Ab Initio Atomic Polarizability Tensors for Organic Molecules

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A recently developed method for deriving anisotropic atomic dipole polarizability tensors has been employed to derive these terms for each of the atoms in seven families of organic compounds: alcohols, alkanes, amides, amines, carboxylic acids, sulfur compounds, and benzene rings. The procedure uses fits to ab initio quantum mechanically computed molecular polarizability data to determine effective atomic polarizability tensor parameters. A new representation is described which uses bond increments, a property of the bonds rather than simply the atomic types, for polarizability components both parallel and perpendicular to the bonds. It is shown to give excellent results as gauged by its reproduction of the exact ab initio polarizabilities. We examine the accuracy of the ab initio isotropic polarizabilities compared to experiment and present a simple scaling procedure for the former. The isotropic approximations to the full anisotropic atomic polarizabilities are compared for differing atom types and bonding environments. The resulting molecular isotropic polarizabilities are also compared where possible with experiment. The present model consistently predicts both experimental isotropic molecular polarizabilities and empirically derived atomic parametrizations precisely within a few percent.

Introduction

It is becoming increasingly recognized that the use of current atomistic methods for modeling the properties of molecules and molecular materials is often severely deficient due to their inability to model polarization effects, that is, the response of the electron distribution to intramolecular and/or intermolecular electric fields. There have been several attempts to include such effects in computing not only the polarizabilities themselves but also properties that depend appreciably on the charge polarization, such as molecular interaction energies.[1,2] These have generally been parametrized as effective atomic polarizabilities, using both empirical[3–6] and ab initio quantum mechanical procedures.[7,8] The results have been inconclusive, largely because there has been considerable disagreement between the values of the atomic polarizabilities as derived and used in differing studies and by differing methods. Also, atomic polarizabilities have been derived for only a limited number of types of molecules. Thus, there is a need for atomistic models that are both accurate and may be applied directly to predicting the properties of large molecules and their assemblages for any type of species.

Recently we have described a new theoretical procedure for determining atomic polarizability tensors in molecules using ab initio quantum calculations either on single molecules or sets of closely related species.[9] The use of ab initio calculations provides a means for describing species for which no experimental data is available, while forming the basis of more detailed models than have previously been possible. Specifically, the method gives the full anisotropic polarizability tensor corresponding to each atom, thereby allowing for an increase in accuracy over simple isotropic polarizability models. The ability to use single molecules, or small sets of closely related

molecules, obviates the need to use large sets of species with frequently dissimilar atomic environments, as is generally required by empirical schemes.

In this paper we briefly review the procedure for deriving effective atomic polarizability tensors using ab initio quantum calculations. A new way of representing atomic polarizabilities is described, which is based on a bond increment description of the contributions to each atom from all other atoms to which it is bonded. This allows the atomic polarizability to vary depending on each atom's bonding environment. We then apply the method to several classes of organic molecules, which were chosen to represent both a comprehensive set of organic compounds and also to provide the parameters needed to model proteins. The resulting molecular polarizabilities are tested by comparing the predicted polarizability tensor elements with the corresponding ab initio values, and by comparing both predicted isotropic polarizabilities with experiment. In particular we examine the extent to which atomic parameters for specific atoms or atom types, such as alkyl carbons, are similar within differing molecular environments, such as alkanes and alkylamines. To determine the extent to which the polarizability bond increments are transferable to additional species, we test the accuracy of the predicted isotropic molecular polarizabilities with the ab initio results for species outside the set used in deriving the parameters. Finally we also examine the magnitude of the anisotropy of the atomic polarizability tensors—an effect that has generally been ignored in previous approaches.

Theory and Methodology

Derivation of Atomic Polarizability Tensors. We have recently described a procedure to determine the effective atomic polarizability tensors for an atom using quantum mechanically computed molecular dipole and quadrupole polarizability tensors and their derivatives with respect to atomic displacements for a single molecule or a set of molecules containing that atom.[9] We require that the atomic dipole polarizability tensor compo-

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nents corresponding to the i and j Cartesian axes on atom a, α_{ij}^a, summed over all the atoms in the molecule equal the total molecular dipole polarizability,

$$\alpha_{ij} = \sum_a \alpha_{ij}^a \qquad (1)$$

where α_{ij} is the ij component of the molecular polarizability. Similarly, if the derivative of the molecular polarizability with respect to a molecular internal coordinate σ is known, then this will equal the sum of the derivatives of the atomic polarizabilities, i.e., the polarizability flux terms $(\partial\alpha_{ij}^a/\partial\sigma)$ corresponding to that coordinate,

$$\frac{\partial\alpha_{ij}}{\partial\sigma} = \sum_a \frac{\partial\alpha_{ij}^a}{\partial\sigma} \qquad (2)$$

These derivatives, which measure the change in polarizability with changes in molecular structure, may be significant in determining molecular polarizability in cases where the equilibrium structure differs significantly from that for which the α_{ij}^a were derived. In computing the molecular polarizabilities as described below, the polarizability fluxes are not included.

Expressions such as (1) and (2) are generally insufficient to obtain all the polarizability tensor components α_{ij}^a and their derivatives for all the atoms in a molecule. However, if A is the molecular dipole−quadrupole polarizability tensor, and $A_{i,jk}$ is the jk dipole−quadrupole component due to an applied electric field in the i direction, then there exist relationships between the $A_{i,jk}$ and the atomic polarizability tensors on atom a, for example for the case $i = x$, as follows:

$$A_{x,xx} = \sum_a [2\alpha_{xx}^a x^a - \alpha_{xy}^a y^a - \alpha_{xz}^a z^a] \qquad (3a)$$

$$A_{x,yy} = \sum_a [2\alpha_{xy}^a y^a - \alpha_{xx}^a x^a - \alpha_{xz}^a z^a] \qquad (3b)$$

$$A_{x,zz} = \sum_a [2\alpha_{xz}^a z^a - \alpha_{xx}^a x^a - \alpha_{xy}^a y^a] \qquad (3c)$$

$$A_{x,xy} = \frac{3}{2}\sum_a [\alpha_{xx}^a y^a + \alpha_{xy}^a x^a] \qquad (3d)$$

$$A_{x,xz} = \frac{3}{2}\sum_a [\alpha_{xx}^a z^a + \alpha_{xz}^a x^a] \qquad (3e)$$

$$A_{x,yz} = \frac{3}{2}\sum_a [\alpha_{xy}^a z^a + \alpha_{xz}^a y^a] \qquad (3f)$$

