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A Distributed Model of the Electrical Response of Organic Molecules

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Correlated ab initio calculations of the electrical properties of a large set of organic molecules have been carried out and used in the selection of transferable parameters in an additive model of electrical response. The set of parameters of the model consists of anisotropic atomic dipole polarizabilities for H, C, N, O, and F atoms in different bonding environments and bond dipole moments. The model uses a distribution of atomic dipole polarizabilities and bond dipoles according to the bonding and structure of a molecule. The model describes a molecule's long-range electrostatic potential and the change in that potential from polarization by an external electrostatic potential. To very good accuracy, it yields mean molecular dipole polarizabilities and magnitudes of dipole moments, and to good accuracy, it yields dipole polarizability anisotropies and dipole moment orientations. The capability of the model reinforces the idea that to a good extent molecular polarization is tied to electronic structure changes at individual atoms. Ultimately, this will aid in modeling the effects of polarization response on other properties.

Introduction

The response of a molecule to an electrical perturbation underlies phenomena from Raman scattering to weak and hydrogen bonding. The capability to reliably model electrical response, primarily polarization, offers connection with a number of forms of molecular spectroscopy. It is not surprising, then, that efforts to model molecular dipole polarizabilities, and sometimes other response properties, go back about a half century. Other properties, such as chemical shielding and nuclear quadrupole coupling, are affected by the polarization of electronic structure,[1] and a more contemporary need is to build a model of these other property changes for use in molecular simulations. Such efforts rely on our models of polarizabilities.

Modeling dipole polarizabilities and other response properties of molecules means using chemical structure, the pattern of bond types and elements in a molecule, as the basis for the property prediction. Usually, this implies a transferable set of parameters associated with specific elements and specific types of bonding. A most natural choice of parameters is those comprising local dipole polarizability tensors. These might be associated with bonds, atoms, functional groups, or some entirely different set of centers and might be isotropic or anisotropic. They might be chosen to "relay" polarization by an implicit interaction (mutual polarization) among them, or they might be chosen to respond only to external electrical influence. With any of these choices, the modeling is meant to represent the response of a molecule's electronic charge cloud to an external electrical perturbation in terms of the net response to a set of ideal, dipole-polarizable points. This is analogous to representing the permanent charge field of a molecule by a set of distributed point multipoles. For both polarization and charge field response, there is ultimately a tradeoff between the soundness of the representation and the computational simplicity of the model, and with that, there have been quite different selections of the above choices in the history of polarization models. The primary objective in this work is a model suitable for long-range intermolecular interaction and for the prediction of molecular dipole polarizability tensors.

What is perhaps the first reported model of polarizabilities associated cylindrical point dipole polarizabilities with specific bonds.[2] Parameters were based on refractive index data and Kerr constant data for a sizable number of molecules from several classes of organic species, and it was shown that mean polarizabilities of the molecules could be obtained to good accuracy by additive contributions from a small number of bond types. Bond polarizabilities were also used in a model by Vogel and co-workers.[3] Hirschfelder, Curtis, and Bird[4] offered a formal analysis supporting additive contributions to the total molecular polarizability. The combination of bonds into functional groups suggests assigning polarizabilities to small groups, and modeling on this basis has been reported.[5]

Assigning polarizabilities to bonds was favored mostly because treating all carbon atoms as identical, for instance, did not prove workable. In ionic crystals, however, atomic centers were the choice in the 1953 model of Tessman, Kahn, and Shockley.[6] If a model is based on additivity (no relay polarization) and if it only generates the molecular or unit cell dipole polarizability, the siting of the polarizable centers is not important; there is no dependence on the geometrical arrangement of those centers. In such models, there is no distinction between using bond centers or atom centers.

