J. Phys. Chem. A **2000,** *104,* 5579−5589

Properties of Atoms in Molecules: Group Additivity

Richard F. W. Bader* and David Bayles

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

Received: December 10, 1999; In Final Form: March 27, 2000

Every property of a molecule is given by the sum of the contributions from each of its constituent atoms or groups, the groups being defined as proper open systems. The observation of "experimental group additivty" requires that in addition to the properties of the groups being additive, the group and its properties be transferable from one molecule to another, different molecule. It is shown that such transferability of a group and its properties is in general, only apparent, being the result of compensatory transferability wherein the changes in the properties of one group are compensated for by equal but opposite changes in the properties of the adjoining group. These compensating changes are in some cases vanishingly small, but even when the energy changes are in excess of 20 kcal/mol, the experimental heat of formation is still predicted to be additive to within 0.1 kcal/mol. The operation of compensatory transferability is illustrated for the linear homologous series of hydrocarbons and polysilanes and for the formation of pyridine from fragments of benzene and pyrazine. The properties considered are the energy and the delocalization of the electrons, the former determined by the one-electron density matrix and the latter by the pair density. It is shown that the transferability of the degree of localization of the electrons to a given group, a property of the pair density, is a result of the conservation of the delocalization of its electrons over the remaining groups in the molecule. The results presented here emphasize the important observation that all the properties of a proper open system—a functional group—whether determined by the first-order density matrix, the pair density, or field-induced charge and current densities, are all functionally related to its form in real space, that is, to its distribution of charge.

Historical Development of Additivity

The realization that the molecular value of some property could be obtained as a sum of group contributions arose not long after the introduction of structural formulas into chemistry, the concept of structure being essential to the definition of a group. In 1855 Kopp[1] showed that the volumes of the normal alkanes at their boiling points were additive, and in the 1880s additive group contributions were obtained for molar refraction[2] and molar polarization.[3] In 1888 Henrichsen [4] demonstrated an apparent, nearly constant contribution from the methylene group to the magnetic susceptibility, work that culminated in the establishment of a general group additivity scheme for the magnetic susceptibility by Pascal and his school by 1910.[5] In the 1930s, the work of Rossini and co-workers[6] added heats of formation of hydrocarbons to the list of molecular properties that followed a group additivity scheme. The more recent compilations of experimental data by Benson and co-workers[7,8] demonstrates the widespread applicability of group additivity rules for the estimation of thermochemical properties. Group additivity, is of course, not always obtained, but its observance as a limiting situation played a fundamental role in the development of the concept central to chemistry—the concept of a functional group—that a given bonded group of atoms exhibits a set of characteristic and measurable properties. Its use enables one to predict the properties of a molecule in terms of the characteristic properties imparted by the groups it contains and to identify the presence of a given group through the same characteristic properties.

Obtaining a physical basis for the concept of a functional group and the associated observation of group additivity had to await the development of the quantum mechanics of a proper open system.[9,10] A proper open system is one that is bounded by a surface $S(\mathbf{r})$ exhibiting a local zero flux in the gradient vector field of the electron density $\rho(\mathbf{r})$, eq 1.

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0 \qquad \forall \mathbf{r} \in S(\mathbf{r}) \tag{1}$$

Such "zero-flux" surfaces partition a molecule into mononuclear spatial regions, that is, into a set of linked atomic-like systems. Equation 1 serves as the boundary condition that enables one to extend quantum mechanics to an open system and thus define all properties and associated theorems for these atomic-like systems. The atoms of chemistry are identified with proper open systems because (1) their properties are characteristic and additive, summing to yield the corresponding values for the molecule, and (2) they are as transferable from one system to another as are the forms of the atoms in real space, that is, as transferable as are their charge distributions. The atomic and group properties defined in this manner have been shown to predict the experimentally determined contributions to the volume, energy, electric polarizability, and magnetic susceptibility in those cases where, as described above, the group contributions are essentially transferable, as well as additive.[11] It is important to realize that while quantum mechanics predicts the properties of the open systems to be additive and to sum to the molecular value in all instances, one obtains "experimental additivity" as described above only when the group is also transferable without apparent change from one system to another. Thus while group properties are always additive, they are not always transferable.

Group Additivity and the Physics of an Open System

The present paper presents a comparative study of the group additivity of energy and electron delocalization exhibited by the linear hydrocarbons with that obtained for the linear silanes.

10.1021/jp9943631 CCC: \$19.00

While the additivity of energy and other properties of the hydrocarbons has been considered previously,[12] the present results are obtained from calculations that exactly satisfy the virial theorem through a self-consistent scaling of the electronic coordinates (SCVS) Since this theorem plays a pivotal role in the definition of the energy of an open system,[9,10] it is important to demonstrate that the previously described results which employed a small empirical correction remain valid. The extent to which electrons are localized or delocalized throughout a system is determined by the operation of the Pauli exclusion principle as contained in the pair density,[13,14] a question of some interest in the understanding of the electronic excitation of the polysilanes.[15] The pair density is the expectation value of a quantum mechanical operator, and its average values are uniquely defined. Questions of electron localization and delocalization are answered with certainty by the physics of an open system, a point demonstrated anew here.

The Essential Physics. The mathematical development of the physics of a proper open system is to be found in a number of sources.[9,10,16] The present discussion presents a synopsis of the essential theorems that determine the physics and hence the properties of an atom in a molecule and form the basis for the concept of a functional group. The primary theorem of an open system is the Ehrenfest force theorem, the theorem that defines the force acting on each element of the electron density and hence on an atom in a molecule. The local expression of this force, the Ehrenfest force density $\mathbf{F}(\mathbf{r})$, has a simple expression in terms of the divergence of the quantum stress tensor $\sigma(\mathbf{r})$, eq 2.

$$\mathbf{F}(\mathbf{r}) = -\nabla\cdot\sigma(\mathbf{r}) \tag{2}$$

As in classical physics, the stress tensor enables one to determine the force imposed on a body arising from the application of a stress at any point. The Ehrenfest force density is a most remarkable quantity: it reduces all of the complex interactions between the electron at $\mathbf{r}$ and the remaining electrons and nuclei in the system, as determined by the many-particle wave function, to a density in real space. This an example of a "dressed property density" —a density dressed by the average interaction, appropriate to the property at hand, of the electron at $\mathbf{r}$ with the remainder of the system.[16] All properties are so described, enabling one to obtain the corresponding atomic contributions by a simple integration of the appropriate density over a region of real space bounded by the appropriate zero-flux surface.

The definition of the force density makes possible the definition of a potential energy density, an essential step in the spatial partitioning of the energy.[9] It was the inability to obtain a partitioning of the potential energies of interaction from physics that caused the failure of previous attempts at partitioning the energy. How does one determine how much of the nuclear−electron attraction, or the electron−electron repulsion, or the nuclear−nuclear repulsion energy belongs to a given atom in a molecule? Physics answers this question through the atomic statements of the Ehrenfest force and virial theorems and their associated dressed density distributions.

Taking the virial of the Ehrenfest force yields a potential energy density, a dressed density that determines the average energy of interaction of the electron at position $\mathbf{r}$ with the remainder of the system. This is accomplished by taking the scalar product of $\mathbf{F}(\mathbf{r})$ with the position vector $\mathbf{r}$, a step formally analogous to letting a force act through a distance to obtain a corresponding energy. This step yields the virial of the Ehrenfest force $\mathbf{r}\cdot\mathbf{F}(\mathbf{r})$, which may be identified with $V(\mathbf{r})$, an electronic potential energy density. Its integral over all space yields the electronic potential energy displayed in eq 3.

$$\int \mathrm{d}\mathbf{r}\ \mathbf{V}(\mathbf{r}) = \langle\hat{V}_{\mathrm{en}}\rangle + \langle\hat{V}_{\mathrm{ee}}\rangle + \langle\hat{V}_{\mathrm{nn}}\rangle - \sum_{\alpha}\mathbf{X}_{\alpha}\cdot\mathbf{F}_{\alpha} = \langle\hat{V}\rangle - \sum_{\alpha}\mathbf{X}_{\alpha}\cdot\mathbf{F}_{\alpha} \tag{3}$$

The symbol $\langle\ \rangle$ denotes the average value of the contained operator−the electron−nuclear, electron−electron, and nuclear−nuclear potential energy operators, respectively—and $\langle\hat{V}\rangle$ is the average of the potential energy operator, the quantity appearing in the expression for the total energy $E = \langle\hat{T}\rangle + \langle\hat{V}\rangle$. The final term in eq 3 is the virial of the Hellmann−Feynman forces on the nuclei. If the molecule is in an equilibrium geometry, this term vanishes and then the integral of the virial of the Ehrenfest force yields the total potential energy $\langle\hat{V}\rangle$. The density $V(\mathbf{r})$ differs from the virial density $\boldsymbol{V}(\mathbf{r})$, whose integral over an atom yields the atomic virial $V(\Omega)$, by a divergence term, $\mathbf{r}\cdot(\nabla\cdot\sigma)$. The integration of the divergence term yields the surface virial of the Ehrenfest force when integrated over an atom, a term which vanishes for the total system with a surface at infinity.

