

Explicit solvent model for spectral shift of acrolein and simulation with molecular dynamics

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Abstract By introducing the concept of spring energy of permanent dipole and taking the conformations of solvent molecules into account, the formulas of electrostatic solvation energy in equilibrium and nonequilibrium are derived from the explicit solvent scheme, with the spatial distribution of the discrete permanent charges and induced dipoles of the solvent molecules involved. The energy change of solute due to the variation of wave function from the case of vacuum to that in solution is estimated by treating the solvent effect as external field in the iteration cycles of the self-consistent field. The expression for spectral shift is deduced and applied to the processes of light absorption and emission in solution. According to the new formulations, the averaged solvent electrostatic potential/molecular dynamics program is modified and adopted to investigate the equilibrium solvation energy of water molecule and spectral shift of acrolein.

Keywords: nonequilibrium solvation, molecular dynamics, spectral shift, explicit solvent model.

Nonequilibrium solvation plays an important role in ultra-fast processes occurring in solution such as electron transfer reactions and light absorption/emission, and it is always an interesting popular topic in theoretical and experimental studies. Since the concept of nonequilibrium solvation was established by Marcus^[1], Mataga^[2] and Lippert^[3] in the 1950s, the continuum model has been a significant method to investigate the nonequilibrium for its two advantages: precisely esti-

imating the electrostatic interaction energy and low computational cost^[4,5]. In the framework of continuum model, the nonequilibrium solvation theory has been developed and many models have been established. Some numerical algorithms, e.g., polarizable continuum model (PCM)^[6] and conductor-like screening model (COSMO)^[7], have been implemented within the quantum mechanics programs such as Gaussian03 and Gamess. Although different authors adopted different methods to achieve the basically consistent expression for the solvation energy of nonequilibrium in the past, the defects in derivation and understanding were pointed out and testified in our recently published papers^[8–12]. Several independent methods, Jackson formula, energy decomposition, and field superposition, were applied to obtaining an identical novel expression for the non-equilibrium electrostatic free energy, which is different from the traditional ones. Consequently, the two-sphere model for the solvent reorganization energy of electron transfer^[8,11], the single sphere model for spectral shifts^[8,9,11], the multipole expansion method^[8,10] and numerical algorithm^[8,12] for nonequilibrium solvation energy were developed.

Although the continuum model is convenient to deal with nonequilibrium solvation, there are still some limitations. Firstly, the continuum model is unable to take the microscopic structures of solvent into account. Secondly, the choices of cavity sphere radius in analytical models and cavity size in the numerical algorithm are relatively arbitrary. Furthermore, the continuum model cannot be used to investigate the dispersion and repulsion energy. Therefore, methods with explicit solvent approaches, such as the quantum mechanism/molecular mechanism (QM/MM) and quantum mechanism/molecular dynamics (QM/MD), are developed to obtain more precise results^[13–15]. In the past, the application of explicit solvent model was mainly focused on the equilibrium solvation, that is to say, the solvent polarization reaches the equilibrium with the charge distribution of the solute in a large time scale. The development of nonequilibrium solvation remains somewhat unsatisfactory at present for the complexity of the interaction between the solute and solvent. In recent years, the explicit solvent model has come into use for the nonequilibrium solvation phenomenon shortly after Franck-Condon transition in solution. Aguilar and co-workers^[16] have done a lot of work on this topic and the averaged solvent electrostatic potential/ molecular dynamics (ASEP/MD) program was coded to explain

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spectral shifts in solution. However, it is found that the inconsistency of energy decomposition in the traditional nonequilibrium solvation theory within the continuum model still exists in the derivation from explicit solvent model^[8,10]. Hence, some defects in the codes of ASEP/MD program need to be modified.

In this work, the correct formula for the nonequilibrium electrostatic solvation energy is introduced at first in the framework of continuum model and the energy components are analyzed based on the solvent polarization decomposed into two parts: orientational and electronic polarization. And then the expressions for the nonequilibrium solvation energy and spectral shifts are achieved with the description of discrete charges in the explicit solvent scheme when the solvent polarization is divided into permanent and induced dipoles. At last, according to the new derivation, the ASEP/MD program is modified to investigate the equilibrium solvation energy of water molecule and the absorption spectral shift of $n \rightarrow \pi^*$ transition in acrolein molecule.

