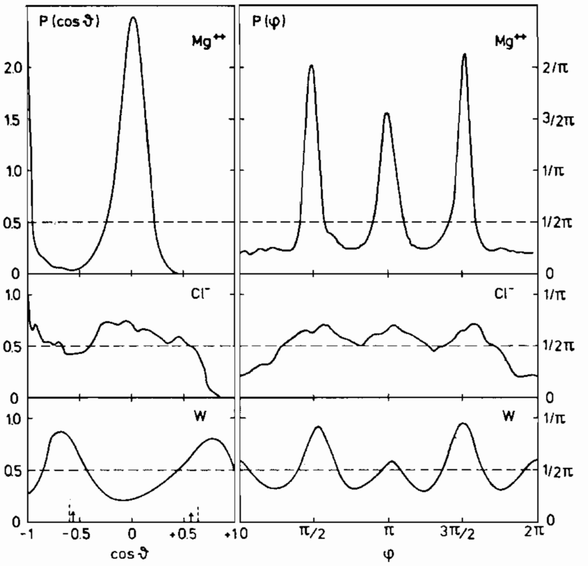

Fig. 1. Probability densities for the polar angle and the azimuth angle of the oxygen atom positions of the six nearest neighbor water molecules around an Mg^{++} and a Cl^- and for the four nearest neighbor water molecules around a central one. The dashed lines indicate uniform distributions.

tion shells of the ions are calculated from the simulation through autocorrelation functions and are compared with experimental results. The spectral densities of the hindered translational and librational motions result from Fourier transformation of the corresponding autocorrelation functions. The dynamic properties can be calculated separately for the water subsystems — hydration water of the cations, the anions and bulk water — and thus provide the possibility of understanding measured macroscopic properties of solutions on a molecular level. The self-diffusion coefficients for the three kinds of water in a LiI solution are given in Table I as an example [3].

TABLE I. Self-diffusion Coefficients for Bulk Water (D^b), Hydration Water of Li^+ (D^+) and of I^- (D^-) in Units of 10^{-5} cm^2/s from an MD Simulation of a 2.2 Molal LiI Solution at 305 °K. D^0 denotes pure water.

i	D^i	D^i/D^0
b	2.85 ± 0.08	0.84
+	1.33 ± 0.10	0.39
–	2.67 ± 0.10	0.78

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Metal Ion Influence on Hydrogen Bonds in Solvent and Ligands

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The application of quantum chemical calculations of the all-electron *ab initio* type to studies of metal influence on neighbouring hydrogen bonds has been extended successively to new and larger model compounds during the past decade. Starting with comparatively small systems accessible to fair methodical accuracy due to the use of larger basis sets, some principal effects have been revealed, such as bond contraction, net bond stabilization, charge transfer effects and the increase of rotational barriers around the hydrogen bond [1, 2]. At the same time, such investigations have proved once more the need for the use of *ab initio* type calculations and the incapability of semiempirical procedures for the treatment of metal–solvent or metal–ligand interactions.

The consideration of slightly larger systems such as *e.g.* ion/water/formamide [3] has shown that the effect of the metal ion extends over a long series of bonds, which implies a need for comparatively large 'subunits' of the molecular (or rather 'supermolecular') system for a conclusive quantum theoretical study. This fact was also revealed by the quantum chemically predicted electronic rearrangements taking place in complexes with more than one ligand with the ability to form chelate structures [4]. For this reason, the applicability of minimal basis sets, allowing an extension of the supermolecular model system to considerably larger subunits, had to be tested. The conclusions of such tests [2, 3] have shown that such basis sets can be used for the evaluation of intermolecular geometrical parameters and relative energy effects, still maintaining sufficient accuracy, especially if basis set error corrections like the counterpoise procedure [5] are employed.

