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Intermolecular electrical response

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Abstract

The understanding of intermolecular electrical response is considered from the standpoint of both interaction energetics and property changes and from evaluation by ab initio calculations and by modeling. The objective of such understanding is to use property changes as better and better probes of behavior associated with intermolecular interaction and to design the most effective potential models for simulation of large molecular aggregations. The inherent transferability of electrical properties and the cooperativity of the complete electrical interaction is advantageous in connecting small cluster behavior with condensed phase behavior. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Progress in the study of intermolecular interaction phenomena over the past decade has been dramatic, and a number of reviews help highlight the diverse theoretical, conceptual, and calculational thrusts that have led to such progress [1–13]. A particular aspect, the nature of electrical response as molecules approach and interact, has been studied to finer and finer levels of detail and this has been done for problems that now range from small clusters to solvent effects to polymers. Significant is that electrical response is taking hold as a means for interpreting and accounting for certain intermolecular behavior, and its rigorous evaluation is increasingly being made a component of simulation and modeling schemes.

The motivation and the utility of working with electrical response is that it involves well-defined properties that are intrinsic to molecules and/or molecular fragments. Hence, its transferability is in place from the start. Another important motivation, especially for future developments, is that electrical response serves as a bridge between classical and quantum mechanical interaction analysis. Electrical response can be carried from a classical or model region into a quantum mechanical region as an external electrostatic potential, something which is incorporated via a one-electron operator. Likewise, the electrostatic potential arising from the species within a quantum mechanical region can be evaluated in the course of the quantum mechanical calculation and that can be naturally added to the electrostatic potentials used in the model region.

A third motivation for careful and detailed treatment of electrical response is that it often seems to be the dominant source of changes in properties, including many that are of enough interest to be sought spectroscopically. Nuclear quadrupole coupling [14], chemical shielding [15,16], and electrical properties themselves [17] have all been shown

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to change in certain cases mostly via electrical influence. Hence, rigorous evaluation of electrical interaction can be used to generate certain property surfaces over intermolecular coordinates. That in turn can make for firmer connections between the theory of intermolecular interaction and a variety of experimental observations and analyses.

2. Electrical response properties of molecules

Electrical response of molecules or of groups of molecules is formally developed via energy derivatives and such response is intrinsic to features of electronic structure. Physically, an electrical perturbation, such as that of a point charge, a field, or a field gradient, is expected to yield some shift or readjustment in an electron cloud of an atom or a molecule, a change which is usually called a polarization of the charge distribution. The dependence of the effect on the strength or size of the charge, the field, or the field gradient quantifies each particular property.

An electrical potential $V(x, y, z)$ arising from some fixed charge distribution is a function of spatial coordinates such that the energy to place a point charge, q, at some point (x', y', z') is $qV(x', y', z')$. The potential can be expressed as a power series in terms of the spatial coordinates relative to a chosen expansion center or origin. The coefficients in the expansion are the value of the potential at the origin, $V_0 = V(0, 0, 0)$, then the three vector components that comprise the electric field, e.g.

$$V_x = \left.\frac{\partial V}{\partial x}\right|_{(0,0,0)},$$

then the nine components that comprise the field gradient tensor, and so on. Conversely, specifying field component values (V_x, V_y, V_z) or field gradient tensor element values (V_{xx}, V_{xy}, and so on) prescribes a particular electrostatic potential, and hence these values are parameters on which the energy of an embedded species will depend. The usual electrical response properties are the derivatives of the energy of a molecule with respect to these parameters continuing through all orders of differentiation. Explicit formulas and definitions are available [17–20].

The first derivatives of the energy with respect to field components of an electrical potential are the components of the dipole moment vector, the derivatives with respect to field gradient components comprise the quadrupole moment tensor, and so on. These first derivative properties are characteristic of the static charge distribution. The first derivatives of these and other properties, which are formally second and higher energy derivatives, reflect *changes* in electronic structure due to an external electrical environment. That is, they reflect polarization or induction of charge.

The dependence of the dipole moment on the strength of an applied field is the dipole polarizability, α, a second derivative property, and to be precise, a second rank tensor. A typical size of an isotropic dipole polarizability of a small molecule is 10 a.u. and with an external field of 0.001 a.u. (5.14×10^6 V/cm), the dipole induced by the field would be 0.01 a.u. (0.0254 Debye). This induced dipole would be the same as that arising from pulling opposite charges of ± 0.002 to the ends of the small molecule, if its length were 5 a.u. (2.6 Å). This suggests that polarization yields a rather small change in the electron density. From the opposite perspective, if there is evidence of a charge shift of this size, it is likely to be something that can be accounted for simply as polarization (induction).

