An Ab Initio Model for Solvent Effects in Organic Molecules[†]

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An ab initio formulation for calculating solvent effects for organic molecules is presented. The solvent effects are treated in two parts using different models for the solvent. For calculating the reaction field the solvent is modeled as a continuum with the cavity determined ab initio as a surface enclosing the solute molecule, which represents the minima of the interaction potential as a solvent molecule approaches a solute molecule at various angles. The interaction potential is calculated using results of ab initio diatomic calculations on various pairs of atoms with frozen asymptotic charge densities. The reaction field contribution from the solvent is evaluated by using the apparent surface charge model with a dense grid of points on the cavity. For the direct interaction we first construct the first shell of solvent molecules around the solute molecule by bringing the solvent molecules as discrete systems to the cavity surface. The corresponding energy (consisting of both the solvent−solute and solvent−solvent interaction) is minimized with respect to both the location of solvent molecules as well as their orientation. The method is demonstrated by application to the *p*-nitroaniline in various solvents. The solvated excitation energies are calculated and compared with experiment. We also compute the solvated polarizabilities and second-order transition moments.

I. Introduction

Several ab initio methodologies now exist that can explain and predict with various degrees of success the energetics and properties of intermediate and large-size organic molecules in the gas phase. However, most experimental measurements of the properties of organic systems are carried out in the solvated phase. It is, therefore, of high interest to develop methods and computational strategies for describing the effects of solvent on the molecular properties.

Early work[1−4] on solvent effects, directed primarily to estimate solvation energies, has led to developments in theoretical chemistry relating to the many-electron description of the solvated molecule. Three distinct models have emerged: (i) one that treats the solvent molecules around the solute molecule on the same footing as the solute, the so-called supramolecular model,[5] (ii) the continuum model,[6] where the solvent is treated as a continuum that surrounds the solute molecule, and (iii) the semicontinuum model.[7−11] In the last two models the solute is supposed to reside in a cavity not accessible by the continuum, although for the semicontinuum model some of the solvent molecules are allowed to exist within the cavity as discrete entities. One important feature of the continuum model is the fact that the solvated molecule induces polarization charges in the solvent that then give rise to an extra field at the position of the solute. This so-called reaction field (RF) is then incorporated in the solute Hamiltonian.

While the supramolecular model is theoretically straightforward, the execution of the model is difficult since for a satisfactory representation of the solvent a large number of solvent molecules need to be considered. The method is primarily employed to study the stochastic effects by adopting empirical laws of interaction (e.g., Lennard-Jones) and then carrying out Monte Carlo or molecular dynamics calculations.

On the other hand, the strictly continuum models, particularly the polarization continuum model (PCM),[12−15] although quite successful for prediction of various solvation-related properties, are fundamentally (but not fatally) flawed theoretically. First, the separation of the solute from its nearest solvent shell molecules is not large enough for the solute to see a continuous solvent. Furthermore, particularly in a polar solvent, the solute fails to see a constant dielectric “constant”, since the Boltzmann factor $\exp(-pE/kT)$ cannot be linearized owing to the dipole moment of the solvent being usually too large. For example, for pNA as the solute with an estimated cavity radius of 10 au and dipole moment of water as 1.5 au the “pE/kT” for *p*-nitroaniline (pNA0 in water turns out to be ∼4.5 at room temperature.

In the present work we shall adopt what can be regarded as a semicontinuum model for the solvent. While the continuum model is retained to obtain the reaction field contribution, the “direct” electrostatic effects between solute and solvent are obtained by constructing the first solvation shell by minimizing enthalpy (with nothing included from the entropy-related forces).

This leads us to the following model: For the continuum part of the solute−solvent interaction we determine the cavity surface ab initio (unlike the continuum models hitherto reported) by letting a solvent molecule approach a solute molecule from various directions and orientations. The corresponding minima are taken as describing the cavity surface. With the cavity so defined the corresponding Poisson equation with the bulk dielectric constant is solved to lead to the “reaction-field”, which is then incorporated in the solute Hamiltonian. Using the cavity as the starting point, we also obtain the direct contribution (as opposed to the “reaction field”) to the total interaction energy from the first solvation shell. In the following we shall present a strictly ab initio formulation of the above model of the solvated phase except for the only empirical parameter, the dielectric constant. We shall then present some actual illustrative calculations on the system (pNA).

