Role of conical intersections in molecular photophysics and photochemistry

Wolfgang Domcke
Department of Chemistry, Technical University of Munich, Garching, Germany

Abstract

Conical intersections play a crucial role in photophysics and photochemistry. At conical intersection seams of electronic potential-energy surfaces, the molecular dynamics is dominated by a complete breakdown of the celebrated Born-Oppenheimer (BO) approximation. Starting from a historical overview of the BO approximation and the concept of conical intersections, this lecture traces the development of methods which allow the computational study of the ultrafast (femtosecond) nonadiabatic dynamics at conical intersections. A brief overview is also given of computational methods for the simulation of time-resolved nonlinear spectra. It is demonstrated that photochemical dynamics can nowadays be scrutinized in unprecedented detail by the interplay of laser spectroscopy and computational chemistry.