

Intermolecular Potential Function for Copper(II)-Water Based on *ab initio* Calculations

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An analytical pair potential function for the system Cu(II)-water has been derived by means of *ab initio* calculation of the corresponding energy surface, using double zeta + polarization basis sets and effective core potentials. Tests on the function show that it should be reliable for use in Monte Carlo or molecular dynamics simulations.

Introduction

In recent years, numerous computer simulations have been performed on aqueous solutions of monovalent and divalent metal ions. Monte Carlo (MC) and/or Molecular Dynamics (MD) simulations [1] have been reported for example on LiCl [2], NaCl [3], BeCl₂ [4], MgCl₂ [5], CaCl₂ [6] and SrCl₂ [7] solutions dealing with the structure of the hydration shell of the ions and spectroscopic data for the ion influence on the solvent. For a comparison with the divalent metal ions, and to evaluate preferential solvation in aqueous solution in analogy to studies on Li⁺–NH₃–H₂O [8] and Na⁺–NH₃–H₂O [9], it is of interest to study also the behaviour of Cu²⁺ in aqueous solution. Cu²⁺ is of particular interest among first series transition metal ions because of the d⁹ configuration and due to its biological importance. In this work, the complete intermolecular potential of Cu²⁺/water interaction is investigated in order to obtain an analytical pair potential function which can serve for MC/MD simulations. In some previous calculations on Cu²⁺/water, Veillard et al. [10] have reported the hydration number and the hydration energy of Cu²⁺, evaluated by small basis set *ab initio* SCF calculations. Sano and Yamatera [11] discussed the optimized geometries and the electron density changes of hexaquo ions of various divalent metals, including Cu²⁺. The Jahn-Teller effect in the hydrated copper(II) ion was studied by White et al. [12], but no complete energy surface has been reported so far.

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Method of Calculation

Copper(II) ion was placed at numerous positions around the water molecule, varying geometrical parameters $0^\circ \leq \Theta \leq 180^\circ$ and $0^\circ \leq \varphi \leq 135^\circ$ (Figure 1). First, five types of geometrical configurations, all having the four atoms of Cu²⁺–H₂O in one plane, and then six nonplanar configurations were calculated. For each configuration, the copper-oxygen internuclear distance was varied from 1.2 Å to 8.0 Å. The water molecule's geometry was kept fixed during all calculations at the experimental values [13] (O–H = 0.9572 Å and H–O–H = 104.52°). The calculations were performed based on the LCAO-MO-UHF-SCF method, with double zeta basis set including

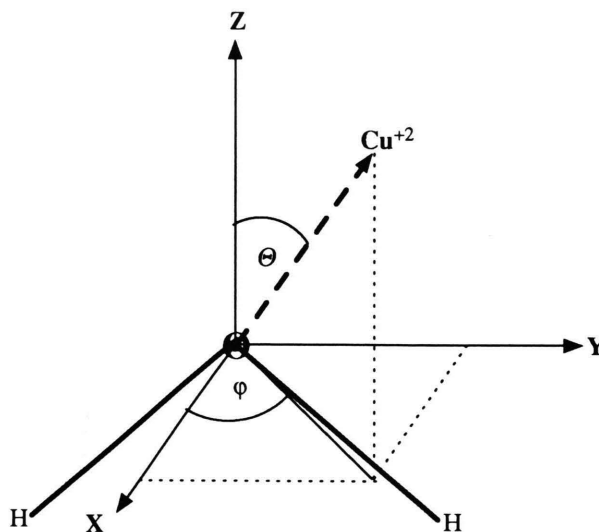


Fig. 1. Definition of geometric variables for copper(II)-water orientations. H₂O molecule in yz plane.

