

Ab Initio Copper–Water Interaction Potential for the Simulation of Aqueous Solutions

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A new *ab initio* effective two-body potential that aims at mimicking the average copper–water interaction energy of the first solvation shell was developed. This new potential, together with the MCY water–water potential and a three-body ion–water–water induction potential, is tested in simulations of gas-phase clusters $[\text{Cu}^{2+}-(\text{H}_2\text{O})_{20}]$ and diluted solutions $[\text{Cu}^{2+}-(\text{H}_2\text{O})_{200}]$ at $T = 298$ K. The results of simulations with conventional *ab initio* pair potentials, with and without three-body induction corrections, are also presented. The different types of copper–water interaction potentials are evaluated comparatively and the efficiency of the newly proposed effective pair potential is discussed. © 1993 by John Wiley & Sons, Inc.

INTRODUCTION

Model potentials that accurately describe the intermolecular interactions are essential in computer simulations of condensed-phase matter.

In the past few years, several ion–water potential energy functions have been proposed, some derived from *ab initio* calculations and other strictly empirical. For the particular case of multivalent transition metal ions in water, it is now widely recognized that *ab initio* pair potentials are inadequate and should be supplemented by higher-order terms.^{1–3} However, there is, as yet, no general agreement on how to include the many-body corrections. As a matter of fact, different authors have suggested different methods of accounting for the many-body energy corrections. An open question is whether three-body nonadditive terms are sufficient for a good description of the solvation or four-body [e.g., ion– $(\text{H}_2\text{O})_3$ terms] and higher-order terms should also be considered. This latter option is usually avoided in practical simulations due to the extra costs involved. In what concerns three-body nonadditive terms, the most general method for their estimation is the *ab initio* calculation of a set of trimers, the three-body correction being calculated as the difference between the interaction energy of the trimer and the sum of the interaction energies of the dimers therein. The extent to which three-body terms may be estimated by an electrostatic calculation of the induction energy has been discussed.^{2a,4–8} One suggestion coming out of these works is that when the nonpairwise additive elec-

trostatic energy is explicitly calculated the remainder interaction energy is likely to be largely pairwise additive, especially in the intermediate to longer range. At shorter distances, the intrinsic nonadditivity of the chemical bond represented by the exchange terms in the usual interaction energy decomposition schemes or in the intermolecular perturbation theories will take a relevant role.

Another type of difficulty with conventional two-body potentials for metallic ion–water interactions comes from the well-known fact that the average ion–water binding energy is markedly lower than the corresponding interaction energy of the ion–water dimer.^{2,9,10a} When a conventional two-body potential is used, this has to be corrected for by the introduction of three-body and higher corrections. If this is not done, the attraction of the water molecules to the metallic ion will be unreasonably high. This unpleasant feature may be avoided if, instead of the conventional *ab initio* two-body potential, an effective potential is introduced that represents the average ion–water interaction energy in typical solvation conditions.

In this work, an effective two-body potential is introduced by fitting a model function to *ab initio* interaction energies of ion–water clusters, while the nonpairwise additive polarization energy is explicitly considered. A comparative study is presented of conventional and effective *ab initio* potentials. In the next section, the two-body potentials are outlined and the parametrization procedure described; the method of evaluation of the three-body induction terms is also presented. The effects of the counterpoise corrections (CPs) on the *ab initio* gas-phase surfaces used in the fitting procedures are also examined.

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The different two- and two-plus three-body model potentials are then tested in simulations of $\text{Cu}^{2+}-(\text{H}_2\text{O})_{20}$ clusters at $T = 298$ K. The most interesting model potentials are also tested in simulations of a diluted Cu^{2+} aqueous solution. Finally, the performance and validity of these models are discussed.

METAL ION-WATER POTENTIALS

Conventional Two-Body *Ab Initio* Potential

The $\text{Cu}^{2+}-\text{H}_2\text{O}$ pair-additive interaction energies are described by a potential function similar to that introduced by González-Lafont et al.¹¹:

$$\begin{aligned}
 V_2 = & c_1[2q_{\text{O}}/r_a + 2q_{\text{H}}(1/r_b + 1/r_c)] \\
 & + c_2[1/r_a^2 - 1/2(1/r_b^2 + 1/r_c^2)] \\
 & + c_3[1/r_a^3 - 1/2(1/r_b^3 + 1/r_c^3)] \\
 & + c_4/r_a^4 + c_5(1/r_b^4 + 1/r_c^4) \\
 & + c_6/r_a^5 + c_7(1/r_b^5 + 1/r_c^5) \\
 & - c_8/r_a^6 - c_9(1/r_b^6 + 1/r_c^6) \\
 & + c_{10}/r_a^{12} + c_{11}(1/r_b^{12} + 1/r_c^{12}) \quad (1)
 \end{aligned}$$

where $q_{\text{O}} (= -0.684)$ and $q_{\text{H}} (= +0.342)$ are atomic charges and r_a , r_b , and r_c are the Cu—O and Cu—H interatomic distances. The coefficients c_i ($i = 1, 2, \dots, 11$) were determined by fitting the two-body V_2 function to *ab initio* calculated interaction energies of the dimer $\text{Cu}^{2+}-\text{H}_2\text{O}$ for five planar and six nonplanar orientations of the water molecule around the Cu(II) ion.¹⁰ The internal geometric parameters of the H_2O molecule are held fixed at the experimental values,¹² i.e., $r_{\text{OH}} = 0.957$ Å and $\angle\text{HOH} = 104.5^\circ$. In the fitting, the same weighting method of ref. 10a was applied to all SCF calculated dimer

points with energies above ca. 394 kJ/mol (0.15 hartree).

