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Iso-Energy Cutoff for the Calculation of Interionic Potential of Mean Force in Water

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Abstract

An iso-energy cutoff scheme is introduced for the calculation of the potential of mean force between two ions in water. The cutoff criterion is based on the optimal interaction of the water dipole with the ion pair, for which analytical expressions are derived. Formulae are also derived to characterize the solvent reorganization contribution to the potential of mean force. Treatment of the contributions from waters outside the cutoff is also discussed.

I. Introduction

Recent computer simulation studies [1-3] showed that the calculated interionic potential of mean force (PMF) can be qualitatively affected by the cutoff scheme (i.e., treatment of distant waters) employed. The main options discussed earlier are spherical cutoff on the ions, minimum image cutoff on the ions or Ewald summation. It has been shown by recent simulations [3] that the use of spherical cutoff on two ions between which the PMF is to be calculated introduces artifactual minima in the PMF. Alternatives schemes like the Ewald summation or the minimum image not only require more computational effort but have their own problems as well [3].

In the following a new cutoff scheme, called iso-energy (IE) cutoff, is proposed that has the following advantages: 1. The cutoff is based on an energy criterion that is designed to work independent of the relative position of the water and is based on both of the ions — this way the artifact discussed in Ref. 3 is expected to be eliminated. 2. It is possible to separate the contributions to the PMF due to solvent reorganization and solvent accessibility. 3. The long range effects can be incorporated after the simulation based on numerical solutions of the Poisson-Boltzmann (PB) equations, e.g., with the DELPHI program [4].

The procedure proposed places a cutoff on the idealized interaction energy of water and the ion pair: the water is represented by a dipole and the energy is calculated assuming that the dipole is in the orientation giving the lowest interaction energy with the charges. For this purpose, the optimal orientation has been derived as a funcion of the ion-ion and ion-dipole distances.

As the volume of the object defined by the IE cutoff varies with the interionic distance, the calculated PMF will contain contributions due to the change in the number of waters the ions interact with. This is a fundamental contribution to the PMF: as the ion pair separates, the number of waters that strongly interact with both ions simultaneously is decreasing. The

estimate of this effect requires the dependence of the volume of the region within the IE surface on the interionic distance. Knowing the density and the ion-water energy at the surface the volume contribution can be obtained.

The contribution from waters outside the cutoff can be obtained from the PB calculation. As this contribution can be calculated independently of the first two, it can be based on local dielectric constants obtained by comparison of the field of the two ions with the mean electric field averaged over the simulation.

