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Properties of atoms in molecules: Dipole moments and transferability of properties

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This paper uses the theory of atoms in molecules to investigate the origin of molecular dipole moments. The dipole moment is given by a sum over the net charge and first moment of every atom in a molecule. The first term leads to a charge transfer contribution μ_c , the second to an atomic polarization contribution μ_a . It is shown that both terms are, in general, of equal importance in determining both the static molecular dipole moment and the moment induced by a nuclear displacement. Models which employ only point charges and corresponding bond moments which follow rigidly the nuclear framework, i.e., models which approximate μ_c and ignore μ_a , are shown to lead to results that are incompatible with the changes that are found to occur in a molecular charge distribution during a nuclear vibration. The dipole moment is shown to be another group property that is transferable between molecules in the normal hydrocarbons. This property, along with the net charge, the energy, the correlation energy (expressed as a functional of the charge density), and the atomic volumes are transferable for methyl and methylene groups because of a corresponding transferability of the distribution of charge over the basins of the atoms in these groups up to their surfaces of zero flux in the gradient vector of the charge density. Transferability of group properties is not a result of the transferability of individual orbitals or geminals, which necessarily have tails lying outside of the group in question. Atoms have no tails and their energy, as is known from experiment, can in certain instances be transferred between systems with changes of less than 1 kcal/mol. The properties of atoms in molecules can be determined experimentally and quantum mechanics predicts these properties, just as it predicts the properties of a total system.

INTRODUCTION

The theory of atoms in molecules defines the average value of an observable over each atom in a molecule. As a result of this partitioning, the molecular average of an observable is given by a sum of atomic contributions. The definition of an atom in a molecule, of the average values of its observables and of their equations of motion are obtained through a generalization of quantum mechanics to a subsystem of some total system.^{1,2} This generalization is unique as it applies only to regions of real space that satisfy a particular constraint on the variation of the action integral of the subsystem, a constraint that requires the subsystem to be bounded by a surface of zero flux in the gradient vector of the charge density

$$\nabla \rho \cdot \mathbf{n} = 0 \quad \text{for every point on the surface.} \quad (1)$$

Because of the principal topological property of a charge distribution for a many-electron system—that it exhibits local maxima only at the positions of nuclei—the quantum boundary condition [Eq. (1)] yields a partitioning of the real space of a molecule into a disjoint set of mononuclear regions or atoms. A very condensed outline of this theory is to be found in a recent issue of this journal³ and a more general nonmathematical review is given in *Accounts of Chemical Research*.⁴

The principle property to be considered in this work is the molecular dipole moment. The dipole moment of a neutral molecule can be expressed in terms of a sum over the net charge $q(\Omega)$ and first moment $\mu(\Omega)$ of every atom Ω in the

molecule,^{5,6} as

$$\begin{aligned} \mu &= \sum_{\Omega} Z_{\Omega} \mathbf{X}_{\Omega} - \int_{\Omega} \mathbf{r} \rho(\mathbf{r}) d\tau \\ &= \sum_{\Omega} [q(\Omega) \mathbf{X}_{\Omega} + \mu(\Omega)], \end{aligned} \quad (2)$$

where \mathbf{X}_{Ω} is the position vector of the nucleus of atom Ω measured from some arbitrary origin. The atomic charge is defined as the sum of the nuclear and average electronic charges

$$q(\Omega) = Z_{\Omega} - \int_{\Omega} \rho(\mathbf{r}) d\tau = Z_{\Omega} - N(\Omega) \quad (3)$$

and the first moment is the atomic average of the electronic position vector $\mathbf{r}_{\Omega} = \mathbf{r} - \mathbf{X}_{\Omega}$:

$$\mu(\Omega) = - \int_{\Omega} \mathbf{r}_{\Omega} \rho(\mathbf{r}) d\tau. \quad (4)$$

While the individual contributions $q(\Omega) \mathbf{X}_{\Omega}$ depend upon the choice of origin, their sum does not, and hence each molecular dipole moment is uniquely determined by a charge transfer contribution arising from the net charge on the atoms

$$\mu_c = \sum_{\Omega} q(\Omega) \mathbf{X}_{\Omega} \quad (5)$$

and a first moment contribution arising from the polarization of the atomic charge densities:

$$\mu_a = \sum_{\Omega} \mu(\Omega). \quad (6)$$

Both terms are equally important in the description of a molecular dipole.^{5,7,8} Relating the static molecular dipole μ to

only the charge transfer term through the assignment of a set of atomic charges is unrealistic as it ignores dipolar contributions arising from the atomic polarizations, the importance of which was shown long ago by Coulson.⁷ Use of such a model corresponds to assuming the molecular charge distribution to be composed of a set of spherically symmetric atomic densities, each centered on its own nucleus, a physically unacceptable model even in the limit of an ionic system.^{9,10} Any use of the spherical atom-charge transfer model in the description of changes in dipole moment accompanying nuclear vibrations, even when modified to include changes in the atomic charges, the so-called atomic fluxes,¹¹ is still less acceptable as it cannot adequately describe the relaxations in the charge density induced by the nuclear motions. Such relaxations may correspond to the density preceding the displaced nucleus thereby facilitating the motion, or it may lag behind the nuclear motion and oppose it.^{12,13} In the electro-optical method (EOM) as applied and extended by Gussoni *et al.*,^{14,15} experimental vibrational intensities are used to fix a set of bond dipoles and changes in these dipoles, the bond dipoles being in turn used to assign a set of atomic charges. Each bond dipole is constrained to be directed along the corresponding internuclear axis and to rigidly follow the motion of this axis. Such a model fails to describe moments arising from atomic polarizations and their changes which, in general, are not directed along a bond axis. In addition, it does not allow for the line of maximum charge density linking a pair of bonded nuclei to not rigidly follow the displaced internuclear axis.^{16(a)} This latter possibility occurs even in systems without nonbonded charge concentrations. Wiberg and Wendoloski^{16(b)} have stressed the importance of nonrigid following of the charge density in the bending of C-H bonds.