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II. Model for Solute−Solvent Interaction

We propose here an approximate framework where the solute−solvent interaction is partitioned into two distinct parts, the electrostatic ΔW_{els} and the polarization $\Delta W_{\mathrm{pol}}{}^{(\mathrm{S,L})}$:

$$\Delta W_{\mathrm{tot}} = \Delta W_{\mathrm{els}} + \Delta W_{\mathrm{pol}}{}^{(\mathrm{S})} + \Delta W_{\mathrm{pol}}{}^{(\mathrm{L})} \tag{1}$$

We shall treat the electrostatic part of the total solute−solvent interaction as a sum of two-body interactions between the constituent atoms of the solute and the solvent molecules. The two-body interactions are obtained ab initio by first computing the diatomic interaction for various pairs of atoms by assuming that their charge distributions are rigidly undisturbed in fully occupied (and, hence, sphericallly symmetric) atomic shells, except for orthogonalization distortion as the solvent molecule approaches the solute. The interaction potential for any pair of atoms can then be shown to have the general form

$$\begin{aligned} V^{(12)} = \Delta E_{\mathrm{core}} + \sum_{\mathrm{v}\subset\mathrm{atom1}}\left[\frac{n_{\mathrm{v}}}{f_{\mathrm{v}}}\Delta h_{\mathrm{v}} + \sum_{\mathrm{v}'\subset\mathrm{atom1}}\left(\frac{n_{\mathrm{v}}n_{\mathrm{v}'}}{f_{\mathrm{v}}f_{\mathrm{v}'}}\right)\Delta J_{\mathrm{vv}'}\right] + \\ \sum_{\mathrm{v}\subset\mathrm{atom2}}\left[\frac{n_{\mathrm{v}}}{f_{\mathrm{v}}}\Delta h_{\mathrm{v}} + \sum_{\mathrm{v}'\subset\mathrm{atom2}}\left(\frac{n_{\mathrm{v}}n_{\mathrm{v}'}}{f_{\mathrm{v}}f_{\mathrm{v}'}}\right)\Delta J_{\mathrm{vv}'}\right] + \\ \sum_{\mathrm{v}\subset\mathrm{atom1}}\ \sum_{\mathrm{v}\subset\mathrm{atom2}} \frac{n_{\mathrm{v}}n_{\mathrm{v}'}}{f_{\mathrm{v}}f_{\mathrm{v}'}}\Delta J_{\mathrm{vv}'} \end{aligned} \tag{2}$$

where n_{v} and $n_{\mathrm{v}'}$ are the numbers of valence electrons on the two atoms and f_{v} and $f_{\mathrm{v}'}$ the degeneracies of the valence shells. The core contribution ΔE_{core}, one-electron parts Δh_{v} and $\Delta h_{\mathrm{v}'}$, and the electron repulsion terms $\Delta J_{\mathrm{vv}'}$, $i, j = 1, 2$, are calculated as the interaction of the "filled shells" using the orbitals of the neutral atoms:

$$\begin{aligned} E_{\mathrm{core}} &= h^{+}\mathbf{D}_0 + \mathbf{D}_0{}^{+}(\mathbf{J} - {}^{1}\!/_{2}\mathbf{K})\mathbf{D}_0 \\ h_{\mathrm{v}} &= h^{+}\mathbf{D}_{\mathrm{v}} + \mathbf{D}_0{}^{+}(\mathbf{J} - {}^{1}\!/_{2}\mathbf{K})\mathbf{D}_{\mathrm{v}} && \text{v on atoms 1, 2} \\ J_{\mathrm{vv}'} &= \mathbf{D}_{\mathrm{v}}{}^{+}(\mathbf{J} - {}^{1}\!/_{2}\mathbf{K})\mathbf{D}_{\mathrm{v}'} && \text{v, v}' \text{ both on the same atom} \\ J_{\mathrm{vv}'} &= \mathbf{D}_{\mathrm{v}}{}^{+}(\mathbf{J} - {}^{1}\!/_{2}\mathbf{K})\mathbf{D}_{\mathrm{v}'} && \text{v and v}' \text{ on different atoms} \end{aligned} \tag{3}$$

where $\mathbf{D}_0$ is the core density matrix of the cores on both centers, $\mathbf{D}_{\mathrm{v}}$ is the valence density matrix on the two centers, with the valence shells fully occupied, and $\mathbf{J}$ and $\mathbf{K}$ are the Coulomb and exchange supermatrices. The interaction contributions are obtained by subtracting off the asymptotic values of these quantities.

