

# Microsolvation of Cl anion by water clusters: Perturbative Monte Carlo simulations using a hybrid HF/MM potential

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## Abstract

We present a study of micro-solvation of Cl anion by water clusters of the size up to seven molecules using a perturbative Monte Carlo approach with a hybrid HF/MM potential. In this approach, a perturbation theory was used to avoid performing full SCF calculations at every Monte Carlo step. In this study, the anion is treated quantum mechanically at the HF/6-31G<sup>\*</sup> level of theory while interactions between solvent waters are represented by the TIP3P potential force field. Analysis on the solvent induced dipole moment of the ion indicates that the Cl anion resides most of the time on the surface of the clusters. Accuracy of the perturbative MC approach is also discussed.

## 1. Introduction

Solvation of ions in aqueous solution is of fundamental importance to chemistry in condensed phases [1,2]. It is often thought that waters sequentially fill the solvation shells as the system approaches bulk-like [3–5]. This infers the ion would prefer to be in the center of water clusters. However, whether the ion preferentially resides on the surface or interior of the cluster depends on the free energy change upon solvation of the ion by the cluster. This free energy change results from the lost of water–water hydrogen bonds and the gain of ion–water hydrogen bonds and the entropy change associated with the process. Depending on this free energy change, the ion could prefer to reside on the surface or interior of the cluster, consequently it would have very different

chemical reactivity. For this reason, structure and reactivity of microsolvated clusters have their own scientific interest beside providing an opportunity for exploring the gradual transition from the gas to liquid phase [6].

Despite advances in ion beam and photoelectron spectroscopy techniques allowing accurate measurements of energetic properties of microhydrated ion clusters as functions of the cluster size, direct inferences on solvent structure around the ion has not been possible [3,4,6,7]. Theoretical modeling would be useful in determining the structure–energy relationships for ion in water clusters. In this study, we focus on microscopic solvation of Cl anion in water clusters. Most theoretical studies [8–19] so far reproduce reasonably the general experimental energetic trend as a function of the cluster size, though fail to provide consistent structural information regarding the preferred location of the ion relative to the cluster and relative importance of specific interactions. Such inconsistency results from different ap-

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proximations employed in different theoretical treatments.

From a theoretical point of view, in order to address this problem correctly, one requires (1) to sufficiently sample the configuration space for accurate statistical averaging of thermodynamics properties and (2) to accurately describe *both* the solvent–solute and solvent–solvent interactions. Previous theoretical studies [8,12–15,17–19] based on molecular dynamics (MD) or Monte Carlo (MC) simulations satisfy the first requirement but not the second one due to the nature of the molecular mechanics (MM) potential force fields used. Ab initio studies [10,11] treat both solvent–solute and solvent–solvent interactions accurately at the same level of quantum mechanical (QM) theory, however, due to the computational demand such studies cannot sufficiently explore the configuration manifold of clusters with more than three waters. Thus, a natural progress would be to improve the accuracy of the interaction potential in classical simulations. In previous MC and MD simulations, the MM potentials consisted of electrostatic and van der Waals interactions between point particles, and sometimes included classical polarization of the solvent and solute. Several studies reported that solvent polarization is less important in determining the preferred location of the ion with respect to the cluster [13,15]. Recent study by Dang and Smith [13] pointed out that the ion polarizability is important though it was treated classically. In this study, the ion polarizability is treated quantum mechanically within the hybrid Hartree–Fock (HF)/MM potential while water molecules are represented by a molecular mechanics force field. A good review on the methodology and applications of the QM/MM approach was recently written by Gao [20].

Performing full SCF calculation at every MC or MD step is computationally expensive. A recently developed perturbative approach [21–23] recognizes the fact that in MC simulations, for certain solvent moves that induce small changes in the solvent–solute electrostatic interaction Hamiltonian, one can approximate the corresponding energy change by the perturbation theory using the wavefunction from the previously accepted full SCF step without having to perform full SCF calculations again. Our previous detailed analysis on the accuracy and efficiency of

this approach indicated that significant improvement in the computational performance with a negligible loss of accuracy can be achieved for small ion–water complexes [23]. Consequently, this approach allows us to treat the solute at HF ab initio level of theory which is more accurate than semiempirical methods used in most applications of the QM/MM method.

