Comparison of Atomic Charges Derived via Different Procedures

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Atomic charges were obtained from *ab initio* molecular orbital calculations using a variety of procedures to compare them and assess their utility. Two procedures based on the molecular orbitals were examined, the Mulliken population analysis and the Weinhold–Reed Natural Population Analysis. Two procedures using the charge density distribution were included: the Hirshfeld procedure and Bader's Atoms in Molecules method. Charges also were derived by fitting the electrostatic potential (CHELPG) and making use of the atomic polar tensors (GAPT). The procedures were first examined for basis set independence, and then applied to a group of hydrocarbons. The dipole moments for these molecules were computed from the various atomic charges and compared to the total SCF dipole moments. This was followed by an examination of a series of substituted methanes, simple hydrides, and a group of typical organic compounds such as carbonyl derivatives, nitriles, and nitro compounds. In some cases, the ability of the charges to reproduce electrostatic potentials was examined. © 1993 by John Wiley & Sons, Inc.

INTRODUCTION

There has been a continuing interest in atomic charges in organic compounds.[1] Most methods of defining charges involve analyses of the results of *ab initio* molecular orbital calculations, and a variety of techniques are available. We were interested in exploring the relationship between the charges obtained using these methods. It is not possible to make use of all of them in a comparison, and so we have selected a representative sample.

Some procedures make use of the basis functions that are used to represent the wave function. The oldest and most widely used of these methods is the Mulliken population analysis,[2] which makes use of the density matrix, assigning diagonal terms belonging to the basis set used for a given atom to that atom. The off-diagonal elements are arbitrarily split between the corresponding atoms. Although widely used, it has long been recognized that the Mulliken procedure has a strong dependence on the basis set (the set of functions, generally Gaussians, assigned to the atoms).[3] An improved procedure that eliminates most of the problems associated with the Mulliken analysis is the Weinhold–Reed Natural Population Analysis (NPA).[4]

An alternate approach is to make use of the charge density distribution. This distribution contains all of the information needed for calculating the properties of the system (i.e., the energy, dipole and higher

moments, etc.) and it may be calculated directly via density functional theory without the use of molecular orbital methods.[5] The use of the charge density ρ has a natural advantage in that it is an observable quantity, but some way in which to define the atoms is required so that the molecular ρ may be converted into an atomic population. One of the earlier methods is that of Hirshfeld, in which a hypothetical "promolecule" is constructed by the superposition of the spherically symmetrized charge density distributions of the isolated atoms. The charge density of the real molecule at each point in space is then divided between the constituent atoms in the same proportions as they contribute charge density to that point in the hypothetical promolecule.[6] The atomic populations are obtained by integrating these charge density contributions over all space. A different approach was taken by Bader in his theory of Atoms in Molecules (AIMs), in which atoms are separated by zero-flux surfaces of grad ρ.[7] In both methods, the atoms become nonspherical, and the charges are the first term of a Taylor's series expansion that includes dipolar, quadrupolar, and higher terms.

Some other different approaches are available. They include charges derived by fitting the electrostatic potential. This is another observable quantity, and represents the energy of a positive test charge at a given position.[8,9] Another procedure makes use of the atomic polar tensors that may be derived experimentally from the intensities of infrared bands, and may be calculated in the context of molecular orbital theory.[10,11]

In the following, we will first present some infor-

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mation on the procedures used in calculating the atomic charges. Then, we will explore the basis set sensitivity of each of these methods and apply them first to a series of hydrocarbons in which there are significant changes in hybridization as judged from their nuclear magnetic resonance (NMR) ^{13}C—H coupling constants. Next, the effect of substituents on charge distributions will be examined using a set of methyl derivatives as well as a set of simple hydrides as examples. Finally, we will examine a set of representative organic compounds to see the relationship (if any) among the calculated charges.

Throughout this study, HF/6-31G* geometries will be used, and 6-31G** and 6-311+ +G** wave functions will be derived using these geometries. In the latter case, six Cartesian d functions were employed. The wave functions, Mulliken populations, NPA analyses, atomic polar tensors, and CHELPG charges were derived using Gaussian 92.[12] The AIM populations were derived using PROAIM.[13] The Hirshfeld charges and GAPT charges were obtained using programs written at Yale.

METHODS OF CALCULATION

As noted above, the Mulliken population is easily obtained from the density matrix that is created as part of the SCF–MO formalism. The NPA procedure[4] is designed to minimize the problems associated with this simple procedure. The analysis begins with an independent symmetric orthogonalization of the basis functions centered on each atom. The resulting basis functions, which have intraatomic orthogonality but not interatomic orthogonality, are then separated into a highly occupied natural minimal basis and a largely unoccupied natural Rydberg basis. The natural minimal basis orbitals are then subjected to an *inter*atomic symmetric orthogonalization. The natural Rydberg basis is then orthogonalized internally and to the natural minimal basis in a somewhat more involved manner. The end result of this process is a set of basis functions that are orthogonal, unlike the original basis functions, yet to as great a degree as possible still retain the atom-centered characteristic of their progenitors.

The Hirshfeld method makes use of a set of spherically symmetrical proatoms* located at the nuclear coordinates of the molecule in question.[6] The value of ρ at any point in space for the molecule is partitioned in accord with the ratio of ρs from the proatoms at that point. The total population for each atom is derived by integrating the terms over all space. The Hirshfeld procedure requires some sort of operational definition for the proatoms, and because these definitions have not always been made

clear in previous publications we have established our own. For those atoms with a half-filled outer shell, an ROHF calculation was performed for the appropriate state. This category includes hydrogen (doublet state; half-filled 1s orbital), nitrogen (quartet state; filled 2s orbital and half-filled 2p shell), and phosphorous (quartet state; filled 3s orbital and half-filled 3p shell). For most of the remaining atoms, generalized valence bond (GVB) calculations were performed in which the partially filled outer p shell orbitals all had equal partial occupancies so as to guarantee spherical symmetry.† For instance, oxygen was forced to have a filled 2s orbital and three 2p orbitals each with an occupancy of 1.333333, while fluorine had partial occupancies of 1.666667 in its 2p shell. These ROHF and GVB calculations necessarily yielded spherically symmetric wave functions.

Carbon, which has particular importance for organic chemists, was given a slightly different treatment. The carbon proatom was derived from the wave function for methane. First, the basis functions for the methane wave function centered at the hydrogen atoms were removed. Then, the occupancies of the valence orbitals were adjusted to 1.000000 for the 2s and the three 2p orbitals. Finally, the wave function was renormalized to yield the correct total integration of six electrons. This normalization was performed on each shell independently, i.e., the core 1s orbital was renormalized to 2.000000, the 2s orbital was renormalized to 1.000000, and the 2p shell was renormalized to 3.000000. The silicon proatom was defined in a similar manner based on the wave function for silane. It makes conceptual sense in that it is the "valence" state of the atom that we would like to have as a reference. Unfortunately, a similar procedure cannot be used for the other atoms because only in the case of a highly symmetric species such as methane will the proatom derived from such a procedure be spherically symmetric. In all cases, the proatoms were calculated at the same basis set as the molecular wave functions for which Hirshfeld charges were desired. Because the center of charge density will usually be displaced from the nuclei, there also will be atomic dipoles that may be calculated along with the charges.[6] This requires the summation over all points of the charge component for a given atom multiplied by its Cartesian displacement from that atom.

In Bader's Theory of Atoms in Molecules, the topology of the charge distribution is used to define atomic regions.[7] Critical points between bonded atoms are first located. They are the points of minimum charge density along a bond, but a maximum

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*It might be noted that nonsymmetric proatoms also may be defined and used to form a promolecule.[14]

in directions normal to the bond. Starting at a critical point, paths for which the charge density decreases most rapidly are developed in all directions normal to the bond. The set of such paths defines a zero-flux surface separating a pair of atoms. A set of these surfaces (one per bond) will separate a molecule into unique atomic regions for which the hypervirial theorem is satisfied. Numerical integration of the charge density within a region gives the population assigned to the given atom. At the same time, other properties such as the atomic dipole and the atomic kinetic energy may also be derived.