It may come as a surprise that the virial of the forces exerted on the electrons should include the nuclear−nuclear repulsion energy $\langle\hat{V}_{\mathrm{nn}}\rangle$ along with the virial of the forces on the nuclei, although how this occurs is easily explained. The major component of the Ehrenfest force is the one exerted on the electrons by the nuclei. Upon taking the virial of the operator describing this force and applying Euler's theorem, one obtains in addition to the corresponding potential energy contribution $\langle\hat{V}_{\mathrm{en}}\rangle$, the virial of the Hellmann−Feynman forces exerted by the nuclei on the electrons, the final term in eq 4.

$$\langle(\sum_{i} - \mathbf{r}_i\cdot\nabla_i\hat{V}_{\mathrm{en}})\rangle = \langle\hat{V}_{\mathrm{en}}\rangle + \sum_{\alpha}\mathbf{X}_{\alpha}\cdot\mathbf{F}_{\mathrm{e}\alpha} \tag{4}$$

The nuclear virial in turn may be expressed in terms of $\langle\hat{V}_{\mathrm{nn}}\rangle$ and the virial of the Hellmann−Feynman forces on the nuclei as in

$$\sum_{\alpha}\mathbf{X}_{\alpha}\cdot\mathbf{F}_{\mathrm{e}\alpha} = \langle\hat{V}_{\mathrm{nn}}\rangle - \sum_{\alpha}\mathbf{X}_{\alpha}\cdot\mathbf{F}_{\alpha} \tag{5}$$

Adding $\langle\hat{V}_{\mathrm{ee}}\rangle$, the virial of the electron−electron Ehrenfest force, to the virial of the electron−nuclear forces in eq 4 then yields the virial of the Ehrenfest force as given in eq 3. The atomic virial theorem, as does the theorem for the total system, equates twice the electronic kinetic energy of an atom to the negative of its virial, $2T(\Omega) = -\boldsymbol{V}(\Omega)$, where the atomic virial consists of the virial of the Ehrenfest forces over the atomic basin and surface. The molecules under study here are in equilibrium geometries. Under these conditions $E(\Omega)$, the energy of atom Ω, equals $-T(\Omega)$ and the total energy E is given by the sum of the atomic energies, as given by

$$E = \sum_{\Omega} E(\Omega), \qquad \text{where } E(\Omega) = -T(\Omega) \tag{6}$$

The discussion has illustrated how the physics of an open system yields dressed densities for the Ehrenfest force and potential energy that, by integration, yield the corresponding atomic contributions, just as integration of the electron density yields the average number of electrons. All properties are so defined and determined including second-order field-induced properties such as the electric polarizability and magnetic susceptibility. The polarization density[12] and the magnetization density[17] are expressed, respectively, in terms of the field-induced first-order density and current density. A forthcoming paper determines the group contributions to the transition probability for the electronic excitation of the silanes, a property determined by integration of the transition density induced by the electromagnetic field, weighted by the dipole operator. All observable properties of a system can be equated to a sum of group contributions using the physics of a proper open system.

Group Additivity of Energy in Hydrocarbons and Silanes

The work of Benson and co-workers[7,8] demonstrated that the group additivity rules for thermodynamic properties extended to systems more complex than homologous series of molecules. For example, the rules predict that the properties of AGGB should be given by the arithmetic mean of the properties of AGGA and BGGB.[8] This type of additivity is demonstrated for the cases G = CH_2, A = H, and B = F, Cl, and I which satisfy the rule of the arithmetic mean to within 1 kcal/mol, using the heats of formation obtained from Benson's experimental tabulation.[7] The SCF and MP2 energies of ACH_2CH_2B,[18] for the systems obtained with G = CH_2 and A, B = CH_3, H, NH_2, OH, and F also satisfy the rule of the arithmetic mean generally, to within 1 kcal/mol. The magnetic susceptibilties of the same molecules also obey the rule of the arithmetic mean to better than 1%. Such a rule applies equally well to the total energies of systems in which the electrons are delocalized, the observed heat of formation of pyridine equaling the mean of the values for benzene and pyrazine to within 0.1 kcal/mol.[7] This example corresponds to the linking of the groups |CHCHCH| and |CHNCH|, the vertical bars denoting the interatomic surfaces defining the two groups, as illustrated in Figure 1. The calculated SCF energies of these molecules satisfy the rule of the mean to 1.6 kcal/mol. While the gross features of the density distributions of the two groups appear very similar, there are small changes in both the geometries and in the group boundaries as a result of a transfer of electronic charge. Similarly, there is a transfer of charge from one fragment to the other in the formation of $ACH_2|CH_2B$ resulting in a shift in the C|C interatomic surface away from the more electronegative of the groups A and B. How is group additivity of the energy and other properties possible in the face of the unavoidable perturbations induced in the groups by their transfer from the parent molecules?

Compensatory Transferability. The addivity of group properties is thus only apparent being the result of *compensatory transferability,* wherein the intergroup transfer of electron density that accompanies the formation of the product molecule results not only in the conservation of charge but also in the conservation of other properties.[12,18,19] Thus energy is conserved if the energy lost by one group equals the energy gained by another. The simplest mechanism that accounts for this behavior is found to be operative in the hydrocarbons. It has been shown that associated with every property is a property density. The perturbation caused by the transfer of density between the groups causes a shift in the interatomic surface that will result in a corresponding transfer of other property densities. If the major changes to the density occur in the region of the newly formed interatomic surface and the surface is between chemically similar groups, across a C|C surface in a hydrocarbon for example, then the constancy in the transferred property densities is understandable. The operation of this type of compensatory transferability requires that the geometrical parameters be insensitive to the displacements of the interatomic surfaces.

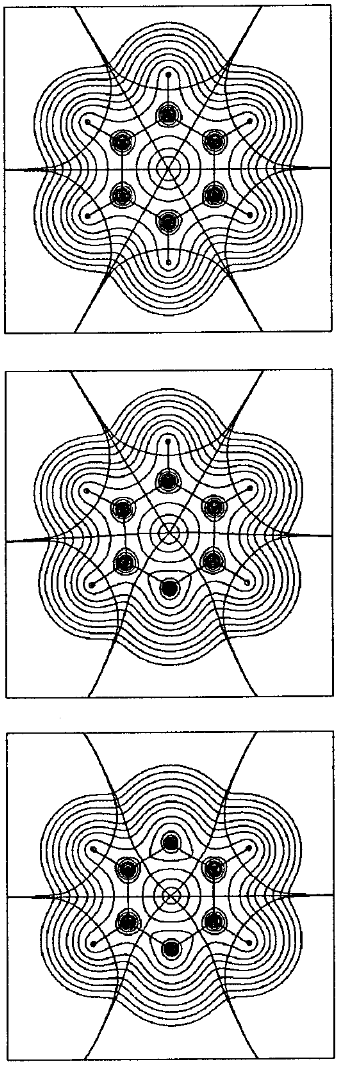

Figure 1. Contour maps of the electron density in the plane of the nuclei for pyridine, the central plot, to be viewed as the addition of the |CHCHCH| group of benzene (upper plot) and the |CHNCH| group of pyrazine. The plots are overlaid with the intersections of the interatomic surfaces and the bond paths. The ring critical point in pyridine is displaced by 0.08 au toward the carbon para to N from the midpoint of the N−C line with a consequent motion of the two C|C boundary surfaces toward the benzene fragment, reflecting a transfer of density to the pyrazine fragment. The contours in these and succeeding plots increase toward beginning with 0.001 au followed by the series 2 × 10^n, 4 × 10^n, 8 × 10^n with n beginning at −3 and increasing in steps of unity.

TABLE 1: Energies and Integration Errors of Hydrocarbons

molecule	E	$(V/T) + 2$	$\Sigma E(\Omega) - E$	$\Sigma N(\Omega) - N$
C_2H_6	−79.257 376	8.000000E−08	0.000 07	0.0004
C_3H_8	−118.303 845	−3.000000E−08	0.000 37	0.0013
C_4H_{10}	−157.350 217	−2.000000E−08	0.000 50	0.0017
C_5H_{12}	−196.396 509	−1.000000E−08	0.000 89	0.0031
C_6H_{14}	−235.442 807	1.000000E−08	0.001 01	0.0035
C_7H_{16}	−274.489 106	1.000000E−08	0.001 39	0.0049

Group Additivity of the Energy. The energies, Tables 1 and 2, and equilibrium geometries, Tables 3 and 4, of the linear hydrocarbons C_nH_{2n+2} and of the silanes Si_nH_{2n+2} were calculated using the 6-311++G(2d,2p) basis set at the single determinant level[20] coupled with a self-consistent virial scaling (SCVS) of the electronic coordinates so that the virial theorem is satisfied, the magnitude of $T/V + 2$ equaling 1×10^{-7} or less for all calculations (Tables 1 and 2). To observe transferability of group properties without change requires transferability of geometrical parameters. The lengths of structurally equivalent C−C and Si−Si bonds differ in general by less than 0.0001 au,

TABLE 2: Energies and Integration Errors of Oligosilanes

molecule	*E*	(*V*/*T*) + 2	Σ*E*(Ω) − *E*	Σ*N*(Ω) − *N*
Si_2H_6	−581.363 570	<1.000000E−08	0.00021	0.0006
Si_3H_8	−871.471 110	1.000000E−08	0.00024	0.0010
Si_4H_{10}	−1161.578 870	<1.000000E−08	0.00076	0.0039
Si_5H_{12}	−1451.686 620	1.400000E−07	0.00097	0.0041
Si_6H_{14}	−1741.794 400	−1.000000E−08	0.00049	−0.0002
Si_7H_{16}	−2031.902 170	<1.000000E−08	0.00116	0.0048

the same being true for the bonds to hydrogen. The length of a C−H bond is greater for a methylene than for a methyl group and is greater by ~0.001 au for a methylene bonded only to other methylenes, as opposed to one bonded to a methyl. The variations in the Si−H lengths are smaller. The bond angles also exhibit only small variations, in general less than 0.05°.

