Limitations of the Molecular Multipole Expansion Treatment of Electrostatic Interactions for C−H···O and O−H···O Hydrogen Bonds and Application of a General Charge Density Approach

Weili Qian and Samuel Krimm*

Biophysics Research Division and Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

Received: October 25, 2004; In Final Form: January 20, 2005

A molecular multipole expansion treatment (up to hexadecapole) is examined for its accuracy in describing hydrogen-bond electrostatic interactions, with particular reference to explaining the differences between blue-shifted C−H···O and red-shifted O−H···O bonds. In interactions of H_2O and CH_4 with point charges at hydrogen-bonding distances, we find that the molecular multipole treatment not only fails to reproduce ab initio energies but also forces on OH or CH bonds, and therefore cannot properly account for the electrostatic component of the interaction. A treatment based on a molecule's permanent charge density and its derivatives and the charge density and its derivatives induced by an external multipole distribution is in full accord with ab initio results, as shown by application to models of the H_2O-H_2O and CH_4-FH systems. Such a charge density approach provides a fundamental basis for understanding the importance of interaction forces in initiating structural change and thereby altering molecular properties.

Introduction

The extensive recent interest in the presence of C−H···O hydrogen bonds in many different systems, and particularly in the instances of observed and predicted (nontraditional) blue shifts in its CH stretch frequencies, has generated a comparable effort to understand the physical origin of this interaction and why its spectroscopic behavior varies from that of the familiar typical hydrogen bonds (e.g., OH···O and NH···O). Such fundamental understanding is important, among other reasons, in enabling the development of valid models for incorporating the CH···O interaction in physically accurate molecular mechanics energy functions.[1]

An underlying theme in understanding frequency shifts due to hydrogen bonding, namely "that electrostatic [i.e., time-invariant] interactions have a significant role", was recognized early,[2] and the basic treatment of this interaction has been elaborated.[3] In the simple case of a molecule interacting with a weak external homogeneous electric field, the interaction energy is determined by energy-related molecular properties, namely the molecular dipole moment and molecular dipole polarizabilities.[3] However, molecular structure changes are triggered by initial interaction forces,[4] which are determined by force-related molecular properties, such as the molecular dipole derivatives and polarizability derivatives, and forces need to be given equal attention in describing these interactions. Different structure and spectroscopic changes, either in different molecules or different bonds, originate from differences in these related properties. For example, the CH and OH bonds of the cis formic acid molecule have different dipole derivative directions.[5] When the molecule interacts with a very weak homogeneous electric field, the initial force on the C → H bond is negative but is positive for the O → H bond, resulting in bond shortening and a blue shift for CH and elongation and a red shift for OH. On the other hand, the induced dipole derivatives from the polarizability derivatives are always parallel to the bonds, and thus the initial force on the CH bond becomes positive at some large field strength when the positive force from the induced dipole derivative overcomes the negative force from the permanent dipole derivative. The analysis of the interaction with the dipole field can be easily extended to higher rank multipole fields. Since the interaction between the molecule and the electric field is purely electrostatic, the classic calculation gives a quite good prediction.[3]

However, in an actual hydrogen bonding case, the situation is more complicated, not only because of the inhomogeneous electric field from the acceptor molecule charge density that acts on the donor molecule but also because of the presence of other interactions that need to be included, e.g., exchange-repulsive, dispersion, charge transfer, and intramolecular intrinsic (i.e., cross-term force constant) effects. Although the electrostatic interaction has been an underlying premise in theoretical approaches to explaining geometric and spectroscopic changes in blue-shifting situations,[5−19] the emphasis has varied, from assigning a major initial role to this interaction[5,6,11−16] (usually associated with accompanying exchange-repulsion[5,13−16]), to viewing the formation of the hydrogen bond in terms of its final structural and electronic impact on the donor molecule (whether through a so-called two-step process,[9,10] a balance between hyperconjugation and rehybridization,[17] or through electron density difference maps[7,8,16]), and to implementing perturbation treatments of the interaction energy.[18,19] As is clear from an electrostatic/exchange-repulsive/intrinsic treatment of the seven equilibrium structures of the formic acid dimer,[15] a very satisfactory accounting of the ab initio C−H···O and OH···O results is possible. Although the blue-shifted hydrogen bonds are not caused by electrostatic interactions alone, the difference between blue- and red-shifted hydrogen bonds originates mainly from these interactions. This perspective also enables us to understand why no qualitative difference is found between blue-shifted (CH) and red-shifted (OH) hydrogen-bond-donor molecular electron density maps upon complexation:

---

* To whom correspondence should be addressed. E-mail: skrimm@umich.edu. Phone: 734-763-8081. Fax: 734-764-3323.

10.1021/jp040683v CCC: $30.25

since both shifts in electron density result mainly from polarization interactions, which are similar, the density difference maps are also expected to be similar.

Despite the success of the dipole and polarizability derivative formulation of the electrostatic interaction,[5,13−15] these are exact only for an external dipole field and the first terms in the multipole expansion treatment, and even though it has been assumed that a complete expansion is a valid description for a hydrogen bond,[13,14,16] this has not been demonstrated. We explore this question with a simple case, a molecule interacting with a point charge distribution, taking water (a red shifting) and methane (a blue shifting) as donor molecules, and putting point charges at the water dimer acceptor molecule nuclear positions and at the FH nuclear positions in $CH_4\cdots FH$. Point charges interacting with a donor molecule as a model of the electrostatic interaction in a blue shifting hydrogen bond study have been used recently,[14] as well as in modeling molecular polarizability.[20] As in our earlier studies,[5,15] and in the spirit of Feynman[4] that "Many of the problems of molecular structure are concerned essentially with forces", we focus on interaction forces as well as energies. Although Stone's distributed multipole analysis (DMA)[3] model produces accurate interaction energies, in the absence of appropriate distributed force-related properties, i.e., multipole derivatives and polarizability derivatives, it cannot properly account for interaction forces. Since a suitable model of the latter kind is not presently available, we first examine the characteristics and limitations of a description based on molecular properties. (Note that forces are determined by molecular derivatives: thus a force on a bond is in fact the molecular dipole moment derivative with respect to the bond coordinate.) We show that in a multipole expansion of the molecular charge distribution (up to hexadecapole), force as well as energy properties do not converge and thus that such an expansion does not capture the full physics of the interaction. With respect to energy, this has been noted before[21] and undoubtedly arises from the breakdown of the expansion when the source of the electric fields (the charge) is too close to the multipoles.

We have therefore explored another approach, a molecular charge density formulation, which involves the interaction between the electron system of the molecule and the external point charge. Such electrostatic interactions involve at least four basic properties of the molecular charge distribution: the permanent charge density, $\rho(r)$; the permanent charge density derivatives, $d\rho(r)/d\lambda$, where λ is a Cartesian or internal coordinate; the induced charge density, $\Delta\rho(r)$; and induced charge density derivatives $d\Delta\rho(r)/d\lambda$. This formulation results in full agreement with the ab initio calculation of the molecule at equilibrium structure with point charges and therefore represents the complete and fundamental physical interaction. Since $d\rho(r)/d\lambda$ (which has been applied to a vibrational mode coupling study[22]) can be represented by the molecular dipole derivative when the molecule interacts with a homogeneous electric field, we expect that $d\Delta\rho(r)/d\lambda$ should behave in a manner analogous to the induced dipole derivative. In this connection, we discuss the extent to which the dipole and polarizability derivative descriptions alone constitute a satisfactory representation of the exact interaction and consider the possibility that a distributed multipole and multipole derivative model can furnish a more complete representation of the electrostatic interactions.

Molecular Multipole Expansion Treatment

The electrostatic properties of a molecule are determined by its interactions with external electric fields. The molecular dipole moments, dipole polarizabilities, and higher order dipole polarizabilities are determined by the interaction energies of the molecule with dipole fields, and the molecular dipole derivatives and all the dipole polarizability derivatives are determined by the interaction forces at nuclear sites with dipole fields. Other high-rank molecular multipoles, polarizabilities, and their derivatives are determined by the interactions of the molecule with the relevant multipole fields. Such molecular multipole properties are associated with the multipole expansion of the electronic charge distribution. They are exact when the molecule interacts with weak external fields. In fact, classical calculations based on molecular multipoles, multipole polarizabilities, multipole derivatives, and multipole polarizability derivatives can predict very accurate interaction energies and interaction forces as long as the electric fields are small.[3]

However, when a molecule interacts with an external charge distribution, the multipole expansion method, viz., the molecular multipole moments interacting with the multipole fields produced by that external charge distribution, has three major problems: divergence,[23,24] truncation, and penetration[25,26] errors. According to Stone's divergence theorem,[3] the divergence sphere for a small molecule is a sphere that contains all nuclear sites. If the external charge distribution is outside this sphere (convergence radius), the interaction energy between the molecular multipoles and the external charge distribution formally converges. In practical calculations, limited multipole moments are used, and therefore, truncation error can arise from the absence of high rank multipole moments. This error, as well as the divergence region, can be significantly reduced if distributed multipoles are used.[3] The last error comes from the penetration effects, which exist when the external charges are within the molecular electron density region. For the systems we study here, water and methane with external point charges, the point charges are located at hydrogen bond acceptor nuclear positions, which are outside the divergence sphere of the hydrogen donor molecule. Although DMA is a good representation of the molecular electron density $\rho(r)$, and a distributed polarizability is a good representation of the molecular linear response function $\chi(r,r')$, they do not suffice to calculate the interaction forces. For example, when a molecule interacts with a dipole field, the interaction forces at atomic sites depend only on the atomic point charges, but atomic charges in DMA are not uniquely defined. We know the interaction forces depend on $d\rho(r)/d\lambda$, but to our knowledge there is no applicable distributed model for $d\rho(r)/d\lambda$. Similarly, there is also no applicable distributed model for $d\Delta\rho(r)/d\lambda$ (a distributed polarizability derivative). Since in this paper we are particularly interested in the satisfactory description of interaction forces, we focus at this stage only on molecular properties. The following formalism and discussion serve as an introduction to and direct comparison with our subsequent charge density treatment.

