$ will be greater than $n_t(\mathrm{A})$, so that the basin term will also produce an increase in $N(\mathrm{A})$. The population of group B will decrease by an identical amount. Equations I–IV thus predict a *qualitative* correspondence between orbital models and the charge density which confirms with chemical intuition in a simple manner for this case.

Another useful perturbation to consider is a simple bond stretch, keeping the populations q_s and q_t constant. Within Hückel theory the resonance integral β is taken to be constant for a given type of bond, which is equivalent to neglecting the effect of bond length changes on the atomic orbital populations. In this approximation, then, the bond length and the orbital populations are independent of each other. (For alternant systems the independence of bond length and atomic orbital populations is maintained when β is allowed to change: a consequence of the vanishing of the "atom-bond polarizability"[11a].) Thus, calculations for the reference molecule at different bond lengths will, within the Hückel model, correspond to a change in R keeping q_s and q_t constant. The density at the bond point is predicted to decrease as the bond is stretched, the rate of decrease being $q_t\rho'_t$ or, for symmetrical bonds, simply ρ'_t. Calculations were carried out at the 6-31G* level for each of the reference bonds used in this paper, keeping all other geometrical parameters at their equilibrium geometry values. Over a range of bond lengths representative of changes induced by substituents, the values of ρ_c are indeed related to the bond length with high precision. The slopes of the graphs are −0.256 for ethane, −0.373 for ethene, and −0.467 for formaldehyde (all in au). The slopes for the CC bonds are useful as they provide us with values for ρ'_t which can be used in eq I, II, and IV.

The predictions concerning the effect of a simple bond stretch on other properties of symmetrical bonds are dictated by symmetry, and eq IB and IVC correctly predict that the bond point will remain at the midpoint and that the populations of A and B will remain at zero.

The differences between the critical values of the reference bonds were discussed in an earlier section. Equations I–IV show how these critical values affect the responses of critical and atomic properties to perturbation. The values of λ_3 are particularly important and differ by more than an order of magnitude between C=C and C=O bonds. The inverse proportionality of the bond point shift to λ_3 leads us to expect that the bond point position of C=C bonds will be much more sensitive to orbital populations than the CO bond point position. This is a quantitative statement of the intuitive suggestion that bond points in regions where the density is "flat"—i.e., of small curvature—are "motile" or easily moved[5] and is of crucial importance in the translation between orbital models and density properties.

Equation IVC shows that the surface contribution to the population change is proportional to δx_c while the basin contribution has no such dependence. The relative importance of these two terms will thus vary with the bond type, and the following sections will show how this difference resolves the apparently counterintuitive values of the populations in certain cases. In unsaturated hydrocarbons the surface term will be large, while similar perturbations of the carbonyl group will produce only small surface contributions to the change in population.

It should be noted that the total molecular dipole can be expressed *exactly* as a sum of atomic contributions by the equation

$$\mu = \sum_{\mathrm{A}} (\mu(\mathrm{A}) - Q(\mathrm{A})X_\alpha) \quad (7)$$

where $\mu(\mathrm{A})$ is the dipole of the charge within the atomic basin measured with the nucleus as origin, and where $Q(\mathrm{A})$ is the net charge on the atom. The presence of atomic dipoles in this equation is unavoidable when modelling a continuous distribution of charge and can lead to discrepancies between charges defined from the electron distribution and charges qualitatively assigned to atoms in "ball-and-stick" representations of molecules, where the molecular dipole is often (but not always) taken to indicate the signs and magnitudes of the charges on the (assumed dipole-less) atoms. In some cases the atomic dipole can in fact be large, reflecting a large asymmetry of the electron distribution in the basin.

Properties of Atoms and Bonds in Hydrocarbons. Table I shows the atomic and critical properties of some prototype hydrocarbon molecules, calculated at the 6-31G*/6-31G* level. The approach developed in the present paper allows an interpretation of these data in terms of simple orbital concepts.

The relative populations of the two hybrid orbitals involved in a given bond in a hydrocarbon molecule reflect the relative electronegativities of the two groups involved in the bond, though in more complicated molecules field effects may influence the relative orbital populations also. Thus, the bond point position should, in general, also be consistent with the relative electronegativities of the two sides of the molecule.[6–8] The data of Table I show this to be so. Also, the basin and surface terms in these bonds reinforce each other's effects, the perturbation being roughly one of a polarization of the bond in question compared to ethane, just as described in the previous section, and so the charges on each side of the molecule qualitatively follow the bond point position.

