

Intermolecular Potential Function Including Anisotropic Terms for Ammonia/Cu²⁺ Based on ab-initio Calculations

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An intermolecular pair potential function for Cu²⁺–NH₃ has been derived based on ab-initio calculations with a ECP-DZV basis set. For copper the original ECP-DZV basis set was modified in order to avoid unwanted charge-transfer effects. The final potential function including anisotropic terms was constructed from a total of 679 configurations.

Introduction

Monte Carlo and Molecular Dynamics simulations become an increasingly valuable tool for the study of electrolyte solutions [1–4]. In order to perform such simulations, accurate analytical intermolecular potential functions are necessary.

The Ammonia-Cu²⁺-system was of particular interest for three reasons: First, from the methodical viewpoint to describe the whole energy surface of this open-shell system with the UHF-formalism, second, as various Cu²⁺–NH₃-complexes are of interest for the inorganic chemist and third, the model character of this system for Cu²⁺-amino acid interactions, recently found to be crucial for catalyzing peptide synthesis in aqueous solutions in possible prebiotic evolution steps [5].

Method of Calculations

To construct the potential function by means of quantum chemical calculations the following steps were performed: (1) selection of representative geometries of the pairs; (2) performance of the SCF-calculations; (3) fitting of the computed interaction energies to a functional form and (4) testing the function.

1. Selection of Geometries

Ammonia was placed with N in the center of a cartesian coordinate system as illustrated in Figure 1.

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The position of the copper was characterized by its distance to N and two rotational angles *A* and *B* around the *Y*-axis and the *Z*-axis.

The energy surface of the system was divided by a grid of 30°-rotational angle steps (*A* and *B*) and the corresponding SCF-energies were calculated for Cu–N-distances from 1.4 up to 10 Å.

The experimental geometry of ammonia was taken as N–H=1.008 Å and H–N–H=107.3° [6].

2. Performance of the SCF-Calculations

The HONDO 7 program [7] was used for the quantum chemical calculations employing the ECP-DZV basis set of Stevens, Basch and Krauss [8] for ammonia. For copper the original ECP-DZV basis set of Hay and Wadt [9] had to be modified because of a charge-transfer effect leading to Cu¹⁺ at larger Cu–NH₃-distances as exemplified in Figure 2.

In order to avoid this effect, the two p-functions with the smallest exponents as well as the two highest s-functions were removed, and the uppermost d-function of the original Cu valence basis set was included in the contraction of the others (see Table 1). The ECP-functions remained unchanged.

With this basis set it was possible to calculate SCF-points for the complete energy surface with strongly

	α_i	c_i
s-Orbital	0.7307	1.0
d-Orbitals	41.34	0.0395247
	11.42	0.1943744
	3.839	0.4005019
	1.230	0.4638820
	0.3102	0.2870209

Table 1. Modified basis set for Cu.

α_i = gaussian orbital exponent,
 c_i = coefficient.

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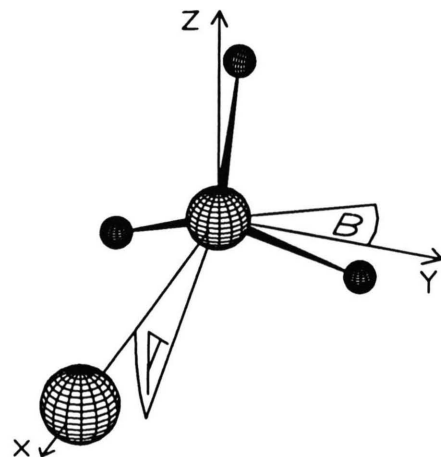


Fig. 1. Geometrical parameters for ammonia/Cu(II) configurations.