The present study has two objectives. One is to examine the structure–energy relationship in  $\text{Cl}^- (\text{H}_2\text{O})_n$  ( $n = 1-7$ ) clusters using the perturbative MC approach with the hybrid HF/MM potential. The other is to provide a closer look at the accuracy of the perturbative MC approach, which is briefly discussed below.

## 2. Perturbative Monte Carlo method for simulations using a hybrid QM/MM potential

In the QM/MM approach, the total effective Hamiltonian is partitioned as

$$H_{\text{eff}} = H^{\text{QM}} + H^{\text{QM/MM}} + H^{\text{MM}}, \quad (1)$$

where  $H^{\text{QM}}$  represents interactions within the quantum region,  $H^{\text{MM}}$  classical interactions within the MM region, and  $H^{\text{QM/MM}}$  interactions between the QM and MM regions. The  $H^{\text{QM/MM}}$  Hamiltonian is given by

$$H^{\text{QM/MM}} = \sum_i \sum_{\alpha} -\frac{q_{\alpha}}{R_{i\alpha}} + \sum_A \sum_{\alpha} \frac{q_{\alpha} Z_A}{R_{A\alpha}} + \sum_{\alpha} \sum_A \left( \frac{A_{\alpha A}}{(R_{\alpha A})^{12}} - \frac{B_{\alpha A}}{(R_{\alpha A})^6} \right), \quad (2)$$

where indices  $i$  and  $A$  run over the solute electrons and nuclei, respectively, while  $\alpha$  runs over all solvent atoms. The first two terms represent electrostatic interactions between solvent atoms and solute electrons and nuclei, respectively. The last term describes solvent–solute van der Waals interactions, denoted as  $E_{s-s}^{\text{vdW}}$  below. The total energy is then expressed as

$$E_{\text{tot}} = \left\langle \Psi \left| H^{\text{QM}} + \sum_i \sum_{\alpha} -\frac{q_{\alpha}}{R_{i\alpha}} \right| \Psi \right\rangle + \sum_A \sum_{\alpha} \frac{q_{\alpha} Z_A}{R_{A\alpha}} + E_{s-s}^{\text{vdW}} + E^{\text{MM}}, \quad (3)$$

where  $E^{\text{MM}}$  is the interaction energy within the MM region and  $\Psi$  is the solute wavefunction. The first

term in Eq. (3) requires solving the electronic Schrödinger equation which is the most time consuming step.

For Monte Carlo simulations, when the solvent molecule  $m$  is moved, the effective Hamiltonian in the first term of Eq. (3) is changed by

$$\Delta H = \sum_i \sum_{\alpha \in m} -q_\alpha \left( \frac{1}{R'_{i\alpha}} - \frac{1}{R_{i\alpha}} \right). \quad (4)$$

If the perturbation given by Eq. (4) is small, we can approximate the corresponding energy change within the first order perturbation theory by

$$\begin{aligned} \Delta E_{\text{tot}} = & \sum_{\mu\nu} P_{\mu\nu} \left\langle \mu \left| \sum_{\alpha \in m} -q_\alpha \left( \frac{1}{R'_{i\alpha}} - \frac{1}{R_{i\alpha}} \right) \right| \nu \right\rangle \\ & + \sum_A \sum_\alpha q_\alpha Z_A \left( \frac{1}{R_{A\alpha}} - \frac{1}{R'_{A\alpha}} \right) \\ & + \Delta E_{s-S}^{\text{vdW}} + \Delta E^{\text{MM}}, \end{aligned} \quad (5)$$

where  $P_{\mu\nu}$  is the density matrix element between the basis functions  $|\mu\rangle$  and  $|\nu\rangle$  from the previous full SCF calculation,  $\Delta E_{s-S}^{\text{vdW}}$  and  $\Delta E^{\text{MM}}$  are the changes in the short range solvent–solute and the solvent–solvent interactions, respectively. The main computational cost in calculating  $\Delta E_{\text{tot}}$  is the evaluation of a small number of one-electron integrals in Eq. (5). Consequently, one can expect significant speed up for perturbative MC calculations comparing to SCF calculations at each MC step.