All molecular multipole parameters are defined by Taylor expansions of the interaction energies and forces with respect to external multipole fields. For a homogeneous (i.e., dipole) electric field, we have

$$\begin{aligned} U &= U(0) + (\partial U/\partial V_\alpha)V_\alpha + \frac{1}{2}(\partial^2 U/\partial V_\alpha \partial V_\beta)V_\alpha V_\beta + \frac{1}{6}(\partial^3 U/\partial V_\alpha \partial V_\beta \partial V_\gamma)V_\alpha V_\beta V_\gamma + \cdots \\ &= U(0) + A_\alpha V_\alpha + \frac{1}{2}B_{\alpha\beta}V_\alpha V_\beta + \frac{1}{6}C_{\alpha\beta\gamma}V_\alpha V_\beta V_\gamma + \cdots \end{aligned} \quad (1)$$

where U is the molecular energy and V_α is the electrostatic potential derivative with respect to Cartesian coordinate component α (i.e., the negative of the electric field). In this article, the same index means summation, e.g., $(\partial U/\partial V_\alpha)V_\alpha = \sum_{\alpha=1}^{3}(\partial U/\partial V_\alpha)V_\alpha$, except where it is explicitly indicated. $A_\alpha = \partial U/\partial V_\alpha$ is the molecular dipole moment α component, $B_{\alpha\beta} = \partial^2 U/\partial V_\alpha \partial V_\beta$ is the negative molecular polarizability tensor $\alpha\beta$ component, $C_{\alpha\beta\gamma} = \partial^3 U/\partial V_\alpha \partial V_\beta \partial V_\gamma$ is the hyperpolarizability tensor $\alpha\beta\gamma$ component, and so on. If the applied field is a higher rank field (e.g., quadrupole), the coefficients *A*, *B*, and *C* are then the high rank multipole moment, polarizability, and hyperpolarizability, respectively (i.e., $A_{\alpha\beta}$ for $V_{\alpha\beta}$, $B_{\alpha\beta\alpha'\beta'}$ for $V_{\alpha\beta}V_{\alpha'\beta'}$, etc.). For the forces ($F = -\partial U/\partial\lambda$), we have

$$F^\lambda = -\partial U/\partial\lambda = -\partial U(0)/\partial\lambda - (\partial^2 U/\partial V_\alpha \partial\lambda)V_\alpha - \frac{1}{2}(\partial^3 U/\partial V_\alpha \partial V_\beta \partial\lambda)V_\alpha V_\beta - \frac{1}{6}(\partial^4 U/\partial V_\alpha \partial V_\beta \partial V_\gamma \partial\lambda)V_\alpha V_\beta V_\gamma + \cdots$$
$$= F_0^\lambda + A_\alpha^\lambda V_\alpha + \frac{1}{2}B_{\alpha\beta}^\lambda V_\alpha V_\beta + \frac{1}{6}C_{\alpha\beta\gamma}^\lambda V_\alpha V_\beta V_\gamma + \cdots \qquad (2)$$

where λ is the atomic Cartesian or internal coordinate. Therefore, the interaction forces are determined by all of the molecular dipole derivatives ($-A_\alpha^\lambda$), dipole polarizability derivatives ($B_{\alpha\beta}^\lambda$), and dipole hyperpolarizability derivatives ($-C_{\alpha\beta\gamma}^\lambda$). For high-rank multipole fields, all definitions are similar. Thus, the physical meaning of the parameters *A*, *B*, and *C* depends on the rank of the applied field; they are just the linear, quadratic, and cubic term coefficients in the Taylor expansion. We already noted[5] that the red-shifted and blue-shifted hydrogen-bond donor OH and CH bonds have different dipole derivative properties: parallel (for OH) and antiparallel (for CH) to the bond direction ($X \rightarrow H$, which is parallel to the local electric field of the acceptor). When the molecule is in a dipole field parallel to the bond, all of the observed structure and spectroscopic properties can be understood very clearly from the balance between the permanent and induced dipole derivatives.

For the systems for which we are presently interested in obtaining molecular multipole properties and checking the validity of the multipole expansion method (H_2O and CH_4), we have done four calculations, all on a model of the molecule interacting with a −0.5e point charge at distances from the origin at the O or C atom and along the OH or CH bond (the z direction) of 3 (a typical hydrogen-bond distance) to 20 Å. In this case, the electric fields are simple: the diagonal and some nonzero off-diagonal fields are

$$V_z = q/r^2,\ V_{zz} = q2/r^3,\ V_{zzz} = q6/r^4,\ V_{zzzz} = q24/r^5,\ V_{xx} = V_{yy} = -q/r^3,\ V_{xxxx} = V_{yyyy} = q9/r^5,\ V_{xxz} = V_{yyz} = -q3/r^4,\ V_{xxyy} = q3/r^5,\ V_{xxzz} = V_{yyzz} = -q12/r^5 \qquad (3)$$

The four calculations (with the −0.5e charge and the isolated equilibrium monomer structures) are:

1. Ab initio calculation of the molecule and point charge.
2. Ab initio calculation of the molecule with the full electric fields up to the hexadecapole field produced by the point charge, as given by eq 3.
3. Ab initio calculations of the molecule with only the diagonal electric field components, viz., V_z, V_{xx}, V_{yy}, V_{zz}, V_{zzz}, V_{xxxx}, V_{yyyy}, and V_{zzzz}.
4. Classical calculation using parameters (i.e., the *A*, *B*, and *C*) derived from the same electric fields as in 3.

Calculation 1 provides quantum-mechanical data for the molecule interacting with a point charge. Calculation 2 provides data based on the molecular multipole expansion method, the validity of which can be checked by comparing 2 with 1. The differences between calculations 2 and 3 show the influence of the off-diagonal electric field (V_{xxz}, V_{yyz}, V_{xxyy}, V_{xxzz}, and V_{yyzz}) contributions. The differences between calculations 3 and 4 show the cross-interaction contributions by the off-diagonal polarizabilities and their derivatives, which would not be included in 4, and the validity of the classical perturbation formula.

TABLE 1: Multipole Parameters for H_2O and CH_4

		H_2O		CH_4	
multipole[a]		energy[b]	force[c]	energy[b]	force[c]
dipole	A_z	0.5186	−0.2308	0.0	0.1812
	B_z	−6.8545	7.6969	−13.6905	9.8542
	C_z	−18.0	54.0	−25.0	49.5
quadrupole	A_{xx}	−5.5944	0.5366	−6.2586	0.3337
	A_{yy}	−3.9042	0.4750	−6.2586	0.3337
	A_{zz}	−3.5668	0.8765	−6.2586	1.5202
	B_{xx}	−21.8471	39.6294	−64.8251	−1.4971
	B_{yy}	−24.2471	39.8294	−64.8456	−1.4871
	B_{zz}	−24.1941	34.4706	−68.9535	−57.8738
	C_{xx}	−2000	500	−2744	−227.5
	C_{yy}	−1000	500	−2948	−157.0
	C_{zz}	−1000	−1500	−3383	−12875
octopole	A_{zzz}	1.3239	2.5673	1.0988	5.9634
	B_{zzz}	−384.1177	3970	1529	−392
	C_{zzz}	0.0	0.0	−613000	−1902500
hexadecapole	A_{xxxx}	−17.5539	2.2265	−41.9214	0.4159
	A_{yyyy}	−15.2747	1.8653	−41.9227	0.4159
	A_{zzzz}	−14.4153	7.9770	−41.2645	17.8965
	B_{xxxx}	−3471	390529	−18515	−2142
	B_{yyyy}	−3706	390294	−19952	−1972
	B_{zzzz}	−3706	391059	−23252	−18132
	C_{xxxx}	0.0	0.0	0	0
	C_{yyyy}	0	0	0	0
	C_{zzzz}	0	0	0	0

[a] General component in eqs 1 and 2. [b] *A*: multipole moment; −*B*: multipole polarizability; *C*: multipole hyperpolarizability. [c] $-A^\lambda$: multipole moment derivative; B^λ: multipole polarizability derivative; $-C^\lambda$: multipole hyperpolarizability derivative. Force on OH bond for H_2O and CH bond for CH_4.

All the calculations were done with Gaussian 98,[27] at the HF/6-311++G** level.