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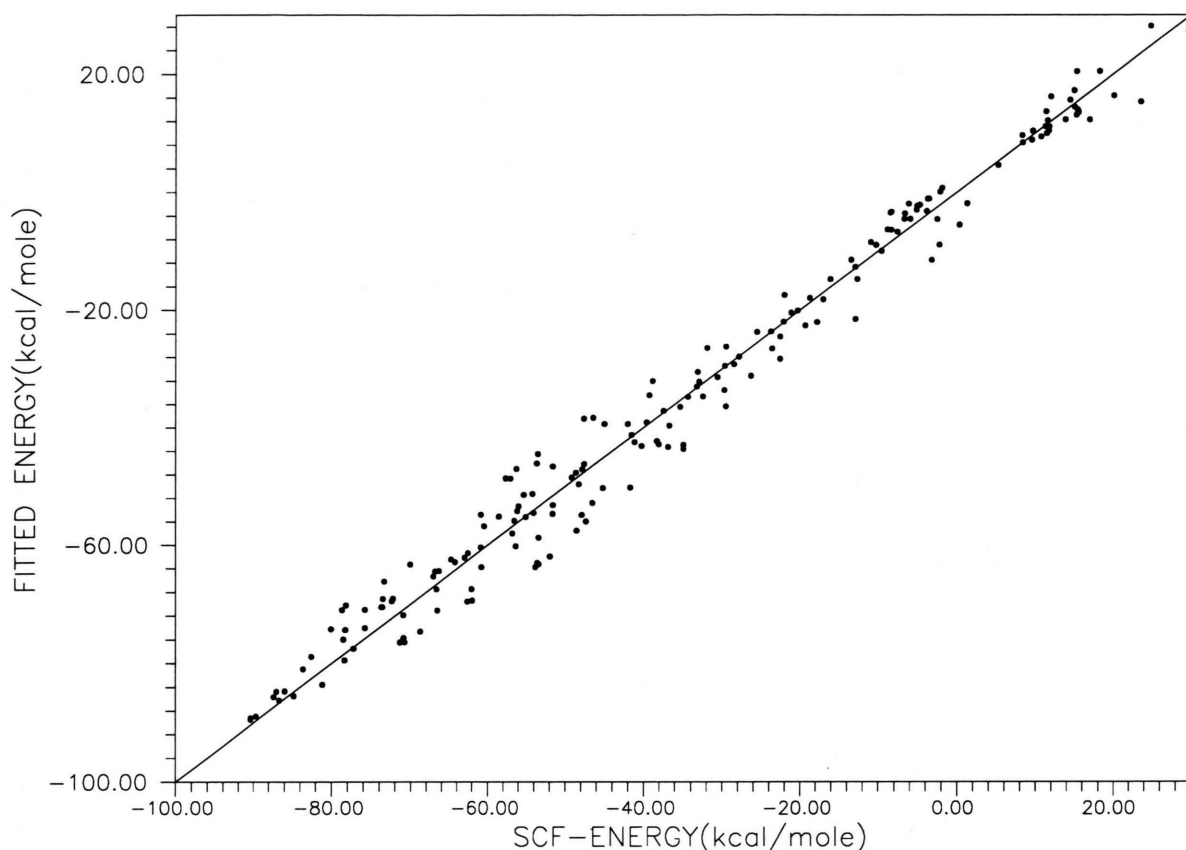


Fig. 2. Comparison of the stabilization energies from *ab initio* calculations (ΔE_{SCF}), and fitted energies (ΔE_{FIT}) with the final fitting parameters given in Table 2.

polarization functions (DZP) and ECP [14] approximation, using a version of the HONDO (7.0) [15] program. For the oxygen atom of water, the basis set was taken from Stevens *et al.* [16] for both core and valence shell electrons, and was augmented by a d-type polarization function of orbital exponent 1.154 [17]. The DZP basis set of Dunning [18] was used for hydrogen. For the Cu^{2+} ion, 18 electrons (the Argon configuration) were included in the core potential. The ECP and the DZV basis set was taken from Hay and Wadt [19].

Fitting of Pair Potential to a Functional Form

After having calculated a total of 173 points of the energy surface, the coulombic energies as obtained from Mulliken population analysis [20] were subtracted from the *ab initio* energies, and the energy

Table 1. Number of SCF-energy points (N), and standard deviation (σ) for each optimization step.

Step	N	σ (kcal/mole)	σ (%)
1	1-173	3.98	4.4
2	174-205	5.20	5.7
3	1-205	4.09	4.5

Table 2. Final optimized parameters for the interaction of O and H atoms of water with Cu(II) ion.

Atom	q_i (a.u.)	A (\AA^{-2} kcal/ mole)	B (kcal/mole)	C (\AA^{-1})
O	-0.60724	-398.69	$5.1996 \cdot 10^4$	-3.6995
H	0.30362	50.379	13.336	-0.16633

