

Beyond the classical nuclei approximation in electronic structure calculations

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First-principles electronic structure calculations played a very important role during the past decade due to their predictive power, and also to their ability to describe complex physical and chemical phenomena, often inaccessible to experiment, in a realistic way. Their feasibility is related to a few quite reasonable approximations: (a) the adiabatic separation of nuclear and electronic degrees of freedom, (b) the classical treatment of atomic nuclei, and (c) various approximations for the electronic exchange and correlation. While a large amount of work has been devoted to electronic correlations, relatively less effort has been put into the quantum treatment of the nuclei, and very little in relaxing the Born–Oppenheimer approximation. In this work I will present some approaches devised in order to move from classical towards quantum nuclei. This acquires particular relevance when dealing with systems constituted by light atoms like H, He and first-row elements. Quantum effects have indeed been observed in molecules (including large molecules such as proteins), in liquids (water), and in solids (high-pressure H and ice, H-bonded molecular solids, etc.)

To include the influence of quantum nuclear delocalization on the electrons it is needed to solve the nuclear Schroedinger equation in the multidimensional ab initio (DFT or another) potential energy surface (PES). Two problems arise at this point: 1) solving the 3N-dimensional nuclear Schroedinger equation (where N is the number of atoms), and 2) mapping the 3N-dimensional PES. This is a formidable task and so it is desirable to find simplified, but still accurate, approaches. Different schemes have been proposed: the ab initio path integral method [1,2], a multicomponent density functional theory [3], and the vibrational self-consistent field method (VSCF) [4]. I will briefly describe the first two, and then concentrate on the VSCF, which we have recently reformulated in a way that extends the present capabilities of the method to include cases in which the quantum geometries are significantly different from the classical ones, e.g. tunnelling [5]. I will present the state of the art and some results for small molecules, and then discuss some possible extensions.

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