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The Response of Electrons to Structural Changes

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The properties of a molecule are determined by the distribution of its electrons. This distribution can be described by the charge density, which is readily obtained from the wave functions derived by ab initio molecular orbital calculations. The charge density may be analyzed in a number of different fashions to give information about the effects of substituents, structural changes, and electronic excitation on the properties of molecules; one common procedure makes use of projection density or charge difference plots. Charge density also may be partitioned among atoms, and by numerical integration over appropriate volume elements one may obtain atomic charges, dipoles, kinetic energies, and other properties of the atoms in a molecule. Many chemical phenomena have been analyzed in terms of charge densities.

ELECTRONS ARE THE GLUE THAT HOLDS MOLECULES TOGETHER. This is readily seen if the total energy of a molecule is decomposed into its components

$$E = T + V_{\text{nn}} + V_{\text{ee}} + V_{\text{ne}}$$

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where T is the kinetic energy of the electrons, V_{nn} is the nuclear-nuclear repulsion, V_{ee} is the electron-electron repulsion, and V_{ne} is the nuclear-electron attraction. The first three terms are destabilizing, and V_{ne} must dominate the total energy if the molecule is to be stable. It then seems appropriate to consider intra- and intermolecular interactions in terms of changes in the charge density (ρ) distribution. The charge density, $\rho(r)$, is readily obtained from the wave functions derived from ab initio molecular orbital (MO) calculations because for real wave functions, $\rho(r) = \psi(r)^2$. This distribution is experimentally accessible from x-ray crystallography and there is good agreement between the experimental charge densities and those derived from calculations (1). Further, all of the properties of a molecule that may be calculated from its molecular wave function can equally well be obtained from the charge density distribution (2).

A common way in which to examine intermolecular and intramolecular interactions makes use of MO theory, and the simplest approach of this type, frontier orbital theory (3), has become popular. A procedure that correlates all of the orbitals of the interacting units will, of course, give the correct result because the total wave function contains all of the information inherent in the charge density distribution. However, when only small subsets of MOs are used, or when some of the interactions, such as electron repulsion, are left out, one cannot be sure that a correct interpretation has been achieved. The charge density serves to describe all of the electrons in a molecule, and analyses of ρ have inherent advantages over MO studies that use less than a complete set of MOs. In addition, there are useful ways in which charge densities may be examined that have no simple counterparts in the use of MOs. In this article we illustrate some of the ways in which the charge density may be used in studying chemical phenomena.

There are two approaches that may be used. In the first, distribu-

tions of ρ for molecules are examined, and, frequently, charge density differences are used to explore the effect of structural changes on the electron distribution. As long as one makes use of good wave functions in obtaining ρ , the results are well defined and noncontroversial. In the second, ρ is partitioned among the atoms in the system in one of several ways. Here, the form of the separation has generated some controversy. Both of these approaches are illustrated below, starting with the molecular charge distribution.

Projection Density Plots

It is readily possible to construct three-dimensional contour diagrams showing a surface of constant ρ for a molecule. However, these diagrams are generally featureless and do not provide much information. For relatively simple molecules, the distribution of ρ may be examined with the use of projection density plots of the type described by Streitwieser (4). Here, a plane is taken that contains most of the interesting parts of the molecule, and the charge density above and below a given point in the plane is summed and assigned to the point. This procedure is carried out for a grid of points in the molecular plane, and contour plots of equal values of the projection density are made. Some plots for simple methyl derivatives are shown in Fig. 1.

In the case of the symmetrical ethane, the two methyl groups share the electron population equally (Fig. 1A). The point along the internuclear axis at which the charge density has the lowest value is indicated by a dark circle. In methyl fluoride, the fluorine has a much higher electronegativity than carbon, and, as a result, there is a shift of charge density toward the fluorine (Fig. 1D). The volume element that might be associated with the fluorine has increased considerably. The opposite effect is seen when the relatively electropositive lithium and silicon are attached to the methyl group. With methyl-lithium, the contours that might be associated with the carbon bond stretch well over toward the lithium (Fig. 1C). The charge density

