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Solvent Effect on the Electronic Structure of Molecules Studied by the Langevin Dipoles/Monte Carlo Approach

Józef Lipiński* and Wojciech Bartkowiak

Institute of Physical and Theoretical Chemistry, I-30, Wyb. Wyspiańskiego 27, Technical University of Wrocław, 50-370 Wrocław, Poland

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A method for calculation of the solvent effect on the molecular electronic ground-state structure of ions and molecules has been presented. In this method, being a modification of the Warshel et al. approach, solvent molecules are represented by a three-dimensional cubic grid of Langevin polarizable point dipoles. The modifications introduced into the original model include (a) the representation of a solute molecule by atomic point charges, dipoles, and quadrupoles, (b) the full (i.e., without dumping) Langevin formula for the polarization, (c) mutual polarization of the solute and the solvent molecules, and (d) the Monte Carlo sampling technique for determination of the optimal position and orientation of the solute molecule. The proposed method has been applied in the calculation of hydration energies for small molecules, ions, α-amino acids, and DNA bases, as well as in calculations of the solvent effect on the electronic spectra of acetone, 4-nitroaniline, and Reichardt's betaine dye.

Introduction

Accurate evaluation of the energies of solvation is important for understanding physical, chemical, and biochemical phenomena in solution. There are many techniques for the theoretical treatment of solvent effects in chemical systems. Excellent reviews have been appeared recently[1−6] which summarize the theoretical developments in this area. Quantum chemical procedures that include a solvent effect are also known.[1,3,4] Most of them introduce an energy operator of the solute molecule (H) in the form

$$H = H^0 + V \tag{1}$$

where H^0 denotes the energy operator for the free molecule and V is the energy of electrostatic interactions between solute and solvent molecules. Various methods have been employed, differing only in the choice of a detailed form of V. The electrostatic part of the solvation energy is defined as the difference between the total energy of the solvated molecule and the total energy of molecule in vacuo

$$\Delta E_{\mathrm{elst}} = \langle\Psi|H^0 + V|\Psi\rangle - \langle\Psi^0|H^0|\Psi^0\rangle \tag{2}$$

and the solvation Gibbs free energy as[3]

$$\Delta G_{\mathrm{sol}} = \langle\Psi|H^0 + V|\Psi\rangle - {}^1/_2\langle\Psi|V|\Psi\rangle - \langle\Psi^0|H^0|\Psi^0\rangle = \Delta E_{\mathrm{elst}} - {}^1/_2\langle\Psi|V|\Psi\rangle \tag{3}$$

The second term on the right-hand side of this equation represents the energy cost of polarizing the solvent, and $\langle\Psi^0|H^0|\Psi^0\rangle$ is the energy of the solute in the gas phase.

In quantum chemical calculations via eq 1 usually "quantum" analogues are used for the classical expression of the interaction energy with environment as compared to the old continuum models of solvation of Born,[7] Onsager,[8] and Kirkwood,[9] the Poisson−Boltzmann (PB) equation,[2,10−13] the reference interaction site model (RISM),[2,14−17] the Langevin dipole (LD) representation of the solvent molecules,[18−20] and Monte Carlo (MC)[5] or molecular dynamics (MD)[5] potentials. Among many theoretical quantum chemical treatments of the solvent effect, we mention here only the most representative. Born's theory or its generalization[21,22] has been used by Klopman,[23,24] Germer,[25] Constanciel et al.,[26−28] and Cramer and Truhlar.[4,29,30] The Onsager reaction field was a base for the so-called self-consistent-reaction-field (SCRF) theory of Tapia and Goscinski[31] and the direct reaction field (DRF) model of van Duijnen et al.,[32−35] whereas the general expression of the reaction field potential of Kirkwood[9] has been used in the calculation scheme by Rinaldi and Rivail[39] and by Christoferssen et al.[40] Recently, a novel approach to the electrostatic solvation energy calculations has been proposed by Klamt et al.[36−38] in their COSMO model. Among the classical continuum models, the polarized continuum model (PCM) first proposed by Miertus, Scrocco, and Tomasi[41,42] is presently probably most widely used for the description of solute−solvent interactions. The electrostatic potential obtained from the numerical solution of PB equations has been incorporated into quantum chemical calculations by Tannor et al.[43] and Chen et al.[44] The hybrid approach—based on the statistical theory of liquids (RISM-SCF)—has been recently published by Hirata and collaborators.[45−47] The Langevin dipole model of solvents was also incorporated into the quantum chemical Hamiltonian and used in calculation of solvation energies and electronic spectra of molecules in solution.[48−50] Combined approaches named QM/MC and QM/MD, in which solute molecules are treated quantum mechanically (semiempirically or ab initio) and solute−solvent and solvent−solvent interactions are evaluated using molecular mechanics potentials, have begun to appear (see e.g. refs 51−62). The incorporation of solvent potentials via eq 1 into quantum chemical packages enables not only calculations of the solvation energy (as was done in the classical calculations) but also exploration of the solvent effect on many chemical and physical properties of solute molecules: geometry, conformational and tautomeric equilibria, dipole moment, molecular spectra (UV, IR, NMR), nonlinear optical properties, and others.