Consider the wave functions of either the isolated solute or solvent molecules: In this work both will be assumed to be closed-shell and, therefore, describable by a single-determinant Hartree−Fock wave function.

$$\Psi = \tilde{A}[\psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta...]/(N!)^{1/2} \tag{4}$$

The orbitals in the LCAO form are given by

$$\psi_i = \sum_{\mathrm{a}} C_{i\mathrm{a}}\varphi_{\mathrm{a}} \tag{5}$$

where φ's are atomic functions. We shall re-express ψ_i's as

$$\psi_i = \sum_{\mathrm{a}} C'_{i\mathrm{a}}\varphi'_{\mathrm{a}} \tag{6}$$

where φ_{a}'s are symmetrically orthogonalized atomic-like orbitals (ALO). Assuming the overlaps $S_{\mathrm{ab}} \equiv \langle\phi_{\mathrm{a}}|\phi_{\mathrm{b}}\rangle$ between the atomic centers to be small, one can write approximately

$$\varphi'_{\mathrm{a}} \cong \varphi_{\mathrm{a}} - {}^{1}\!/_{2}\sum_{\mathrm{b}} S_{\mathrm{ab}}\varphi_{\mathrm{b}} \tag{7}$$

One can then show that

$$C'_{i\mathrm{a}} \cong C_{i\mathrm{a}} + {}^{1}\!/_{2}\sum_{\mathrm{b}} S_{\mathrm{ab}}C_{i\mathrm{b}} \tag{8}$$

such that the Mulliken's charges are given approximately as

$$\rho_{\mathrm{a}} = 2\sum_{i}(C'_{i\mathrm{a}})^2 \tag{9}$$

In other words, Mulliken's charge is simply the occupancy in a "symmetrically orthogonalized" ALO representation of the Hartree−Fock wave function.

The valence charge density of either solute or solvent is given by the following expression

$$\begin{aligned} \rho(r) &= \sum_{\mathrm{a}} Z_{\mathrm{a}}\delta(r - R_{\mathrm{a}}) - \sum \mathbf{D}_{\mathrm{al,bm}}\phi_{\mathrm{al}}\phi_{\mathrm{bm}} \\ \mathbf{D}_{\mathrm{al,bm}} &= 2\sum_{i} c_{i\mathrm{al}}c_{i\mathrm{bm}} \end{aligned} \tag{10}$$

where $\mathbf{D}_{\mathrm{al,bm}}$ is the valence density matrix and Z_{a} is the nuclar charge (minus the core). Since the Coulomb integrals involving the off-diagonal differential overlap $\phi_{\mathrm{al}}\phi_{\mathrm{bm}}$ are, in general, very small, we retain only the diagonal terms in eq 10. Furthermore, we introduce the following approximation for valence shells with degenerate subshells such as the p shells:

$$\sum_{\mathrm{l}\subset\mathrm{v}} \mathbf{D}_{\mathrm{al,al}}(\phi_{\mathrm{al}})^2 \approx \Big(\sum_{\mathrm{l}\subset\mathrm{v}} \mathbf{D}_{\mathrm{al,al}}\Big)\frac{1}{f_{\mathrm{v}}}\sum_{\mathrm{l}\subset\mathrm{v}}(\phi_{\mathrm{al}})^2 = \frac{n_{\mathrm{v}}}{f_{\mathrm{v}}}\sum_{\mathrm{l}\subset\mathrm{v}}(\phi_{\mathrm{al}})^2 \tag{11}$$