The perturbative approach outlined above generates an approximate configuration ensemble. To ensure that such an ensemble is close to the exact one, the perturbative walk needs to be corrected to the exact path after a certain number of perturbative moves. This is done by performing full SCF calculations to update the solute wavefunction after every given number of perturbative solvent moves, denoted as NPMOVE. Detailed analysis on the average errors as functions of NPMOVE will provide insight in both accuracy and efficiency of this approach.

### 3. Computational details

In all MC simulations of  $\text{Cl}^- (\text{H}_2\text{O})_n$  clusters, the anion was treated quantum mechanically at the HF/6-31G\* level. Even at this level of theory, the

calculated polarizability of  $\text{Cl}^-$  anion of  $6.305 \text{ \AA}^3$  is too large compared to the experimental value of  $3.690 \text{ \AA}^3$  [24]. Water–water interactions were modeled by the TIP3P model [25]. Solvent–solute van der Waals parameters were taken from the OPLS force field [26]. These parameters were fitted to a point charge description for  $\text{Cl}^-$  anion. Recently, Freindorf and Gao [27] have optimized vdW parameters for the QM/MM potential. These new parameters are expected to be more accurate and will be used in our future applications of the HF/MM potential. All clusters were first equilibrated at  $25^\circ\text{C}$  by  $10^6$  classical steps where  $\text{Cl}^-$  was treated as a point charge following by  $2 \times 10^5$  quantum steps. Equilibrium properties were averaged over  $2 \times 10^5$  quantum steps. For the analysis of the accuracy of the perturbative approach, for each cluster, several MC simulations were performed, each with a different value of NPMOVE. All calculations were done using our interface between the G92/DFT [28] and BOSS [29] programs.

## 4. Results and discussion

### 4.1. Energetics

Calculated binding enthalpies of  $\text{Cl}^-$  in water clusters are listed in Table 1 and also shown as

Table 1  
Enthalpies of binding,  $\Delta H$  (kcal/mol), and average errors in solvent–solute electrostatic energy,  $\Delta E_{\text{elS}}$  (kcal/mol) for  $\text{Cl}^- (\text{H}_2\text{O})_n$  clusters

$n$	$-\Delta H$					$\Delta E_{\text{elS}}$	
	Expt. <sup>a</sup>	This work <sup>b</sup>	JS93 <sup>c</sup>	PB91 <sup>d</sup>	ANK93 <sup>e</sup>		DS93 <sup>f</sup>
1	14.7	13.4	12.7		13.3	13.4	0.05
2	27.7	26.5	25.2		26.0	25.6	0.06
3	39.5	37.4	37.3		38.1	37.1	0.08
4	50.1	47.4	49.2	49.7	49.7	48.4	0.09
5	59.6	57.3	60.4	58.5	60.7	57.9	0.08
6	68.4	67.5	71.5	69.1	71.2	66.6	0.08
7	76.5	75.4	81.4	76.8	81.2		0.07

<sup>a</sup> Ref. [7].

<sup>b</sup> NPMOVE = 20, the calculated uncertainties are 0.2–0.4 kcal/mol.

<sup>c</sup> Ref. [15]. The reported uncertainties are 0.1–0.2 kcal/mol.

<sup>d</sup> Ref. [17,18]. The reported uncertainties are 1.5–2.4 kcal/mol.

<sup>e</sup> Ref. [8]. The reported uncertainties are 0.3–2.5 kcal/mol.

<sup>f</sup> Ref. [13]. The reported uncertainties are 0.5–1.8 kcal/mol.