1 Theoretical foundation of nonequilibrium solvation

1.1 Continuum model

For the ultra-fast processes in solution, the solvent polarization equilibrates with the solute charge distribution ρ_1 , with an electrostatic dielectric constant ϵ_s before the Franck-Condon transition. In this case, the electrostatic potential of the system is denoted by Φ_1^{eq} . Thus this equilibrium state is denoted by $[\rho_1, \Phi_1^{\text{eq}}]$. After the electronic transition of the solute molecule, the solute charge distribution is changed to ρ_2 quickly and the corresponding nonequilibrium potential Φ_2^{non} is yielded. This nonequilibrium state is denoted by $[\rho_2, \Phi_2^{\text{non}}]$. During this transition process, the orientational polarization will maintain the status of the previous equilibrium state for the slow response. However, the electronic polarization can be adjusted quickly and reaches the new equilibrium with the final charge distribution of the solute for its fast response. Therefore the nonequilibrium can be considered as the superposition of two equilibrium states^[8], i.e.

$$[\rho_2, \Phi_2^{\text{non}}] = [\rho_1, \Phi_1^{\text{eq}}] + [\Delta\rho, \Delta\Phi_{\text{op}}], \quad (1)$$

where $\Delta\rho = \rho_2 - \rho_1$ represents the change of solute charge from equilibrium to nonequilibrium, and $\Delta\Phi_{\text{op}}$ is the potential due to $\Delta\rho$ in the solvent with the optical dielectric constant ϵ_{op} . Thus according to the relation-

ship $\Phi_2^{\text{non}} = \Phi_1^{\text{eq}} + \Delta\Phi_{\text{op}}$, the electrostatic free energy of nonequilibrium state can be expressed as^[8]

$$G_2^{\text{non}} = \frac{1}{2} \int_V \rho_1 \Phi_1^{\text{eq}} dV + \frac{1}{2} \int_V \Delta\rho \Delta\Phi_{\text{op}} dV + \frac{1}{2} \int_V \Delta\rho \Phi_1^{\text{eq}} dV + \frac{1}{2} \int_V \rho_1 \Delta\Phi_{\text{op}} dV = \frac{1}{2} \int_V \rho_2 \Phi_2^{\text{non}} dV. \quad (2)$$

Eq. (2) shows that the expression of nonequilibrium electrostatic free energy is similar in form to that in equilibrium^[8-12]. Therefore, we focus on the discussion of nonequilibrium state, and the final expression can be applied to the equilibrium state directly. In terms of electric field and electric displacement, eq. (2) can be changed to^[8-10]

$$G_2^{\text{non}} = (1/8\pi) \int_V \mathbf{E}_2^{\text{non}} \cdot \mathbf{D}_2^{\text{non}} dV, \quad (3)$$

where $\mathbf{E}_2^{\text{non}} = \mathbf{E}_2^{\text{c}} + \mathbf{E}_2^{\text{p}}$ and $\mathbf{D}_2^{\text{non}} = \mathbf{E}_2^{\text{c}} + \mathbf{E}_2^{\text{p}} + \mathbf{P}_2^{\text{non}}$ represent the total electric field strength and electric displacement respectively, \mathbf{E}_2^{c} and \mathbf{E}_2^{p} are the field strengths due to solute charge and polarization charge in nonequilibrium respectively, and $\mathbf{P}_2^{\text{non}}$ is the total polarization in nonequilibrium. In continuum model, $\mathbf{P}_2^{\text{non}}$ can be divided into orientational polarization $\mathbf{P}_{2,\text{or}}$ and electronic polarization $\mathbf{P}_{2,\text{op}}$. The electronic polarization arrives at the equilibrium with the solute charge of the final state for fast response, but the response of orientational polarization is slow, hence we have $\mathbf{P}_{2,\text{or}} = \mathbf{P}_{1,\text{or}}$. Accordingly, the total polarization field \mathbf{E}_2^{p} is the sum of orientational and electronic polarization fields, that is, $\mathbf{E}_2^{\text{p}} = \mathbf{E}_{2,\text{or}} + \mathbf{E}_{2,\text{op}}$ with $\mathbf{E}_{2,\text{or}} = \mathbf{E}_{1,\text{or}}$. Therefore, the total electrostatic free energy of nonequilibrium is composed of several parts: the self-energy of the solute charge, the orientational polarized charge and the electronic polarized charge, i.e.