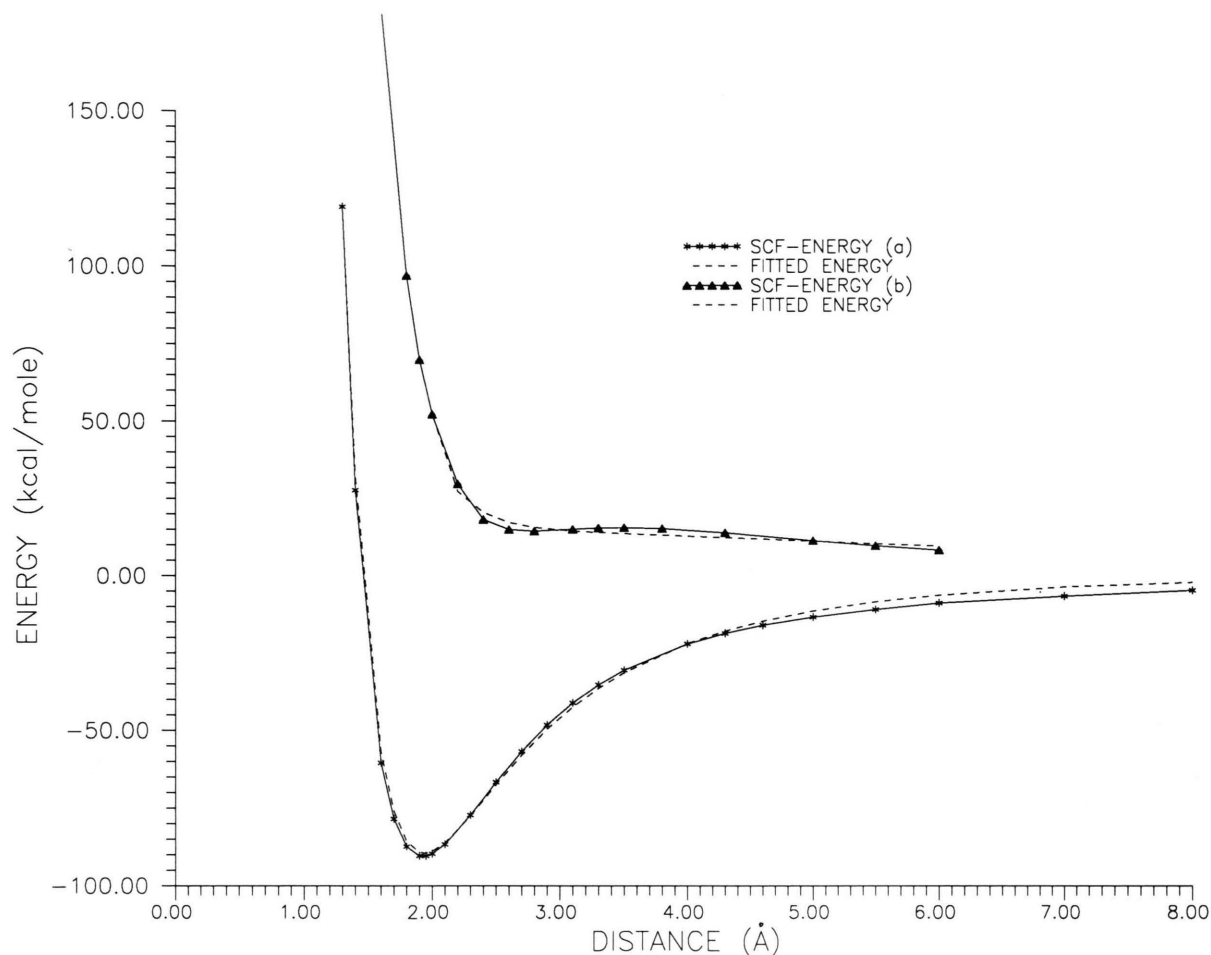


Fig. 3. a, b. Curve-fitting features of some copper(II)-water orientations; (a) $\Theta = 0^\circ$, $\varphi = 0^\circ$ (C_{2v}); (b) $\Theta = 180^\circ$, $\varphi = 0^\circ$; (c) $\Theta = 37.74^\circ$, $\varphi = 90^\circ$; (d) $\Theta = 127.74^\circ$, $\varphi = 90^\circ$; (e) $\Theta = 30^\circ$, $\varphi = 0^\circ$; (f) $\Theta = 60^\circ$, $\varphi = 0^\circ$.

points of the differences less than 30 kcal/mole were included in the fitting using a multidimensional non-linear least-squares procedure to a functional of the form

$$\Delta E(r) = \sum_{i=1}^3 \frac{q_m q_i}{r_{im}} + \sum_{i=1}^3 \left(\frac{A_{im}}{r_{im}^2} + B_{im} \exp\{C_{im} r_{im}\} \right),$$

where r_{im} is the distance between the i -th atom of water and copper(II) ion in Å, q_i and q_m are the charges of hydrogen and oxygen of water and copper ion, respectively, obtained by Mulliken population analysis [20] in the SCF calculations of the isolated systems. These q -values were kept constant throughout the calculations. A_{im} , B_{im} and C_{im} are the fitting parameters for the interactions between Cu^{2+} and oxygen or hydrogen of water.