with similar expressions for fields applied in the y and z directions. In addition, if atom b is displaced in the x direction, then, for example, (3a) gives the derivative

$$\frac{\partial A_{x,xx}}{\partial x^b} = 2\alpha_{xx}^b + \sum_a \left[2\left(\frac{\partial\alpha_{xx}^a}{\partial x^b}\right)x^a - \left(\frac{\partial\alpha_{xy}^a}{\partial x^b}\right)y^a - \left(\frac{\partial\alpha_{xz}^a}{\partial x^b}\right)z^a\right] \quad (4)$$

with similar expressions for displacements in the y and z directions. So, if the field is applied in the x, y, and z directions, the relations of the form given by (3) provide a total of 18 equations for the α_{ij}^a. Combining these with the derivatives of A along the three Cartesian coordinates for each atom (or along the molecular internal coordinates), for a molecule with N atoms,

gives as many as $18(1 + 3N - 6)$ or $18(3N - 5)$ equations for the atomic polarizabilities for each molecule. These alone are sufficient to uniquely determine the atomic polarizabilities in some cases either for single molecules or small families of structurally related species. Notice that (4) again includes not only the polarizabilities but also the polarizability flux terms, such as $(\partial\alpha_{xx}^a/\partial x^b)$.

Although (3) and (4) are rich sources of unique quantum mechanical results for deriving an atomic polarizability model, in practice for most molecules we have found it necessary to include molecular polarizability data in the fit and to introduce several approximations. These approximations are described in the following sections.

Bond Increment Method. To make the resulting parametrization more transferable among different kinds of molecular environments, and to facilitate its later application to computing the properties of large molecular systems, we employ a bond increment approach. This is a common way of parametrizing atomic partial charges. In the case of charges, we can write the atomic partial charge on atom a, q^a, as

$$q^a = q_0^a + \sum_{b \neq a} \delta_q^{ab} \qquad (5)$$

where q_0^a is a formal atomic charge (zero except for ions), δ_q^{ab} is the contribution to the charge on atom a due to atom b, and the sum extends over all molecular bonds to atom a. In this way the atomic partial charge for each atom depends on its molecular environment as expressed by the contributions of all the atoms to which it is bonded. This model has the additional useful property that the sum of all the δ_q^{ab} will be zero for neutral molecules if we require $\delta_q^{ba} = -\delta_q^{ab}$ for each bond between dissimilar atoms and $\delta_q^{ab} = 0$ between atoms that are chemically equivalent. (There are similar relations for the bond increment representations of the higher static atomic multipoles.)

Similarly we can write the atomic polarizability tensor α^a for each atom a as the sum over the contributions from each atom b to which it is bonded,

$$\alpha^a = \sum_{b \neq a} \delta^{ab} \qquad (6)$$

The δ^{ab} summed over all atoms a and b will give the total molecular polarizability. However in this case, there is no a priori relationship between δ^{ab} and δ^{ba}, and δ^{ab} will in general be nonzero between atoms that are related by symmetry or are chemically similar. So, for atomic polarizabilities, a large number of bond increment parameters result. We therefore make the additional approximation that the bonds have cylindrical symmetry. Thus if the x Cartesian axis is oriented along the bond, we have

$$\delta_\perp^{ab} = \delta_{yy}^{ab} = \delta_{zz}^{ab} \qquad (7a)$$

$$\delta_{xy}^{ab} = \delta_{xz}^{ab} = \delta_{yz}^{ab} = 0 \qquad (7b)$$

which in the case of terminal atoms gives

$$\alpha_{yy}^a = \alpha_{zz}^a \qquad (8a)$$

$$\alpha_{xy}^a = \alpha_{xz}^a = \alpha_{yz}^a = 0 \qquad (8b)$$

for each terminal atom, where $\delta_\perp^{ab}$ is the contribution perpendicular to the bond axis from atom b to atom a. So, using

TABLE 1: Types Assigned to Atoms in Various Functional Groups

atom type	molecular connectivity
c	carbon (sp^3) in alkanes
c″	carbonyl carbon except in amides
c′	carbonyl carbon in amides (connected to nitrogen)
cp	carbon in aromatic rings
h	hydrogen connected to carbon or sulfur
h*	hydrogen connected to oxygen or nitrogen
n	nitrogen in amides
na	nitrogen (sp^3) in amines
o	doubly connected oxygen
o′	carbonyl oxygen
s	sulfur (sp^3) doubly connected

(1)−(4), it is necessary to determine only two quantities, the parallel and perpendicular bond increment parameters $\delta_{\parallel}^{ab}$ and $\delta_{\perp}^{ab}$, for the bond increment for each bonded atom pair. However, unlike the case of charge bond increments, for which one can set $\delta_q^{ba} = -\delta_q^{ab}$, polarizability bond increments in the forward and backward directions are unrelated, so that δ_{ij}^{ba} and δ_{ij}^{ab} need to be determined independently.

Polarizability Flux Constrains. In using equations such as (3) and (4), it is sometimes found that there is still not sufficient quantum mechanical information to completely determine all the atomic polarizability increments without further constraints on the polarizability flux increments such as on $\partial\delta_{\parallel}^{ab}/\partial r^{cd}$ where r^{cd} is a bond length between atoms c and d. It was found useful to impose three types of constraints on the flux parameters. First, all fluxes due to changes in bond length, $\partial\delta_{\perp}^{ab}/\partial r^{cd}$ and $\partial\delta_{\parallel}^{ab}/\partial r^{cd}$, were included unless the $a-b$ bond and the $c-d$ bond do not share a common atom. Second, all polarizability flux terms involving a bond angle, $\partial\delta_{\perp}^{ab}/\partial\theta^{cde}$ and $\partial\delta_{\parallel}^{ab}/\partial\theta^{cde}$ where θ^{cde} is the bond angle formed by atoms c, d and e, were not included unless the $c-d-e$ angle includes the bond $a-b$. Third, the fluxes due to the torsions and out-of-plane deformations were not included. Approximating these types of polarizability flux terms to zero, as well as using the

bond increment representation, in general had little or no effect on the quality of the fit to the ab initio data.