Theoretical Outline

Classical LD/MC Technique. In the present work, the solvent effect was taken into account using a modified Langevin

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dipole (LD) model developed by Warshel and collaborators.[6,48-50] Below, we shall give a description of the modifications introduced in the original model. Solvent molecules are represented in the LD model by a three-dimensional cubic grid of polarizable point dipoles as described in refs 48−50. The solvent dipoles are located on a regular cubic grid (with Δ spacing) which is extended around the center of mass of the solute up to a radius of sphere R, typically 12−18 Å, and deleting all grid points whose distance from the closest solute atom is smaller than the sum of the corresponding solute atom and solvent van der Waals radii (i.e., $r_{\mathrm{vdW}} + \Delta/2$). The sphere (with R radius) is then surrounded by a bulk solvent which is treated as a dielectric continuum with the dielectric constant of the bulk solvent (ϵ). Each solvent dipole (an ith molecule) is polarized by the local field resulting from a set of charges, dipoles, and quadrupoles located on the atoms of the solute molecule, as well as from other solvent dipoles. Thus, the total field on the ith Langevin dipole can be expressed as

$$(\bar{E}_i)^n = \bar{E}_i^0 + (\bar{E}_i^{\mathrm{LD}})^n \tag{4}$$

where $\bar{E}_i^0$ is the field produced by the solute molecule and $\bar{E}_i^{\mathrm{LD}}$ is the field produced by other solvent molecules. The latter parameter is calculated self-consistently, $(\bar{E}_i^{\mathrm{LD}})^0 = 0$. In an nth iterative step, the polarization (expressed by the dipole moment of an ith solvent molecule) is approximated by the Langevin-type function

$$(\bar{\mu}_i^{\mathrm{LD}})^{n+1} = (\bar{e}_i)^n |\mu_{\mathrm{s}}| [\coth z_i - z_i^{-1}]^n \tag{5}$$

where $\bar{e}_i$ is the unit vector in the direction of E_i, μ_{s} is the permanent dipole moment of the solvent molecules, and

$$z_i = \frac{|\mu_{\mathrm{s}}||E_i|}{kT} \tag{6}$$

where k is the Boltzmann constant and T denotes absolute temperature.

Warshel advocated a simpler version of this model, in which in eq 4 the fields from other dipoles are neglected, and a dumping distance-dependent factor $d(r_i)$ is introduced into eq 6 to give eq 6a

$$z_i = \frac{|\mu_{\mathrm{s}}||E_i^0|}{kTd(r_i)} \tag{6a}$$

These approximations diminish greatly the computation time, but our experience shows that they also introduce several restrictions. First, final results depend strongly on the form of $d(r)$, and the extension to other solvent molecules is also restricted. Second, in this simpler procedure only the magnitude of the Langevin dipole, but not its direction, is optimized, which means that the contributions to the field from other point dipoles are not correctly treated.

In the modification of the method used in this paper, the electrostatic potential and the electric field around the solute molecule were calculated using so-called cumulative atomic multipole moments (CAMM).[63] In this approach, each ith atom of the solute molecule is represented by a scalar net atomic charge (q), a vector of atomic dipole ($\boldsymbol{\mu}$), and a tensor of atomic quadrupole ($\mathbf{Q}$), according to

$$q_i = Z_i - \sum_{I\in i}^{\mathrm{AO}} \sum_{J}^{\mathrm{AO}} P_{IJ} S_{IJ} \tag{7}$$

$$\mu_i^u = \sum_{I\in i}^{\mathrm{AO}} \sum_{J}^{\mathrm{AO}} P_{IJ} (S_{IJ} u_i - \langle I|u|J\rangle) \tag{8}$$

$$Q_i^{uv} = \sum_{I\in i}^{\mathrm{AO}} \sum_{J}^{\mathrm{AO}} P_{IJ} (u_i \langle I|v|J\rangle + v_i \langle I|u|J\rangle - u_i v_i S_{IJ} - \langle I|uv|J\rangle) \qquad (u, v = x, y, z) \tag{9}$$

where Z_i stands for the atomic core charge, P_{IJ} is the density matrix element, and $\langle I|x^k y^l z^m|J\rangle$ denotes the multipole integral in the atomic orbital basis with Cartesian operators defined relative to a atomic origin. In the LD model, the solvation free energy depends on the position and orientation of the solute molecule, placed in a cubic grid of polarizable solvent molecules. In the calculations reported in this paper, the optimum position and orientation of the solute molecule was determined using the Monte Carlo (MC) sampling method;[64] hereafter, the modification of the model will be referred to as the LD/MC technique. The maximum linear displacements (δr) and maximum rotation angle ($\delta\xi$) of the solute molecule (treated at this step as a rigid body) were chosen to bring the acceptance ratio near 0.5, in order to achieve a reasonable convergence. In most simulations, we used $\delta r = 0.05{-}0.10$ Å, and $\delta\xi = 5{-}10°$. In each MC step, permanent and induced dipole moments of each solvent molecule, as well as the electric potential and electric field vector produced by all solvent molecules on each atom of the solute, were iteratively calculated using eqs 4−6. In addition to the polarization of the permanent solvent dipoles, the induced solvent dipoles are also considered. These induced dipoles were calculated by the usual approximation:

$$\bar{\mu}_{i,\mathrm{LD}}^{\mathrm{ind}} = \alpha_{\mathrm{LD}} \bar{E}_{i,\mathrm{LD}}^n \tag{10}$$

where α_{LD} is the polarizability of the solvent molecules and $\bar{E}_{i,\mathrm{LD}}$ is the electric field on the ith solvent molecule. This field is calculated self-consistently considering the field from solute atomic charges, atomic dipoles, and atomic quadrupoles (obtained from CAMM's, see above) as well as the permanent and induced solvent dipoles.