Along with the dipole moment, most other properties of a molecule will be affected by an external electrical environment. For instance, the nmr chemical shielding, which is a second derivative property, may have an important first derivative with respect to electric field strength, a property often referred to as the shielding polarizability [15,16,21–34]. Clearly, polarizabilities of magnetic and other properties lengthen the list of electrical responses. The extent to which properties display an electrostatic influence has something to do with how the charge distribution is shifted because of a field, field gradient, or such pieces of a potential. Hence, the molecular dipole polarizability, α, or local dipole polarizabilities stand as crucial electrical response properties in that these most directly, and usually most sizably, determine the shift of charge that might occur because of a field.

3. Ab initio evaluation of properties

The most rigorous theoretical evaluation of

electrical response properties is via ab initio calculations. Calculational methods for the direct determination of derivatives of the energy offer convenient ways of carrying out the ab initio calculations, but in any case, the definition of properties as energy derivatives means they can be obtained numerically. These are generally referred to as finite field approaches, though the techniques work with fields, charges, field gradients, and so on. Whether by direct determination or by finite fields, the accuracy of the property evaluation depends on the same two things that control the reliability of ab initio potential energy surfaces, (i) the quality of the basis set and (ii) the quality of the treatment of electron correlation. How these factors affect the accuracy of an evaluation of a response property, though, does not have to follow how they affect the accuracy of a potential energy surface.

To describe response properties such as the polarizability, basis sets must be flexible enough to describe the slight polarization changes in electronic structure. This is accomplished with diffuse valence and extensive polarization function sets. Ideally, these augment a good quality core/valence basis so as not to unbalance the description of the polarization from that of the unperturbed electronic structure. The correlation consistent basis sets of Dunning and coworkers [35,36] are among available bases that include a number of extended sets suited to property evaluation or that are easily augmented for this purpose. Very large, multiply polarized bases have been used in a number of very critical evaluations [37–39].

At the SCF level for closed shell species, all magnetic and electrical properties to any order of differentiation can be calculated directly through solution of the differentiated Hartree–Fock equations [25,40]. This means multipole hyperpolarizabilities, which are third derivatives, and second hyperpolarizabilities, which are fourth derivatives, and so on are all calculable, and in fact, a demonstration through ninth derivatives has been given [41]. Derivatives can also be obtained directly from correlated levels of treatment, though these are often to low order. Finite field treatments are always available for the evaluation of derivatives.

Electron correlation affects electrical response properties, and in certain ways, the role of correlation on properties tracks with its role in potential energy surfaces. Where nondynamical correlation is important for the potential surface, it is likely to be important for electrical properties. It is also the case that correlation tends to be more important for higher order derivatives, though care must be taken because a deficient basis can exaggerate the correlation effect. For small, light molecules that are covalently bonded and near their equilibrium structure, correlation tends to have an effect of 1–5% on the first derivative properties (dipole, quadrupole, etc.) [42] and around 5–15% on the second derivative properties (polarizabilities) [43–50]. A still greater correlation effect, around 25% and more, may be found for third derivative properties (hyperpolarizabilities), though sometimes the sizable percentage effects are with relatively small tensor elements. When the bonding has ionic character, the correlation effect on hyperpolarizabilities tends to be significant. For instance, in lithium hydride, the dipole hyperpolarizability β at equilibrium is reduced to about half its size with the neglect of correlation effects even though the correlation effect on α is only about 15% [51]. The nondynamical correlation effect is fairly well determined at the simple MP2 (Moeller-Plesset) [52] or MBPT-2 (many-body perturbation theory) [53]. For example, in five small covalent molecules chosen as a test set, the mean deviation of α-elements obtained with MP2 from those obtained with a coupled cluster level of treatment was 2% [54].

As a final point in discussing the evaluation of response properties, we include something that might be called an ab initio *classical* calculation. This refers to a rigorous, nonapproximate solution of mutual (hyper)polarization equations for some collection of species with specific multipole moments and (hyper)polarizabilities. Means for doing this to any order of multipole [55] and to any order of hyperpolarization have been developed [56]. Hence, from the beginning level of classical electrical analysis, though with the neglect of intermolecular quantum effects, induced moments in a charge distribution (molecule) and associated fields and field gradients can be obtained. From that information and ab initio or other values for property polarizabilities (e.g. nmr shielding polarizabilities), property changes due to electrical influence can be evaluated.