Calculations 1−3 are straightforward. In deriving all multipole moments, polarizabilities, and their derivatives up to hexadecapole, for simplicity only diagonal terms were considered. To determine the *A*, *B*, and *C* parameters, a total of 12 electric fields were applied: V_α, $V_{\alpha\alpha}$, $V_{\alpha\alpha\alpha}$, and $V_{\alpha\alpha\alpha\alpha}$ for $\alpha = x$, *y*, and *z*. From the analytically calculated energies *U* (eq 1) and forces F^λ (eq 2), all the parameters can be computed numerically. In these calculations, the applied fields were in the order of 10^{-3} a.u. for the dipole (D) and quadrupole (Q), 10^{-4} for the octopole (O), and 10^{-5} for the hexadecapole (H) fields. For a given α, the V_α are varied and the ab initio calculated energies (or forces) are fit to a Taylor expansion. The coefficient of the leading term is the molecular dipole moment, *A* (or the negative molecular dipole derivative, A^λ), the coefficient of the quadratic term is the negative polarizability tensor, *B* (or the polarizability derivative, B^λ), and the coefficient of the cubic term is the hyperpolarizability tensor, *C* (or the negative hyperpolarizability derivative, C^λ). When the applied fields are $V_{\alpha\alpha}$, $V_{\alpha\alpha\alpha}$, and $V_{\alpha\alpha\alpha\alpha}$, the *A*, *B*, and *C* parameters are for the quadrupole, octopole, and hexadecapole quantities, respectively. These quantities are listed in Table 1 for the H_2O and CH_4 molecules.

From this table and eqs 2 and 3, we see the following. The molecular dipole derivatives ($-A_z^\lambda$) for the OH (0.2308) and CH (−0.1812) bonds have opposite directions, respectively parallel to the OH bond (and resulting in a positive, or elongating, force) and antiparallel to the CH bond (and resulting

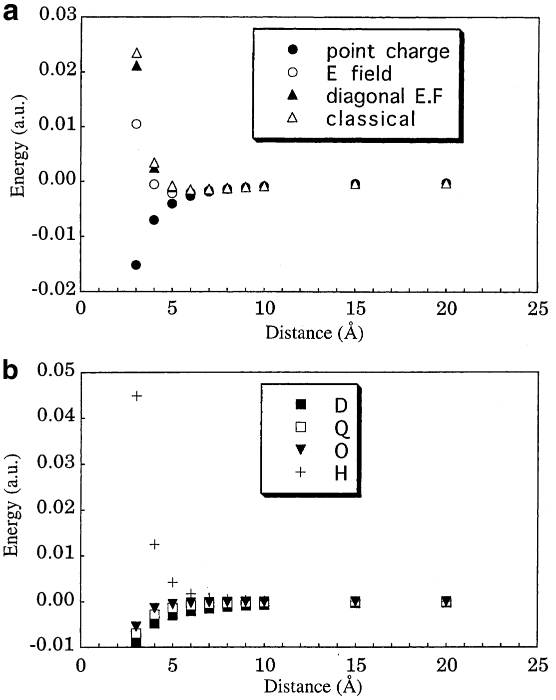

Figure 1. Interaction energies (in a.u.) of an H_2O molecule as a function of the distance (in Å) of a $-0.5e$ point charge from the O atom along an O−H direction. (a) Based on four calculations (see text): ab initio, point charge (1), ●; ab initio, full electric field (2), ○; ab initio, diagonal electric field (3), ▲; classical, diagonal electric field (4), △. (b) Based on four component fields in classical calculation: dipole (D), ■; quadrupole (Q), □; octopole (O), ▼; hexadecapole (H), +.

in a negative, or contracting, force). However, the induced dipole derivatives from the dipole polarizability derivatives (the B_z^λ terms), both being negative, result in positive, i.e., elongating, forces. For the quadrupole V_{zz} field, with similar negative parameters for OH (−0.8765) and CH (−1.5202) for the permanent quadrupole derivatives, both bonds experience negative (contracting) forces. However, from the induced quadrupole derivatives, the OH bond experiences a positive force, whereas the CH bond experiences a negative force. Therefore, when the molecule interacts with a quadrupole field, we can expect the bond length changes of OH and CH to have different features. We turn now to the application of these results to the specific molecule-point charge interactions.

Water. The variation of energy with distance of the point $-0.5e$ charge from the O atom along the O−H (z) axis is shown in Figure 1a for each of the four calculations. We see that when the distance is larger than 9 Å the interaction energies from all calculations are exactly the same. As the distance decreases, the energy from (ab initio) calculation 1 becomes increasingly negative, whereas those from the other calculations increasingly depart and below ~5 Å are going positive. The off-diagonal field contributions, comparing calculations 2 and 3, are quite large at short distances, whereas a comparison of calculations 3 and 4 shows that the cross-interactions are not significant.

More detailed information is provided by 4, which, since classical, can give the contributions from the individual D, Q, O, and H fields. These are shown in Figure 1b. Noting the signs of the V_α in eq 3, we see that permanent interaction energies for D (with parameter 0.5186) and O (with parameter 1.3239) are negative Although the Q_{zz} (i.e., A_{zz} for energy) component has a positive interaction energy, the negative contributions from Q_{xx} (A_{xx}) and Q_{yy} (A_{yy}) (since V_{xx} and V_{yy} are positive) overcome Q_{zz}, resulting in a total negative Q interaction energy. The induction energies for D, Q, and O are negative, so we have a total negative interaction energy. It is interesting that the D + Q energy is very close to the ab initio energy from 1. All diagonal H components have positive interaction energy. At large distances, this energy contribution is minimal, but at short distances, it is much larger than the other interaction energies, resulting in the wrong total interaction energy trend and dominating the whole interaction energy. This behavior is clear evidence of the breakdown of the multipole expansion method at short (comparable to hydrogen-bond) distances.

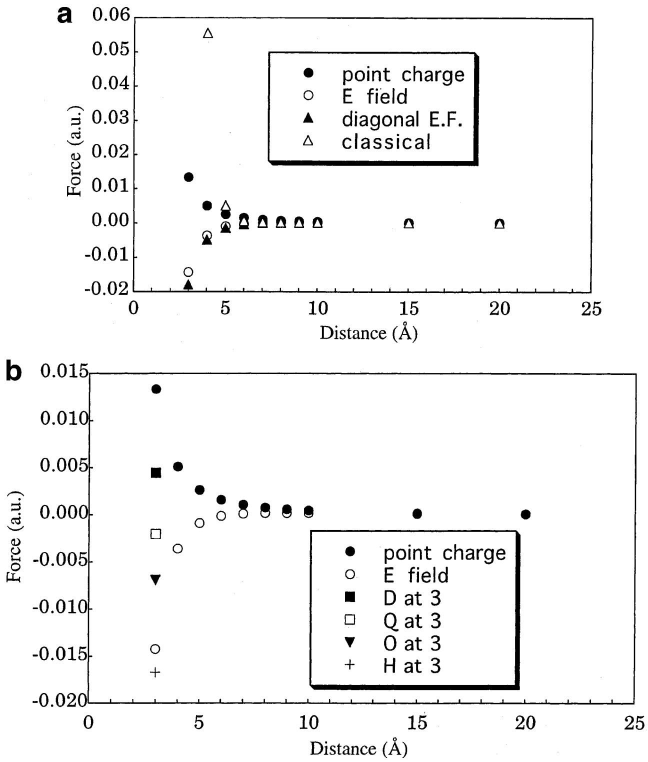

Figure 2. Interaction forces on an H_2O molecule OH bond (as in Figure 1). (a) Based on four calculations (see Figure 1 caption). (b) Full calculations 1 and 2, plus ab initio calculation 2 for individual fields at 3 Å.

The variation of initial force with distance for each of the four calculations is shown in Figure 2a. At distances larger than ~7 Å, all calculations give similar results, ~0. At 5 Å, the calculated forces start to diverge, with the wrong trend from the multipole expansion calculations: forces from 1 keep going up moderately, forces from 2 and 3 keep going down, and forces from 4 go up explosively. From the molecular multipole derivatives, we can see that the dipole derivative gives a positive force contribution. Since $V_{zz} = -2V_{xx} = -2V_{yy}$, the magnitude of $2dQ_{zz}/dr$ (i.e., A_{zz} for force) is larger than $dQ_{xx}/dr + dQ_{yy}/dr$, and therefore, we have a total negative force from the permanent quadrupole derivative. The O and H permanent derivatives also contribute negative forces, so that the total force from the permanent multipole derivatives depends on the balance between the positive force from D and the negative force from Q + O + H. This analysis is consistent with the trends in 2 and 3. The separate calculation 2 forces from D, Q, O, and H are shown in Figure 2b at 3 Å and compared to the total 2 and total 1, qualitatively confirming this mechanism (the small quantitative difference is due to the absence of off-diagonal and cross-term interactions in the sum D + Q + O + H). The negative rather than the positive calculation 1 forces must be mainly attributed, as in the case of the energy, to the distorting influence of the H field at very short distances, again revealing the basic inadequacy of the multipole expansion approach. The

