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Quantum Transition State Theory

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The main idea of Wigner's transition state theory (TST) is to compute reaction rates from the flux through a dividing surface placed between reactants and products. In order not to overestimate the rate the dividing surface needs to have the no- recrossing property, i.e. reactive trajectories cross the dividing surface exactly once, and nonreactive trajectories do not cross it at all. The long standing problem of how to construct such a diving surface for multi-degree-of-freedom systems was solved only recently using ideas from dynamical systems theory. Here a normal form allows for a local decoupling of the classical dynamics which leads to the explicit construction of the phase space structures that govern the reaction dynamics through transition states. The dividing surface is spanned by a normally hyperbolic manifold which is the mathematical manifestation of the transition state as an unstable invariant subsystem of one degree of freedom less than the full system. The mere existence of a quantum version of TST is discussed controversially in the literature. The key isssue is the presence of quantum mechanical tunneling which prohibits the existence of a local theory analogous to the classical case. Various approaches have been devloped to overcome this problem by propagating quantum wavefunctions through the transition state region. These approaches have in common that they are computationally very expensive which seriously limits their applicability. In contrast the approach by Roman Schubert, Stephen Wiggins and myself is local in nature. A quantum normal form allows us to locally decouple the quantum dynamics to any desired order in Planck's constant. This yields not only the location of the scattering and resonance wavefunctions relative to the classical phase space structures, but also leads to very efficient algorithms to compute cumulative reaction probabilities and Gamov-Siegert resonances which are the quantum imprints of the transition state.