Quantum Mechanical Calculations. As in our earlier study, the equations of the form of (1)−(4) were solved for each molecule, using Spackman's "polarization" basis set[10] and the Hartree−Fock approximation. We used the Gaussian90 program[11] to compute the structures and molecular multipole values. The molecular structures were computed in the HF/6-31G* level of approximation.[12] In determining the A tensor, a uniform electric field with a magnitude of 0.005 atomic units was applied along each Cartesian coordinate, and derivatives of the elements of the A matrix were found numerically by displacing the atoms in both the positive and negative directions by 0.005 Å along the internal coordinates. Derivatives of the molecular dipole polarizability were found similarly. Thus, by using (1)−(4), we determined dipole and quadrupole polarizabilities, and the derivatives of their components with respect to each internal coordinate. These were fit to obtain the $\delta_{\parallel}^{ab}$ and $\delta_{\perp}^{ab}$ terms. Weighting factors were adjusted in order to fit all the computed properties with roughly the same relative errors. All molecular dipole and quadrupole polarizabilities were assigned a weight of 100, except for the quadrupole polarizabilities of the amines and the sulfur compounds (assigned a weight of 20) and the benzene molecule (given a weight of 1). All dipole and quadrupole polarizability derivatives were given a weight of 1 except the alcohols (given a weight of 2). The atoms were assigned the standard types as used in the CFF force field.[13] The specific atom types used here are defined in Table 1.

We have applied this method to determine ab initio polarizability bond increment parameters for seven classes of organic compounds: alcohols, alkanes, amides, amines, carboxylic acids, phenyl rings, and sulfur compounds. Phenyl rings are represented here by the benzene molecule. Excluding benzene, the specific molecular structures employed in deriving the bond increments for each class of compounds are shown in Figure 1, referred to hereinafter as the training set.

Training Compounds
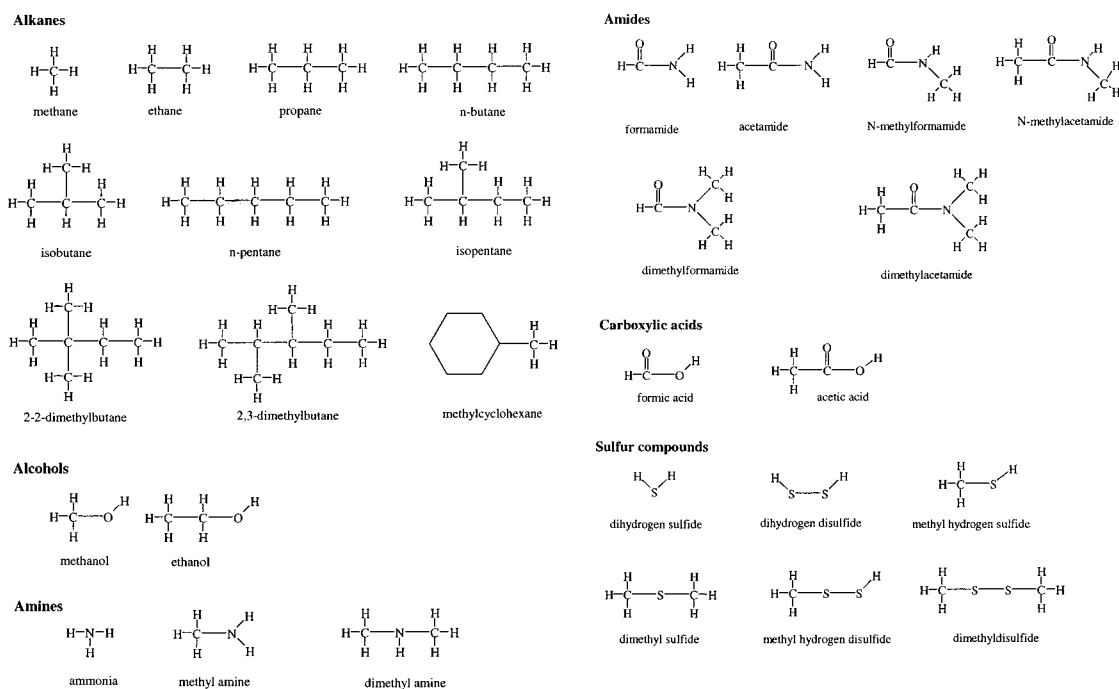
Figure 1. Molecules used in the training set to derive the atomic polarizability tensor parameters.

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TABLE 2: Ab Initio Polarizability Bond Increments Parallel and Perpendicular to the Bond

bond[a]		polarizability component ($Å^3$)	
		parallel	perpendicular
h	c	0.538	0.239
c	h	0.223	0.247
c	c	0.655	0.035
h	cp	0.431	0.138
cp	cp	1.198	0.410
o′	c′	1.391	0.592
c′	n	1.234	0.587
n	c′	1.099	0.458
h	c′	0.530	0.124
c′	h	0.000	0.222
h*	n	0.425	0.164
n	h*	0.000	0.162
c	c′	0.492	−0.077
c′	c	0.422	0.000
c	n	0.393	−0.061
n	c	0.727	0.000
o′	c″	1.276	0.580
o	c″	0.983	0.488
c″	o	1.039	0.753
h	c″	0.473	0.137
h*	o	0.413	0.138
c	c″	0.447	−0.091
o	c	1.037	0.561
c	o	0.205	0.042
na	c	0.648	0.109
c	na	0.455	0.094
h*	na	0.418	0.185
na	h*	0.290	0.362
s	c	1.965	1.047
c	s	0.998	−0.057
h	s	0.677	0.263
s	h	1.351	1.229
s	s	2.622	0.799

[a] Polarizability is donated to the first atom from the second in the order given. The two directions are equivalent except where specified otherwise in the text. Bond increments constrained to zero are not listed.

TABLE 3: Summary of the Deviations in Fitting the Bond Increment Polarizability Tensor Model to ab Initio Tensor Components for the Various Functional Groups

functional group	rms relative (%) deviations			
	polarizabilities		polarizability derivatives	
	dipole[a]	quadrupole	dipole	quadrupole
alcohols	2.9 (0.42)	12.0	19.5	19.5
alkanes	2.3 (0.97)	17.9	28.6	19.1
amides	3.9 (0.68)	11.4	39.6	26.4
amines	2.6 (0.50)	18.8	22.0	19.4
benzene	0.5 (0.00)	0.0	55.0	29.6
carboxy acids	5.3 (0.95)	12.5	46.7	26.2
sulfur cmpds	5.7 (0.67)	32.9	27.5	22.9
average rms	3.2	15.1	34.1	23.3

[a] Value in parentheses is the rms relative percentage deviation in the isotropic molecular polarizabilities.