$$G_2^{\text{c}} = (1/8\pi) \int_V \mathbf{E}_2^{\text{c}} \cdot \mathbf{E}_2^{\text{c}} dV, \quad (4)$$

$$G_{2,\text{or}} = (1/8\pi) \int_V \mathbf{E}_{2,\text{or}} \cdot \mathbf{E}_{2,\text{or}} dV, \quad (5)$$

$$G_{2,\text{op}} = (1/8\pi) \int_V \mathbf{E}_{2,\text{op}} \cdot \mathbf{E}_{2,\text{op}} dV, \quad (6)$$

the interaction energy between solute charge and orientational polarized charge

$$G_{2,\text{c-or}} = (1/4\pi) \int_V \mathbf{E}_2^{\text{c}} \cdot \mathbf{E}_{2,\text{or}} dV, \quad (7)$$

the interaction energy between solute charge and electronic polarized charge

$$G_{2,c-op} = (1/4\pi) \int_V \mathbf{E}_2^c \cdot \mathbf{E}_{2,op} dV, \quad (8)$$

the interaction energy between the orientational and electronic polarized charges

$$G_{2,or-op} = (1/4\pi) \int_V \mathbf{E}_{2,or} \cdot \mathbf{E}_{2,op} dV, \quad (9)$$

and the spring energy of the orientational and electronic polarizations^[8,10]

$$\begin{aligned} G_{2,or}^{\text{spring}} &= (1/2) \int_V \mathbf{P}_{2,or} \cdot \mathbf{E}_2^{\text{non}} dV \\ &= -(1/8\pi) \int_V \mathbf{E}_{2,or} \cdot \mathbf{E}_2^{\text{non}} dV \\ &= -(1/8\pi) \int_V \mathbf{E}_{2,or} \cdot (\mathbf{E}_2^c + \mathbf{E}_{2,or} + \mathbf{E}_{2,op}) dV \\ &= -(1/2)G_{2,c-or} - (1/2)G_{2,or-op} - G_{2,or}, \quad (10) \\ G_{2,op}^{\text{spring}} &= (1/2) \int_V \mathbf{P}_{2,op} \cdot \mathbf{E}_2^{\text{non}} dV \\ &= -(1/8\pi) \int_V \mathbf{E}_{2,op} \cdot \mathbf{E}_2^{\text{non}} dV \\ &= -(1/8\pi) \int_V \mathbf{E}_{2,op} \cdot (\mathbf{E}_2^c + \mathbf{E}_{2,or} + \mathbf{E}_{2,op}) dV \\ &= -(1/2)G_{2,c-op} - (1/2)G_{2,or-op} - G_{2,op}. \quad (11) \end{aligned}$$

The sum of the above contributions gives the expression for total electrostatic free energy in nonequilibrium as

$$\begin{aligned} G_2^{\text{non}} &= G_2^c + (1/2)(G_{2,c-or} + G_{2,c-op}) \\ &= (1/8\pi) \int_V \mathbf{E}_2^c \cdot (\mathbf{E}_2^c + \mathbf{E}_{2,or} + \mathbf{E}_{2,op}) dV \\ &= (1/8\pi) \int_V \mathbf{E}_2^c \cdot \mathbf{E}_2^{\text{non}} dV. \quad (12) \end{aligned}$$

With simple derivation, the equality between eq. (3) and eq. (12) can be testified^[8]. This indicates that the solvation energy of equilibrium and nonequilibrium can be analyzed reasonably by introducing the concept of spring energy. Subtracting the self-energy of solute charge from eq. (12), the nonequilibrium solvation energy of the system can be expressed as

$$\begin{aligned} \Delta F_2^{\text{non}} &= G_2^{\text{non}} - G_2^c = (1/2)(G_{2,c-or} + G_{2,c-op}) \\ &= (1/8\pi) \int_V \mathbf{E}_2^c \cdot (\mathbf{E}_{2,or} + \mathbf{E}_{2,op}) dV. \quad (13) \end{aligned}$$

The electrostatic self-energy of solute is usually calculated by quantum chemistry program. Similarly, the solvation energy of equilibrium can be given by

$$\Delta F_1^{\text{eq}} = (1/8\pi) \int_V \mathbf{E}_1^c \cdot (\mathbf{E}_{1,or} + \mathbf{E}_{1,op}) dV. \quad (14)$$

It is seen that the electrostatic free energy and solvation energy of the solute-solvent system for both equilibrium and nonequilibrium have no difference in

form^[8-12].