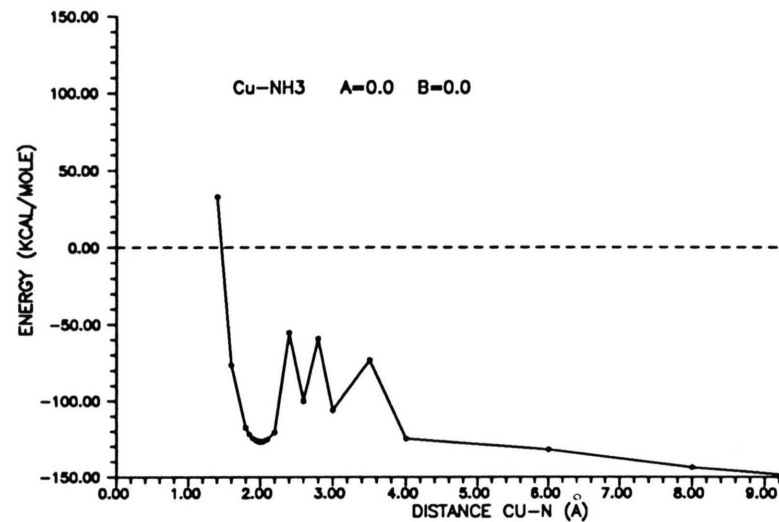


Fig. 2. The SCF-energies in the global minimum for the Cu^{2+} -ammonia system with the Cu-valence basis set of Hay and Wadt. The two rotational angles A and B are 0. The values for the charge on Cu taken from the Mulliken-Population-Analysis indicate that Cu^{2+} changes to Cu^{1+} at larger Cu-NH₃-distances (more than 4 Å).

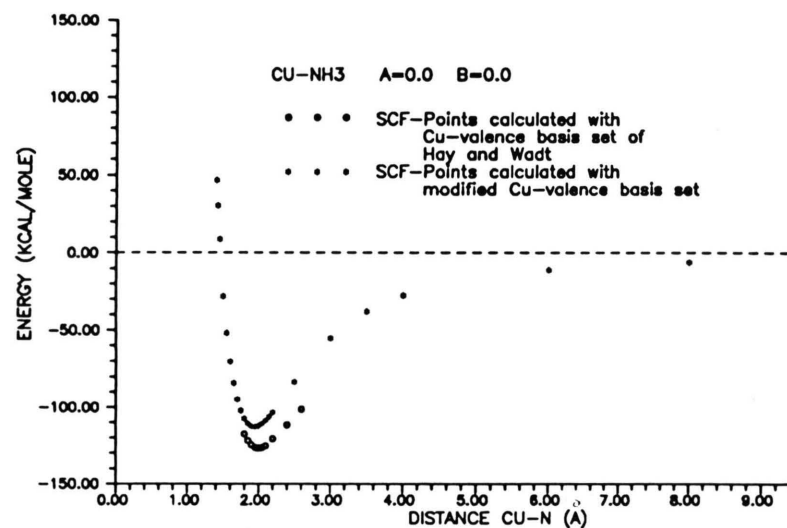


Fig. 3. Representation of the global minimum with different Cu-valence basis sets.

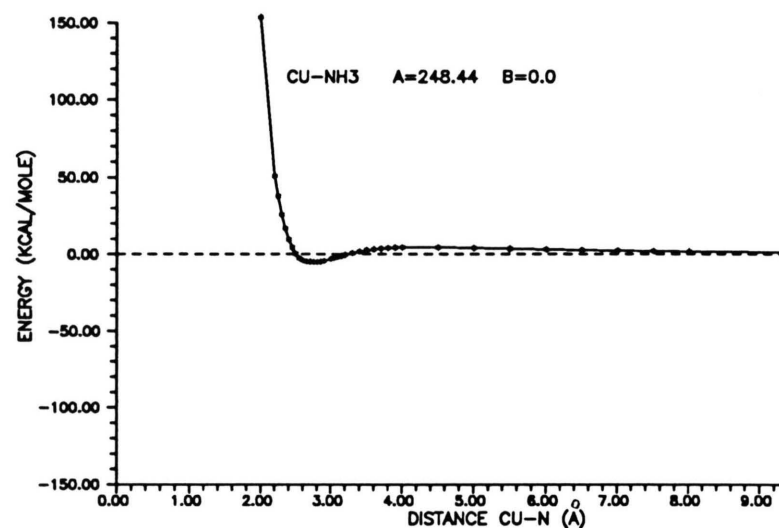


Fig. 4. Potential curve for the approach of Cu^{2+} towards hydrogen of ammonia along the N-H-axis.

reduced charge transfer effects. Figure 3 gives an illustration of the influence on the energy caused by the modification in the basis set.

The minimum was found to be -126.6 kcal/mole at a Cu–N-distance of 2.0 Å for the original basis set, compared to -112.6 kcal/mol and a Cu–N-distance of 1.95 Å for the modified basis set. As the calculations were carried out to develop a potential function for simulations, this rise of 11% could be tolerated, as the absolute energy values do not play such an important role for evaluation of structural properties. The deviation of the minimum distance of 0.05 Å may have more influence in this aspect but seems still acceptable. More reliable data could have been obtained only by the inclusion of further ligand molecules in the SCF calculations [10], leading to enormous computational efforts.