Methane shows that the methyl group donates charge to hydrogen, a result that has been discussed before.[18] Together with

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(18) Wiberg, K. B.; Wendolowski, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 6561–6563.

the high degree of transferability of the topologically defined groups between hydrocarbon molecules,[19] this result sets the trend for other bonds. The hydrogens on ethane are more negative than those in methane as a result of replacing H by Me. The charges on the hydrogens of ethene and ethyne are increasingly positive, and the bond point position moves closer to the proton as the electronegativity of the carbon bonding hybrid increases. An improvement in basis set alters the absolute values of the charges slightly but does not significantly alter the trends observed.[18]

In propene, the methyl group donates electrons to the vinyl fragment more than do the hydrogens, whose charges all lie between 0 and +0.01 electrons. The methyl group is positively charged, again reflecting the greater electronegativity of the sp^2 carbon than the sp^3. Further, the CH_2 group is slightly negative, another reflection of the electron donating influence of the methyl group.

In butadiene the terminal CH_2 group is slightly negative, which is contrary to electronegativity expectations. The bond point position does, however, reflect the electronegativities of the two fragments of the molecule, being closer to the CH_2 carbon nucleus. Equation IVC suggests that this lack of concert between the bond point position and the group charge is a reflection of the basin contribution to the charge and most likely originates with the π orbital contribution to the population. This suggestion is confirmed by a separate look at the σ and π contributions to the CH_2 charge, which show the σ component to be +0.012 and the π component to be −0.018. Thus, in cases where the π distribution is polarized, the atomic charges may carry different information from the bond point positions.

The density at the bond point confirms the suggestion that the total orbital population ($q_s + q_t$) in each bond remains essentially constant in these molecules, as ρ_c correlates well with the bond length alone. The best fit line is (in atomic units)

$$\rho_c = 1.054 - 0.278R \tag{8}$$

with a correlation coefficient of −1.000 and a standard deviation for the slope of 0.001. Such a correlation has been previously reported and discussed as part of a study of a wider range of hydrocarbons at the STO-3G basis set.[8] The values of the slope and intercept are both somewhat greater in magnitude for the 6-31G* basis set than for STO-3G. The slope of eq 8 is between those for the bond stretches of ethane and ethene reported above.

The allyl cation was mentioned in the introduction as a case where the atomic charges appear to be counter intuitive. The analysis of the relationship between orbital concepts and topological features of the electron density presented here shows that the orbital and resonance pictures are completely consistent with the actual electron distribution as described by its atomic charges, which were presented in the introduction. The STO-3G basis set substantially underestimates the values of λ_3 for CC bonds as compared to better basis sets,[4] which means that the STO-3G charges will exaggerate the surface contribution to the atomic charges relative to the basin contribution. The sensitivity of the bond point position to basis set quality has been discussed elsewhere.[18,20] The *qualitative* comparison between the π orbital model and the calculated distribution will, however, not be affected by improvement of basis set.

The large π electron deficiency of the terminal carbons causes them to be very electronegative, and so they withdraw σ charge inductively from the central carbon and from the terminal hydrogens. The central carbon, now depleted of σ electrons, takes charge in turn from the hydrogen attached to it. The small λ_3 curvature of the CC bond in hydrocarbons (especially at the STO-3G level[4]) and the concomitant large shift in bond points means that it is the surface term, which involves the σ charge alone, which determines the net population on the atom and *not* the π distribution. Thus, the charges assigned purely on the basis of π orbital models do not and should not correspond directly to the topologically defined total atomic charges. The "formal" charges deduced from π orbital models contribute only to the basin term of eq IVC. They also determine the relative electronegativities of the atoms in the molecule, which in turn determine the bond point positions which, through the surface term of equation IVC, have a large influence on the atomic charges in cases where λ_3 is small. This interpretation is supported by the observation that the π population in each CH_2 group is, in a 6-31G* wave function,[10] found to be 0.50. The Hückel prediction is confirmed. The interesting case of the alkyl ions has been studied by using a better basis set,[19] and the qualitative conclusions are not altered.

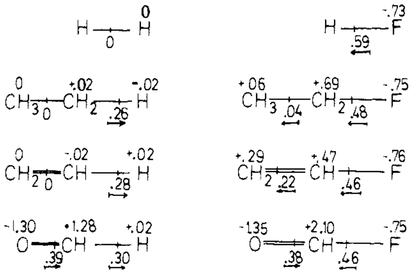

Figure 5. The atomic or group charges (above the molecule) and the bond point position measured relative to the bond midpoint (below the molecule) showing the effects of fluorine substitution. All data are in atomic units, and the arrows underneath the bond point shift mark the direction of shift relative to the bond midpoint.

