substituted benzenes and the $b_{2g}(\pi_3^*)$ orbital of benzene.[3b] For each of the molecules studied, the third electron affinity lies between −4.45 and −5.12 eV. The relative positions are in accord with our earlier discussion of inductive and resonance effects.

To provide an overview of the effects of substitution on the unfilled as well as filled orbitals, we present in Figure 2 a correlation diagram of the anion and cation states. For the latter, the splitting of the $e_{1g}(\pi)$ orbital of benzene into the $b_1(\pi)$ and $a_2(\pi)$ orbitals has been the subject of several investigations[17] employing photoelectron spectroscopy. We have not indicated the positions of the third π ionization potentials since, for some of the substituted benzenes, the assignment is still open to question.

These studies indicate that ETS provides a complement to photoelectron spectroscopy in yielding information about the shifts of levels due to substituent effects. Although the shifts in anion energies can be interpreted in terms of the same concepts invoked for cation states, the variations in anion lifetime are poorly understood and warrant further investigation.

Acknowledgment. We acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

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(2) The sign of the electron affinity is taken by convention to be negative for an unstable anion.

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(4) P. D. Burrow and K. D. Jordan, *Chem. Phys. Lett.*, **36**, 594 (1975).

(5) These spectra are acquired by passing a high resolution electron beam through a cell containing gas at sufficient density to scatter approximately 60% of the electron beam. The unscattered, or *transmitted*, portion of the beam, which is collected, is related to the total scattering cross section. To enhance the visibility of sharp variations in the scattering cross section, the derivative of the transmitted current with respect to energy is plotted as a function of the electron impact energy.

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(7) For a discussion concerning the identification of this state, see S. F. Wong and G. J. Schulz, *Phys. Rev. Lett.*, **35**, 1429 (1975).

(8) We infer from the characteristics of the spectra and our instrumental energy resolution that the lifetimes of the anions studied here correspond to spreads in energy in excess of 0.04 eV.

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(12) The vibrational spacing of the ground state anions of C_6H_5OH, $C_6H_5OCH_3$, $C_6H_5NH_2$, C_6H_5F, C_6H_5Cl, and C_6H_5Br is 120, 125, 120, 115, 125, and ~125 meV, respectively. Of the modes which are energetically possible, we favor the $a_2(\nu_{17a})$ ring puckering vibration. The excitation of this mode is consistent with the charge distribution of the $a_2(\pi^*)$ orbital.

(13) The existence of temporary anion states in benzene and certain of its derivatives was first inferred by R. N. Compton, L. G. Christophorou, and R. H. Huebner, *Phys. Lett.*, **23**, 656 (1966), using the SF_6 electron scavenger technique. The splitting of the degenerate benzene anion states under substitution was studied by L. G. Christophorou, D. L. McCorkle, and J. G. Carter, *J. Chem. Phys.*, **60**, 3779 (1974), using the trapped electron method. Neither of these techniques is sensitive to sharp structure in the scattering cross section and thus only a rather crude bound on the EA's can be determined in general. Furthermore, signals arising from direct vibrational excitation may also be present. The results described in the latter reference are not in good agreement with those of the present work nor are they consistent with known resonance and induction effects.

(14) I. Nenner and G. J. Schulz reported only a bound for the EA of C_6H_5F of >-1.0 eV.

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On the Development of Quantum Mechanical Solvent Effect Models. Macroscopic Electrostatic Contributions

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Abstract: Identification of the various kinds of interactions that are expected between a molecule and its environment is carried out and a model for the estimation of macroscopic electrostatic solvent effects using ab initio quantum mechanics is presented. Evaluation of all integrals in closed form when a spherical Guassian basis set is employed is shown to be possible and initial applications to CH_4, C_2H_6, C_3H_8, and n-C_4H_{10} in a n-hexane solvent are described. The need for inclusion of an additional potential to constrain the electrons within a sphere is described. It is shown how this constraining potential may be chosen to minimize the effect on the calculated interaction energy, while achieving the desired goal of constraining the electrons. Also, a strong dependence on choice of sphere radius is noted. Finally, the analysis necessary for inclusion of such a solvent effect model into a semiempirical formalism is described.

Interactions among molecular species clearly form one of the dominant and most pervasive preoccupations of chemists. However, not only the making and breaking of chemical bonds, but the effect of the environment on the physical and chemical properties of nonreactive systems, where lesser magnitude forces typically are involved, requires a detailed description of intramolecular interactions. Hence, the desirability of developing general approaches that will allow discussion of the various possible intermolecular interactions is self-evident.

In spite of the obvious need for such capabilities, previous approaches to the problem[1-23] have typically required serious approximations to be made, either in the model itself or in the techniques used to evaluate the model, so that computational tractability of the procedure is obtained. The current work formulates an approach that employs ab initio quantum mechanics, either directly or by the use of wave functions and concepts derived from ab initio studies, in order to evaluate more accurately some of the various interactions that might be expected.

In the following sections, the various kinds of interactions that might be expected between a molecule and its environment are discussed, using solute–solvent interactions as the particular vehicle for the discussion. The formulation of a quantum mechanical approach for evaluating one of the important types of interactions, i.e., electrostatic interactions between the solute and bulk solvent, is given within the framework of Hartree–Fock theory and using wave functions derived therefrom. Applications to several prototype systems are also described, which allow assessment of the assets and deficiencies of the approach, and the size and nature of systems to which it may be applicable.