The CHELP analysis of electrostatic potentials to derive atomic charges was developed by Chirlian and Francl,[8] and represents a least-squares fit of charges to the calculated electrostatic potential outside the van der Waals surface for the molecule. In the original implementation, the electrostatic potentials were not sampled uniformly, and the results were not rotationally independent. This could be removed by appropriate sampling, and the charges thus derived will be referred to as CHELPG.[9]

Atomic polar tensors have been used for some time, particularly by King,[10] to derive effective charges. Cioslowski has made use of the theoretically calculated atomic polar tensors, and has defined the charge at a given atom as one third of the norm of rank one of the atomic polar tensor of that atom.[11]

REQUIREMENTS FOR A SATISFACTORY REPRESENTATION OF CHARGE

Before presenting the results of our calculations, it would seem appropriate to specify what is meant by an atomic charge and propose some criteria for deciding whether or not a given set of charges are satisfactory. One definition of atomic charges requires that the atoms be spherically symmetrical and nuclear centered. This type of definition will be convenient for calculating intermolecular Coulombic interactions of the types used in many force fields such as those in AMBER and CHARM, and which are used in statistical mechanics Monte Carlo simulations of solutions. The CHELP definition is an example of a method making use of spherically symmetrical atoms.

Other definitions of atomic charge make use of more physically reasonable nonspherical atoms. The shape of atoms in molecules may be usefully seen in projection density plots, and they are shown for methyllithium and methyl fluoride in Figure 1. These compounds were chosen to represent extremes of electronegativity differences with respect to carbon. It can be seen that in methyl fluoride the charge density associated with the fluorine moves toward the carbon, whereas in the carbon—lithium bond the density associated with the carbon moves toward the lithium. Both the NPA and AIM definitions of charge correspond to nonspherically symmetrical atoms. One characteristic of these definitions is that the center of charge density does not coincide with the nuclear positions, which results in atomic dipoles and higher moments at each atom. While the pro-atoms in the Hirshfeld procedure are spherically symmetrical, the assignment of charges ultimately relies on the integration of the total SCF density. Thus, the Hirshfeld atoms also have centers of charge that differ from the nuclear coordinates and can have dipole and higher moments associated with them.
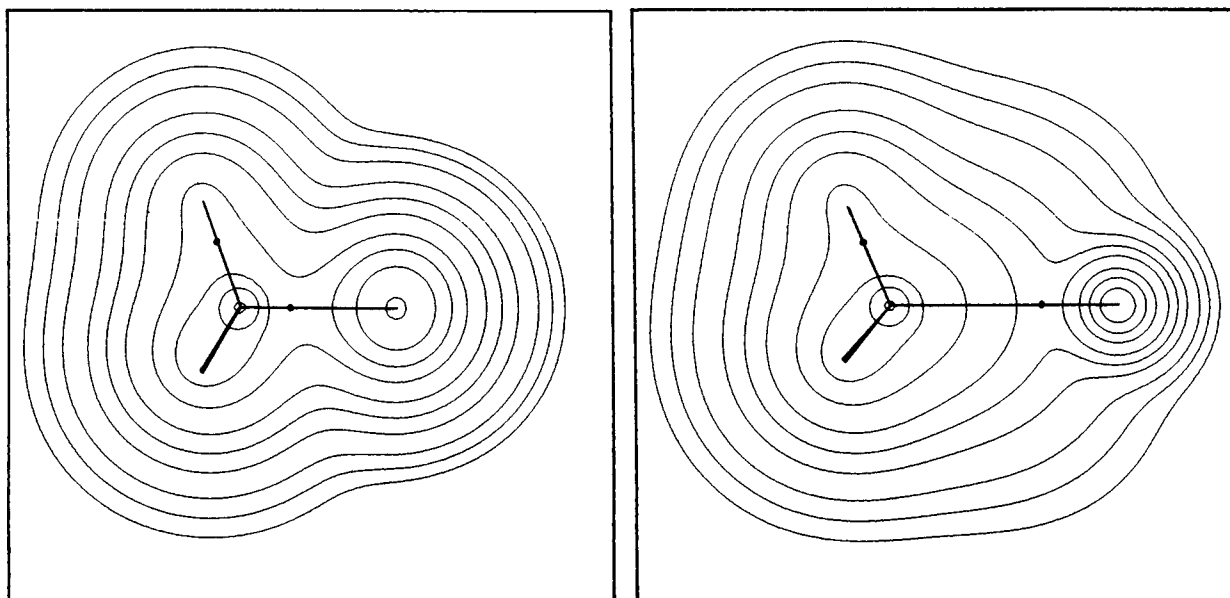

Figure 1. Projection density plots for methyl fluoride (a) and methyllithium (b). The C—X bond critical points are shown as dark circles. Note the polarization of the methyl group toward the lithium and away from the fluorine.

What criteria might reasonably be used in assessing the usefulness of a given definition of atomic charge? We propose the following:

1. It should be relatively independent of the basis set used in the calculations so long as it is of reasonably high quality (i.e., not STO-3G). Although changes in basis set can lead to small changes in charge density distribution that may be energetically important, the distribution of charge between a given pair of atoms is not much affected, and thus the atomic charges should have only a small dependence on basis set.
2. The calculated charges should reproduce reasonable trends due to electronegativity differences. Thus, in changing from CH_3 to NH_2, OH, and F as substituents the charge on the atom to which they are attached should become more positive.
3. The calculated charges should approximately reproduce the dipole moment of the molecule. In the case of methods using spherically symmetrical atoms, the dipole moment should be obtained directly from the charge-coordinate products. In the case of methods using nonspherically symmetrical atoms, the atomic dipoles created by the charge distribution also should be included. This is especially true for atoms having lone pairs because they contribute large atomic dipoles.
4. The charges should approximately reproduce the molecular electrostatic potential map outward from the van der Waals surface of the molecule. It should be derived from just the charges with spherically symmetrical atoms and from the charges, atomic dipoles, and higher moments in the other cases.

The first of these criteria may be examined using the data in Table I. There are a number of molecules for which the Mulliken populations are strongly affected by the basis set used. In the case of isobutene, the Mulliken charge for the central carbon goes from +0.1 with 6-31G* wave functions to +1.0 for 6-311++G** wave functions. Here, the problem is well understood. The inclusion of diffuse functions at a center serves to improve the charge density distribution not only at that center but also at some adjacent centers. Thus, it is not appropriate to assign the density matrix elements for all of the functions at a given center to that center.

The NPA analysis provides a marked improvement. Here, the charges for isobutene and acetic acid are essentially basis set independent. The same is true for all of the other procedures used in this article.

ATOMIC CHARGES FOR HYDROCARBONS

As organic chemists, we are particularly interested in how structural constraints and hybridization af-

Table I. Effect of basis set on calculated charges.

Compound	Atom	Mulliken		NPA		Hirshfeld		AIM		GAPT		CHELPG	
		6-31G**	6-311++G**	6-31G**	6-311++G**	6-31G**	6-311++G**	6-31G**	6-311++G**	6-31G**	6-311++G**	6-31G**	6-311++G**
Isobutene	Me	+0.014	-0.249	+0.030	+0.013	+0.001	+0.007	+0.033	+0.037	+0.006	+0.017	-0.028	-0.030
	CH_2	-0.084	-0.661	-0.031	-0.043	-0.066	-0.063	-0.031	-0.023	-0.146	-0.170	-0.214	-0.236
	C	+0.056	+1.150	+0.002	+0.018	+0.064	+0.048	-0.033	-0.050	+0.135	+0.136	+0.271	+0.296
Acetic acid	Me	+0.063	+0.003	-0.013	+0.001	+0.075	+0.078	+0.174	+0.189	+0.042	+0.051	-0.022	-0.023
	C	+0.720	+0.338	+0.987	+0.952	+0.374	+0.350	+1.909	+1.816	+1.318	+1.367	+0.891	+0.947
	=O	-0.553	-0.399	-0.698	-0.689	-0.381	-0.370	-1.405	-1.349	-0.870	-0.911	-0.636	-0.672
	-O-	-0.592	-0.250	-0.797	-0.754	-0.248	-0.237	-1.339	-1.303	-0.826	-0.838	-0.687	-0.715
	H	+0.362	+0.307	+0.518	+0.489	+0.181	+0.179	+0.657	+0.649	+0.336	+0.331	+0.454	+0.462

Table II. Calculated atomic charges for hydrocarbons, HF/6-31G**//HF/6-31G*.