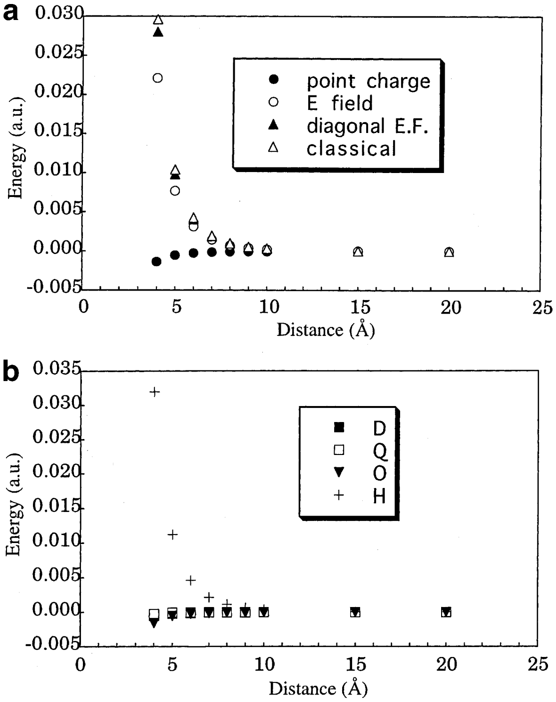

Figure 3. Interaction energies (in a.u.) of a CH_4 molecule as a function of distance (in Å) of a $-0.5e$ point charge from the C atom along a C−H direction. (a) Based on four calculations (see text): ab initio, point charge (1), ●; ab initio, full electric field (2), ○; ab initio, diagonal electric field (3), ▲; classical, diagonal electric field (4), △. (b) Based on four component fields in classical calculation: dipole (D), ■; quadrupole (Q), □; octopole (O), ▼; hexadecapole (H), +.

source of the huge positive force in the classical calculation (at a value of 1.045 at 3 Å, orders of magnitude off the scale of Figure 2a) also resides in the H term, which contributes 1.032 au at 3 Å. Thus, the positive contributions from the induced multipole derivatives are not representative of the polarization when the electric field is large, and are particularly sensitive to the H component at distances where in effect the charge begins to penetrate the molecular charge distribution.

Methane. The energy variations with distance for calculations 1−4 are shown in Figure 3a. Again we see that the multipole expansion calculation has the wrong trend: the energies from 1 become more negative as the distance decreases, but all of the other energies keep going up. Since the differences between 2, 3, and 4 are small, we can base our discussion on 4. In Figure 3b, the contributions from D, Q, O, and H are shown. The wrong trend again comes from the H contribution. Because there is no dipole moment, and the Q_{xx}, and Q_{yy} components cancel the Q_{zz} contribution, the contributions from the permanent D and Q are zero. Similar to water, O has a negative but H has a positive contribution from the permanent part, the balance between O and H determining the total interaction energy from the permanent multipoles. All induction contributions are negative, though small, the trend from D + Q + O being correct at short distances. The permanent H contribution dominates the interaction energy and gives the wrong results, very similar to the case of the water interaction energy.

The variation of force on the CH bond is shown in Figure 4a. Calculation 1 shows that this interaction force is negative at distances larger than 6 Å, and when the distance decreases the interaction force increases and becomes positive. From the figure, we can see that any multipole method cannot reproduce such a turning feature: even for the dipole part, at 4 Å distance the contribution from the induced dipole derivative cannot overcome the contribution from the permanent dipole derivative.

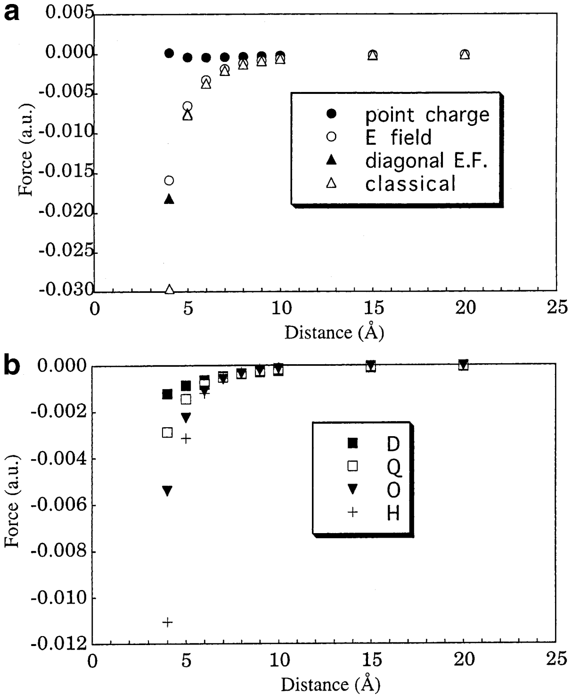

Figure 4. Forces on an CH_4 molecule CH bond (as in Figure 3). (a) Based on four calculations (see Figure 3 caption). (b) Based on four component fields in classical calculation (see Figure 3 caption).

In addition, all Q, O, and H induced multipole derivatives have negative force contributions. The individual 4 contributions from D, Q, O, and H are shown in Figure 4b.

All calculations, whether for red- or blue-shifted groups, show that at large distances the interaction between a point charge and a molecule can be modeled by the multipole expansion method, the high-order multipole contributions are small, and the interaction is dominated by the dipole term (or first nonzero multipole term). When the distance becomes smaller, the high-order multipoles play more important roles. Within the hydrogen-bond region, the high-order multipole contributions are too large to provide a correct description of the electrostatic interaction.

Charge Density Treatment

As we have seen, the molecular multipole expansion method fails in short distance interactions, such as the hydrogen bond, and a distributed multipole treatment still lacks the addition of distributed multipole derivatives that would enable a satisfactory treatment of interaction forces. A more basic theory is desirable to gain insight into this problem, and we have therefore explored an approach based on the influence of the charge density properties of a molecule on its interaction with an external multipole distribution.

In density functional theory, the interaction energy of an N electron system with an external perturbing electrostatic potential $V(\vec{r})$ is[28−30]

$$U(V(\vec{r})) = \int\left[\frac{\delta U(V(\vec{r}))}{\delta V(\vec{r})}\right]V(\vec{r})\,\mathrm{d}\vec{r} + \frac{1}{2}\int\int\frac{\delta^2 U(V(\vec{r}))}{\delta V(\vec{r})\delta V(\vec{r}\,')}\,V(\vec{r})V(\vec{r}\,')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' + \frac{1}{6}\int\int\int\frac{\delta^3 U(V(\vec{r}))}{\delta V(\vec{r})\delta V(\vec{r}\,')\delta V(\vec{r}\,'')}\,V(\vec{r})V(\vec{r}\,')V(\vec{r}\,'')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,'\,\mathrm{d}\vec{r}\,'' + \cdots \quad (4)$$

where

$$\frac{\delta U(V(\vec r))}{\delta V(\vec r)} = \rho(\vec r) \tag{5}$$

is the electron density,

$$\frac{\delta^2 U(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')} = \chi(\vec r,\vec r\,') \tag{6}$$

is the linear response function,

$$\frac{\delta^3 U(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')\delta V(\vec r\,'')} = \gamma(\vec r,\vec r\,',\vec r\,'') \tag{7}$$

is the quadratic response function, and so on. From eq 5, we have

$$\frac{\delta^2 U(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')} = \frac{\delta \rho(\vec r)}{\delta V(\vec r\,')}$$

and therefore

$$\Delta\rho_1(\vec r) = \int \frac{\delta\rho(\vec r)}{\delta V(\vec r\,')} V(\vec r\,')\,\mathrm{d}\vec r\,' = \int \chi(\vec r,\vec r\,')V(\vec r\,')\,\mathrm{d}\vec r\,' \tag{8}$$

which is the induced electron density from the linear response function with the perturbation $V(\vec r)$. Similarly,

$$\Delta\rho_2(\vec r) = \int\!\!\int \gamma(\vec r,\vec r\,',\vec r\,'')V(\vec r\,')V(\vec r\,'')\,\mathrm{d}\vec r\,'\,\mathrm{d}\vec r\,'' \tag{9}$$

is from the quadratic response function, and so on.

If the perturbations are from some external distributed point multipoles, $M_{ka}(\vec R_k)$ (following the Applequist notation[31]), all multipole moment components can be put in a one-dimensional array, $a = 0$ for the point charge, $a = 1-3$ for the dipole, $a = 4-9$ for the quadrupole, $a = 10-19$ for the octopole, $a = 20-34$ for the hexadecapole, and so on. For an electrostatic potential $V(\vec r)$ from M_k with its related T tensor,[32] we have $V_k(\vec r) = \sum_a M_{ka}T_a(\vec R_k,\vec r)$, and the total electrostatic potential from all point multipoles is $V(\vec r) = \sum_{k,a} M_{ka}T_a(\vec R_k,\vec r)$. Inserting these into eq 4, we have

$$\begin{aligned} U(V(\vec r)) &= \int\left[\frac{\delta U(V(\vec r))}{\delta V(\vec r)}\right] M_{ka}T_{ka}(\vec r)\,\mathrm{d}\vec r + \\ &\quad \frac{1}{2}\int\!\!\int \frac{\delta^2 U(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')} M_{ka}T_{ka}(\vec r)M_{lb}T_{lb}(\vec r\,')\,\mathrm{d}\vec r\,\mathrm{d}\vec r\,' + \cdots \\ &= A_{ka}M_{ka} + \frac{1}{2}B_{klab}M_{ka}M_{lb} + \\ &\quad \frac{1}{6}C_{klmabc}M_{ka}M_{lb}M_{mc} + \cdots \end{aligned} \tag{10}$$