The approximation involves (for the p-type valence shell) neglecting the part of the interaction corresponding to the "d" component of the charge density, hence of the order of $O(1/R^4)$ or higher. Specializing the indices a and b, respectively, to denote the solute and solvent atoms, one can write the total electrostatic interaction energy as

$$\Delta W_{\mathrm{els}}{}^{\mathrm{L-S}} = \sum_{\mathrm{a,b}}\left[V^{(\mathrm{ab})} + \frac{(Q_{\mathrm{a}} - Z_{\mathrm{a}})(Q_{\mathrm{b}} - Z_{\mathrm{b}})}{R_{\mathrm{ab}}}\right] \tag{12}$$

where Z_{a} and Z_{b} are the nuclear charges, the quantities Q_{a}, Q_{b}, ... are the total Mulliken population densities at the centers a and b and (ab) denotes the diatom involving the atoms a and b. $V^{(\mathrm{ab})}$ is calculated using eq 2 where the valence occupancies $\{n_{\mathrm{v}}\}$'s are replaced by the partial Mulliken population for the valence shells {v}.

Thus, we use the following recipe to obtain the various two-body potentials required for a given problem: First, we decide upon a common level of basis for all calculations. (For the present work we have chosen the 6-31G basis.) We consider various pairs of atoms at various internuclear separations. Using the orbitals obtained from atomic calculations, we first symmetrically orthonormalize them. With all the shells filled (i.e., with the same electronic configurations as the respective rare gas atoms of the rows to which the atoms belong), the various parameters ΔE_{core}, Δh_{v}, $\Delta J_{\mathrm{vv'}}$, etc. are obtained and then fitted to the following analytical forms:

$$f_{ij}(R) = \frac{\exp(-\zeta_{ij}R)}{R}\sum_{n=0}^{3} A_{n,ij}R^n \tag{13}$$

III. Solute−Solvent Polarization Energy

To calculate the polarization contribution, we notice that the polarizing field is very inhomogeneous and, therefore, it is inaccurate to represent the polarization contribution in terms of the "total" polarizabilities of the solvent and solute molecules. We use instead the following approach: We write the total polarization energy as the second-order perturbed energy:

$$\Delta E_{\mathrm{pol}} = -\sum_{\mathrm{a}\subset \mathrm{S}} \frac{\left\langle \phi'^{(n)}_{\mathrm{a}} \left| \sum_{\mathrm{b}\subset \mathrm{L}} \frac{Z_{\mathrm{b}} - Q_{\mathrm{b}}}{R_{\mathrm{ab}}^{3}} \mathbf{R}_{\mathrm{ab}}\cdot\mathbf{r} \right| \phi_{\mathrm{a}} \right\rangle^2}{E_{\mathrm{a}}^{(n)} - E_0} - \sum_{\mathrm{a}\subset \mathrm{L}} \frac{\left\langle \phi'^{(n)}_{\mathrm{a}} \left| \sum_{\mathrm{b}\subset \mathrm{S}} \frac{Z_{\mathrm{b}} - Q_{\mathrm{b}}}{R_{\mathrm{ab}}^{3}} \mathbf{R}_{\mathrm{ab}}\cdot\mathbf{r} \right| \phi_{\mathrm{a}} \right\rangle^2}{E_{a}^{(n)} - E_0}$$

$$= -{}^{1}/_{2}\sum_{\mathrm{a}\subset \mathrm{S}} \alpha_{\mathrm{a}} \mathbf{F}_{\mathrm{a}}^{(\mathrm{L})}\cdot\mathbf{F}_{\mathrm{a}}^{(\mathrm{L})} - {}^{1}/_{2}\sum_{\mathrm{a}\subset \mathrm{L}} \alpha_{\mathrm{a}} \mathbf{F}_{\mathrm{a}}^{(\mathrm{S})}\cdot\mathbf{F}_{\mathrm{a}}^{(\mathrm{S})} \tag{14}$$

where

$$\mathbf{F}_{\mathrm{a}}^{(\mathrm{S})} = \sum_{\mathrm{b}\subset \mathrm{L}} \frac{Z_{\mathrm{b}} - Q_{\mathrm{b}}}{R_{\mathrm{ab}}^{3}}\mathbf{R}_{\mathrm{ab}},\ \mathbf{F}_{\mathrm{a}}^{(\mathrm{L})} = \sum_{\mathrm{b}\subset \mathrm{S}} \frac{Z_{\mathrm{b}} - Q_{\mathrm{b}}}{R_{\mathrm{ab}}^{3}}\mathbf{R}_{\mathrm{ab}} \tag{15}$$