The quantum calculations were carried out at the UHF level using the Gaussian 90 program.¹³ The *ab initio* effective core potentials (ECP) and double-zeta valence basis set developed by Hay et al.¹⁴ were used for the Cu(II) ion. For the oxygen and hydrogen atoms, the double-zeta all-electron basis set of Dunning et al.¹⁵ was used. From these calculations, a global energy minimum of -401.08 kJ/mol was found for the dipole-oriented C_{2v} configuration (the configuration with angle α equal 0° of Fig. 1 in ref. 10b) of the $\text{Cu}^{2+}-\text{H}_2\text{O}$ dimer at a Cu—O distance of 1.94 Å. These values are comparable to those reported in the literature,^{2b,3a} although they appear to be a bit high.

To assess the effects of the basis set superposition errors (BSEEs)¹⁶ on the present two-body interaction energies, SCF calculations of all dimer configurations were repeated with CP corrections. These corrections were determined with standard techniques¹⁷ by recomputing the monomer (Cu^{2+} , H_2O) energies with the basis set of the entire dimer at all its Cu—O distances.

The new $\text{Cu}^{2+}-\text{H}_2\text{O}$ energy points were then fitted to the same function of eq. (1), thus leading to a two-body CP-corrected potential ($V_2\text{CP}$). All the necessary parameters of the potential functions used here (V_2 and $V_2\text{CP}$) as well as the rms errors of the fits are collected in Table I.

As shown in Table I, the rms distances between the V_2 or $V_2\text{CP}$ potentials and their respective *ab initio* points are fairly small; they correspond to about 3% of the energy minima calculated for the $\text{Cu}^{2+}-\text{H}_2\text{O}$ dimer. By direct minimization on the fitted function, it was checked that no false minima exist that might have been introduced by the fitting process.

Table I. Final parameters for the ion-water, uncorrected and CP-corrected, two-body potential functions.

Parameter	Potential ^a			
	V_2	V_{eff}^b	$V_2\text{CP}$	$V_{\text{eff}}\text{CP}^b$
c_1	$+0.10950 \times 10^1$		$+0.11557 \times 10^1$	
c_2	-0.38764×10^1		-0.37995×10^1	
c_3	$+0.10568 \times 10^3$		$+0.10360 \times 10^3$	
c_4	-0.99579×10^3	-0.10049×10^4	-0.95013×10^3	-0.96488×10^3
c_5	-0.41881×10^1		-0.13858×10^2	
c_6	$+0.35082 \times 10^4$	$+0.36694 \times 10^4$	$+0.32749 \times 10^4$	$+0.34890 \times 10^4$
c_7	$+0.57407 \times 10^2$		$+0.11050 \times 10^3$	
c_8	$+0.41369 \times 10^4$	$+0.45033 \times 10^4$	$+0.37605 \times 10^4$	$+0.42548 \times 10^4$
c_9	$+0.11015 \times 10^3$		$+0.18970 \times 10^3$	
c_{10}	$+0.51389 \times 10^5$	$+0.51138 \times 10^5$	$+0.33453 \times 10^5$	$+0.51022 \times 10^5$
c_{11}	$+0.19452 \times 10^4$		$+0.29720 \times 10^4$	
n	237	20	233	20
σ	10.5	3.79	10.3	3.25

The number (n) of energy points used and the standard deviations (σ) of the fits are also shown.

^aEnergies in hartrees when bond distances are in bohrs.

^bThe parameters c_1 , c_2 , c_3 , c_5 , c_7 , c_9 , and c_{11} of these effective potentials are equal to the corresponding V_2 parameters.

Effective Two-Body *Ab Initio* Potential

It is well known that conventional *ab initio* pair potentials do generally overestimate the average interaction energy as determined on simulations of aqueous ionic solutions.^{2,4-8} On the other hand, they are likely to be accurate enough only for the description of the interactions at longer distances, outside the first hydration shell, but not within it. An *ab initio* effective pair potential is now derived to describe the metal-water interaction in the first hydration shell region.

The quantum interaction energy was calculated for a set of octahedral $\text{Cu}^{2+}-(\text{H}_2\text{O})_6$ clusters (with Th symmetry) for different metal-water distances, keeping the water molecules at fixed geometries.¹² The effective copper-water interaction energies are calculated from these interaction energies after deduction of the relevant water-water interactions calculated at the same level. All the quantum energies were evaluated by the same UHF method with ECP and basis sets taken again from refs. 14 and 15.

The quantum copper-water interaction energy values were then fitted to the same analytic function as in eq. (1) above. Parameters $c_1, c_2, c_3, c_5, c_7, c_9,$ and c_{11} are kept fixed at the same values (see Table I) as they act upon metal-hydrogen distances and the water molecules are kept at the same orientation in all configurations considered; parameters $c_4, c_6, c_8,$ and c_{10} are adjusted to best fit the new data associated to radial symmetric expansions of the first shell.

The BSSE were again investigated for all *ab initio*-computed interaction energies. To illustrate the effects of the CP corrections, the final uncorrected and CP-corrected full binding energies of the Cu^{2+} clusters considered for the fits are plotted in Figure 1 for several Cu-O distances. To evaluate the effect of the BSSEs on the two-body interactions, the uncorrected and CP-corrected binding energies of the above clusters, at this level of approximation, are also plotted in Figure 1.

The BSSEs seem to be slightly more important for the $n = 6$ full-body binding energies (2-8%) than for the corresponding two-body energies (2-5%). From the results of Figure 1, it can be noted that the uncorrected calculations overestimate the values of the interaction energies, although at large Cu-O distances ($r_{\text{CuO}} \geq 3.0 \text{ \AA}$) the two sets of energies differ little. It is also interesting to note that the full-body binding energies are practically equal to the two-body binding energies for large Cu-O distances, i.e., distances corresponding to regions outside the first shell, and this corroborates once more the idea that pair potentials may be used at least to describe these regions. However, in the region of the first solvation shell the overestimation by the two-body potential is ca. 30%.

