Plenary Talk PV III Tue 9:00 e415

Potential energy surfaces and Berry phases from the exact factorization: A rigorous approach to non-adiabatic dynamics — •E.K.U. Gross — Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem, Israel

Some of the most fascinating phenomena in physics and chemistry, such as the process of vision, as well as exciton dynamics in photovoltaic systems occur in the so-called non-adiabatic regime where the coupled motion of electrons and nuclei beyond the Born-Oppenheimer approximation is essential. To tackle the problem we deduce an exact factorization [Abedi et al, PRL 105, 123002 (2010)] 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 two wave functions lead to a unique definition of exact potential energy surfaces as well as exact geometric phases and, hence, provide an ideal starting point to study non-adiabatic phenomena. The successful prediction of laser-induced isomerization processes [Agostini et al, JPCL 8, 3048 (2017)], the description of decoherence [Min et al, PRL 115, 073001 (2015)], calculations of the molecular Berry phase beyond the Born-Oppenheimer approximation [Min et al, PRL 113, 263004 (2014)] and accurate predictions of nonadiabaticity in vibrational spectroscopy [Scherrer et al, PRX 7, 031035 (2017); Requist et al, PRB 99, 165136 (2019)] will demonstrate the power of the new approach.