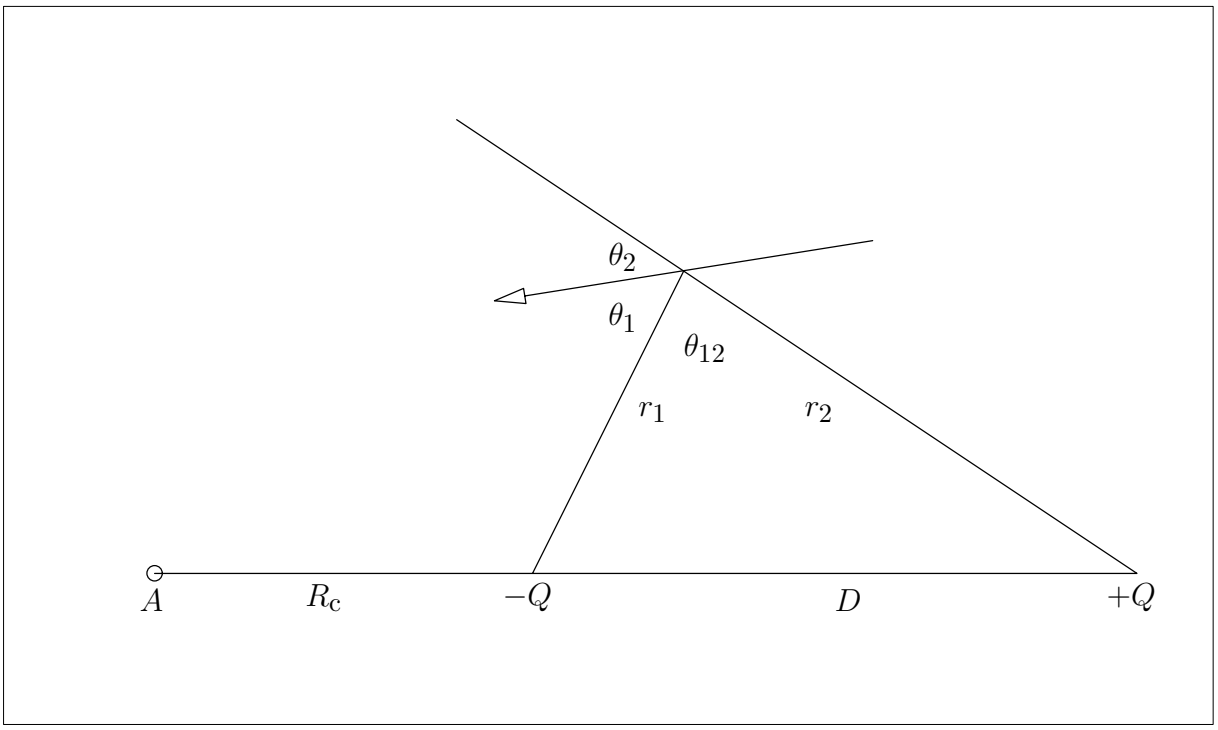

Fig. 1. Definition of the angles θ_1 and θ_2 used for the determination of the optimal ion-dipole interaction.

II. Theory

A. Cutoff formalism

The interaction between a dipole μ and a charge Q at a distance r is given as

$$E_{Q\mu} = -Q\mu\cos\theta/r^2 \tag{1}$$

with $\mu = |\mu|$ and θ being the angle between the dipole μ and the line between the ion and the dipole. For a dipole μ interacting with charges Q and sQ (s being +1 or -1) at a distance r_1 and r_2 from the dipole, respectively (see Figure 1. for the case s=-1), the interaction energy is given as

$$E_{Q\mu}(r_1, r_2, D) = -Q\mu(\cos\theta_1/r_1^2 + \cos\theta_2/r_2^2), \tag{2}$$

where

$$\cos(\theta_1 + \theta_2) = -s(D^2 - r_1^2 - r_2^2)/(2r_1r_2) = \alpha, \tag{3}$$

i.e., for $s = +1$, the dipole points between the two ion-dipole line and for $s = -1$, it points outside (as shown on Figure 1).

Using the Lagrange multiplier method to minimize the energy subject to the constraint of Eq.(3) leads to the system of equations

$$(\partial/\partial\theta_i)\{E_{Q\mu} + \lambda[\cos(\theta_1 + \theta_2) - \alpha]\} = 0 \quad (i = 1, 2) \tag{4}$$

giving

$$Q\mu \sin\theta_i / r_i^2 - \lambda \sin(\theta_1 + \theta_2) = 0 \quad (i = 1, 2) \tag{5}$$

or

$$\sin\theta_i = -r_i^2 (1 - \alpha^2)^{1/2} \lambda / Q\mu \quad (i = 1, 2) \tag{6}$$

λ can be determined by substituting Eq.(6) into the constraint [Eq.(3)] and using trigonometric identities:

$$\alpha = \cos(\theta_1 + \theta_2) = \cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2$$
$$= \{[1 - r_1^4 (1 - \alpha^2)\lambda^2/(Q\mu)^2][1 - r_2^4 (1 - \alpha^2)\lambda^2/(Q\mu)^2]\}^{1/2}$$
$$- r_1^2 r_2^2 (1 - \alpha^2)\lambda^2/(Q\mu)^2. \tag{7}$$

Solving Eq.(7) for λ^2 gives

$$\lambda^2 = (Q\mu)^2/(2\alpha r_1^2 r_2^2 + r_1^4 + r_2^4) \tag{8}$$

Substitution of Eqs.(6) and (8) into the identity

$$\cos\theta_i = \pm(1 - \sin\theta_i^2)^{1/2} \tag{9}$$

gives

$$\cos\theta_i = sg_i\{1 + r_i^2[D^4 + (r_1^2 - r_2^2)^2 - 2D^2(r_1^2 + r_2^2)]/$$
$$[4r_{i'}^2(r_1^4 + r_2^4 - s \times r_1 r_2 (D^2 - r_1^2 - r_2^2))]\}^{1/2} \tag{10}$$

where $i' = 3 - i$ (i.e., the other one).