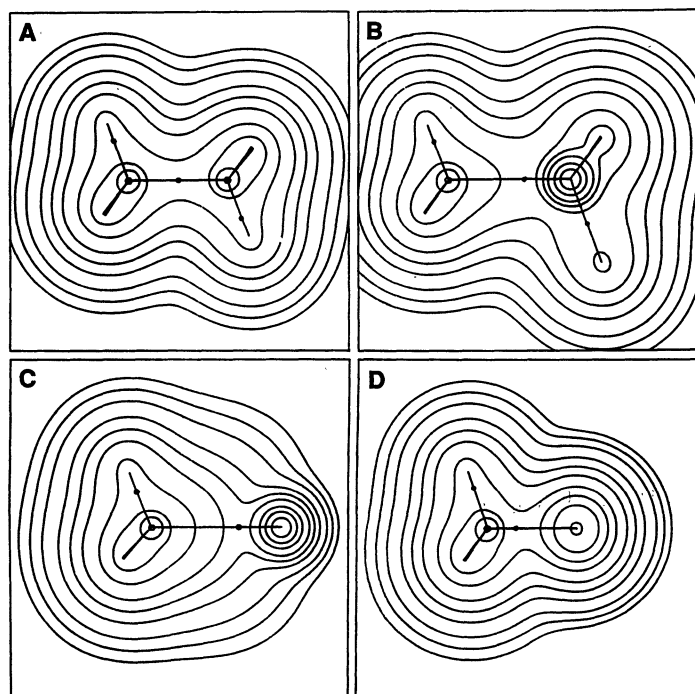


Fig. 1. Projection density plots for (A) ethane, (B) methylsilane, (C) methyl lithium, and (D) methyl fluoride. The methyl group is to the left in each case, and one methyl hydrogen is in the plane at the upper left. The points along bonds that have a minimum value of ρ are shown as dark circles.

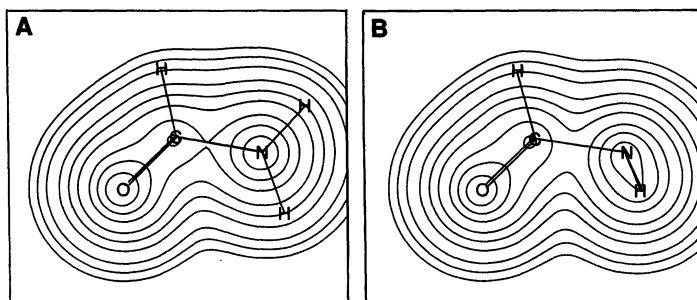
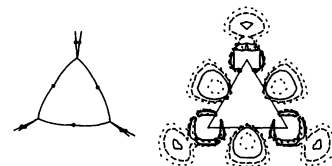


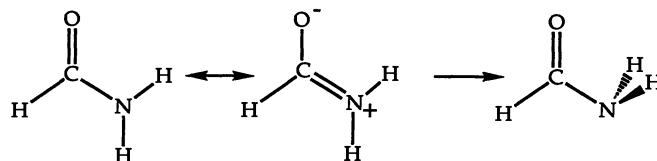
Fig. 2. Projection density plots for the π electrons of (A) planar formamide and (B) 90° rotated formamide.

Fig. 3. Cyclopropane. The bond paths are shown on the left, and the positive regions of the deformation density (charge density less than for spherically symmetrical atoms) are shown on the right. The deformation density for the C-C bonds lies outside the line drawn between the carbons.



reaches a minimum value of only 0.04 e/bohr^3 along the Li-C bond, which may be contrasted with a value of about 0.25 e/bohr^3 for most bonds involving first row elements. Thus, the best description of methyl lithium is $\text{CH}_3^- \text{Li}^+$ with little covalent character (5). The charge shift is not as severe with methylsilane (Fig. 1B), but again there is a clear shift in charge density from silicon to carbon and from silicon to hydrogen.

A variety of questions may be examined with the use of projection density plots. Formamide provides one example (6). The relatively large C-N rotational barrier in amides is generally considered to be an example of a resonance effect in which a dipolar structure helps stabilize the planar form, making rotation more difficult.



Scheme 1

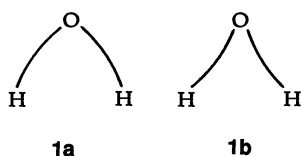
If this were correct, one would expect a significant change in the charge density distribution on going from the planar to rotated forms. The projection densities for π electrons of the two rotamers are shown in Fig. 2. Important changes occur in the region of the C-N bond. However, the charge density contours in the vicinity of the oxygen are virtually the same for the two forms. This result, along with the large dipole moment for carbonyl compounds and calculations of electron populations (7), suggests that the carbonyl group might best be written as $\text{C}^+ \text{O}^-$. The barrier then results from an interaction between the nitrogen and the electron deficient carbon. The acidity of carboxylic acids (8) also is easily explained with the use of this structure for the carbonyl group.

