

## A DFT Benchmark Study on Ionic Liquids

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**Abstract:** Ionic Liquids (IL) is a class of substance generally formed by organic cations and inorganic anions which make them liquid at the room temperature. The wide range of possible combinations of cations and anions can result in solvents with many interesting and different properties and applications.[1] Due to its high polarity, low coordination number and almost zero vapor pressure, the IL are able to solvate both organic and inorganic compounds besides being more easily recyclable than common industrial solvents, which highlights its economical and friendly environment characteristics.[2] All these features have brought a lot of attention to IL from both experimental and theoretical point of views.[3] From the theoretical perspective, the majority of the quantum mechanical studies have used Density-Functional Theory (DFT) without, however, a consensus about which functional, and even basis set functions, best describes the microscopic features of IL.[4,5] In this work, the most common ion pair combinations forming IL were investigated with different DFT functionals and basis set functions. The results were compared with a benchmark high-level calculation composed of Coupled-Cluster Method extrapolated to a complete basis set and experiment if possible.[6] The set of selected functionals includes pure and hybrid ones with and without long range dispersion correction, while the basis sets comprise double and triple zeta added with polarization and diffuse functions. The solvent effect was implicitly included in all calculations as well as the counterpoise correction for the basis set superposition error on ionic pairs. The long range corrected functionals with triple zeta basis sets including polarization and diffuse functions show the best agreement with the benchmark high-level calculation indicating they should be the method of choice as starting point calculations of more complex and/or large IL systems and molecular mechanics simulations.

**Key-words:** ionic liquids, density-functional theory, benchmark.

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