The Effects of Fluoro Substitution. Figure 5 shows the atomic charges and bond point properties for hydrogen, ethyl, vinyl, and formyl fluoride, in addition to the hydrogen analogues. Fluorine disturbs the charge density of an adjacent bond more than other substituents of similar simplicity[15] and so provides a useful introduction to the study of substituent effects on the electron distribution.

The CF bond is very similar in each molecule. The net charge transfer between fluorine and the rest of the molecule is almost identical in all cases. The electronegativity of the fluorine pushes the CF bond point right up against the core of the carbon atom, and so minor differences between the different groups do not alter the situation significantly. Any back polarization of π electrons does not result in net charge transfer to the vinyl or formyl groups.

The similarity between the molecules is not maintained as we look at the bonds within the substrate group. The position of the critical point and the charge transfer between the CHF group and the Me, CH_2, or O fragments reflect the predictions of eq I. In vinyl fluoride the inductive effect produces a large shift in bond point toward the CH_2 group which makes that group positively charged. In ethyl fluoride the bond point is shifted by a factor of more than 5 less than in vinyl fluoride, which is qualitatively what we would expect from eq I. The charge on the methyl group is again fixed by the surface term and is positive. Formyl fluoride behaves in a fundamentally different manner. The bond point is shifted only slightly toward the oxygen, again as expected from the inductive effect. The population on the oxygen is *more* negative than that in formaldehyde, however. This can be interpreted by noting that the basin contribution to the population change is likely to be the determining factor in this case as a result of the small value of δx_c. The fluorine atom will polarize the CO π bond away from itself and so increase the π charge on the oxygen, which in this case determines the net charge on the atom. The different orbital interpretation of the atomic charge in this case and also in the case of hydrocarbons is obvious and demonstrates the need for an analysis such as the present one to provide a reliable method of translating between the two languages if misinterpretation is to be avoided.

Confirmation of the correctness of the interpretation of the atomic charges in formyl fluoride and vinyl fluoride can be obtained by looking separately at the σ and π contributions to the net charges. These are presented in Table III and demonstrate that in the case of vinyl fluoride it is indeed the σ charge which determines the final outcome, while in the case of formyl fluoride the π charge is the decisive factor.

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(19) Bader, R. F. W. *Can. J. Chem.* **1986**, *64*, 1036–1045.

(20) Edgecomb, K. E.; Boyd, R. J. *Int. J. Quantum. Chem.* **1986**, *29*, 959–973.

Table III. σ and π Contributions to Fluorine Substituent Effects on Atomic Charges, Together with Bond Point Position[a]

	H	F
	$XCH{=}CH_2$	
$Q(CH_2)$	0.000	0.288
$Q_\sigma(CH_2)$	0.000	0.288
$Q_\pi(CH_2)$	0.000	0.000
$r(CH_2)$	1.244	1.017
δx_c	0.000	0.219
	$XCH{=}O$	
Q(O)	-1.295	-1.349
$Q_\sigma(O)$	-0.735	-0.703
$Q_\pi(O)$	-0.560	-0.646
r(O)	1.509	1.479
δx_c	-0.390	-0.379

[a] All data are in au.

Table IV. Truncation Errors in the Taylor Series Approximation to Bond Point Position and Density, from 6-31G*/6-31G* Calculations[a]

	bond		
	C—C	C=C	C=O
displacement produced by F	0.04	0.22	0.01
$\Delta(x_c)$	0.00	0.02	0.002
$\rho_c(F) - \rho_c(H)$	0.02	0.01	0.03
$\Delta(\rho_c)$	0.00	0.001	0.000

[a] See text for explanation.

Conclusions

The present paper has shown that trends in atomic charges and properties of bond points calculated directly from the electron density and defined by the theory of atoms in molecules can be interpreted in terms of "chemical" concepts based on simple orbital models of electronic structure. The interpretation must take into account the character of the unperturbed bond as summarized by its critical values. In particular, the value of the positive principal curvature, along the bond path, is crucial in the orbital interpretation of atomic charges.