Traditionally, dipole moments have been discussed and categorized in terms of bond dipoles. The vector addition of bond dipoles is useful in the elucidation of molecular structures.¹⁷ There is no unique way of decomposing a dipole moment of a polyatomic molecule into a set of bond moments. In addition, there is the further problem of treating the presence of moments arising from atomic polarization associated with the presence of nonbonded pairs of electrons. One may attempt to include the moments arising from these atomic polarizations in the associated bond moment or treat them as separate entities. The ultimate usefulness of the bond moment concept is dependent upon the extent to which the assigned moments are independent of their environment and are transferable between molecules. In spite of the above shortcomings, the method of bond moments has and continues to serve a useful purpose.¹⁷

In addition to using Eq. (2) to obtain an atomic understanding of molecular dipoles and their dependence on nuclear displacements, it is a further purpose of this paper to show to what extent theory can recover the principal features of the bond moment model. It is the atom and its properties that are defined by quantum mechanics and while no attempt is made to reduce the total moment to a sum of bond contributions, it is possible to rewrite just the charge transfer contribution to μ as a sum of bond contributions. This serves two purposes: it maximizes the mapping of the model onto

theory and in addition, it serves to isolate and emphasize the contributions ignored by the model, those from the atomic polarizations.

The transferability of moments between systems can be understood and illustrated by summing the properties for a grouping of atoms linked by a set of bond paths to obtain corresponding property values for a functional group. Such a group is again bounded by a surface of zero flux in the gradient vector of the charge density and as such, is a quantum subsystem with well defined properties. Most importantly, the theory of atoms in molecules can determine to what extent the atomic properties, including net charges and atomic dipoles, are transferable between molecules. The atoms of theory are the most transferable pieces of a system that one can define in real space and they thus maximize the transfer of information between systems. The most important characteristic of an atom is that the constancy in its properties, and hence in its contribution to the properties of the total system, is observed to be directly determined by the constancy in its distribution of charge. While it is not surprising that this relationship should obtain for properties determined directly by the charge density, it is found to hold for the energy of the atom as well, a quantity determined by the first-order density matrix and not just its diagonal elements. Thus when the distribution of charge over an atom is the same in two different molecules, i.e., when the atom or some functional grouping of atoms is the same in the real space of two systems, then the atom or group makes the same contribution to the total energy of both systems.^{1,18}

Examples of near perfect transferability of atoms and functional groupings of atoms and their properties between molecules have been given.^{19,20} Indeed, it was the observation that the transferability of the charge density is paralleled by a corresponding constancy in the kinetic energy density for a subsystem bounded by a zero flux surface that led to their discovery and ultimate quantum justification.¹⁸ This observation shows that the average kinetic energy of such a subsystem $T(\Omega)$ exhibits the same constancy and transferability as does its distribution of charge. Assuming the existence of a subsystem virial theorem, this observation implies that the total energy of the subsystem $E(\Omega)$ is also conserved along with its charge distribution, since by this theorem $E(\Omega) = -T(\Omega)$. It has since been demonstrated that these subsystems or atoms are quantum systems, the virial theorem does indeed apply (as do all theorems derived from the Heisenberg equation of motion for any observable), and thus conservation of the average kinetic energy of the atom demands conservation and transferability of its total energy as well.²¹ Most recently, the methyl and methylene groups of saturated hydrocarbons that are responsible for the well documented energy additivity scheme found for these molecules have been identified with the atoms of theory.^{19,20} It is shown here that the dipole moments of the methyl and methylene groups are also transferable between the same hydrocarbon molecules.

It is to be emphasized that transferability of group properties is a consequence of the transferability of the one-density matrix over spatial regions bounded by zero flux surfaces. This automatically implies transferability of the

charge density, the diagonal elements of this density matrix.²³ Transferability of group properties is not a consequence of a corresponding transferability of the individual orbitals or geminals that are used to construct the density matrices. By their very nature, orbitals and geminals extend over the total space of a system and even when chosen in some localized form, will have "tails" that belong to different environments of the group in question as the group is transferred between systems. This problem has recently been discussed and illustrated by Reed and Weinhold²⁶ using the natural bond orbital analysis.²⁷ What is remarkable, is that in spite of these unavoidable changes in the individual orbitals or geminals, the sum of their contributions to the density matrix can be transferable. As a result, an atom can exhibit a transferability of form in the one-density matrix (in the neighborhood of its diagonal elements) over its entire basin up to its atomic surface of zero flux sufficient to ensure a change in energy between systems of less than a kcal/mol. Atoms have no tails and what is most remarkable is that this constancy in their properties, which is illustrated in this paper, is obtained in spite of changes in their neighboring fragments. This essential property of the chemical atom has its basis in the observation that an atom of theory responds only to changes in the total (Ehrenfest) force exerted on its charge distribution and not to changes in the individual contributions to this force, changes which are large even between closely related systems be they members of a homologous series or chemically similar in structure.^{1,18,20} If it were not for this property of responding only to the total force, there would be no chemically recognizable atoms or functional groups.

HYDROCARBONS AND TRANSFERABLE PROPERTIES

The experimental heats of formation of the homologous series of hydrocarbons $\text{CH}_3(\text{CH}_2)_m\text{CH}_3$ can be fitted to the following relationship^{28,29}:

$$\Delta H_f(298) = 2\Delta H_f(\text{CH}_3) + m\Delta H_f(\text{CH}_2) \quad (7)$$

beginning with $m = 0$. The first contribution is one-half of the heat of formation of ethane, equal to -10.12 kcal/mol and the second is the increment in heat content for the methylene group, with a value of -4.93 kcal/mol. Calculated single determinant SCF energies (without zero-point energy corrections^{30(a)}) at both the 6-31G*/6-31G* and 6-31G**/

6-31G* levels of approximation satisfy a corresponding relationship

$$E = 2E(\text{CH}_3) + mE(\text{CH}_2), \quad (8)$$

with an error comparable to or less than the experimental one.^{19,20}

Hydrogen is slightly more electronegative than carbon in saturated hydrocarbons and the order of the group electron withdrawing ability in hydrocarbon molecules without geometric strain is $\text{H} > \text{CH}_3 > \text{CH}_2 > \text{CH} > \text{C}$.^{19,20} In ethane, methyl is bonded to methyl while in the other molecules of the series it is bonded to methylene from which it withdraws charge. Table I lists the populations and energies of the methyl groups for $m > 0$ relative to their values in ethane. To within the accuracy of the numerical integrations,^{30(b)} the energy and population of the methyl group are constant when it is bonded to a methylene group. Thus, the CH_3 group is the same in all of the members of the homologous series past ethane.