The total energies of both sets of molecules were fitted using linear regression analysis to obtain an equation for the total energy in each series of molecules as a function of the number of methylene or silylene groups, the parameter *p*. The expressions for the energies in au are

$$E(C_nH_{2n+2}) = -79.25747 - 39.04634p$$
$$E(Si_nH_{2n+2}) = -581.36346 - 290.10773p \qquad (7)$$

$R^2 = 1.000\,00$ for both series. The fact that the energies fit such linear relationships implies the operation of compensatory transferability. Reference to Tables 1 and 2 shows that the intercept for each equation corresponds to the energy of the first member of each series, $p = 0$, to within 0.0001 au, that is to twice the energy of the methyl or silyl groups, the slope equaling the apparent additive energy of the repeating methylene or silylene group. With A = C or Si, the empirical relations in eq 7 may be reexpressed as

$$E(A_nH_{2n+2}) = 2E(AH_3) + pE(AH_2) \qquad (8)$$

The groups in both series will be denoted collectively by the symbols $|AH_3$ and $|AH_2|$. Even if the perturbations incurred by the addition of each such succeeding group is damped by a single $|AH_2|$ group as required for simple compensatory transferability, there are necessarily two kinds of $|AH_3$ groups; those in the parent compounds with $p = 0$ and those bonded to an $|AH_2|$ group in succeeding members of the series. There are three kinds of $|AH_2|$ groups; the one bonded to two $|AH_3$ groups when $p = 1$; those bonded to a single $|AH_3$ group, as found in molecules with $p > 1$, and those bonded to only other $|AH_2|$ groups, as found in molecules with $p \geq 3$. This proposed division of the groups mimics the division that is determined by the transferability of their geometrical parameters (Tables 3 and 4). The fitting of the energies to expressions that formally relate them to single values for $E(AH_3)$ and $E(AH_2)$, as in eq 8, therefore requires that any intergroup transfer of electron density resulting from this differentiation between otherwise identical groups results in a corresponding transfer of energy density.

Compensatory Transferability in Hydrocarbons and Silanes. The operation of compensatory transferability is best demonstrated by giving the difference between the energy of each successive group relative to its standard energy $E(AH_3)$ or $E(AH_2)$ and showing that the differences sum to zero. These data, along with the charges $q(AH_3)$ and $q(AH_2)$, are given in Table 5 for the hydrocarbons and in Table 6 for the silanes. Tables 1 and 2 also list the differences—the integration errors—between the sums of the integrated populations and energies for all the atoms in each molecule and the corresponding molecular values. The errors generally increase with the size of the molecule, exhibiting a maximum value of 0.005*e* in the population and 0.9 kcal/mol in the energy for $n = 7$ where the molecular values are equated to the sum of 23 atomic contributions.

TABLE 3: Bond Lengths and Angles of Hydrocarbons

C_2H_6 D_{3d}							
r(C−C)	1.5244	∠(H−C−C)	111.21	*r*(C−H)	1.0835	∠(H−C−H)	107.68
C_3H_8 C_{2v}							
r(C1−C2)	1.5250	*r*(C2−H)	1.0851	∠(H−C1−C2)	111.08	∠(H−C2−C1)	109.35
r(C1−H′)	1.0835	∠(C1−C2−C3)	112.96	∠(H′-C1−H)	107.77	∠(H−C2−H)	106.26
r(C1−H)	1.0845	∠(H′-C1−C2)	111.34	∠(H−C1−H)	107.62		
C_4H_{10} C_{2h}							
r(C1−C2)	1.5249	*r*(C2−H)	1.0861	∠(H′-C1−H)	107.74	∠(H−C2−H)	106.20
r(C2−C3)	1.5258	∠(C1−C2−C3)	113.23	∠(H−C1−H)	107.64		
r(C1−H′)	1.0834	∠(H′-C1−C2)	111.29	∠(H−C2−C1)	109.37		
r(C1−H)	1.0844	∠(H−C1−C2)	111.13	∠(H−C2−C3)	109.21		
C_5H_{12} C_{2v}							
r(C1−C2)	1.5250	*r*(C3−H)	1.0870	∠(H′-C1−H)	107.74	∠(H−C3−C2)	109.23
r(C2−C3)	1.5258	∠(C1−C2−C3)	113.21	∠(H−C1−H)	107.63	∠(H−C3−H)	106.14
r(C1−H′)	1.0834	∠(C2−C3−C4)	113.53	∠(H−C2−C1)	109.33		
r(C1−H)	1.0844	∠(H′-C1−C2)	111.28	∠(H−C2−C3)	109.26		
r(C2−H)	1.0860	∠(H−C1−C2)	111.14	∠(H−C2−H)	106.21		
C_6H_{12} C_{2h}							
r(C1−C2)	1.5250	*r*(C2−H)	1.0859	∠(H−C1−C2)	111.14	∠(H−C2−H)	106.21
r(C2−C3)	1.5260	*r*(C3−H)	1.0869	∠(H′-C1−H)	107.74	∠(H−C3−C2)	109.17
r(C3−C4)	1.5257	∠(C1−C2−C3)	113.20	∠(H−C1−H)	107.63	∠(H−C3−C4)	109.28
r(C1−H′)	1.0835	∠(C2−C3−C4)	113.51	∠(H−C2−C1)	109.33	∠(H−C3−H)	106.16
r(C1−H)	1.0844	∠(H′-C1−C2)	111.28	∠(H−C2−C3)	109.27		
C_7H_{16} C_{2v}							
r(C1−C2)	1.5250	*r*(C3−H)	1.0869	∠(H−C1−C2)	111.14	∠(H−C3−C2)	109.18
r(C2−C3)	1.5259	*r*(C4−H)	1.0868	∠(H′-C1−H)	107.73	∠(H−C3−C4)	109.29
r(C3−C4)	1.5259	∠(C1−C2−C3)	113.20	∠(H−C1−H)	107.63	∠(H−C3−H)	106.15
r(C1−H′)	1.0835	∠(C2−C3−C4)	113.50	∠(H−C2−C1)	109.33	∠(H−C4−C3)	109.23
r(C1−H)	1.0844	∠(C3−C4−C5)	113.48	∠(H−C2−C3)	109.27	∠(H−C4−H)	106.17
r(C2−H)	1.0860	∠(H′-C1−C2)	111.28	∠(H−C2−H)	106.21		