$$\bar{E}_{i,\mathrm{LD}}^n = \bar{E}_i - \sum_{j\neq i} \frac{1}{r_{ij}^{\ 3}} (\bar{\mu}_{j,\mathrm{LD}}^{\mathrm{ind},n-1} - 3(\bar{r}_{ij} \bar{\mu}_{j,\mathrm{LD}}^{\mathrm{ind},n-1}) \bar{r}_{ij}/r_{ij}^{\ 2}) \tag{11}$$

The dipole moments of all solvent molecules induce a dipole moment on the ith atom of the solute molecule according to eq 12,

$$\bar{\mu}_{i,\mathrm{sol}}^{\mathrm{ind}} = \alpha_{i,\mathrm{sol}} \bar{E}_i^{\ \mathrm{LD}} \tag{12}$$

where $\alpha_{i,\mathrm{sol}}$ is the polarizability of the ith solute atom and $\bar{E}_i^{\mathrm{LD}}$ is the electric field produced by all permanent LD solvent dipoles on the ith solute atom. The total electrostatic solvation free energy (ΔG_{sol}) can then be determined as the sum of the following contributions:

$$\Delta G_{\mathrm{sol}} = \Delta G_{\mathrm{LD}} + \Delta G_{\mathrm{ind,sol}} + \Delta G_{\mathrm{ind,LD}} + \Delta G_{\mathrm{bulk}} \tag{13}$$

where

$$\Delta G_{\mathrm{LD}} = -{}^1\!/_2 \sum_i^N \bar{\mu}_i^{\ \mathrm{LD}} \bar{E}_i^{\ 0} \tag{14}$$

$$\Delta G_{\mathrm{ind,sol}} = -{}^1\!/_2 \sum_i^{\text{sol atoms}} \bar{\mu}_{i,\mathrm{sol}}^{\mathrm{ind}} \bar{E}_i^{\mathrm{LD}} \tag{15}$$

$$\Delta G_{\mathrm{ind,LD}} = -{}^1/_2\sum_i^N \bar{\mu}_{i,\mathrm{LD}}^{\mathrm{ind}}\bar{E}_i^0 \tag{16}$$

$$\Delta G_{\mathrm{bulk}} = -\frac{0.5Q^2}{R}\left(1-\frac{1}{\epsilon}\right) - \frac{0.5M^2(2\epsilon-2)}{R^3(2\epsilon+1)} \tag{17}$$

and ΔG_{LD} is the free energy of the permanent Langevin dipoles in the electrostatic field from solute charges, dipoles, and quadrupoles, $\Delta G_{\mathrm{ind,sol}}$ is the free energy of the solute induced dipoles, and $\Delta G_{\mathrm{ind,LD}}$ denotes the free energy of the solvent induced dipoles. ΔG_{bulk} is the free energy of solvation of the solute molecule and solvent molecules by the bulk solvent outside the sphere (with R radius) of explicit LD dipoles evaluated using the sum of the Born's formula and/or Onsager equation. Q, M, and R denote the total charge, total dipole moments, and radius of sphere, respectively, and ϵ is the bulk dielectric constant of the solvent. In eq 13 we neglected contributions from dispersion, repulsion, and cavitation terms because the ΔG_{cav} values are approximately equal to the $\Delta G_{\mathrm{disp-rep}}$ magnitudes (in absolute values). Therefore, these terms are nearly compensated or are slightly positive (1−2 kcal/mol) in summation, and the solvation energy is mainly represented by electrostatic terms. Moreover, these terms are strongly dependent on method used in cavitation energy calculations and parametrization scheme employed in evaluation of dispersion−repulsion contribution. However, these terms must be included in the calculation of solvation free energy in a nonpolar solvents. Work in this direction is currently in progress.

In our approach, solvent (water) is modeled by the experimental values of the molecular dipole moment ($\mu_s = 1.85$ D), the molecular polarizability ($\alpha_{\mathrm{LD}} = 1.45$ Å^3), the dielectric constant ($\epsilon = 78$), and grid spacing ($\Delta = 3.0$ Å). The grid radius (R) was chosen so the number of solvent molecules considered in calculations amounted to ca. 250−300. The atomic polarizabilities of the solute atoms (see eq 12) are taken from empirical method based on the additivity of atomic polarizability.[65,66] The values of the solute atomic van der Waals radii r_{vdW} are adopted from Luzhkov and Warshel study[48] (r_{vdW} [Å]: H, 1.2; C, 2.0; N, 1.4; O, 1.3).

