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Aspects of conical intersections: Dynamics, bound states embedded in the continuum and short-lived electronic states

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Conical intersections are omnipresent in polyatomic molecules and their presence gives rise to the most severe breakdown of the Born-Oppenheimer approximation. Several general aspects of conical intersections and of the dynamics through them will be addressed. Particular attention will be paid to the question what happens to the potential energy surfaces if the electronic states are metastable. In addition, it is shown that nuclear dynamics on coupled potential surface can lead to bound states embedded in the continuum. Non-Born-Oppenheimer effects are responsible for the binding of these states. Once the Born-Oppenheimer approximation is introduced, these states at best become resonances which decay via potential tunnelling. The tunnelling is completely suppressed by the coupling between the electronic states. Another important issue which will be touched upon is dynamics in the presence of conical intersections in macrosystems. Here, the number of modes is extremely large and, nevertheless, their impact close to the intersections cannot be neglected. It is shown that effective modes can be derived which reproduce exactly the short-time dynamics of the whole macrosystem at low cost. Numerical examples are given.

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