The 1972 work of Applequist and co-workers[7] was an important step in the understanding of molecular electrical response because it gave a more detailed model, one that did not assume additivity. Instead, atoms were taken as interacting such that polarization of one atom in a molecule could be "relayed" to the next via its induced dipole, and to the next, and so on. This approach introduces an implicit dependence of the overall polarization response on the geometrical arrangement of the polarizable sites because a geometry change will change the extent to which polarization is relayed. Applequist recognized that isotropic atomic polarizabilities could be chosen according to the type of bonding environment. Thus, a carbonyl

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carbon atom was allowed to be different from an alkane or nitrile carbon, for example. This removes one of the earlier notions for favoring bond over atom centers in models because it explicitly incorporates effects of different types of chemical bonding. Applequist's model has application to more than the dipole polarizability and the refractive index. The distribution of polarizabilities means that the modeled system can respond to a nonuniform field with the induction of a quadrupole or higher multipole moment. That is, the distribution of dipole polarizable centers implies a response corresponding to a molecular quadrupole polarizability and higher multipole polarizabilities. The distribution also makes possible the evaluation of optical rotation, as Applequist developed in a subsequent report,[8] and vibrational Raman scattering. The model parameters that Applequist gave were derived using largely refractive index data for a set of organic molecules.

A return to the use of cylindrical bond polarizabilities is found in a model by Camail et al. that allowed for mutual, interatomic polarization[9] as in Applequist's model. In 1979 Birge[10] replaced the isotropic atomic polarizabilities in Applequist's model with anisotropic tensors. The increased number of parameters improved the reliability of the model. (Bode and Applequist have recently analyzed[11] how isotropic atomic polarizabilities can reproduce molecular anisotropies.)

A characteristic of nonadditive models is parameter values smaller than those of additive models, sometimes 50% smaller, and this is because the relay polarization enhances the net response to an external field. Achieving the same overall molecular polarizabilition calls for smaller values if mutual interatomic polarization is incorporated than if it is not. However, for largely the same reason, mutual interatomic polarization models can exhibit a breakdown where additive models do not. It is possible for a singularity to arise in the mutual polarization equations implying an infinite value for the polarizability. This does not occur with an additive model of polarization. Such breakdown is not necessarily a problem in application, and Thole has considered a type of scaling of the interaction to overcome the difficulty.[12] A further difference between additive and nonadditive models is that nonadditive models can achieve anisotropic molecular polarizabilities from isotropically polarizable atoms,[11] but additive models must have anisotropic polarizabilities for the constituent atoms.

In 1979, Miller and Savchik produced a model[13] of the mean dipole polarizabilities of molecules from additive atomic polarizabilities expressed in terms of empirically chosen parameters related to the square root of the atom's polarizability. An updated set of parameters and a very extensive test set were reported[14] in 1990 along with comparisons to bond or functional group polarizability models. Further development allowed for anisotropy at each of the centers and semiempirical incorporation of interatomic effects.[15] Ab initio calculations on dipole polarizabilities reported by Liu and Dykstra[16] in 1987 showed a near additivity of atom polarizabilities for a number of ABH_n molecules (A, B = Li, C, N, O, and F) upon adjustment for multiple bonding. Laidig, Bader and co-workers[17,18] used ab initio calculations via the atoms in molecules approach to demonstrate additivity of atomic polarizabilities for a series of hydrocarbons. Ab initio technology has been devised by Stone[19] to extract analytically a distribution of point-polarizable centers. Recently, Applequist[20] has extended his model by allowing for explicit charge transfer in the polarization response following the approach of Olson and Sundberg.[21] Importance of this has been found in aromatic systems, and application has been made to fullerenes.[22]

TABLE 1: Comparison of Model Molecular Dipole Polarizabilities (au)[a]

molecule	model/expt	α (mean)	α_1	α_2	α_3
CH_2O	expt[34,35]	16.54	18.63	12.35	18.63
	model[7,8]	16.56	19.17	6.28	24.23
	model[10]	15.61	20.85	8.71	17.28
	model[11]	15.20	19.93	6.22	19.53
	model[13−15]	18.22			
	this work	15.91	20.67	11.81	15.25
NH_2CHO	expt[36]	27.56	35.36	*b*	*b*
	model[7,8]	27.51	46.36	27.26	8.91
	model[11]	25.31	41.61	25.45	8.95
	model[13−15]	25.98			
	model[12]	25.64	32.80	27.26	16.87
	this work	28.29	32.62	29.69	22.56
CH_3CN	expt[37,38]	30.23	38.74	25.98	25.98
	model[7,8]	28.05	45.01	19.57	19.57
	model[10]	27.96	39.75	22.07	22.07
	model[13−15]	30.10			
	model[12]	28.70	37.93	24.09	24.09
	this work	28.54	37.81	23.90	23.90
HCOOH	expt[39]	22.40			
	model[13−15]	23.42			
	this work	21.47	25.92	22.82	15.69

[a] Polarizabilities reported in other than atomic units have been converted to au. [b] $\alpha_2 + \alpha_3 = 47.31$.