Incorporation of the LD/MC Model into Quantum Chemical Calculations. The permanent and induced dipole moments of the solvent molecules obtained in the MC run generate the averaged (in the meaning of the MC method) electrostatic potential and electric field vector on each atom of the solute molecule. Thus, the total potential V acting on solute atoms is a sum of averaged potential due to the permanent (V_{perm}) and induced (V_{ind}) dipole moments of solvent molecules:

$$V = V_{\mathrm{perm}} + V_{\mathrm{ind}} \tag{18}$$

These average values of the electrostatic potential and electric field vector are introduced into eq 1, and after the usual SCF calculation, new atomic charges, atomic dipoles, and atomic quadrupoles have been obtained, which generate new potentials (V_{perm} and V_{ind}), which are then incorporated into eq 1 to give new charges, dipoles, and quadrupoles. By repeating these calculations, we obtain new solvent potentials, etc., until self-consistency is reached. From the standard SCF calculation and CI procedure we obtain energies of the electronic ground state E_{g} and any excited electronic states E_{e} in the forms

$$E_{\mathrm{g}} = \langle\Psi_{\mathrm{g}}|H^0 + V_{\mathrm{perm,g}} + V_{\mathrm{ind,g}}|\Psi_{\mathrm{g}}\rangle \tag{19}$$

$$E_{\mathrm{e}} = \langle\Psi_{\mathrm{e}}|H^0 + V_{\mathrm{perm,g}} + V_{\mathrm{ind,g}}|\Psi_{\mathrm{e}}\rangle \tag{20}$$

where index "g" in the potentials $V_{\mathrm{perm,g}}$ and $V_{\mathrm{ind,g}}$ denotes that they are obtained from the ground-state multipole distribution of the solute molecule. However, as noted by Luzkhov and Warshel,[48] the expression for E_{e}, eq 20, contains the term $\langle\Psi_{\mathrm{e}}|V_{\mathrm{ind,g}}|\Psi_{\mathrm{e}}\rangle$, which gives nonphysical interaction between the solute in the excited state and the solvent ground state induced potential. The "true" excited-state energy will be obtained with the Hamiltonian in which $V_{\mathrm{ind,g}}$ is replaced by $V_{\mathrm{ind,e}}$, i.e., $H^0 + V_{\mathrm{perm,g}} + V_{\mathrm{ind,e}}$. This can be approximately done by perturbation theory applied to energy E_{e}. Treating operator (V') in the form

$$V' = V_{\mathrm{ind,e}} - V_{\mathrm{ind,g}} \tag{21}$$

as a perturbation, we can estimate—to the first order perturbation theory—the "true" energy of the excited state ($E_{\mathrm{e,t}}$) as equal to

$$E_{\mathrm{e,t}} \cong E_{\mathrm{e}} + \langle\Psi_{\mathrm{e}}|V_{\mathrm{ind,e}}|\Psi_{\mathrm{e}}\rangle - \langle\Psi_{\mathrm{e}}|V_{\mathrm{ind,g}}|\Psi_{\mathrm{e}}\rangle \tag{22}$$

(We neglected the higher order energy corrections, assuming that these terms are small; however, we have not tested this assumption.)

The solvation energy of the excited states is evaluated using the ground-state solvent configurations, since the absorption of light is faster than the reorientation time of the permanent dipoles of the solvent and allowing only the induced dipoles to be reoriented. Thus, in the calculation of the electronic transition of a solute molecule in a field of polarizable solvent molecules, we must include the change of the energy necessary to polarize the solvent in the excited and ground state, ΔE_{ind}, of the solute molecule by the solvent induced dipoles:

$$\Delta E_{\mathrm{ind}} = E_{\mathrm{ind,e}} - E_{\mathrm{ind,g}} = -{}^1/_2[\langle\Psi_{\mathrm{e}}|V_{\mathrm{ind,e}}|\Psi_{\mathrm{e}}\rangle - \langle\Psi_{\mathrm{g}}|V_{\mathrm{ind,g}}|\Psi_{\mathrm{g}}\rangle] \tag{23}$$

Finally, the electronic transition energy in solution is calculated from eq 24

$$\Delta E_{\mathrm{eg}}(\mathrm{sol}) = E_{\mathrm{e,t}} - E_{\mathrm{g}} + \Delta E_{\mathrm{ind}} = \Delta E_{\mathrm{eg}}(\mathrm{sol,CI}) + {}^1/_2\langle\Psi_{\mathrm{e}}|V_{\mathrm{ind,e}}|\Psi_{\mathrm{e}}\rangle - {}^1/_2\langle\Psi_{\mathrm{g}}|V_{\mathrm{ind,g}}|\Psi_{\mathrm{g}}\rangle + \langle\Psi_{\mathrm{g}}|V_{\mathrm{ind,g}}|\Psi_{\mathrm{g}}\rangle - \langle\Psi_{\mathrm{e}}|V_{\mathrm{ind,g}}|\Psi_{\mathrm{e}}\rangle \tag{24}$$

where $\Delta E_{\mathrm{eg}}(\mathrm{sol,CI})$ is the transition energy calculated directly from the CI procedure

$$\Delta E_{\mathrm{eg}}(\mathrm{sol,CI}) = \langle\Psi_{\mathrm{e}}|H^0 + V_{\mathrm{perm,g}} + V_{\mathrm{ind,g}}|\Psi_{\mathrm{e}}\rangle - \langle\Psi_{\mathrm{g}}|H^0 + V_{\mathrm{perm,g}} + V_{\mathrm{ind,g}}|\Psi_{\mathrm{g}}\rangle \tag{25}$$

