(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:

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

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

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