



18th December 2013 - 2:00 p.m.
CFEL-bldg. 99, seminar room I

Jhon Fredy Pérez-Torres

Institut für Chemie und Biochemie, Freie Universität Berlin

***Electronic flux densities in vibrating H_2^+
in terms of vibronic eigenstates***

The calculation of the electronic flux density (EFD) associated with vibrational motion in the electronic ground state of a molecular system is a challenge, because the customary practice of describing the state in the Born–Oppenheimer approximation (BOA) gives *real* electronic wave function, for which the EFD vanishes [1]. Here we solve the problem in terms of accurate vibronic energy eigenstates ψ_n of the *complete* Hamiltonian of H_2^+ [2]. The total wave function, expressed as a linear combination of the ψ_n is used to compute an accurate EFD, which is compared with approximate EFD computed by scaled coupled–channels (SCCh) approach within the framework of the BOA [3]. Analysis of the flux densities close to the turning points shows that the nuclear wave packet takes longer time (1.4 fs) to change its direction compared to the electronic one (1 fs). On the other hand, analysis of the highly excited stationary states (not included for the computation of the EFD) suggests that resonant states can appear, presumably due to the correlation between the electronic and nuclear motion, i.e., due to non adiabatic effects. This feature calls for investigation of the non Born-Oppenheimer states with energies above the dissociation threshold.

[1] E Schrödinger, *Ann. Phys. (Leipzig)* **81**, 109 (1926).

[2] J F Pérez-Torres, *Phys. Rev. A* **87**, 062512 (2013).

[3] D J Diestler, A Kenfack, J Manz, B Paulus, J F Pérez-Torres and V Pohl, *J. Phys. Chem. A* **117**, 8519 (2013).