We recently completed a set of ab initio calculations to obtain SCF-level dipole polarizability tensors for about 40 organic molecules.[23] We found that the SCF values could be reproduced to 10% and better by a simple model with additive, anisotropic, point-polarizable atomic centers. The ab initio calculations were done at a chosen set of standard geometries. For this report, correlated ab initio calculations have been used to refine the quality and the usefulness of the parameter set. We find that the choice of the model (additive, anisotropic atomic centers) is equally workable with the data set of correlated values, and one may thereby anticipate using the model choice with any consistent set of higher quality calculated or experimental values that may be available in the future.

It is clear that the choice of additivity of polarizabilities in modeling impacts the range of applications. Optical properties, Raman amplitudes, and so on either are not predictable at all with this choice or are not well-predicted; for such objectives, relay of polarization effects along a molecular backbone are needed [see, for instance, refs 24−27], or else the model needs some other means of giving proper variation with molecular geometry. Additive models are not excluded from such objectives if there is explicit incorporation of geometry dependence. The advantage of additive models, avoiding the comparatively costly computational solution of mutual polarization equations, may outweigh the generality of application of nonadditive models. Lengthy simulations requiring repeated electrical interaction analysis will benefit from additive models, and several molecular potential schemes used in simulations do already incorporate polarizabilities,[28−32] usually as isotropic, atomic, point-polarizable centers. Our first aim in modeling molecular polarizabilities is for application in long-range, intermolecular interaction,[33] and so in this report, we focus on using the body of ab initio data for additive modeling.

Assessment of the effectiveness of the modeling approaches may be found in the original reports, and overall, predictive schemes have yielded mean dipole polarizabilities to 10% and sometimes better. Some have yielded more detailed pcitures of molecular electrical response (optical properties, quadrupole polarizabilities, and so on). Table 1 is a limited comparison of selected approaches for several molecules. Some differences are expected among models because of differences in the geometries used, though overall the results from the models are in fair to good agreement with the available experimental values.

Calculational Approach

In the ab initio calculations used to generate the data set for modeling, the basis sets were mostly the ELP (electrical properties) sets given by Liu and Dykstra.[16] These have diffuse s- and p-type functions added to a Dunning−Huzinaga[41] triple-ζ (TZ) core-valence set, plus three sets of d-polarization functions on atoms other than hydrogen. For hydrogen, there are two p-polarization functions. We used a set of molecules containing up to four C, N, O, or F atoms as in the previous study.[23] To control variances in properties arising from differences in geometries of certain bond types, the molecular geometries used a standard set of bond lengths and bond angles as approximate equilibrium structures.[23]

Our model selection was to use anisotropic, additive (non-relay) atomic centers for the dipole polarizability. The model parameters, which are the diagonal tensor elements for these atomic centers, were obtained by a least-squares fit of the individual tensor elements obtained from ab initio calculation at the level of second-order perturbation theory[42] (MP2 or MBPT-2) using finite field evaluation of the energy derivatives. The fitting coefficients were the *xx*, *yy*, and *zz* elements of the polarizability tensors of the constituent atoms. Different atomic tensors were allowed for elements in different bonding environments or different hybridization. Certain symmetry constraints were imposed. For instance, the two components perpendicular to the triple bond of an sp-type carbon were constrained to be the same. Using 99 diagonal tensor elements for 33 small molecules, 25 parameters were obtained by least-squares adjustment.

The typical effect of electron correlation on multipole polarizabilities of covalent molecules amounts to 5−15%.[43−49] To assess the MP2 level of correlation treatment, calculations were carried out for five small to intermediate sized organic molecules with two more complete correlation treatments. One was the coupled cluster (CC) expansion[50−54] including single and double substitutions (CCDS). The other was the approximate coupled cluster method[55,56] (ACCDS). In all correlated treatments, the calculation of the dipole polarizabilities was accomplished by numerical differentiation of energies obtained with finite, uniform electric fields included in the molecular Hamiltonian. In most cases, the field strengths were 0.0001, 0.0002, 0.0003, 0.0004, 0.001, 0.002, 0.003, 0.006, 0.007, 0.008, 0.008, 0.009, and 0.010 au, and the dipole polarizability was obtained from a least-squares fit of the energy to a fourth-order polynomial in the field component. Numerical precision was checked, in part, by comparing the SCF results obtained in this way with the corresponding analytical values obtained via analytical differentiation.