where the coefficients are defined as

$$A_{ka} = \int\left[\frac{\delta U(V(\vec r))}{\delta V(\vec r)}\right] T_{ka}(\vec r)\,\mathrm{d}\vec r = \int \rho_0(\vec r)T_{ka}(\vec r)\,\mathrm{d}\vec r \tag{11}$$

$$\begin{aligned} B_{klab} &= \int\!\!\int \frac{\delta^2 U(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')} T_{ka}(\vec r)T_{lb}(\vec r\,')\,\mathrm{d}\vec r\,\mathrm{d}\vec r\,' = \\ &\quad \int\!\!\int \chi(\vec r,\vec r\,')T_{ka}(\vec r)T_{lb}(\vec r\,')\,\mathrm{d}\vec r\,\mathrm{d}\vec r\,' \end{aligned} \tag{12}$$

$$\begin{aligned} C_{klmabc} &= \int\!\!\int\!\!\int \frac{\delta^3 U(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')\delta V(\vec r\,'')} \times \\ &\quad T_{ka}(\vec r)T_{lb}(\vec r\,')T_{mc}(\vec r\,'')\,\mathrm{d}\vec r\,\mathrm{d}\vec r\,'\,\mathrm{d}\vec r\,'' \\ &= \int\!\!\int\!\!\int \gamma(\vec r,\vec r\,',\vec r\,'')T_{ka}(\vec r)T_{lb}(\vec r\,')T_{mc}(\vec r\,'') \times \\ &\quad \mathrm{d}\vec r\,\mathrm{d}\vec r\,'\,\mathrm{d}\vec r\,'' \end{aligned} \tag{13}$$

The high-order coefficients are defined similarly.

When only point charges are involved, we have $M_{k0} = q_k$, $T_{k0} = 1/|\vec r - \vec R_k|$, and $A_{k0} = \int[\delta U(V(\vec r))/\delta V(\vec r)]T_{k0}(\vec r)\,\mathrm{d}\vec r = \int\rho_0(\vec r)/|\vec r - \vec R_k|\,\mathrm{d}\vec r$, which is the electrostatic potential at $\vec R_k$ from the permanent electron density ρ_0, and $A_{k0}q_k$ is the interaction energy between q_k and ρ_0. The B coefficient is $B_{kl00} = \int\!\int[\delta^2U(V(\vec r))/\delta V(\vec r)\delta V(\vec r\,')]\,T_{k0}(\vec r)T_{l0}(\vec r)\,\mathrm{d}\vec r\,\mathrm{d}\vec r\,'$, and since $\Delta\rho_1(\vec r) = \int\!\int[\delta^2U(V(\vec r))/\delta V(\vec r)\delta V(\vec r\,')]\,T_{l0}(\vec r\,')\,\mathrm{d}\vec r\,' = \int\!\int\chi(\vec r,\vec r\,')/|\vec r - \vec R_l|\,\mathrm{d}\vec r\,'$ is the induced electron density from a unit point charge at location $\vec R_l$, we have $B_{kl00} = \int\Delta\rho_1(\vec r)/|\vec r - \vec R_k|\,\mathrm{d}\vec r$, which is the electrostatic potential at $\vec R_k$ from the electron density induced by a unit point charge at $\vec R_l$. Therefore, 1/2 $B_{kk00}q_kq_k$ is the induction energy between point charge q_k and the system electron density $\rho_0(\vec r)$, and 1/2 $B_{kl00}q_kq_l$ is the cross-induction energy, or the interaction energy between the induced electron density $\Delta\rho_1(\vec r)$ from point charge q_k and the point charge q_l, and vice versa.

Let λ be a parameter like a nuclear Cartesian or an internal coordinate; then for the interaction force ($F^\lambda = -\partial U/\partial\lambda$), the analogue to eq 2 becomes

$$\begin{aligned} F^\lambda(V(\vec r)) &= \int\left[\frac{\delta F^\lambda(V(\vec r))}{\delta V(\vec r)}\right] V(\vec r)\,\mathrm{d}\vec r + \\ &\quad \frac{1}{2}\int\!\!\int \frac{\delta^2 F^\lambda(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')} V(\vec r)V(\vec r\,')\,\mathrm{d}\vec r\,\mathrm{d}\vec r\,' + \\ &\quad \frac{1}{6}\int\!\!\int\!\!\int \frac{\delta^3 F^\lambda(\mathbf{V}(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')\delta V(\vec r\,'')} \\ &\quad V(\vec r)V(\vec r\,')V(\vec r\,'')\,\mathrm{d}\vec r\,\mathrm{d}\vec r\,'\,\mathrm{d}\vec r\,'' + \cdots \end{aligned} \tag{14}$$

where

$$\frac{\delta F^\lambda(V(\vec r))}{\delta V(\vec r)} = -\frac{\delta \mathrm{d}U(V(\vec r))}{\delta V(\vec r)\mathrm{d}\lambda} = -\frac{\mathrm{d}\rho(\vec r)}{\mathrm{d}\lambda} = -\rho^\lambda(\vec r) \tag{15}$$

is the negative electron density derivative,

$$\frac{\delta^2 F^\lambda(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')} = -\frac{\delta^2 \mathrm{d}U(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')\mathrm{d}\lambda} = -\frac{\mathrm{d}\chi(\vec r,\vec r\,')}{\mathrm{d}\lambda} = -\chi^\lambda(\vec r,\vec r\,') \tag{16}$$

is the negative linear response function derivative, and

$$\frac{\delta^3 F^\lambda(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')\delta V(\vec r\,'')} = -\frac{\delta^3 \mathrm{d}U(V(\vec r))}{\delta V(\vec r)\delta V(\vec r\,')\delta V(\vec r\,'')\mathrm{d}\lambda} = -\frac{\mathrm{d}\gamma(\vec r,\vec r\,',\vec r\,'')}{\mathrm{d}\lambda} = -\gamma^\lambda(\vec r,\vec r\,',\vec r\,'') \tag{17}$$

is the negative quadratic response function derivative. We also have

$$\Delta\rho_1{}^\lambda(\vec r) = \int \frac{\delta\rho^\lambda(\vec r)}{\delta V(\vec r\,')} V(\vec r\,')\,\mathrm{d}\vec r\,' = \int \chi^\lambda(\vec r,\vec r\,')V(\vec r\,')\,\mathrm{d}\vec r\,' \tag{18}$$

which is the induced electron density derivative from the linear response function derivative, and

$$\Delta\rho_2{}^{\lambda}(\vec{r}) = \int\int \gamma^{\lambda}(\vec{r},\vec{r}',\vec{r}'')V(\vec{r}')V(\vec{r}'')\,\mathrm{d}\vec{r}'\,\mathrm{d}\vec{r}'' \quad (19)$$

which is the induced electron density derivative from the quadratic response function derivative. For external distributed point multipoles $M_{ka}(\vec{R}_k)$

$$\begin{aligned} F^{\lambda}(V(\vec{r})) = {} & \int\left[\frac{\delta F^{\lambda}(V(\vec{r}))}{\delta V(\vec{r})}\right] M_{ka}T_{ka}(\vec{r})\,\mathrm{d}\vec{r} + \\ & \frac{1}{2}\int\int \frac{\delta^2 F^{\lambda}(V(\vec{r}))}{\delta V(\vec{r})\delta V(\vec{r}')} M_{ka}T_{ka}(\vec{r})M_{lb}T_{lb}(\vec{r}')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}' + \cdots \\ = {} & A^{\lambda}_{ka}M_{ka} + \frac{1}{2}B^{\lambda}_{klab}M_{ka}M_{lb} + \\ & \frac{1}{6}C^{\lambda}_{klmabc}M_{ka}M_{lb}M_{mc} + \cdots \end{aligned} \quad (20)$$

where

$$A^{\lambda}_{ka} = \int\left[\frac{\delta F^{\lambda}(V(\vec{r}))}{\delta V(\vec{r})}\right]T_{ka}(\vec{r})\,\mathrm{d}\vec{r} = -\int \rho^{\lambda}(\vec{r})T_{ka}(\vec{r})\,\mathrm{d}\vec{r} \quad (21)$$

$$\begin{aligned} B^{\lambda}_{klab} = {} & \int\int \frac{\delta^2 F^{\lambda}(V(\vec{r}))}{\delta V(\vec{r})\delta V(\vec{r}')} T_{ka}(\vec{r})T_{lb}(\vec{r}')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}' = \\ & -\int\int \chi^{\lambda}(\vec{r},\vec{r}'')T_{ka}(\vec{r})T_{lb}(\vec{r}')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}' \end{aligned} \quad (22)$$

$$\begin{aligned} C^{\lambda}_{klmabc} = {} & \int\int\int \frac{\delta^3 F^{\lambda}(V(\vec{r}))}{\delta V(\vec{r})\delta V(\vec{r}')\delta V(\vec{r}'')} \times \\ & T_{ka}(\vec{r})T_{lb}(\vec{r}')T_{mc}(\vec{r}'')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}'\,\mathrm{d}\vec{r}'' \\ = {} & -\int\int\int \gamma^{\lambda}(\vec{r},\vec{r}',\vec{r}'')T_{ka}(\vec{r})T_{lb}(\vec{r}')T_{mc}(\vec{r}'') \\ & \mathrm{d}\vec{r}\,\mathrm{d}\vec{r}'\,\mathrm{d}\vec{r}'' \end{aligned} \quad (23)$$