General Description of Solute–Solvent Interactions

When considering the possible interactions between a solute molecule and the surrounding solvent, two qualitatively different kinds of interactions can be identified. The first of these, which represents interactions that occur at relatively short distances in the vicinity of the solute, will be referred to as "microscopic" interactions. The other type of interactions, which will be referred to as "macroscopic" interactions, consists of longer range interactions and can be thought of as the interactions between the solute and the bulk solvent, the latter of which may be treated as a continuum instead of discrete molecules. Using this approach, one must identify the nature of both the microscopic and macroscopic interactions and develop criteria for determining where microscopic interactions can be legitimately replaced by macroscopic interactions.

At the microscopic level, where the solute and each solvent molecule is treated explicitly, several kinds of interactions can be identified. These include electrostatic, polarization, charge transfer, exchange polarization, and correlation effects. Of these, the use of Hartree–Fock theory[24,25] with a suitably flexible basis set allows calculation of electrostatic and polarization effects simply by examining the individual solute and solvent molecules in the presence of each other. If, in addition, the system of solute and solvent molecules is treated as a "supermolecule", where the molecular orbitals are allowed to be delocalized over the entire system of solute and solvent molecules, then charge transfer and exchange polarization effects can also be included. An approach which utilizes the properties of spherical Gaussian basis orbitals for the description of these effects is described in the following paper. Of course, correlation effects require the introduction of configuration interaction or equivalent techniques, which are not treated in the current studies.

In the case of macroscopic interactions, we shall consider the possible interactions between a solute molecule and a solvent, the latter of which is considered to consist of a continuous, polarizable dielectric having macroscopic characteristics, e.g., a dielectric constant. Among the interactions that can be expected to be of importance in this category are electrostatic interactions, cavity energy, solvent relaxation effects, and short-range repulsive and dispersion forces.[1-5] Electrostatic interactions arise from the polarization of the dielectric by the solute, resulting subsequently in a "reaction field" which acts back upon the solute. The cavity energy arises because the volume occupied by the discrete solute molecule (or solute plus several discrete solvent molecules) needs to be excluded from the macroscopic dielectric and the cavity energy is that which is required to create such a cavity within the continuous dielectric. Solvent relaxation terms arise from the tendency of the dielectric to relax in time from its polarized form, while short-range repulsive effects are those encountered by the electrons of the molecules inside the cavity as they reach the outer edge.

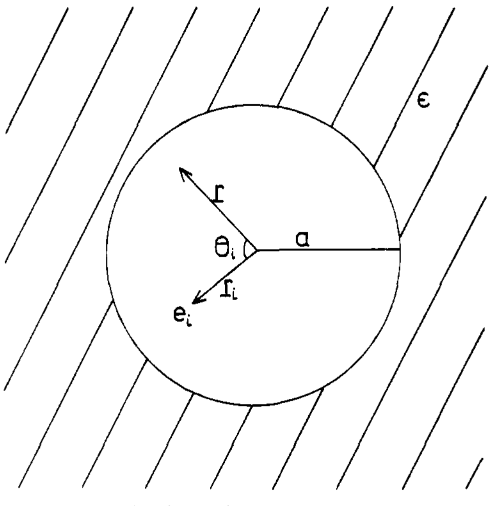

Figure 1. Depiction of the classical electrostatic model of Kirkwood.

The current studies are focussed toward formulation and application of ab initio quantum techniques for examining electrostatic interactions, both macroscopic and microscopic. The discussion in this paper and the next describes a formulation and application of ab initio techniques to several aspects of these effects, using floating spherical Gaussian orbitals[26] (FSGO) as the basis set. Particular attention is given to the desirability for applicability to large molecular systems.

Macroscopic Electrostatic Interactions

The method developed here[27] starts from a classical model due to Kirkwood[2] to deduce an appropriate quantum mechanical operator for description of the electrostatic potential due to the bulk solvent which affects a solute molecule.[28]

The classical model is one in which the solvent is described as a polarizable dielectric continuum, characterized by its static dielectric constant ϵ. The solute molecule is represented by M point charges (e_i), situated at fixed points (r_i) inside a sphere of radius "a" (see Figure 1). By solving the appropriate electrostatic equations inside and outside the sphere and applying the boundary conditions that are needed, Kirkwood found

$$V_\mathrm{I}(\mathrm{r}) = \sum_{k=1}^{M} \frac{e_k}{|\mathrm{r} - \mathrm{r}_k|} + \sum_{k=1}^{M} \left(\frac{e_k}{a}\right) \times \sum_{l=0}^{\infty} \left[\frac{(l+1)(1-\epsilon)}{\epsilon(l+1)+l}\right]\left(\frac{rr_k}{a^2}\right)^l P_l(\cos\vartheta_k) \qquad (1)$$

where $V_\mathrm{I}(\mathrm{r})$ is the potential at any point inside the sphere. The first set of terms arises from the point charges inside the sphere and the second set of terms arises because the point charges polarize the dielectric external to the sphere, and this polarized dielectric creates an additional contribution to the total potential inside the sphere.