Thus, the solvent shift $\Delta E_{\mathrm{shift}}$ is equal to

$$\Delta E_{\mathrm{shift}} = \Delta E_{\mathrm{eg}}(\mathrm{sol}) - \Delta E_{\mathrm{eg}}(\mathrm{gas,CI}) \tag{26}$$

where $\Delta E_{\mathrm{eg}}(\mathrm{gas,CI})$ denotes the transition energy calculated in the absence of an intervening solvent potential

$$\Delta E_{\mathrm{eg}}(\mathrm{gas,CI}) = \langle\Psi^0{}_{\mathrm{e}}|H^0|\Psi^0{}_{\mathrm{e}}\rangle - \langle\Psi^0{}_{\mathrm{g}}|H^0|\Psi^0{}_{\mathrm{g}}\rangle \tag{27}$$

This procedure of calculation will be referred to as quantum-mechanical LD/MC (QM/LD/MC). It corresponds to the "perm,ind" model of Luzkhov and Warshel;[48] see eq 18 in their paper. Recently, the method presented here has been used in the calculation of solvent effects on nonlinear optical pro-

TABLE 1: Calculated (LD/MC) and Observed Hydration Free Energies (in kcal/mol) for Neutral Molecules

molecule	ΔG_{LD}	$\Delta G_{ind,LD}$	$\Delta G_{ind,sol}$	ΔG_{bulk}	ΔG_{sol}	exp[a]
H_2O	−4.9	−0.7	−0.3	−0.6	−6.5	−6.3
NH_3	−3.3	−0.8	−0.8	−0.1	−5.1	−4.3
$(CH_3)_2CO$	−3.0	−0.7	−0.9	−0.2	−4.8	−3.8
CH_3OH	−2.5	−0.5	−0.4	−0.2	−3.7	−5.1
CH_3CN	−4.0	−1.0	−0.3	−0.3	−5.6	−3.9
CH_3NH_2	−2.6	−0.2	−0.3	−0.3	−3.4	−4.5
CH_3COOH	−4.1	−0.6	−0.2	−0.7	−6.3	−6.7
imidazole	−4.0	−0.9	−0.4	−0.2	−5.5	−5.9,[b] −10.2
C_6H_6	−0.1	−0.0	−0.0	−0.1	−0.2	−0.9
PhOH	−3.2	−0.9	−0.4	−0.3	−4.8	−6.6
CH_3CONH_2	−5.4	−1.2	−0.6	−0.3	−7.5	−9.7
$PhNH_2$	−2.6	−0.6	−0.8	−0.4	−4.4	−4.9
PhCN	−3.7	−1.0	−0.6	−0.4	−5.7	−4.8

[a] Cited from ref 4 and from Alkorta, I.; Villar, H. O.; Perez, J. J. *J. Comput. Chem.* **1993**, *14*, 620. Cabani, S.; Giani, P.; Molica, V.; Lepori, L. *J. Solution Chem.* **1981**, *10*, 563. Ben-Naim, A.; Marcus, Y. *J. Chem. Phys.* **1984**, *81*, 2016. Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109. [b] Estimated in ref 22.

TABLE 2: Calculated (LD/MC) and Observed Hydration Free Energies (in kcal/mol) for Ions

ion	ΔG_{LD}	$\Delta G_{ind,LD}$	$\Delta G_{ind,sol}$	ΔG_{bulk}	ΔG_{sol}	exp[a]
H_3O^+	−65.2	−19.9	−1.7	−14.6	−101.5	−104
HO^-	−61.3	−15.4	−0.3	−16.0	−93.0	−106
$HCOO^-$	−52.8	−13.6	−0.5	−15.3	−82.2	−80
NH_4^+	−50.6	−16.9	−0.3	−13.8	−81.6	−79
NO_2^-	−51.3	−12.9	−0.2	−12.5	−76.9	−72
CH_3COO^-	−48.4	−11.2	−1.0	−15.2	−75.8	−77
$CH_3NH_3^+$	−46.3	−10.6	−0.7	−15.8	−73.3	−70
CN^-	−47.9	−12.2	−0.1	−12.6	−72.8	−77
CH_3O^-	−45.7	−10.4	−0.3	−14.8	−71.2	−95
imidazolium	−37.8	−8.1	−0.3	−14.1	−60.3	−62

[a] Cited from Alkorta, I.; Villar, H. O.; Perez, J. J. *J. Comput. Chem.* **1993**, *14*, 620.

perties[67−69] and in calculations of solvatochromic shifts in the electronic spectra of benzimidazole-based betaines.[70,71]

Results and Discussion

The SCF and CI procedures and CAMM's calculations have been realized using our semiempirical GRINDOL[72] program, being a modified version of the NDO-like approach. The method enables calculation of ground- and excited-state properties with acceptable agreement with relevant experimental studies for isolated molecules and molecular complexes within the unified parametrization scheme (see e.g. refs 67−72 and references therein).

Hydration Energies. Hydration free energies for all molecules were calculated by both methods presented here, but only results from "classical" calculations (i.e., using the LD/MC method) are given. The QM/LD/MC method produces similar results, except for slightly smaller values of induction terms due to the underestimation of atomic polarizabilities by the GRINDOL method.

Small Molecules and Ions. The free energies of hydration for 13 molecules and 10 ions are shown in Tables 1 and 2. (The AM1[73] calculated gas phase structure of molecules and ions was assumed for all calculations.) The computed hydration energies are in reasonable agreement with experimental data, the standard deviation between calculated and experimental values for neutral and ionic species being only 0.9 and 3.8 kcal/mol, respectively.

