Non-adiabatic Berry connection, the mediator of energy, momentum, and angular-momentum transfer between electrons and nuclei

E.K.U. Gross

The Hebrew University of Jerusalem, Edmond Safra Campus, Jerusalem, Israel

The quantum dynamics of molecules and solids often involves an electronic excitation followed by nuclear motion on a somewhat slower time scale. Some of the most fascinating phenomena in physics and chemistry, such as the process of vision or the Nobel-prize-winning femto-chemistry experiments of Ahmed Zewail are of this kind. Also processes in molecular junctions may be similar, when an applied voltage leads to an electron current through the junction which then triggers nuclear motion, e.g. a perpetual rotation of the molecule representing a nano "water wheel". What is common to these processes is that, after electronic excitation, energy, momentum or angular momentum is transferred from the electronic to the nuclear subsystem (and sometimes back). Usually these processes are non-adiabatic, i.e. they cannot be described by the motion of nuclei on a single Born-Oppenheimer surface. To tackle this situation we deduce an exact factorization [1] of the fully correlated electron-nuclear wave function into a purely nuclear part and a many-electron wave function which parametrically depends on the nuclear coordinates and which has the meaning of a conditional probability amplitude. The variational principle leads to formally exact equations of motion for these two wave functions. The electronic equation is involves non-Hermitian operators which yield a very efficient way to describe and control electronic decoherence [2] in laser-induced isomerization processes. The dynamics of the nuclear subsystem is described by a time-dependent Schroedinger equation which contains a single time-dependent scalar potential energy surface and a vector potential which has the structure of a Berry connection. It turns out that this "non-adiabatic Berry connection" plays a crucial role in the transfer of energy, momentum and angular momentum from the electronic subsystem to the nuclei. In the classical limit, and likewise in the nuclear Ehrenfest equations, the vector potential leads to an electric-like force and to a Lorentz force with a magnetic-like field given by the associated Berry curvature. Consequences of these unusual forces will be explored [3]. The exact vector potential leads to a molecular "non-adiabatic Berry phase" whose calculation does not invoke the Born-Oppenheimer approximation. The value of this exact Berry phase, depending on system, may differ significantly from the standard Born-Oppenheimer molecular Berry phase.[4]

[1] A. Abedi, N.T. Maitra, E.K.U. Gross, Phys. Rev. Lett. 105 (2010) 123002.

[2] S.K. Min, F. Agostini, E.K.U. Gross, Phys. Rev. Lett. 115 (2015) 073001.

[3] A. Scherrer, F. Agostini, D. Sebastiani, E.K.U. Gross, R. Vuilleumier, Phys. Rev. X 7 (2017) 031035.

[4] S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, Phys. Rev. Lett. 113 (2014) 263004.