Although the approach presented in this paper clarifies many of the aspects of the relationship between orbital concepts and the electron distribution, some important questions concerning the utility of atomic charges deserve further investigation. Large atomic dipoles may be expected in unsaturated hydrocarbons, as the shifts in bond points will produce highly asymmetric atomic basins. The atomic charges may not provide a good estimate of the total molecular dipole on their own and must be combined with atomic dipoles and possibly higher multipoles in order to produce a reasonable estimate of the electrostatic field produced by the molecular charge distribution. It must be remembered, however, that the atomic charges are defined directly in terms of the electronic charge distribution and so cannot be dismissed as artefacts of some model. When they fail to reproduce molecular dipoles, this is an indication that the "ball-and-stick" model, which we use to guide our thoughts and which tacitly assumes that molecules can be well-represented by a collection of spherical charges, is failing, and that higher atomic multipoles are essential for a description of the molecule's electrostatic field.

Finally, it should be pointed out that the approach to the interpretation of electron distributions described here can be extended easily to other quantities. The ellipticity of a bond[4] describes its deviation from cylindrical symmetry and has been interpreted as a density analogue of the "π character" of simple orbtal models.[4] Equations can be derived for the ellipticity in an analogous way to those for x_c and ρ_c. Further, the laplacian of the electron distribution has recently been shown[3,21,22] to be useful in gaining additional insight into the fine structure of the electron distribution in molecules as well as to predict sites of attack in ionic reactions. The critical points of the laplacian obey equations which are exactly analogous to those for critical points of the density itself, and such a treatment helps reveal the connections between the behavior of the laplacian of the electron density and the underlying changes in the density itself. These points will be amplified in a later publication.

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Appendix

In this appendix I will derive I–IV of Table II that relate Hückel perturbations to changes in the position of the bond point, the value of the density at the bond point, and the atomic charges.

Within the simple bond orbital picture of Figure 4 the density of the unperturbed bond is given, at the bond point x_c^0, by eq 4

$$\rho_c^0 = q_s\rho_s^0 + q_t\rho_t^0 \qquad \text{(A1)}$$

where ρ_s^0 is the density of the basis function ϕ_s with unit occupancy at x_c^0. The changes of nuclear positions are expressed as

$$X_A \rightarrow X_A + \delta R_A$$
$$X_B \rightarrow X_B + \delta R_B \qquad \text{(A2)}$$

If, in addition, the populations of the basis functions are changed then the density becomes

$$\rho(x) = (q_s + \delta q_s)\rho_s(x - \delta R_A) + (q_t + \delta q_t)\rho_t(x - \delta R_B) \qquad \text{(A3)}$$

First let us derive the equations for the position of the bond point in this new density, x_c. Its position can be related to that of the bond point in the reference density (x_c^0) by using the Taylor series expansion about x_c^0 to describe ρ_s and ρ_t.[15] It is convenient to introduce two new variables

$$x_c - \delta R_A = x_c^0 + \delta x_s$$
$$x_c - \delta R_B = x_c^0 + \delta x_t \qquad \text{(A4)}$$

so that the density at the bond point x_c is given by

$$\rho(x_c) = (q_s + \delta q_s)(\rho_s^0 + \rho'_s\delta x_s + \lambda_s\delta x_s^2/2) + (q_t + \delta q_t)(\rho_t^0 + \rho'_t\delta x_t + \lambda_t\delta x_t^2/2) \qquad \text{(A5)}$$

x_c can now be found by requiring that $\partial\rho/\partial x_c = 0$, which to first order in the assumed small quantities δq_s, δq_t, and δx_c is

$$0 = (q_s\rho'_s + q_t\rho'_t) + (\delta q_s\rho'_s + \delta q_t\rho'_t) + (q_s\lambda_s\delta x_s + q_t\lambda_t\delta x_t) \qquad \text{(A6)}$$

or as $$q_s\rho'_s + q_t\rho'_t = \partial\rho^0(x_c^0)/\partial x = 0 \qquad \text{(A7)}$$

and $$q_s\lambda_s + q_t\lambda_t = \partial^2\rho^0(x_c^0)/\partial x^2 = \lambda_3 \qquad \text{(A8)}$$

$$0 = (\delta q_s\rho'_s + \delta q_t\rho'_t) - (q_s\lambda_s\delta R_A + q_t\lambda_t\delta R_B) + \lambda_3\delta x_c \qquad \text{(A9)}$$

where $\delta x_c = x_c - x_c^0$. Rearranging gives

$$\delta x_c = -(\delta q_s\rho'_s + \delta q_t\lambda_t)/\lambda_3 + q_t\lambda_t(\delta R_B - \delta R_A)/\lambda_3 \qquad \text{(A10)}$$