1.2 Explicit solvent model

In explicit solvent model, the solvent polarization is divided into permanent dipole and induced dipole similar to the treatment in the continuum model. Therefore, the solvation energy of nonequilibrium can be expressed as

$$\begin{aligned} \Delta F_2^{\text{non}} &= G_{2,pe} + G_{2,in} + G_{2,in-pe} + G_{2,c-pe} + G_{2,c-in} \\ &\quad + G_{2,pe}^{\text{spring}} + G_{2,in}^{\text{spring}} + G_{2,c}^{\text{dist}}, \quad (15) \end{aligned}$$

where $G_{2,pe}$, $G_{2,in}$ and $G_{2,in-pe}$ are the self-energy of solvent permanent dipole and induced dipole and the interaction energy between them, $G_{2,c-pe}$ and $G_{2,c-in}$ stand for the interaction energy between the permanent and induced dipoles and the solute charge, $G_{2,pe}^{\text{spring}}$ and $G_{2,in}^{\text{spring}}$ denote the spring energy of permanent and induced dipoles respectively, and $G_{2,c}^{\text{dist}}$ is the energy change for the variation of the solute wave function due to the solvent effect. The subscripts “pe” and “in” refer to permanent and induced dipoles respectively. In the past years, the spring energy of the permanent dipole was ignored inappropriately and the permanent dipole was treated as free charge by some authors^[16-18]. However, for the arrangement in order of solvent molecules due to the solute field, both the vector sum of all solvent permanent dipoles and the averaged field acting on the solvent molecule are obviously not zero. Therefore, the permanent dipole should have the spring energy similar to orientational polarization. In our treatment, the permanent dipole is represented by the discrete distribution of permanent charge brought by each atom of all the solvent molecules. Therefore, the self-energy of the permanent dipole and induced dipole of solvent can be expressed as

$$G_{2,pe} = \frac{1}{2} \sum_i q_{2,i} V_{2,i}^q, \quad G_{2,in} = -\frac{1}{2} \sum_j \mu_{2,j} \cdot \mathbf{E}_{2,j}^{\mu}, \quad (16)$$

where $q_{2,i}$ is the permanent charge brought by the i th solvent atom, $V_{2,i}^q$ is the potential at the i th solvent atom generated by the other permanent charges of the solvent, the subscript “ i ” represents the number of solvent atom, $\mu_{2,j}$ and $\mathbf{E}_{2,j}^{\mu}$ stand for the induced dipole at the centroid of the j th solvent molecule and the field strength at this point generated by the other induced dipoles, and the subscript “ j ” denotes the number of the

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solvent molecules. The interaction energy between the permanent and induced dipoles of solvent can be expressed as

$$G_{2,\text{in-pe}} = -\sum_j \boldsymbol{\mu}_{2,j} \cdot \mathbf{E}_{2,j}^q, \quad (17)$$

where $\mathbf{E}_{2,j}^q$ is the field strength at the j th solvent molecule generated by all permanent charges. The interaction energy between the solvent permanent and induced dipoles and the solute charge has the forms of

$$G_{2,\text{c-pe}} = \sum_i q_{2,i} V_{2,i}^c, \quad G_{2,\text{c-in}} = -\sum_j \boldsymbol{\mu}_{2,j} \cdot \mathbf{E}_{2,j}^c, \quad (18)$$

where $V_{2,i}^c$ is the potential at the i th solvent atom due to the solute charge distribution in nonequilibrium and $\mathbf{E}_{2,j}^c$ is the field strength at the j th solvent molecule due to the solute charge. By introducing the tensor of molecular polarizability $\bar{\alpha}_j$, similar to electronic polarization, the spring energy of induced dipole can be expressed as

$$\begin{aligned} G_{2,\text{in}}^{\text{spring}} &= \sum_j \frac{\boldsymbol{\mu}_{2,j} \cdot \bar{\alpha}_j^{-1} \cdot \boldsymbol{\mu}_{2,j}}{2} = \frac{1}{2} \sum_j \boldsymbol{\mu}_{2,j} \cdot \mathbf{E}_{2,j} \\ &= \frac{1}{2} \sum_j \boldsymbol{\mu}_{2,j} \cdot (\mathbf{E}_{2,j}^q + \mathbf{E}_{2,j}^u + \mathbf{E}_{2,j}^c) \\ &= -\frac{1}{2} G_{2,\text{in-pe}} - G_{2,\text{in}} - \frac{1}{2} G_{2,\text{c-in}}. \end{aligned} \quad (19)$$