Derivation of Polarizability Bond Increments

All the resulting polarizability bond increment values $\delta_{\parallel}^{ab}$ and $\delta_{\perp}^{ab}$ are listed in Table 2. Table 3 shows the precision with which the ab initio quantities—the molecular dipole and dipole−quadrupole polarizability tensors and their derivatives with respect to the molecular internal coordinates for all the species in the training set—are fit by these polarizability bond increments. Dipole polarizabilities are represented better than the quadrupole terms (3.2% and 15.1% root-mean square (rms) deviations, respectively) and, as expected with our choice of weighting factors, the polarizabilities are fit better than their derivatives (34.1% and 23.3%). Isotropic dipole polarizabilities

Test Compounds
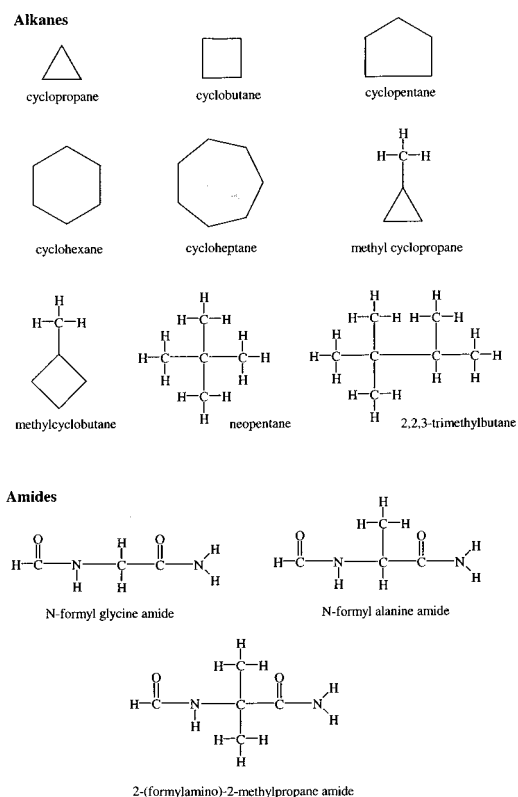
Figure 2. Molecules used to test the atomic polarizability tensor parameters.

(in parentheses) are fit better than the individual tensor components. However, the quality of the fit is approximately the same for all seven functional groups.

The remainder of this paper will focus on examining the computed polarizability bond increments and the atomic and molecular polarizabilities derived from them. Of the seven classes of compounds, the alkanes and the amides were examined in especial detail, since they form families of extended molecular structures, and there are also numerous experimental and previous theoretical studies available for comparison. We focus primarily on the extent to which the bond increments reproduce the ab initio quantities. To verify that the resulting parameters can *predict* molecular polarizabilities in addition to fitting the data, we examined an additional set of alkane and amide molecules that were not used in the fitting. We will refer to these additional compounds as the test set. The molecular structures in the test set are shown in Figure 2.

In the following sections we will discuss the results of the derivation of the polarizability terms for each family of molecules separately, focusing on aspects of the calculations that are unique to that family. For purposes of comparison, it is useful to use the isotropic polarizabilities for both the molecules and the individual atoms, i.e. the polarizability averaged over all directions. The isotropic polarizability for a molecule is given by $\alpha_{iso} \equiv (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$, and similarly for atom a, $\alpha_{iso}{}^a \equiv (\alpha_{xx}{}^a + \alpha_{yy}{}^a + \alpha_{zz}{}^a)/3$. The atomic polarizabilities of terminal atoms are characterized by two terms, $\delta_{\parallel}^{ab}$ and $\delta_{\perp}^{ab}$, for the polarizability components perpendicular and parallel to the terminal bond. The polarizabilities of nonterminal atoms will generally be characterized by completely anisotropic atomic polarizability tensors, since they contain contributions from two or more other atoms.

TABLE 4: Ab Initio and Bond Increment Values for the Molecular Isotropic Dipole Polarizabilities for the Alkane Molecules in the Training Set

molecule	polarizability (Å³)		
	ab initio	bond increments[a]	% deviation
methane	2.310	2.311 (0.001)	0.04
ethane	3.976	3.949 (−0.027)	−0.27
propane	5.649	5.688 (−0.061)	−0.50
n-butane, *anti*	7.340	7.226 (−0.113)	−0.89
n-butane, *gauche*	7.274	7.226 (−0.048)	−0.05
isobutane	7.312	7.226 (−0.085)	−0.45
n-pentane	9.039	8.865 (−0.174)	−1.23
isopentane	8.951	8.865 (−0.086)	−0.17
2,2-dimethylbutane	10.550	10.530 (−0.047)	−0.81
2,3-dimethylbutane	10.542	10.503 (−0.039)	−0.79
methylcyclohexane	11.606	11.470 (−0.136)	−0.16
overall[b]		(0.088)	0.53

[a] Absolute differences from ab initio are given in parentheses. [b] Rms differences (in parentheses) and average of absolute percentage differences.

It is useful in many cases to compare both the ab initio and the modeled isotropic molecular dipole polarizabilities with experiment. Several compilations of these experimental values have been published. In particular, a recent compilation by Gussoni, Rui, and Zerbi[14] gave isotropic polarizabilities of 650 small organic molecules, as well as analyzing the trends among the polarizabilities. The data were obtained from the Lorenz−Lorenz equation,[15] which relates the molecular polarizability to the molar index of refraction. These data are corrected where necessary for normal dispersion, but generally not for effects of temperature, pressure, nor the frequency of the light source employed. For consistency we will use the values recommended by Gussoni et al. for all molecules, except where otherwise noted.

Alkanes. The molecules chosen to represent the alkanes varied in size from methane to methylcyclohexane. As given in Table 2, the polarizabilities for the alkanes with our cylindrically symmetric bond increment model are given by four quantities: $\delta_{\parallel}^{CH}$, $\delta_{\parallel}^{CC}$, $\delta_{\perp}^{CH}$, and $\delta_{\perp}^{CC}$. As an initial test we computed each of the components of the molecular dipole polarizability tensors of each molecule using the bond increments, and compared them with the components of the ab initio polarizability tensor. The deviations between the two were found to be nearly independent of the size of the molecule, and to range from 0.0% for methane to 4.4% for n-pentane. As shown in Table 3, the overall rms deviation in the tensor components was 2.3%.

Another way of gauging the quality of the model is by using the isotropic molecular polarizabilities. Table 4 lists the ab initio polarizabilities and those found using the bond increments for the eleven alkane species. The differences between the two are in parentheses, and the last column gives the percentage deviation. Differences range from 0.001 Å³ (0.04%) for methane to 0.174 Å³ (1.23%) for n-pentane. The overall rms deviation is 0.088 Å³, corresponding to an average relative deviation of only 0.53%.