3. Development of Potential Function and Fitting of the Energies

After having calculated 629 SCF-points in the geometries mentioned in section 1 it became obvious that ammonia is strongly polarized in certain configurations. Figure 4 shows the potential curve for the approach of Cu^{2+} along the N–H-axis towards H. Instead of being a purely repulsive curve, weak stabilizing energies at Cu–H-distances around 1.7 Å (minimum: -4.9 kcal/mole) were obtained. The Mulliken-Population-Analysis (MPA) [11] for the corresponding SCF-points indicates negative charges for the hydrogen (-0.476 atomic units).

This polarization effect becomes weaker, and no stabilization is observed anymore when Cu^{2+} approaches H along a straight line with an angle of more than 10° to the N–H-axis, although the corresponding H still remains negatively charged.

Because of this phenomenon and the fact that first attempts to fit the SCF-energies to commonly used isotropic potential functions did not give satisfactory results, anisotropic, angular dependent atom-atom interaction terms were introduced into the analytical potential function.

Considerations on the nature of this term were based on two assumptions: (a) ammonia hydrogens are polarized along the N–H bonds, nitrogen in the direction of the molecular dipole, and (b) the pair interaction between Cu^{2+} and an atom of ammonia is an ion/induced dipole interaction corresponding to a $1/r^3$ -term.

If the two vectors Cu^{2+} –H and N–H are perpendicular to each other, the polarization along the N–H-axis and the ion/induced dipole interaction (μ_k) becomes zero. The associated energy can be expressed as

$$E \cong \frac{\langle \mu_k | r_k \rangle}{||r_k||^3}, \quad (1)$$

μ_k = induced dipole, r_k = Cu–H-distance, $k = 1, 2, 3$ for the hydrogens of ammonia.

$|\mu_k\rangle$ is given by

$$|\mu_k\rangle = \langle \text{NH}_k | r_k \rangle \frac{|\text{NH}_k\rangle}{||\text{NH}_k||} \frac{A_k}{||r_k||}, \quad (2)$$

where A_k is the fitting parameter including the polarizability α . Division by r_k is necessary since the induced dipole is dependent on the electric field, which is proportional to the reciprocal distance to Cu^{2+} .

Equation (1) can be written now as

$$E \cong \frac{|r_k\rangle}{||r_k||^3} \left[\langle \text{NH}_k | r_k \rangle \frac{|\text{NH}_k\rangle}{||\text{NH}_k||} \frac{A_k}{||r_k||} \right]. \quad (3)$$

After inclusion of $1/||\text{NH}_k||$ into the parameter A_k , the following expression for the pairwise interaction between Cu^{2+} and the hydrogens of ammonia results:

$$E = A_H \frac{\langle \text{NH}_k | r_k \rangle^2}{||r_k||^5} = A_H \frac{\text{ANG}_k}{||r_k||^3} \quad (4)$$

with

$$\text{ANG}_k = \frac{\langle \text{NH}_k | r_k \rangle^2}{||r_k||^2};$$

$k = 1, 2, 3$ for the hydrogens of ammonia.

Following further assumption (a), that the nitrogen polarization will be always in the direction of the symmetry axis of the molecule, the pair interaction term between Cu^{2+} and N can be written as

$$E = A_N \frac{\langle U | r_N \rangle^2}{||r_N||^5} = A_N \frac{\text{ANG}_N}{||r_N||^3} \quad (5)$$

with

$$\text{ANG}_N = \frac{\langle U | r_N \rangle^2}{||r_N||^2},$$

r_N = distance Cu–N, $|U\rangle$ = unit vector in direction of the symmetry axis of ammonia.

The first set of 629 Cu^{2+} – NH_3 interaction energies was then fitted, using a multidimensional non-linear least-squares procedure by means of the Levenberg-Marquard minimizing algorithm [12], to a functional

of the form

$$E = \sum_{k=1}^4 A_k \frac{ANG_k}{r_k^3} + B_k \frac{1}{r_k^4} + C_k \frac{1}{r_k^5} + D_k \cdot \exp(r_k \cdot E_k) + F \frac{q_k \cdot q_m}{r_k}, \quad (6)$$

where r_k is the distance between the k -th atom of ammonia and Cu^{2+} . q_k and q_m are the net charges of an atom k of ammonia and the Cu^{2+} -ion, respectively, in atomic units, obtained from the Mulliken-Population-Analysis in the SCF-calculations for the isolated subsystems. A_k , B_k , C_k , D_k , E_k , and F are the fitting parameters for the interaction between Cu^{2+} and N or H atoms of ammonia. Only one value for the coulombic parameter F was used, valid for both the Cu^{2+} -N and Cu^{2+} -H interactions.

