Energy-density relationships for the treatment of ion solvation within density-functional theory

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Useful energy-density relationships, connected with the embedding of singly charged postive or negative atomic ions in polar solvents, are developed. The insertion of the atomic charged system into the polarizable host is modeled through successive isoelectronic processes at the nucleus, involving a varying nuclear charge. In this way, the controversial procedure of selecting appropriate ionic radii, involved in the calculation of solvation energies through the Born formula, is avoided and replaced by integration in [0,]. The approximate expressions, derived from a variational procedure proposed by Levy [J. Chem. Phys. 68, 5298 (1978); 70, 1573 (1979)], are reformulated within the nuclear-transition-state model. The classical reaction field expression for the insertion energy is recovered. The quality of the approximations made are discussed within the frame of the Kohn-Sham formulation of density-functional theory.