This transferable methyl group is more stable relative to methyl in ethane by an amount $\Delta E = -10.5 \pm 0.5$ kcal/mol and its electron population is greater by an amount $\Delta N = 0.018 \pm 0.001 e$.^{19,20} The charge and energy gained by the methyl group is taken from the methylene group. What is remarkable, and what accounts for the additivity observed in this series of molecules, is that the energy gained by methyl is equal to the energy lost by methylene. Table I lists the energies of the methylene groups relative to the incremental value $E(\text{CH}_2)$, Eq. (8), the energy of the standard methylene group. In propane, where it is bonded to two methyls, the energy of the methylene group is $E(\text{CH}_2) - 2\Delta E$ and its net charge is $+2\Delta N$ where ΔE is identical to the ΔE defined above for methyl measured relative to the energy of the standard methyl group. In butane, a methylene is bonded to a single methyl, its energy is $E(\text{CH}_2) - \Delta E$ and its charge is $+\Delta N$. The corresponding groups in pentane and hexane, those bonded to a single methyl, have the same properties as the methylene group in butane. Thus, the charge transfer to methyl is damped by a single methylene group and the central methylene groups in pentane and hexane should have a zero net charge and an energy equal to the increment $E(\text{CH}_2)$. The properties of these "standard" methylene groups are listed under separate columns in Table I. This is what is found to within the uncertainties in the integrated values of the atomic properties. Therefore, methylene

TABLE I. Group properties in hydrocarbons (6-31G**/6-31G*).

Molecule	Methyl group properties ^a					Methylene group properties ^b				
	$\Delta N(\text{CH}_3)$ (e)	$\Delta E(\text{CH}_3)$ (kcal/mol)	$ \mu(\text{CH}_3) ^c$ (a.u.)	e^d (a.u.)	Molar volume (cm ³)	$\Delta N(\text{CH}_2)$ (e)	$\Delta E(\text{CH}_2)$ (kcal/mol)	$ \mu(\text{CH}_2) ^c$ (a.u.)	e^d (a.u.)	Molar volume (cm ³)
Ethane	0.000	0.0	0.253	-0.3456	19.77					
Propane	-0.017	-10.9	0.244	-0.3484	19.73	0.037	+21.7	0.307	-0.3180	14.18
Butane	-0.018	-10.8	0.243	-0.3486	19.70	0.019	+10.8	0.305	-0.3208	14.12
Pentane	-0.017	-9.9	0.249	-0.3486	19.71	0.019 0.001	+10.9 0.0	0.310 0.304	-0.3210 -0.3238	14.08 13.98
Hexane	-0.018	-9.9	0.245	-0.3485	19.74	0.020 0.000	+10.6 -1.1	0.306 0.300	-0.3208 -0.3237	14.09 14.03

^a Differences are relative to methyl group in ethane.

^b Differences are relative to standard methylene group. The entries beginning with propane are for CH_2 groups bonded to one methyl group. The set beginning with pentane are for CH_2 groups bonded only to other CH_2 groups.

^c Calculated with carbon nucleus as origin.

^d Correlation energy calculated using a density functional, Ref. 32(b).

groups bonded only to other methylenes as found in pentane, hexane, and all succeeding members of the series, possess a zero net charge and contribute the standard increment $E(\text{CH}_2)$ to the total energy of the molecule. The underlying reason for the observation of additivity in this series of molecules is the fact that the change in energy for a change in population, the quantity $\Delta E/\Delta N$, is the same for both the methyl and methylene groups. The small amount of charge shifted from methylene to methyl makes the same contribution to the total energy.

The hydrocarbons also demonstrate²⁰ that the constancy and transferability of group properties is a result of the separate transferability of the distribution of charge and one-density matrix over each of the regions of space bounded by a zero flux surface in the gradient vector of the charge density—over each separate atom. The same reference gives data which demonstrate that this transferability is obtained in spite of very large changes in the individual contributions to the potential energy of each atom that is incurred when the methyl group is transferred between the members of the homologous series. The same study shows that changes in the charge distribution of a group leads to corresponding changes in its energy, an observation that accounts for the origin of strain energy in cyclic systems. The charge distribution of the methylene group in cyclopropane, for example, differs slightly from that of the standard methylene group as a result of decrease in the extent of charge transfer from C to H. The energy of the group is consequently found to increase by 9.6 kcal/mol, just the value required to account for a strain energy of ~ 29 kcal/mol in cyclopropane. Not only does the theory define the energy of an atom in a molecule, the energies and energy differences so obtained are the ones familiar to chemists.

All properties of the methyl and methylene groups in this homologous series of molecules exhibit the same pattern of transferable values as do their energies and populations. The behavior of the group dipoles (Table I), for example, parallels that of the energy and charge. These values are calculated with the carbon nucleus of the group as origin. The magnitude of the moment for the methyl group is unique for ethane but nearly constant for the remaining molecules. The methylene groups again exhibit two transferable values, one for the methylene attached to a single methyl and another, slightly smaller, for a methylene attached only to other methylenes. The magnitude of the methylene moment in propane is within the average of the values for the methylenes bonded to a single methyl. In all cases the hydrogens form the negative end of the group dipole. The directions of these moments are also transferable. The dipole moment of the methyl group is parallel to the bond path linking the neighboring carbon nucleus to within 0.5° through the series. The direction of the methylene moment, in those cases where it is not dictated by symmetry, lies 0.05° off the axis bisecting the HCH angle in pentane, and 1.1° and 1.2° off this axis in butane and hexane, respectively. These group moments, along with the group charges, can be used in Eq. (2) to determine the total dipole moment of a hydrocarbon molecule in exactly the same way that atomic values are used. The total calculated moments of propane and pentane in the to-

tally staggered conformations are 0.0237 and 0.0230 a.u., respectively. They are directed along the twofold symmetry axis bisecting the central HCH angle with the positive end in the direction of the methylene hydrogens in propane and the reverse in pentane. The total moments are thus dominated by the moments and charges of the methyl groups. The magnitude of the experimental moment for propane, determined by a Stark effect on the microwave spectrum, is 0.0327 a.u.³¹

A number of density functionals for the correlation energy have been investigated in this laboratory.^{32(a)} The one which gives the best overall results for both atoms and molecules is one recently proposed by Langreth *et al.*^{32(b)} It is a complicated functional of the charge density involving gradient corrections. The values of this functional for the methyl and methylene groups are listed in Table I under the heading ϵ as another example of a property which exhibits constant values for the transferable methyl group and the two kinds of transferable methylene groups. Some time ago Lie and Clementi³³ suggested that the Hartree–Fock energy be corrected for the correlation energy error through the use of a density functional for the latter quantity. While a functional expression for the correlation energy which gives chemical accuracy is yet to be forthcoming, it is clear that when such a functional becomes available, the theory of atoms in molecules will make possible the determination of the total energies of the groups responsible for the additivity schemes of chemistry and total energies of large molecules will be predicted using groups and properties defined by theory.