To obtain a two-body CP-corrected effective po-

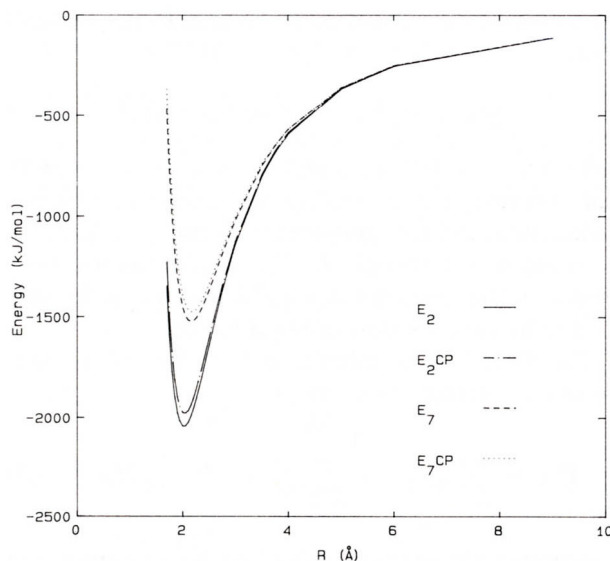


Figure 1. Total interaction energy for the $\text{Cu}^{2+}-(\text{H}_2\text{O})_6$ cluster as a function of the Cu-O distance. The full cluster-uncorrected (E_7) and CP-corrected ($E_{7\text{CP}}$) and the two-body uncorrected (E_2) and CP-corrected ($E_{2\text{CP}}$) *ab initio* binding energies are shown.

tential (V_{effCP}), the fitting procedure was repeated with the new CP-corrected energies. The optimized values of the parameters of the two effective potentials (V_{eff} and V_{effCP}) are listed in Table I, together with the standard mean square errors of the fits. Again, it was checked that no artificial minima were introduced by the fitting procedure.

Three-Body Induction Terms

Water polarization^{4-8,18} is known to have a marked influence on the structure of liquid phases (e.g., the dipole moment of water in gas phase, $\mu = 1.9D$, is clearly different from that of bulk water, $\mu \geq 2.2D$). It is thus to be expected that explicit consideration of the polarization cannot be avoided, especially in the simulation of the neighborhood of an ion. It should be noticed that many-body effects and, particularly, polarization effects are included, in average, in the effective potential above. The explicit treatment of polarization proposed here allows a finer discrimination among different conformations adopted by the water molecules around the metal ion. From preliminary quantum studies on $\text{Cu}^{2+}-(\text{H}_2\text{O})_n$ ($n = 6$ and 8) clusters,^{10a} it appears that the most important nonpairwise-additive energy comes from three-body terms, and so the only correction discussed here is a three-body nonadditive polarization energy.

Following the work of Clementi and coworkers,⁴ the three-body nonadditive energy is approximated by an induction energy based upon a classic water-bond polarizability model.¹⁹ The water molecules are considered rigid, but polarizable, in such a way that

bond dipoles are induced according to the expression:

$$\underline{\mu}_{bK} = \alpha_{\perp} \underline{E}_{bK} + \delta \underline{u}_{bK} (\underline{u}_{bK} \cdot \underline{E}_{bK}) \quad (2)$$

where α_{\perp} ($= 3.91$ a.u.) and δ ($= \alpha_{\parallel} - \alpha_{\perp} = 1.42$ a.u.) represent, respectively, the perpendicular polarizability and the anisotropy of the polarizability of bond b in molecule K . \underline{E}_{bK} is the electric field vector at the midpoint of bond b and \underline{u}_{bK} is the unit vector in the direction of bond b .

The field \underline{E}_{bK} is calculated in terms of the surrounding permanent charges:

$$\underline{E}_{bK} = \sum_{J \neq K} \underline{E}_{bK,J} = \sum_{J \neq K} \sum_{j \in J} q_j \cdot \underline{R}_{bK,jJ} / R_{bK,jJ}^3 \quad (3)$$

where q_j is the point charge of center j on molecule J ($q(\text{Cu}^{2+}) = +2.0$ a.u., $q(\text{O}) = -0.684$ a.u. and $q(\text{H}) = +0.342$ a.u.), $\underline{R}_{bK,jJ}$ is the distance vector pointing from the center of J to the midpoint of bond b of molecule K . Note that the index J refers to the copper ion or to another water molecule.

It should be noticed⁵ that the electric field \underline{E}_{bK} above is that produced by permanent charges alone and that the set of charges used for water have an associated dipole moment similar to the experimental value in the gas phase.¹⁸ This means that the polarization on each water molecule is assumed to be due to the surrounding point charge distribution and, at this stage, to avoid further expensive calculations the polarization caused by the induced dipoles on the other molecules is disregarded.

The nonadditive induction energy is then given by

$$U_{\text{ind}} = -1/2 \sum_{b,K} \underline{\mu}_{bK} \cdot \underline{E}_{bK} \quad (4)$$

Substituting eqs. (2) and (3) in the above equation, two types of triple sums that depend upon products $q_j q_i$ can be found:

- The first is associated with ion–water–water terms as j and i may either be the Cu(II) ion or an atom belonging to a water molecule different from K .
- The second is associated with water–water–water terms as j and i are atoms belonging to water molecules J and I , both different from molecule K .

The first of these sums can be thought of as a three-body correction for the Cu^{2+} – H_2O pair potential and the latter one as a three-body correction for the H_2O – H_2O pair potential.