Experimental isotropic polarizabilities are known for at least six of these species. The results are listed in the second column of Table 5, with the ab initio values in the next column. The deviations are given in parentheses, with the percentage deviations in the last column. The ab initio values are consistently smaller, the deviations ranging from 8.5% for n-pentane to 11.2% for methane with an average deviation of 9.3%, suggesting that the ab initio results should be scaled up by a factor of approximately 1.10 to reproduce the experimental values.

TABLE 5: Comparison of Experimental and ab Initio Molecular Isotropic Dipole Polarizabilities for Alkanes

molecule	polarizabilities (Å³)		
	experiment	ab initio[a]	% difference
methane	2.60	2.31 (−0.29)	−11.2
ethane	4.40	3.98 (−0.42)	−9.5
propane	6.23	5.65 (−0.58)	−9.3
n-butane	8.02	7.34 (−0.68)	−8.5
isobutane	8.01	7.31 (−0.70)	−8.7
n-pentane	9.88	9.04 (−0.84)	−8.5
average		(0.58)	−9.3

[a] Absolute deviations from experiment in parentheses.

TABLE 6: Empirical and Quantum Mechanically Determined Atomic Polarizabilities Previously Reported for Alkanes Compared with the Present Results

method	polarizabilities (Å³)	
	c	h
empirical (Miller[5])	1.116	0.392
empirical (No et al.[6])	1.051	0.389
QM (Ferraro et al.[7])	0.85	0.40
QM (Zhou and Dykstra[8b])	1.822	
present work (unscaled)	0.957−0.967	0.338
present work (scaled)[a]	1.052−1.064	0.372

[a] Scale factor = 1.10 from scaling the ab initio total molecular polarizability.

For the alkanes, isotropic atomic polarizabilities (based essentially on atom types) have been derived by several authors using both experimental data and quantum mechanical calculations. Four of these—two empirical and two quantum mechanical—are collected in Table 6. These are compared with the atomic polarizabilities computed using the bond increments, with and without the scale factor of 1.10, in the fifth and sixth rows of data. Note that the values for the carbon atom from the present work span a range, since they employed bond increments to represent differing molecular environments. However the range is quite narrow (0.012 Å³) indicating that a model using atom types instead of increments could in principle be accurate across the entire set of alkane molecules. The two empirical approaches, by No et al.[6] and by Miller,[5] and the quantum mechanical (Hartree−Fock) values by Ferraro et al.,[7] are all in substantial agreement with each other and with our bond increment results. However the value for carbon of 1.822 Å³ reported by Zhou and Dykstra,[8b] based on SCF quantum calculations, is larger by about a factor of nearly two. (Earlier work by Stout and Dykstra,[8a] which employed quantum calculations including electron correlation, found even larger values, for example 1.930 Å³ with the coupled cluster approximation.) The relatively large values obtained by Stout and Dykstra as well as those from Zhou and Dykstra arise because these two studies constrained the polarizabilities of all the hydrogens to be zero, thus implicitly including the contributions of the hydrogens in with the heavier atoms in fitting the molecular polarizabilities.[8b,16]

Thus, from the values in this table, there is a consensus that the isotropic atomic polarizability of a hydrogen atom in an alkane, α_{iso}^H, is between 0.3 and 0.4 Å³, and α_{iso}^C for an sp³ hybridized carbon atom is about 1 Å³ (neglecting the values of Stout and Dykstra[8a] and Zhou and Dykstra[8b]).

It should be pointed out that other authors have reported isotropic atomic polarizabilities for alkanes. However, the values generally show considerable dissimilarities among the different studies and from all those presented herein. Thus, Gao et al.,[17] using an empirical approach based on simulations of liquids, reported $\alpha_{iso}^H = 0.124$ Å³ and $\alpha_{iso}^C = 0.649$ Å³. Nakagawa[18]

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TABLE 7: Ab Initio and Bond Increment Values for the Molecular Isotropic Dipole Polarizabilities for the Amide Molecules in the Training Set

	polarizability (Å^3)		
molecule	ab initio	bond increments[a]	% deviation
formamide	3.461	3.457 (−0.004)	−0.12
acetamide	5.067	5.036 (−0.030)	−0.59
N-methylformamide, *trans*	5.091	5.164 (0.073)	1.43
N-methylformamide, *cis*	5.155	5.164 (0.009)	0.17
N-methylacetamide, *trans*	6.726	6.743 (0.017)	0.25
N-methylacetamide, *cis*	6.703	6.743 (0.040)	0.60
N,N-dimethylformaide	6.817	6.817 (0.053)	0.78
N,N-dimethylacetamide	8.405	8.450 (0.045)	0.54
overall[b]		(0.040)	0.56

[a] Absolute differences from ab initio are given in parentheses. [b] rms differences (in parentheses) and average of absolute percentage differences.

reported that α_{iso}^H and α_{iso}^C are about equal, for example 0.582 Å^3 and 0.557 Å^3, respectively, based on quantum calculations at the MP2 level in propane. Both of these approaches relied on studying the nonuniform electric fields formed by point charges. Thus it appears that the point-charge models are not of the same level of accuracy as the others, and so comparisons with them will not be included in our discussion of the following families of molecules.

Amides. As shown in Figure 1, the training set for the amides consisted of eight species, containing between one carbon (formamide) to three carbon atoms (dimethylacetamide). Bond increments are required for all bonds to the amide carbon (c′), oxygen (o′), and nitrogen (n), and the hydrogen bonded to the amide nitrogen (h*). For example for *N*-methylformamide, the atom types are related to the structure as follows:
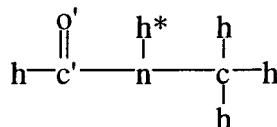
Parallel and perpendicular components are required for six bond types, not including those that may be transferred from the alkanes. In solving for the atomic polarizabilities and their derivatives, it was found that an additional constraint on the bond increments was needed to derive a unique solution. In this case, for the amide carbon atom, we set $\delta_{||}^{n-h*} = \delta_{||}^{co} = \delta_{||}^{ch} = \delta_{\perp}^{n-c} = \delta_{\perp}^{co} = \delta_{\perp}^{ch} = 0$. However, the increments in the reverse direction, such as $\delta_{||}^{h*-n}$, were retained. By examining the quality of the fit, this was found to be a very good approximation. For example Table 3 shows that, using this approach, the components of the molecular dipole and quadrupole polarizability tensors were fit with rms deviations of 3.9% and 11.4% respectively, results which are comparable to the other families of molecules.