TABLE 3: Calculated (LD/MC) and Observed[a] Hydration Free Energies (in kcal/mol) for α-Amino Acids

amino acid	ΔG_{LD}	$\Delta G_{ind,LD}$	$\Delta G_{ind,sol}$	ΔG_{bulk}	ΔG_{sol}	exp[a]
asp	−10.9	−2.6	−1.5	−0.3	−15.3	−10.9
arg	−9.4	−2.3	−1.7	−0.4	−13.8	−10.9
glu	−8.4	−2.0	−0.9	−0.2	−11.5	−10.2
his	−8.1	−1.8	−1.1	−0.3	−11.3	−10.3
asn	−7.9	−1.8	−0.9	−0.2	−10.8	−9.7
ser	−7.2	−1.8	−1.2	−0.3	−10.5	−5.1
thr	−6.3	−1.5	−0.7	−0.3	−8.8	−4.9
leu	−5.7	−1.4	−0.8	−0.4	−8.3	2.3
hpr	−5.7	−1.3	−0.6	−0.3	−7.9	
lys	−5.4	−1.3	−0.8	−0.3	−7.8	−9.5
gly	−5.2	−1.2	−0.6	−0.2	−7.2	
ile	−4.6	−1.2	−0.4	−0.2	−6.4	
tyr	−4.4	−1.1	−0.5	−0.2	−6.2	−6.1
val	−3.9	−1.0	−0.6	−0.2	−5.7	2.0
trp	−3.6	−0.9	−0.5	−0.3	−5.3	−5.9
ala	−3.2	−0.8	−0.3	−0.3	−4.6	1.9
phe	−2.4	−0.5	−0.4	−0.2	−3.5	−0.8

[a] Wolfenden, R.; Anderson, L.; Cullis, P. M.; Southgate, C. C. B. *Biochemistry* **1981**, *20*, 849. Cited after Wesson, L.; Eisenberg, D. *Protein Sci.* **1992**, *1*, 227. Note that "experimental" data cited in this table refer to vapor-to water free energies of transfer for amino acid side chain analogues.

TABLE 4: Calculated (LD/MC) Hydration Free Energies (in kcal/mol) for Nucleic Acid Bases

molecule	ΔG_{LD}	$\Delta G_{ind,LD}$	$\Delta G_{ind,sol}$	ΔG_{bulk}	ΔG_{sol}
A	−4.3	−1.0	−0.5	−0.2	−6.1
T	−9.6	−2.3	−0.2	−0.1	−12.8
G	−11.4	−2.6	−1.3	−0.3	−15.6
C	−10.3	−2.4	−1.1	−0.4	−14.2
AT(HB)	−10.1	−2.5	−1.1	−0.3	−14.0
GC(HB)	−11.7	−2.7	−1.4	−0.2	−16.0
AT(ST)	−8.0	−1.9	−0.8	−0.3	−11.0
TA(ST)	−8.7	−2.1	−1.0	−0.4	−12.2
GC(ST)	−10.0	−2.4	−1.0	−0.3	−13.7
CG(ST)	−13.4	−3.2	−1.3	−0.5	−18.4

α-*Amino Acids.* The calculated hydration energies of some α-amino acids for experimental geometries (taken from the compilation presented in ref 74) and compared with experimental data for amino acid side chain molecules are presented in Table 3. The calculated values of ΔG_{sol} exhibit a reasonable correlation with experimental data, but this agreement has to be taken with care because the correct calculation of solvation energies for species such as α-amino-acids, with several local conformational equilibria and low-energy barriers between conformations, should be conducted by examining the complete conformational energy surface and calculation of the Boltzmann-weighted free energy of hydration. It should be noted that there is a substantial induction energy contribution to the total hydration energies, ranging from 20 to 30%.

Nucleic Acid Bases. Table 4 presents the calculated free energies of hydration for the nucleic acid bases of DNA and their hydrogen-bonded (HB) and stacked (ST) complexes. The geometries of isolated bases as well as their complexes are taken from experimental studies of B-DNA.[75] However, no experimental results are available to test the theoretical results. Therefore, in Table 5 we compare our results with those from other works. Our calculations indicate that hydration energies decrease in the order G > C > T > A. The same results have been obtained by Miller and Kollman,[76] Elcock et al.,[77] and Young and Hiller;[78] however, other sequences of the relative hydration energies appear also (see Table 5). Moreover, the absolute values of hydration free energies obtained by various authors are also different. Thus, a more systematic, detailed, and sophisticated study of this problem is clearly needed. Similarly, as in the case of α-amino acids, an important induction contribution to the total solvation free energy is noted. The hydration free energies for the HB complexes (see Table 4) of base pairs arranged in the Watson−Crick configurations

TABLE 5: Comparison of Relative Hydration Free Energies (in kcal/mol) for Nucleic Acid Bases Obtained with Different Methods (Absolute Hydration Energies in Brackets)

method	A	T	C	G
QM/MM[a]	[−5.1] 0.0	−3.4	−11.2	−8.4
FDPB OPLS[b]	[−10.8] 0.0	0.4	−6.0	−8.9
FDPB CHARMM[b]	[−10.3] 0.0	2.3	−0.9	−5.0
FDPB AMBER[b]	[−10.7] 0.0	−8.4	−7.6	−16.6
AM1−SM2[c]	[−20.9] 0.0	7.6	2.2	−3.4
SCRF[d]	[−6.5] 0.0	−2.1	−6.5	−9.6
FEP AMBER[e]	[−12.6] 0.0	5.1	−0.1	−7.0
AMBER/TI[f]	[−12.0] 0.0	−0.4	−6.4	−10.4
FEP OPLS[g]	[−11.6] 0.0	−1.5	−8.5	−10.1
this work	[−6.1] 0.0	−6.7	−8.1	−9.5

