CARL VON OSSIETZKY universität OLDENBURG
Institut für PHYSIK

PHYSICAL COLLOQUIUM

INVITATION

Monday, 25.11.2019, 4.15 p.m., W2-1-148

speaks

Prof. Dr. Volker Engel,

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about

"Coupling of electrons and nuclei in molecules: from adiabatic Born-Oppenheimer dynamics to non-adiabatic motion at conical intersections"

The Born-Oppenheimer separation of electronic and nuclear motion is one of the most fundamental approximations applied in the theoretical description of molecules. Although it gives excellent results in many cases, it fails in calculating certain observables. Examples are the expectation values of electron momenta or electronic ux densities. The latter situations strongly contradict the concept of an adiabatic motion where the electrons smoothly adapt to the moving nuclei, as it is assumed in the Born-Oppenheimer case. It is, however, possible to circumvent these errors [1,2]. There exist many cases where the BO approximation breaks down. This is encounter, e.g., in the vicinity of avoided crossings or conical intersections of potential energy surfaces. In such regions the coupling of electronic and nuclear motion induces a strong population transfer between different electronic states. We investigate such non-adiabatic motion for systems where the timedependent Schrödinger equation for the coupled motion can be solved numerically. It is found that the quantum motion of the electron-nuclear density in regions with large non-adiabatic couplings is unexpectedly smooth [3,4]. It is then possible to treat the dynamics classically in the complete phase space of electronic and nuclear degrees of freedom [5,6].

1. Albert, J., Hader, K., Engel, V., On the calculation of time-dependent electron ux within the Born-Oppenheimer approximation: A ux-ux reection prin- ciple, J. Chem. Phys. 147,241101 (2017).

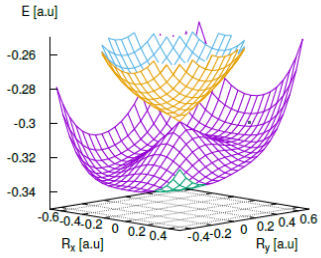

FIG. 1. Conical intersection between two potential energy surfaces in electronically excited states

2. Schaupp, T., Engel, V., On the calculation of time-dependent electron momenta within the Born-Oppenheimer approximation, J. Chem. Phys. 150, 164110 (2019). 3. Hader, K., Albert, J., Gross, E.K.U., Engel, V., Electron-nuclear wave-packet dynamics through a conical intersection, J. Chem. Phys. 146, 074304 (2017). 4. Albert, J., Hader, K., Engel, V., Coupled electron-nuclear quantum dynamics through and around a conical intersection, J. Chem. Phys. 147, 064302 (2017). 5. Albert, J., Kaiser, D., Engel, V., Adiabatic and non-adiabatic electron-nuclear motion: Quantum and classical dynamics, J. Chem. Phys. 144, 171103 (2016). 6. Schaupp, T., Engel, V., A classical ride through a conical intersection, J. Chem. Phys. 150, 034301 (2019).

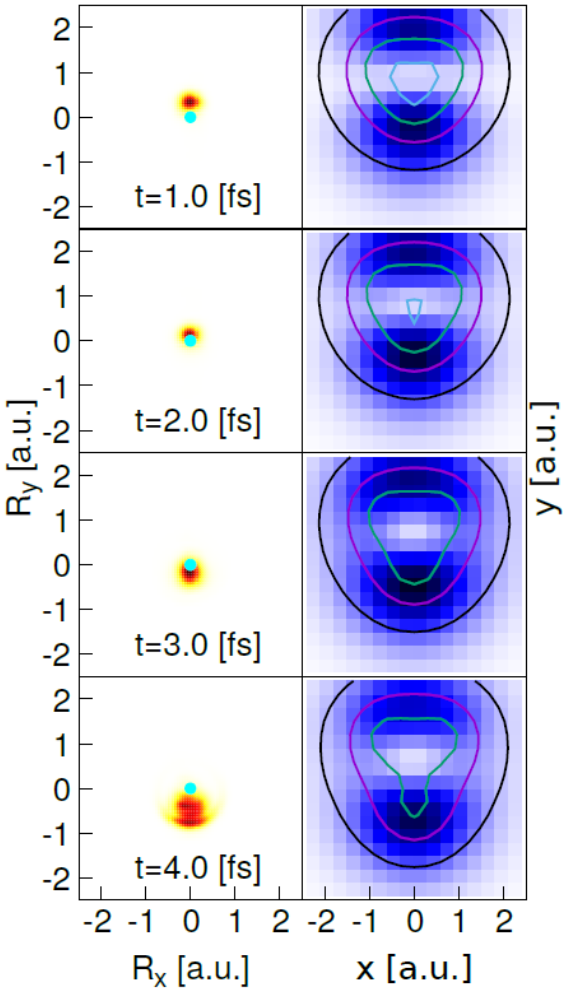

FIG. 2. Nuclear (left hand panels) and electronic (right hand panels) density dynamics through a conical intersection. No substantial changes are observed during the passage. The blue circles indicate the position of the conical intersection.

All interested persons are cordially invited.

Sgd. Prof. Dr. Matthias Wollenhaupt