Bond Properties

The projection densities are not so useful for more complex molecules, and the charge density distribution is frequently examined in other ways. One simply defined and useful quantity is the

bond path, which is the path of maximum charge density between a pair of bonded atoms (9). The charge density is a maximum near any nucleus, and, for a bond between two atoms, the charge density decreases when proceeding away from either of the nuclei. These bond paths provide a proper description of the directionality of bonds and frequently do not coincide with the conventional bonds, that is, straight lines drawn between nuclei. The deviation between the bond paths and the line between nuclei can become quite large in a molecule such as cyclopropane (Fig. 3), in which the extra charge density for the C–C bonds lies outside the triangle formed by the three carbons. The deviation of the bond paths is conveniently expressed in terms of a bond path angle, the angle between a pair of bond paths at a given nucleus. In the case of cyclopropane, the C–C–C bond path angle is 78°, which is 18° larger than the conventional angle (10).

Deviations between bond path angles and conventional angles may be found in cases other than small ring compounds. The bond angles in simple compounds such as water, ammonia, hydrogen sulfide, and phosphine have been the subject of considerable discussion (11). The conventional angle in water is 104.5°, significantly smaller than the tetrahedral angle (109.5°). This has been attributed to a repulsive interaction between the hydrogens and the lone pairs, forcing the H–O–H angle to become smaller than tetrahedral. Alternatively, one might postulate that the lone pairs should be placed in orbitals having as much *s* character as possible in order to stabilize them. The O–H bonds would then be formed largely from *p* orbitals, the “ideal” angle would be closer to 90°, and the observed angle would result from repulsion between the hydrogens. A distinction between these views may be made with the use of the bond path angles. In the first case, repulsion with the lone pairs would push the hydrogens inward and the bond path angle would be larger than the conventional angle (1a). In the second case, H–H repulsion would lead to a conventional angle that is larger than the bond path angle (1b). Although the calculated angles vary a little with the size of the basis set used in the calculations, in all cases, the bond path angle is less than the conventional angle by 5° (Table 1) (12). Therefore, the second view appears to be correct. The same is found with ammonia, where the bond path is 3° less than the conventional angle.



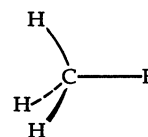
Hydrogen sulfide and phosphine have the opposite behavior. Here, the difference between the two angles is about 3°, but the bond paths bend inward, rather than outward. In these cases, the bonds to hydrogen are relatively long, minimizing H–H repulsion. The lone pair repulsion appears to be the more important term.

Bent's rule (13) is a useful guide in considering the effect of substituents on structures. It is assumed that an electronegative group would prefer to be bonded to an orbital with high *p* character because *p* orbitals are not as strongly bound as *s* orbitals. Fluorine is the most electronegative atom, and a large effect on hybridization would have been expected when it is bound to carbon, as in methyl fluoride. Increased *p* character in the C–F bond should lead to increased *s* character in the C–H bonds and larger H–C–H bond angles (the *sp*² angles are 120°, whereas the *sp*³ angles are 109.5°). As a result, the H–C–F angle should decrease. However, the observed (conventional) H–C–F angle is 108.9° (14), close to the

Table 1. Bond path angles for some hydrides. $\angle\text{HMH}$ is the conventional bond angle, α is the angle between the bond paths at the center nucleus, and $\Delta\alpha$ is the difference between these two values.

Compound	Basis set	Angles (degrees)		
		$\angle\text{HMH}$	α	$\Delta\alpha$
Water	6-31G*	105.41	100.36	5.05
	6-31G**	105.92	101.04	4.88
	6-31++G**	107.06	102.15	4.91
Ammonia	6-31G*	107.20	103.95	3.25
	6-31G**	107.53	104.45	3.08
	6-31++G**	108.79	106.30	2.49
Hydrogen sulfide	6-31G*	94.36	97.77	-3.40
	6-31G**	94.38	97.98	-3.60
	6-31++G**	94.36	97.99	-3.63
Phosphine	6-31G*	95.40	98.84	-3.44
	6-31G**	95.54	98.91	-3.37
	6-31++G**	95.65	99.01	-3.36

tetrahedral value. The apparent disagreement is removed when one examines the bond path angles (15). Here, the H–C–F angle becomes 106.7°, in good agreement with expectation. The bent bond is caused by a repulsive interaction between the fluorine and the hydrogens.