The sign of the square root, sg_i, can be determined as follows. Assuming $r_1 \leq r_2$, sg_1 is always positive ($\theta_1 < \pi/2$). As the angle between the two ion–dipole lines, θ_{12}, can be obtained unequivocally from the law of cosines, a convenient criterion of requiring the negative sign is that for $s = -1$, $\theta_1 + \theta_{12} < \pi/2$ and for $s = +1$, $\theta_1 + (\pi - \theta_{12}) < \pi/2$.

A few special cases can be immediately solved:

$$\text{Case1}: \quad r_2 - r_1 = D : \theta_1 = 0 \ \text{ and } \ \theta_2 = 0$$

$$\text{Case2}: \quad r_2 + r_1 = D : \theta_1 = 0 \ \text{ and } \ \theta_2 = \pi$$

$$\text{Case3}: \quad r_2 = r_1 : \theta_1 = \theta_2. \tag{11}$$

The result for Case 1 can be used to relate the IE cutoff to the conventional spherical cutoff. For a water on the interionic line outside the ions at the conventional cutoff distance R_c from the closer ion (and $D + R_c$ distance from the other), the cutoff energy $E^c_{Q\mu}(D, R_c)$ is

$$E^c_{Q\mu}(D, R_c) = Q\mu[1/R_c^2 + s/(R_c + D)^2]. \tag{12}$$

Therefore, the IE cutoff that gives a reasonable correspondance to the spherical cutoff around the ions with radius R_c would neglect ion–water interactions whenever