To obtain the potential energy (U) due to the interaction of the solute molecule and solvent medium, one forms

$$U = \tfrac{1}{2} \int \rho(\mathrm{r}) V(\mathrm{r}) \mathrm{d}\mathrm{r} \qquad (2)$$

where $\rho(\mathrm{r})$ is the charge distribution of the molecule and $V(\mathrm{r})$ is the potential describing the interaction. In the classical model of Kirkwood, the charge distribution is represented by

$$\rho(\mathrm{r}) = \sum_{j=1}^{M} e_j \delta(\mathrm{r} - \mathrm{r}_j) \qquad (3)$$

and the appropriate potential $V(\mathrm{r})$ is the second set of terms in $V_\mathrm{I}(\mathrm{r})$ in eq 1. Evaluation of eq 2 then gives

$$U = \tfrac{1}{2} \sum_{j=1}^{M} e_j V(\mathbf{r}_j) \qquad (4)$$

or

$$U = \tfrac{1}{2} \sum_{j=1}^{m} \sum_{k=1}^{M} \left(\frac{e_j e_k}{a}\right) \times \sum_{l=0}^{\infty} \left[\frac{(l+1)(1-\epsilon)}{\epsilon(l+1)+l}\right] \left(\frac{r_j r_k}{a^2}\right)^l P_l(\cos\vartheta_{jk}) \qquad (5)$$

where ϑ_{jk} is the angle between $\mathbf{r}_j$ and $\mathbf{r}_k$. Note that the sums over j and k both extend over all particles.

In order to convert the above exact classical expression into a corresponding quantum mechanial operator, one replaces the classical point charge distribution by the corresponding quantum mechanical charge distribution. This has the effect in eq 5 of simply changing $\mathbf{r}_j$, $\mathbf{r}_k$, and ϑ_{jk} from fixed quantities to variables, resulting in the conversion of U into a quantum mechanical operator, $\mathcal{U}$. Using atomic units,[29] $\mathcal{U}$ can then be written in more familiar form as a sum of nuclear-nuclear, nuclear-electron, and electron-electron terms, i.e.,

$$\mathcal{U} = \sum_{l=0}^{\infty} \left[\frac{(l+1)(1-\epsilon)}{(l+1)\epsilon+l}\right]\left(\frac{1}{a}\right) \times \left\{\frac{1}{2}\sum_{\alpha,\beta}^{P} Z_\alpha Z_\beta \left(\frac{R_\alpha R_\beta}{a^2}\right)^l P_l(\cos\vartheta_{\alpha\beta}) - \sum_{\alpha}^{P}\sum_{i}^{S} Z_\alpha \left(\frac{R_\alpha r_i}{a^2}\right)^l P_l(\cos\vartheta_{\alpha i}) + \frac{1}{2}\sum_{i,j}^{S}\left(\frac{r_i r_j}{a^2}\right)^l P_l(\cos\vartheta_{ij})\right\} \qquad (6)$$

or

$$\mathcal{U} = \sum_{l=0}^{\infty} \mathcal{U}_l \qquad (7)$$

In eq 6, P nuclei and S electrons have been assumed, with the nuclear positions ($\mathbf{R}_\alpha$, $\mathbf{R}_\beta$) assumed to be fixed.

Considering several terms in $\mathcal{U}$ explicitly, the terms in $\mathcal{U}_0$ can be written as

$$\mathcal{U}_0 = -\tfrac{1}{2}(Q^2/a)(1-(1/\epsilon)) \qquad (8)$$

where Q is the net charge on the solute molecule. This is simply the Born charging term and vanishes for neutral molecules.

The terms corresponding to $l = 1$ can be written as

$$\mathcal{U}_1 = -\frac{1}{2}\left[\frac{2(\epsilon-1)}{2\epsilon+1}\right]\left(\frac{\mu^2}{a^3}\right) \qquad (9)$$

where μ^2 is the square of the dipole operator,

$$\boldsymbol{\mu} = \sum_{\alpha}^{P} Z_\alpha \mathbf{R}_\alpha - \sum_{i}^{S} \mathbf{r}_i \qquad (10)$$

If μ is taken as the sum of the permanent dipole moment and an induced moment and the operator nature of μ^2 is ignored, then the reaction field model due to point dipoles derived by Onsager[3] is obtained.

The model represented by eq 6 is seen to have several important attributes not possessed in previous models. In particular, the model is one in which *all* multipole terms of the reaction field are included, and the model is not limited to monopole and/or dipole terms. Second, the use of an operator instead of the corresponding classical quantities allows nonclassical (i.e., quantum mechanical) effects to be included in the treatment.

Finally, this formulation includes electrostatic macroscopic solvent terms in the Hamiltonian, with concomitant effect on the wave function, instead of applying a solvent effect correction to the free molecule charge distribution.[2]

In the treatment of the classical model, it is assumed that all point charges will be confined within the sphere of radius "a". However, it is convenient computationally, if not essential, for the wave function that is determined to extend everywhere, at least in principle. This computational need contradicts not only the classical model, but also the actual situation in a liquid, where the electrons of a particular molecule are confined essentially to that molecule by short-range overlap repulsive forces due to electrons of other molecules.