In this paper, we study the interaction between point charges and a molecule, so eqs 10 and 20 become

$$U(q(\vec{R}_k)) = A_k q_k + \frac{1}{2}B_{kl}q_k q_l + \frac{1}{6}C_{klm}q_k q_l q_m + \cdots \quad (24)$$

$$F^{\lambda}(q(\vec{R}_k)) = A^{\lambda}_k q_k + \frac{1}{2}B^{\lambda}_{kl}q_k q_l + \frac{1}{6}C^{\lambda}_{klm}q_k q_l q_m + \cdots \quad (25)$$

Because the $\rho_0(\vec{r})$, $\chi(\vec{r},\vec{r}')$, $\gamma(\vec{r},\vec{r}',\vec{r}'')$, $\rho_0{}^{\lambda}(\vec{r})$, $\chi^{\lambda}(\vec{r},\vec{r}')$, and $\gamma^{\lambda}(\vec{r},\vec{r}',\vec{r}'')$ are all properties of the isolated molecule, for given external point multipole distributions (at $\vec{R}_k$) the *A*, *B*, and *C* (eqs 11−13*)* and A^{λ}, B^{λ}, and C^{λ} (eqs 21−23) have very clear physical meanings and could be calculated if the above six molecular functions were known, and the molecular interaction energies and interaction forces could be predicted accordingly. In the absence of full knowledge of these quantities, however, we can obtain the *A*, *B*, and *C* directly. We can see the similarities between eqs 1 and 2 and eqs 24 and 25. The same symbols *A*, *B*, and *C* are used since they are the linear, quadratic, and cubic Taylor expansion coefficients, although the actual physical meanings of *A*, *B*, and *C* depend on the external electric fields (in the first case) or the external point multipole distributions (in the second case). They both can be determined from ab initio calculations. Because no multipole expansion is involved in the charge density treatment, there are no divergence, truncation, or penetration problems. In ab initio calculations, the contributions to the interaction energies and forces from nuclear charges are included, and since no polarization exists for a nuclear charge, nuclear charge effects will appear only in the linear term:

$$U(q(\vec{R}_k)) = \sum_{i=1}^{N} \frac{Z_i q_k}{|\vec{R}_k - \vec{R}_i|} = A^{Z}_k q_k \quad (26)$$

$$\vec{\mathrm{F}}^{i}(q(\vec{R}_k)) = \frac{Z_i q_k(\vec{R}_i - \vec{R}_k)}{|\vec{R}_k - \vec{R}_i|^3} = \vec{A}^{Z}_k q_k \quad (27)$$

where the Z_i's are the N nuclear charges. The interaction energy among external charges is not included in our definition (but is included in Gaussian ab initio calculations), since we define the cross-interaction between point charges by polarization and not by the direct interaction.

As a first step, we compute all *A*, *B*, and *C* coefficients from eqs 24 and 25 for some specific interesting configurations. We model the electrostatic interactions in $H_2O\cdots H_2O$ and $CH_4\cdots FH$ dimers by hydrogen donor molecules together with acceptor point charges located at the second water atomic sites and at the FH sites, with the ab initio intermolecular geometry, respectively. The monomer structures are the isolated minimum energy structures. When there is more than one point charge, there are cross-interactions among the sites. Such a nonadditive effect comes from polarization, the induced charge distribution from one site interacting with point charges at other sites. In this study, only the cross-interactions are considered which involve two sites, the high-order cross-interactions involving more then two sites not being included. The H_2O calculations were done with Gaussian 98,[27] the CH_4 calculations with GAMESS.[33]

Water Dimer. Similar to the electric field method, all parameters were derived by numerical calculations. For parameters related to the acceptor O atom site, the point charge was put on the O site and from ab initio calculated energies and forces the *A*, *B*, and *C* parameters were derived. When the two point charges were put on the O and H atoms, the cross-terms for these atoms could be derived, the HH cross-terms being derived in the same way.

The calculated parameters for each site as well as the cross-interaction terms are listed in Table 2. The *A* parameter is simply the electrostatic potential from the permanent charge distribution; the *B* parameter is related to the electrostatic potential from the induced charge distribution. The difference between the parameters for the O and H sites reflects the distance effect. The parameters for the OH bond force are very different: *A* being much larger than *B* means that the interaction with the charge density derivative is the large and dominating interaction force. Since the charge at O in the hydrogen bond is negative, the interaction force is positive and this contributes to bond elongation. (The counteracting force of the positive H atom interactions is not large enough to overcome the elongating force from the O atom, nor in the actual dimer does the exchange-repulsion contracting force from the O atom counterbalance the net electrostatic elongating interaction.)

Using these parameters with an O (potential-derived) charge of −0.8196e, the ab initio and classical calculated values of the energy are listed in Table 3 and the respective OH forces in Table 4. The classical calculation provides the different interaction energy components and thus gives more detailed information: the permanent charge interaction energies are the leading term, the diagonal induction energies are all negative, whereas the contributions from the O and H atom cross-interactions are positive. The excellent agreement of the classical with ab initio results is evident (the calculation up to quadratic terms being best). The OH bond interaction force is dominated by the permanent charge derivatives, all of the induction contributions

TABLE 2: Charge Density Expansion Parameters for H_2O[a]

	energy				force[c]			
parameter[b]	O[d]	H[d]	OH[e]	HH[e]	O[d]	H[d]	OH[e]	HH[e]
A	0.02714	0.015475			−0.4268	−0.3387		
B	−0.01234	−0.005237	−0.00787 0.56174[f]	−0.00490 0.35027[f]	−0.004083	−0.01587	−0.0132	−0.01829
C	−0.0043	−0.00099			0.03555	0.01245		

[a] Based on point charges located at hydrogen-bond acceptor positions. [b] In eqs 24 and 25. [c] Force on the OH bond (to be multiplied by 10^{-2}). [d] Diagonal terms in the interaction. [e] Cross-interaction terms involving these two atoms. [f] Point charge to point charge self-interaction.

TABLE 3: Water Energies:[a] Calculated Classical Components[b] Based on Charge Density Properties Compared to ab Initio

component	O atom	H atom	total 1[c]	total 2[d]
linear	−0.02224	0.00634	−0.00956	
quadratic				
induction	−0.00414	−0.00044	−0.00502	
cross[e]	0.00446[f]	−0.31852[g]	−0.31406	
total[h]			−0.32864	−76.38206
cubic				
induction	0.00040	−0.00001	0.00038	
cross[i]			−0.00056	
total[j]			−0.32883	−76.38226
ab initio				−76.38206

[a] Water molecule interacting with three point charges (−0.8196e, 0.4098e, and 0.4098e) located at hydrogen-bond acceptor positions, in a.u. [b] Based on eq 24. [c] Interaction energies only. [d] Interaction plus isolated monomer energies. [e] Includes all cross-terms plus the self-energy of the point charge interactions. [f] All cross interactions. [g] Total point charge to point charge interaction energy. [h] Linear + quadratic terms. [i] Includes all cross-terms. [j] Linear + quadratic + cubic terms.

TABLE 4: Water OH Forces:[a] Calculated Classical Components[b] Based on Charge Density Properties Compared to ab Initio

component	O atom	H atom	total
linear	3.4983	−1.3881	0.7221
quadratic			
induction	−0.0137	−0.0133	−0.0403
cross[c]			0.0581
total[d]			0.7398
cubic			
induction	−0.0326	0.0014	−0.0298
cross[c]			0.0552
total[e]			0.7653
ab initio			0.7383

[a] Water molecule interacting with three point charges (−0.8196e, 0.4098e, and 0.4098e) located at hydrogen-bond acceptor positions, in a.u. (to be multiplied by 10^{-3}). [b] Based on eq 25. [c] Includes all cross-terms. [d] Linear + quadratic terms. [e] Linear + quadratic + cubic terms.

TABLE 5: Charge Density Expansion Parameters for CH_4[a]

	energy[c]			force[c]		
parameter[b]	F[d]	H[d]	FH[e]	F[d]	H[d]	FH[e]
A	0.09524	0.04094		0.16861	0.1463	
B	−0.58988	−0.23990	−0.37560	0.71487	0.2647	0.4347
C	−0.1098	−0.0245		0.2392	0.0577	

[a] Based on point charges located at positions of F and H atoms. [b] In eqs 24 and 25. [c] In a.u. (to be multiplied by 10^{-2}). [d] Diagonal terms in the interaction. [e] Cross-interaction terms involving these two atoms.

TABLE 6: CH_4 Energies:[a] Calculated Classical Components[b] Based on Charge Density Properties Compared to ab Initio

component	F atom	H atom	total 1[c]	total 2[e]
linear	−0.44764	0.19241	−0.25523	
quadratic				
induction	−0.65152	−0.26497	−0.91649	
cross	0.82970		0.82970	
total			−0.34203	
cubic				
induction	0.01899	−0.00424	0.01475	
cross			−0.01360	
total[d]			−0.34088	−40.20951
ab initio				−40.20951

[a] CH_4 molecule interacting with two point charges (−0.47e and 0.47e) located at F and H positions, in a.u. (to be multiplied by 10^{-3}). [b] Based on eq 24. [c] Interaction energies only. [d] Includes all terms. [e] Interaction plus isolated monomer energies (not to be multiplied by 10^{-3}).