Compound	Atom	Mulliken	NPA	Hirshfeld	AIM	GAPT[a]	CHELPG
Methane	C	−0.473	−0.880	−0.007	+0.244	+0.073	−0.333
	H	+0.118	+0.220	+0.002	−0.061	−0.018	+0.083
Ethane	C	−0.335	−0.647	+0.021	+0.237	+0.147	−0.010
	H	+0.112	+0.216	−0.007	−0.079	−0.049	+0.003
Ethylene	C	−0.254	−0.419	−0.009	+0.082	−0.041	−0.280
	H	+0.127	+0.210	+0.005	−0.041	+0.021	+0.140
Acetylene	C	−0.233	−0.244	−0.067	−0.121	−0.212	−0.259
	H	+0.233	+0.244	+0.067	+0.121	+0.212	+0.259
Propane	C1	−0.330	−0.646	+0.014	+0.225	+0.126	−0.211
	Ha	+0.111	+0.222	−0.006	−0.079	−0.050	+0.036
	Hb	+0.109	+0.213	−0.009	−0.082	−0.046	+0.045
	C2	−0.216	−0.432	+0.047	+0.220	+0.178	+0.272
	H	+0.109	+0.216	−0.014	−0.092	−0.073	−0.051
Cyclopropane	C	−0.261	−0.454	+0.001	+0.104	+0.054	−0.228
	H	+0.131	+0.227	−0.001	−0.052	−0.027	+0.114
Cyclopropene	C1	−0.141	−0.199	−0.005	−0.084	−0.106	−0.142
	H	+0.158	+0.234	+0.034	+0.040	+0.091	+0.144
	C3	−0.242	−0.455	−0.013	+0.247	+0.152	−0.075
	H	+0.104	+0.193	−0.023	−0.080	−0.061	+0.035
Cyclobutene	C1	−0.131	−0.214	−0.003	−0.005	−0.040	−0.168
	H	+0.132	+0.217	+0.004	−0.038	+0.025	+0.107
	C3	−0.241	−0.441	+0.023	+0.191	+0.126	+0.069
	H	+0.120	+0.219	−0.012	−0.075	−0.055	−0.005
Bicyclo[1.1.0]butane	C1	−0.147	−0.251	−0.012	−0.061	−0.123	−0.032
	H	+0.146	+0.242	+0.010	−0.009	+0.008	+0.098
	C2	−0.241	−0.427	+0.012	+0.186	+0.190	−0.336
	Ha	+0.126	+0.225	+0.001	−0.055	−0.004	+0.149
	Hb	+0.116	+0.211	−0.011	−0.062	−0.070	+0.121
[1.1.1]Propellane	C1	−0.014	−0.064	−0.079	−0.105	−0.329	−0.287
	C2	−0.276	−0.436	+0.031	+0.137	+0.214	−0.025
	H	+0.143	+0.239	+0.011	−0.033	+0.003	+0.108
Bicyclo[1.1.1]pentane	C1	−0.133	−0.211	+0.041	+0.102	+0.077	+0.197
	H	+0.112	+0.222	−0.012	−0.073	−0.080	−0.005
	C2	−0.203	−0.431	+0.012	+0.153	+0.115	−0.295
	H	+0.109	+0.212	−0.016	−0.088	−0.056	+0.083
Tetrahedrane	C	−0.164	−0.257	−0.031	−0.049	−0.105	−0.128
	H	+0.164	+0.257	+0.031	+0.049	+0.105	+0.128

[a]GAPT charges obtained at HF/6-31G*//HF/6-31G*.

fect the charge distribution in hydrocarbons. Representative data are shown in Table II. One may first be struck with the range of carbon charges calculated for methane, going from −0.880 to +0.244! We have tried to see how the differences in the calculated charges vary, giving the results shown in Table III. The hydrogen charges were examined because they have a multiplicative effect on the carbon charges, making the latter charges more variable. It can be seen that whereas the hydrogen charges derived by the different procedures vary considerably in each comparison the difference between the

charges for a pair of procedures was fairly constant with relatively small average deviations. The smallest average deviation was found in comparing Mulliken and Hirshfeld charges, and the NPA–Hirshfeld charge comparison also gave a small average deviation. However, in no case did the average deviation exceed 0.05 e, and in 6 of the 15 comparisons it was less than 0.03 e. Thus, although the numerical values may be different, the hydrogen charges tend to have relatively constant differences between procedures. It may be noted that the CHELPG charges have the largest deviation from the other sets of charges.

Table III. Differences between hydrogen charges for hydrocarbons; average values of A-B.

A	B				
	NPA	Hirshfeld	AIM	GAPT	CHELPG
Mulliken	−0.093 ± 0.013	0.128 ± 0.013	0.172 ± 0.020	0.137 ± 0.035	0.048 ± 0.040
NPA		0.220 ± 0.010	0.265 ± 0.032	0.230 ± 0.046	0.141 ± 0.048
Hirshfeld			0.044 ± 0.025	0.009 ± 0.039	−0.079 ± 0.044
AIM				−0.035 ± 0.018	−0.124 ± 0.038
GAPT					−0.089 ± 0.036

PROCEDURES TO DERIVE ATOMIC CHARGES

Dipole moment derivatives derived from experimentally determined intensities of infrared bands are consistent with a bond dipole in the sense C^+—H^- for methane and ethane and in the sense C^-—H^+ for acetylene.[16] The reversal is presumably a result of the change in hybridization at carbon. The AIM and GAPT charges are in agreement with these bond moments. The Hirshfeld population analysis also describes these changes reasonably faithfully, yielding a small bond dipole in the sense C^+—H^- for ethane, a significant bond dipole in the sense C^-—H^+ for acetylene, and almost no bond dipole for ethylene.

The NPA charges appear to give a large C—H bond dipole in the opposite sense from that found experimentally. However, Reed and Weinhold have shown that if one corrects for the atomic dipole at carbon that results from the centroid of charge being displaced from the nuclear position their population analysis also is in agreement with a methane bond dipole in the sense C^+—H^-.[17]

The CHELPG charges have some serious deficiencies. There are presumably no atomic dipole terms, and yet they lead to relatively large positive charges at hydrogens. In the case of propane, one might expect the two carbons to be similar, but they are found to have opposite signs. The same is true for the carbons of bicyclo[1.1.0]butane. Further difficulties with the CHELPG charges will be seen when the atomic charges for methyl derivatives are examined.

Dipole moments for simple hydrocarbons are usually fairly small, reflecting the small difference in electronegativity between carbon and hydrogen. However, in some cases they may approach 1 D. In the group of hydrocarbons in Tables I and II, cyclopropane, bicyclobutane, and isobutene all have significant dipole moments. They have been examined along with cyclobutene as an example of a hydrocarbon with a small dipole moment in Table IV. In each case, the dipole moment was calculated from the atomic charges and atomic coordinates. With the AIM charges, it is necessary also to include the sum of the atomic dipoles, and they are given in the table. Atomic dipoles can also be calculated easily using

the Hirshfeld method[6] and they are given in the table as well. It also gives the dipole found in the SCF calculation from which the wave function was obtained.

In general, there is a fairly good agreement between the SCF dipoles and those calculated from the atomic charges. The AIM and Hirshfeld dipoles agree with the SCF dipoles as long as the atomic dipole contributions are included, and this should always be the case. Similarly, the CHELPG charges reproduce the SCF dipoles as would be expected. With some of the other procedures, there were significant deviations from the SCF dipoles. Thus, the GAPT dipoles are seriously in error with cyclobutene and bicyclobutane, and the dipoles calculated from the NPA charges show significant deviations for isobutene and cyclobutene. The magnitude of the Mulliken population-derived dipoles are too large for isobutene and too small for bicyclobutane. In summary, the three procedures that uniformly give satisfactory dipole moments are AIM, Hirshfeld, and CHELPG. It should be noted that in addition to AIM and Hirshfeld most of the other procedures at least in principle should lead to atomic dipoles. However, whereas they are readily defined for AIM and Hirshfeld, this does not appear to be the case for the other methods.

CHARGES FOR SUBSTITUTED METHANES

We have examined the AIM charges for a variety of methyl derivatives[18] and compared them with the charges for ethyl, isopropyl, and butyl derivatives.[19] The charges at the substituted carbons in these groups of compounds were found to be linearly related. Therefore, it should be satisfactory to examine just the methyl derivatives in comparing the several methods of defining charges. The results for a set of MeX derivatives where X = Li, BeH, BH$_2$, CH$_3$, NH$_2$, OH, and F are given in Table V. Again, there is a range of charges for a given substituent. One might first note that the CHELPG charges for methylamine, methanol, and methyl fluoride are essentially the

**Table IV.** Calculated dipole moments for hydrocarbons.

Method	Isobutene	Cyclopropene	Cyclobutene	Bicyclo[1.1.1]butane
SCF	−0.481	−0.556	−0.042	−0.737
Mulliken	−0.748	−0.430	−0.006	−0.561
NPA	−0.216	−0.537	−0.174	−0.772
Hirshfield				
Charge	−0.407	−0.679	0.138	−0.181
At. dipole	−0.076	0.122	−0.178	−0.556
Total	−0.482	−0.557	−0.040	−0.737
AIM				
Charge	−0.315	−0.096	−0.264	0.132
At. dipole	−0.181	−0.464	0.229	−0.857
Total	−0.496	−0.560	−0.035	−0.724
GAPT	−0.573	−0.620	0.426	−0.057
CHELPG	−0.441	−0.564	−0.028	−0.665

Table V. Calculated methyl group charges for methyl derivatives, HF/6-31G**//HF/6-31G*.