On the other hand, the spring energy of the permanent dipoles has the form of

$$\begin{aligned} G_{2,\text{pe}}^{\text{spring}} &= -\frac{1}{2} \sum_i q_{2,i} (V_{2,i}^q + V_{2,i}^u + V_{2,i}^c) \\ &= -\frac{1}{2} G_{2,\text{in-pe}} - G_{2,\text{pe}} - \frac{1}{2} G_{2,\text{c-pe}}. \end{aligned} \quad (20)$$

In solution, the energy change of solute molecule due to the variation of wave function is

$$G_{2,\text{c}}^{\text{dist}} = \langle \Psi_2 | \mathbf{H} | \Psi_2 \rangle - \langle \Psi_2^0 | \mathbf{H} | \Psi_2^0 \rangle, \quad (21)$$

where Ψ_2^0 and Ψ_2 are the in-vacuum and in-solution solute wave functions, \mathbf{H} is Hamiltonian in vacuum. It should be emphasized that $\langle \Psi_2 | \mathbf{H} | \Psi_2 \rangle$ is not the total energy in vacuum or in solution and eq. (21) only stands for the energy change of solute molecule itself for the distortion of the wave function caused by the solvent surroundings. Substituting eqs. (16)–(21) into eq. (15), the simple form of the electrostatic solvation energy of nonequilibrium is given by

$$\Delta F_2^{\text{non}} = \frac{1}{2} (G_{2,\text{c-pe}} + G_{2,\text{c-in}}) + G_{2,\text{c}}^{\text{dist}}. \quad (22)$$

It is seen that the spring energy of the permanent di-

poles as given by eq. (20) cancels the self-energy of permanent dipoles, the half of interaction energy between permanent and induced dipoles, and the half of interaction energy between the solute charge and permanent dipoles, so the self-energy of the permanent dipoles disappears in eq. (22). However, ignoring the spring energy of permanent dipole, other authors derived the following form different from eq. (22)^[17]:

$$\begin{aligned} \Delta F_2^{\text{non}}(\text{A}) &= G_{2,\text{pe}} + \frac{1}{2} G_{2,\text{in-pe}} + G_{2,\text{c-pe}} \\ &\quad + \frac{1}{2} G_{2,\text{c-in}} + G_{2,\text{c}}^{\text{dist}}. \end{aligned} \quad (23)$$

It is obvious that the above equation cannot be reduced to the equilibrium form when the equilibrium condition is reached. According to the derivation of eq. (22), the solvation energy of equilibrium can be written as

$$\begin{aligned} \Delta F_1^{\text{eq}} &= \frac{1}{2} (G_{1,\text{c-pe}} + G_{1,\text{c-in}}) + G_{1,\text{c}}^{\text{dist}} \\ &= \frac{1}{2} \left(\sum_i q_{1,i} V_{1,i}^c - \sum_j \boldsymbol{\mu}_{1,j} \cdot \mathbf{E}_{1,j}^c \right) \\ &\quad + \langle \Psi_1 | \mathbf{H} | \Psi_1 \rangle - \langle \Psi_1^0 | \mathbf{H} | \Psi_1^0 \rangle. \end{aligned} \quad (24)$$

Because the spectral shift $\Delta h\nu$ is defined as the difference of solvation energy between nonequilibrium and equilibrium^[8–12], we have

$$\Delta h\nu = \Delta F_2^{\text{non}} - \Delta F_1^{\text{eq}} = \frac{1}{2} (\delta_{\text{c-pe}} + \delta_{\text{c-in}}) + \delta_{\text{c}}^{\text{dist}}, \quad (25)$$

where $\delta_{\text{c-pe}} = G_{2,\text{c-pe}} - G_{1,\text{c-pe}}$, $\delta_{\text{c-in}} = G_{2,\text{c-in}} - G_{1,\text{c-in}}$ and $\delta_{\text{c}}^{\text{dist}} = G_{2,\text{c}}^{\text{dist}} - G_{1,\text{c}}^{\text{dist}}$. Eq. (25) is valid for both the absorption and emission. For the absorption case, the subscripts “2” and “1” stand for the nonequilibrium excited state and equilibrium ground state respectively. For the emission or fluorescence spectrum, the subscripts “2” and “1” stand for nonequilibrium ground state and equilibrium excited state. Aguilar *et al.*^[17] also gave the formula for the spectral shift as

$$\Delta h\nu(\text{A}) = \frac{1}{2} \delta_{\text{in-pe}} + \delta_{\text{c-pe}} + \frac{1}{2} \delta_{\text{c-in}} + \delta_{\text{c}}^{\text{dist}}. \quad (26)$$

Since the energy components in nonequilibrium are not appropriately understood, the formula of spectral shift given in eq. (26) looks unreasonable, and this defect also emerges in coding the ASEP/MD program.