Table 7 lists the isotropic molecular polarizabilities obtained from the ab initio calculations and with the bond increments for the eight amide species in the training set. The ab initio polarizabilities range from 3.461 Å^3 for formamide to 8.405 Å^3 for *N,N*-dimethylacetamide, the differences between the ab initio and bond increment values varying from 0.004 Å^3 (0.12%) in formamide to 0.073 Å^3 (1.43%) in trans *N*-methyformamide. These are quite similar to the deviations found for the alkanes (Table 4). The rms and average relative deviations are 0.040 Å^3 and 0.56%, compared to 0.088 Å^3 and 0.53% found for the alkanes.

Experimental isotropic polarizabilities are known for at least five of these species, as listed in Table 8. The ab initio values

TABLE 8: Comparison of experimental and ab Initio Molecular Isotropic Dipole Polarizabilities of Amides

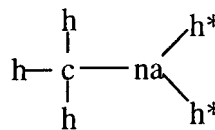|	polarizabilities (Å^3)		
molecule	experiment	ab initio[a]	% difference
formamide	4.08	3.46 (−0.62)	−15.2
acetamide	5.67	5.07 (−0.60)	−10.6
N-methylformamide, *trans*	5.91	5.09 (−0.82)	−13.9
N-methylacetamide, *trans*	7.82	6.73 (−1.09)	−13.9
N,N-dimethylformamide	7.81	6.82 (−0.99)	−12.7
average		(−0.82)	−13.3

[a] Absolute deviations from experiment in parentheses.

are smaller than experiment by amounts ranging from 10.6% (acetamide) to 15.2% (formamide) for an average difference of 13.3%. This suggests that the ab initio values should be scaled up by a factor of 1.15, compared to a scale factor of 1.11 for the alkanes.

Table 9 shows the isotropic atomic polarizabilities for the amide atom types from the tables of empirical parameters by No et al.[6] and by Miller,[5] the values without and with scaling, and the ab initio values reported by Zhou and Dykstra.[8b] Note that all the previously reported methods require all the sp^3 hybridized carbon atoms to share the same polarizabilities, as well as all carbonyl carbons, all amide nitrogens, and all the hydrogens. Based on our present calculations, this may be a reasonable approximation for the carbon atoms. However the amide nitrogens span a range of about 30% between the differing bonding environments, and the hydrogens attached to carbonyl carbon or nitrogen have significantly smaller polarizabilities (0.298 Å^3 and 0.289 Å^3) than those attached to alkane carbons (0.389 Å^3). Again the bond increment atomic polarizabilities are in quite reasonable agreement with both set of empirical values. However the values found by Zhou and Dykstra[8b] for the carbons and nitrogen are again considerably larger than those from the other studies, while the carbon oxygen value (0.464 Å^3) is much smaller, as expected for the reasons cited above.

Other Families of Molecules. For the remaining molecules we will focus primarily on the isotropic atomic polarizabilities for purposes of comparing with the values reported by other authors and of examining trends between families of compounds.

Amines. The ammonia, methylamine, and dimethylamine molecules were used to derive the bond increment parameters for the bonds to the amine nitrogen (na). In these species there are four atom types: na, c, h, and h*, the h* representing hydrogen bonded to nitrogen. So, for example, methylamine would be assigned atom types as follows:

Thus, there are parallel and perpendicular components for two additional bond types: c−na and na−h*, or four additional bond increments. Interestingly, when these are applied to the set of amines, the isotropic polarizability of the nitrogen is found to vary appreciably between different bonding environments, decreasing from 1.013 Å^3 in ammonia to 0.964 Å^3 in methylamine and 0.915 Å^3 in dimethylamine, for a total decrease of about 10%. This is in contrast to the alkanes, for which a variation of only about 1% was found among the molecules examined. The experimental polarizability of ammonia is 2.14 Å^3, while the ab initio value is 1.80 Å^3, or 15.9% lower. This leads to a scale factor for the ab initio results of 1.19. The resulting isotropic atomic polarizabilities are given in Table 10,

TABLE 9: Empirical and Quantum Mechanically Determined Atomic Polarizabilities Previously Reported for Amides Compared with the Present Results

method	polarizabilities (Å^3)							
	c′	o′	n	h(c′)	h*	c(c′)	c(n)	h(c)
empirical (Miller[5])	1.369	0.739	0.851	0.392	0.392	1.116	1.116	0.392
empirical (No et al.[6])	1.077	0.829	1.020	0.389	0.389	1.051	1.051	0.389
QM (Zhou and Dykstra[8b])	1.671	0.464	1.296			1.822	1.822	
present work (unscaled)	0.943−0.950	0.858	0.888−1.156	0.259	0.251	0.830	0.808	0.338
present work (scaled)[a]	1.084−1.098	0.987	1.021−1.329	0.298	0.289	0.954	0.929	0.389

[a] Scale factor = 1.15 from scaling the ab initio total molecular polarizability.

TABLE 10: Empirical and Quantum Mechanically Determined Isotropic Atomic Polarizabilities Previously Reported for Amines Compared with the Present Results

method	polarizabilities (Å^3)		
	na	h*	c
empirical (Miller[5])	1.077	0.392	1.116
empirical (No et al.[6])	1.020	0.389	1.051
QM (Zhou and Dykstra[8b])	1.321−1.490		1.822
present work (unscaled)	0.915−1.013	0.262	0.932
present work (scaled)[a]	1.089−1.205	0.312	1.109

[a] Scale factor = 1.19 from scaling the ab initio total molecular polarizability.

which lists the scaled and unscaled values, along with some of the values that have been reported by other authors.

Alcohols and Carboxylic Acids. These two functional groups were combined in the fit since they both contain the C−O−H moiety. Bond increment terms are required for two additional atom types: o (doubly connected oxygen) and o′ (carbonyl oxygen). For example, acetic acid is assigned atom types as follows:
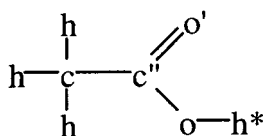
In computing the bond increment parameters for the acids and alcohols, it was found necessary to impose the constraints $\delta^{c''-o'} = \delta^{c''-h} = \delta^{o-h*} = \delta^{c''-c} = 0$ (contributions to c″ from o′, etc.) for the parallel and perpendicular components. However the contributions in the reverse directions, $\delta^{o'-c''}$, $\delta^{h-c''}$, δ^{h*-o}, and $\delta^{c''-c}$, were determined.

Comparison of the experimental isotropic polarizabilities for formic acid, acetic acid, methanol, and ethanol (3.32, 5.15, 3.21, and 4.92 Å^3) with the ab initio values (2.74, 4.37, 2.77, and 4.44 Å^3 respectively) gives an average difference of 0.57 Å^3 or 14.0%, indicating that the ab initio values should be scaled up by a factor of 1.16.