TABLE 4: Bond Lengths and Angles of Oligosilanes

Si_2H_6 D_{3d}							
r(Si−Si)	2.3731	r(Si−H)	1.4768	∠(H−Si−Si)	110.27	∠(H−Si−H)	108.66
Si_3H_8 C_{2v}							
r(Si1−Si2)	2.3745	r(Si2−H)	1.4798	∠(H−Si1−Si2)	110.12	∠(H−Si2−Si1)	109.18
r(Si1−H′)	1.4764	∠(Si1−Si2−Si3)	112.07	∠(H′-Si1−H)	108.69	∠(H−Si2−H)	107.96
r(Si1−H)	1.4769	∠(H′-Si1−Si2)	110.60	∠(H−Si1−H)	108.56		
Si_4H_{10} C_{2h}							
r(Si1−Si2)	2.3744	r(Si2−H)	1.4800	∠(H′-Si1−H)	108.71	∠(H−Si2−H)	107.81
r(Si2−Si3)	2.3762	∠(Si1−Si2−Si3)	112.19	∠(H−Si1−H)	108.64		
r(Si1−H′)	1.4766	∠(H′-Si1−Si2)	110.66	∠(H−Si2−Si1)	109.29		
r(Si1−H)	1.4767	∠(H−Si1−Si2)	110.04	∠(H−Si2−Si3)	109.08		
Si_5H_{12} C_{2v}							
r(Si1−Si2)	2.3746	r(Si3−H)	1.4802	∠(H′-Si1−H)	108.70	∠(H−Si3−Si2)	109.16
r(Si2−Si3)	2.3761	∠(Si1−Si2−Si3)	112.21	∠(H−Si1−H)	108.63	∠(H−Si3−H)	107.67
r(Si1−H′)	1.4766	∠(Si2−Si3−Si4)	112.41	∠(H−Si2−Si1)	109.31		
r(Si1−H)	1.4767	∠(H′-Si1−Si2)	110.67	∠(H−Si2−Si3)	109.02		
r(Si2−H)	1.4798	∠(H−Si1−Si2)	110.04	∠(H−Si2−H)	107.88		
Si_6H_{12} C_{2h}							
r(Si1−Si2)	2.3747	r(Si2−H)	1.4798	∠(H−Si1−Si2)	110.04	∠(H−Si2−H)	107.88
r(Si2−Si3)	2.3763	r(Si3−H)	1.4800	∠(H′-Si1−H)	108.70	∠(H−Si3−Si2)	109.19
r(Si3−Si4)	2.3759	∠(Si1−Si2−Si3)	112.22	∠(H−Si1−H)	108.63	∠(H−Si3−Si4)	109.10
r(Si1−H′)	1.4767	∠(Si2−Si3−Si4)	112.42	∠(H−Si2−Si1)	109.30	∠(H−Si3−H)	107.74
r(Si1−H)	1.4768	∠(H′-Si1−Si2)	110.68	∠(H−Si2−Si3)	109.02		
Si_7H_{16} C_{2v}							
r(Si1−Si2)	2.3747	r(Si3−H)	1.4800	∠(H−Si1−Si2)	110.04	∠(H−Si3−Si2)	109.18
r(Si2−Si3)	2.3763	r(Si4−H)	1.4798	∠(H′-Si1−H)	108.70	∠(H−Si3−Si4)	109.09
r(Si3−Si4)	2.3761	∠(Si1−Si2−Si3)	112.22	∠(H−Si1−H)	108.63	∠(H−Si3−H)	107.76
r(Si1−H′)	1.4767	∠(Si2−Si3−Si4)	112.41	∠(H−Si2−Si1)	109.30	∠(H−Si4−Si3)	109.02
r(Si1−H)	1.4768	∠(Si3−Si4−Si5)	112.38	∠(H−Si2−Si3)	109.02	∠(H−Si4−H)	107.78
r(Si2−H)	1.4798	∠(H′-Si1−Si2)	110.68	∠(H−Si2−H)	107.88		

TABLE 5: Net Charges and Energies of Methyl and Methylene Groups Relative to Standard Values[a]

molecule	$q(CH_3)$	$q(CH_2)$	$q(CH_2)^b$	$\Delta E(CH_3)$	$\Delta E(CH_2)$	$\Delta E(CH_2)^b$
ethane	−0.000			0.0		
propane	−0.016	0.033		−9.5	18.8	
butane	−0.016	0.017		−8.9	8.7	
pentane	−0.016	0.017	0.002	−8.7	9.1	−1.5
hexane	−0.016	0.017	0.001	−8.6	9.4	−1.1
heptane	−0.016	0.017	0.002	−8.6	9.4	−0.9
			0.001[c]			−0.8[c]

[a] $E(CH_3) = -39.628\,73$ au, $E(CH_2) = -39.046\,34$ au using linear regression fit of the molecular energies of the series. [b] This CH_2 is bonded only to other methylenes. [c] Fourth carbon in heptane.

The data for the hydrocarbons indicate the presence of two kinds of methyl groups and three methylenes, as anticipated above. Hydrogen is slightly more electronegative than a saturated carbon atom, with $q(H) = -0.061e$ in a methyl group and $-0.080e$ in the central methylene in heptane. As a result, methyl withdraws charge from methylene and the net charge on $|CH_3$, $q(CH_3)$, changes from 0 in ethane to a constant value of $-0.016e$ in the remaining molecules (Table 5). Because of this charge transfer, the interatomic surface is not equidistant between the carbon of methyl, C1, and the adjacent carbon, C2, of methylene but is shifted toward C2. A bond critical point (BCP) marks the intersection of the interatomic surface with the bond path and defines the bonded radius of an atom, the distance from the nucleus to the BCP. This is illustrated in Figure 2, which compares the density distributions of the methyl and neighboring methylene groups for $n = 6$ and 7. The values of the radii, $r_b(C1) = 1.447$ au and $r_b(C2) = 1.435$ au, quantify the small shift in the interatomic surface toward the methylene group, a displacement too small to be discernible in Figure 2. The bond critical point is equidistant between the C nuclei for the remaining C−C bonds with $r_b(C) = 1.442$ au, leading one to anticipate that there is no transfer of density between the methylene groups. Electronic charge is transferred to methyl primarily from the adjacent methylene, the charge of $+0.033e$ on $|CH_2|$ in propane being twice that for the succeeding methylenes that are bonded to but a single methyl. While the methylenes that are bonded only to other methylenes have a zero net charge to within the integration error, they do exhibit a small and consistent loss of electronic charge of $\sim 0.001e$.

The transfer of density to the methyl groups leads to a decrease in their energies (an increase in their stability) by 9.5 kcal/mol in propane and to an essentially constant decrease of 8.7 ± 0.01 kcal/mol in the remaining molecules. The unique $|CH_2|$ group in propane exhibits twice the increase in energy found for the $|CH_2|$ groups bound to a single methyl, as anticipated for the model in which a single methylene quenches the perturbation. The increase in energy of these $|CH_2|$ groups in molecules for $n > 4$ exceeds the decrease for the $|CH_3$ groups by an amount that is offset by the small departures recorded for the methylene groups bonded only to other methylenes. If the perturbing effect of $CH_3|$ is completely damped by its neighboring $|CH_2|$ group, the remaining methylene groups would exhibit zero net charge and zero deviation from the standard energy $E(CH_2)$ It appears that a single methylene group does not completely quench the electron-withdrawing perturbation of the methyl group, but the deviations from the standard value $E(CH_2)$ for the central $|CH_2|$ groups for $n \geq 5$ are less than the uncertainty in the integrated energies.

While perfect transferability is theoretically an unattainable limit,[9] it appears to be attainable both experimentally and computationally to within the associated uncertainties. Thus, following the compensatory transfer of charge and energy density from $|CH_2|$ to $CH_3|$ for $n > 2$, the resulting groups are predicted by the present and previous calculations[12,19] to be transferable without significant change from $n = 4$ onward. One should bear in mind that the total energy of a methyl or methylene group is of the order of 2.5×10^4 kcal/mol and that these groups, when transferred between structurally equivalent

TABLE 6: Net Charges and Energies of Silyl and Silylene Groups Relative to Standard Values[a]

molecule	$q(SiH_3)$	$q(SiH_2)$	$q(SiH_2)^b$	$\Delta E(SiH_3)$	$\Delta E(SiH_2)$	$\Delta E(SiH_2)^b$
disilane	0.000			0.0		
trisilane	0.008	−0.015		1.9	−3.9	
tetrasilane	0.017	−0.015		2.8	−3.0	
pentasilane	0.015	−0.005	−0.015	2.3	−1.7	−1.7
hexasilane	0.013	−0.007	−0.005	2.2	−2.0	−0.3
heptasilane	0.014	−0.007	−0.007	2.0	−2.2	−0.7
			0.004[c]			1.0[c]

[a] $E(SiH_3) = -290.681\ 73$ au, $E(SiH_2) = -290.107\ 73$ au using linear regression fit of the molecular energies of the series. [b] This SiH_2 is bonded only to other silylenes. [c] Fourth silicon in heptasilane.

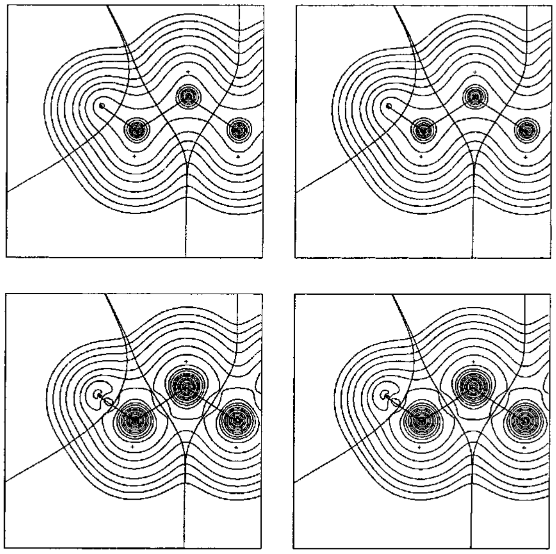

Figure 2. Contour plots of the electron densities (upper plots) and kinetic energy densities for the $CH_3|CH_2|CH_2$-group in hexane on the left and heptane on the right showing the interatomic surfaces and bond paths in the plane containing the nuclei of H−C−C−C. The positions of out-of-plane nuclei are indicated by open crosses. Corresponding plots are completely superimposable, illustrating the concurrent transferability of the electron and kinetic energy densities of the methyl and methylene groups in the homologous series of hydrocarbons for $n > 3$. The kinetic energy density is the positive definite form given by the action of the operator $(\hbar^2/2m)\nabla\cdot\nabla'$ on the first-order density matrix $\gamma(\mathbf{r},\mathbf{r}')$, followed by setting $\mathbf{r} = \mathbf{r}'$. *When the form of a group is the same in two different molecules, it contributes identical amounts to all properties in both molecules.*

positions, exhibit energy changes of less than 1 kcal/mol, experimentally and theoretically. This transferability is illustrated in Figure 2, which displays the electron density and the positive-definite kinetic energy density[9] for a methyl and its neighboring methylene group in hexane and heptane. The contour plots of both functions are completely and separately superimposable over each of the groups, as the reader may verify with the help of a duplicating machine. The methyl and bonded methylene group are each calculated to possess the same average number of electrons to within 0.0002 e and the same average energies to within 0.06 kcal/mol for methyl and 0.4 kcal/mol for methylene, the energy of the group equaling the negative of its electronic kinetic energy, eq 6, obtained by integration of the kinetic energy density. These results closely parallel those obtained previously with wave functions that do not exactly satisfy the virial theorem.[12,19] The results obtained using a slightly larger basis set[12] than that used here (yielding a standard energy for methyl equal to −39.62953 au compared to the present value of −39.62873 au) yielded values of $q(CH_3)$ and $\Delta E(CH_3)$ equal to $-0.018e$ and −10.5 kcal/mol, respectively.