The conventional and bond path angles for a methyl group attached to a number of first row elements are shown in Table 2 (12). The order of the bond path angles fits well with the usual ideas of electronegativity. In these cases, the bond lengths also should respond to changes in hybridization (bonds with higher *s* character are shorter), and bond lengths are found to be related to the bond path angles. Again, the difference between the bond path and conventional angles may be attributed to steric interactions.

The changes in bond lengths (16) in the series methyl fluoride (1.383 Å), methylene fluoride (1.360 Å), fluoroform (1.335 Å), and carbon tetrafluoride (1.319 Å) have been discussed in terms of negative hyperconjugation and other effects (17). However, the hybridization effect noted above can easily account for these changes if one remembers that bond lengths increase with increasing *p* character (18). With methyl fluoride, the carbon orbital to the

Table 2. Bond path angles (degrees) for some substituted methanes. 1nc compounds are listed in order of increasing bond path angle, α . $\angle\text{HCM}$ is the conventional bond angle and $\Delta\alpha = \angle\text{HCM} - \alpha$ (Me, methyl).

Compound	Angle	α	$\angle\text{HCM}$	$\Delta\alpha$
MeN ₂ ⁺	HCN	101.17	104.98	3.81
MeNH ₃ ⁺	HCN	104.71	108.10	3.39
MeF	HCF	106.68	109.17	2.49
MeNC	HCN	107.42	109.79	2.20
MeCN	HCC	108.26	109.79	1.53
MeC≡CH	HCC	109.43	110.61	1.18
MeMe	HCC	110.25	111.20	0.95
MeCF ₃	HCC	110.41	109.40	-1.01
MeO ⁻ Li ⁺	HCO	111.20	112.55	1.35
MeBeH	HCB	112.77	112.07	-0.70
MeLi	HCLi	113.37	112.56	-1.81
MeO ⁻	HCO	116.77	116.52	-0.25

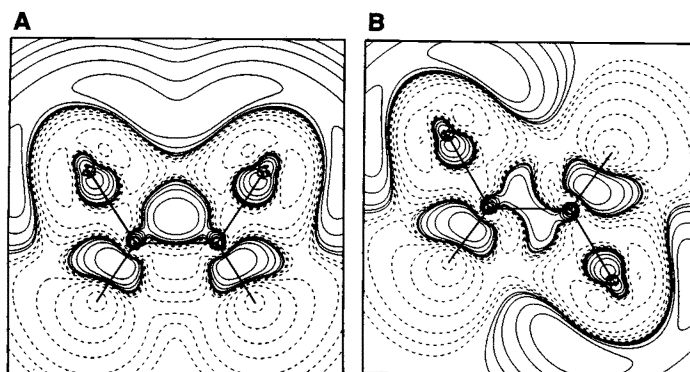


Fig. 4. Charge density difference plots for (A) *cis*- and (B) *trans*-1,2-difluoroethene. The solid contours indicate regions that gain charge density on going to the larger basis set, and the dashed contours indicate regions that lose charge density.

fluorine, would have a maximum *p* character, resulting in a longer bond. The two fluorines in difluoromethane must share the extra *p* character donated by the carbon, and the bond length would decrease. Finally, with carbon tetrafluoride, the carbon has returned to *sp*³ hybridization and the *p* character of each fluorine has been reduced. The C–F bonds in carbon tetrafluoride are the shortest in the series.

Charge Density Plots

The total charge density in any molecule is large. Therefore, the small changes caused by structural or other modification are often obscured when the total charge densities are compared. Here, charge density difference plots become useful. Two types of difference plots are in common use. In the first, the charge densities for the two cases being compared are subtracted and suitable plots are prepared. In the second, the charge density for a model system (such as a set of atoms placed at the appropriate locations) is subtracted from the system in question. In x-ray crystallography, plots of this type are known as deformation density plots (Fig. 3) (19). The choice of the appropriate model system for the latter