Table 1
AAC model parameters for molecular dipole polarizabilities [68]

Center type	αTensor parameters[a]	
	Element	Value
C (sp^3)	xx=yy=zz	12.2956
C (sp^2)	xx	19.2020
	yy	11.5156
	zz	9.4305
(O)=C (sp^2)	xx=zz	13.4126
	yy	6.9980
(C)=C=(C)	xx	35.5897
	yy=zz	7.4611
(O)=C=	xx	17.7597
	yy=zz	6.9922
C (sp)	xx	24.8616
	yy=zz	6.0858
(H)C (sp)	xx	15.3058
	yy=zz	9.5618
(H_2)N (sp^3)	xx=yy=zz	8.9117
(H)N (sp^3)	xx	17.2036
	yy=zz	6.4847
N (sp^2)	xx	11.9376
	yy	8.1553
	zz	6.1498
N (sp)	xx	1.2229
	yy=zz	4.5402
O=	xx	5.4717
	yy=zz	1.9600
—O—	xx=yy=zz	3.4970
F	xx=zz	0.6948
	yy	−0.9010

[a] The tensor parameters are defined with respect to a reference orientation for each center. That reference orientation is with the highest order bond of the given center type aligned with the x-axis. Hence, the x-axis is along the double bond of a carbon with sp^2 bonding environment. The y and z axes are equivalent for all but sp^2 centers (i.e., axial symmetry). For sp^2 centers, the y-axis of the reference orientation is in the plane of the atoms to which the center is bound, whereas the z-axis is perpendicular to this plane.

4. Modeling response properties

A considerable effort over several decades has gone into modeling molecular properties and especially into modeling a key response property, the dipole polarizability. Model schemes have been based on bond contributions [57,58], atomic contributions [59–62] and group contributions [63] in additive schemes. Results of ab initio calculations have confirmed a good degree of additivity [64–68] and we have set up a very simple additive atomic centers (AAC) model for molecular dipole polarizabilities based on ab initio values of the α tensors of a test set of molecules [54,67–68]. We note that odd-order dipole response properties, such as the dipole moment and the first dipole hyperpolarizability, β, vanish for isolated atoms by symmetry, whereas even-order properties, such as α and the second hyperpolarizability, γ, do not. On this basis, AAC uses atom centered contributions to a molecular α or γ, but not β. Since the properties that are zero by symmetry for an isolated atom develop into non-vanishing properties in a molecule through electronic density changes within a bonding region, a bond site representation might be used for the odd-order properties. With AAC, one identifies atoms in a molecule according to their bonding environment and then assigns a local α to the atom as the model of the local response property. The assigned values (Table 1) have been developed from ab initio calculations at the MP2 level. The molecular α is the tensor sum of the local αs. For small molecules at least, this simple scheme reproduces molecular ab initio values of the tensors rather nicely, and for the isotropic response, it is even better. Several examples are in Table 2. In the absence of other information, AAC quickly provides values that serve as reasonable guesses even for larger molecules.

Models can incorporate intramolecular polarization [69–71] by going beyond the assumption of additivity. In 1972, Applequist presented a non-additive model [69] in which the polarization of one atom could be relayed to the next via its induced dipole moment, and so on. It is useful to recognize that this incorporation of intramolecular polarization implies higher order response as the energy in the presence of an applied field will depend on higher powers of the external field strength. At the same time, there is an equivalent additive approach to modeling the higher order response, and it is to represent the higher order properties, e.g. the hyperpolarizabilities, as a separate additive set. Of course, the number of model parameters grows with the number of separate properties.

5. Response to interaction

When two or more molecules approach, the interaction involves energetic changes and also electronic

Table 2
AAC model dipole polarizability tensor elements vs ab initio values (in a.u.) [68]