The extent of charge transfer to the hydrogens is much greater in the silanes than in the hydrocarbons: $q(H) = -0.06$ to $-0.08e$ in the hydrocarbons and $-0.72e$ in the silanes, accounting for the differences in the gross features of their charge distributions, as illustrated for propane and trisilane in Figure 3. The excess negative charge on H imparts a diffuse nature to its charge distribution, the average volume[21] of H in a silane equaling 95.6 au as opposed to a value approximately half as large, or 51.0 au, in the hydrocarbons. Unlike the hydrocarbons where $q(H)$ is more negative in $|CH_2|$ than it is in $|CH_3$ by $0.02e$, the value of $q(H)$ is essentially independent of position in the silanes exhibiting a variation of only $0.001e$. The values of the density and its Laplacian at a C−H BCP are characteristic of a shared interaction with $\rho_b = 0.29$, au $\nabla^2\rho_b = -1.12$ au, whereas those for Si−H are characteristic of a polar interaction with $\rho_b = 0.12$, au $\nabla^2\rho_b = +0.18$ au. The critical point data for the C−C and Si−Si shared interactions reflect their relative strengths, with $\rho_b = 0.25$ au, $\nabla^2\rho_b = -0.62$ au for C−C while Si−Si has a smaller accumulation of density and greatly reduced charge concentration with $\rho_b = 0.09$ au, $\nabla^2\rho_b = -0.14$ au, Figure 3.

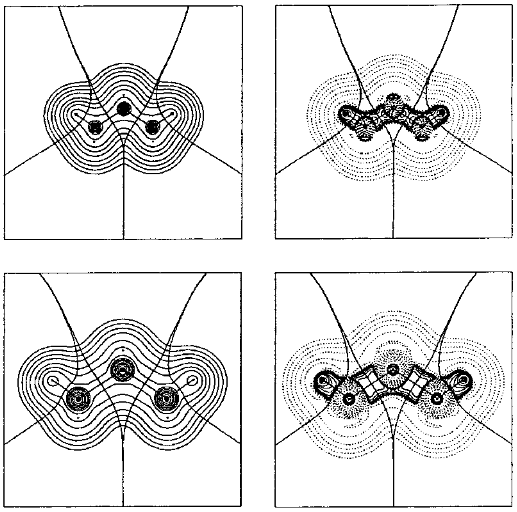

Figure 3. Contour plots of the electron density and its Laplacian in propane (upper plots) and trisilane in the plane of the carbon or silicon nuclei overlaid with interatomic surfaces and bond paths. Solid contours denote $\nabla^2\rho < 0$, a concentration of electronic charge. These diplays account for the differing chemistry of a saturated hydrocarbon compared to a silane by demonstrating the very polar character of the latter molecule compared to the former. Note how the position of the bond critical point, where the density attains its minimum value along the bond path, equally partitions the valence density of a C−H bond, while approaching the core density of Si in a Si−H bond. The larger core density on silicon results in a decrease in the nuclear attractive force acting on the valence electrons, and ρ_b for Si−Si is less than half of the value for C−C. Not only is there a large charge separation between the hydrogens and the silicon atoms giving $q(Si) = +2.2e$ and $+1.4e$ for terminal and central silicons, the valence shell of charge concentration in the Laplacian distribution of a silicon atoms is missing except for the bonded concentration shared with another Si, enhancing its already large electrostatic susceptibility to nucleophilic attack.

TABLE 7: Changes in Population and Energy in Forming Pyridine from |CHCHCH| and |CHNCH|[a]

	$\|C\alpha H\|N\|C\alpha H\|$ from pyrazine				$\|C\beta H\|C\gamma H\|C\beta H\|$ from benzene					
	Cα	H	$\|C\alpha H\|$	N	Cβ	H	$\|C\beta H\|$	Cγ	H	$\|C\gamma H\|$
ΔN	−0.013	+0.012	−0.001	+0.025	+0.007	−0.011	−0.004	+0.001	−0.017	−0.016
ΔE	+9.9	−4.3	+5.6	+8.8	−11.3	+3.7	−7.6	−10.8	+3.9	−6.9

[a] The C atoms are labeled α, β, and γ with respect to the position on the N atom. ΔN is units of electronic charge and ΔE is in kcal/mol.

The BCP data exhibit only small changes throughout both series of molecules, ρ_b varying by ±0.001 au and $\nabla^2\rho_b$ by ±0.01 au.

While compensatory transferability is operative in the silanes as in the hydrocarbons, the net charges and the deviations in the energies from the standard values of $|SiH_3$ and $|SiH_2|$ do not exhibit the regularity found for the corresponding groups in the hydrocarbons and the deviations from the standard values, particularly for the energies, are of lesser magnitude. The $|SiH_3$ group behaves oppositely to $|CH_3$ and transfers charge to its bonded $|SiH_2|$ group, so that $q(SiH_3) > 0$ for $n > 2$. In addition, the charge is not of constant magnitude, but increases by a factor of 2 for $n > 3$. The values of $q(SiH_2)$ are all negative. In trisilane, a single $|SiH_2|$ group compensates for the charge lost by both $|SiH_3$ groups, and its charge is equal to $q(SiH_2)$ in tetrasilane, where each $|SiH_2|$ accepts charge from a single $|SiH_3$ group. The magnitude of $q(SiH_2)$ for a group bonded to $|SiH_3$ for $n \geq 5$ is reduced by a factor of 2−3 compared to $n = 3$ or 4. Aside from the value for the central group for $n = 5$, the net charges on the remaining $|SiH_2|$ groups bonded only to other silylene groups are within or close to being within the integration error and they approach the limiting form of an unperturbed group.

The deviations in the energies from the standard value reflect the transfer of charge between the groups. Thus $\Delta E(SiH_3) > 0$ and $\Delta E(SiH_2) < 0$, corresponding to the small transfer of charge from the silyl to the silylene groups. The magnitudes of the energy changes are smaller by a factor of 3 or 4 for the SiH_3 groups and for the SiH_2 groups bonded to a single silyl group than the changes for the corresponding groups in the hydrocarbons. Small perturbations appear to be transmitted to the central SiH_2 groups, the largest change appearing in pentasilane, which is perturbed to the same extent as is the $|SiH_2|$ group linked to a single silyl group. The value of $\Delta E(SiH_2)$ for the central group in heptasilane is calculated to be positive, in line with the its predicted small loss of charge. The calculated charges and energy changes for the central $|SiH_2|$ groups in hexa- and heptasilane are within the integration error, and these groups are sensibly transferable between systems without change. The variations in the deviations from the standard populations and energies recorded in Table 6 should be viewed in terms of the groups' total populations of 16 and 17 e and total energies of $\sim 1.8 \times 10^5$ kcal/mol, to realize that the silyl and silyene groups, with the exception of disilane, are sensibly transferable.

Compensatory Transferability in Formation of Pyridine. The perturbations are more severe in the synthesis of pyridine from the appropriate groups in benzene and pyrazine (Figure 1). However, even here, one is struck by the similarity in the forms of the groups in pyridine, compared to those in their parent molecules. The |CHNCH| group of pyrazine gains 0.024 e from |CHCHCH| of benzene and undergoes an energy increase of 20.0 kcal/mol, the energy of the benzene fragment decreasing by an almost equal amount, 22.0 kcal/mol. Thus the changes in the two groups nearly compensate one another and the energy in this case is conserved to ~2 kcal/mol (actually 1.6 kcal/mol in terms of the total calculated energies, the 0.4 kcal/mol difference resulting from the accumulated atomic integration errors) The directions of charge and energy transfer are opposed in this example, and the changes in density caused by the linking of the two groups are not confined to the region of the newly formed interatomic surfaces. They are instead spread over all the atoms of both groups, Table 7, a result of significant geometrical changes caused by the linking of the groups. The lengths of the new Cα|Cβ bridging bonds undergo a decrease of 0.001 au, and the BCPs are shifted 0.017 au toward Cβ of the benzene fragment, in accordance with the direction of the transfer of electronic charge. The CβCδCβ angle decreases by 1.3° from 120° and the CαNCα angle opens by 1.1° from its value of 116.7° in pyrazine. While N gains 0.025 e, it is destabilized as are its bonded CH groups, as a result of the C−N lengths increasing by 0.005 au. The C−C lengths of |CHCHCH| decrease by the same amount and the three CH groups are stabilized, despite a loss of electronic charge. There is a compensation of the changes incurred within each CH group, the changes in the population and energy being of opposite sign for carbon and its bonded hydrogen (Table 7).