and $\{\phi_{\mathrm{a}}\}$ and $\{\phi_{\mathrm{a}}'\}$ are respectively the localized occupied and virtual orbitals (symmetrically orthogonalized) for the atom a, E_0 is the Hartree−Fock energy, $E_{\mathrm{a}}^{(n)}$ represents the excited energy when the electron occupying ϕ_{a} is promoted to $\phi_{\mathrm{a}}'^{(n)}$, $\{\alpha_{\mathrm{a}}\}$'s are the atomic polarizabilities of the atoms in the environment of their respective molecules, and R_{ab} is the separation between atoms a and b.

IV. Determination of the Cavity Geometry

In this work the cavity surface is defined as consisting of the set of points where the solute−solvent interaction potential attains its minimum as the solvent molecule approaches the solute molecule along the line joining their charge centroids (CC). We can justify this definition in the following way: Although only a solitary solvent molecule is considered in our definition, the interaction minima in terms of the solvent solute molecules approaching each other's CC should lie very close to those in the presence of the neighboring solvent molecules since intuitively only the interaction along the radial direction is dependent almost exclusively on the solute−solvent interaction. A further corroboration of the present definition is obtained (see below) where we actually build the first solvation shell around a solvent molecule. It turns out that despite solvent−solvent interaction the surface traced out by the centers of the molecules in the first solvation shell continues to be approximately the cavity surface, as defined above. We are currently exploring a more direct verification of this model by doing molecular dynamics on a solute molecule embedded in an assemblage of solvent molecules and then studying the time-averaged shape and size of the first solvation shell.

In determining the cavity according to the present model, we proceed as follows: We draw a large imaginary sphere around the solute molecule with the center at the centroid of the Mulliken charges defined by

$$\mathbf{R}_{\mathrm{S}}^{\mathrm{CC}} = \sum_{\mathrm{a}} |Z_{\mathrm{a}} - Q_{\mathrm{a}}|\mathbf{R}_{\mathrm{a}} / \sum_{\mathrm{a}} |Z_{\mathrm{a}} - Q_{\mathrm{a}}| \tag{16}$$

We then place the centroid (similarly defined) of the solvent molecule at various points of the surface of this sphere and let it approach radially. The interaction energy is minimized at every radial distance by optimizing the solvent molecular orientation (not the relative positions of the atoms within the solvent molecule, which are kept frozen). The motivation of using the charge centroids is to ensure that the quadrupole terms for most systems of interest (e.g., the centrosymmetric ones) are small. This is important in determining the RF contributions.

Using the cavity surface as the starting point we build up the first solvation shell as follows: (1) Add a solvent molecule to the cavity surface with its CC on the cavity surface. Orient the molecule to attain minimum in energy. (2) Add another one likewise to the cavity surface. Optimize both its orientation as well as location of CC on the cavity surface to attain energy minimum. (3) More molecules are similarly added until energy actually goes up. (4) Go back to the first solvent molecule and optimize the location as well as orientation in the presence of all the assembled molecules. We repeat the same operation (4) for other molecules and so on until energy becomes stationary. (5) As a final check on the bona fide nature of the first solvation shell, we now allow out-of-cavity surface displacement of individual solvent molecules. If any molecule is found to reach a minimum energy at a point deviating by more than 10% from its cavity surface solvent−solute distance, this is taken as an indication that the molecule does not belong to the first solvation shell. We then have to reoptimize (carry out step (4)) the solvation shell with the molecule taken out. This is an expensive part of the calculations. Fortunately, our preliminary finding detects no substantial deviation of the locations of the CC's of the solvent molecules from the cavity surface.