The idea of defining the shape of a molecule for its non-bonded interaction with other molecules in terms of a particular outer contour of the charge density was made some time ago.³⁴ This method of determining the van der Waals' envelope of a molecule has proven useful in the elucidation of crystal structures³⁵ and is now finding use in drug design studies. Closely associated with the notion of shape is a measure of the volume occupied by a molecule.³⁶ The molar volume is one of the earliest examples of a property that can be expressed in terms of additive group contributions, the hydrocarbons again providing the first examples. Table I gives the volumes of the methyl and methylene groups for the homologous series of hydrocarbons, the atomic volume being defined by the region of space enclosed by the intersection of the atomic surface of zero flux and the 0.001 a.u. envelope of the charge density.³⁷ This property exhibits the same characteristics of group transferability as do the other properties discussed for the hydrocarbons. Atomic volumes and van der Waals' envelopes can be determined for hydrocarbons of any chain length from the charge distributions of the standard methyl and methylene groups defined by theory. Experimentally, it is found that the CH_2 group makes an additive contribution of 22.0 cc to the molar volume of a hydrocarbon at its boiling point.³⁸ The molar volume of the transferable methylene group as determined by theory, when corrected to take into account the free volume between molecules,³⁹ yields a value of 21.9 cm^3 .

The measured value of -4.93 kcal/mol for the additive contribution of the methylene group to the heat of formation of a hydrocarbon is as much an observable property of these

TABLE II. Vibrationally induced dipoles and their charge transfer and atomic moment contributions.

	$\Delta\mu/\Delta S$ (D/Å or D/rad)	$\Delta\mu_c$	$\Delta\mu_a$ (a.u.)	$\Delta\mu$
CH ₄ stretch	0.975 ± 0.003	+ 0.0453	- 0.0615	- 0.0163
CH ₄ bend	0.364 ± 0.003	+ 0.0475	- 0.0654	- 0.0179
SiH ₄ stretch	2.115 ± 0.003	- 0.0283	- 0.0073	- 0.0356
SiH ₄ bend	2.263 ± 0.003	- 0.3097	+ 0.2000	- 0.1097

molecules as are their spectra or ionization potentials. *The properties of atoms in molecules can be determined experimentally.* It is a straightforward matter to use quantum mechanics to relate a spectroscopically measured energy to the theoretically defined difference in energy between two states of a system. In a less direct but no less rigorous manner, the same quantum mechanics relates the difference in the heats of formation of butane and pentane to the corresponding theoretically defined energy of the methylene group.

VIBRATIONALLY INDUCED MOLECULAR DIPOLE MOMENTS

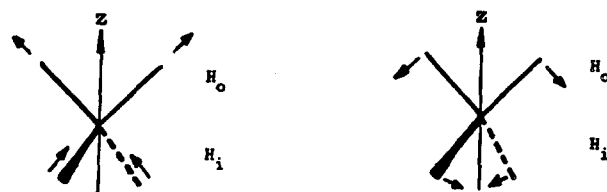
The vibrationally induced molecular dipole moments for the infrared active modes of methane, silane, and ethylene are related to the changes in the atomic charge distributions. A calculation of the infrared intensities for these same modes, together with those in acetylene, ethane, and the ammonium ion, has recently been given by Wiberg and Wendoloski.⁴⁰ Wiberg and co-workers have combined theoretically determined force fields with experimentally measured frequencies and band intensities in the determination, assignment, and discussion of the dipole moment derivatives in the relatively complex molecules pyridine,⁴¹ cyclopropene,⁴² and cyclohexane.⁴³ The present results, as were the previous ones,⁴⁰ are from 6-31G**/6-31G** calculations. The calculated dipole moments (Table II) induced by the antisymmetric stretching and bending modes of CH₄ (as illustrated in Table III) are the average values for five displacements of the protons ranging from 0.01 to 0.04 a.u. and for changes in the HCH angles of 2.5°, 5.0°, and 7.5°. The results for SiH₄ are the averages over two displacements and two angle changes. The quantitative agreement with the experimental values is, as previously discussed,⁴⁰ fair but the results are qualitatively correct: the intensities are greater for silane than for methane and the intensity of the bending mode is greater than that for the stretching mode in the former with the reverse being true in the latter.⁴⁴

Table III lists the charge on the carbon, silicon, and hydrogen atoms in the equilibrium geometries and the changes in these charges for the antisymmetric stretch with a proton displacement of 0.04 a.u. and antisymmetric bend with a 5.0° change in H-A-H angle for both methane and silane. Also listed is the nonvanishing component and its change for the atomic first moment of each of the atoms. The change in μ and the separate changes in the charge transfer and atomic polarization contributions for these same motions are given in Table II. The electronic population on hydrogen increases in both molecules when the A-H bond is

TABLE III. Vibrationally induced changes in atomic charges and moments in CH₄ and SiH₄ 6-31G**/6-31G**.