The comparison of correlation treatments is shown in Table 2. Water, a small molecule, shows the more substantial differences in dipole polarizability between MP2 and higher levels of treatment. The larger organic molecules show a relatively small change between MP2 results and the high-level CCDS and/or ACCDS results. On that basis, we expect that, for the molecules in our set, use of MP2 values rather than those of higher level treatments introduces a 2−3% error, and that is within the anticipated reliability of the model.

We carried out several calculations to check whether lingering basis deficiencies were greater at the MP2 level than at the SCF level. A basis set designated ELP+ has an additional d-polarization function on atoms other than hydrogen[57] in order to provide greater flexibility for describing polarization. Table 3 gives the polarizabilities with the ELP and ELP+ basis sets for four molecules. Very small changes from basis set enlargement resulted, and the changes at the MP2 level are comparable with those at the SCF level. Hence, the ELP basis was used in all subsequent calculations.

TABLE 2: Electron Correlation Effects on Dipole Polarizabilities

		α (au)			
molecule	tensor element[a]	SCF	MP2	ACCDS	CCDS
H_2O	*xx*	8.345	9.564	9.176	9.235
	yy	9.134	9.967	9.733	9.771
	zz	7.850	9.613	9.059	9.148
CH_2NH	*xx*	28.34	28.51	28.05	28.57
	yy	20.47	22.06	21.43	21.92
	zz	16.06	16.68	16.17	16.22
C_2H_6	*xx*	27.90	29.31	28.56	
	yy = *zz*	25.76	26.48	26.10	
cis-N_2H_2	*xx*	24.33	22.73	22.86	
	yy	16.56	18.26	17.72	
	zz	13.49	13.97	13.64	
C_2H_2	*xx*	32.39	31.16	31.03	
	yy = *zz*	19.24	18.90	18.56	
mean dev from ACCDS[b] (%)		4.1	2.4		1.1

[a] Geometries and orientations with respect to the axes have been given previously.[23] The indicated equivalence of tensor elements is by symmetry. [b] The mean deviation is the average of the absolute percent difference for the tensor elements with respect to values obtained from ACCDS calculations.

TABLE 3: Basis Set Augmentation Effects on Dipole Polarizability Tensor Elements

	tensor	α (au)			
molecule	element[a]	SCF/ELP	SCF/ELP+	MP2/ELP	MP2/ELP+
C_2H_6	*xx*	27.90	27.99	29.31	29.44
	yy = *zz*	25.76	25.81	26.48	26.52
CH_3CCH	*xx*	49.27	49.38	48.93	49.01
	yy	28.52	28.55	28.65	28.57
CH_2NH	*xx*	28.34	28.34	28.51	28.55
	yy	20.47	20.52	22.06	22.09
	zz	16.06	16.06	16.68	16.62
C_2H_2	*xx*	32.39	32.26	31.16	31.19
	yy = *zz*	19.24	19.25	18.90	18.78

[a] Geometries and orientations with respect to the axes have been given previously.[23] The indicated equivalence of tensor elements is by symmetry.

Results and Discussion

Table 4 gives the diagonal components of the dipole polarizability tensors from ab initio calculation and from the model of additive atomic center (AAC) contributions. The errors in this model based on MP2 values are of the same size as those in the prior model based on SCF values.[23] For the mean or isotropic polarizabilities, the average of the magnitude of the percentage difference between the MP2 and model values is 2.3%. That this agreement is better than that for individual tensor elements indicates that the AAC model has greater errors in the orientational features (i.e., anisotropy) of the polarization response than in its size. Table 5 lists the full set of parameter values obtained at the SCF level and with correlation effects at the MP2 level. The most significant correlation effects on the parameter values involve bonding to oxygen and nitrogen atoms.