Equation A10 takes on a slightly simpler form if we measure the shift relative to the bond midpoint, in which case it is equal to half the difference between the bonded radii of the atoms (i.e., the distance from the nucleus to the bond point). The bonded radius of atom A to the bond point with B will be denoted $r_B(A)$. In this case, $-\delta R_A = \delta R_B = \delta R/2$, and we have equation IA of Table II; which shows how changes to orbital populations and to bond lengths affect the bond point position

$$\delta x_c = (q_t\lambda_t - q_s\lambda_s)\delta R/2\lambda_3 - (\delta q_s\rho'_s + \delta q_t\rho'_t)/\lambda_3 = (r_B(A) - r_A(B))/2 \qquad \text{(IA)}$$

The changes in bonded radii of the atoms follow immediately, simply by choosing the origin to remain fixed at one nucleus. For instance the change in radius of atom A is given by

$$\delta r_B(A) = q_t\lambda_t\delta R/\lambda_3 - (\delta q_s\rho'_s + \delta q_t\rho'_t)/\lambda_3 = \delta x_c + q_s\lambda_s\delta R/\lambda_3 \qquad \text{(IIA)}$$

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(21) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800–3810, 3811–3819.

(22) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1985**, *106*, 1594–1605.

As pointed out in the text, the CC bonds of ethane and ethene are symmetrical about the bond point, the populations of their atomic orbitals are both unity, and the curvatures λ_s and λ_t are both $\lambda_3/2$, so that the dependence of δx_c on R vanishes, as of course it should. Further, $\rho'_s = -\rho'_t$, so that we have the simpler expressions

$$\delta x_c = \rho'_t(\delta q_s - \delta q_t)/\lambda_3 \qquad \text{(IB)}$$

$$\text{and} \qquad \delta r_B(A) = \delta R/2 + \rho'_t(\delta q_s - \delta q_t)/\lambda_3 \qquad \text{(IIB)}$$

An equation for ρ_c can be written down straight from eq A5 above. Carrying only first-order terms, we can write

$$\rho_c = \rho_c^0 + (\delta q_s\rho_s^0 + \delta q_t\rho_t^0) + q_s\rho'_s\delta x_s + q_t\rho'_t\delta x_t \qquad \text{(A11)}$$

$$\delta\rho_c = (\delta q_s\rho_s^0 + \delta q_t\rho_t^0) - (q_s\rho'_s\delta R_A + q_t\rho'_t\delta R_B) \qquad \text{(A12)}$$

The result of Table II follows

$$\delta\rho_c = (\delta q_s\rho_s^0 + \delta q_t\rho_t^0) - q_t\rho'_t\delta R \qquad \text{(IIIA)}$$

Simplications of this equation again occur for ethane, ethene, and other symmetrical bonds where $q_s = q_t = 1$, so that $\rho_s^0 = \rho_t^0 = \rho_c^0/2$, leaving

$$\delta\rho_c = (\delta q_s + \delta q_t)\rho_c^0/2 - \rho'_t\delta R \qquad \text{(IIIB)}$$

In this equation, $\rho(x)$ in the valence region has been approximated by a constant, rather than by the quadratic model used in the estimation of bond point position. The correspondence between orbital models and the density at the critical point is a superposition of the changes in populations and the change in bond length, so that in those cases where the bond length change is small ρ_c gives us an indication of whether charge has been added to or removed from the bond.

The next step is to derive the results relating orbital models and bond point properties to the change in atomic population, $\delta N(A)$, which can be written as

$$\delta N(A) = \sum_i \left\{\delta q_i\cdot\int_{A^0}\rho_i(x)\,d^3x + q_i\cdot\delta\int_{A^0}\rho_i(x)\,d^3x\right\} + \int_{\delta A}\rho^0(x)\,d^3x + \int_{\delta A}\delta\rho(x)\,d^3x \qquad \text{(A13)}$$

where the sum is now over *all* basic functions, ϕ_i. Neglecting the second-order contribution, the equation can be rewritten as

$$\delta N(A) \approx \sum_i\{\delta q_i\cdot n_i(a^0) + q_i\cdot\delta n_i(A)\} + \sum_{B->A}\delta r_B(A)N(S) \qquad \text{(A14)}$$

where the density along the bond path has again been approximated as constant, where $n_i(A^0)$ is the population of basis function ϕ_i within the basin of A in the reference molecule, and where $N(S)$ is the integral of the density over the surface separating atoms A and B, called the surface population.