Atom	Stretched geometry ^a		Equilibrium geometry ^a		Bent geometry ^a	
	$\Delta q(\Omega)$	$\Delta\mu(\Omega)$	$q(\Omega)$	$\mu(\Omega)$	$\Delta q(\Omega)$	$\Delta\mu(\Omega)$
Methane						
H _o	+ 0.95	+ 0.04	- 6.16	- 6.52	+ 0.73	- 0.32
H _i	- 1.21	- 0.03	- 6.16	+ 6.52	- 0.53	- 0.31
C	+ 0.52	- 6.17	+ 24.64	0.00	- 0.40	- 5.28
Silane						
H _o	+ 0.64	+ 0.37	- 74.54	+ 25.36	+ 0.29	- 4.15
H _i	- 0.63	+ 0.41	- 74.54	- 25.36	- 0.19	- 3.96
Si	- 0.02	- 2.29	+ 298.16	0.00	- 0.20	- 3.78

^a Differences are with respect to equilibrium geometry. All quantities in atomic units $\times 10^2$.



shortened or the H-A-H angle is decreased. In methane this has the effect of creating a charge transfer moment in the direction of shortened bonds or in the direction of the hydrogens with the smaller bond angle. It is important to realize that the charge transfer contribution to a change in the dipole moment induced by a motion of the nuclei has two sources either of which may be dominant: the induced moment can be determined by the direction of the interatomic transfer of charge as found in methane, or it may reflect the direction of the displacement of charged atoms within the molecule. The latter is found in silane wherein the transfer of charge between the hydrogens caused by nuclear displacements is quite small relative to the net negative charge carried by each of the hydrogen atoms when a proton is displaced.

In the antisymmetric stretch in methane the change in population for the carbon atom is quite small compared to the changes for the hydrogen atoms. Just the reverse is true for the changes in the atomic first moments, the values for the hydrogens being close to zero while the charge distribution of the carbon atom is strongly polarized to yield a large first moment whose direction is counter to the charge transfer moment. This relaxation of the atomic charge distribution in the vicinity of the carbon nucleus is the largest single change caused by the antisymmetric motion of the nuclei and it dominates the induced dipole moment for this mode. Thus, there are two opposing charge transfers induced by the antisymmetric stretch: charge in the outer region of the distribution is transferred from the outwardly to the inwardly displaced protons while in the interior of the molecule an even larger amount of charge is transferred in the opposite direction within the carbon atom.

The extent of charge transfer between the hydrogens caused by the antisymmetric bending motion in methane is smaller by about a factor of 10 while the polarizations of the hydrogens are larger by about the same factor compared to the corresponding changes found for the stretching motion.

The direction of the charge transfer moment is determined by the changes in the hydrogen atom charges as it was in the stretching mode, but the overall change in dipole is again dominated by a counterpolarization of the charge density of the carbon atom and the direction of the final moment corresponds to a flow of negative charge in the direction of the opened bond angle. It should be emphasized that the shift in the centroid of negative charge of the carbon atom away from its nucleus induced by these vibrations and, as monitored by $\Delta\mu(C)$, is a physical result and not an artifact of the partitioning method. Atomic point charges and the changes in these charges as described by "atomic fluxes" are unable to describe the two opposing outer and inner charge relaxations accompanying the antisymmetric stretch and bend in methane.

There is a significant transfer of charge from silicon to the hydrogens in silane and the charge distributions of the hydrogens are strongly polarized toward the central nucleus. The value of ρ at a bond critical point in a C–H bond is 0.268 a.u. compared to 0.119 a.u. for Si–H and the corresponding values of $\nabla^2\rho$ are -1.055 and 0.297 a.u., respectively. These values show that in a C–H bond, the charge density is contracted towards and accumulated along the bond path to give a shared accumulation of charge between the C and H nuclei. In a Si–H bond, on the other hand, the charge density is contracted towards each of the nuclei and away from the interatomic surface, to give separate concentrations of charge in the Si and H basins. The characteristics of the Si–H bond approach those of the ionic limit and thus represent the other extreme of bonding from that found in methane.¹⁰ A discussion of the differences between the distributions of charge in C–H and Si–H bonds has been given previously.⁴⁵

The vibrationally induced dipole changes in silane are dominated by the spatial displacements of the relatively large and localized distributions of negative charge of the hydrogen atoms rather than by relaxations in the density resulting from either interatomic charge transfer or atomic polarizations. Table III indicates that there is a transfer of charge from the outwardly to the inwardly displaced hydrogens in the antisymmetric stretch, the net charge of silicon remaining essentially constant. The magnitude of the charge transfer is, however, very small compared to the net charge on each of the hydrogens. Because of this, the direction of the charge transfer dipole is opposite to the direction of the interatomic transfer of charge, being instead determined by the displacement of all four negatively charged hydrogens in the positive z direction. The silicon atom does polarize in the direction counter to the transfer of charge, but its contribution to the dipole is considerably reduced by both sets of hydrogens polarizing in the opposite direction, in the direction opposite of the displacement of the protons. The net result is that the induced dipole moment is primarily the result of the displacement of the negatively charged hydrogen atoms.

The magnitudes of the interatomic charge transfers are even smaller for the antisymmetric bending mode than for the stretching mode. Thus $\Delta\mu_c$ is again dominated by the displacements of the large, negatively charged hydrogen

atoms and it points in the direction of the hydrogens which bend inwards. Just as in methane, the atomic polarizations are larger relative to the interatomic charge transfers in the bending than in the stretching modes. In silane all of the atoms polarize so as to counter the dipole resulting from the displacements of the net charges of the hydrogens. The dipole induced by the bending motion is in the direction of the charge flow determined by the displacements of the hydrogens but with only one-third its magnitude as a result of the opposed atomic polarizations.

The polarization of the central atom plays an important role in determining the induced dipoles in silane and the dominant role in methane. In the bending modes of both molecules, this polarization of the central atom in the direction of the opened bond angle, causes the bond path angle²⁰ at the carbon or silicon nucleus (the limiting angle subtended at a nucleus by two bond paths) to lag behind a 5° change in the geometrical or so-called bond angle by 1.5° in methane and 1.2° in silane. The resulting bent bond paths illustrate the nonrigid following of the density in the bending modes and provide an alternative interpretation of the charge relaxations of the carbon and silicon atoms accompanying these nuclear motions.^{16(b),40} A model which assumes bond dipoles rigidly attached to internuclear axes and which does not allow for any polarization of the central atom cannot describe these relaxations of the density.