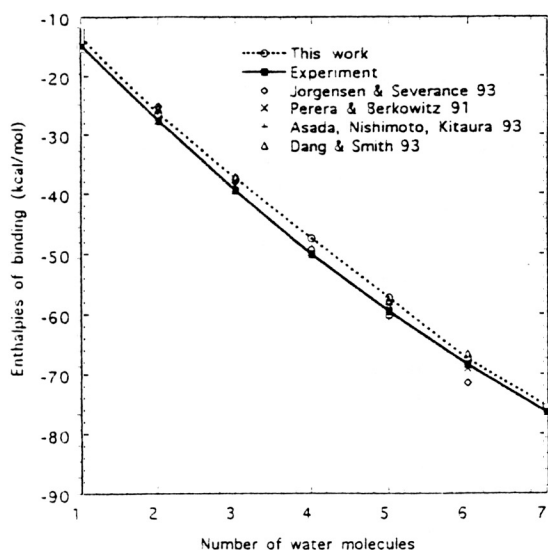


Fig. 1. Plot of the calculated and experimental enthalpies of binding (kcal/mol) of  $\text{Cl}^-(\text{H}_2\text{O})_n$  as functions of the cluster size.

functions of cluster size in Fig. 1 along with experimental data [7] and previously calculated values [8,13,15,17,18]. Our calculated binding enthalpies are slightly smaller (less negative) than the experimental data, though they are within the range of other calculated values. It should be noted that quantum mechanical effects, particularly the zero-point energy motions, have been found to be substantial at low temperatures by Gai et al. [14]. Even at room temperature, zero-point energy effects decrease the binding enthalpies by about 0.7 kcal/mol per water molecule. Consequently, such effects would deviate classical MD and MC results further from experimental observations. This is an evidence for the uncertainty in the molecular mechanics force fields used in simulations. Even in our simulations, such uncertainty also exists, particularly in the solvent-solute vdW parameters.

#### 4.2. Solvation structure

Solvation structures of  $\text{Cl}^-(\text{H}_2\text{O})_n$  clusters have been a debating issue. Most simulations yield the preferred location of the Cl anion to be near the surface of the clusters at room temperature. Furthermore, Perera and Berkowitz [17–19] based on their molecular dynamics (MD) simulations concluded that

solvent polarization is essential. However, Monte Carlo (MC) simulations done by Jorgensen and Severance [15] without including solvent polarization also predicted surface localization of  $\text{Cl}^-$ . Dang and Garrett [13] using MD simulations obtained similar surface solvation structure, however, found that such results are sensitive to solute polarization and not to solvent polarization. Recent MC simulations of Asada, Nishimoto and Kitaura [8] indicated that even though surface states are lower in binding enthalpies, interior states are entropically more favorable and mostly populated at 300 K. These results [8] appear to be in conflict with other MD and MC simulations, however were supported by recent ab initio quantum mechanical calculations for a small number of equilibrium structures for clusters up to six waters [11]. However, for the  $\text{Cl}^-(\text{H}_2\text{O})_6$  cluster, there are more than 40 distinct local minima found and all are important for determining relative stability of interior and surface locations of the ion at finite temperatures [13]. To infer this structural information, one can calculate the average distance between the ion and the center of mass of the water cluster. In the present study, we found that the ion remains on the surface of the water cluster most of the time, thus supporting earlier findings by Dang and Garrett [13] and by Jorgensen and Severance [15]. In addition, since the Cl anion wavefunction is also available, we present a different analysis on this issue though indirect. This analysis based on the fact that the Cl anion wavefunction is polarized in the asymmetric field of point charges and thus leads to an induced dipole moment. If the ion is in the interior of the cluster, such induced dipole moment should be very small whereas it should be large and close to that of the  $\text{Cl}^--\text{H}_2\text{O}$  complex if the ion is on the surface. The average solvent induced dipole moment as a function of the cluster size is shown in Fig. 2. This result leads to the same conclusion as above.