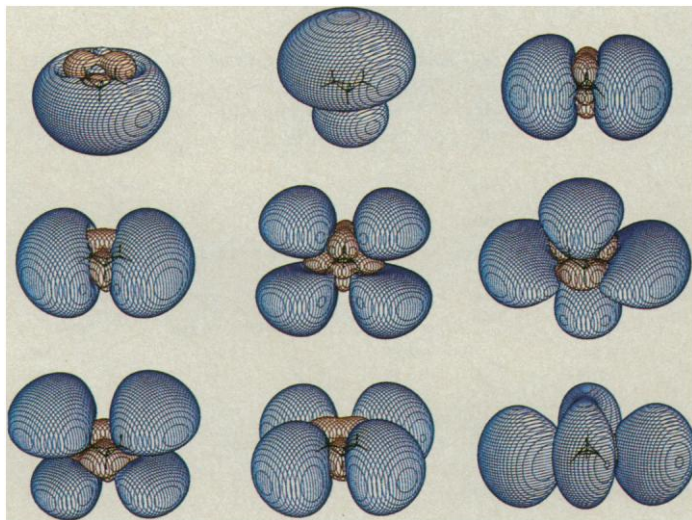


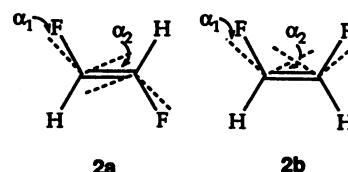
Fig. 5. Charge density difference plots for the first nine excited states of bicyclobutane. The blue contours correspond to regions that gain charge density in the excited states, and the red contours show the region that loses charge density. All correspond to the formation of the bicyclobutane radical cation plus a loosely bound Rydberg electron. The contours are drawn at the 1×10^{-4} e/bohr³ level.

Fig. 6. Charge density difference plots for the first three excited states of ethylene. The upper row gives the difference between the excited state and the ground state, and the bottom row gives just the depletion region. The third state corresponds to the π - π^* transition.



approach, such as spherical atoms, or atoms in prepared valence states, has been the subject of considerable controversy (20). The discussion below focuses on the first type of difference plot.

In the 1,2-disubstituted ethylenes, the *trans* arrangement is normally preferred to the *cis* arrangement, presumably because the groups have a repulsive interaction when close to each other. This repulsion can be seen in the structures in which the bond angles in the *cis* form are larger than those in the *trans* form. However, in the case of 1,2-difluoroethylene, the *cis* arrangement (2b) is preferred by 1 kcal/mol (21). It was noted above that fluorine has a large effect on bond path angles. The bond path angles were examined for the difluoroethylenes (22).



The differences between the bond paths and the conventional bonds for the *trans* form (2a) are $\alpha_1 = 1.12^\circ$ and $\alpha_2 = 3.27^\circ$, whereas for the *cis* form $\alpha_1 = 1.04^\circ$ and $\alpha_2 = 5.85^\circ$. With the *cis* isomer, the C–C bond paths are bent in the same direction and maintain good overlap, but in the *trans* form they are bent in opposite directions, which leads to reduced overlap and weaker bonding (23).

Charge density difference maps help support this argument. The calculations using the 6-31G* basis set led to a lower energy for the *trans* form, but with a larger basis set (6-31+G* and larger), the correct order was found. The charge density in the molecular plane was calculated for the two basis sets and subtracted. The difference plot should show where the electrons moved so as to make the *cis* the more stable form. The effect of the larger basis set is to shift electrons into the bonding regions between nuclei (Fig. 4). With the C–C bonds, the extra charge density for the *cis* form corresponds to the directions of the bond paths given above. The same is true for the *trans* isomer, and here the bond has a sigmoidal shape corresponding to reduced overlap and a weaker bond (24).

Charge density difference plots can be used to study electronically excited states. Electronic excitation is a vertical process; that is, the nuclear positions are the same in the initially formed excited state as for the ground state. Therefore, one could learn much about the nature of the excited states if their wave functions were available. One problem with the description of the excited states is that all configurations can interact that have the same symmetry and are formed by promotion of an electron from a filled molecular orbital to one of the unoccupied orbitals, and the correct excited state wave functions are a linear combination of the above. Foresman and Pople (25) have developed a procedure for obtaining the appropriate excited states and the corresponding density matrices from which the charge density distribution can be constructed. A second problem with excited states is that the set of atomic orbitals used in the calculation must be appropriate for the representation of both the ground state and excited state wave functions. The latter are

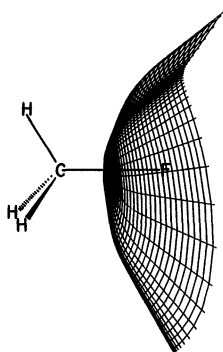
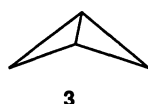


Fig. 7. Partitioning surface for the C-F bond of methyl fluoride.

often quite diffuse, and appropriate atomic orbitals must be included in the set used for the calculations.