Molecule	Percentage difference in $\langle\alpha\rangle$	Tensor element	Ab initio	AAC	Percentage difference
NH_2CH_3	12.1	*xx*	26.60	21.21	20.3
		yy	22.97	21.21	7.7
		zz	22.83	21.21	7.1
C_2H_2	2.7	*xx*	32.29	30.61	5.2
		yy=*zz*	19.23	19.12	0.6
C_2H_4	4.8	*xx*	36.87	38.40	−4.2
		yy	24.75	23.03	6.9
		zz	22.76	18.86	17.1
C_2H_6	7.1	*xx*	27.90	24.59	11.9
		yy=*zz*	25.76	24.59	4.5
HNCO	−3.1	*xx*	33.18	35.17	−6.0
		yy	16.32	17.11	−4.8
		zz	15.84	15.10	4.7
HCOOH	11.8	*xx*	26.77	22.38	16.4
		yy	19.20	18.87	1.7
		zz	14.91	12.46	16.5
CH_3CN	0.2	*xx*	37.70	38.38	−1.8
		yy=*zz*	23.37	22.92	1.9
		zz	14.91	12.46	16.5
H_2CCCH_2	−5.6	*xx*	65.17	73.99	−13.5
		yy=*zz*	29.37	28.41	3.3
		zz	18.55	19.08	−2.9
CO_2	−0.4	*xx*	25.58	28.70	−12.2
		yy=*zz*	12.39	10.91	11.9
		zz	21.34	18.38	13.9
$CH_2C_3H_2$	1.7	*xx*	113.81	109.58	3.7
		yy	36.46	37.95	−4.1
		zz	34.23	33.78	1.3
		yy=*zz*	28.52	27.94	2.0
NH_2COOCH_3		*xx*	39.46	43.59	−10.5
	−3.2	*yy*	43.95	40.08	8.8
		zz	30.30	33.66	−11.1
$F_2C{=}CH_2$	−0.4	*xx*	35.45	37.57	−6.0
		yy	25.01	23.45	6.2
		zz	20.48	20.25	1.1

structure changes. Among closed shell molecules, the first influence on electronic structure as molecules approach at long-range is likely to be an electrostatic effect arising from the charge fields of the interacting species. This effect is an increasingly important research pursuit on its own, particularly for property changes due to solvent molecule interactions or cages [72]. Such influence has been found to be the case for properties such as dipole hyperpolarizability [17], and for long-range intramolecular NMR chemical shielding [15,16]. Analysis of electrical polarization response has also been used to account for changes in the second hyperpolarizability of hexatriene molecules arranged as in a segment of solid state polyacetylene [73].

In the study of a subtle property, the nuclear quadrupole coupling constants of weakly bound clusters [14], a hybrid calculation helped reveal the nature of the effect. The charge field of one molecule was built into a one-electron operator that was used in the evaluation of the nuclear quadrupole coupling constant of the partner molecule. The ab initio calculations on the monomers were done separately, and the success of this approach indicates a nice connection between a classical environment, the partner's charge field, and a local quantum mechanical

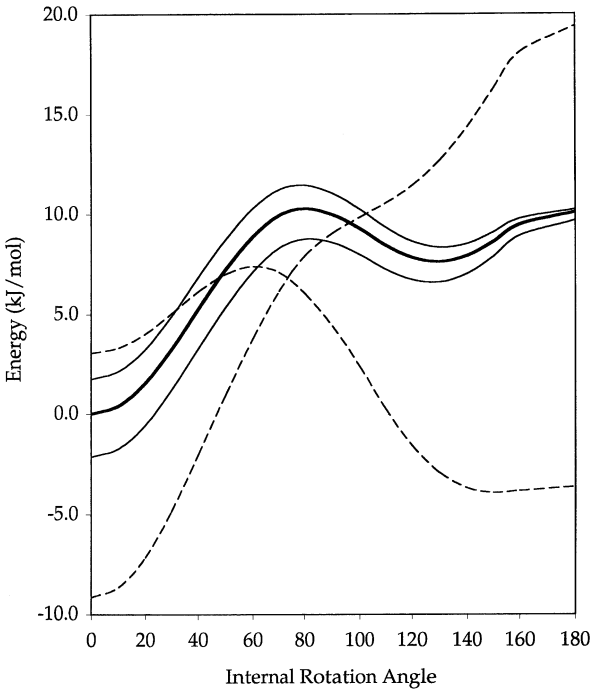


Fig. 1. Internal rotation potentials about the C—C axis for glycine obtained from MP2 calculations with a cc-pVTZ basis set [74]. The z-direction, defined perpendicular to the C—C rotation axis and oriented at $\phi/2$, where ϕ is the internal rotation angle (horizontal axis), is used for the choices of electrical perturbations. Internal rotation potentials are shown for external fields, V_z, and field gradients, V_{zz}. The thick solid line is for no electrical perturbation. The thinner solid lines are for $V_z = -0.002$ a.u. (upper) and $V_z = 0.002$ a.u. (lower). The broken lines are for $V_{zz} = 0.002$ a.u. (upper on the right) and $V_{zz} = -0.002$ (lower on the right).

treatment. The result of this study was to show a correlation between interaction strength and effect on nuclear quadrupole coupling through a series of clusters, and the calculational results were in very good agreement with experimentally determined values.