The analysis is next applied to the B_{1u} and B_{3u} bending modes and the B_{3u} and B_{2u} stretching modes of ethylene. These modes are illustrated in Fig. 1. The calculated dipole moment derivatives given in Table IV are for atomic displacements from the 6-31G**/6-31G** optimized equilibrium geometry required to yield an overall change of 0.1 \AA in the corresponding normal coordinate.⁴⁶ The calculated values are seen to be in good agreement with experiment. The atomic charges on C and H in the equilibrium geometry are $+0.080$ and $-0.040 e$, respectively, and the changes in these charges resulting from the vibrationally induced interatomic charge transfers are indicated in Fig. 1, multiplied by 1000. As discussed more fully below, the electronegativity of carbon relative to hydrogen increases as the s character of the C–H bond is increased and this is reflected in the decreased hydrogen population in ethylene compared to its value in methane. The C–C bond has a large ellipticity showing that the charge density along the C–C bond path is preferentially accumulated in the plane perpendicular to the plane of the nuclei, the " π " plane. The curvature of ρ in this plane at the bond critical point is of smaller magnitude than that in the plane of the nuclei. This shows that the distribution of charge in the π plane is most diffuse and most easily polarized. It is expected and found that the nuclear motions in this molecule lead to the formation of large atomic moments on the carbons as a result of deformations of this density.

Table V lists the total charge transfer moment and the total, as well as the separate contributions from the carbons and hydrogens, to the atomic polarization moment induced by these vibrations. The charge transfer moment is equated to a sum of C–H and C–C bond dipoles defined as $q(H)(X_H - X_C)$ and $Q(C1)(X_{C1} - X_{C2})$, respectively, the lat-

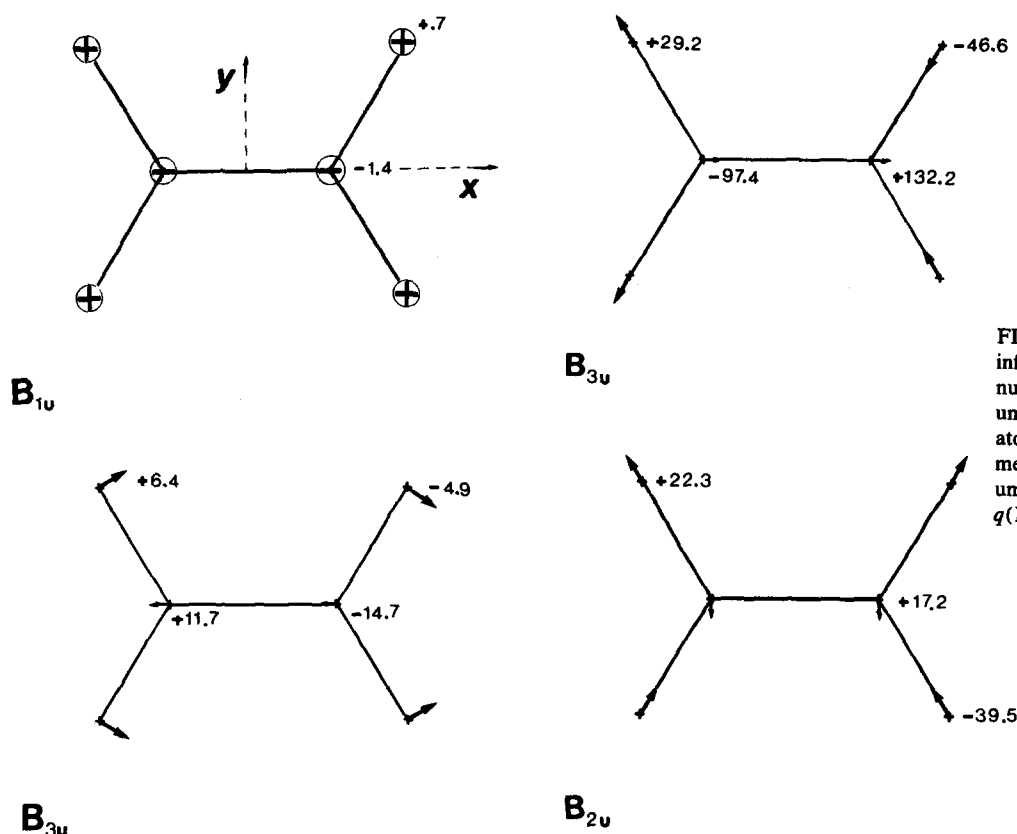


FIG. 1. Schematic representations of four infrared active modes in ethylene. The numbers are the changes in the equilibrium charges of the carbon and hydrogen atoms caused by the atomic displacements, multiplied by 1000. The equilibrium charges are $q(\text{C}) = +0.080 e$ and $q(\text{H}) = -0.040 e$.

ter term being different from zero only when the carbons are no longer equivalent. The charge $q(\text{H})$ is the atomic charge on hydrogen, a terminal atom, and it is assumed to be linked to an equal and opposite charge on the carbon. The charge $Q(\text{C1})$ appearing in the carbon-carbon bond dipole is equal to the atomic charge on carbon, plus the sum of the charges on the hydrogen atoms bonded to it. This method of assigning bond dipoles through the partitioning of the atomic charge of a multiply bonded atoms leads to a unique set of charges only in a system which does not contain any rings or cages which are either unsymmetrical or which contain more than one kind of atom.⁴⁷ However, the use of bond dipoles leads to contributions to the charge transfer moment whose individual values are independent of the choice of origin.

There is but a small charge transfer from the hydrogens to each carbon in the out-of-plane B_{1u} bending mode with the result that the directions of the C-H bond dipoles are determined by the displacement of the negatively charged hydrogen atoms. These bond dipoles are small relative to the atomic moments induced in the carbon atom charge distributions. The partial inversion about carbon that occurs as a result of the out-of-plane displacement of the hydrogens polarizes the charge distribution of this atom in the opposite direction. It is this polarization of the carbon atom charge distributions that determines the direction of the induced dipole, all other contributions shifting negative charge in the opposite direction, as well as being significantly smaller in

magnitude. This "back" polarization of the carbon atom density may also be interpreted as incomplete following by the density of the displaced nuclei, one that leads to the C-H bond paths lagging behind the motion of the corresponding internuclear axis.^{16(b)} This relaxation is similar to that found for the bending mode in methane.

Attempts to account for the direction of the dipole induced by the out-of-plane C-H bending motions in terms of the atomic charge-bond dipole models such as EOM¹⁴ have been the source of much discussion of the direction of charge transfer between carbon and hydrogen.^{15,16,40} In an atomic charge-bond dipole model with rigid following and no allowance for the atomic polarizations, one is forced to make the assignment C^-H^+ to account for the observed direction of the dipole. This is the relative charge assignment obtained in a Mulliken population analysis and Gussoni¹⁵ has pointed out that the charges assigned on the basis of the EOM model are usually in agreement with the Mulliken orbital charges. One may, however, extend the Mulliken atomic population analysis to include the correspondingly defined atomic polarizations and recover the calculated dipole moment, i.e., include the neglected terms in the atomic point charge model. The contributions to the dipole moment changes for the out-of-plane bending mode calculated in this manner are the bracketed numbers in Table V. The hydrogens are now predicted to be polarized to a greater extent than the unsaturated carbons and the carbons are assigned polarizations corresponding to a shift of charge in the direction of the displaced

TABLE IV. Vibrationally induced dipoles in ethylene.