2 Test calculation

2.1 Equilibrium solvation energy of water molecule

The ASEP/MD program^[16] by Aguilar and coworkers combines the high-level quantum calculation by

Gaussian98 or Hondo99 with molecular dynamics calculation by Moldy program. The solute molecule can be treated by quantum chemistry program and the conformation and energy of the solvent molecules is calculated by the molecular dynamics method^[19]. The ASEP/MD program is modified and our new derivation is coded into this program in this work. For the pure solvent and solution, two methods can be adopted to calculate the solute-solvent system.

The first one is full coupling method, but it is valid for the pure solvent only. In this method, the solute molecule in vacuum is calculated at first by Gaussian98 or Hondo99 program and the obtained charge population of solute molecule is assigned to the solvent molecule. According to the intermolecular Lennard-Jones potential and the initial charges brought by the solvent atoms, the N stable conformations of the solvent molecules can be obtained by the Moldy program^[19]. Then the solute cavity is divided into n space grids, and the averaged potential V_1 at these grids can be obtained by the total potential generated by all solvent molecules of the N stable conformations. At the same time, the conformations of solvent molecules and charges brought by the solvent atoms in the range of cut-off radius should be averaged on the number of conformations, and the potential V_2 can be calculated, which is generated by the charges brought by the solvent atoms of the averaged conformation. The potential difference $V_1 - V_2$ can be fitted by the 60 point charges on the surfaces of two concentric spheres (Fig. 1) and the new quantum calculation is carried out with the external field due to two components: the charges brought by the solvent atoms of the averaged conformation in the cut-off radius and the 60 point charges. Hence the newly calculated charge population and geometry of the solute are

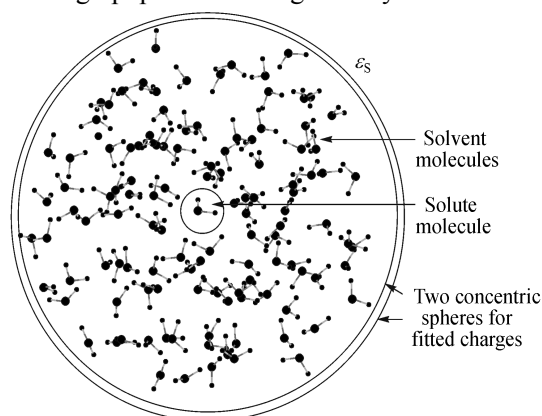


Fig. 1. Two concentric spheres for fitted charges in ASEP/MD program.

assigned to the solvent molecule once again and the second dynamics calculation can be executed. The above cycles will not stop unless the convergence criterion is satisfied. Because the geometry and charge distribution of each solvent molecule are the same as those of the solute in this method, the induced dipoles of the solvent molecules are essentially considered by assigning the result of the solute treated with quantum calculation to the solvent molecules.

The second one is polarized medium method. Firstly, the quantum calculation for the solute molecule and the dynamic calculation for solvent molecules are carried out and then the induced dipoles can be calculated for each solvent conformation according to the molecular polarizability. The charges brought by the solvent atoms are permanent ones in this method and the averaged potential V_1 at the grids in the solute cavity can be achieved with the potential due to the permanent charges and induced dipoles of all the solvent conformations dividing the number N of solvent conformations. The conformations and permanent charges of solvent molecules in the cut-off radius are averaged and then the potential V_2 is obtained. The potential difference $V_1 - V_2$ fitted by the 60 point charges on the surfaces of two concentric spheres includes the contribution from the induced dipoles of the solvent molecules. Then the 60 point charges and the averaged permanent charges of the solvent molecules are introduced into the quantum calculation for the solute as an external field and a new geometry and charge population of the solute molecule can be obtained. Hence the induced dipoles and fitted charges are renewed and the cycles will not stop unless the convergence is reached. In this method, the charges brought by the solvent atoms keep constant and the induced dipoles of the solvent molecules are investigated by introducing the molecular polarizability. This method is valid for both pure solvent and solution. By considering the Van der Waals interaction energy G_2^{vdw} , ASEP/MD program gives the expression of the final solvation energy $\Delta F_{2,\text{total}}^{\text{non}}$ as

$$\Delta F_{2,\text{total}}^{\text{non}} = \Delta F_2^{\text{non}} + G_2^{\text{vdw}}. \quad (27)$$