[a] Gao, J. *Biophys. Chem.* **1994**, *51*, 253. [b] Mohan, V.; Davis, M. E.; McCammon, J. A.; Pettitt, B. M. *J. Phys. Chem.* **1992**, *96*, 6428. [c] Cramer, C. J.; Truhlar, D. G. *Chem. Phys. Lett.* **1992**, *198*, 74. [d] Young, P. E.; Hillier, I. H. *Chem. Phys. Lett.* **1993**, *215*, 405. [e] Bash, P. A.; Singh, U. C.; Langridge, R.; Kollman, P. A. *Science* **1987**, *236*, 564. [f] Miller, J. L.; Kollman, P. A. *J. Phys. Chem.* **1996**, *100*, 8587. [g] Elcock, A. H.; Richards, W. G. *J. Am. Chem. Soc.* **1993**, *115*, 7930.

are, at least, qualitatively acceptable as compared to the results of Cieplak and Kollman.[79] However, the hydration free energies for the stacked complexes are markedly underestimated as compared to the results of Cieplak and Kollman. On the other hand, the stacking geometries are characterized by a flat potential surface for rotation of one base with respect to the other,[80] and as a consequence the B-DNA stacked conformation, used in our calculations, may be inappropriate in simulation studies in a polar solvent.

Electronic Spectra. Solvatochromic shifts of electronic transitions are widely used for the exploration of solute−solvent interactions in solution.[81−85] The applicability of the QM/LD/MC method has been tested on the calculation of solvent effects on the electronic transitions of three molecules which their low-lying singlet electronic transition representing a small blue shift (acetone), a large red shift (4-nitroaniline, PNA), and a very large blue shift [(2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenolate, known as Reichardt's betaine dye)]. The ground-state geometries of all molecules have been optimized using the AM1 method of Dewar et al.[73] The electronic transitions, oscillator strengths, and dipole moments have been evaluated using the GRINDOL[72] package including the configuration interaction (CI), with 600 (Reichardt's betaine dye) or all (acetone, PNA) singly excited configurations included. The number of solvent (water) molecules taken into account in the calculations amounted to ca. 250 in the case of acetone and PNA and to 450 in the case of Reichardt's betaine dye. We have neglected the contributions due to the dispersion term, which gives a red shift, estimated to be relatively unimportant for polar solutes.[84,85] The results of these calculations are presented in Table 6.

Acetone. As the solvent polarity increases, the n−π*(S_1 state in Table 6) transition moves toward higher energy (blue shift). In water, the computed blue shift of this transition is equal to $\tilde{\nu}_{max} = 1270$ cm^{-1}, which agrees favorably with experimental data $\tilde{\nu}_{max} = 1560$ cm^{-1} [86] and QM/MM calculations of Gao,[87] 1694 cm^{-1}, or De Bolt and Kollman[88] molecular dynamics calculations, 1680 cm^{-1}. Fox and Rösch[89] reported calculations based on the continuum model of PCM. These authors noted that the calculated shift is strongly dependent on the cavity radius and/or cavity scaling factor.

4-Nitroaniline (PNA). In studying the electronic transition process, our approach was tested by the PNA molecule selected as a molecule undergoing a very large dipole moment change in approaching the first π−π* excited state (S_1 state in Table 6). The calculated dipole moment in the ground and the first exited state of the isolated molecule is $\mu = 7.1$ and 14.3 D, respectively, very well correlating with the experimental values of $\mu = 6.2$ and ca. 16 D.[82] As expected, the dipolar charge transfer excited state is more stabilized by the polar solvent, resulting in a red shift of the transition energy. The calculated (Table 6) red shift for this state ($\Delta\tilde{\nu}_{max} = 5753$ cm^{-1}) lies between the experimental values published by Millefiori et al.[90] and by Suppan.[82] Similar results for solvatochromic shifts of PNA have been obtained by Karelson and Zerner[91] and by Fox and Rösch.[92]

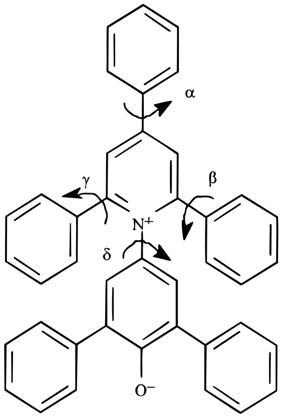

Figure 1. Structure of Reichardt's betaine dye.