$$E_{Q\mu}(r_1, r_2, D) \geq E^c_{Q\mu}(D, R_c). \tag{13}$$

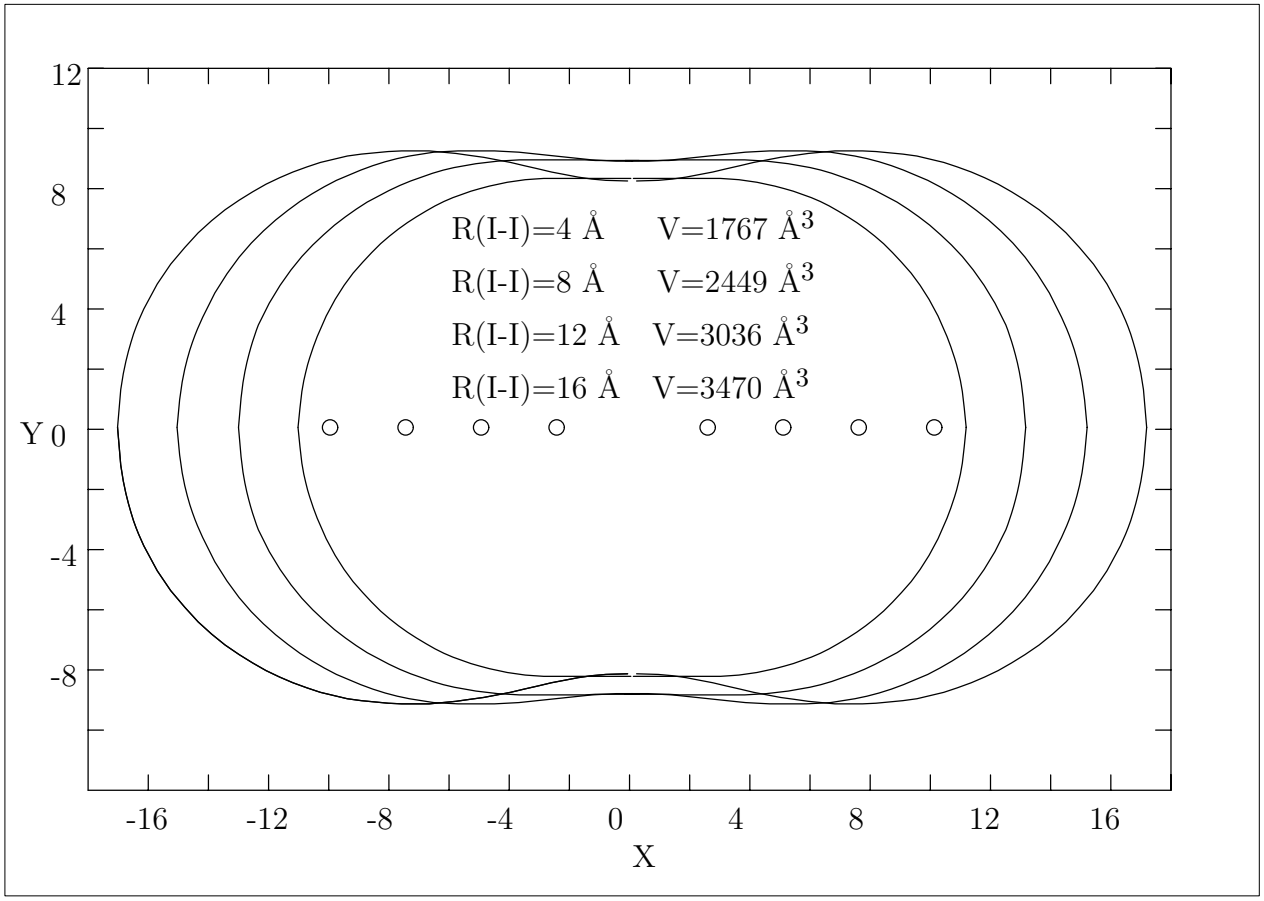

Fig. 2. The IE surfaces corresponding to $R_c = 9$ Å spherical cutoff for interionic distances D=4, 8, 12 and 16 Å.

Figure 2. shows the shape of the cutoff region defined by Eq.(13) for several different D values. Note that with this choice the cutoff energy will vary with the interionic distance (it increases inmagnitude as the ions separate). This reflects the fact that increasing the separation of the ion pair increases its dipole moment. Application of the electrostatic long-range correction (through the PB equation) will (ideally) compensate for any artifact that the dependence of the cutoff energy on the ion-ion distance might introduce. An alternative would keep

$E^c_{Q\mu}(D) = E^c_{Q\mu}(D_\mathrm{o})$ with a selected ion–ion distance D_o (say, the closest possible), but this would result in a larger volume variation.

B. Estimating the solvent reorganization term

Even if the solvent formed an unperturbed continuum around the ions, the variation in the number of solvents interacting with the two ions introduces a driving force between the ions. This would be the case with (most) any kind of cutoff. The choice of the IE cutoff provides a mean for estimating this contribution to the PMF, as described below.

The contribution to the PMF from the changing number of interacting solvents when the IE cutoff is applied with cutoff value $E^\mathrm{o}_{Q\mu}(D)$, $W_V(D)$, can be used to obtain an estimate of the solvent reorganization contribution as $W(D) - W_V(D)$. $W_V(D)$ can be obtained as

$$W_V(D) = \int_{D_\mathrm{min}}^{D} E^c_{Q\mu}(D)\rho\partial V(D')/\partial D' dD' \tag{14}$$

where ρ is the density of the water, as the waters in the region representing the volume change from $V(D)$ to $V(D+dD)$ are all within infinitesimal distance of the surface and thus their energy is $E^c_{Q\mu}$.

The volume of the area within the IE surface can be obtained as

$$V(D) = \int_{-\infty}^{\infty} [y(x,D)]^2 \pi dx \tag{15}$$

where the ion pair is assumed to lie along the x axis and $y(x)$ is the point on the IE surface at x. For x outside the cutoff region, $y(x) = 0$. The dependence of y on x is defined through the relation

$$S(r_1, r_2, D) = E_{Q\mu}(r_1, r_2, D) - E^c_{Q\mu}(D) = 0 \tag{16}$$

that, does not lend itself to expressing y explicitly, therefore a numerical solution is required. Fortunately, $y(x)$ turned out to be single-valued for the cases examined.