The resulting isotropic atomic polarizabilities are shown in Table 11. The results are similar to those for the amides shown in Table 9. The polarizability of the carbonyl oxygen is found to be appreciably greater than that of the acidic oxygen (0.942 for atom type o′ vs 0.757 Å^3 for o respectively after scaling). All carbon atoms again have about the same values. The scaled polarizability of the polar hydrogen (h*) is about 0.3 Å^3 both when the hydrogen is bonded to nitrogen in amides and when bonded to oxygen in acids.

In the case of formic acid, there are two conformers (*cis* and *trans*). This allows us to examine the conformational dependence of the atomic polarizabilities. The bond increment model gives very nearly the same isotropic polarizabilities for the two conformers. However, since both structures are planar, this is a case where we may solve the equations, such as (3) and (4), exactly and directly without using bond increments.[9] (We have,

however, imposed cylindrical symmetry on the bonds to the o′ and h atoms.) The results are shown in Table 12. Comparing with the values in Table 11, all the polarizabilities are found to be quite close to those from the bond increment model. The largest differences between the two structures is for the doubly connected oxygen (o), which decreases from 0.651 to 0.607 on going from *cis* to *trans*, compared with the bond increment value of 0.653 for both structures. For the o′ and h* atom types, the *cis* and *trans* polarizabilities are very similar to each other and to the bond increment values.

Sulfur Compounds. As shown in Figure 1, six species were used in deriving the bond increment parameters (s−c, h−s, and s−s bonds in Table 2) for compounds containing doubly connected sulfur. The resulting isotropic polarizabilities are given in the third row of Table 13. The sulfur polarizabilities span a range from 2.540 to 2.760 Å^3 or about 9% depending on the molecular connectivity. Comparing experimental polarizabilities for hydrogen sulfide and dimethyl sulfide[19] (3.83 and 7.53 Å^3, respectively) with the ab initio values (3.31 and 6.73 Å^3, respectively) shows that the experimental values are larger by an average of 0.66 Å^3 or 12%. This suggests that the ab initio values should be scaled up by a factor of 1.12. The scaled atomic polarizabilities are shown in the fourth row of Table 13. The hydrogen polarizability (0.449 Å^3) is significantly higher than in the compounds of lighter elements (for example 0.372 Å^3 in alkanes).

Benzene. In determining the polarizability bond increments for benzene rings, we imposed the constraint that the hydrogen contribution to the carbon polarizability $\delta^{cp - h}$ (but not δ^{h-cp}, the carbon contribution to the hydrogen) was set to zero. As shown in Table 3, the ab initio dipole polarizability tensor of benzene is reproduced with an accuracy of 0.5% by the bond increments (components parallel and perpendicular to the ring 11.388 and 5.683 Å^3, respectively, from the ab initio method and 11.354 and 5.751 Å^3 from the bond increments). The isotropic polarizability (9.487 Å^3) was precisely reproduced by the bond increments.

The resulting atomic polarizabilities are shown in the third row of Table 14. The experimental isotropic polarizability for the benzene molecule is 10.39 Å^3 while the ab initio value is 9.49 Å^3, corresponding to a scale factor for the ab initio values of 1.09. The scaled atomic polarizabilities are given in the fourth row of the table. Note that the polarizability of the aromatic carbon atom is now about 30% larger than that in the alkanes.

Testing the Polarizability Bond Increments

Alkanes. The precision of the fit to the data is generally not sufficient to establish the accuracy and reliability of a theoretical procedure. It is desirable to show that the resulting values may be applied to additional molecules of interest. For the alkanes and amides we therefore selected sets of compounds that have significantly different structures than those used in deriving the polarizability bond increments. Table 15 gives the results for

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TABLE 11: Empirical and Quantum Mechanically Determined Isotropic Atomic Polarizabilities Previously Reported for Alcohols and Carboxylic Acids Compared with the Present Results

	polarizabilities (Å³)						
method	c″	o′	o	h*	h(c″)	c(c″)	c(o)
empirical (Miller[5])	1.369	0.739	0.780	0.392	0.392	1.116	1.116
empirical (No et al.[6])	1.077	0.829	0.728	0.389	0.389	1.015	1.051
QM (Zhou and Dykstra[8b])	1.671	0.464	0.518			1.822	1.822
present work (unscaled)	0.849	0.812	0.653	0.249	0.230	0.806	0.814−0.816
present work (scaled)[a]	0.985	0.942	0.757	0.289	0.267	0.935	0.944−0.947

[a] Scale factor = 1.16 from scaling the ab initio total molecular polarizability.

TABLE 12: Atomic Polarizabilities of the Cis and Trans Conformers of Formic Acid, Found without Imposing Bond Increment Constraints

	polarizabilities (Å³)	
atom type	cis	trans
c″	0.844	0.843
o′	0.795	0.817
o	0.607	0.651
h*	0.247	0.223
h	0.250	0.265

TABLE 13: Empirical and Quantum Mechanically Determined Isotropic Atomic Polarizabilities Previously Reported for the Sulfur Compounds Compared with the Present Results

	polarizabilities (Å³)	
method	s	h
empirical (Miller[5])	3.056	0.392
empirical (No et al.[6])	3.316	0.389
present work (unscaled)	2.540−2.760	0.401
present work (scaled)[a]	2.845−3.091	0.449

[a] Scale factor = 1.12 from scaling the ab initio total molecular polarizability.

TABLE 14: Empirical and Quantum Mechanically Determined Isotropic Atomic Polarizabilities Previously Reported for Benzene Compared with the Present Results

	polarizabilities (Å³)	
method	cp	h
empirical (Miller[5])	1.369	0.392
empirical (No et al.[6])	1.499	0.254
present work (unscaled)	1.345	0.236
present work (scaled)[a]	1.466	0.257

[a] Scale factor = 1.09 from scaling the ab initio total molecular polarizability.

the ab initio and bond increment isotropic dipole polarizabilities of nine test compounds. These are also shown in Figure 2. They were chosen to include more rings and highly branched compounds than in the training set.

Table 15 lists the ab initio and bond increment isotropic molecular polarizabilities for the test set molecules. The overall rms deviation between ab initio and bond increment polarizabilities is 0.112 Å³ for an average relative deviation of 1.34%, compared to 0.088 Å³ and 0.53% for the training set used to derive the bond increments. However, the four largest deviations correspond to the four three- and four-membered ring compounds, which are generally the most difficult to model with any parametrization that is also to be employed for the straight-chain alkanes. When the small ring compounds are excluded from the comparison, the deviation is only 0.046 Å³, or 0.54%, essentially the same as that in the training set.