Since the mean polarizabilities are particularly well represented by a sum of mean atomic polarizabilities, we may view

TABLE 4: Model and MP2 Calculated Dipole Polarizability Tensor Elements (au)

molecule	polariz element	MP2 value	model value	% diff
NC−CN	xx	50.28	49.57	−1.4
	$yy = zz$	21.93	21.76	−0.8
	mean	31.38	31.03	−1.1
CH_3CN	xx	37.99	37.81	−0.5
	$yy = zz$	23.87	23.90	0.1
	mean	28.58	28.54	−0.1
HNCO	xx	39.10	42.25	8.1
	yy	17.59	18.98	7.9
	zz	17.18	17.16	−0.1
	mean	24.62	26.13	6.1
NH_2CHO	xx	36.16	32.62	−9.8
	yy	31.00	29.69	−4.3
	zz	21.14	22.56	6.7
	mean	29.43	28.29	−3.9
CH_2NH	xx	28.51	27.72	−2.8
	yy	22.06	21.68	−1.7
	zz	16.68	16.41	−1.6
	mean	22.42	21.94	−2.2
CH_2O	xx	20.08	20.67	3.0
	yy	17.34	15.25	−12.0
	zz	12.79	11.81	−7.7
	mean	16.74	15.91	−4.9
CH_2CO	xx	45.32	48.42	6.9
	yy	22.09	22.90	3.7
	zz	22.85	19.45	−14.9
	mean	30.08	30.26	0.6
trans-CH_2CHCHO	xx	58.04	54.54	−6.0
	yy	39.92	40.88	2.4
	zz	28.50	30.51	7.1
	mean	42.15	41.98	−0.4
CH_2CCO	xx	78.71	82.89	5.3
	yy	29.46	29.57	0.4
	zz	26.10	26.12	0.1
	mean	44.75	46.19	3.2
HCOOH	xx	27.00	25.92	−4.0
	yy	23.86	22.82	−4.4
	zz	16.40	15.69	−4.4
	mean	22.42	21.47	−4.2
CH_3COOH	xx	37.34	35.27	−5.5
	yy	36.95	39.51	6.9
	zz	26.37	28.71	8.9
	mean	33.55	34.50	2.8
CH_3CCH	xx	48.93	50.98	4.2
	$yy = zz$	28.65	28.32	−1.2
	mean	36.14	35.88	1.3
trans-$(CHO)_2$	xx	35.11	33.99	−3.0
	yy	36.34	37.87	4.2
	zz	20.64	23.61	14.4
	mean	30.67	31.82	3.8
C_2H_4	xx	34.33	33.89	−1.3
	yy	25.29	25.60	1.2
	zz	22.64	18.71	−17.4
	mean	27.42	26.07	−4.9
C_2H_2	xx	31.16	32.49	4.3
	$yy = zz$	18.90	17.85	−5.6
	mean	22.99	22.73	−1.1
C_4H_4	xx	101.07	102.79	1.7
	yy	37.29	38.93	4.4
	zz	34.54	32.03	−7.3
	mean	57.63	57.92	0.5
C_2H_6	xx	29.31	26.05	−11.1
	$yy = zz$	26.48	26.05	−1.6
C_2H_6	mean	27.42	26.05	−5.0
CO_2	xx	30.41	35.21	15.8
	$yy = zz$	13.62	12.55	−7.8
	mean	19.21	20.11	4.6
OC_3O	xx	105.02	97.41	−7.3
	$yy = zz$	26.06	26.87	3.1
	mean	52.38	50.38	−3.8
FHCO	xx	23.92	21.71	−9.3
	yy	18.28	16.23	−11.2
	zz	13.32	12.90	−3.1
	mean	18.51	16.95	−8.4
FCC−CCH	xx	80.95	82.29	1.7
	$yy = zz$	30.19	29.14	−3.5
	mean	47.11	46.85	−0.5
$F_2C{=}CH_2$	xx	35.57	35.97	1.1
	yy	27.32	27.55	0.8
	zz	21.57	20.89	−3.2
	mean	28.15	28.14	−0.1
HCC−CHO	xx	55.17	54.95	−0.4
	yy	32.71	34.24	4.7
	zz	25.50	27.11	6.4
	mean	37.79	38.76	2.6
CH_2CHCN	xx	49.30	48.31	−2.0
	yy	44.36	46.85	5.6
	zz	28.84	29.58	2.6
	mean	40.83	41.58	1.8
C_4H_2	xx	79.12	75.91	−4.1
	$yy = zz$	30.32	30.60	0.9
	mean	46.59	46.59	−1.9
$HCC{-}CHCH_2$	xx	68.83	65.66	−4.6
	yy	43.80	47.08	7.5
	zz	33.68	34.00	1.0
	mean	48.77	48.92	0.3
CH_3CHO	xx	32.63	30.02	−8.0
	yy	32.14	31.96	−0.6
	zz	23.45	24.83	5.9
	mean	29.41	28.93	−1.6
cis-FHC−CHF	xx	35.21	35.97	2.2
	yy	27.13	27.55	1.6
	zz	21.33	20.89	−2.0
	mean	27.89	28.14	0.9
$CH_3{-}CH_2F$	xx	26.92	27.12	0.8
	yy	26.39	26.99	2.3
	zz	27.03	27.14	0.4
	mean	26.78	27.09	1.1
$CH_2F{-}CH_2F$	xx	28.07	28.19	0.4
	yy	28.76	27.94	−2.9
	zz	25.99	28.24	8.7
	mean	27.61	28.12	1.9
cis-N_2H_2	xx	22.72	21.54	−5.2
	yy	18.26	17.76	−2.8
	zz	13.97	14.12	1.1
	mean	18.32	17.81	−2.8
NH_2CH_3	xx	28.88	28.66	−0.8
	yy	24.09	23.78	−1.3
	zz	22.64	23.78	5.0
	mean	25.20	25.40	0.8
NH_2CCH	xx	49.82	53.58	7.6
	yy	26.31	26.05	−1.0
	zz	26.72	26.05	−2.5
	mean	34.28	35.23	2.8

