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Institutsseminar

Phase or Faith: The Molecular Aharanov-Bohm Effect in Unimolecular Reactions

Prof. Hua Guo

Department of Chemistry and Chemical Biology
University of New Mexico – United States of America

It is a standard practice in chemistry to consider reaction dynamics as nuclear motion on an adiabatic potential energy surface based on the Born-Oppenheimer approximation. This approximation, which forms a cornerstone of modern chemistry, rests on the large disparity between electronic and nuclear masses. However, it also engenders a geometric phase in electronic wavefunction when encircling a conical intersection. While non-adiabatic transitions are known to occur between different adiabatic states near a conical intersection in such processes as internal conversion, it is still commonly believed that the adiabatic dynamics can be reasonably approximated by this single-state adiabatic model. We demonstrate that adiabatic dynamics of photodissociation and unimolecular reactions can be strongly influenced by the geometric phase associated with a conical intersection along the reaction pathway, even when the energy is much lower than the crossing point. This so-called molecular Aharonov-Bohm effect can be thought as a quantum interference, which can significantly affect not only the tunneling lifetimes, but also product state distributions. These results suggest important caveats to adiabatic treatments of reaction dynamics.

References

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Hörsaal G **14:00 Uhr** **22.01.2020**