For $E^c_{Q\mu}(D) = E^c_{Q\mu}$, the expression for $W_V(D)$ simplyfies into

$$W_V(D) = E^c_{Q\mu}\rho[V(D) - V(D_\mathrm{min})]. \tag{17}$$

For the variable $E^c_{Q\mu}(D)$ case, the derivative $\partial V/\partial D$ can be expressed as

$$\partial V/\partial D = \int_{-\infty}^{\infty} \partial\{[y(x)]^2\}/\partial D \pi dx \tag{18}$$

and using the law of the derivative of an implicit function we obtain

$$\partial\{[y(x)]^2\}/\partial D = 2y(x)\partial[y(x)]/\partial D$$

$$= -2y(x)[(\partial S(r_1, r_2, D)/\partial D)/(\partial S(r_1, r_2, D)/\partial y)], \tag{19}$$

where

$$\partial S(r_1, r_2, D)/\partial D = \partial E_{Q\mu}(r_1, r_2, D)/\partial D - \partial E^c_{Q\mu}(D)/\partial D$$
$$= \sum_{i=1,2} -(\partial \cos\theta_i/\partial D)/r_i^2 - 2/(R_c + D)^3 \tag{20}$$

and

$$\partial S(r_1, r_2, D)/\partial y = \partial E_{Q\mu}(r_1, r_2, D)/\partial y$$
$$= \sum_{i=1,2} (\partial E_{Q\mu}(r_1, r_2, D)/\partial r_i)(\partial r_i/\partial y) = \sum_{i=1,2} -(\partial(\cos\theta_j/r_j^2)/\partial r_i)(y/r_i)$$
$$= \sum_{i=1,2} -\{[\partial(\cos\theta_i/r_i^2)/\partial r_i)] + [(\partial \cos\theta_{i'}/\partial r_i)/r_{i'}^2]\}(y/r_i)$$
$$= \sum_{i=1,2} -\{[(\partial \cos\theta_i/\partial r_i)/r_i^2 - 2\cos\theta_i/r_i^3))] + [(\partial \cos\theta_{i'}/\partial r_i)/r_{i'}^2]\}(y/r_i) \tag{21}$$

The derivatives of $\cos\theta_i$ in Eqs.(20) and (21) are given by the following expressions:

$$\partial \cos\theta_i/\partial D = \{[(r_i^2(D^3 - D(r_i^2 + r_{i'}^2))]/[r_{i'}^2 \text{ DEN}] +$$
$$[sDr_i^3 \text{ NUM}]/[r_{i'} \text{ DEN}^2]/2\}/(2\cos\theta_i) \tag{22}$$

$$\partial \cos\theta_i/\partial r_i = \{[r_i \text{ NUM} + 2r_i^3(r_i^2 - r_{i'}^2 - D^2)]/[2r_{i'}^2 \text{ DEN}]$$
$$-[r_i^2 \text{ NUM}(4r_i^3 - sr_{i'}(D^2 - r_i^2 - r_{i'}^2(2s+1)))]/[4r_i^2 \text{ DEN}^2]\}/(2\cos\theta_i) \tag{23}$$

$$\partial \cos\theta_i/\partial r_{i'} = \{-[2r_i^2 r_{i'}^2(r_i^2 - r_{i'}^2 + D^2) - r_i^2 \text{ NUM}]/[2r_{i'}^3 \text{ DEN}]$$
$$-[r_i^2 \text{ NUM}(4r_{i'}^3 - sr_i(D^2 - r_i^2 - r_{i'}^2(2s+1)))]/[4r_{i'}^2 \text{ DEN}^2]\}/(2\cos\theta_i), \text{`} \tag{24}$$

where the abbreviations NUM and DEN have been introduced:

$$\text{NUM} = D^4 + (r_1^2 - r_2^2)^2 - 2D^2(r_1^2 + r_2^2) \tag{25}$$

$$\text{DEN} = r_1^4 + r_2^4 - s \times r_1 r_2(D^2 - r_1^2 - r_2^2). \tag{26}$$

The integrations with respect to D and x in Eqs.(14) and (15) have to be performed numerically, as the integrand itself is obtained from a numerical procedure.

III. Summary

A computationally accessible description is provided for an iso-energy cutoff for the interaction of a water molecule with an ion pair. Its use in simulations for the interionic PMF allows post-simulation determination of the contributions from waters outside the cutoff and formulae are also given for the determination of the structural contribution of the water to the PMF.

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