these predictions as coming from a condensed model, one with only 12 parameters, the isotropic α's in Table 5. A potential limitation of this model is for systems with extensive conjugation. Large dipole polarizabilities in such species arise with delocalized π-bonding[58−60] that gives rise to sizable end effects, and these would call for different model parameters for centers near the ends of the molecule. This is also viewed as a nonlinearity of the polarizability with respect to chain length, and there are a number of critical reports on this problem [see, for instance, refs 58−67].

The energetic response of a molecule to an external electrical perturbation involves the permanent charge field, often more so than the polarizabilities. The ab initio calculations that have been carried out at the MP2 level provided a small data set for modeling permanent charge fields. A thorough investigation of the ability to represent the charge fields using a collection

TABLE 5: Comparison of Model Atomic Polarizabilities from SCF and MP2

atom type[a]	tensor element	model parameter (au) SCF	model parameter (au) MP2	mean α (au) SCF	mean α (au) MP2
C(sp^3)	*xx* = *yy* = *zz*	12.6564	13.0251	12.656	13.025
C(sp^2)	*xx*	18.2329	16.9460	13.360	13.033
	yy	12.3669	12.8003		
	zz	9.4811	9.3525		
(O)=C(sp^2)	*xx*	21.7843	27.7495	12.636	14.348
	yy = *zz*	8.0615	7.6479		
=C=	*xx*	38.6488	34.4512	17.267	15.926
	yy = *zz*	6.5759	6.6639		
C(sp)	*xx*	22.0207	21.7066	11.713	11.484
	yy = *zz*	6.5589	6.3728		
(H)C(sp)	*xx*	16.9912	16.2460	11.669	11.366
	yy = *zz*	9.0073	8.9266		
N(sp^3)	*xx*	12.7286	15.6301	10.698	12.377
	yy = *zz*	9.6829	10.7504		
N(sp^2)	*xx*	11.4124	10.7721	8.682	8.903
	yy	7.9852	8.8798		
	zz	6.6483	7.0578		
N(sp)	*xx*	3.4935	3.0782	3.982	4.030
	yy = *zz*	4.2261	4.5052		
O=	*xx*	2.2372	3.7288	1.738	2.878
	yy = *zz*	1.4878	2.4532		
−O−	*xx*	5.8440	8.9236	3.825	5.561
	yy = *zz*	2.8153	3.8802		
F	*xx*	−0.2885	0.9216	0.135	1.036
	yy = *zz*	0.3468	1.0936		