Here, the contribution of cavitation energy to solvation energy is not taken into account. In equilibrium case, we only need to change the subscript “2” to “1” in eq. (27).

The above two methods are both used to estimate the equilibrium solvation energy for water molecule with

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water solvent. The quantum calculation for the solute is carried out at the level of HF/6-31++G** with Gaussian98 program by using the above two methods. In the first method, the initial charge of the solvent oxygen atom is assigned to -0.808 , i.e. $q(\text{O}) = -0.808$, and that of hydrogen atom is $q(\text{H}) = 0.404$. According to the precise result of the solute quantum calculation, the charges brought by the solute and solvent atoms will not stop changing unless the convergence is reached in the first method. Here 214 solvent molecules are adopted and the cut-off radius is 9 \AA . We consider 100 conformations of the solvent molecules^[16,18]. In the second method, $q(\text{O})$ of solvent molecule is assigned to -0.716 and $q(\text{H})$ is 0.358 , which are permanent charges and will not change during the iteration. The induced dipoles are estimated by introducing the polarizability tensor. The contribution to potential of both permanent charges and induced dipoles in the second method is equal to that of atomic charge distribution of the solvent molecules in the first method. Thus the initial assignment of the atomic charge is not equal for the two methods. The other parameters in the second method are the same as those in the first method. The calculated results are listed in Table 1.

The equilibrium solvation theory with continuum model can give the reasonable explanation for the experimental observation at present. Therefore, the result by PCM method at the level of HF/6-31++G** by Gaussian98 program is obtained. With the modified ASEP/MD program, the above mentioned methods, full coupling and polarized medium give the solvation energy of -50.50 and -45.94 kJ/mol respectively. Comparing with -52.54 kJ/mol from PCM method without considering cavitation energy, our result looks reasonable. Involving the cavitation energy of 18.60 kJ/mol at the level of HF/6-31++G**, the total solvation energy in our case is -31.90 and -27.34 kJ/mol respectively by full coupling and polarized medium methods. These values are very close to the total solvation energy of -33.94 kJ/mol obtained by PCM. Not cognizing appropriately the energy component of the spring energy, eq.

(23) ought to involve the energy term of self-energy of the permanent dipoles, but this self-energy part was ignored in Aguilar's test calculations, without explanation^[18].

2.2 Absorption spectral shift of acrolein molecule

It is assumed that the cavitation energy of the solute remains the same in both equilibrium and nonequilibrium, so it does not affect the spectral shift and solvent reorganization energy in electron transfer reactions. The polarized medium method is adopted to estimate the absorption spectral shift of acrolein molecule in water. The geometry optimization for acrolein in vacuum is carried out by CASSCF method with 6 valence electrons in 5 orbitals with the basis sets of 6-31G(d) in Gaussian98, and the obtained charge population is listed in Fig. 2. For the dynamic simulation with Moldy program, the solvent is represented by 214 TIP3P water molecules and the cut-off radius is 9 \AA . The permanent charges for the solvent molecule are $q(\text{O}) = -0.716$ and $q(\text{H}) = 0.358$. Taking 100 conformations from the dynamic simulation into account and introducing the molecular polarizability tensor, the permanent charges averaged on the number of solvent conformations and the fitted 60 charges on the two concentric sphere surfaces are calculated. The new charge distribution is achieved by treating the two parts of solvent charges as the external field in the quantum calculation (see Fig. 2 for the final results). The values of spectral shift for $n \rightarrow \pi^*$ transition of acrolein are listed in Table 2.