Amides. As shown in Figure 2, the three amide test species consisted of *N*-formylglycineamide, *N*-formylalanineamide, and

TABLE 15: Ab Initio and Bond Increment Values for the Molecular Isotropic Dipole Polarizabilities for the Alkane Molecules in the Test Set

	polarizability (Å³)		
molecule	ab initio	bond increments[a]	% deviation
cyclopropane	5.035	4.916 (−0.119)	−2.36
cyclobutane	6.694	6.554 (−0.140)	−2.09
cyclopentane	8.224	8.193 (−0.031)	−0.50
cyclohexane	9.851	9.831 (−0.020)	−0.89
cycloheptane	11.452	11.470 (0.017)	0.05
methylcyclopropane	6.727	6.554 (−0.173)	−2.57
methylcyclobutane	8.391	8.193 (−0.198)	−2.36
neopentane	8.953	8.865 (−0.088)	−0.98
2,2,3-trimethylbutane	12.107	12.142 (0.035)	0.29
overall[b]		(0.112)	1.34
overall excluding 3- and four-membered rings[b]		(0.046)	0.54

[a] Absolute differences from ab initio are given in parentheses. [b] rms differences (in parentheses) and average of absolute percentage differences.

TABLE 16: Ab Initio and Bond Increment Values for the Molecular Isotropic Dipole Polarizabilities for the Amide Molecules in the Test Set

	polarizability (Å³)		
molecule	ab initio	bond increments[a]	% deviation
FGLY[b]	7.899	7.890 (−0.009)	−0.11
FALA[c]	9.456	9.528 (0.072)	0.76
FAMPAM[d]	11.022	11.167 (0.145)	1.32
overall[e]		(0.094)	0.73

[a] Absolute differences from ab initio are given in parentheses. [b] *N*-formylglycineamide. [c] *N*-formylalanineamide. [d] 2-(formylamino)-2-methylpropaneamide. [e] rms differences (in parentheses) and average of absolute percentage differences.

2-(formylamino)-2-methylpropaneamide. These were chosen to include both larger molecules than those in the training set, and also those with substituents on the alpha carbon atom. The ab initio and the bond increment isotropic molecular polarizabilities are compared in Table 16. The largest difference is found for 2-(formylamino)-2-methylpropaneamide, for which the ab initio polarizability is 11.022 Å³ and the bond increment value is 11.167 Å³, for a difference of 0.145 Å³ or 1.32%. For the three compounds the rms deviation is 0.094 Å³ corresponding to an average absolute relative deviation of 0.73%. This is comparable to the training set compounds, for which the overall deviations are 0.040 Å³ and 0.56%.

The results for the test compounds may be summarized by comparing the differences between the ab initio and bond increment molecular polarizability tensor components and isotropic polarizabilities. As was shown in Table 3, for the alkane training set, the rms deviation in the tensor components is 2.3% and in the isotropic value 0.97%. For the test set of compounds these deviations are 2.6% and 1.05% excluding the small ring compounds. Similarly for the amides, the deviation

for the training set is 3.9% and 0.68% for the tensor components and isotropic value, respectively. For the test set this is 3.9% and 0.88%. Therefore, as measured by both the tensor components and the isotropic approximation, the bond increments are reasonably transferable from the training to the test set of molecules.

Conclusions

In this paper we have applied a new procedure for computing effective atomic dipole polarizability tensors to seven types of organic compounds. A new way of representing the atomic terms was proposed, polarizability bond increments, which reduces the number of quantities that must be determined while maintaining the anisotropy of each atomic tensor. It also allows a more transferable description by including the effects of the local molecular connectivity. Thus, it should be suitable for predicting the properties such as conformational energies and binding affinities in large molecular systems such as proteins.

Dipole and quadrupole polarizabilities and their derivatives with respect to internal coordinates were computed quantum mechanically and used to derive bond increments for polarizability parallel and perpendicular to the bonds for a training set of 29 compounds. The results were examined by comparing both tensor components of the molecular dipole polarizabilities and the isotropic values computed ab initio with the bond increment results. We also compared the resulting atomic polarizabilities in the isotropic approximation with those that have been reported previously, both based on quantum calculations and using experimental data. Finally, we computed the polarizability tensor components and isotropic polarizabilities for a test set of 12 additional molecules using the bond increments, and showed that the same level of accuracy relative to the ab initio results was obtained as for the training set. Overall the ab initio polarizabilities were reproduced with an accuracy of 3.5% for the tensor components and 0.77% for the isotropic values.

Comparison of the isotropic atomic polarizabilities obtained with the bond increments with those proposed by other authors shows that, although there is considerable disagreement with and among the quantum mechanically derived terms that have been reported previously, our scaled results are in agreement with both the empirical values reported by Miller[5] and by No et al.[6] The three methods agree that the polarizabilities for the hydrogens are all about 0.4, the first row atoms are all in the range of roughly $1.0-1.3$, and sulfur is about 3. To our knowledge this is the first ab initio quantum mechanical treatment that consistently gives isotropic atomic polarizabilities in substantial agreement with the empirical values.

Using the present bond increment approach also allows an appreciable increase in accuracy over the isotropic atomic polarizability model. First, bond increments allow the same atom to have different polarizabilities in different bonding environments, such as the 10% variation that was noted among the nitrogen atom values in the various amines. Second, the results of applying this type of approach include the anisotropy of the

polarization tensor on each atom. Table 2 shows that the anisotropy is always appreciable, the polarizability along the bond always being at least roughly twice that perpendicular to the bond. This was also observed in the quantum calculations by Stout and Dykstra.[8a] In some cases, such as for nitrogen and sulfur, the differences between the two components can be considerably greater. This means that a computed interaction energy with an ion or another molecule that took place primarily along a terminal bond and relied on an isotropic model would obtain a polarization contribution that contains a serious inaccuracy.

Perhaps the most significant conclusion from the agreement of our quantum mechanically determined isotropic atomic polarizabilities with the empirical values is that it indicates that our atomic polarizabilities are accurate *individually*. This is a much more stringent requirement than requiring that their sums, as represented by the total molecular polarizabilities, are accurate. As we noted previously,[9] accuracy of the individual atomic terms should be necessary for any model that is to be used to compute localized properties, such as interaction energies. Therefore the type of model presented here should find broad application to a range of computed properties, particularly for large organic molecules and polymers.

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