[a] The atom type is the element listed specific to any hybridization listed and to any attached atom shown in parentheses.

of atom-centered and/or bond-centered dipoles has been reported by Williams.[68] He used a technique referred to as the potential-derived charge method with dipoles restricted to be along the direction of the bond direction and to be unrestricted. Bond dipole components were determined for each individual bond in a series of hydrocarbons. We believe the efficacy of using bond placement for point dipoles in a model of the permanent charge field is already clear, and of course, bond dipoles are currently used in molecular mechanics to calculate intramolecular energy as well as intermolecular energy.[69] Thus, we used our dipole moment data to find bond dipoles as model parameters.

We have chosen to use bond dipoles placed at the center of each bond and oriented along the bond, and then the bond dipole parameters were obtained by a least-squares fit of the ab initio molecular dipoles. Sixteen bond dipole parameters were obtained with the available data, and these are given in Table 6 along with corresponding values obtained from SCF-level dipole moment values. Table 7 gives the ab initio calculated values for the components of the molecular dipole moments along with the corresponding values obtained from the model. In most cases, the components of the dipole moment were well represented. However, for some species, the component of the dipole moment vector perpendicular to the molecular axis/plane showed a rather substantial deviation from the ab initio calculated values. The usefulness of the model is assessed, in part, by the errors in the magnitude and the angle of the dipole moment vectors with respect to the ab initio calculations. As seen in Table 7, though individual vector components may show large percentage errors, the magnitude of the dipole moment can be predicted generally to better than 10%, except for those molecules with very small dipoles, and there the absolute size of the error remains small. Furthermore, the difference between the angle of the dipole moment vector obtained from the model and the dipole moment vector obtained from ab initio calculations ranges up to 10°.

Conclusions

The collection of correlated ab initio calculations performed for 33 H, C, N, O, and F molecules provides a unique set of data for analyzing electrical response in addition to offering values of the polarizabilities of these molecules. The use of the same, moderately high-level methodology (ELP basis with MP2 treatment of correlation) and the use of geometries based on a standard set of bond lengths and angles serve to critically isolate the electronic contributions to the dipole moments and polarizabilities. This means we can examine models of the electronic contributions free from dynamical and environmental effects intrinsic in a set of experimental data, free from approximating static polarizabilities from optical polarizabilities, free from different error sources among results from using calculations at different levels, and so on. The calculations provide the data for making the most direct assessment—with any model—of the purely electronic contributions to the polarization response of molecules comparable to those in the test set. To our knowledge, this has been done only once before, and that was with calculations at the SCF level.[23] With correlation effects included in this study, and with modeling of the charge field in terms of bond dipoles, a more reliable and complete model has been generated.

The physically significant conclusion of this work comes from how well overall molecular dipole polarizability tensors can be found on the basis of additive contributions from atomic centers. On this, our results reinforce a rather widely held view that the polarization response of molecules arises mostly from the dense charge regions *around* atomic nuclei. It is linked to the bonding only through the way in which the bonding affects the charge density around an atom; for instance, carbon atoms contribute mean polarizabilities around 13 au, with a range from 11.4 au for sp-hybridization to 15.9 au for an allenic carbon. Then, to the extent of the 2.3% mean error in isotropic polarizabilities of the AAC model, polarization at one atomic center is independent of that at another center.

The dipole moment analysis, though not as involved as that done for polarizabilities, reinforces the choice of bond center

TABLE 6: Model Bond Dipole Parameters Obtained from SCF and MP2 Values (au)

bond type/dipole direction	model parameter values SCF	model parameter values MP2	bond type/dipole direction	model parameter values SCF	model parameter values MP2
H→C	−0.0149	−0.0098	C(sp^2)→C=	0.4228	0.4475
H→N or H→O	−0.6460	−0.6140	O→C−C	1.2098	0.9957
F→C	0.6642	0.5476	O→C= or O→C−N	1.3177	1.0484
O→C	0.3339	0.2768	O→C−X, X = H, O, F	1.1767	0.9786
N→C	0.1014	−0.0031	N→C(sp^2)	0.8525	0.7313
C(sp^3)→C	−0.1100	−0.1277	FC(sp)→C(sp)	0.1963	0.1509
C(sp^3)→C≡ or C(sp^3)→C=	0.1208	0.1479	N→C(sp)	1.6546	1.4980
C(sp^2)→C−	−0.1408	−0.0965			