We use bicyclobutane (3) as an example because it has received considerable experimental and theoretical study (26). The energies were calculated with a set of atomic orbitals that included two sets of diffuse orbitals in addition to the normal types of orbitals (6-311(2+)-G*), and the transition energies were found to be in reasonable agreement with experiment. The charge density distributions of the excited states were calculated and subtracted from that of the ground state. The changes in charge density between the ground state and the first nine excited states are shown in Fig. 5, where the blue contours correspond to regions in which there is greater charge density than in the ground state, and the red contours correspond to regions in which the charge density has been depleted on excitation. The blue contours have a strong resemblance to the atomic orbitals, going from *s* to the three *p* orbitals and then to the *d* orbitals. Subsequent excited states involve *f*-type orbitals. The red contours resemble the contours found in comparing the ground state with the radical cation formed by removing one electron from bicyclobutane. Geometry optimization for the first excited state yielded a geometry that was close to that for the radical cation. The excitation process then corresponds roughly to ionization of an electron to give the bicyclobutane radical cation, with capture of the electron in an atom-like (Rydberg) orbital.



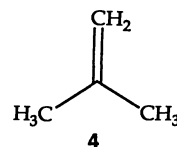
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With ethylene, one would expect to find at least one valence transition, corresponding to $\pi\text{-}\pi^*$ excitation (where the π electrons are those out of the plane of the molecule). An examination of the first 20 excited states showed that most were Rydberg states and corresponded to the formation of a radical cation and a Rydberg electron. The $\pi\text{-}\pi^*$ excited state was different from the others (Fig. 6) in the nature of the charge depletion region. These density difference plots now have the possibility of distinguishing between Rydberg and valence states and of showing the predominant nature of each. It also is possible to carry out geometry optimization for the

excited states to determine their equilibrium geometry and to calculate their vibrational frequencies (23). These sorts of data should make it possible to examine photochemical processes in much more detail than has been possible.

Atoms in Molecules

Many schemes have been proposed for separating the charge density in a molecule into populations that may be assigned to atoms. One of the earliest is the Mulliken population analysis (27), which assigns the diagonal density matrix components to the atoms and splits the off-diagonal elements between the atoms involved. This procedure frequently has a strong dependence on the choice of basis set. In the case of isobutene (4), the population for the central carbon was +0.1 with the 6-31G* basis set and +1.0 with the larger 6-311++G** basis set. The usual ideas concerning the relative electronegativities of sp^2 - versus sp^3 -hybridized carbons (the two methyl groups) would suggest that the central carbon should have a small negative charge, which is opposite to the Mulliken population. The problems with this type of population have been recognized by a number of workers, including Mulliken (28).



4

Methods for calculating populations can be placed in two categories. The first category is based on atomic orbitals that are assigned to specific atoms (29), whereas the second is based on partitioning of the charge density (30, 31). The major problem with the first approach is that atomic orbitals no longer belong to specific atoms when molecules are formed, and part of an atomic orbital of

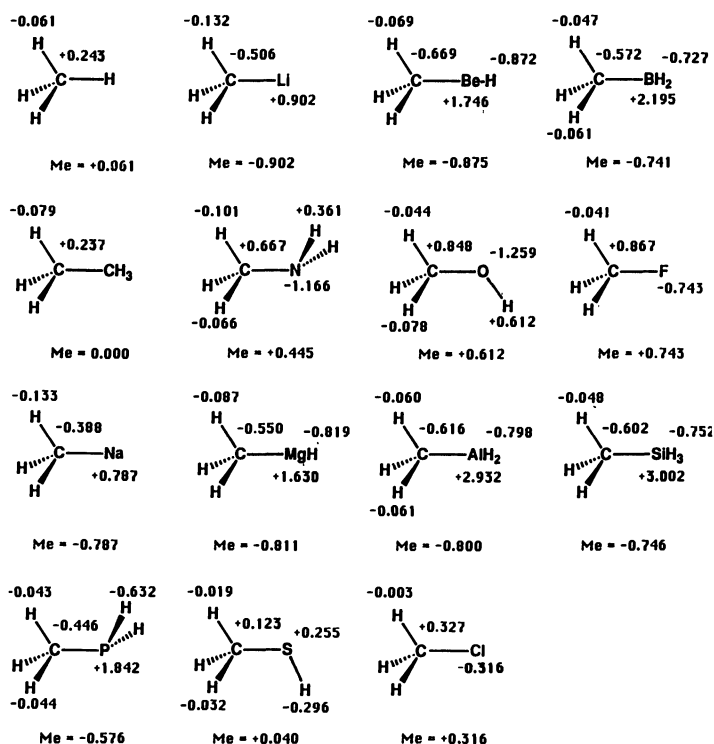
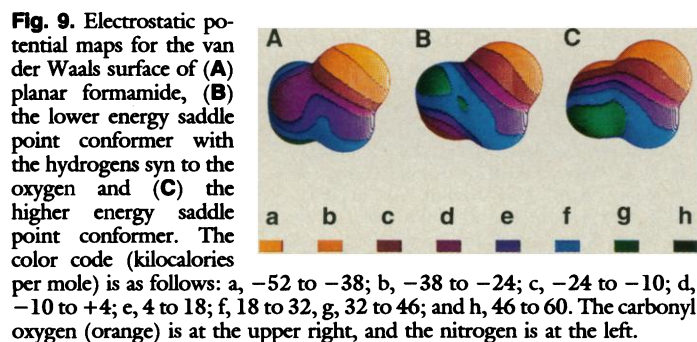