TABLE 7: CH_4 CH Forces:[a] Calculated Classical Components[b] Based on Charge Density Properties Compared to ab Initio

component	F atom	H atom	total
linear	−0.79248	0.68762	−0.10486
quadratic			
induction	0.78958	0.29236	1.08194
cross[c]	−0.96035		−0.96035
total[d]			0.016733
cubic			
induction	−0.04139	0.00998	−0.03141
cross[c]			0.02736
total[e]			0.01268
total[f]			0.01271
ab initio			0.01240

[a] CH_4 molecule interacting with two point charges (−0.47e and 0.47e) located at F and H positions, in a.u. (to be multiplied by 10^{-3}). [b] Based on eq 25. [c] Includes all cross-terms. [d] Linear + quadratic terms. [e] Linear + quadratic + cubic terms. [f] Calculated plus ab initio isolated molecule CH bond force.

being relatively small. Again we see that the classical calculation can very accurately reproduce the ab initio value, with the quadratic treatment giving best agreement.

Methane-FH. The charge density expansion parameters are listed in Table 5. For the energy, and different from the water case, the diagonal *B* parameters are large, indicating that CH_4 is much more easily polarized. The off-diagonal *B* parameter is negative, so we have a positive cross-interaction energy. We can see from this that all interactions are important. For the force parameters, the linear parameter *A* has an opposite sign to that of water, indicating that a negative point charge causes a contracting force. The quadratic parameter *B* shows that the induction interaction always causes an elongating force. The net force will be the balance between these. This is exactly the same as CH_4 in a dipole field. The agreement of the classical and ab initio calculations of the energy and force with (potential derived) point charges −0.47e (F) and 0.47e (H) are given in Tables 6 and 7 and are seen, as expected, to be excellent. (We have seen in the formic acid dimer[15] that both positive and negative electrostatic C−H forces can occur, and because this net result is generally small and the exchange-repulsive interaction always contributes a generally large negative force, the total initial force in an actual hydrogen bond leads to contraction and a resulting blue shift.)

Discussion

We have seen that, at hydrogen-bonded distances, the molecular multipole expansion fails to account for electrostatic interaction energies and forces, particularly as higher order multipoles are included. Stone and Alderton have given a very detailed analysis of convergence properties of molecular and distributed multipoles. [34] Another perspective on this is gained by comparing the relative magnitudes of these terms. For the point charge, we can see (eq 3) that$V_{zzzz}/V_{zzz} = 4/r$, $V_{zzzz}/V_{zz} = 12/r^2$, and $V_{zzzz}/V_z = 24/r^3$. For water, we have from the multipoles (A_α in Table 1) $M_{zzzz} = -14.4$, $M_{zzz} = 1.3$, $M_{zz} = 3.6$, and $M_z = 0.5$. Since the ratio of the H interaction energy to others is $U(\mathrm{H})/U(\mathrm{O}) = V_{zzzz}M_{zzzz}/V_{zzz}M_{zzz} = 44.3/r$, $U(\mathrm{H})/U(\mathrm{Q}) = 48/r^2$, and $U(\mathrm{H})/U(\mathrm{D}) = 691/r^3$, and the hydrogen bond $r \sim 3$ Å $= 5.7$ bohr, we find that $U(\mathrm{H})/U(\mathrm{O}) = 7.8$, $U(\mathrm{H})/U(\mathrm{Q}) = 1.5$, and $U(\mathrm{H})/U(\mathrm{D}) = 3.7$. Obviously these ratios are too large, and the expansion method does not apply. For CH_4, there is no dipole moment, the quadrupole makes no contribution, and with $M_{zzz} = 1.1$, $M_{zzzz} = -41.3$, and the hydrogen bond r being ~ 4 Å, the ratio $U(\mathrm{H})/U(\mathrm{O}) = 19.9$. This is also too large, and the expansion breaks down.

The interaction forces depend on molecular multipole derivatives, which show convergence properties similar to those of the multipoles. Thus, for the water OH bond force, with the field ratios $V_{zzzz}/V_z = 24/r^3$ and $V_{zzz}/V_z = 6/r^2$, and the derivative ratios $M^\lambda_{zzzz}/M^\lambda_z = 34.7$ and $M^\lambda_{zzz}/M^\lambda_z = 11.1$, the ratio of interaction forces is $F(\mathrm{H})/F(\mathrm{D}) = V_{zzzz}M^\lambda_{zzzz}/V_zM^\lambda_z = (9.41/r)^3$ and $F(\mathrm{O})/F(\mathrm{D}) = V_{zzz}M^\lambda_{zzz}/V_zM^\lambda_z = (8.16/r)^2$. For a point charge at the hydrogen bond distance $r \sim 3$ Å $= 5.7$ bohr, the contributions from the hexadecapole and octopole derivatives are much larger than that from the dipole derivative, resulting in a wrong interaction force. For the CH bond in CH_4, $M^\lambda_{zzzz}/M^\lambda_z = 98.8$, $M^\lambda_{zzz}/M^\lambda_z = 32.9$, and $M^\lambda_{zz}/M^\lambda_z = 8.4$, and we find that $F(\mathrm{H})/F(\mathrm{D}) = (13.3/r)^3$ and $F(\mathrm{O})/F(\mathrm{D}) = (14.0/r)^2$. At $r \sim 4$ Å $= 7.6$ bohr, the interaction force ratio of hexadecapole and octopole to dipole is also much larger than 1. Since the convergence radii of H_2O (OH bond length) and CH_4 (CH bond length) are smaller than the hydrogen bond distances for these systems, the discrepancies from ab initio must come from truncation and penetration errors.

It is interesting that, although at the hydrogen-bonding distance the high-order multipole expansion does not work, the low-order multipoles usually give a correct trend and a good value. For example, we show in Figure 5a that the D + Q multipole description of the water energy is very close to the ab initio results. In the case of the OH interaction force, Figure 5b, although the trend is correct, even the D term (let alone D + Q) does not match the ab initio value; however, it may not be difficult to adjust the polarization parameter to fit the ab initio force. For CH_4, the D and Q terms are zero, but it is interesting that the octopole can roughly reproduce the ab initio interaction energy (Figure 6a). For the CH force (Figure 6b), however, the trends from all terms are incorrect; a stronger induced dipole derivative would be needed to reproduce the ab initio force. Clearly, each molecular system has its own characteristics with respect to such possible approximations.

Our energy results are consistent with previous studies.[21,25,26] For example, the molecular multipole divergence in intermolecular interactions was reported by Fowler and Buckingham,[21] with a common acceptance that distributed multisite multipoles can improve the convergence of the molecular electrostatic potential (MEP). Stone et al.[34] showed that the magnitudes of multipoles at each site converge (i.e., decrease) very quickly by the DMA method, which then improves the MEP convergence dramatically. We can see from our results that this is

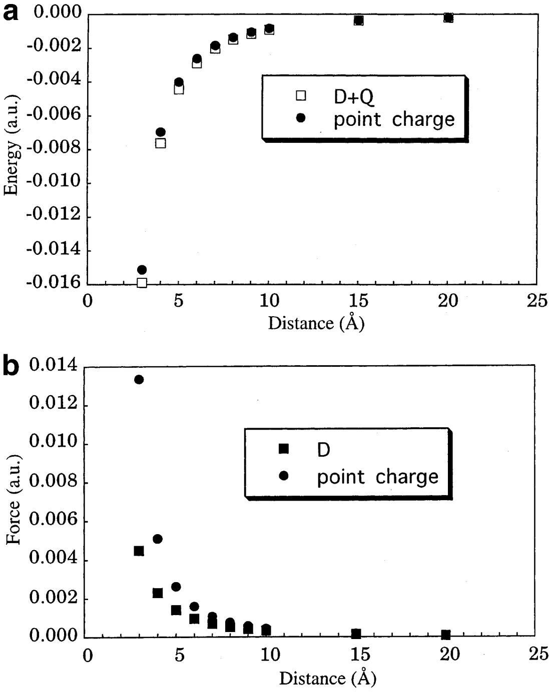

Figure 5. Comparison of H_2O/point charge and partial multipole/point charge calculations. (a) Energies (in a.u.) as a function of the distance (in Å) of ab initio, point charge (1), ●, and classical, diagonal electric field (4) for dipole (D) plus quadrupole (Q) terms, □. (b) Force (in a.u.) on OH bond as a function of distance (in Å) of ab initio, point charge (1), ●, and classical, diagonal electric field (4) for dipole (D) term, ■.