To account for this situation, an additional repulsive potential has been introduced, which constrains the electrons to remain substantially inside the sphere, but without introducing any discontinuities into the wave function. One form for this potential that has been found convenient in the current studies is

$$C = \sum_{i=1}^{S}\left(\frac{r_i}{a}\right)^n \qquad (11)$$

since this function remains small inside the sphere but rises rapidly outside. The value of n should be greater than any power of l required in $\mathcal{U}$ in eq 6 so that, if the sum over l is terminated with $l = m$, then $n \gg m$. This "penalty function" (C) will then override the terms in $\mathcal{U}$ (which have the form $(r_i/a)^{2l}$), causing the electrons to be constrained to be essentially inside the sphere.

Another of the advantages of the model expressed by eq 6 and 11 is its ease of incorporation into typical ab initio quantum mechanical studies. In particular, since $\mathcal{U}$ is a sum over zero-, one-, and two-electron operators only, and since C is a sum only over one-electron operators, incorporation into the framework of Hartree-Fock theory is straightforward. To do this, one defines a modified Hamiltonian ($\mathcal{H}'$) by

$$\mathcal{H}' = \mathcal{H} + \mathcal{U} + C \qquad (12)$$

where $\mathcal{H}$ is the usual free molecule Hamiltonian.[24,25] Then, an energy optimization using a self-consistent field approach on $\mathcal{H}'$ is employed to obtain the wave function for the solute in the presence of the bulk solvent.

However, it is desirable that both of the mean values $\langle\mathcal{U}\rangle$ and $\langle C\rangle$ should be monitored to insure that the constraint energy $\langle C\rangle$ remains much smaller than the solvation energy. Assuming that to be the case, the energy due to interaction of the solute with the solvent medium is given by:

$$E_S = E' - \langle C\rangle - E \qquad (13)$$

where E' is the energy associated with $\mathcal{H}'$ and E is the energy of the solute in the absence of the solvent, i.e., associated with $\mathcal{H}$.

It should be noted that the modified Hamiltonian $\mathcal{H}'$ contains two parameters, ϵ and "a". In principle, neither of these parameters need to be assigned arbitrarily. For example, if the sphere size is allowed to increase (with concomitant addition of appropriate numbers of explicit solvent molecules) until the potential exerted on the solute molecule is the same whether calculated using discrete solvent molecules or the continuum model, then use of the bulk dielectric constant for the solvent may be justifiable. In slightly greater detail, the static dielectric constant is appropriate for U_0 since no dynamics are involved but, for the remaining terms, the instantaneous polarization of the solvent is required and the high frequency dielectric constant is appropriate. Also, the sphere radius that is appropriate for use is determinable, at least in principle, using this procedure. However, practical difficulties currently associated with treatment of large numbers of explicit solvent molecules may require arbitrary assignments of the sphere radius (with corresponding errors associated with the use of bulk values for the dielectric constant).

Evaluation of Integrals

The evaluation of integrals involved in $\mathcal{H}'$ are, as usual,

Table I. Effect of Constraint Function on Calculated Solvent Effect for the Case of Ethane in *n*-Hexane

n	$(E' - \langle C \rangle)$ (E_a)	E_s, kcal/mol
8	−67.37537	−17.0179
10	−67.37538	−17.0242
12	−67.37539	−17.0304
14	−67.37539	−17.0304
16	−67.37539	−17.0304

simplified considerably if spherical Gaussian functions (FSGO) are used for the basis set. In particular, the basis orbitals (G_i) chosen for use are defined by

$$G_i = N_i \exp\{-(\mathrm{r} - \mathbf{R}_i)^2/\rho_i{}^2\} \qquad (14)$$

where N_i is a normalization constant, ρ_i is the "orbital radius" of the FSGO, and $\mathbf{R}_i$ is the origin of the FSGO, relative to some arbitrary origin.

The integrals that are required for calculation of $\mathcal{H}'$, in addition to the usual integrals that arise, have the forms

$$\mathrm{I} = \langle G_i(1) | R_\alpha{}^m r_1{}^m P_m(\cos\vartheta_{\alpha 1}) | G_j(1) \rangle \qquad (15)$$

$$\mathrm{II} = \langle G_i(1) | r_1{}^{2m} | G_j(1) \rangle \qquad (16)$$

$$\mathrm{III} = \langle G_i(1) G_k(2) | \, r_1{}^m r_2{}^m P_m(\cos\vartheta_{12}) | G_j(1) G_l(2) \rangle \qquad (17)$$

The first integral (I) arises from the nuclear–electronic term in U, while the second integral (II) arises from the electron–electron term when the electrons coincide and also from C if the power of n is taken as even. The third term (III) arises from the electron–electron term in U when the electrons are different. Defining

$$\mathbf{A}_{ij} = (\rho_j{}^2 \mathbf{R}_i + \rho_i{}^2 \mathbf{R}_j)/(\rho_i{}^2 + \rho_j{}^2) \qquad (18)$$

$$S_{ij} = \langle G_i | G_j \rangle \qquad (19)$$

and $\vartheta_{\alpha,ij}$ to be the angle between $\mathbf{R}_\alpha$ and $\mathbf{A}_{ij}$, and $\vartheta_{ij,kl}$ to be the angle between $\mathbf{A}_{ij}$ and $\mathbf{A}_{kl}$, then all of the required integrals are easily evaluated in closed form and are given by

$$\mathrm{I} = S_{\mathrm{ij}} \cdot R_\alpha{}^m A_{ij}{}^m P_m(\cos\vartheta_{\alpha,ij}) \qquad (20)$$