Mode	$\left \frac{\partial \mu}{\partial S} \right ^a$	
	Calc.	Expt. ^b
B_{1u} bend	0.442	0.402
B_{3u} bend	0.097	0.116
B_{3u} stretch	0.286	0.234
B_{2u} stretch	0.356	0.296

^a All values in atomic units. The results for the B_{1u} bend and B_{3u} bends are in a.u./rad.

^b From Ref. 46.

protons, an unphysical result in terms of any orbital or hybridization model and a result at odds with the actual measured polarization of the total charge density in the vicinity of a carbon nucleus. Reed and Weinhold²⁶ point out that while a population analysis based on a set of natural atomic orbitals leads to the charge assignment C^-H^+ , $q_H = +0.24 e$, the expectation value of the dipole moment operator over the natural bond orbital for the C-H bond, yields a bond dipole moment with the sense C^+H^- , the result argued for some time by Wiberg.^{16,40}

While it is not clear what an orbital based atomic population is or what relation it has to the any physical property of the total charge distribution (recall that Mulliken⁴⁸ himself disowned his method of assigning atomic populations because they bore no relation to the actual spatial distribution of charge), the populations, and moments, indeed all properties of an atom in a molecule as defined by the quantum zero flux boundary condition, have a clear physical meaning. There is a well-defined region of real space associated with each nucleus. In the case of the bending mode in ethylene, it is clear from the very small changes in the atomic population and moment for hydrogen that there are no major shifts or changes in the charge density in the regions of the protons in the B_{1u} bending mode, however, one defines the atomic boundaries. What the atomic moments show is that there is a major polarization of the charge density in the vicinity of each carbon nucleus in a direction opposite to the displacement of the protons, an effect that is evident in the

charge distribution for the distorted geometry. There is no way one can map this polarization onto a bond dipole, and as the single largest change in the charge distribution for the most intense mode in ethylene, it cannot be simply ignored and its role replaced by a set of fictitious point charges of incorrect sign tied to and moving rigidly with the nuclei.

In the B_{3u} in-plane bending mode there is a transfer of charge between the methylene groups, the one with the opened bond angle losing charge to the one with the closed angle, similar to the behavior found in methane. The result is a large charge transfer moment, with the C-C bond moment making the largest contribution. The carbons also polarize to a significant extent in the direction of their displacement, the direction counter to the charge transfer, and the atomic moments nearly cancel with the bond dipoles to yield a small induced dipole moment.

The behavior of the hydrogens with respect to charge transfer in the B_{3u} stretching mode is also similar to that observed in methane, with the inwardly and outwardly displaced hydrogens gaining and losing charge, respectively. The associated carbons behave in the opposite manner and the large resultant C-C bond dipole cancels two-thirds of the moment arising from the C-H bond dipoles. The carbons again polarize to a significant degree, this time in a direction counter to their displacement and these atomic polarization dominate the final induced dipole. By far the largest atomic moments are found for the B_{2u} stretching mode wherein the charge distributions of both carbons polarize in the opposite direction to their displacement—the density relaxes so as to oppose the motion of the carbon nuclei. Again as is observed in methane, the inwardly displaced hydrogens gain charge at the expense of the carbons and the outwardly displaced hydrogens. This interatomic transfer of charge results in the formation of large C-H bond dipoles oppositely directed to the atomic moments of the carbons. The direction of the induced moment is, however, again determined by the atomic moments of the carbons. The single dominant factor determining these vibrationally induced dipole moments in ethylene is the atomic moment resulting from the polarization of the relatively loosely bound density on the unsaturated carbon atoms, a physical phenomenon that, in general, is not describable in terms of bond dipoles.

TABLE V. Vibrationally induced changes in atomic and bond moments^a for ethylene 6-31G**/6-31G** for 0.1 Å mode displacements.

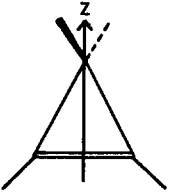
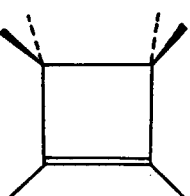
Mode	Axis of moment ^b	μ_a		μ_c				
		$\mu(C_1) + \mu(C_2)$	$\Sigma\mu(H)$	sum of atomic moments	$\mu(C-C)$	$\Sigma\mu(C-H)$	sum of bond moments	μ
B_{1u} out-of-plane bend	<i>z</i>	+ 6.02 (− 4.09) ^c	− 0.48 (+ 4.70)	+ 5.54 (+ 0.61)	0.00 (0.00)	− 1.18 (+ 3.80)	− 1.18 (+ 3.80)	+ 4.42
B_{3u} symmetric bend	<i>x</i>	+ 8.77	+ 1.60	+ 10.37	− 6.13	− 3.24	− 9.37	+ 0.97
B_{3u} symmetric stretch	<i>x</i>	+ 8.84	− 0.10	+ 8.74	+ 9.55	− 15.36	− 5.81	+ 2.86
B_{2u} antisymmetric stretch	<i>y</i>	− 23.20	− 0.08	− 23.28	0.00	+ 19.82	+ 19.82	− 3.56

^a All quantities in atomic units $\times 10^2$.

^b See Fig. 1 for coordinate axes.

^c Values calculated using a Mulliken population analysis including Mulliken atomic polarizations.

TABLE VI. Atomic populations and first moments* 6-311G**/6-31G** (Ref. 56).