The higher $1/r^n$ terms can be interpreted as compromise in the description of higher ion/induced-multipole interactions, the exponential part represents the repulsive forces at short distances.

4. Testing the Function

The analytical potential function was tested in two aspects. First, the procedure proposed by Beveridge [13] was used. An additional set of 50 randomly distributed SCF points was calculated, and the ability of the function to reproduce the energies of these 50 points was tested by comparing the standard deviation (σ_{test} in kcal/mole) of these points with σ of the previously calculated points. Afterwards, these 50 points were included into the set of the others and the parameters of the function were reoptimized. The standard deviation was determined again, and as the result was satisfactory, a plot of the SCF-energies versus the energies predicted by the function with the final parameter set was drawn in order to check for exceptional aberrations.

N	σ	N_{test}	σ_{test}
629	3.29	50	3.17
679	3.27		

Table 2. Fitting characteristics.

Atom	q	A	B	C	D	E	F
N	-0.76353	-43.685	-1118.1	553.60	80846.0	-3.6878	1.8318
H	0.25451	-128.73	-292.67	417.67	75.863	-1.0377	1.8318

Table 3. Final parameters of potential (energies in kcal/mole, distances in Å).

In a second test the final function was searched for artificial minima. This was done with a computer program checking the whole space around ammonia with an angular variation (the two rotational angles A and B as in Fig. 1) of 10° within distances from 0.1 up to 10 Å. No such minima were found.

Results

Table 2 shows N , the number of configurations included in the fitting procedure, σ , the corresponding standard deviation of these points in kcal/mole as well as N_{test} and σ_{test} .

In Table 3 the final set of parameters for the interaction of H and N atoms of ammonia with Cu^{2+} is listed. The analytical potential function (Eq. (6)) with this set of parameters delivers the energies in kcal/mole.

In Fig. 5 the SCF-energies are plotted versus the energies predicted by the function with this parameter set.

Figure 6a displays some potential curves for attractive geometries of the system obtained from the SCF-calculations and their representation by the potential function. All of them are reproduced very well, the minima of all 22 curves being identical for SCF and function results. Figure 6b illustrates two repulsive configurations. Figure 6c demonstrates the special case for the approach of Cu^{2+} towards H along the N-H-axis.

The function underestimates this local minimum ($A = 248.44$, $B = 0.0$) which is not an undesirable result (cf. Section 3) as in the SCF-calculations Cu^{2+} and ammonia are treated in the gas phase without any other molecules or charges simulating a corresponding electric field around them. In solution the polarisation effects in ammonia should be weaker because of the existence of other molecules in the surroundings and consequently, these local minima should become less pronounced or disappear.

Summarizing all results, the description of the Cu^{2+} - NH_3 -system by the given analytical potential function can be considered as satisfactory for its use in statistical simulations, especially if mainly structural

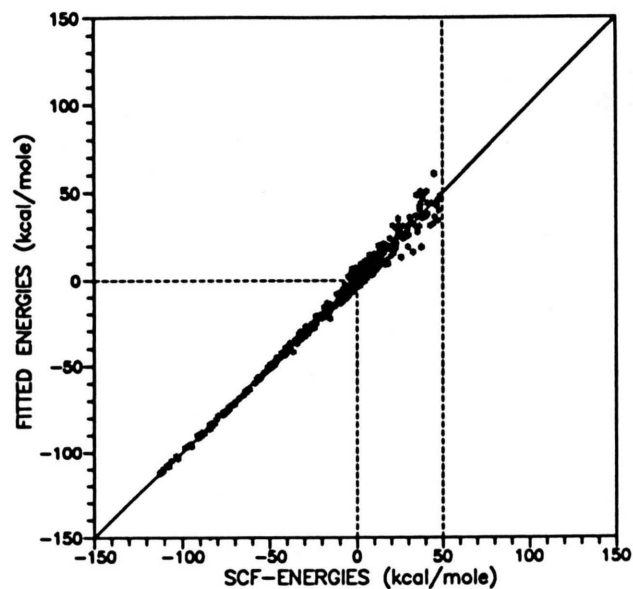


Fig. 5. Calculated vs. fitted energies.