$$\mathrm{II} = S_{ij} \left\{ \binom{2m+1}{1} \frac{\gamma(m + 1/2)}{\beta^m \Gamma(1/2)} + \binom{2m+1}{3} A_{ij}{}^2 \frac{\Gamma(m - 1/2)}{\beta^{m-1}\Gamma(1/2)} + \binom{2m+1}{5} A_{ij}{}^4 \frac{\Gamma(m - 3/2)}{\beta^{m-2}\Gamma(1/2)} + \ldots + A_{ij}{}^{2m} \right\} \qquad (21)$$

$$\mathrm{III} = S_{ij} S_{kl} A_{ij}{}^m A_{kl}{}^m P_m(\cos\vartheta_{ij,kl}) \qquad (22)$$

$$\beta = \alpha_i + \alpha_j = (\rho_i{}^2 + \rho_j{}^2)/\rho_i{}^2 \rho_j{}^2 \qquad (23)$$

where $\binom{n}{k}$ is the binomial coefficient, $R_\alpha{}^m$ and $A_{ij}{}^m$ are the moduli of $\mathbf{R}_\alpha{}^m$ and $\mathbf{A}_{ij}{}^m$, respectively, and $\Gamma(x)$ is the Γ function, defined as

$$\Gamma(x) = \int_0^\infty t^{x-1} e^{-t} \, \mathrm{d}t$$

At this point, several computational aspects are of interest to note. In particular, integrals I and II are one-electron integrals and thus give rise to only $\sim n^2$ integrals if n basis functions are used. Relative to the approximately n^4 electron repulsion integrals in $\mathcal{H}$, the integrals arising from I and II do not add significantly to the total integral evaluation time and do not increase storage requirements at all. Integral III gives rise to $\sim n^4$ integrals in much the same manner as for usual electron repulsion integrals. However, as indicated in eq 22, only overlap integrals are involved and evaluation of the modified error function ($F_0(x)$) is not needed. Since these overlap integrals are also needed elsewhere in the calculations, reevaluation in this context is not needed. Also, since one of the primary factors in determining whether a usual electron repulsion integral is effectively zero is the overlap of orbitals, inclusion of integrals from III is not expected to change the number of nonzero integrals that need to be stored. Finally, each of I–III are computed and added to appropriate integrals in $\mathcal{H}$ during the integral evaluation stage and do not need to be altered later. Thus, I–III are not needed separately during the SCF stage. Thus, the net effect of inclusion of macroscopic electrostatic effects on the total SCF calculation is a small increase in total computational time and estimation of macroscopic electrostatic solvent effects for molecular systems approximately as large as possible for free molecules is expected to be relatively straightforward.

Investigation of Prototype Systems

In order to assess the characteristics of this model, several studies on prototype systems were carried out. So that these initial studies might be carried out on systems where the model is expected to be applicable without unnecessary complications, a series of hydrocarbons in nonpolar solvent have been chosen. In particular, the hydrocarbons methane, ethane, propane, and *n*-butane have been studied in a solvent of *n*-hexane.

The Hartree–Fock SCF calculations for the isolated molecules, as well as those in modified form for the molecules in a hexane solvent, have employed the ab initio molecular fragment procedure,[30] which is described in detail elsewhere.[31,32] For each of the solute molecules studied here, the original FSGO basis that was determined in studies[32] of CH_4 was employed for each carbon atom environment to facilitate comparisons. The same basis was used in both the free molecule and molecule-in-hexane studies. The dielectric constant for hexane was taken as 1.890, the static (bulk) value. The nuclear geometries used in these studies were taken from the electron diffraction studies of Kuchitsu[33] and no geometric relaxation was allowed.

The first study was designed to measure the effect of the sphere-constraining potential (C) on the electrostatic solvent effect. This study was carried out using ethane in hexane and the value of n in eq 11 was varied, but kept even for ease of integration. It was found in preliminary studies[27] that inclusion of terms in eq 7 through $\mathcal{U}_3$ was sufficient to insure convergence to a few tenths of a kilocalorie, which implies that values of n greater than 6 are needed in eq 11. The results for various choices of $n > 6$ are summarized in Table I. For these studies, the origin of the sphere was taken at the midpoint of the C–C bond in C_2H_6 and the radius of the sphere was taken as the distance from the origin to any of the hydrogen atoms plus 1.67 times the van der Waals radius of H. Further discussion of the choice of sphere radius is given below. As is apparent from the data in the table, both the total energy of the solvated system ($E' - \langle C \rangle$) and the electrostatic solvent energy (E_s) are insensitive to the value of n after $n > 10$ and they converge rapidly to constant values. Consequently, the value of $n = 12$ was chosen for all subsequent studies.