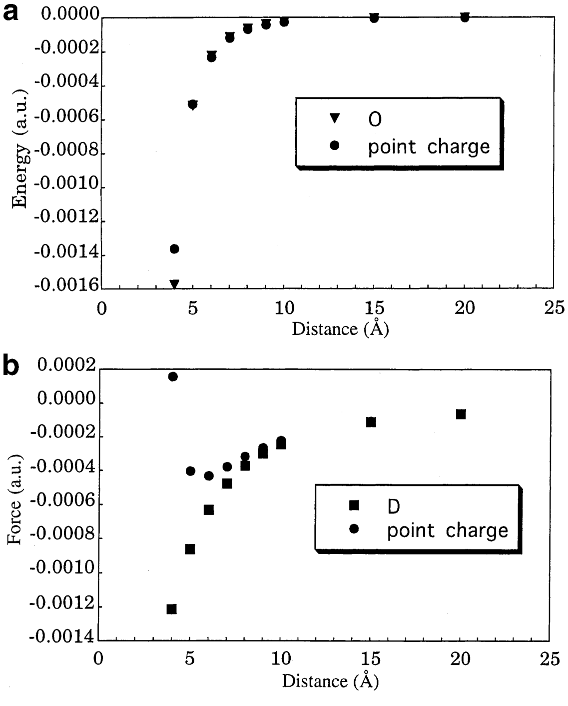

Figure 6. Comparison of CH_4/point charge and partial multipole/point charge calculations. (a) Energies (in a.u.) as a function of the distance (in Å) of ab initio, point charge (1), ●, and classical, diagonal electric field (4) for octopole (O) term, ▼. (b) Force (in a.u.) on CH bond as a function of distance (in Å) of ab initio, point charge (1), ●, and classical, diagonal electric field (4) for dipole (D) term, ■.

crucial for the multipole expansion method. Popelier et al.[23,24] also show that the atomic multipoles from AIM (atoms in molecules) work very well in intermolecular interactions because each atom has an atomic basin that is defined in real space and corresponds to a formal convergence radius. Unfortunately, distributed models for molecular force-related properties are still at a very early stage of development.[35−37]

In the charge density expansion method, the response functions and response function derivatives are six- (linear) or nine- (quadratic) dimensional and are complicated. For our purpose, the differences between blue- and red-shifted hydrogen-bond donor molecule electrostatic properties are important, and can be studied by the defined A, B, and C parameters for a specific configuration. The interaction energy and forces between a point charge and a molecule can be accurately reproduced by a classical calculation based on the derived parameters. The differences in A^{λ}'s reflect the differences in ρ^{λ}'s, which are more precise than dipole derivatives. More detailed properties of these parameters will be given in a subsequent paper.[38]

Conclusions

The molecular multipole expansion treatment to describe the electrostatic interaction properties of CH⋯O and O−H⋯O hydrogen bonds fails because high-order multipoles cause large discrepancies (divergences) in interaction energies and forces. This is fundamentally a result of the inadequacy of such an expansion when the source of the electric field (from the acceptor molecule) in effect penetrates the electron density distribution of the donor atoms.

We have explored an approach in which in effect one examines the interactions of the charge density of the donor molecule to an external multipole distribution established by the acceptor molecule. Such a treatment gives an exact reproduction of the ab initio results, thus implicitly including the penetration effect. The difference between blue- and red-shifted hydrogen bonds is seen to reside in the fact that, for the former (CH), the interaction of a negative (acceptor) charge with the permanent charge density derivative of the donor results in a negative force on the CH bond while the interaction with the induced charge density derivative results in a positive force, whereas for the latter (OH), both forces are positive. In addition, from the charge density treatment, we see that the penetration produces a positive force for both CH and OH bonds.[38] Therefore, the OH bond always has a large positive force, whereas CH has a small negative or positive force depending on the balance between these three forces. As we pointed out,[5,15] the dipole derivative properties of the hydrogen-bond donor OH and CH bonds (more exactly, the charge distribution derivative properties) are different in the actual hydrogen-bonding environment: the OH bond has a large positive electrostatic interaction force, which overcomes the negative force from the exchange−repulsive interaction, resulting in bond elongation; the CH bond has a weak positive or even a negative electrostatic force, depending on the balance between permanent and induced charge derivatives, that, working with the exchange-repulsive interaction, makes it possible to shorten the bond.

Finally, and simply, to what should be attributed the origin of a blue-shifted hydrogen bond? As a hydrogen bond forms, the interaction energy must be negative, which is the same for blue-shifted or red-shifted hydrogen bonds, arising mainly from electrostatic interactions, including the polarization interaction. Therefore, their linear response functions are similar. However, the opposite behavior of CH and OH bonds is a structure-related change, which, as pointed out by Feynman,[4] depends essentially on forces, in this case on the fact that their charge density derivatives with respect to these bonds are different. Thus, although both types of bonds share qualitatively (and roughly quantitatively) similar exchange-repulsive interactions, the exhibited difference resides basically in their dissimilar electrostatic interactions.

In light of these studies, the future challenge, particularly for energy function development,[1] will be to develop a distributed multipole and multipole derivative model that can simultaneously account for interaction energies and forces and can be applied in intermolecular interaction studies.

Acknowledgment. This research was supported by NSF Grants MCB-0212232 and DMR-0239417.

References and Notes

(1) Palmo, K.; Manfors, B.; Mirkin, N. G.; Krimm, S. *Biopolymers* **2003**, *68*, 383−394.

(2) Liu, S.; Dykstra, C. E. *J. Phys. Chem.* **1986**, *90*, 3097−3103.

(3) Stone A. J. *The Theory of Intermolecular Forces*; Clarendon: Oxford, 1996; Chapter 2.

(4) Feynman, R. P. *Phys. Rev.* **1939**, *56*, 340−343.

(5) Qian, W.; Krimm, S. *J. Phys. Chem. A* **2002**, *106*, 6628−6636.

(6) Dinur, U. *Chem. Phys. Lett.* **1992**, *192*, 399−406.

(7) Gu, Y.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411−9432.

(8) Scheiner, S.; Kar, T. *J. Phys. Chem. A* **2002**, *106*, 1784−1789.

(9) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253−4264.

(10) van der Veken, B. J.; Herrebout, W. A.; Szostak, R.; Shchepkin, D. N.; Havlas, Z.; Hobza, P. *J. Am. Chem. Soc.* **2001**, *123*, 12290−12293.

(11) Masunov, A.; Dannenberg, J. J.; Contreras, R. H. *J. Phys. Chem. A* **2001**, *105*, 4737−4740.

(12) Delanoye, S. N.; Herrebout, W. A.; van der Veken, B. J. *J. Am. Chem. Soc.* **2002**, *124*, 7490−7498.

(13) Hermansson, K. *J. Phys. Chem. A* **2002**, *106*, 4695−4702.

(14) Pejov, L.; Hermansson, K. *J. Chem. Phys.* **2003**, *119*, 313−324.

(15) Qian, W.; Krimm, S. *J. Phys. Chem. A* **2002**, *106*, 11663−11671.

(16) Li, X.; Liu, L.; Schlegel, H. B. *J. Am. Chem. Soc.* **2002**, *124*, 9639−9647.

(17) Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. *J. Am. Chem. Soc.* **2003**, *125*, 5973−5987.

(18) Herrebout, W. A.; Delanoye, S. N.; van der Veken, B. J. *J. Phys. Chem. A* **2004**, *108*, 6059−6064.

(19) McDowell, S. A. C. *Chem. Phys.* **2004**, *301*, 53−60.

(20) Celebi, N.; Angyan, J. G.; Dehez, F.; Millot, C.; Chipot, C. *J. Chem. Phys.* **2000**, *112*, 2709−2717.

(21) Fowler, P. W.; Buckingham, A. D. *Chem. Phys. Lett.* **1991**, *176*, 11−18.

(22) Moran, A.; Mukamel, S. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 506−510.

(23) Kosov, D. S.; Poplier, P. L. A. *J. Phys. Chem. A* **2000**, *104*, 7339−7345.

(24) Popelier, P. L. A.; Rafat, M. *Chem. Phys. Lett.* **2003**, *376*, 148−153.

(25) Freitag, M. A.; Gordon, M. S.; Jensen, J. H.; Stevens, W. J. *J. Chem. Phys.* **2000**, *112*, 7300−7306.

(26) Piquemal, J.-P.; Gresh, N.; Giessner-Prettre, C. *J. Phys. Chem. A* **2003**, *107*, 10353−10359.

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(28) Parr, R. G.; Yang W. *Density-Functional Theory of Atoms and Molecules*; Oxford University: New York, 1989.

(29) Savin, A.; Colonna, F.; Pollet, R. *Int. J. Quantum Chem.* **2003**, *93*, 166−190.

(30) Morita, A.; Kato, S. *J. Am. Chem. Soc.* **1997**, *119*, 4021−4032.

(31) Applequist, J. *J. Math. Phys.* **1983**, *24*, 736−741.

(32) Dykstra, C. E. *J. Comput. Chem.* **1988**, *9*, 476−487.

(33) Schmidt, M. W.; Bandyopadhyay, P.; Boatz, J. A.; Elbent, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

(34) Stone, A. J.; Alderton, M. *Mol. Phys.* **1985**, *56*, 1047−1064.

(35) Dinur, U.; Hagler, A. T. *J. Chem. Phys.* **1989**, *91*, 2949−2958.

(36) Dinur, U.; Hagler, A. T. *J. Chem. Phys.* **1989**, *91*, 2959−2970.

(37) Dinur, U. *J. Comput. Chem.* **1991**, *12*, 91−105.

(38) Qian, W.; Krimm, S. to be published.