1st principle simulations of ions in water solutions: Bond structure and chemistry in the hydration shells of highly charged ions

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Methods of direct simulation (Monte Carlo and molecular dynamics) have provided new insights into the structure and dynamics of electrolyte solutions. However, these methods are limited by the difficulty of developing reliable ion-solvent and solvent-solvent potential interactions in the highly perturbed hydration region. To model the interactions in this region methods of simulation that are based on the direct on the fly solution to the electronic Schrödinger equation (ab-initio molecular dynamics, AIMD) are being developed. However, 1st principle methods have their own problems because the solution to the electronic structure problem is intractable unless rather uncontrolled approximations are made (e.g. density functional theory, DFT) and there is high computational cost to the solution to the Schrödinger equation. To test the accuracy of AIMD methods we have directly simulated the XAFS spectra for a series of transition metal ions Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. Despite DFT's well know deficiencies, the agreement between the calculated XAFS spectra and the data is almost quantitative for these test ions. This agreement supports the extension of the interpretation well beyond that of the usual XAFS analysis to include higher-order multiple scattering signals in the XAFS spectra, which provide a rigorous probe of the first shell distances and disorders. Less well resolved features of the spectra can still be analyzed and are related to 2nd shell structure. The combination of XAFS measurements and the parameter free AIMD method leads to new insights into the hydration structure of these ions. While strictly local DFT +gga provides excellent agreement with data, the addition of exact exchange seems to provide slightly better structural agreement. The computational complexity of these calculations requires the development of simulation tools that scale to high processor number on massively parallel supercomputers. Our present algorithm scales to nearly 100,000 processors. However, even with high scaling the time to solution is very long. We are also developing and testing new methods to improve the performance of simulation and new sampling methods that more efficiently explore phase space and can reach longer time frames. Results of calculation of the hydration structure and dynamics of highly charges ions and free energy calculations of ion association will be presented.