TABLE 6: Calculated Solvent Effects on the Absorption Maxima ($\tilde{\nu}_{max}$, in cm^{-1}), Oscillator Strengths (*f*), and Dipole Moments (μ, in D) for Acetone, PNA, and Reichardt's Betaine Dye

solute	state	$\tilde{\nu}_{max}$ (gas phase)	*f*	μ	$\tilde{\nu}_{max}$ (water)	*f*	μ
acetone	S_0	0.0		3.8	0.0		4.6
	S_1	35 478	0.0	0.7	36748	0.0	1.4
PNA	S_0	0.0		7.1	0.0		9.0
	S_1	30 501	0.3560	14.3	24748	0.3332	19.4
Reichardt' betaine	S_0	0.0		16.8	0.0		24.3
	S_1	11 344	0.3167	2.4	20500	0.0254	5.6
	S_2	20 406	0.0243	0.2			
	S_3	25 325	0.3315	16.3	25793	0.3765	23.5
	S_4	29 737	0.2973	12.9	30777	0.6493	25.0
	S_5	31 775	0.1067	6.9	30938	0.2570	22.0
	S_6	34 030	0.0392	12.3	32404	0.2951	28.8
	S_7	34 418	0.6461	17.1	36836	0.1148	19.7
	S_8	35 208	0.0325	14.9	37301	0.0948	21.1
	S_9	37 208	0.0330	13.4	40523	0.0926	23.3
	S_{10}	38 793	0.0482	12.5	41406	0.7526	25.8
	S_{11}	40 994	0.0236	15.6	42041	0.1325	25.6
	S_{12}	41 202	0.3674				
	S_{13}	41 724	0.5207				

Reichardt's Betaine Dye. In the electronic ground state, Reichardt's betaine molecule (see Figure 1) exhibits a large dipole moment (16.8 D, see Table 6). (The experimental ground-state dipole moment of related betaine dye [(2,6-di-*tert*-butyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide], is $\mu_g = 14.8$ D.[93]) There is dramatic change of dipolarity upon excitation to the first excited (π−π*) state (S_1 state in Table 6). The calculated dipole moment in this state ($\mu_e = 2.4$ D, see Table 6) is smaller than experimental value obtained by Liptay[94] ($\mu_e = 6.2$ D). Thus, this intramolecular charge transfer (CT) absorption band is strongly solvent dependent, resulting in very large hypsochromic shifts of the CT band with increasing solvent polarity. For instance, the long-wavelength absorption band of the pyridinium-*N*-phenolate betaine dye shifts from $\lambda_{max} = 810$ nm in diphenyl ether to 453 nm in water.[81,83] Unfortunately, there is no experimental gas phase spectrum available for Reichardt's betaine dye because of the low volatility of this zwitterionic compound. The UV/vis absorption spectrum in nonpolar solvents shows three peaks below 25 000 cm^{-1} (see fig. 6.2. in ref 83). These peaks are located at about $\tilde{\nu}_{max}$ = 11 000−12 000, 21 000, and 25 000 cm^{-1}. The next two strong bands are located at $\tilde{\nu}_{max}$ = 32 000 cm^{-1}(log ϵ = 4.8) and about 41 000 cm^{-1}. On going to polar solvents, the first absorption band is strongly blue-shifted with diminished intensity. The polarity of the solvent does practically not change the UV/vis spectrum in the range above $\tilde{\nu}_{max}$ = 30 000 cm^{-1}. For the gas phase, the calculated first absorption maximum at $\tilde{\nu}_{max}$ = 11 344 cm^{-1} correlates well with the experimental value obtained in nonpolar solvents.[83] A shoulder observed at about 21 000 cm^{-1} can be identified as the calculated weak charge-transfer transitions at $\tilde{\nu}_{max}$ = 20 406 cm^{-1} (see Table 6). The next observed strong absorption band at $\tilde{\nu}_{max}$ = 25 000 cm^{-1} can be interpreted as due to a strong, locally excited state, without change of the dipole moment (S_3 state in Table 6). The broad (30 000−40 000 cm^{-1}), intense absorption band with an maximum at about $\tilde{\nu}_{max}$ = 32 000 cm^{-1} can be regarded as a superposition of many closely-lying transitions. (In Table 6 only more intense transitions are presented.) It should be noted that these latter transitions do not markedly change the dipole moment. This result may be used as an explanation for the small solvent effect observed for this broad band.[83] The lowest energy transition of this betaine dye undergoes a very large blue shift in going from the gas phase to water as solvent. The energy of the low-lying singlet transition is shifted by $\Delta\tilde{\nu}_{max}$ = 9156 cm^{-1} (Table 6) and can be compared to the experimental shifts[81,83] of 9730 cm^{-1} on going from diphenyl ether (nonpolar solvent) to water (polar solvent). The weak transition observed in nonpolar solvents at ca. 21 000 cm^{-1} is absent in polar solvents (see Table 6). The direct calculation of the UV/vis spectrum shows that in the region of 30 000−40 000 cm^{-1} a rather small solvent effect is expected. The position of the long-wavelength intramolecular CT absorption of this dye has been calculated by various methods.[95−98] However, the full electronic spectrum of this betaine dye in various solvents has been published only by Zerner et al.[95] Their results are qualitatively consistent with our calculations.

Conclusions

This paper presents a method for the calculation of the solvent effect on electronic structure of ions and molecules. The LD/MC and QM/LD/MC procedures employed in this paper are capable of being applied to the calculation of hydration free energy of small molecules, ions, α-amino acids, and nucleotide bases of DNA. The QM version of the LD/MC method also enables to estimate the solvent effect on the electronic spectra and dipole moments of acetone, 4-nitroaniline, and Reichardt's betaine dye. Generally, a good agreement between calculated and experimental data has been obtained.

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