Next, the effect of sphere radius choice was studied, again using the example of ethane in hexane. The results of these studies are summarized in Table II. The sphere radius was taken as the origin-to-hydrogen distance as before plus the van der Waals radius of H scaled by multiplication by the values of the scale factor. As is apparent from the data, there is a marked dependence of the solvent effect on the sphere radius choice. Since it was not possible in a practical manner to determine the appropriate sphere radius by inclusion of sufficient explicit solvent molecules inside the sphere as described earlier, an arbitrary assignment was necessitated. In the remaining

Table II. Effect of Sphere Radius Choice on Calculated Solvent Effect for the Case of Ethane in *n*-Hexane

Scale factor	Radius (a_0)	$(E' - \langle C \rangle)$ (E_a)	E_s, kcal/mol
1.0	5.1859	−67.42673	−49.24
1.25	5.7528	−67.39868	−31.65
1.5	6.3197	−67.38267	−21.60
1.75	6.8866	−67.37288	−15.45
2.0	7.4535	67.36654	−11.47
2.25	8.0203	−67.36224	−8.78
2.5	8.5872	−67.35922	−6.88

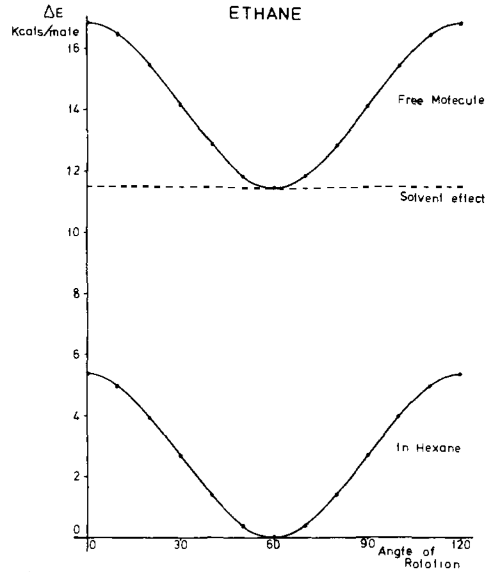

Figure 2. Electrostatic solvent effect on ethane rotational barrier.

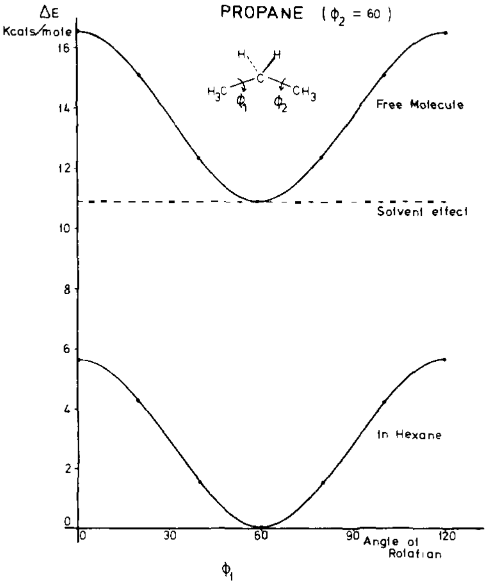

Figure 3. Electrostatic solvent effect on propane (ϕ_2 = 60°).

calculations, the sphere origin was taken as the center of mass of the solute molecule, and the radius was taken as the distance from the origin to the farthest atom plus twice the van der Waals radius of that atom.

In order to investigate the effect of the hexane solvent on conformation, the series of molecules, CH_4, C_2H_6, C_3H_8, and n-C_4H_{10}, was studied, using the sphere radius and other choices discussed previously. The results of these studies are summarized in Figure 2-6. In each case, the zero energy has been taken as the minimum energy in the presence of hexane, and the zero angle of rotation is taken as the eclipsed position of hydrogen atoms on adjacent carbon atoms. Of particular interest in these figures is the change in solvent effect (i.e., the "differential solvent effect") with conformation, which is shown as a dashed line in each figure. It is seen that, for ethane (Figure 2) and for the conformations of propane in which ϕ_2 = 60° (Figure 3), there is no differential solvent effect. On the other hand, for propane with ϕ = 0° (Figure 4) and for both butane cases studied (Figures 5 and 6), there is a noticeable differential solvent effect.

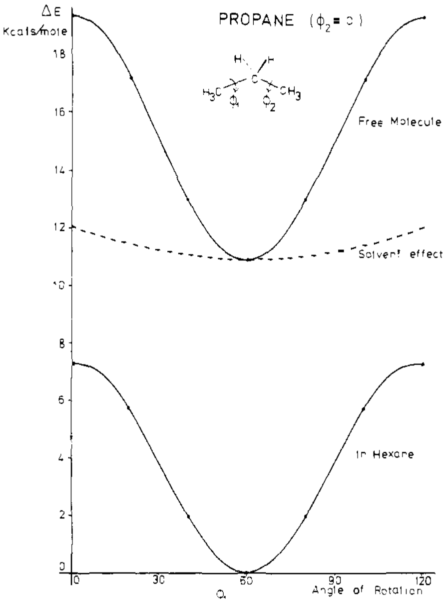

Figure 4. Electrostatic solvent effect on propane (ϕ_2 = 0°).

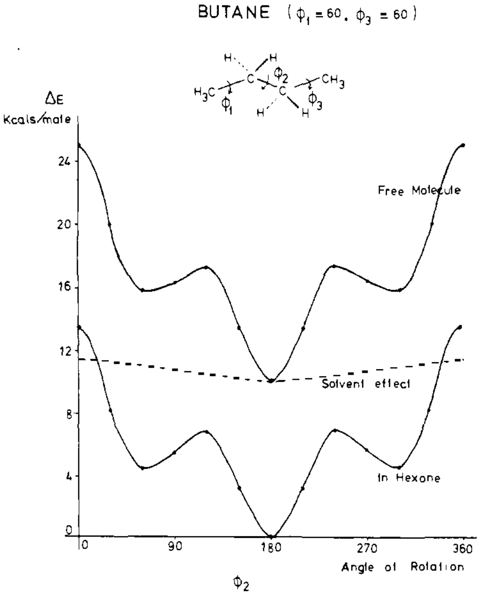

Figure 5. Electrostatic solvent effect on n-butane (ϕ_1 = 60°, ϕ_3 = 60°).