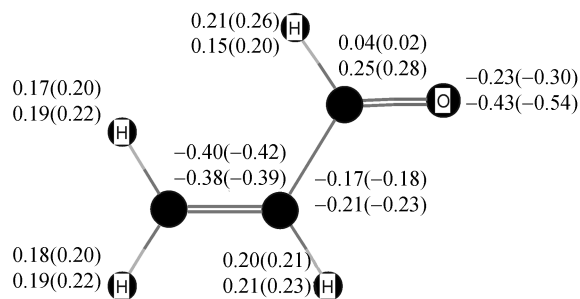


Fig. 2. Net charges condensed on the atoms of acrolein molecule. The upper for excited state and the lower for ground state. Data in brackets are in solution.

Table 1 Different energy contributions to the solvation energy of water molecule (Unit: kJ/mol)

Method	$\frac{1}{2} G_{1,c-pe}^a$	$\frac{1}{2} G_{1,c-in}^a$	$G_{1,c}^{dist a}$	$G_1^{vdw a}$	$\Delta F_{1,total}^{eq a}$	$\Delta F_{1,total}^{eq (A)^b}$	$\Delta F_{1,total}^{eq (H)^c}$
Full coupling	-119.97	0	25.75	43.72	-50.50	-90.50	-52.54
Polarized medium	-65.67	-15.93	14.76	20.90	-45.94	-80.67	

a) Results by the modified ASEP/MD program, cavitation energy not involved; b) results by the original ASEP/MD program, cavitation energy not involved^[18]; c) result by the PCM method at the level of HF/6-31++G** with Gaussian98 program, cavitation energy not involved.

Table 2 Dipole moments and spectral shift of absorption in solution (kJ/mol)

	$\mu_g^a)$	$\mu_e^a)$	$\frac{1}{2}\delta_{c-pe}^a)$	$\frac{1}{2}\delta_{c-in}^a)$	$\delta_c^{dist a)}$	$\Delta h\nu^a)$	$\Delta h\nu (A)^b)$	$\Delta h\nu (P)^c)$	$\Delta h\nu (H)^d)$	$\Delta h\nu (exp)^e)$
Polarized medium	4.00	1.98	9.45	2.93	8.07	20.45	25.50	31.77	41.38	18.81

a) Results by modified ASEP/MD program, the unit for the dipole moment is Debye; b) results by the original ASEP/MD program^[17]; c) results by PCM^[20]; d) hybrid continuum/discrete solvent model^[20]; e) see ref. [17].

The $n \rightarrow \pi^*$ transition energy of acrolein molecule in vacuum is 3.97 eV with Gaussian98 program, very close to the experimental value of 3.94 eV. The solute dipoles of ground state and excited state in solution are 4.0 and 1.98 Debye respectively. Compared with 2.87 Debye for ground state and 1.06 Debye for excited state in vacuum, the solute dipoles change to larger values in the solvent surroundings. The conformations of the solvent molecules and Lennard-Jones potential are thought invariant during the transition of the solute molecule, hence the van der Waals interaction will keep constant from equilibrium to nonequilibrium. Keeping solvent structure corresponding to the excited state as the same as that in ground state, the modified ASEP/MD program gives the spectral shift of 20.45 kJ/mol, a little larger than the experimental value of 18.81 kJ/mol. However, the original ASEP/MD program gives a value of 25.50 kJ/mol^[17] for this quantity, and PCM also predicts an overestimated value of 31.77 kJ/mol^[20]. Besides, a value of 41.38 kJ/mol was obtained from hybrid continuum/discrete solvent model^[20]. It can be concluded that traditional theories of nonequilibrium solvation will overestimate the spectral shift of acrolein by using both continuum model and explicit solvent model, for the defects on understanding the energy components of nonequilibrium state.

3 Conclusion

Based on the study of nonequilibrium solvation with continuum model, similar physical ideology is applied to the explicit solvent model. It is found that the defects on the conventional derivation of the nonequilibrium solvation free energy by continuum model still exist when explicit solvent model is used. Hence, according to the reasonable decomposition of the energy in solute-solvent system and introducing the concept of spring energy, the new formula for the nonequilibrium solvation energy is established by rectifying the mistake of ignoring the existence of spring energy of permanent dipoles. The new formula is adopted to establish the expression for spectral shift without distinguishing absorption from emission. Our new formulas are different from the traditional ones. With the new

treatments, ASEP/MD program is modified and applied to the calculation of equilibrium solvation energy of water molecule and the spectral shift of acrolein. The results show that our new formula can give reasonable explanation for the experimental value and solve the problem of overestimation of the spectral shift in traditional models.

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