Fig. 8. Atomic charges for substituted methanes (Me, methyl).

Table 3. Group charges (electrons) for the allyl cation.

Group	σ	π	Total
CH (center)	+0.304	+0.008	+0.312
CH ₂ (terminal)	-0.152	+0.496	+0.344
All	0.000	+1.000	1.000



one atom may play an important role in describing the charge density at a nearby atom. A problem with the second approach is that of defining unique volume elements. This problem has been resolved by Bader in the development of his theory of atoms in molecules (31).

In this theory, one first locates the bond critical points, which are the points of minimum charge density along the bond paths (the dark circles in Fig. 1). Starting at a given critical point, one develops rays normal to the bond path for which the charge density decreases most rapidly. The set of such rays forms a surface (Fig. 7) that separates the two atoms forming the bond. These surfaces are obtained for all of the bonds in a molecule and serve to separate the molecule into a set of atomic domains. Numerical integration of the charge density within a given volume element gives the electron population for that atom. The kinetic energy, atomic dipole components, and other properties may be obtained in the same fashion. In the case of compounds containing rings such as cyclopropane, the ring critical points (points of minimum charge density within the ring) are also located and help define the atomic domains.

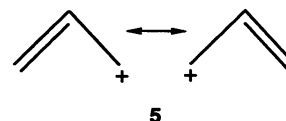
The effect of substituents in methyl derivatives has received extensive investigation (32). The atomic charges derived with the theory of atoms in molecules are summarized in Fig. 8. They are in good accord with the electronegativity of the substituents. Hydrogen is just slightly more electronegative than an sp^3 -hybridized carbon, and with methane and ethane the C-H bond dipole has the sense C^+H^- (33). The most electronegative element, fluorine, has the largest atomic charge. Although it may seem surprising to think of methyl fluoride as a polar molecule, carbon and hydrogen have similar electronegativities, and it is not surprising to think of hydrogen fluoride as a polar molecule. Part of the increased charge at fluorine arises from its increased volume as the bond critical point shifts toward the carbon (Fig. 1).

The large difference in electronegativity between carbon and silicon is readily apparent, and, correspondingly, the Si-H bonds have considerable polar character in the sense Si^+H^- . The second row elements are, in general, considerably less electronegative than those in the first row. Lithium and sodium atoms have very small electronegativities, and, as a result, there is a large charge transfer from the metal to carbon. Therefore, organolithium and organosodium compounds are best regarded as $CH_3^-Li^+$ and $CH_3^-Na^+$, respectively.

The atomic charges may be used in examining a variety of chemical phenomena. For example, with formamide the electron population at oxygen changes by only 0.05 e from the planar to rotated forms, whereas there is a much larger shift of electron population between the carbon and nitrogen. Again, this shows that the oxygen is not much affected by rotation about the C-N bond.

In the case of planar conjugated molecules, it is often useful to examine the σ (in plane) and π electrons separately. Allyl cation (5), when treated by π -electron theories, is found to have 0.5 π electrons at each of the terminal carbons and one π electron at the central

carbon. However, when all of the electrons are examined, the σ electrons shift so as to decrease the differences in charge (Table 3) (34). This result should not be surprising. When the terminal carbons become π -electron deficient, they become more electronegative, and the σ electrons in the C-C and C-H bonds shift toward these carbons. This type of σ - π polarization is a very common phenomenon (35).