The formation of the $ACH_2|CH_2B$ systems also exhibits changes in energy and charge relative to the parent molecules that extend over all the atoms.[18] In systems which mix dissimilar atoms the compensatory transferability is not the result of related flows of charge and energy densities across a boundary between chemically similar atoms. Instead, there is an extended response throughout both groups that minimizes the resulting changes in their properties. Benson and Buss[8] likened group additivity in $ACH_2|CH_2B$ to the additive contributions to the properties of a solution obtained from individual solute molecules as the concentration approached infinite dilution, believing the $CH_2|CH_2$ bridge provided sufficient separation such that A did not perturb B. This is not the case. Even three intervening $|CH_2|$ groups are not sufficient to completely damp a perturbation, the energies of X = OH and F changing by 2 and 4 kcal/mol, respectively, when $H{-}(CH_2)_2{-}X$ is transformed into $H{-}(CH_2)_3{-}X$.[17] Compensatory transferability, which does account for the additivity in these systems, appears to be the consequence of the operation of a Le Chatelier-like principle: each of the transferred groups does change, but each responds to the presence of the other in such a way as to minimize the resulting perturbation. Recognizing the operation of such a principle provides a rationalization for the ubiquitous occurrence throughout chemistry of groups exhibiting characteristic properties.

Transferability of Localization and Delocalization Indices. The quantum mechanical pair density in conjunction with the definition of an atom in a molecule provides a precise determination of the extent to which electrons are localized to a given atom or delocalized over any pair of atoms.[13,14] Does a property determined by the pair density exhibit the same degree and pattern of transferable behavior as do the group properties determined by the electron density and the one-electron density matrix? While the Ehrenfest force and its virial are expressible in terms of the one-electron density matrix through the stress tensor $\boldsymbol{\sigma}(\mathbf{r})$, they include the forces and energies of repulsion acting between the electrons, properties determined by the pair density. The stress tensor, however, has the property of isolating the essential physics of the force acting on an electron and its virial, and it clearly does not contain all of the information contained in the pair density. Thus there is no a priori reason to expect that a property determined solely and completely by the pair density will exhibit the same degree of transferability as do the force and its virial and hence the energy of the atom.

The spatial localization of the electron is determined by the localization of the density of the Fermi hole, the physical manifestation of the exclusion principle. The Fermi hole has a simple physical interpretation: it provides a description of how the density of an electron of given spin, called the reference electron, is spread out from a preassigned point into the space of another same-spin electron, thereby excluding the presence of an identical amount of same-spin density.[13] It is a negative quantity, as it decreases the amount of same spin density throughout space and its integration over the space of the second electron yields − 1, corresponding to the removal of one same-spin electron. If the density of the Fermi hole is maximally localized in the vicinity of the reference point, then all other same-spin electrons are excluded from this vicinity and the reference electron is localized. For a closed-shell molecule, the result is a localized α,β pair, since all other β electrons will be similarly excluded from the same region. Contrariwise, the electron can go wherever its Fermi hole goes and if the Fermi hole of an electron when referenced to a given atom is delocalized into the basin of a second atom, then the electron is shared between them.

These ideas are made quantitative through the appropriate integration of the pair density to determine the total Fermi correlation that is contained within the basin of a single atom A, the quantity $F(\mathrm{A,A})$, or the correlation that is shared between the basins of atoms A and B, the quantity $F(\mathrm{A,B})$ At the Hartree−Fock level of theory, $F(\mathrm{A,A})$ is obtained by integrating the exchange density for two same-spin electrons over atom A, while for $F(\mathrm{A,B})$ the coordinates of one electron are integrated over atom A and the coordinates of the other over atom B. The delocalization of electrons between atoms A and B is determined by the extent to which electrons on A are exchanged with those on B. We shall assume a closed-shell molecule, and from this point on the symbols $F(\mathrm{A,A})$ and $F(\mathrm{A,B})$ will refer to the equal contributions to the Fermi correlation from electrons of both spin states. $F(\mathrm{A,A})$ is a measure of the extent to which the $N(\mathrm{A})$ electrons of atom A are localized within its basin, that is, the extent to which they exchange with electrons within atom A. Its limiting value is $-N(\mathrm{A})$, corresponding to complete containment of the Fermi correlation for the $N(\mathrm{A})$ electrons to the basin of atom A. Similarly, $F(\mathrm{A,B})$ is a measure of the number of electrons of either spin, referenced to atom A, that are delocalized onto atom B with a corresponding definition of $F(\mathrm{B,A})$ which necessarily equals $F(\mathrm{A,B})$[13]

The magnitude of $F(\mathrm{A,A})$ is termed the *localization index* $\lambda(\mathrm{A})$, and in general, $\lambda(\mathrm{A}) < N(\mathrm{A})$, emphasizing that $N(\mathrm{A})$ denotes an average population, the result of other electrons exchanging with the electrons in A. The ratio $|F(\mathrm{A,A})|/N(\mathrm{A})$, whose limiting value is unity, is the fraction of the total Fermi correlation required for the complete localization of the $N(\mathrm{A})$ electrons to A. The extent to which $|F(\mathrm{A,A})| < N(\mathrm{A})$ is a measure of the delocalization of the electrons of A onto other atoms. The sum $F(\mathrm{A,B}) + F(\mathrm{B,A}) = \delta(\mathrm{A,B})$, termed the *delocalization index*, is a measure of the total Fermi correlation shared between the atoms, that is, the number of shared electrons.[14] The total Fermi correlation equals $-N$, that is, $\sum_{\mathrm{A,B}} F(\mathrm{A,B}) = -N$, and one may view the Fermi hole as a correction for the self-pairing of each electron. Because of this property of the Fermi correlation, one obtains the following useful partitioning of the atomic population of atom A:

$$F(\mathrm{A,A}) + \sum_{\mathrm{B}} F(\mathrm{A,B}) = -N(\mathrm{A}) \quad \text{for} \quad \mathrm{B} \neq \mathrm{A} \tag{9}$$

or, equivalently, since the localization and delocalization indices sum to N

$$\lambda(\mathrm{A}) + \sum_{\mathrm{B}} \left(\frac{1}{2}\right) \delta(\mathrm{A,B}) = N(\mathrm{A}) \quad \text{for} \quad \mathrm{B} \neq \mathrm{A} \tag{10}$$

These relationships enable one to determine what fraction of the electron population of A is localized to A and to what extent it is delocalized onto other atoms in the molecule.

Only Fermi correlation is operative at the Hartree−Fock level and the delocalization index then equals unity for a single pair of electrons equally shared between two identical atoms A and A′. The electron pairing predicted by the Hartree−Fock model of the pair density is found to be remarkably successful in recovering the Lewis model. The Hartree−Fock delocalization values for the C−C bonds in ethane and ethylene are 1.0 and 1.9, respectively, and 3.0 in N_2. The delocalization indices for such homopolar interactions decrease with the addition of Coulomb correlation, as it disrupts the pairing of electrons between the atoms. Thus with the addition of Coulomb correlation, the values for $\delta(\mathrm{C,C'})$ decrease to 0.83 for ethane and to 1.42 for ethylene. The values we report here are obtained at the Hartree−Fock level, and they will represent upper bounds to the number of Lewis electron pairs shared between equivalent atoms.[22]

Structurally equivalent C|C and Si|Si bonded interactions yield identical values for the delocalization index. In the hydrocarbons, $\delta(\mathrm{C,C})$ decreases from 0.992 in ethane to a constant value of 0.978 for the bond between methyl and methylene and equals 0.966 for the remaining interior bonds between the carbons of successive methylenes. The values of $\delta(\mathrm{C,H})$ are 0.965 ± 0.002 in methyl and 0.946 ± 0.002 for methylene. The delocalization indices are smaller in the silanes than in the hydrocarbons. The value of $\delta(\mathrm{Si,Si})$ increases from 0.738 in disilane to 0.762 in trisilane, equaling 0.760 for the remaining Si−Si interactions. The values of the delocalization index for the polar Si−H interactions are substantially less than unity, $\delta(\mathrm{Si,H}) = 0.549 \pm 0.001$ in the silyl group and 0.619 ± 0.001 in the silylene group.

Of more immediate interest is the degree of transferability of the localization and delocalization indices for each group through the series of molecules. The tableaux in Tables 8and 9 summarize this information. A diagonal element equals $\lambda(\mathrm{A})$ for the indicated group while an off-diagonal element gives $^1/_2\delta(\mathrm{A,B})$, the contribution to the delocalization index between groups A and B and referred to hereafter as $d(\mathrm{A,B})$ Thus, as required by eq 10, the sum of the values in any column equals $N(\mathrm{A})$, the population of the group, and the off-diagonal entries indicate how the population of A is spread over the remaining groups.

