

# Potential energy surfaces and Berry phases beyond the Born-Oppenheimer approximation

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Some of the most fascinating phenomena in Chemistry and Physics, such as the process of vision, exciton dynamics in photovoltaic systems, as well as phonon-driven superconductivity occur in the regime where the non-adiabatic coupling of electronic and nuclear motion is essential. To tackle such situations, one has to face the full Hamiltonian of the complete system of electrons and nuclei. We deduce an exact factorization [1] of the full electron-nuclear wavefunction into a purely nuclear part and a many-electron wavefunction 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] that provides an avenue to make the fully coupled electron-nuclear system tractable for very large systems.

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