Compound	Mulliken	NPA	Hirshfeld	AIM	GAPT[a]	CHELPG
Methyllithium	−0.419	−0.821	−0.464	−0.902	−0.669	−0.767
Methylberylium hydride	−0.229	−0.741	−0.150	−0.876	−0.398	−0.305
Methylborane	−0.069	−0.209	−0.014	−0.741	−0.228	−0.205
Ethane	0.000	0.000	0.000	0.000	0.000	0.000
Methylamine	+0.176	+0.174	+0.086	+0.444	+0.230	+0.281
Methanol	+0.300	+0.315	+0.143	+0.647	+0.405	+0.264
Methyl fluoride	+0.408	+0.429	+0.211	+0.743	+0.550	+0.277

[a]GAPT charges obtained at HF/6-31G*//HF/6-31G*.

same, whereas they would be expected to differ significantly due to the changes in electronegativity. The other methods for calculating populations do give the expected trends.

Electronegativity

Electronegativity
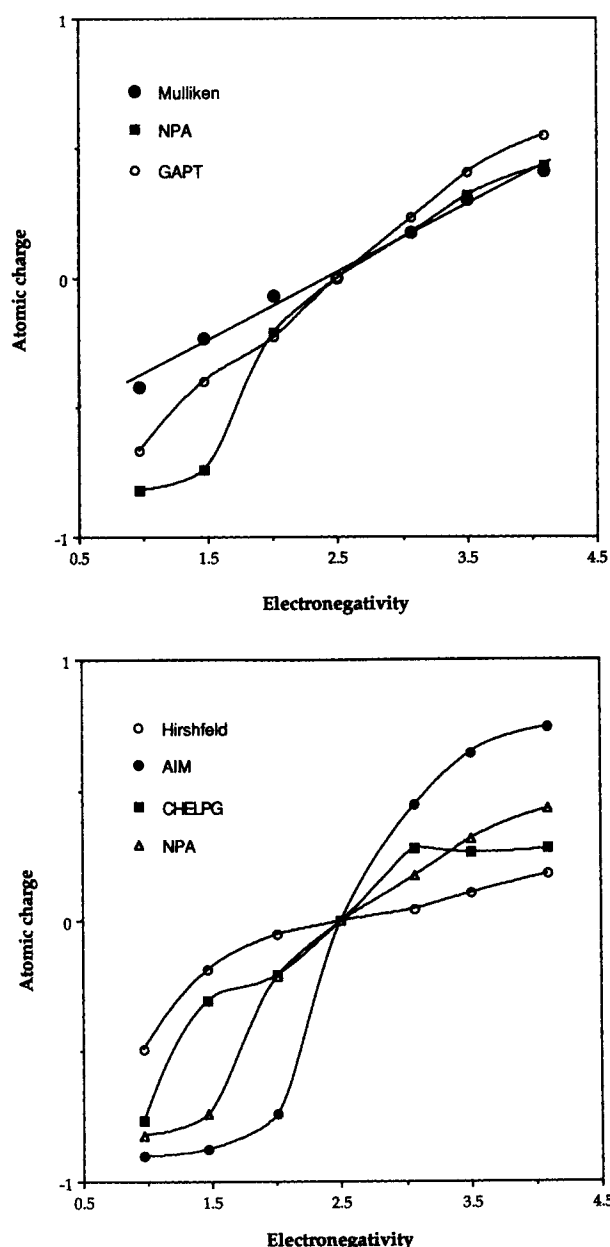
Figure 2. Relationship between the calculated charges and the electronegativities of the attached atoms for the methyl derivatives.

The CHELPG charges at first appeared attractive in that they reproduce the molecular dipole moments and electrostatic potentials. However, in view of the lack of response to changes in electronegativity, and the problems noted with the hydrocarbons, they cannot be recommended for studies of substituent effects or other intramolecular interactions. The problem may arise, at least in part, from treating the charge distribution in the vicinity of each nucleus as if it were spherically symmetrical, when in fact this charge distribution is usually highly anisotropic. As a result, neighboring atoms must be modified to allow the anisotropy of the electrostatic potential to be reproduced. The CHELPG charges are, however, useful in estimating intermolecular Coulombic interactions, and they might best be thought of as a set of empirical quantities that are designed to reproduce these interactions.

In examining the charges calculated by the other methods, it is convenient to see how they are related to the electronegativities of the substituents. This is shown in Figure 2. Except for the CHELPG charges, there is the expected change in charge with increasing electronegativity. However, the charges do not change in a linear fashion. The AIM charges give the largest deviation from linearity, and small changes in electronegativity will lead to relatively large changes in population. The AIM procedure is a topological analysis of the charge density (ρ), and in common with all topological analyses it begins with locating the critical points in ρ (the points for which the derivatives of ρ are zero). The critical point between a pair of atoms will lie on the surface that separates the two atoms. It is a sensitive function of the changes in ρ caused by electronegativity differences.* As a result, the volume associated with a given atom increases quickly with an increase in electronegativity, and this in turn leads to a large increase in the electron population.

It has been stated[21] that the AIM charges are "too large." This would be true if they represented "point charges" for spherically symmetrical atoms. However, it can be seen in Figure 1 that atoms in molecules are far from symmetrical. As a result, there

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*The location of the bond critical point has been used as a measure of electronegativity differences.[20]

Table VI. Calculated atomic charges for simple hydrides, HF/6-31G**//HF/6-31G*.

Compound	r	E(6-31G**)	Atom	Mulliken	NPA	Hirshfeld	AIM	GAPT[a]	CHELPG
LiH	1.6360	−7.98134	H	−0.194	−0.726	−0.402	−0.909	−0.647	−0.748
			Li	+0.194	+0.726	+0.402	+0.909	+0.647	+0.748
BeH$_2$	1.3342	−15.76691	H	−0.109	−0.588	−0.179	−0.873	−0.369	−0.366
			Be	+0.218	+1.176	+0.359	+1.747	+0.739	+0.733
BH$_3$	1.1884	−26.39287	H	−0.077	−0.127	−0.063	−0.719	−0.211	−0.236
			B	+0.230	+0.380	+0.189	+2.158	+0.634	+0.709
CH$_4$	1.0838	−40.20170	H	+0.118	+0.220	+0.002	−0.061	+0.073	+0.083
			C	−0.473	−0.880	−0.007	+0.244	−0.018	−0.333
NH$_3$(C$_3$V)	1.0025	−56.19553	H	+0.263	+0.378	+0.095	+0.371	+0.164	+0.356
			N	−0.790	−1.133	−0.285	−1.113	−0.492	−1.069
NH$_3$(D$_3$H)	0.9884	−56.18675	H	+0.287	+0.400	+0.101	+0.434	+0.246	+0.497
			N	−0.861	−1.201	−0.302	−1.300	−0.739	−1.490
H$_2$O(C$_2$V)	0.9473	−76.02357	H	+0.336	+0.486	+0.164	+0.617	+0.300	+0.400
			O	−0.672	−0.972	−0.327	−1.235	−0.600	−0.801
H$_2$O(D*H)	0.9246	−75.96893	H	+0.409	+0.585	+0.205	+0.751	+0.563	+0.626
			O	−0.818	−1.170	−0.410	−1.502	−1.126	−1.251
HF	0.9109	−100.01155	H	+0.392	+0.565	+0.240	+0.754	+0.425	+0.453
			F	−0.392	−0.565	−0.240	−0.754	−0.425	−0.453
SiH$_4$	1.4753	−291.23084	H	−0.167	−0.213	−0.118	−0.743	−0.322	−0.161
			Si	+0.667	+0.853	+0.471	+2.975	+1.275	+0.644

[a]GAPT charges obtained at HF/6-31G*//HF/6-31G*.

are atomic dipoles that should be considered. The methyl and X atomic dipoles for methyllithium and methyl fluoride are

$$\underset{-3.72}{H_3C \!\longrightarrow\! Li} \qquad \underset{+1.86 \quad +0.81}{H_3C \!\longleftarrow\! F}$$

With methyllithium, the sum of the atomic dipoles is −3.72 and the charge distance product gives a moment of +9.48 D. The sum is +5.67 D, in good agreement with the SCF value of 5.72 D. For methyl fluoride, the sum of the atomic dipoles is +2.67 D and the charge distance product gives −4.66 D, for a sum of −1.98 D. Again, this is in good agreement with the SCF value of −1.98 D. The same sort of analysis can be carried out using the charges and atomic dipoles derived from the Hirshfeld method, and the results are equally good.