The values of $\lambda(\mathrm{A})$ for both the methyl and methylene groups are essentially unchanged through the series of hydrocarbons, with an uncertainty of ±0.002 in $\lambda(\mathrm{CH_3})$ and ±0.001 in $\lambda(\mathrm{CH_2})$ Like certain other properties, such as group polarizability and magnetic susceptibility, the λ values do not differentiate between the three different methylene groups, as do their populations and energies. The electrons of a methyl group are delocalized over other groups to the extent of 7.5% and those of a methylene group by approximately twice that amount, 15.7%. Referring to the results for $n = 7$, the delocalization of the electrons of a

TABLE 8: Localization and Delocalization Indices for Hydrocarbons

C_2H_6

	$C1H_3$
$C1H_3$	8.344
C2H3	0.656
sum	8.999

C_3H_8

	$C1H_3$	$C2H_2$
$C1H_3$	8.342	0.615
$C2H_2$	0.615	6.736
$C3H_3$	0.058	0.615
sum	9.016	7.966

C_4H_{10}

	$C1H_3$	$C2H_2$
$C1H_3$	8.341	0.614
$C2H_2$	0.614	6.735
$C3H_2$	0.051	0.582
$C4H_3$	0.009	0.051
sum	9.015	7.982

C_5H_{12}

	$C1H_3$	$C2H_2$	$C3H_2$
$C1H_3$	8.341	0.614	0.051
$C2H_2$	0.614	6.735	0.581
$C3H_2$	0.051	0.581	6.734
$C4H_2$	0.008	0.044	0.581
$C5H_3$	0.001	0.008	0.051
sum	9.014	7.982	7.997

C_6H_{14}

	$C1H_3$	$C2H_2$	$C3H_2$
$C1H_3$	8.341	0.614	0.051
$C2H_2$	0.614	6.735	0.580
$C3H_2$	0.051	0.580	6.734
$C4H_2$	0.007	0.045	0.580
$C5H_2$	0.001	0.006	0.044
$C6H_3$	0.000	0.001	0.007
sum	9.014	7.981	7.997

C_7H_{16}

	$C1H_3$	$C2H_2$	$C3H_2$	$C4H_2$
$C1H_3$	8.341	0.613	0.050	0.008
$C2H_2$	0.613	6.735	0.601	0.039
$C3H_2$	0.0050	0.601	6.734	0.600
$C4H_2$	0.008	0.039	0.600	6.733
$C5H_2$	0.001	0.007	0.045	0.600
$C6H_2$	0.000	0.001	0.006	0.045
$C7H_3$	0.000	0.000	0.001	0.006
sum	9.013	7.994	8.037	8.032

TABLE 9: Localization and Delocalization Indices for Oligosilanes

Si_2H_6

	$Si1H_3$
$Si1H_3$	16.431
$Si2H_3$	0.563
sum	16.994

Si_3H_8

	$Si1H_3$	$Si2H_2$
$Si1H_3$	16.414	0.544
$Si2H_2$	0.544	14.924
$Si3H_3$	0.031	0.543
sum	16.989	16.011

Si_4H_{10}

	$Si1H_3$	$Si2H_2$
$Si1H_3$	16.402	0.541
$Si2H_2$	0.541	14.915
$Si3H_2$	0.027	0.527
$Si4H_3$	0.005	0.028
sum	16.976	16.010

Si_5H_{12}

	$Si1H_3$	$Si2H_2$	$Si3H_2$
$Si1H_3$	16.404	0.541	0.027
$Si2H_2$	0.541	14.905	0.524
$Si3H_2$	0.027	0.524	14.906
$Si4H_2$	0.004	0.024	0.524
$Si5H_3$	0.000	0.005	0.026
sum	16.976	15.998	16.008

Si_6H_{14}

	$Si1H_3$	$Si2H_2$	$Si3H_2$
$Si1H_3$	16.407	0.542	0.027
$Si2H_2$	0.542	14.907	0.524
$Si3H_2$	0.027	0.524	14.897
$Si4H_2$	0.004	0.024	0.523
$Si5H_2$	0.001	0.004	0.024
$Si6H_3$	0.000	0.001	0.004
sum	16.981	16.002	15.999

Si_7H_{16}

	$Si1H_3$	$Si2H_2$	$Si3H_2$	$Si4H_2$
$Si1H_3$	16.404	0.541	0.026	0.003
$Si2H_2$	0.541	14.906	0.524	0.024
$Si3H_2$	0.026	0.524	14.898	0.522
$Si4H_2$	0.004	0.026	0.522	14.887
$Si5H_2$	0.001	0.004	0.026	0.522
$Si6H_2$	0.000	0.000	0.004	0.027
$Si7H_3$	0.000	0.000	0.000	0.004
sum	16.977	16.000	16.001	15.990

methyl group decays monotonically with distance, decreasing to effectively zero for a group separated by four intervening groups, the same being true for a methylene group. The value of $N(CH_3)$ is constant for $n > 2$, and thus the delocalization contributions for a given group must sum to the same value for each molecule with the added proviso that the delocalization onto each of the groups bonded to it must also be the same throughout the series for this property to be completely transferable. This conservation of the delocalization index requires that the values of all $d(1,x)$ with $x = 2$ to $n - 1$, be the same for the molecule with n carbons as for the next with $n + 1$ carbons and that the value of $d(1,n)$ in C_n equal the sum $d(1,n) + d(1,n+1)$ in C_{n+1}. This is indeed the case. Consider for example, pentane. The values of $d(1,2)$ and $d(1,3)$ are the same as those found for butane, and $d(1,4)$ for butane is equal to the sum of the delocalizations $d(1,4)$ and $d(1,5)$ for pentane.

The methylene groups exhibit the same transferable behavior irrespective of their position along the chain, the values of $\lambda(CH_2)$ exhibiting variations of less than 0.2%. One again notes the operation of the conservation of the delocalization index, with $d(3,6)$ in hexane equaling the sum of $d(3,6)$ and $d(3,7)$ in heptane, the values of $d(3,1)$ to $d(3,5)$ being the same in both molecules. The same conservation principle operates within a given molecule: the value of $d(4,7)$ in heptane equals the sum of the values for $d(3,6)$ and $d(3,7)$, while $d(3,7)$ in turn equals the sum of $d(2,6)$ and $d(2,7)$ The demonstrated principle of conservation of delocalization is a necessary result for the transferability of the properties of the pair density averaged over an atom or group. If the value of $F(\mathrm{A,A})$ and hence the localization of the electrons to a group A is transferable from one molecule to another, as found here for both the methyl and methylene groups, then the number of delocalized electrons, as given by $\sum_{\mathrm{B}} F(\mathrm{A,B})$, must also be not only conserved, but partitioned among the remaining groups in such a manner as to maintain their transferable values.

The values of $\lambda(\mathrm{SiH_3})$ and $\lambda(\mathrm{SiH_2})$ for $n > 2$ are constant to within 0.01. The electrons are 96.6% localized on a silyl group, a value greater than the 93.1% found for the silylene groups. Thus the electrons are more localized in the silanes than in the hydrocarbons, where the percent localizations of the methyl and methylene groups are 92.5% and 84.2%, respectively. This result is anticipated on the basis of the very polar nature of the SiH interaction, $q(\mathrm{H}) = -0.72e$, compared to that in CH, $q(\mathrm{H}) = -0.07e$ (Figure 2). The silyl and silylene groups exhibit the same conservation of delocalization as found for the hydrocarbons. The delocalization of the electrons on a silyl group does not extend beyond four silylene groups as found for the methyl group, and its delocalization over the neighboring groups exhibits the requisite transferable behavior, the delocalization of the electrons in the $|\mathrm{SiH_3}$ groups in hexa- and heptasilane being identical, for example. Similar observations apply to the $|\mathrm{SiH_2}|$ groups which exhibit the same delocalizations over the three adjacent groups irrespective of their position in the chain.

The same pattern of transferable behavior is found for the "source" function, a function that determines the contribution to the density $\rho(\mathbf{r})$ at a given point $\mathbf{r}$ from any spatial region.[23] Since the density at a C−H bond critical point (BCP) in a methyl group is unchanged for all members with $n > 2$, the contribution to $\rho(\mathbf{r})$ at the BCP from the source function averaged over the methyl group must, like $\lambda(\mathrm{CH_3})$, be constant throughout the series and, additionally, the contributions from successive groups must be the same in succeeding members of the series, with the contribution from the final group with n carbons being equal to the sum of the final two contributions in the succeeding member.

The intracule and extracule functions of the pair density are the probability densities for the interparticle distance and the center of mass of an electron pair, respectively.[24] They are being increasingly employed in the study of electron correlation. Fradera et al.[25] have studied these functions and their associated Laplacian distributions to determine their relevance in determining the spatial localization of electron pairs. These functions are incapable of providing information about the sharing of electrons between specific pairs of atoms or their degree of localization within individual atomic basins, the properties of interest here. To quote these authors, "The fact that several electron−electron interactions may contribute to close regions in space introduces an additional difficulty when trying to perform a precise interpretation of the maps and attempt a quantitative study of the contribution of each particular interaction."