It should be noted that the present model does not account for the short-range three-body exchange corrections that are related to nonclassic overlap effects.^{2a,4a,8} Normally, these corrections have been

introduced^{4a,8} by three-body terms fitted to the non-additive interaction energies of ion–(H_2O)₂ trimers. Apart from the needed big amount of expensive quantum calculations on Cu^{2+} –(H_2O)₂ trimers, the nonadditive fitting process can also be extremely difficult. However, an average of the many-body exchange effects is already implicit in the newly proposed effective potential. This, of course, is not true for the simulations that use the conventional two-body V_2 potential, even when this is supplemented by the above three-body polarization terms [eq. (4)].

It should be made clear that to apply expression (4) on simulations with the effective potential the effective copper–water interaction to be used in the fitting process has to be recalculated. This interaction is now determined by extracting the water–water interactions and the three-body induction terms from the interaction energies of the Cu^{2+} –(H_2O)₆ clusters considered in the section on two-body *ab initio* potential. Two sets of copper–water effective interactions were computed: on the first, only the ion–water–water terms were removed, and on the second all the three-body induction was removed. This will also allow us to examine which of the polarization terms, three-body ion–(H_2O)₂ or (H_2O)₃, are more important to adequately reproduce the ionic solution.

The two sets of copper–water energies were again fitted with the same V_2 parameters fixed (as described earlier) to obtain the effective pair potential V_{effI} , to be used when this two-body effective energy is supplemented by the ion–(H_2O)₂ polarization terms, and the effective pair potential V_{effT} , to be used when this two-body effective energy is supplemented by the ion–(H_2O)₂ and (H_2O)₃ polarization terms. Table II shows the fitted parameters for these two functions.

A similar procedure was used to determine CP-corrected pair potentials V_{effI} and V_{effT} , but they are not shown here as the results obtained in the simulations were essentially unchanged.

Table II. Optimized parameters for the ion–water two-body effective potentials to be used in the simulations with induction.

Parameter	Potential ^a	
	V_{effI}^b	V_{effT}^b
c_4	-0.10027×10^4	-0.10074×10^4
c_6	$+0.36228 \times 10^4$	$+0.36603 \times 10^4$
c_8	$+0.44304 \times 10^4$	$+0.44962 \times 10^4$
c_{10}	$+0.51189 \times 10^5$	$+0.51150 \times 10^5$

V_{effI} is the effective potential calculated from the Cu^{2+} –(H_2O)₆ cluster interaction energy deflated by water–water interactions and copper–water–water induction energies. V_{effT} is similarly calculated but the water–water–water induction energies are also considered.

^aEnergies in hartrees when bond distances are in bohrs.

^bThe standard deviations of the fits are 3.96 and 3.68 kJ/mol, respectively.

RESULTS AND DISCUSSION

The different potentials described in the previous section are tested, first by the study of the energetic and structural properties of a $\text{Cu}^{2+}-(\text{H}_2\text{O})_{20}$ cluster in Monte Carlo (MC) simulations at 298 K. Then, the same properties are analyzed for a diluted aqueous solution of Cu^{2+} by MC simulations of a $\text{Cu}^{2+}-(\text{H}_2\text{O})_{200}$ complex.

All MC simulations were carried out with a (NVT) ensemble using the Metropolis algorithm.²⁰ Cubic boundary conditions with a minimum image cutoff²¹ have been used throughout.

In the cluster simulations, 2×10^6 steps were carried out; the first half of the run was considered to be for equilibration and all statistical averages are based upon the last half run. For the diluted solution, the $\text{Cu}^{2+}-(\text{H}_2\text{O})_{200}$ complex was confined to a cubic box of length 18.1 Å and a spherical cutoff at 9.1 Å for the polarization terms was introduced. In this case, especially in the simulations with many-body potentials, an equilibration of up to 2×10^6 steps was done prior to the statistical production period. This equilibration has been confirmed by checking of the standard deviations of the properties along the run and by some tests with longer runs or different starting configurations.

In all simulations, the MCY potential²² was used for the water–water two-body interactions. This potential was chosen to have only *ab initio* type potentials in the simulations, i.e., potentials entirely derived from *ab initio* computations. On the other hand, the MCY potential has already proved to give a reasonable description of water in condensed state (4).

Ion–Water Cluster Simulations

As a starting point, the results of $\text{Cu}^{2+}-(\text{H}_2\text{O})_{20}$ simulations using the conventional two-body $\text{Cu}^{2+}-\text{H}_2\text{O}$ potential (V_2) are compared with those that use the new effective two-body $\text{Cu}^{2+}-\text{H}_2\text{O}$ potential (V_{eff}). At the same time, the importance of the CP correction is analyzed by its effect on the simulations. To this end, simulations are run with the conventional and effective *ab initio* potentials modified to account for the CP correction. The end results of the four simulations (applying V_2 , V_{eff} , $V_2\text{CP}$, and $V_{\text{eff}}\text{CP}$ for the copper–water pair interactions) are summarized in Table III.

Notice that the coordination numbers shown in Table III were determined not only by integrating the radial Cu–O distribution functions but also by analyzing their distribution along the simulations. Thus, when more than one coordination number is depicted for a particular simulation it means that more than one structure was found on the analysis of the distribution of coordination numbers. Table III

Table III. Simulation results for the $\text{Cu}^{2+}-(\text{H}_2\text{O})_{20}$ system at 298 K using different two-body ion–water potentials.

Potential	Energies ^a (kJ/mol)	Oxygen ^b position (Å)	Hydrogen ^b position (Å)	Hydration ^c number
V_2	–165.40	2.15	2.75	8–9
	26.78	(1.95)		
	–192.18			
$V_2\text{CP}$	–162.13	2.15	2.70	8–9
	26.97	(1.96)		
	–189.10			
V_{eff}	–133.42	2.25	2.90	8
	16.42	(2.09)		
	–149.84			
$V_{\text{eff}}\text{CP}$	–131.54	2.25	2.90	8
	17.95	(2.09)		
	–149.49			

^aEnergies per water molecule for the total, water–water, and ion–water interactions.