Quality Test of the Function

The function obtained from the first SCF-data set was tested using the procedure of Beveridge *et al.* [21]. A total of 32 copper(II)-water configurations were chosen outside the first set of data but within the ranges of $\Theta = 0^\circ$ to 90° and $\varphi = 0^\circ$ to 45° . The interaction energies ΔE_{FIT} for these additional configurations were evaluated from the optimized function, followed by quantum chemical calculation for the same configurational points. The quality of the intermolecular potential function was then evaluated by comparing the ΔE_{FIT} and ΔE_{SCF} values. To improve the quality of the function, the additional SCF energy points were then included in the fitting procedure.

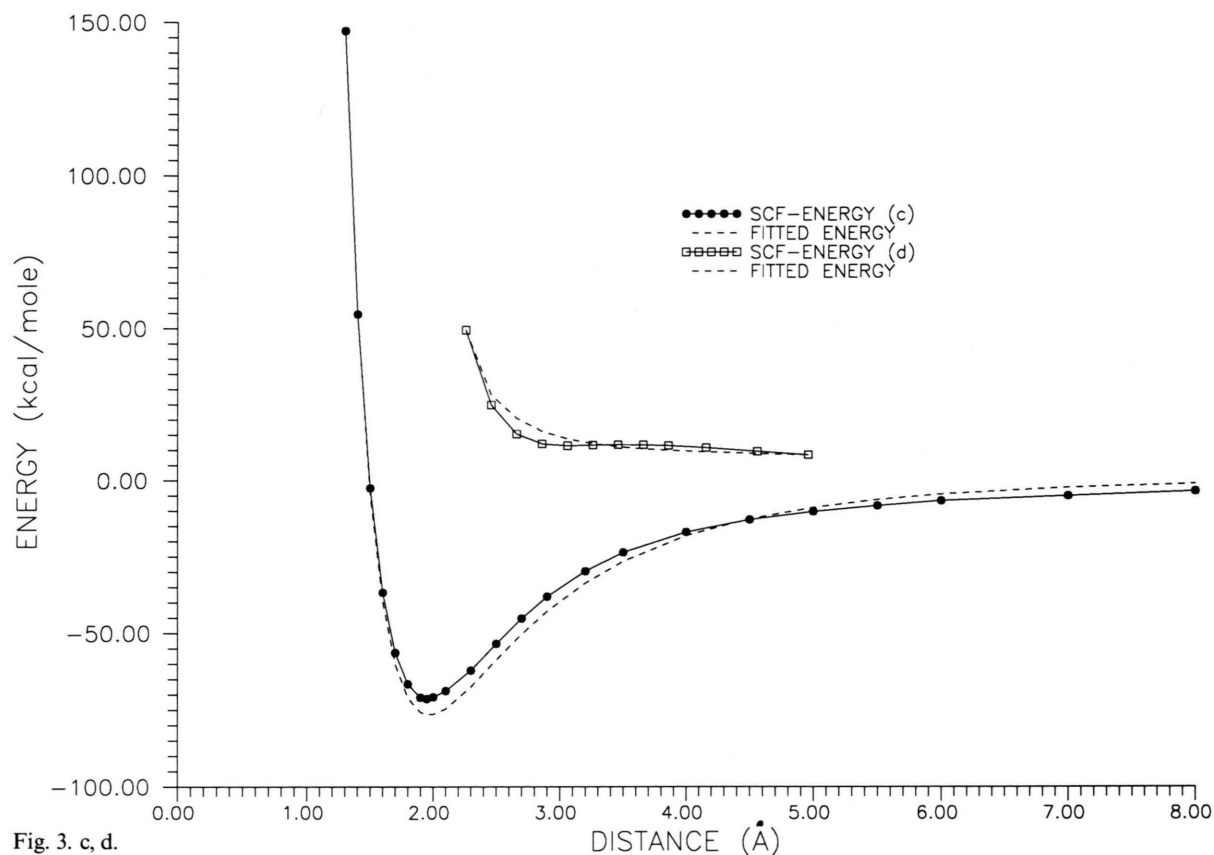


Fig. 3. c, d.

Results and Discussion

For the initial 173 SCF-data points on the energy surface, the standard deviation of the function values was 3.98 kcal/mole, corresponding to 4.4%. The standard deviation of the values predicted by the function from the corresponding *ab initio* calculated energies for the further 32 chosen test points was 5.20 kcal/mole. This result indicates that the interaction of Cu^{2+} with water is already well represented by the function. After inclusion of these points, the standard deviation was 4.09 kcal/mole (4.5%), thus remaining practically identical. 35% of the total 205 energy points were from the minimum region of the energy surface within internuclear distances from 1.7 Å to 3.0 Å, and 19% were from repulsive regions.