CHARGES FOR SIMPLE HYDRIDES

To go along with the methyl derivatives, we also have examined a series of related simple hydrides at the same theoretical level, giving the data summarized in Table VI. The hydrogen charges calculated using any of the methods studied here change in the expected way with increased electronegativity of the attached atom. They also are related to the hybridization of the attached atom, as can be seen in the comparisons of ammonia with its planar counterpart and water with its linear counterpart. In the normal forms, the lone-pair electrons will be placed in orbitals having high s-character, thus decreasing the s-character in the bonds to hydrogen. The distorted forms require the lone pair to be in a p-orbital, increasing the s-character in the bonds to hydrogen

and decreasing the electron population at the hydrogens.

In view of the similarity in electronegativity between carbon and hydrogen, one might reasonably expect that the methyl charges for the methyl derivatives and the hydrogen charges for the hydrides would be related. This has been examined giving the data shown in Table VII. It can be seen that linear relationships are found in many cases with slopes near unity. The largest exception is the Mulliken charges, for which the slope is only 0.777, and the GAPT and CHELPG charges also give slopes that differ significantly from unity. The two best correlations were found with the NPA (slope = 0.95, r^2 = 0.99) and AIM charges (slope = 1.02, r^2 = 1.00) (Fig. 3).

CHARGES FOR TYPICAL ORGANIC COMPOUNDS

The following compounds were examined: formaldehyde, acetaldehyde, acetone, formamide, acetonitrile, nitromethane, and vinylamine. The data are given in Table VIII. The fluoromethanes also were examined (Table IX). Although the numerical values

Table VII. Correlation between hydrogen charges for HX and methyl charges for MeX.

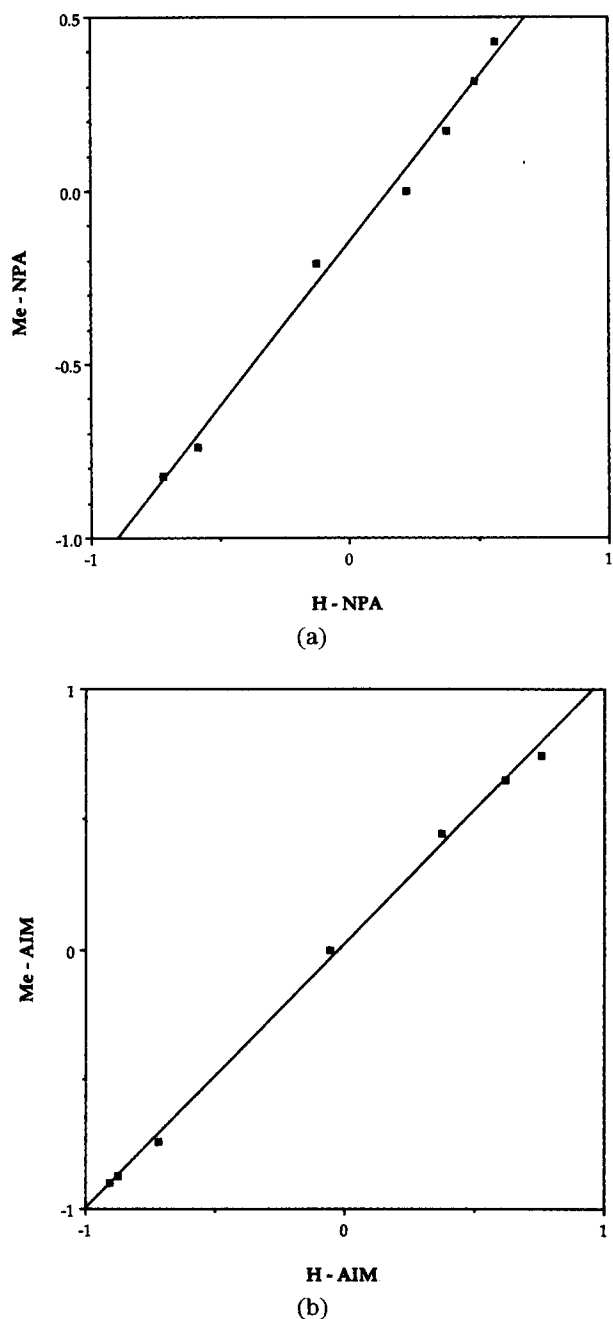| Population	Slope	r^2
Mulliken	0.777	0.947
NPA	1.046	0.992
Hirshfeld	0.959	0.973
AIM	0.979	0.998
GAPT	0.893	0.974
CHELPG	1.154	0.982

Figure 3. Relationship between hydrogen charges for hydrides and methyl charges for the corresponding methyl derivatives for the NPA analysis (a) and the AIM procedure (b).

of the charges vary considerably between the different charge definitions, we were interested in seeing if there were any consistent trends. Therefore, we have examined the correlations among the charges for these compounds and for ethane as a typical hydrocarbon. The results are shown in Table X. Not surprisingly, the best correlation was between the Mulliken and NPA charges with $r^2 = 0.99$ (Fig. 4). There also was a good correlation between the Hirshfeld and AIM charges ($r^2 = 0.95$), which is encouraging because both were derived by integration of charge density, although with different defi-

nitions of the volume elements (Fig. 4). There also were reasonable correlations between the Mulliken and the Hirshfeld ($r^2 = 0.94$) and AIM charges ($r^2 = 0.94$) and between the Hirshfeld and GAPT charges ($r^2 = 0.95$). However, in many cases the correlation was poor, with r^2 less than 0.9. This was particularly true with the correlations involving the CHELPG charges and to a lesser extent with the GAPT charges.

The slopes of the correlations are also of interest (Table X). It can be seen that the Hirshfeld charges change much less than any of the others, and the CHELPG charges also give relatively small slopes when plotted against any of the other sets of data. The NPA and AIM charges are correlated with a slope near unity.

The charges at fluorine in the fluoromethanes have been of special interest to us (Table IX).[22] It is interesting to note that the NPA, AIM, and GAPT charges at fluorine are independent of the number of fluorines and that the Mulliken, Hirshfeld, and CHELPG charges change by relatively small amounts through the series. We have proposed that the increasing charge at carbon with increasing fluorine substitution is the major factor leading to the stability of the polyfluoroalkanes.[22]

The planar and rotated formamide and planar and rotated vinylamine provide interesting comparisons between the different methods of defining populations. On going from the planar to the rotated form of the latter, the terminal methylene group is calculated to lose electron population with all the methods except AIM. The latter gives a small change in population in the opposite direction. The same trend is seen with formamide, in which the amide nitrogen is calculated to lose charge on rotation using most methods but is calculated to gain charge using AIM.

The reasons for the differences among the methods for defining populations can readily be seen by examining "planar" and rotated vinylamine. In the conventional view, one writes the following resonance structures to describe planar vinylamine:
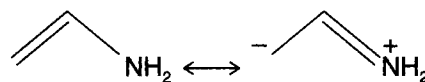
Here, one anticipates some shift of lone-pair density into the C—C double bond. On rotation, the π interaction will be lost, and there should be a shift of π density back to the nitrogen. However, the σ system also is involved in the process. In the planar form, the lone pair at nitrogen is placed in an orbital with high p-character so that it can interact with the double bond. The bond from nitrogen to carbon will then be formed using $\sim$ an sp^2 orbital. On rotation, the lone pair will be placed in an orbital with high s-character (as is found with amines) and the bond from nitrogen to carbon will be formed using an orbital with high p-character. In this rotated form,

Table VIII. Calculated charges for assorted organic molecules, HF/6-31G**//HF/6-31G*.