V. Reaction Field

Consider now the effect of the solvent on the solute Hamiltonian. Let us denote the total potential as $\phi(\mathbf{r})$, created by the solute and solvent treated as a continuum at a given point $\mathbf{r}$ in space (in the cavity or outside). Then the polarization induced in the dielectric is given by

$$\mathbf{P} = -\frac{(\epsilon - 1)}{4\pi}\nabla\phi \tag{17}$$

Thus, one obtains

$$\phi(\mathbf{r}) = \phi_0(\mathbf{r}) - \int_{\mathrm{L}} \mathbf{P}\cdot\nabla_{\mathbf{R}}\left(\frac{1}{|\mathbf{r} - \mathbf{R}|}\right) \mathrm{d}^3\mathbf{R}$$

$$= \phi_0(\mathbf{r}) + \frac{(\epsilon - 1)}{4\pi}\int_{\mathrm{L}} \nabla_{\mathbf{R}}\phi(\mathbf{R})\cdot\nabla_{\mathbf{R}}\left(\frac{1}{|\mathbf{r} - \mathbf{R}|}\right) \tag{18}$$

whence

$$\phi(\mathbf{r}) = \phi_0(\mathbf{r}) + \frac{\epsilon - 1}{4\pi}\int_{\mathrm{CS}} \frac{\partial\phi}{\partial n_{\mathbf{R}}}\frac{1}{|\mathbf{r} - \mathbf{R}|}\,\mathrm{d}S \qquad \mathbf{r}\text{ in cavity} \tag{19}$$

using Gauss's theorem. The direction of the normal "n_R" is from the cavity outward into the solvent. Using the boundary conditions

$$\phi(\mathbf{r}-0)=\phi(\mathbf{r}+0)$$
$$\left(\frac{\partial\phi}{\partial n}\right)_- = \epsilon\left(\frac{\partial\phi}{\partial n}\right)_+ \tag{20}$$

one can then obtain an equation involving only the surface charges:

$$\frac{\partial\phi}{\partial n_{\mathbf{r}}}=\frac{\partial\phi_0}{\partial n_{\mathbf{r}}}+\frac{\epsilon-1}{4\pi\epsilon}\int_{\mathrm{CS}}\frac{\partial\phi}{\partial n_{\mathbf{R}}}\frac{\partial}{\partial n_{\mathbf{r}}}\frac{1}{|\mathbf{r}-\mathbf{R}|}\,\mathrm{dS} \tag{21}$$

In the above ϕ_0 is the potential in free space:

$$\phi_0=\sum_{\mathrm{a}}\frac{Z_{\mathrm{a}}-Q_{\mathrm{a}}}{|\mathbf{r}-\mathbf{R}_{\mathrm{a}}|}$$
$$\cong\frac{\mu\cdot\mathbf{R}}{R^3} \tag{22}$$

where $\{Q_{\mathrm{a}}\}$ are the net Mulliken charges on the various atoms and $\{R_{\mathrm{a}}\}$ denotes the position of the a-th nucleus, μ is the dipole moment of the solute, and R is the distance from its CC. The notation "CS" denotes cavity surface. We solve for $\partial\phi/\partial n$ iteratively from the eq 20 by breaking the CS into tesserae.[12-15] Since the cavities turn out to be nearly spherical and large enough such that the linear (i.e., the dipolar) terms predominate, we start with a value of $\partial\phi/\partial n$ given by

$$\frac{\partial\phi}{\partial n}=-\frac{6\epsilon}{2\epsilon+1}\frac{\mu\cdot\mathbf{n}}{R^3} \tag{23}$$

which is the value for a spherical cavity of radius R enclosing a central dipole moment μ.

VI. Application to the *p*-Nitroaniline (pNA) Molecule

We shall demonstrate the solvation scheme developed above by applying it to calculate the solvated excitation energies, polarizabilities, and the second-order transition moments for the *p*-nitroaniline molecule and compare with other theoretical results.[6] The ab initio formalism we adopt to generate wave functions is the modified sum-over-states (MSOS)[16] approach developed recently. Briefly, the method starts by first selecting a set of highest occupied molecular orbitals (HOMO) and a set of lowest unoccupied molecular orbitals (LUMO) and carrying out a configuration interaction (CI) calculation consisting of all single excitations from the HOMO's to the LUMO's. Using the resulting states as the starting point, we correct them by incorporating both the single excitations excluded in the above CI (viz., those from lower occupied orbitals to higher unoccupied ones and vice versa) as well as double excitations by a first-order perturbative approach. The quantities we shall concentrate in this work are the excitation energies, particularly those corresponding to the excitation of the ground state to the lowest charge-transfer state. Also, we shall calculate the diagonal polarizability components $\alpha_{ij} = \{\alpha_{xx}, \alpha_{yy}, \alpha_{zz})$ and the second-order transition moments $S_{ij}{}^{\mathrm{b}}$, of importance to two-photon absorption, defined by