TABLE 7: Calculated and Model Dipole Moment Components (au)

molecule	dipole moment element	SCF	MP2	model	model-MP2 orientation[a] (deg)	difference: magnitude[b] (%)
CH_3CN	*x*	−1.676	−1.533	−1.636	6.7	1.6
HNCO	*x*	−0.828	−0.711	−0.695	1.4	4.0
	y	0.564	0.522	0.484		
NH_2CHO	*x*	−1.264	−1.188	−1.181	1.0	1.8
	y	−1.082	−0.910	−0.873		
CH_2NH	*x*	0.434	0.379	0.363	1.1	6.7
	y	0.543	0.526	0.484		
CH_2CO	*x*	−0.910	−0.611	−0.611	0.0	0.0
trans-CH_2CHCHO	*x*	−1.482	−1.209	−1.228	6.0	0.8
	y	−0.353	−0.335	−0.205		
CH_2O	*x*	−1.150	−0.942	−0.990	0.0	5.1
CH_2CCO	*x*	−1.422	−1.020	−1.059	0.0	3.7
HCOOH	*x*	0.486	0.426	0.426	7.3	7.4
	y	−0.416	−0.294	−0.220		
CH_3CCH	*x*	−0.307	−0.279	−0.279	0.0	0.0
FHCO	*x*	−0.792	−0.651	−0.664	2.8	1.5
	y	−0.492	−0.492	−0.453		
FCC−CCH	*x*	0.560	0.412	0.557	0.0	35.2
$F_2C{=}CH_2$	*x*	−0.801	0.625	−0.711	0.0	13.8
CH_2CHCN	*x*	−1.062	−0.888	−0.783	2.1	7.1
	y	−1.376	−1.232	−1.174		
CH_3CHO	*x*	−0.885	−0.765	−0.698	4.2	1.0
	y	−0.956	−0.784	−0.830		
cis-FHC−CHF	*y*	1.227	1.027	−0.930	0.0	9.5
CH_3CH_2F	*x*	−0.388	−0.369	−0.334	1.3	6.6
	y	−0.644	−0.541	−0.513		
cis-N_2H_2	*y*	1.208	1.159	1.154	0.0	0.4

[a] The difference in degrees between the orientation of the dipole moment vector of the molecule from the MP2 calculations and the orientation of the resultant vector obtained from adding the model bond dipole vectors. All the differences of 0.0 are necessarily a consequence of molecular symmetry. [b] The percentage difference in the magnitude of the dipole moment from the model compared to the MP2 ab initio value.

over atomic dipoles to represent molecular charge fields. The dense charge cloud in the vicinity of an atomic nucleus in this context is so uniform as to not be the primary source of a local dipole; rather the difference in charge density *along* a bond is. It is possible that a general modeling rule holds: Properties that are nonzero for an isolated atom (e.g., polarizability, second hyperpolarizability) are likely to be best represented with atomic contributions, whereas properties that are zero because of symmetry (uniformity) for an isolated atom (dipole moment, dipole hyperpolarizability) call for bond contributions. We think this may be an important key to modeling certain magnetic and electromagnetic properties.

The practical conclusion of this work is in representing electrical response properties of small and moderate sized organic molecules for long-range intermolecular interaction. We have previously shown that the AAC model can provide a good share of the energetic response of a molecule to a nonuniform electric field (i.e., a field gradient), and with the capability of AAC to reproduce correlated molecular dipole polarizability tensors, the accurate energetic contribution from interaction with a uniform field is assured.

A final result of this investigation concerns correlation effects. Model values in Table 5 are given both for SCF and MP2 data sets. In many cases, the correlation effect on parameters is less than 1.0 au. However, there are larger changes for centers that are multiply bonded. Hence, the typically greater correlation effect on polarizabilities often seen for molecules with multiple bonds can be directly associated with the electron distribution or electron correlation of the atoms in those bonds. At the least, we can thereby better anticipate the errors of SCF calculations of polarizabilities and can understand the type of active orbital spaces needed in correlated calculations targeting very precise determinations of dipole polarizabilities.

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