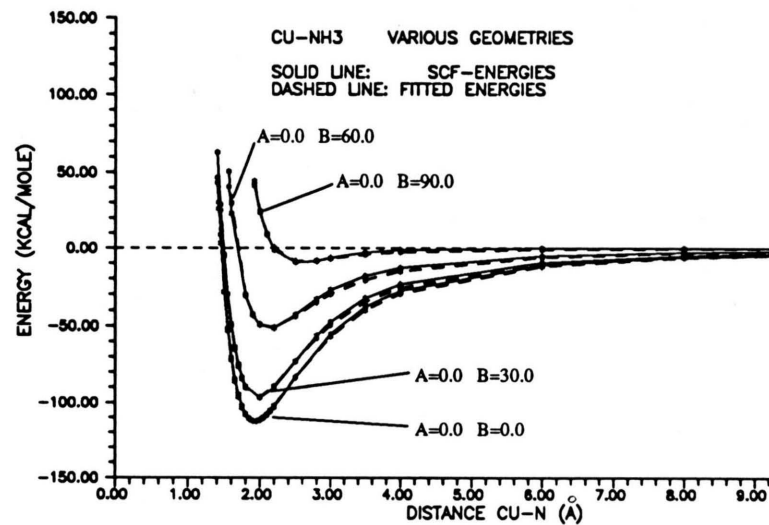


Fig. 6a-c. Potential curves for various geometries. a) Attractive parts of energy surface.

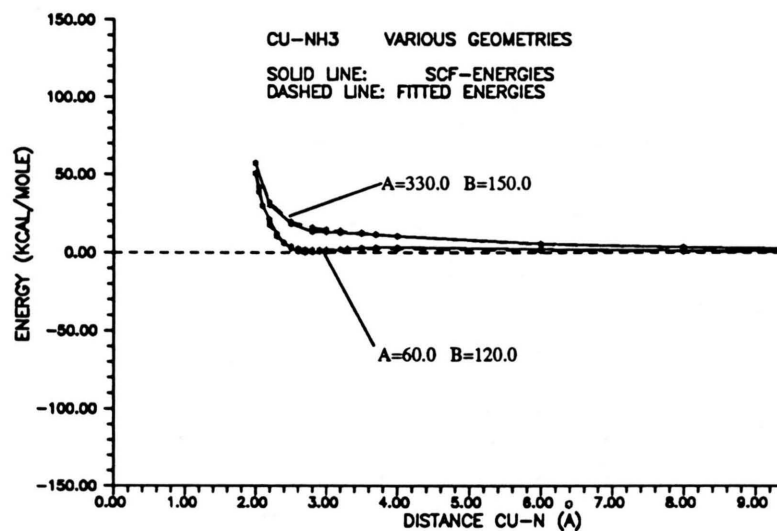


Fig. 6b. Repulsive parts of energy surface.

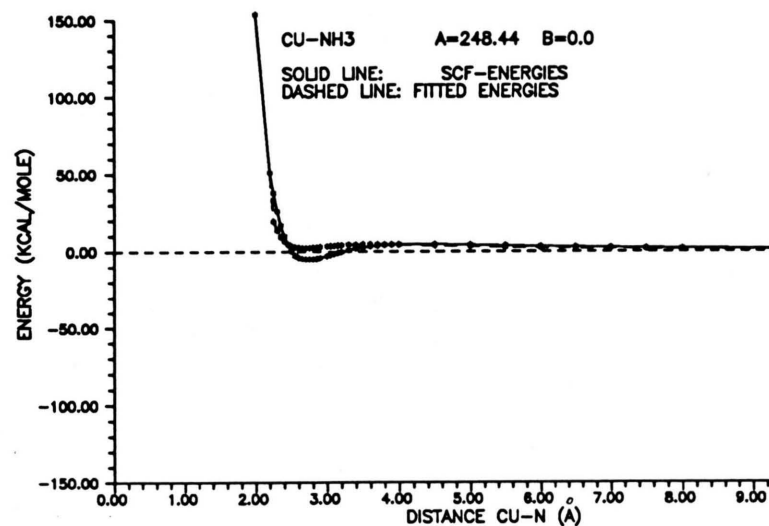


Fig. 6c. Direct approach on H-N-axis.

properties are targetted. It should be mentioned at this point, that three-body effects can be expected to play a non-negligible role, according to extended SCF calculations on $\text{Cu(II)}(\text{H}_2\text{O})_n$ ($n=2 \dots 8$) clusters [14, 15]. For accurate simulation work, the pair potential function presented here might have to be augmented, therefore, by corresponding correction terms.

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