$$\alpha_{ij}=\sum_{\mathrm{a}}\left[\frac{\langle 0|\mu_i|\mathrm{a}\rangle\langle \mathrm{a}|\mu_j|0\rangle}{\Delta E_{\mathrm{a}}-\omega}+\frac{\langle 0|\mu_j|\mathrm{a}\rangle\langle \mathrm{a}|\mu_i|0\rangle}{\Delta E_{\mathrm{a}}+\omega}\right]$$
$$S_{ij}^{\mathrm{b}}=\sum_{\mathrm{a}}\left[\frac{\langle 0|\mu_i|\mathrm{a}\rangle\langle \mathrm{a}|\bar{\mu}_j|\mathrm{b}\rangle+\langle 0|\mu_j|\mathrm{a}\rangle\langle \mathrm{a}|\bar{\mu}_i|\mathrm{b}\rangle}{\Delta E_{\mathrm{a}}-(\Delta E_{\mathrm{b}}/2\}}\right] \tag{24}$$

where

$$\bar{\mu}_j=\mu_j-\langle 0|\mu_j|0\rangle \tag{25}$$

and the summation is over the intermediate single and double excitations.

In calculating the solvated values for the above quantities, we neglect the dynamical effects entirely, assuming that the cavity surface remains rigidly unaffected under the time-dependent perturbations involved. Also the static dielectric constants are used throughout (in line with previous formulations of the continuum models), the rationale being that our calculations are primarily directed to describing the ground state of the solute + solvent system. While the excited state energies calculated are the vertical ones, only the electronic parts of the polarizability and two-photon transition moments of the solute molecule are targeted. It can be argued that since we are interested in "vertical" (in the Franck−Condon sense) excitation energies, we are justified in using frozen cavity surfaces in the way we have defined them (as representing the location of the CC's of the solvent molecules in the first solvation shell). For the properties α_{ij} and $S_{ij}{}^{\mathrm{b}}$ (calculated only for the solute) the above approximation implies neglecting the contributions from the nuclear motion in the solute. According to past calculations[17] of polarizabilities on isolated molecules in the visible range of photon energies, the nuclear contributions have rarely been found substantial. This is, however, not quite true for hyperpolarizabilities. For pNA our value (as well as Luo et al.'s[6] RPA value) for the polarizability agrees fairly well with experiment.[18]

Our MSOS calculations are carried out with a double-ζ basis with polarization (DZP) with d (0.2). In Table 1 we present the excitation energies and polarizabilities (under static conditions and for the photon energy of 0.06 hartrees), and in Table 2, the second-order transition moments for various solvents. We compare the calculated excitation energies with those available from experiments wherever available. The R_{av} values (shown in the third column) represent the mean radii of the cavities as obtained ab initio from the calculations on the ground state of pNA in the various solvents (whose dielectric constants appear in the second column). They vary significantly from solvent to solvent. However, in general, the cavities retain an approximately spherical shape except for a few small regions where R deviates from R_{av} quite markedly (as much as 30%), which represents the purely reaction field contributions to the charge-transfer excitation energy. The fifth column in Table 1 represents the total lowering of the excitation energy as solvents of increasing polarity are considered, with the reaction field contributions calculated in the present work shown in brackets. It is to be noted that, with regard to the direct electrostatic effect contributions, these are calculated with the first solvation shell constructed around the solute molecule for the ground state without the continuum around it. The same solvation shell in terms of the nuclear positions was used in calculating the contribution for the excited state. In other words, we have assumed that the direct effects are small except for the nearest-