^bPosition of the maxima on the first peaks of the radial ion–oxygen and ion–hydrogen distribution functions. The global r_{CuO} minima of the ion–water two-body potentials are also given in parentheses.

^cCalculated by integrating the radial ion–oxygen distribution function up to its first peak minimum.

shows that, although the simulation with the V_{eff} potential gives lower (by ca. 25%) average energies for all two-body interactions, both potentials (V_{eff} and V_2) lead to almost similar structural features for the first hydration shell of the Cu(II) ion. Therefore, the V_{eff} potential, although much weaker than V_2 , it is still not able to reproduce the Cu^{2+} experimental coordination number.^{23–25} As expected, the Cu–O peaks of both simulations are centered at larger distances than the corresponding minima of the *ab initio* $\text{Cu}^{2+}-\text{H}_2\text{O}$ potentials. The minimum of the V_{eff} two-body potential is further out (2.09 Å) than the one of the V_2 potential (1.95 Å), and thus its simulation presents a larger Cu–O radius for the first hydration shell. It is worth noting here that the basis set used in this study may be responsible for the larger Cu–O distances of the global SCF minima of the Cu^{2+} –water dimer or hexamer, taking into account other *ab initio* studies.^{2b,3a} This is expected to affect the results of the simulations with the V_2 or the V_{eff} potential, but only in what concerns the positions of the maxima of the radial distribution functions (RDFs) peaks of the hydration shells of the Cu(II) ion. In fact, judging from our previous results^{10a} and other theoretical work^{2,3} it is unlikely that the use of another basis set will give the correct coordination number for Cu^{2+} in simulations with a simple two-body potential. It should also be remarked that, with the present ECP Cu^{2+} basis set, special care had to be taken in the quantum calculations (especially for certain $\text{Cu}^{2+}-\text{H}_2\text{O}$ dimer configurations) to avoid states different from the 2-D ground state (e.g., $\text{Cu}^+-\text{H}_2\text{O}^+$ states). Essentially,

the same charge-transfer problems have been reported on SCF calculations of copper–water dimers or trimers for a similar basis set.^{3a}

From Table III, it can also be seen that the results of the simulations are insensitive to the CP corrections. The only result to keep in mind is that the CP-uncorrected simulations are likely to overestimate the total average binding energy of the cluster (by up to 2%; see Table II), while the structural features of the hydration shells of the Cu(II) ion in water are strictly unchanged. To estimate how the three-body induction forces may change the above two-body results, MC simulations of the $\text{Cu}^{2+}-(\text{H}_2\text{O})_{20}$ cluster have been repeated including the three-body potentials described in the section on three-body induction terms. As said above, the effects of the CP corrections were again analyzed on those simulations but, as no particular differences came out of them, the results are not presented here.

In Table IV, the results obtained by applying the V_2 two-body potential with three-body induction terms of the type ion–water–water ($V_2 + I$) or ion–water–water plus water–water–water terms ($V_2 + T$) are compared with those with the V_{eff} instead of the V_2 potential ($V_{\text{effI}} + I$ and $V_{\text{effT}} + T$). These results clearly indicate that three-body polarization forces are important and can lower the coordination number of the Cu(II) ion. A similar conclusion has been reached by Rode et al.^{3a} on their simulations of the Cu(II) ion using a corrected copper–water pair potential, as discussed below.

Table IV. Effect of the three-body induction terms on the simulated first coordination shell of the $\text{Cu}^{2+}-(\text{H}_2\text{O})_{20}$ system at 298 K.

Potential ^a	Energies ^b (kJ/mol)	Oxygen ^c position (Å)	Hydrogen ^c position (Å)	Hydration ^d number
$V_2 + I$	-140.63	2.10	2.75	6
	-151.60	(1.95)		
	10.97			
$V_2 + T$	-136.72	2.15	2.75	6–7
	-156.59	(1.95)		
	16.34			
$V_{\text{effI}} + I$	-125.47	2.10	2.75	6
	-136.35	(1.94)		
	10.88			
$V_{\text{effT}} + T$	-124.13	2.15	2.75	6
	-136.76	(1.96)		
	12.63			

^aSee the section on metal ion–water potentials and Tables I and II for details on the potentials. The consideration of the ion–water–water induction terms is indicated by I, while the consideration of these and the water–water–water induction terms is indicated by T.

^bEnergy per water molecule for the total interactions, total two-body interactions, and total three-body interactions.

^{c,d}See footnotes b and c, respectively, in Table III.

By comparing the energy results of Tables III and IV, it can be noticed that the inclusion of the three-body terms produces a decrease in the total energy due not only to the repulsive total three-body contributions but also to the observed decrease of the total two-body energy. This may be explained by the less favorable situation, in terms of two-body energies, of an octahedral cluster when compared with a cubic hydrated cluster (see Figs. 3 and 4 below). It can also be seen that, as expected,^{2b,4a,10a} the most important three-body forces are the ones of the type ion–water–water. In particular, the inclusion of the three-body $(\text{H}_2\text{O})_3$ terms leaves the coordination number of the Cu(II) ion practically unchanged, although the ion–oxygen RDF peak positions are displaced to larger Cu–O distances. A more detailed insight into the magnitude of the three-body forces can be attained by decomposing the total three-body energies of Table IV into their components. This leads to positive values (+17.6 kJ/mol for $V_2 + T$ and 12.2 kJ/mol for $V_{\text{effT}} + T$) for the contributions of the $\text{Cu}^{2+}-(\text{H}_2\text{O})_2$ terms and negative values (-1.2 kJ/mol for $V_2 + T$ and -0.3 kJ/mol for $V_{\text{effT}} + T$) for the contributions of the $(\text{H}_2\text{O})_3$ terms. These values certainly show how small are the contributions of the $(\text{H}_2\text{O})_3$ induction forces in relation to those of $\text{Cu}^{2+}-(\text{H}_2\text{O})_2$. A similar conclusion was achieved in previous quantum studies of Cu^{2+} -hydrated clusters.^{2b,10a}