To estimate the incremental solvent effect due to elongation of the hydrocarbon chain, we note that the solvent effect for CH_4 is calculated to be −8.4 kcal/mol, and from Figures 2-6 it can be seen that the solvent effect for ethane is −11.5 kcal/mol, for C_3H_8 it is in the range −10.9 to −12.1 kcal/mol (depending upon conformation), and for n-(C_4H_{10} it is in the range −10.1 to −11.5 kcal/mol. After appropriate averaging over different conformations, it is expected that the incremental effect of adding additional CH_2 groups will be quite

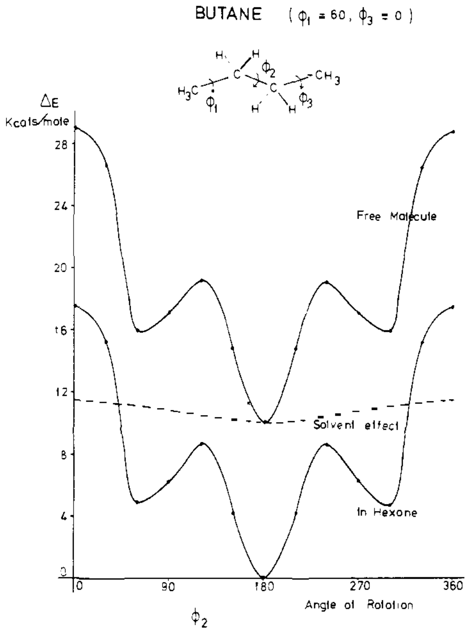

Figure 6. Electrostatic solvent effect on *n*-butane (ϕ_1 = 60°, ϕ_3 = 0°).

small. This is in qualitative agreement with a incremental free energy change of −0.849 kcal/mol observed experimentally[34] for hydrocarbons in a hexane solvent.

Discussion

The model and examples described above indicate that it is possible to formulate a satisfactorily general quantum mechanical model for macroscopic electrostatic effects that is also computationally tractable and convenient. In order to illustrate the connection to other approaches, as well as to point out other characteristics of the model, several additional comments are appropriate.

First, the generality of the model is clear, since terms corresponding to all multipole effects are included, at least in principle, in eq 6. Since most existing models include at most dipole effects, and since higher order terms have been found, at least in these initial studies, to be nonnegligible, such generality of the model seems quite advantageous. Also, even if terms only up to and including dipole effects are included, there are significant differences from dipole models that are typically used. In particular, the use of the operator form of μ in μ^2 gives rise to new terms of the r_i^2 type that are not present in a classical point dipole model. This means that $\mathcal{U}_1$ may give rise to a nonzero contribution to the solvent effect, even if the solute does not contain a permanent dipole moment. Such an effect occurred in the initial studies[27] of He in CCl_4. This suggests that the quantum mechanical dipole term also includes some interactions of the van der Waals type.[35]

As seen in the studies of prototype systems, one of the main difficulties of this model is the a priori assignment of sphere radius. While it is possible in principle to use criteria like the equality of the calculated potential at points within the solute using a microscopic or macroscopic description of the solvent, the practical application of such ideas is not generally feasible at present. This difficulty is further exacerbated by the strong dependence of the calculated solvent effect on sphere radius choice. Hence, while the choice of the distance of the farthest atom from the origin plus twice the van der Waals radius may be a convenient choice that gives rise to reasonable values of the calculated solvent effect, the arbitrariness of such a choice remains, and comparisons of calculated data with experimental data other than trends is not appropriate without extreme care. Of course, use of appropriate statistical mechanical concepts[8,11] in addition are necessary for comparison to experimental data.

Some of the difficulties in choice of C and sphere radius can, however, be rationalized by reference to a more detailed microscopic model of the solvent. In particular, the form of the penalty function C can be related to the form of the overlap repulsions from the solvent molecules, since these determine the localization of the electrons on the solute. A typical form for this repulsive potential is

$$V = A(r - a)^{-12}$$

where A is a constant, r is the distance from the center of the solute sphere, and a is the distance from this center to the nucleus of the nearest solvent atom. While this cannot be fitted exactly by a potential of the form of C, it can be fitted approximately in any appropriate region. The significant region will be the neighborhood of $r = a - v$, where v is the van der Waals radius of the solvent atom or molecule, since this is where the repulsion begins to be effective. To fit the steep rise of the potential, the derivatives are equated at $r = a - v$, i.e.,

$$\left(\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}r}\right)_{r=a-v} = \left(\frac{1}{C}\frac{\mathrm{d}C}{\mathrm{d}r}\right)_{r=a-v}$$

This yields, for the exponent n in C,

$$n = 12((1/v) - (1/a))$$

Thus, the choice of $n = 12$ for a cavity radius choice such that $a \gg v$ and $v \sim 1$ is directly rationalized. Since this a/v relationship will typically be the case, the contraint energy ($\langle C \rangle$) can be interpreted as being proportional to the overlap repulsion effect of the solute electrons with the solvent.