Compound	Atom	Mulliken	NPA	Hirshfeld	AIM	GAPT[a]	CHELPG
Formaldehyde	C	+0.245	+0.325	+0.259	+1.365	+0.800	+0.496
	O	−0.432	−0.577	−0.298	−1.297	−0.675	−0.478
	H	+0.093	+0.126	+0.020	−0.034	−0.063	−0.009
Acetonitrile	C	−0.371	−0.745	+0.057	+0.346	+0.176	−0.207
	H	+0.180	+0.266	+0.032	+0.006	+0.026	+0.103
	C	+0.285	+0.322	+0.148	+1.170	+0.134	+0.406
	N	−0.454	−0.374	−0.301	−1.532	−0.389	−0.509
Nitromethane	C	−0.191	−0.478	+0.114	+0.564	+0.235	−0.298
	H	+0.187	+0.252	+0.044	+0.020	+0.030	+0.145
	H	+0.181	+0.248	+0.039	+0.024	+0.034	+0.135
	N	+0.550	+0.651	+0.297	+0.464	+1.259	+0.864
	O	−0.454	−0.460	−0.266	−0.548	−0.796	−0.491
Acetaldehyde	C	+0.379	+0.513	+0.269	+1.292	+0.853	+0.620
	O	−0.475	−0.606	−0.329	−1.328	−0.740	−0.539
	H	+0.091	+0.130	+0.007	−0.051	−0.089	−0.048
	C	−0.435	−0.759	+0.014	+0.183	−0.033	−0.256
	H	+0.160	+0.245	+0.015	−0.020	+0.003	+0.088
	H	+0.140	+0.239	+0.012	−0.040	+0.003	+0.068
Acetone	C	+0.501	+0.685	+0.284	+1.219	+0.864	+0.761
	O	−0.516	−0.627	−0.353	−1.349	−0.783	−0.589
	C	−0.421	−0.748	+0.006	+0.181	−0.038	−0.373
	H	+0.159	+0.248	+0.013	−0.021	−0.001	+0.104
	H	+0.135	+0.235	+0.008	−0.048	+0.000	+0.091
Formamide	C	+0.562	+0.670	+0.312	+1.977	+1.304	+0.790
	O	−0.562	−0.702	−0.393	−1.392	−0.904	−0.619
	H	+0.097	+0.129	+0.021	−0.035	−0.056	−0.023
	N	−0.732	−0.944	−0.192	−1.476	−0.854	−0.987
	H	+0.322	+0.427	+0.128	+0.471	+0.252	+0.435
	H	+0.312	+0.420	+0.124	+0.456	+0.257	+0.404
Formamide 90°	C	+0.473	+0.671	+0.336	+1.756	+1.075	+0.950
	O	−0.452	−0.617	−0.325	−1.343	−0.775	−0.618
	H	+0.122	+0.143	+0.024	−0.006	−0.040	−0.063
	N	−0.734	−1.012	−0.256	−1.223	−0.632	−1.065
	H	+0.295	+0.407	+0.110	+0.408	+0.186	+0.398
Vinylamine	N	−0.713	−0.910	−0.235	−1.326	−0.705	−0.865
	H	+0.283	+0.399	+0.104	+0.402	+0.211	+0.352
	H	+0.284	+0.395	+0.103	+0.403	+0.180	+0.369
	C	+0.140	+0.044	+0.109	+0.511	+0.573	+0.303
	H	+0.136	+0.207	+0.013	−0.037	+0.007	+0.090
	C	−0.361	−0.558	−0.082	+0.149	−0.321	−0.650
	H	+0.123	+0.219	−0.005	−0.044	+0.031	+0.173
	H	+0.109	+0.204	−0.009	−0.060	+0.024	+0.228
Vinylamine 90°	N	−0.708	−0.942	−0.257	−1.219	−0.506	−0.934
	H	+0.272	+0.388	+0.093	+0.374	+0.155	+0.361
	C	+0.049	−0.018	+0.090	+0.494	+0.294	+0.339
	H	+0.114	+0.186	−0.007	−0.063	−0.049	−0.001
	C	−0.261	−0.433	−0.022	+0.103	−0.112	−0.465
	H	+0.139	+0.220	+0.007	−0.018	+0.043	+0.200
	H	+0.123	+0.211	+0.003	−0.045	+0.019	+0.140

[a]GAPT charges obtained at HF/6-31G*//HF/6-31G*.

Table IX. Calculated charges for fluoromethanes, HF/6-31G**//HF/6-31G*.

Compound	Atom	Mulliken	NPA	Hirshfeld	AIM	GAPT[a]	CHELPG
Fluoromethane	C	+0.087	−0.095	+0.169	+0.869	+0.719	+0.171
	F	−0.407	−0.429	−0.211	−0.743	−0.550	−0.277
	H	+0.107	+0.175	+0.014	−0.042	−0.056	+0.035
Difluoromethane	C	+0.561	+0.562	+0.318	+1.506	+1.304	+0.482
	F	−0.380	−0.429	−0.185	−0.744	−0.576	−0.263
	H	+0.100	+0.149	+0.026	−0.009	−0.076	+0.022
Trifluoromethane	C	+0.944	+1.120	+0.444	+2.193	+1.790	+0.644
	F	−0.350	−0.421	−0.162	−0.744	−0.576	−0.230
	H	+0.106	+0.142	+0.041	+0.047	−0.061	+0.047
Tetrafluoromethane	C	+1.313	+1.620	+0.563	+2.951	+2.202	+0.814
	F	−0.328	−0.405	−0.141	−0.737	−0.551	−0.203

[a]GAPT charges obtained at HF/6-31G*//HF/6-31G*.

Table X. Correlations among the carbon charges.

X	Y	Slope	Intercept	r^2
Mulliken	NPA	1.396	0.134	0.989
	Hirshfeld	0.324	0.128	0.941
	AIM	1.539	0.767	0.943
	GAPT	1.289	0.424	0.901
	CHELPG	0.805	0.084	0.789
NPA	Hirshfeld	0.228	0.160	0.916
	AIM	1.086	0.917	0.925
	GAPT	0.895	0.551	0.856
	CHELPG	0.585	0.160	0.820
Hirshfeld	AIM	4.609	0.185	0.946
	GAPT	3.959	−0.083	0.952
	CHELPG	2.388	−0.217	0.777
AIM	GAPT	0.812	−0.192	0.900
	CHELPG	0.487	−0.280	0.726
GAPT	CHELPG	0.561	−0.139	0.706

the nitrogen will be less electron withdrawing than in the minimum energy structure and there will be a shift in σ electron density away from the nitrogen. Thus, the σ and π charge shifts will be in opposite directions.

This may be seen in charge density difference plots (Fig. 5). Here, the charge density for the planar form is subtracted from that of the rotated form. In the left-hand plot, just the charge density in the molecular plane is considered. It can be seen that the charge density in the terminal methylene group is indeed greater in the rotated form than in the planar form in the σ system. The right-hand plot shows the difference in projection densities.[23] The latter is formed by projecting all of the charge density above and below the molecular plane onto this plane. Now, the rotated form has diminished charge density at the methylene group, and this is the consequence of including the π charge density. Thus, the σ and π shifts do occur in opposite directions, and in this case the π density has the larger effect in the vicinity of the methylene carbon.

The atoms in molecules approach is a topological procedure and, as noted above, one first locates the critical points in ρ. In examining the charge density, the critical point is determined by the charge distribution along a bond, and for a planar molecule the critical points will be in the molecular plane. Thus, with vinylamine the critical point moves away from the nitrogen on going from the rotated to the planar form, and the volume associated with the nitrogen increases. This leads to an increase in the electron population assigned to the nitrogen. In the other procedures, the volume associated with the atoms does not change in the same fashion, and it can be seen that if the volume associated with the nitrogen were constant the electron population at nitrogen would be greater in the rotated form than in the equilibrium structure. This accounts for the difference between the AIM charges and the other charges for vinylamine.
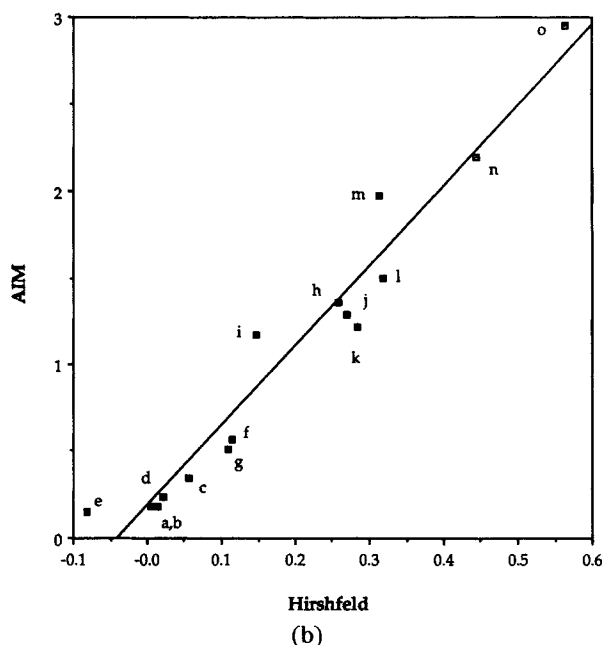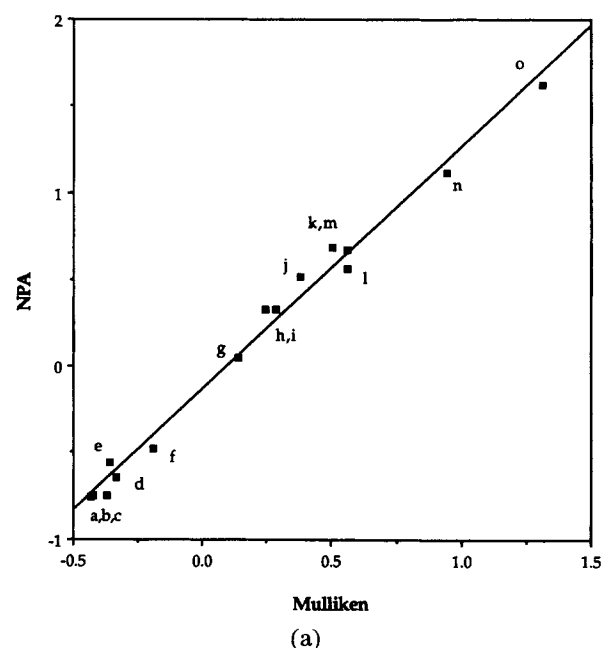