It is important to underline here that a careful analysis of the distribution of coordination numbers for the first Cu^{2+} shell achieved in the $V_2 + T$ simulation did not show exclusivity of the number six, as structures with seven water molecules were also found. On the other hand, a similar analysis performed on the results of the $V_{\text{effT}} + T$ simulation always gives six as the coordination number. Thus, it seems that many-body exchange nonadditive terms are also essential to correctly describe the coordination number of this ion and they appear to be conveniently averaged in the effective potential as used here. In fact, other simulation studies on ion hydration^{4a,8} showed that at least the ion–water–water exchange terms have to be included to obtain energy results in agreement with experimental measurements.

Aqueous Ionic Simulations

As the results of the last section show that the hydration structure around the Cu(II) ion is properly described by simulations that only include the ion– $(\text{H}_2\text{O})_2$ polarization terms, the $(\text{H}_2\text{O})_3$ polarization terms were neglected on the simulations of the Cu^{2+} -diluted solution to avoid expensive calculations. Four simulations of a $\text{Cu}^{2+}-(\text{H}_2\text{O})_{200}$ complex were done, two with only two-body potentials (V_2 and V_{eff}) and the other two with two- plus three-

body ion—(H₂O)₂ polarization potentials ($V_2 + I$ and $V_{\text{effI}} + I$).

In Table V, the main results obtained here are confronted with a selection of experimental and theoretical results. There is a general agreement between our results and the other theoretical results, although our Cu—O distances seem to be a bit too large. In fact, in what concerns the Cu—O RDF peak distances the MC theoretical two-body plus neighbor ligand three-body correction (NL) results of Rode et al.^{3a} agree better with those observed experimentally.^{24,25} As these authors used the same MCY water-water potential, this may arise from our two-body potentials, which have larger Cu—O distances for the global Cu²⁺—H₂O dimer minimum. On the other hand, the corrected pair potential of Rode et al.^{3a} has a high energy barrier on regions where the water molecules are at distances from the central ion of ca. 2–2.2 Å as this is the chosen region to consider the NL corrections, and this can also explain their somewhat shorter Cu—O RDF distances.

It should be emphasized that although our results and those of Rode et al.^{3a} in Table V give a coordination number of six for the solvated Cu(II) ion none of them leads to the exact structure observed experimentally, a distorted octahedral arrangement for the six water molecules. This means that explicit three-body interactions are strictly needed to prevent overestimations of the coordination number of the Cu(II) ion but are not enough to describe other effects such as the Jahn–Teller effect.

In Table V, the hydration enthalpy of the Cu(II) ion (ΔH_{hydr}), determined by taking the energy difference between the aqueous ionic simulation and a liquid water simulation at the same conditions, is presented. In all cases, the agreement with experimental results²³ becomes better as many-body potentials are incorporated, but it is still overestimated. It should be noticed that, although high, the hydration values of the V_{eff} and $V_{\text{effI}} + I$ simulations are closer to the experimental values than those found on the V_2 and $V_2 + I$ simulations. As the energetic trends are better represented by the effective potentials, and the structural results are similar, these types of potentials should thus be preferred. Notice, however, that the experimental results refer to a distorted octahedral structure, which is not the one obtained here. This may explain the discrepancy found for the hydration energy results. Nevertheless, to get more accurate results for the Cu(II) hydration enthalpy simulations carried out in the NPT ensemble should be performed.

The radial distribution functions obtained on the three-body $V_2 + I$ and $V_{\text{effI}} + I$ simulations are similar. The Cu—O and Cu—H RDFs, together with their running coordination number, $N(R)$, for the $V_{\text{effI}} + I$ simulation are shown in Figure 2. From this figure, one can see that both RDF first peaks are well defined and the Cu—H peak is moved outward with respect to the Cu—O peak.

This shows that the oxygens on the first hydration shell are well oriented toward the central Cu(II) ion

Table V. Structural and thermodynamic results of copper (II) in water at 298 K calculated by the MC simulation of Cu²⁺—(H₂O)₂₀₀.

Method	Energies ^a (kJ/mol)	ΔH_{hydr}^b (kJ/mol)	Oxygen ^c position (Å)	Hydrogen ^c position (Å)	Hydration ^d number
Theor. MC: This work					
V_2	−56.732	−3755.0	2.10	2.75	8–9
V_{eff}	−53.298	−3068.0	2.20	2.85	8
$V_2 + I$	−53.630 (1.376)	−3133.0	2.05	2.70	6
$V_{\text{effI}} + I$	−52.976 (1.358)	−3004.0	2.10	2.70	6
Theor. MC: Rode et al. ^c					
2-body	—	—	2.10	2.80	8
2-body + NL	—	—	1.95	2.65	6
Exp.					
X-ray ^g	—	−2100.0 ± 20 ^f	(1.93–2.00) _{eq} ^h (2.28–2.60) _{ax}	—	4 or 4 + 2
Neutron diffraction ⁱ	—	—	(1.96–1.97) _{eq} (2.60) _{ax}	4 or 4 + 2	—

^aEnergy per water molecule for the total two-body interactions. In the case of the simulations where the induction potential is included ($V_2 + I$ and $V_{\text{effI}} + I$), the values for the total three-body interactions are also given in parentheses.