Conclusion

This paper has illustrated how the quantum mechanics of a proper open system provides a basis for understanding the widespread occurrence of group additivity found for both static and field-induced properties, a corollary of the identification of the open systems with the functional groups of chemistry. Group additivity is a consequence of compensatory transferability: the necessary changes incurred in the density, energy, and other properties of one group being compensated for by equal and opposite changes in the properties of the group to which it is linked. This compensating behavior suggests the operation of a Le Chatelier-like principle, a cooperative effect wherein each group responds to the perturbations engendered by a change in its neighboring groups in such a way as to minimize the resultant changes in properties of the new system. The changes in the zero-flux surface a group shares with a neighboring group resulting from the perturbations associated with transfer are necessarily transmitted to the basin of the open system, the basin and surface properties of a proper open system being linked by the principle of stationary action.[9,18] Thus the essentially perfect transferability of the methyl group from hexane to heptane is reflected in the constancy of the zero-flux surface it shares with the methylene group (Figure 2).The possibility of constructing a polypeptide by linking amino acid residues is a consequence of this interdeterminancy of basin and surface properties. The pair of amidic surfaces of zero flux that bound each residue in the peptide chain are very nearly mirror images of one another, and their properties are insensitive to a change in the identities of the groups attached to the α-carbon atom of the neighboring residues.[18]

All the properties of a proper open system are determined by its distribution of charge. This includes properties determined by the pair density and the first-order density matrix, the latter as illustrated in Figure 2, which shows the paralleling transferability of the electron density $\rho(\mathbf{r})$ and the kinetic energy density $G(\mathbf{r})$ for the methyl and methylene groups that appear interchangeable between hexane and heptane. It was the observation of this parallel behavior of $\rho(\mathbf{r})$ and $G(\mathbf{r})$ over spatial regions bounded by zero-flux surfaces that suggested the possibility of partitioning the energy of a molecule into atomic contributions by assuming the existence of a virial theorem for an atom in a molecule, allowing one to equate $E(\Omega)$ to $-T(\Omega)$.[26]

While there is no theoretical proof that the local form of the electron density determines a system's properties, the statement is but a reflection of the dictum that properties follow form in real space. Two identical atoms, whether isolated or bound in different molecules, possess identical properties. The same physics governs a bound or an isolated system, a bound atom differing from an isolated one only in that its zero-flux surface lies partly or completely at finite distances from its nucleus and is open to the transmission of property fluxes. Even properties generated by the response of a system to externally applied electric or magnetic field exhibit a degree of transferability that is once again determined by the corresponding transferability in the form of the unperturbed atom or group. The first-order density $\rho^{(1)}(\mathbf{r})$ induced by an electric field determines the polarizability density $-e\mathbf{r}\rho^{(1)}(\mathbf{r})$ and the first-order current density $\mathbf{j}^{(1)}(\mathbf{r})$ induced by a magnetic field determines the magnetizability density $\mathbf{r} \times \mathbf{j}^{(1)}(\mathbf{r})$[27] The atomic averages of these densities, when referenced to the nucleus, yield transferable polarizabilities[12] and magnetic susceptibilities[17] for the methyl and methylene groups of the linear hydrocarbons, and one must conclude, on the basis of these observations, that the form of $\rho(\mathbf{r})$ over an open system determines even the field-induced charge and current densities, as well as properties determined by the first- and second-order density matrices.

Figure 4 displays the electron density distributions for hepatane and heptasilane showing the interatomic surfaces that define the methyl and methylene groups. We now understand that all the properties of both molecules are the respective sums of the properties of the individual component groups and that these properties are, directly or indirectly, determined by the form of the electron density for each group, by the form of the group in real space. Thus two groups that look the same within

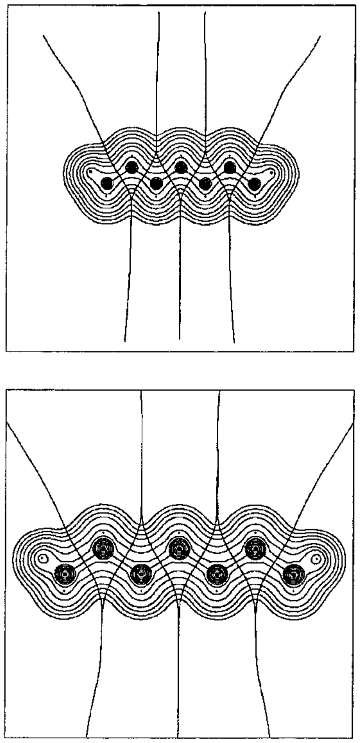

Figure 4. Contour plots of the electron density for the heptane and heptasilane molecules showing the interatomic surfaces of zero flux that define the methyl and methylene groups in the former and the silyl and silylene groups in the latter. Each group makes a contribution to every property of the molecule that is determined by the expectation value of the corresponding operator for an open system. Essentially identical groups, such as the central $|AH_2|$ group and its bonded neighbors in both molecules, contribute identical amounts to all properties.

either molecule make identical contributions to its molecular properties. This understanding is unique to the physics of a proper open system.[28]

References and Notes

(1) Kopp, H. cf. Glasstone, S. *Textbook of Physical Chemistry*, 2nd ed.; Van Nostrand: New York, 1946; p 524.

(2) Bruhl, J. W. *Leibigs Ann. Chem.* **1880**, *200*, 139; *Leibigs Ann. Chem.* **1880**, *203*, 1, 255.

(3) Le Fevre, R. J. W. in *Advances in Physical Organic Chemistry*; Gold, V., Ed.; Academic Press: New York, 1965; Vol. 3, p 1.

(4) Henrichsen, G. *Wied. Ann.* **1888**, *34*, 186.

(5) Pascal, P. *Ann. Chim. Phys.* **1910**, *19*, 5. Pascal, P.; Gallais, F.; Labarre, S. F. *Acad. Sci.* **1961**, *252*, 2644.

(6) Rossini, F. D. *J. Res. Natl. Bur. Stand. (U.S.)* **1931**, *6*, 37; *J. Res. Natl. Bur. Stand. (U.S.)* **1931**, *7*, 329; *J. Res. Natl. Bur. Stand. (U.S.)* **1934**, *13*, 21. Prossen E. J.; Johnson, W. H.; Rossiini, F. D. *J. Res. Natl. Bur. Stand. (U.S.)* **1946**, *37*, 51.

(7) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

(8) Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1958**, *29*, 546.

(9) Bader, R. F. W. *Atoms in Molecules—A Quantum Theory*; Oxford University Press: Oxford, UK, 1990.

(10) Bader, R. F. W. *Phys. Rev. B* **1994**, *49*, 13348.

(11) Bader, R. F. W.; Popelier, P. L. A.; Keith, T. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 620.

(12) Bader, R. F. W.; Keith. T. A.; Gough, K. M.; Laidig, K. E. *Mol. Phys.* **1992**, *75*, 1167.

(13) Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 7391.

(14) Xavier, F.; Austen, M. A.; Bader, R. F. W. *J. Phys. Chem.* **1999**, *103*, 304.

(15) Plitt, H. S.; Downing, J. W.; Raymond, M. K.; Balaji, V.; Michl, J. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1653. Michl, J.; Miller, R. D. *Chem. Rev.* **1989**, *89*, 1359.

(16) Bader, R. F. W. *Can. J. Chem.* **1998**, *76*, 973.

(17) Keith, T. A.; Bader, R. F. W. *J. Chem. Phys.* **1993**, *99*, 3669, 3683.

(18) Bader, R. F. W.; Martín, F. J. *Can. J. Chem.* **1998**, *76*, 284.

(19) Wiberg, K. B.; Bader, R. F. W. Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(21) Bader, R. F. W.; Carroll, M. T.; Cheeseman, J. R.; Chang, C, *J. Am. Chem. Soc.* **1987**, *109*, 7968.

(22) Previous workers using indices that are equivalent to the delocalization index defined here at the Hartree−Fock level, identify δ(A,B) with a bond order between A and B: Ángyán, I.; Loos, M.; Mayer, I. *J. Phys. Chem.* **1994**, *98*, 5244. Fulton, R. L. *J. Phys. Chem.* **1993**, *97*, 7516. However, electrons are delocalized over every pair of atoms in a molecule and not just those linked by a bond path whose presence is required for two atoms be bonded to one another. Assuming the existence of a "bond" between every pair of atoms in a molecule is not physically justified. One may however, make the association of δ(A,B) with a bond order for atoms linked by a bond path, the situation for the bonded interactions discussed here.

(23) Bader, R. F. W.; Gatti, C. *Chem. Phys. Lett.* **1998**, *287*, 233.

(24) Thakkar, A. J.; Smith, V. H. *Chem. Phys. Lett.* **1976**, *42*, 476.

(25) Fradera, X.; Duran, M.; Mestres, J. *J. Chem. Phys.* **1997**, *107*, 3576.

(26) Bader, R. F. W,; Beddall, P. M. *J. Chem. Phys.* **1972**, *56*, 3320.

(27) Jameson, C. J.; Buckingham, A. D. *J. Chem. Phys.* **1980**, *73*, 5684.

(28) Bader, R. F. W. *Can. J. Chem.* **1999**, *77*, 86.