(a)

(b)

Figure 4. Relationship between carbon charges. (a). NPA and Mulliken charges. (b). AIM and Hirshfeld charges. The compounds are: (a), acetone (Me); (b), acetaldehyde (Me); (c), acetonitrile (Me); (d) ethane; (e), vinylamine (CH_2); (f), nitromethane (Me); (g) vinylamine (CH); (h) formaldehyde; (i), acetonitrile (CN); (j), acetaldehyde (CO); (k), acetone (CO); (l), difluoromethane; (m), formamide; (n), fluoroform; (o), carbon tetrafluoride.

Formamide presents a more complex picture. The Mulliken populations suggest that the charge shift on rotation about the C—N bond is between C and O, whereas the NPA populations suggest that it is between N and O and the AIM populations suggest that it is between N and C. A more satisfactory way in which to examine these charge shifts is via an examination of density difference plots. Figure 6
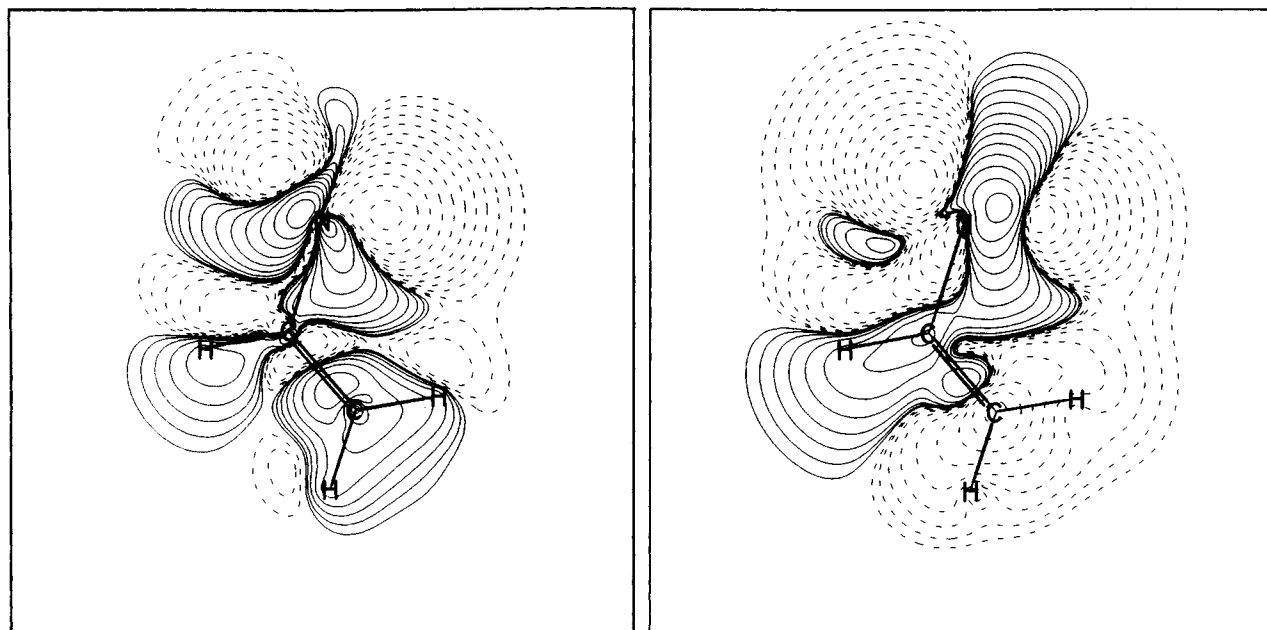
Figure 5. 2-D charge density difference plots for vinylamine (rotated—"planar"). The left-hand plot is for the plane of the vinyl group (i.e., just the σ electrons) and the right-hand plot is for the projection densities that include the π-electrons. Increased charge density for the rotated form is shown with solid lines.

shows such a plot for the oxygen of formamide, and corresponds to the rotated minus planar conformers in which the C—O bond was maintained at the planar value but the rest of each structure was allowed to take its preferred geometry. It can be seen that there is a small π shift away from the oxygen and a small σ shift toward it. Integration of the charge gave a 0.08-e π shift and a 0.03-e σ shift in the opposite sense, for a net change of only 0.05 e. Much larger changes were found in the region of the C—N bond, and here there were significant shifts in π charge toward the nitrogen from the carbon and in σ charge toward the carbon from the nitrogen. The population assigned to each of these atoms then will depend on whether the atom sizes are retained
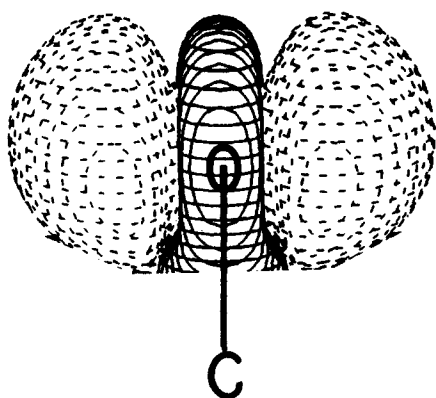
or if the sizes of the atoms are allowed to change in response to changes in electronegativity.

It was suggested above that the electrostatic potential (EP) would be another useful quantity in testing the population methods. The CHELPG charges reproduce the EP outward from the van der Waals surface, and this is expected because these charges were derived by a least-squares fit to the calculated EP. To test the other procedures, we have chosen four common molecules—water, acetone, methyl fluoride, and nitromethane—and calculated the EP maps. The results are shown in Figure 7 for acetone, which is representative of the group. Plots for the other compounds are available by request to the authors. The region inside the van der Waals surface is deleted in each case, and only the EP outside this region will be considered. The calculations are given for the Mulliken, NPA, Hirshfeld, AIM, GAPT, and CHELPG charges. In the cases of the Hirshfeld and AIM charges, where the atomic dipoles also may be obtained, the plots show the EP potential both for just the charges and then for the charges plus atomic dipoles.