^bComputed as $\Delta H_{\text{hydr}} = (\Delta U[\text{Cu}^{2+} - (\text{H}_2\text{O})_{200}]) - (\Delta U[(\text{H}_2\text{O})_{200}])$.

^{c,d}See footnotes b and c, respectively, in Table III.

^eResults of Rode et al.^{3a} for Cu²⁺—(H₂O)₂₀₀, using an ion–water two-body *ab initio* potential or an ion–water two-body *ab initio* potential with neighbor ligand corrections.

^fRef. 23.

^gRef. 24.

^hEquatorial and axial r_{CuO} distances.

ⁱRef. 25.

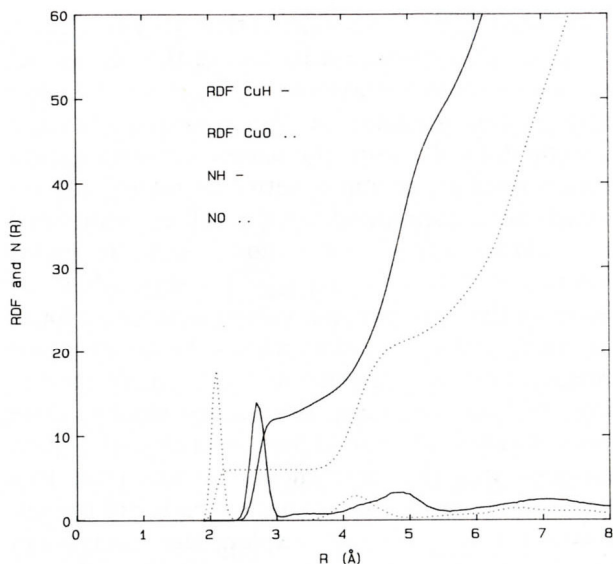


Figure 2. Ion-hydrogen (RDF CuH) and ion-oxygen (RDF CuO) radial distribution functions and their respective running coordination numbers (NH and NO) for the simulation of a diluted Cu^{2+} solution at 298 K using the $V_{\text{eff}} + I$ potential.

and the hydrogens point away from it. The fact that the Cu—O RDF comes down to zero after its first peak and stays vanishingly small for more than 1 Å suggests that the first solvation shell is stable and the water exchange with the second shell will be small indeed. It is also interesting to note that the integration of the first peak of the Cu—H RDF function gave a value of ca. 12, that is, the hydrogens corresponding to the six oxygens appearing in the first Cu^{2+} shell. The Cu—O and Cu—H peaks emerging on the radial distribution functions at $R > 3.5$ Å may be associated with a second hydration shell that seems to be much less rigid than the first.

To further clarify the role of the most important three-body induction forces, the ion— $(\text{H}_2\text{O})_2$ forces, the total interaction energies for typical Cu^{2+} clusters are plotted as a function of the Cu—O distance in Figures 3 and 4. These clusters are the Cu^{2+} — $(\text{H}_2\text{O})_6$ regular octahedral cluster (T_h symmetry) obtained on the many-body simulations and the Cu^{2+} — $(\text{H}_2\text{O})_8$ distorted cubic cluster (S_8 symmetry) obtained on the two-body simulations. To directly compare the two clusters, the energy of the Cu^{2+} — $(\text{H}_2\text{O})_6$ cluster was supplemented by the total interaction energy of two water molecules on the region of the second shell ($3.5 \text{ \AA} \leq R \leq 5 \text{ \AA}$). These interaction energies were extracted from the results of the simulations with the two-body and two- plus three-body potentials, namely, V_2 and $V_2 + I$ (Fig. 3) and V_{eff} and $V_{\text{eff}} + I$ (Fig. 4). In both figures, one can see that the three-body forces are much more important in the case of the cubic cluster than they are for the octahedral cluster. On the other hand, the equilibrium Cu—O distances predicted by the pair potentials are decreased when the three-body

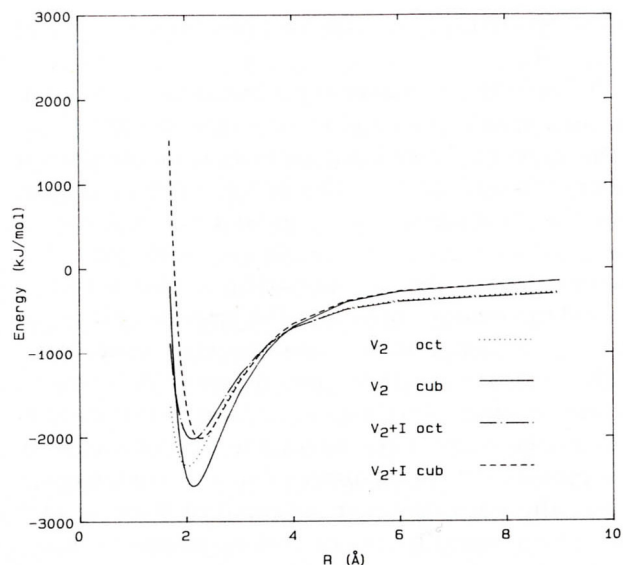


Figure 3. Total interaction energies for the Cu^{2+} — $(\text{H}_2\text{O})_6$ (**oct**) and Cu^{2+} — $(\text{H}_2\text{O})_8$ (**cub**) clusters as a function of their Cu—O distance. The interaction energies are computed using the V_2 two-body potential or the two- plus three-body $V_2 + I$ potential for the copper-water interactions, together with the MCY two-body potential for the water-water interactions.

forces are taken into account. It is also interesting to notice that the effect of the three-body corrections are less pronounced for the V_{eff} results (especially in the case of the octahedral cluster) than those of the V_2 potential. This may be explained by considering the magnitude of the three-body induction