In Fig. 2, the stabilization energies obtained from quantum chemical calculations (ΔE_{SCF}) are plotted versus those obtained from the function (ΔE_{FIT}) with the final parameters in Table 2. An important parameter indicating the quality of the function is the correlation between the position of the energy minima of ΔE_{SCF} and ΔE_{FIT} . To illustrate this agreement, potential curves of some directions are displayed in Figure 3. They show the relation to be satisfactory, even in the repulsive region.

Finally, false minima of the function were searched within the range of distance 1.0 to 10.0 Å (the usual cut-off distance of simulations). No artificial minima were found within these limits.

The global minimum of the potential surface was found to be -90.39 kcal/mole at a Cu^{2+} -O distance of 1.95 Å in C_{2v} symmetry.

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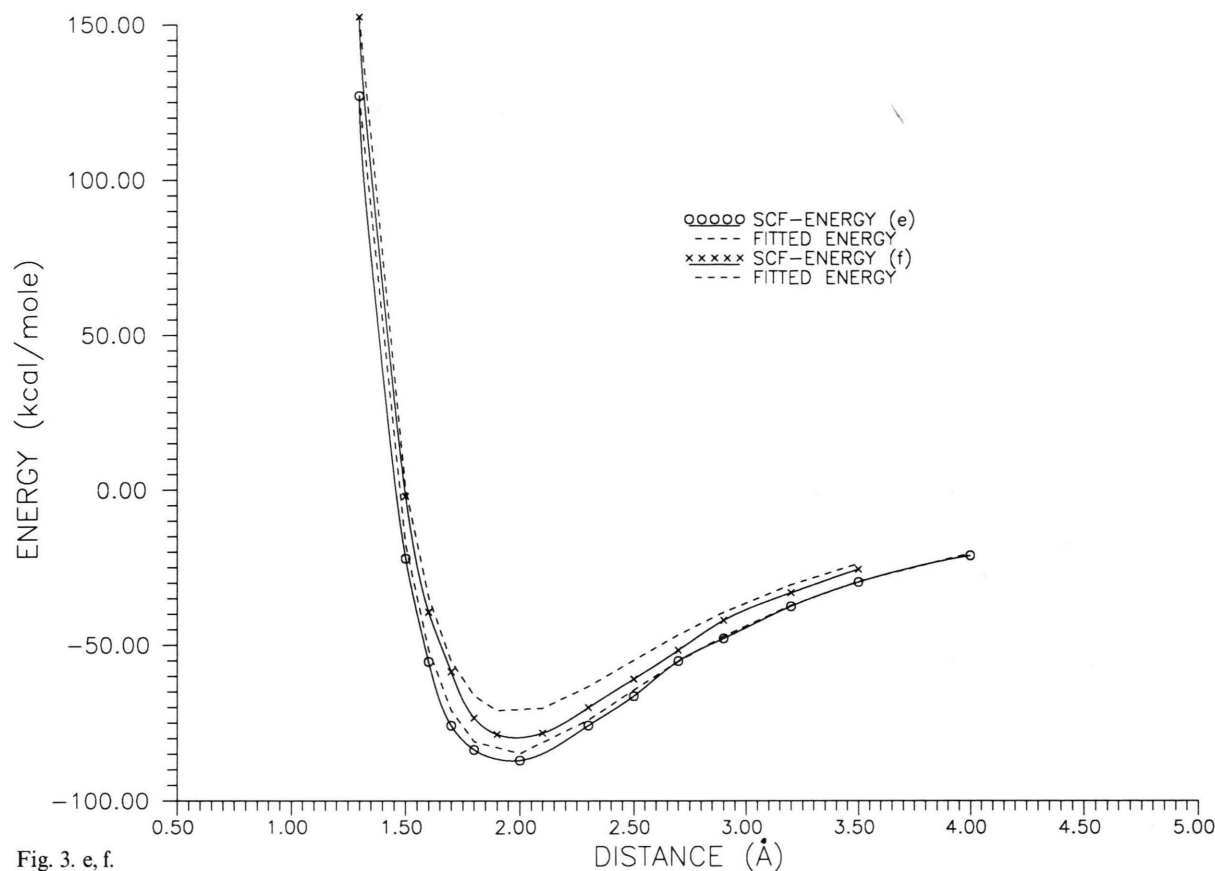


Fig. 3. e, f.

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