A rather direct electrical response is a conformational change. For example, the interconversion energetics of glycine can be noticeably affected by the presence of a field gradient, as shown by calculational results in Fig. 1. A field gradient, such as that which might arise from the charge field of surrounding molecules, adds wiggles to an interconversion surface and this is largely because of how the molecule's quadrupole changes in the course of the internal rotation [74].

An important consequence of intermolecular electrical response is an interaction energy among approaching molecules. Of course, electrical response alone is incomplete because close-in repulsion, dispersion, and possibly other elements are at work. Attempts to model intermolecular interaction have had good success through focusing to some extent on the electrical response, or stated differently, on the electrical interaction energies. Along with many system-specific models, such as for water molecules, there are a good number of models designed to represent and treat many different molecules. Among these is the Buckingham–Fowler model [75], which has been quite effective in accounting for the geometries of numerous van der Waals clusters [1,3]. It uses the DMA (distributed multipole analysis [76,77]) representation of the permanent charge fields to obtain the electrostatic interaction energy. Assigned hard spheres comprise the repulsive part of the potential. A more flexible close-in potential was used in Spackman's model [78–80] which had electrical interaction energies based on a partitioned multipole moment analysis. In my development of the molecular mechanics for clusters (MMC) [81] model, there was strong emphasis on the electrical component of

intermolecular interaction The idea was to utilize intrinsic molecular electrical properties because they can be obtained or are available for the individual monomers and because they are automatically a transferable potential element. MMC combines the interaction of the permanent charge fields, via permanent moments that are either central or distributed as appropriate, with the contribution due to polarization and hyperpolarization for an overall electrical energy term. This is added to dispersion and exchange elements represented with simple atom–atom potentials. There has been moderate to good success in connecting model predictions to spectroscopic data of mixed trimers and larger clusters [82–87], for instance.

Many-body effects or cooperative energetic contributions arise from polarization and are straightforward to incorporate by iterative (or other) solution of the classical mutual polarization/hyperpolarization equations. No new properties are needed for higher order vs 2-body terms and transferability is automatic because it is tied to molecular properties. An interesting example of the effect of mutual polarization is the contraction of separation distances in long chains of HCN molecules and the magnitude of the induced dipoles [81,88–91].

A special value of extensive treatment of electrical response in intermolecular interaction is that it enables incorporation of external electrical environments, such as those of an applied field or field gradient. Much as there can be an influence on conformation of a molecule such as glycine, there will also tend to be structural effects on clusters. Calculations where this has been considered have been done for the trimer of water [91] and for ice Ih [92–94], with the latter study providing clear insight on the enhancement of water's dipole in ice. This is a significant frontier because when combined with dynamical simulation, calculations may be feasible for engineering desired effects in aggregation, condensation, and so on from selective introduction of external electrical environments.

We note that an alternate to the discrete molecular approach for representing the surrounding environment of a solvent is the use of an isotropic dielectric medium. The medium can respond to explicitly treated molecules via its dielectric response. At short range, effects will be averaged relative to representing a solvent as discrete molecules, though at some range it appears advantageous to combine the two approaches [95].

A recent development that involves electrical response is targeted at reactions in solution and solvent effects on chemical properties. It is the effective fragment potential (EFP) by Day et al. [96,97] wherein 'active' molecules are treated by ab initio electronic structure methods apart from 'spectator' molecules of the solvent. The effective potentials that replace the spectator molecules in the ab initio treatment include Coulomb interactions, polarization and exchange repulsion. For the spectator segment of the approach, the permanent moment interactions are corrected by a screening function to account for charge penetration effects. This approach can be used for small, weakly bound clusters [97–99] as well as for reactions in solvents.

6. Summary and outlook

Electrical response in intermolecular interaction needs to be understood to the level of accurately predicting property changes. That objective offers the greatest capability for structural and dynamic simulations and it offers a particularly powerful way to connect quantum mechanical treatment with classical treatment of extended systems. The transferability of electrical properties and the many-body contributions from polarization are valuable for models which can be used from small cluster problems to condensed phases. Overall, the capability developing from electrical response analysis may lead to predictions of a molecular engineering sort: conformational control, alignment in clustering and deposition, and perhaps molecular switches. For instance, crossbar switching may underly new computer architectures [100] at a fast molecular level [101], and a possibility is that controlling molecular orientation or conformation electrically could be used to set data bits.

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