Molecule	$q(\text{C})$		$q(\text{H})$
Standard CH_2	+ 0.142		− 0.071
Cyclobutane	+ 0.117		− 0.057
Cyclopropane	+ 0.046		− 0.023
Ethylene	+ 0.022		− 0.011
$q(\Omega)$	$\mu(\Omega)$	$q(\Omega)$	$\mu(\Omega)$
− 0.052	− 0.081	− 0.046	− 0.057
+ 0.193	− 0.262	+ 0.133	− 0.076
			
− 0.117	+ 0.055	− 0.034	+ 0.063
+ 0.072	+ 0.070	− 0.007	+ 0.090
$\mu_c = -0.032$		$\mu_c = +0.104$	
$\mu_a = -0.171$		$\mu_a = -0.072$	
$\mu = -0.206$		$\mu = +0.032$	

* All quantities in atomic units. Only the components of the atomic moments along the C_2 symmetry axes (z axis) are listed.

DIPOLE MOMENTS OF STRAINED CYCLIC HYDROCARBONS

Cyclopropene and cyclobutene present an interesting contrast in moments as the negative end of the dipole of the three-membered ring compound is directed away from the double bond and is large in magnitude while the four-membered ring system the anticipated behavior is observed, with the double bond forming the negative end of the dipole which, in addition, is small in magnitude.^{49–51} These results find explanation in terms of the increased electronegativity of a carbon atom which is subjected to geometric strain.

The hybridization model predicts that the smaller bond angles found in hydrocarbons with angular strain should result in an increase in the p character of the strained C–C bonds and hence in an increase in the s character of the associated C–H bonds.^{52,53} Orbital theories, in turn, predict the electronegativity of a carbon to increase relative to that of its bonded hydrogen with an increase in the s character of its bonding hybrid orbital.⁵⁴ In this way, one can account for the increase in electronegativity of carbon relative to hydrogen which accompanies the introduction of strain into a cyclic system, an increase which is reflected in the atomic populations of hydrocarbon molecules. This effect has recently been well documented in a study of the atomic properties in hydrocarbons,²⁰ a study that included acyclic molecules, normal and branched, three- to six-membered cyclic molecules, bicyclic molecules from bicyclobutane to bicyclooctane, the small ring propellanes together with cubane and tetrahedrane.

Further examples of the increase of electronegativity with strain is provided by the atomic populations given in Table VI as determined from 6-311G**/6-31G**⁵⁵ calculations. In addition to the results for the two unsaturated ring systems are populations for cyclopropane, cyclobutane, and

ethylene.⁵⁶ (These results may be compared with the more extensive study referred to above which was done using 6-31G*/6-31G* calculations by subtracting 0.028 electronic charges from the hydrogen populations and adjusting the carbon populations accordingly.)⁵⁷

The atomic charges on carbon and hydrogen in the standard transferable methylene group of a normal hydrocarbon are + 0.142 and − 0.071 e , respectively. The atomic populations for cyclobutane and cyclopropane illustrate the transfer of charge from H to C which occurs within the methylene group as a system is subjected to an increasing degree of angular strain. The charges for cyclopropane are closer to those for the CH_2 group in ethylene than they are to the values for the standard methylene group, a result in accord with the orbital models and with the similarity in other of its properties such as bond length and bond angle, C–H¹³C coupling constant and the C–H force constant, bond dissociation energy, and pK_a value with those for ethylene.²⁰ The most electronegative carbon atoms in this series of molecules are the ethylenic carbons in the most strained molecule, cyclopropene followed by the corresponding atoms in cyclobutene. These atoms are negatively charged as a consequence of their hybridization and the presence of ring strain. They withdraw charge from their bonded hydrogen atoms and, in particular, from the methylenic carbon atoms. In addition to the methylenic carbons bearing larger positive charges than in the saturated systems, the methylenic hydrogen atoms in cyclopropene bear a relatively large negative charge. These charges can be rationalized by invoking an ion pair resonance structure for cyclopropene consisting of the stable cyclopropenium cation and a hydride ion. Because of the large net charges on both the hydrogens and carbon atoms of the methylene groups in the unsaturated compounds, these groups possess moments that are considerably

larger than those found in their saturated parent compounds. The magnitudes of the CH_2 group moments with the carbon as origin are 0.542 and 0.359 a.u., respectively, for cyclopropene and cyclopropane and 0.589 and 0.258 a.u. for cyclobutene and cyclobutane.

The charge transfer moment in cyclopropene is relatively small as this moment of the methylene group, with the hydrogens as its negative end, cancels out the corresponding moments of the ethylenic CH groups wherein the hydrogens form the positive end. The atomic dipole term is, however, large in cyclopropene. The atomic moments of the central methylene group are all outwardly directed and lie on the symmetry axis, while the principle moment of an ethylenic carbon, of magnitude 0.184 a.u., makes no contribution as it is directed along the corresponding C–C axis. The net result is a substantial dipole moment with its negative end directed away from the double bond. The calculated value of 0.525 D is in fair agreement with the experimental value of 0.454 D.⁵⁹

The calculated value of the dipole moment for cyclobutene is in the proper direction and, like the experimental value, is of small magnitude, the two values being 0.081 and 0.132 D,⁶⁰ respectively. Because of the reduced strain and consequent reduction in charge transfer found in cyclobutene, the charge transfer and atomic moments are more nearly equal and of opposite sign. None of the principal atomic moments is directed along the symmetry axis and the direction of the dipole is determined by the charge transfer term. In this molecule the carbon and hydrogens of the ethylenic bond are both of negative sign and their contributions to the charge transfer term add. Thus, in cyclobutene, the double bond forms the negative end of the dipole.

CONCLUSIONS

This paper has provided further examples of group properties that are transferable between different molecules including, in particular, the dipole moment. They further illustrate the important observation that transferability of properties is the result of the transferability of the distribution of charge over regions of space bounded by surfaces of zero flux in the gradient vector of the charge density. Since the energy is included among these properties, it follows that the transferability of the charge density over such a region of space demands a corresponding transferability of the one-density matrix. The methyl and methylene groups as defined by theory provide experimental confirmation of the theorem of Hohenberg and Kohn⁶¹ which states that the energy is a functional of the charge density—a theorem that would appear to apply to regions of space bounded by surfaces of zero flux in the gradient of the charge density.

The molecular dipole moment is expressible in terms of a sum over the net charge and first moment of every atom. It has been determined that both the charge transfer moment, as determined by the interatomic charge transfer, and the atomic polarization moments are equally important in determining the dipole moment. Attempts to understand the origin of static or vibrationally induced moments using a model that ignores the contributions of the atomic polarizations leads to results that are not compatible with the observed properties of theoretically determined charge distributions.

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