In addition, while precise assignment of the cavity radius has the difficulties mentioned above, estimation of reasonably narrow limits for the cavity radius can be found relatively easily. In particular, the distance from the origin to the farthest nucleus plus the van der Waals radius of that atom is the lowest possible limit. Also, the largest possible sphere radius is this distance plus the van der Waals radius of the nearest solvent atom. From the form of the penalty function used, it is expected that the optimum choice will be closer to the larger value.

It should also be noted that the magnitude of the stabilization energy may also be affected by the choice of sphere radius and other factors. In particular, since the contributions to $\mathcal{U}$ are proportional to inverse powers of the sphere radius, more folded conformations (with a smaller sphere radius) will experience larger effects. However, since the differential effects observed here (e.g., in butane) stabilize extended conformers instead of folded ones, these effects do not appear to be due simply to the change in sphere radius associated with the change in conformation. As to the magnitude of the stabilization energy found, it would appear to be exaggerated. This may be due to the fact that no individual solvent molecules were included within the sphere. Alternatively, the use of small basis sets may also be expected to overemphasize the calculated stabilization energy. Clearly, additional studies with explicit introduction of solvent molecules must be carried out, along with basis set extension studies, before this particular point can be resolved.

Finally, it is of interest to examine how one might incorporate such a model into a semiempirical formalism. As an example of such an analysis inclusion of eq 6 and 11 and analysis of the assumptions leading to the CNDO/2 SCF equations[36] result in a change in the form of the Fock matrix elements from

$$F_{\mu\mu} = U_{\mu\mu} + (P_{\mathrm{AA}} - \tfrac{1}{2}P_{\mu\mu})\gamma_{\mathrm{AA}} + \sum_{\mathrm{B}(\neq \mathrm{A})} (P_{\mathrm{BB}}\gamma_{\mathrm{AB}} - Z_{\mathrm{B}}\gamma_{\mathrm{AB}}) \quad (24)$$

and

$$F_{\mu\nu} = \beta_{\mathrm{AB}}{}^{0} S_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} \gamma_{\mathrm{AB}} \quad (\mu \neq \nu) \tag{25}$$

to

$$\begin{aligned} F_{\mu\mu}{}' = {} & U_{\mu\mu}{}' + (P_{\mathrm{AA}} - \tfrac{1}{2} P_{\mu\mu}) \\ & \times \left[\gamma_{\mathrm{AA}} + \sum_{l=0}^{\infty} \frac{(l+1)(1-\epsilon)}{(l+1)\epsilon + l} \left(\frac{1}{a^{2l+1}} \right) \gamma_{\mathrm{AA}}{}^{(l)} \right] \\ & + \sum_{\mathrm{B}(\neq \mathrm{A})} (P_{\mathrm{BB}} - Z_{\mathrm{B}}) \left[\gamma_{\mathrm{AB}} + \sum_{l=0}^{\infty} \frac{(l+1)(1-\epsilon)}{(l+1)\epsilon + l} \right. \\ & \left. \times \left(\frac{1}{a^{2l+1}} \right) \gamma_{\mathrm{AB}}{}^{(l)} \right] \end{aligned} \tag{26}$$

and

$$\begin{aligned} F_{\mu\nu}{}' = {} & (\beta_{\mathrm{AB}}{}^{0})' S_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} \\ & \times \left[\gamma_{\mathrm{AB}} + \sum_{l=0}^{\infty} \frac{(l+1)(1-\epsilon)}{(l+1)\epsilon + l} \left(\frac{1}{a^{2l+1}} \right) \gamma_{\mathrm{AB}}{}^{(l)} \right] \end{aligned} \tag{27}$$

where

$$\begin{aligned} & \int \int \phi_{\mu}(1)\, \phi_{\nu}(1) r_1{}^{l} r_2{}^{l} P_l(\cos \vartheta_{12}) \phi_{\lambda}(2) \phi_{\sigma}(2) \mathrm{d}\tau_1 \mathrm{d}\tau_2 \\ & \qquad = \gamma_{\mathrm{AB}}{}^{(l)} \delta_{\mu\nu} \delta_{\lambda\sigma} \end{aligned} \tag{28}$$

and ϕ_{μ}, ϕ_{ν} are on atom A and $\phi_{\lambda}, \phi_{\sigma}$ are atom B. The $U_{\mu\mu}{}'$ and $(\beta_{\mathrm{AB}}{}^{0})'$ term will contain, in addition to the usual CNDO terms, the contributions from C.

Hence, it is seen that the effect of the solvent arises both in one- and two-electron terms (through $U_{\mu\mu}{}'$, $(\beta_{\mathrm{AB}}{}^{0})'$ and the terms in $\gamma_{\mathrm{AB}}{}^{(l)}$). However, the dependence of the model on the sphere constraining terms is now implicit in $U_{\mu\mu}{}'$ and is no longer explicitly revealed in the model. In addition, methods of evaluation of $U_{\mu\mu}{}'$, $(\beta_{\mathrm{AB}}{}^{0})'$, and $\gamma_{\mathrm{AB}}{}^{(l)}$ must be devised by comparison with available experimental data before use is possible. Nevertheless, the applicability of the model within a semiempirical framework is clear.

Further characterization of the model (e.g., basis set dependence), as well as application to problems of chemical and biological interest, is underway and will be reported at a later date.

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