

Potential energy surfaces and Berry phases from the exact factorization: A rigorous approach to non-adiabatic dynamics

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The starting point of essentially all modern electronic-structure techniques is the Born-Oppenheimer (BO) approximation. It not only makes calculations feasible, the motion of nuclear wave packets on the lowest BO potential energy surface often provides us with an intuitive picture of chemical reactions and, for small-amplitude motion, yields an excellent way to determine vibrational spectra. To go beyond the adiabatic limit is notoriously difficult. Here we present a novel approach to non-adiabatic effects that is based on the exact factorization [1] of the full electron-nuclear wave function into a purely nuclear part and a many-electron wave function which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude. The equations of motion for these wavefunctions lead to a unique definition of *exact* potential energy surfaces as well as *exact* geometric phases, both in the time-dependent and in the static case. We discuss a case where the exact Berry phase vanishes although there is a non-trivial Berry phase for the same system in Born-Oppenheimer approximation [2], implying that in this particular case the Born-Oppenheimer Berry phase is an artifact. In the time-domain, whenever there is a splitting of the nuclear wavepacket in the vicinity of an avoided crossing, the exact time-dependent surface shows a nearly discontinuous step [3]. This makes the classical force on the nuclei jump from one to another adiabatic surface, reminiscent of Tully surface hopping algorithms. Based on this observation, we propose novel mixed-quantum-classical algorithms whose unique feature is that the trajectories are coupled. Without recourse to Tully surface hopping and without any added decoherence correction, the new algorithm provides a rather accurate, (much improved over surface hopping) description of decoherence [4]. This is demonstrated for the photo-induced ring opening of oxirane [5]. We present a multi-component density functional theory [6,7] that provides an avenue to make the fully coupled electron-nuclear system tractable for very large systems. Finally, we use the approach to deduce an ab-initio electron-phonon interaction, and we explore the possibility of describing non-adiabatic effects in, e.g., proton transfer by R-dependent nuclear masses [8].

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