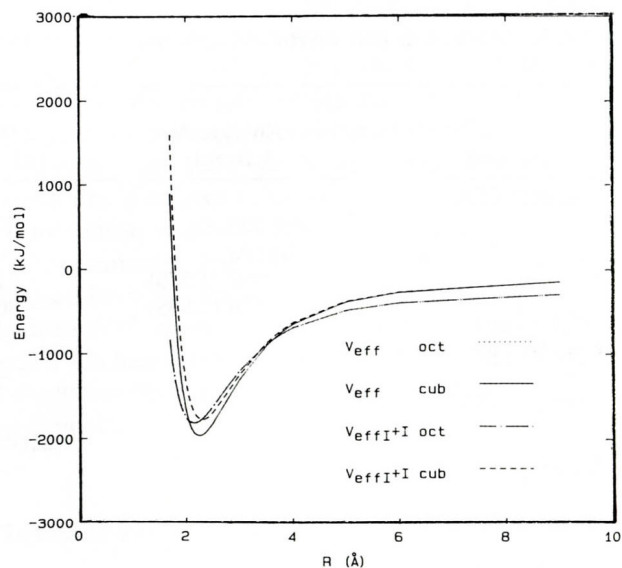


Figure 4. Total interaction energies for the Cu^{2+} — $(\text{H}_2\text{O})_6$ (**oct**) and Cu^{2+} — $(\text{H}_2\text{O})_8$ (**cub**) clusters as a function of their Cu—O distance. The interaction energies are computed using the V_{eff} two-body potential or the two- plus three-body $V_{\text{eff}} + I$ potential for the copper-water interactions, together with the MCY two-body potential for the water-water interactions. Notice that the lines of the V_{eff} and the $V_{\text{eff}} + I$ potentials for the octahedral (**oct**) cluster are coincident.

energies with respect to the two-body energies and by the fact that the V_{eff} pair potential does include some average of the many-body terms.

CONCLUSIONS

In this article, a study is presented of the structural and energetic features of ion–water clusters and diluted aqueous solutions of the Cu(II) ion using MC simulations with several types of interaction potentials. The ion–water cluster simulations revealed some interesting characteristics in agreement with earlier *ab initio* results^{2b,10a} and other MC simulations.^{3a} From the $\text{Cu}^{2+}-(\text{H}_2\text{O})^{20}$ cluster simulation results reported in the last section, the following may be concluded.

1. *Ab initio* conventional or effective $\text{Cu}^{2+}-\text{H}_2\text{O}$ pair potentials are inadequate to describe the interactions of copper ion in water. When the conventional two-body potentials are used in the simulation of ion–water clusters, the equilibrium metal ion–water distance increases due to the repulsion among the water molecules of the first shell.
The effective two-body potential proposed here is constructed in such a way that the gaseous $\text{Cu}^{2+}-(\text{H}_2\text{O})_n$, $n = 6, 8$, clusters do have the correct (quantum calculated) metal–water distance. However, when the same effective potential is used for the simulation of diluted solutions the interactions between the clusters and the external water molecules leads to the expansion of the Cu–O distance in the first solvation shell, which, in turn, may lead to the incorrect prediction of the coordination number 8.
2. The BSSE on the *ab initio* energy points used on the fits of the potentials do have some importance (up to ca. 10%) but do not appear to have relevant effects upon the results of the subsequent simulations.
3. The inclusion of the three-body nonadditive effects will tend to lower the coordination number of the Cu(II) ion in MC simulations. In what concerns the induction nonadditive effects, the main contributions come from the ion–water–water terms as the water–water–water terms are much smaller.
4. If rigorous energetic results are desired, then some sort of repulsive exchange nonadditivity should also be included on the simulations.

Interesting observations can also be extracted from the Cu(II) solution simulations. With the two-body and two- plus three-body potentials used (V_2 , $V_2 + I$, V_{eff} and $V_{\text{eff}} + I$; see above), neither the exact coordination structure of the Cu(II) ion in solution (distorted octahedron) nor the exact radius of its first shell (see Table V) are found. To get a distorted

structure on the Cu(II) solution simulations, some information on the “Mexican hat” type of potential surface²⁶ is probably needed in the potential model used.

However, an energetic improvement is obtained on the effective $V_{\text{eff}} + I$ simulations when compared to the results obtained on the conventional $V_2 + I$ simulations. Thus, *ab initio* effective potentials of the type proposed here seem to be more adequate to model the copper–water interactions in solution.

Rode et al.^{3a} obtained structural results of the same level of accuracy as ours with their technique of neighbor ligand corrections. In this method, for each water molecule within a sphere of a given cutoff radius (chosen at 4 Å) neighbor ligand water molecules are searched in the region $2.0 \text{ \AA} \leq R_{\text{CuO}} \leq 2.2 \text{ \AA}$ and a correction is then applied that is made to depend just upon the O–O distance and is modeled by fitting to SCF calculations with the first water molecule fixed at $R_{\text{CuO}} = 2.0 \text{ \AA}$. The physical rationalization of this technique and of the particular positions chosen for the water ligands deserves further exploration. One consequence is that for the typical octahedral and cubic conformations the estimated interaction energy has an unphysical high potential barrier for expansions through the 2.0–2.2 Å radial region. This is likely to make this method inappropriate for molecular dynamics simulations.

Finally, it should be mentioned that the effective pair potential proposed here might be improved by increasing the number of configurations used in the fit with nonoctahedral ones, for example, those of typical cubic Cu^{2+} clusters.

The conventional two- plus three-body induction potential ($V_2 + I$) might be improved by the consideration of nonadditive three-body exchange effects, but this is outside the goals of the present article.

Ewald sums²¹ to describe the copper–water interactions that are still strong at large distances from the central ion are likely to improve the results presented here.

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