The data of *ab initio* calculations for ion/ligand interaction form the basis of three main approaches to more complex systems:

(1) The evaluation of pair and three-body potentials, representing the basis for the construction of interaction potentials used in methods like Monte Carlo or Molecular Dynamics calculations on large ensembles of ions and molecules and/or macromolecules [*e.g.* 6–8].

(2) The 'static' treatment of large supermolecular species with small basis sets for the evaluation of geometries, binding energies, electron density distribution and other data for solvated ions or ion/ligand complexes.

(3) The possibility of the construction of supermolecular electrostatic perturbation fields representing the influence of molecules at larger distances from the ion and/or directly involved ligand [9, 10].

Among these methods, numbers 2 and 3 are especially suitable to reveal some effects of the metal ions on surrounding solvent and other ligand molecules.

For the demonstration of the use of small basis sets in combination with electrostatic potentials, solvation of ions in water and some nonaqueous solvents are mentioned [9, 10]. The treatment of crystal growth also seems to be a promising field of application for this approach [11].

The application of calculations of the type 2 mentioned above for the study of metal ion influence on hydrogen bonds in base pairs of nucleic acids [12–14] seems to be another useful example of the capability of theoretical approaches in the field of bioinorganic chemistry. These examples also demonstrate, however, the importance of basis set error corrections and hence a careful methodical control in the course of such investigations.

An example of cooperative experimental and quantum chemical research can be given in the field of ion/peptide interactions, where experimental data for biological protein/metal complexes are compared with metal complexes of small peptides, which on the other hand are accessible again to *ab initio* calculations with minimal basis set.

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Some Remarks on Solvent and Conformational Effects

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Let us now consider a classical electrostatic problem, *i.e.* the evaluation of the reaction-field potential due to an arbitrary point-charge distribution placed inside a vaccum cavity, surrounded by a homogeneous and isotropic dielectric medium. Analytical solutions are available for simple cavity shapes (*e.g.* Sphere, Ellipsoid), and numerical ones in more general cases [1, 2].

If one is interested in the study of a solution, a sensible balance between speed and accuracy can be achieved by treating some solvent molecules as granular (*i.e.* inside the cavity) and others as the continuum; if a sufficiently large number of solute molecules is taken into account, then the 'reaction-field contribution' is only a minor correction [1].

Let us consider some simple reaction (*in vacuo*): A + B → products; over the last 10–20 years, physically more realistic calculations have been carried out taking solvent molecules into account (in some way or another, see above); by and large, it has been found that agreement with experiments tends to improve as the number of solvent molecules increases [3, 4].

For some simple molecules, reasonably accurate torsional potentials have been obtained by fitting experimental data and/or quantum mechanical calculations, and simulation studies were carried out allowing for both intra-molecular and solvent interactions. In the case of CH_3OH (torsional barrier ≈ 5 KJ/mol) no significant differences were detected for the angular probability distribution function between dilute vapour, pure liquid and aqueous solutions [5]. As for $CH_3{-}CH_2{-}CH_2{-}CH_3$, small but appreciable differences could be detected between dilute vapour, pure liquid and solutions in CCl_4 or H_2O [6]. As for H_2O_2, the torsional potential exhibits a minimum at $\approx 0.625\pi$ radians, a *trans*-maximum at ≈ 5 KJ/mol and a *cis*-maximum at ≈ 30 KJ/mol, both above the minimum: interconversion of the two minima is only likely to occur via the *trans*-conformer. Simulation calculations were carried out in water solution (both discrete molecules and 'reaction field correction' alone), and their results turned out to be in broad qualitative agreement. The peak in the angular probability distribution function was shifted to $\approx 0.5\pi$ radians, and the probability ratio was found to be:

$$\left(\frac{W_{cis}}{W_{trans}}\right)_{\text{solv.}} \Bigg/ \left(\frac{W_{cis}}{W_{trans}}\right)_{\text{vapour}} \approx 10^4\text{–}10^6$$

Thus, interconversion is now only likely to occur via the *cis*-conformer [7].