#### 4.3. Accuracy of the perturbative MC approach

RMS errors in the solvent-solute electrostatic interaction energy for three given sizes of the perturbative interval (NPMOVE = 20, 100, and 1000) plotted versus the cluster size are shown in Fig. 3. We found that as the perturbative interval increases, the RMS errors also increases but remains less than 0.25

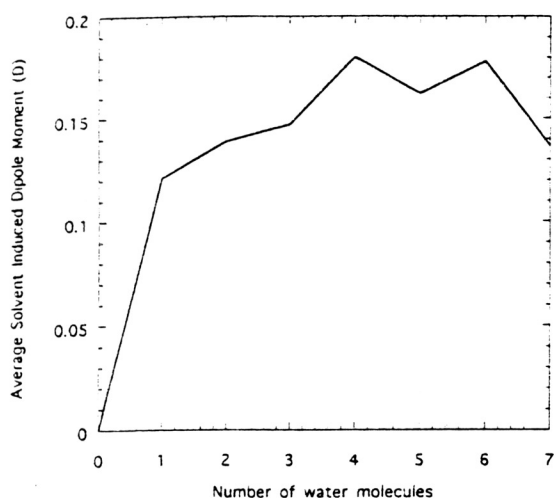


Fig. 2. Plot of the average solvent induced dipole moment (Debye) of the  $\text{Cl}^-$  anion as a function of the cluster size.

kcal/mol. This is consistent with our previous finding [23]. The new results here are on the cluster size effects. For the perturbative interval of 20, RMS errors are nearly independent of the cluster size. For larger intervals, there is a small size dependence. In particular, RMS errors increase with the cluster size. To study size effects, one wants this RMS error to be size-independent. In this case, the perturbative interval near 20 should be used. In our study all solvent

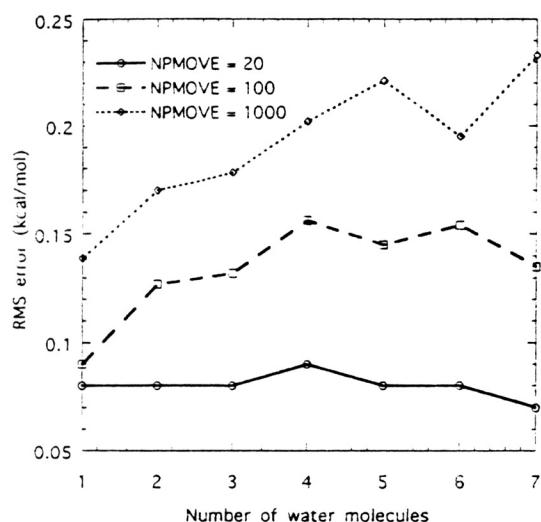


Fig. 3. Plot of the RMS errors in the solvent-solute electrostatic interaction for different perturbative intervals (NPMOVE) as functions of the cluster size.

moves were treated equal. However, for water molecules farther from the solute one expects smaller perturbative errors. In particular, typical solvent moves change solute-solvent interaction energy by an amount proportional to  $R^{-3}$ . Therefore, several perturbative MC moves of water molecules in the outer solvation shells would yield similar error to one MC move of water molecules in the first solvation shell. By using this fact, one can introduce a distance-dependent weighting function to effectively increase NPMOVE interval without loss of accuracy. More analysis on distance-dependence of perturbative errors are needed and will be discussed in our future study.

## 5. Conclusion

We have presented perturbative Monte Carlo simulations using a hybrid HF/MM potential for studying the energy-structure relationship for microsolvation of  $\text{Cl}^-$  anion in clusters of up to seven water molecules. In this case, the ion was treated quantum mechanically at the HF/6-31G\* level of theory while the TIP3P potential was used for interactions between waters. Analyzing the solvent induced dipole moment of the ion, we conclude that the  $\text{Cl}^-$  anion resides on the cluster surface most of the time. Furthermore, the error analysis shows no cluster-size dependence for perturbative intervals of about 20. Further analysis is still needed for designing a distance-dependent weighting function to optimize the perturbative interval for a given accuracy.

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