Coherence as a probe of non-Born-Oppenheimer dynamics

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The breakdown of the Born-Oppenheimer approximation, associated with avoiding crossings and conical intersections of potential-energy surfaces, is known as a driving force of ultrafast photochemistry. While its theoretical description is well established, unambiguous interpretations of experimental measurements remain challenging, especially for larger multidimensional systems.

Coherence, as a superposition of quantum states, represents a microscopic property carrying information on the states character and origin. Once detected as oscillatory signatures in time-resolved spectroscopic signals, it turns into an informative macroscopic observable.

In this contribution I will discuss two examples of how the detected coherence can serve as a probe of the strongly coupled electron-nuclear motion. In the first example, the pseudo-Jahn-Teller effect in pentafluorobenzene leads to the periodic change of excited-state electronic character along the out-of-plane nuclear motion and can be detected as long-lived oscillations in, e.g., time-resolved photoelectron spectra.[1] In the second example, coherent signatures recorded in two-dimensional optical signals of pentacene crystals help to shed light on how the electronic process known as singlet fission is accelerated by nuclear dynamics.[2]

References:

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