as previously observed [2], but also for the radical anion of toluene, where the experimental splitting constants determined by ESR in solution [5] denote a preferential stabilization of ψ_A, in agreement with the result we obtain for a medium with $\epsilon \geqslant 3.5$.

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Solvent–Solvent Interactions in First Neighbour Models for Aqueous Electrolyte Solutions

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First neighbour models (FNM) as a useful tool for the interpretation of the structure function of liquids are widely used more recently in X-ray diffraction studies. Their basic concept is to calculate a model structure function by assuming regular polyhedra for the nearest neighbours in the liquid, varying the structural parameters while the best fit with the experimental curves is reached [1].

A lot of FNM's have been applied for aqueous electrolyte solutions, but the basic interest is connected with the description of hydration phenomena. As a consequence, the assumption for the solvent–solvent interactions to be identical with those in pure water, is commonly accepted [2]. In this version (FNM1) a difference curve after subtraction of the experimental structure function of the pure water from that of the solution will serve for the models of hydration and ion association. Significant changes in the solvent structure are shown, however, *e.g.* by the molecular dynamics study of aqueous halide solutions [3]. In a modified version, FNM2, we assign a tetrahedron to the first neighbours of the 'free' solvent molecules (not included in the hydration shells). An increasing in the first neighbour distances ~2.91–2.96 Å instead of 2.84 Å in pure water and their rms deviations make us possible to characterize the structure making and structure breaking role of the cations [4]. In a third version, FNM3, the assumption of symmetry is also dropped.

As a consequence, the coordination numbers can change, and for the alkali chloride solutions they may differ significantly from those of FNM2, determined by the symmetry of the given polyhedra (Table I). These features of the models are tested even by the pair-correlation functions derived from the FNM's.

TABLE I.

	FNM2	FNM3	
CN_{ww}	4.0	3.0	2 *M* KCl
r_{ww} (Å)	2.94	2.97	
l_{ww} (Å)	0.103	0.20	
CN_{ww}	4.0	3.5	4 *M* KCl
r_{ww} (Å)	2.94	2.99	
l_{ww} (Å)	0.109	0.20	

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A Theoretical Approach to the Evaluation of the Contribution of Many-Particle Interactions to Distribution Functions and Thermodynamics

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The time-averaged coordination number of a fluid is no less than four. It means that any interaction includes at least three particles situated at short distances from each other. There is no doubt that wave functions of all particles involved are mutually disturbed. Therefore, the interaction energy is not pair-additive. Accordingly, we attempted to evaluate the contribution of the non-additivity to the pair correlation function and thermodynamic functions of a fluid in the simplest case of triplet interactions.

The Hamiltonian is as follows:

$$H = ½ \sum_{i,j} \psi_{ij} + \frac{1}{3!} \sum_{i,j,k} \psi^*_{ijk}$$

where ψ_{ij} is the pair (undisturbed by the presence of other particles) potential, ψ^*_{ijk} is the non-additive part (perturbation) of the triple interaction potential. The solution of the problem was achieved in the framework of the BBGKY method and using the functional expansion of the Hamiltonian in non-additive three-particle potentials for diluted solutions both neutral and charged particles.

Theoretical Study on Solvation of a Neutral Molecule: N_2. Two Different Approaches

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A wide investigation has been performed in view of a theoretical study of the solvation of neutral molecules. N_2 as a test molecule and HF, H_2O, NH_3, CH_4 as solvents have been chosen.

In the former approach, the contour maps of interaction energy between N_2 and one solvent molecule have been evaluated, with fast semiempirical methods (Extended Hückel and CNDO), and compared with each other, in order to find a reliable but not too expansive calculation method. For N_2–H_2O interactions, a map has been computed also *ab initio.* The maps are shown, and qualitative and quantitative differences are discussed.

The latter approach rests on building up clusters with one molecule of N_2 surrounded by a number (2 to 8) of solvent molecules and finding the structure of such clusters by energy minimization.

From the reported structures it results that they are determined mainly by steric factors, so that clusters optimized by means of different methods are quite similar.

Solvent Extrusion: A Pathway from Solvent Separated Ion Pairs to Tight Ion Pairs

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A simple model of two oppositely charged ions, embedded in a sea of hard sphere solvent dipoles (whose centers are fixed on a lattice) is implemented to study the recombination of ions in solution. The first step is the passage from 'solvent separated' ion pair to 'intimate' or 'tight' ion pair. A preliminary two dimensional calculation (restricted to purely electrostatic terms) of the potential energy surface for such a recombination reveals two minima, as required by the experimental observations of Winstein and others.

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I.R. Experimental Studies of Dynamical Aspects of Water Structure: Effects of H–D Substitution and of Small Solutes

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Results on i.r. absorption spectra of H_2O, D_2O and electrolytic solutions and their thermal modifications are presented. From the data, some parameters can be obtained which are suitable for a description of dynamical aspects of water structure. Solute induced changes of these parameters provide a quantitative, although phenomenologic description of the water–solute interaction.