TABLE 1: Excitation Energies and Polarizabilities of *p*-Nitroaniline for Various Solvents[a]

solvent/ method	ϵ_0	R_{av} (bohrs)	E_{exc} (cm^{-1})	ΔE_{exc} (cm^{-1})	α	
					$\omega = 0.0$	$\omega = 0.06$
gas	1.0					
PW[b]			38432		104.5	107.5
RPA[c]			41802*		93.9	
exp[d]			35090			
benzene	2.21					
PW[b]		12.3		−1822 (−659)	104.7	107.9
RPA[c]		9.8		−1234	100.8	
hexanol	13.3					
PW[b]		12.5		−2459 (−780)	104.6	107.7
RPA[c]		9.8		−2727	108.9	
acetone	20.7					
PW[b]		11.3		−2283 (−1076)	104.7	107.9
RPA[c]		9.8		−2880 −3646*	109.7	
exp[e]				−7900		
methanol	32.6					
PW[b]		10.9.		−2689 (−1405)	104.9	108.1
RPA[c]		9.8		−2969 −3780*	110.3	
exp[e]				−8061		
DMF	36.7					
PW[b]		11.8		−2634 (−1120)	104.7	107.9
RPA[c]		9.8		−2985 −3806*	110.4	
exp[e]				−8849		
water	78.5					
PW[b]		10.1		−2700 (−1603)	105.0	108.3
RPA[c]		9.8		−3074	110.9	

[a] Polarizabilities are in atomic units, photon enrgies in hartrees. The numbers in parentheses correspond to the reaction field contributions in the present calculations. The starred values are based on multiconfiguration RPA in ref 6. [b] Present work. [c] Reference 6. [d] Reference 18. [e] Reference 19.

TABLE 2: Second-Order Transition Moments for Various Solvents (au) for the Two Strongest Two-Photon States[a]

medium	ΔE_{exc}	root no.	S_{xx}	S_{xy}	S_{yy}	ΔE_{exc}	root no.	S_{xx}	S_{xy}	S_{yy}
gas	0.088	2	−14.9	3.1	142.2	0.113	5	−3.9	2.9	141.7
benzene	0.086	2	−18.2	3.2	160.0	0.112	5	−2.4	3.1	150.0
3-hexanol	0.087	2	−18.1	3.1	153.5	0.112	5	−2.8	3.0	147.1
acetone	0.086	2	−18.1	3.2	156.7	0.112	5	−2.6	3.1	148.6
methanol	0.087	2	−18.1	3.1	153.0	0.112	5	−2.9	3.0	146.8
DMF	0.087	2	−18.1	3.0	150.2	0.112	5	−3.1	3.0	145.5
water	0.087	2	−18.1	3.0	149.0	0.112	5	−3.2	3.0	144.9

[a] Excitation energies are in hartrees.

lying solvent molecules and that in accordance with the Franck−Condon principle all the nuclei are frozen in their ground-state positions.

The starred numbers represent the multiconfiguration RPA excitation energies. The sixth and the seventh columns show the polarizabilities (static and dynamic with a photon energy of 0.06 hartrees, respectively) in the ground state.

We note that the RPA[6] excitation values are in general larger than the MSOS values (most likely because of the choice of a smaller cavity radius than those derived in the preset work), both of which are larger than the experimental[18,19] values. Moreover, while the RPA calculations only consider the reaction field, in our calculations for solvated cases, on the other hand, the reaction field contributions reflect only a small part of the total excitation energies, a major part coming directly from the interaction between the solute and the solvent molecules of the first solvation shell. The experimental solvated excitation energies[19] are based on λ_{max} values and probably represent vibronic transitions and should not be taken too literally, although correlation seems to improve the agreement somewhat, as exhibited by the multiconfiguration RPA values. The RPA-based polarizabilities are much more sensitive to solvent environments than ours, probably because of the larger reaction field. According to our calculations, while the polarizabilities are quite weakly influenced by the presence of the solvents, the effect on the two-photon amplitudes is quite strong. Furthermore, there is an approximate inverse relationship between the polarity of the solvent and the two-photon intensities.

It is to be pointed out that the above calculations are preliminary in nature and are aimed at introducing the concept of ab initio cavity surface and demonstrating the importance of various effects not necessarily included or differentiated in earlier formulations, specially those that result from the direct electrostatic interaction between the solute molecule and the first solvation shell. A more detailed study covering a broad range of molecules and based on a more sophisticated description of the wave function is currently in progress. Since a direct comparison with experiment at this stage is clearly too ambitious for the properties we are interested in, our first attempt will be to carry out supermolecular calculations on smaller systems and compare the results based on the simplified approach presented here.

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