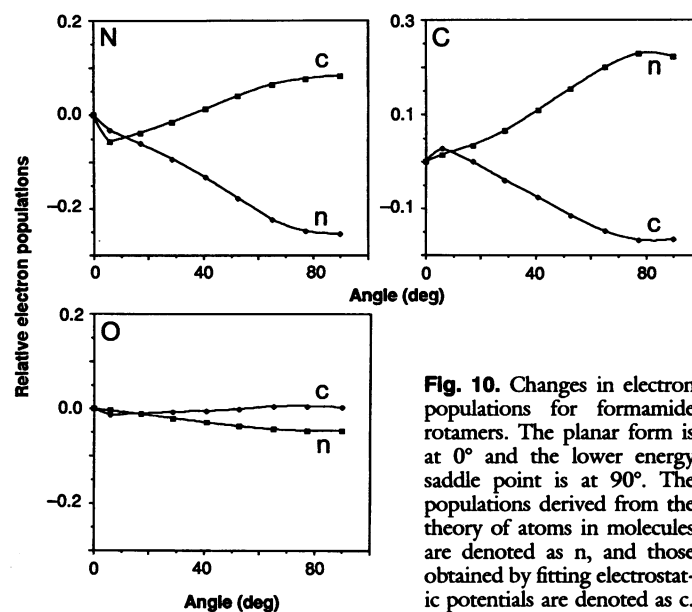


It should be recognized that the charges obtained in this fashion must not be thought of as point charges for atoms. They are, rather, the first terms for a Taylor series expansion, with the atomic dipole components as the second term. The atoms defined by the theory do not have the center of charge density coincident with the nuclear positions, and thus atomic dipoles and higher moments are associated with the charges. Although the charges may in some cases appear large, they provide the expected response to changes in electronegativity and hybridization.

Electrostatic Potentials and Effective Charges

Another well-defined quantity is the electrostatic potential, which is the energy of a positive test charge at a given location. A negative value of the electrostatic potential corresponds to a region that might be expected to interact with protons or other electrophiles. It may readily be calculated from the molecular wave function. The electrostatic potential is thought to be an important component in the intermolecular interaction between molecules (36), and therefore attempts have been made to estimate the potential based on point charges assigned to atoms. The reverse may also be done; point charges may be derived that can best represent the electrostatic potential derived from the wave functions (36).

Formamide provides an interesting example. The electrostatic potential at the van der Waals surface for the molecule may be represented by three-dimensional plots (Fig. 9). In the planar form, the most negative potential is found at the oxygen, and another



region of somewhat smaller negative potential is found at the location of the lone-pair orbital at nitrogen. Rotation to the 90° transition structure leads to a small change in the electrostatic potential at oxygen and a 90° rotation of the negative potential region at nitrogen. Although the potential at nitrogen is seen to be markedly anisotropic, it is possible to reproduce the potential with a set of effective atomic charges corresponding to spherical atoms with the center of charge coincident with the nucleus (6, 36).

A comparison of the changes, in formamide rotamers, of the electron populations derived from the theory of atoms in molecules and of the effective charges derived from the electrostatic potential is shown in Fig. 10. Both criteria indicate that there is no significant change at oxygen on rotation (compare with Fig. 2). However, the two go in opposite directions for carbon and nitrogen. The reason for the difference lies in the definition of the atoms. The charges derived by integration of the charge density represent the atoms as seen by their nuclei, and these atoms are markedly nonspherical. The nitrogen in the planar form has a relatively high electronegativity because it uses sp^2 hybrid orbitals, whereas the nitrogen in the rotated form has a lower electronegativity because it uses orbitals with high p character. As a result, the nitrogen in the planar form has a larger electron population than in the rotated form.

The effective charges derived by fitting the electrostatic potential correspond to nonphysical spherical atoms and also rely on charges on other atoms to reproduce the anisotropy of the electrostatic potential. The charge assigned to the nitrogen reflects the need to reproduce the effect of the lone pair in the rotated form. Although nonphysical, the effective charges are a convenient first approximation for fitting intermolecular interactions involving just pair potentials. The electrostatic potential may also be reproduced by the quantities derived from the theory of atoms in molecules. However, in addition to the charges, one also must include the atomic dipole and quadrupole terms, which are readily calculated. The choice of which approach to use then depends on the purpose for which the data are obtained. For intramolecular interactions, the populations derived from the theory of atoms in molecules are to be preferred. However, for intermolecular interactions, the effective charges derived by fitting the electrostatic potential often provide the more convenient parameters.

Conclusions

The analysis of charge density distributions can be useful for studying chemical phenomena. It frequently allows one to visualize the changes that occur in a fashion that is not readily possible from an examination of the MOs for the system in question. In addition, such analyses allow the calculation of electron populations, energies, and other properties of the atoms in the molecule. These quantities often provide useful information concerning intramolecular interactions.

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