The first term of eq A14 describes the change in orbital populations, evaluated over the unperturbed basin. The third term is the contribution from the change in volume of the atom produced by a shift in critical point position. The second ($\delta n_i(A)$) term arises from the fact that basis functions are considered to be "attached" to their nuclear centers in orbital models, so that if a bond length changes then the proportion of an orbital centered on nucleus B that is inside the basin of A will change, the proportion decreasing as the bond is lengthened. Its value, within a first-order approximation and calculated with the origin at the nucleus of atom A, is

$$\delta n_i(A) = -\delta R\cdot\int dS\rho_i(x) \equiv -n_i(S)\cdot\delta R \qquad \text{(A15)}$$

The origin-dependence of this term cancels with that of $\delta r_B(A)$ to give a final result for $\delta N(A)$ that is independent of origin.

Equation A14 can be rephrased solely in terms of atomic orbital populations by using the eq IA above

$$\delta N(A) = \sum_i\{n_i(A)\delta q_i + q_i\cdot\delta n_i(A)\} + \sum_{B\to A} N(S)[q_t\lambda_t\delta R - (\delta q_s\rho'_s + \delta q_t\rho'_t)]/\lambda_3 \qquad \text{(A16)}$$

where s and t refer to the σ bonding orbitals of the AB bond only.

It was pointed out in the text that this result correctly predicts the independence of populations of each half of a symmetrical molecule to a bond stretch as a result of the cancellations of the nonzero parts of the first and second terms. In asymmetrical bonds, even though the two relevant terms of eq IVA do not exactly cancel, they will still oppose each other, and their net effect will be assumed to be small. With this approximation, then, the general result for changes to atomic populations simplifies to

$$\delta N(A) = \sum_i n_i(A)\delta q_i - \sum_{B\to A} N(S)(\delta q_s\rho'_s + \delta q_t\rho'_t)/\lambda_3 \qquad \text{(IVA)}$$

In this equation, the first summation refers simply to the basin of the unperturbed atom, while the second arises purely from shifts in the atomic surfaces caused by a shift of the associated bond point. These two terms will therefore be called "basin" and "surface" contributions, respectively. In the case of symmetrical bonds, the surface terms simplify to give

$$\delta N(A) = \sum_i n_i(A)\delta q_i - \sum_{B\to A} N(S)\rho'_t(\delta q_s - \delta q_t)/\lambda_3 \qquad \text{(IVB)}$$

In the case of an atom or group with only one finite bounding surface, a case which includes the methyl group in substituted ethanes or the CH_2 group in substituted ethenes, eq IB can be used to emphasize the dependence of the atomic charge on the bond point position and to complete the derivations of the equations of Table II.

$$\delta N(A) = \sum_i n_i(A)\cdot\delta q_i + N(S)\cdot\delta x_c \qquad \text{(IVC)}$$

The approximation of the charge density about the bond point by a Taylor series expansion truncated at quadratic terms, or simply by a constant, introduces errors into eq I–IV that, if large enough, will make them of very limited use. Figure 3 shows the charge densty and its approximation for the bonds studied in this paper. The region over which the approximation must be tested is the region over which the bond point moves in response to perturbation. The fluoro substituent exerts a larger perturbation on the charge density than most other substituents,[15] and so the bond point shift in response to fluorine substitution provides a suitable range to test.

The error in the density and in the bond point position is shown in Table IV along with the changes in those quantities produced by the fluoro substituent. The error in the density ($\Delta\rho_c$) is simply the difference between the exact and approximate densities of the *unperturbed* bond at a displacement equal to the bond point shift produced by fluoro substitution. The error in the bond point position ($\Delta(x_c)$) is estimated to be the distance from the exact unperturbed density at the displacement of the bond point produced by fluoro substitution to the point at which the approximate density reaches the same value of ρ. In all cases the error is seen to be less than 10% of the total change (and often much less), which is sufficient accuracy for the purpose of studying qualitative models.

Registry No. HCHO, 50-00-0; CH_2CH_2, 74-85-1; CH_3CH_3, 74-84-0; CH_4, 74-82-8; CH_3CHCH_2, 115-07-1; $CH_2CHCHCH_2$, 106-99-0; $FCHCH_2$, 75-02-5; FCHO, 1493-02-3.