To facilitate comparisons, the 8.0-kcal/mol contours are indicated by dark circles. Each contour represents a factor of two increase in energy. In addition, the rms deviations between the exact SCF EP and the EP derived from each of the various sets of charges have been computed and are given in Table XI. The averages were taken over the 20 Bohr by 20-Bohr square grids plotted in Figure 7, but excluded all points within the Merz–Kollman van der Waals radius[24] of any atom. The first plot (a) gives the SCF directly calculated EP, against which the

Figure 6. 3-D charge density difference plots for the oxygen of rotated formamide minus planar formamide. Increased charge density for the rotated form is shown with solid lines. The contour level is 1.5 × 10^{-3} e/B^3.
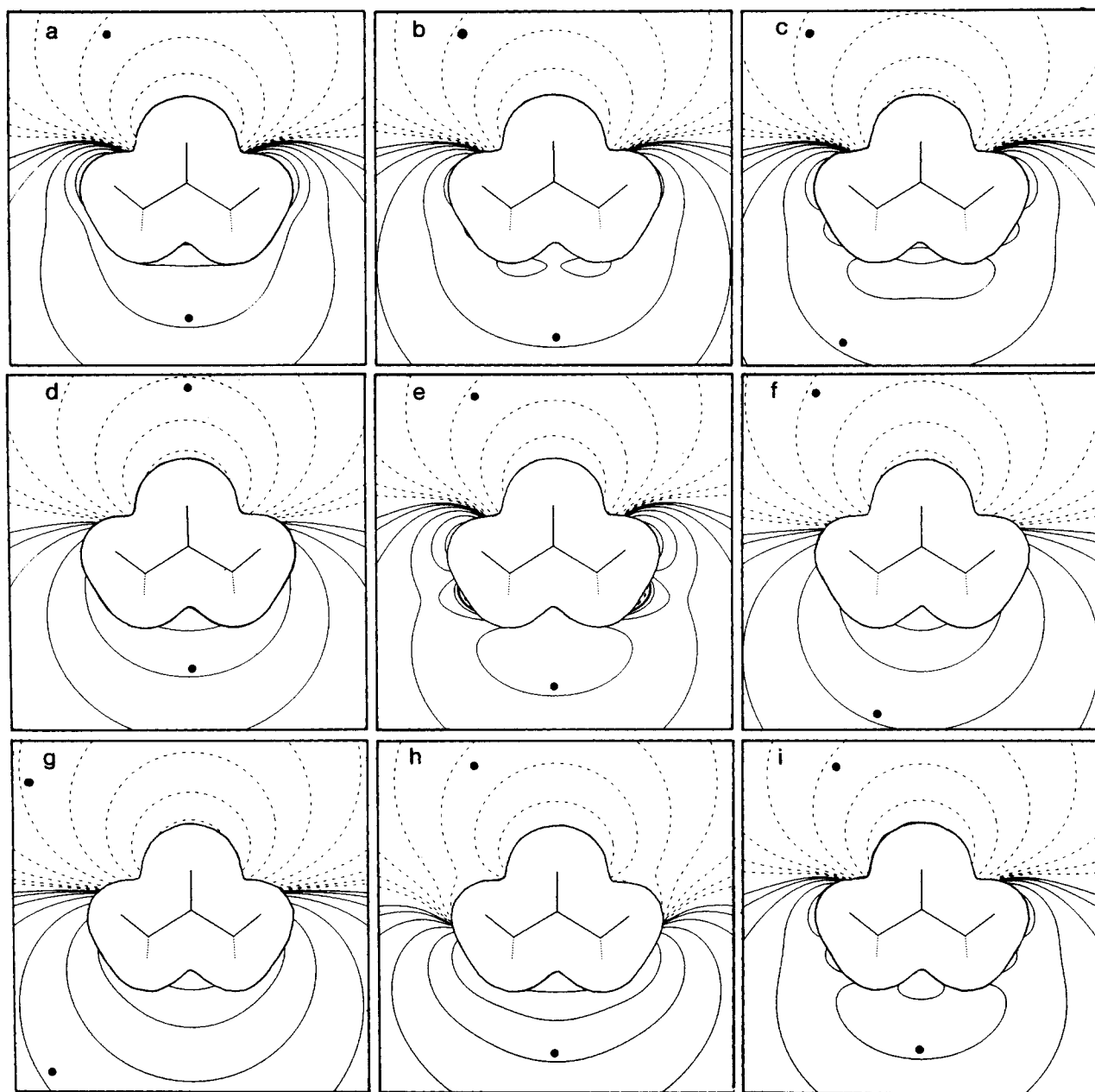
Figure 7. Calculated electrostatic potential maps for acetone. The contours differ in energy by factors of two, and the 8-kcal/mol contour is marked with dark circles. The plots are derived from: (a), the SCF calculation; (b), Mulliken charges; (c), NPA charges; (d), Hirshfeld charges; (e), Hirshfeld charges and atomic dipoles; (f), GAPT charges; (g), AIM charges; (h), AIM charges and atomic dipole; and (i), CHELPG charges.

Table XI. rms deviations between charge-derived and SCF electrostatic potentials, in kcal/mol.

Compound	Monopoles Only						Monopoles and Dipoles	
	Mulliken	NPA	Hirshfeld	AIM	GAPT	CHELPG	Hirshfeld	AIM
Water	2.13	3.32	6.46	6.83	2.90	1.75	1.86	1.30
Fluoromethane	5.05	6.82	2.26	11.45	6.09	1.07	1.74	2.44
Acetone	2.10	4.91	3.49	18.79	5.07	1.52	1.89	3.79
Nitromethane	7.36	6.09	4.30	13.44	9.08	1.65	2.97	6.17
Methyllithium	8.96	5.64	6.75	14.14	6.98	4.10	3.87	7.09
Formamide	3.37	4.92	5.59	15.06	7.31	1.78	1.76	3.03
Formamide 90°	3.68	4.18	6.22	15.72	7.89	1.97	2.59	2.80
Average	4.66	5.13	5.01	13.63	6.47	1.98	2.38	3.80
Average*[a]	3.95	4.84	4.72	12.77	6.04	1.62	2.14	3.26

[a]Average* is the average when the single worst case for each column is excluded.

others should be compared. It can be seen that the Mulliken (b) and NPA charges (c) lead to electrostatic potentials that are too large. The Hirshfeld charges (d) lead to too small an EP, but when the atomic dipoles are included (e) they are close to the SCF values. The AIM charges (g) lead to EPs that are too large, but here, again, the inclusion of the atomic dipoles leads to values close to SCF. The inclusion of the atomic quadrupoles further improves the fit and brings it close to that obtained in the SCF calculations.[25] The inclusion of quadrupole moments would presumably lead to a similar improvement in the EP computed from the Hirshfeld charge moments. The GAPT charges (f) lead to EPs similar to those found in the NPA analysis, and the CHELPG charges (i) reproduce the SCF values fairly well.

The more successful fits to the SCF EPs make use of the Hirshfeld or AIM charges and atomic dipoles, or the CHELPG charges. It is likely that the NPA procedure also would give a good fit if the atomic dipoles were included. However, they are not so readily defined.

CONCLUSIONS

It must first be recognized that no one procedure is "best" for all purposes. The Mulliken, NPA, and GAPT charges are closely related (although not with unit slopes) using the 6-31G* basis set. The Mulliken populations using other basis sets would probably not give a similarly good correlation (cf. Table I). Of the three, the NPA charges are probably the more satisfactory. A potential problem with the GAPT charges is that Hartree–Fock calculations usually give atomic polar tensors that are significantly different than those determined experimentally via analyses of intensities of infrared bands.[26] Therefore, the charges derived from experimental data may be different than those obtained by calculations at the Hartree–Fock level.

Most of the methods studied had difficulty in giving atomic charges that could reproduce both the dipole moments and the electrostatic potentials of a representative set of molecules in a satisfactory manner. However, the AIM and Hirshfeld methods provide a natural definition of atomic dipoles and higher terms, and if these are included the electric moments and electrostatic potentials of the molecules are well reproduced. The CHELPG method also yields charges that lead to satisfactory electrostatic potentials at long distances, as it was designed to do. However, as noted above, they have other difficulties. These findings carry an important message: The charge distribution in a molecule is much too anisotropic to be successfully modeled by any single set of atom-centered charges unless only long-distance interactions are of interest. Otherwise, it is

necessary to include at least atomic dipole terms, and possibly higher terms as well. In this sense, methods of population analysis that conveniently provide these higher moments have an advantage over those that do not.

Although the calculated charges for a given compound vary considerably between methods of defining charge, there is often a reasonable correlation of the changes in charge with structure, especially with the NPA, Hirshfeld, and AIM charges.

Our preference is for the AIM charges. For organic compounds, it is among the best in representing the polarization of CH bonds (both sign and magnitude). It is applicable not only to the results of *ab initio* MO calculations but also to charge densities derived from experimental X-ray crystallographic data[27] and to the results of completely numerical density functional theory calculations in which the idea of atomic and molecular orbitals does not appear.[28] In addition, it allows the calculation of a variety of properties of atoms such as their kinetic and potential energies, and ^{13}C NMR chemical shifts.[29]

Although the CHELPG charges do not respond to substituents and other structural changes in the same way as the other types of charges, they are perhaps the more useful quantities in studying intermolecular interactions because they reproduce the electrostatic potentials using only atom-centered charges. As noted above, they might best be considered as a set of empirical quantities that are designed to reproduce the electrostatic potential, rather than as charges in the usual sense.

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