

CHAPTER OVERVIEW

3: Time-Evolution Operator

Dynamical processes in quantum mechanics are described by a Hamiltonian that depends on time. Naturally the question arises how do we deal with a time-dependent Hamiltonian? In principle, the time-dependent Schrödinger equation can be directly integrated choosing a basis set that spans the space of interest. Using a potential energy surface, one can propagate the system forward in small time-steps and follow the evolution of the complex amplitudes in the basis states. In practice even this is impossible for more than a handful of atoms, when you treat all degrees of freedom quantum mechanically. However, the mathematical complexity of solving the time-dependent Schrödinger equation for most molecular systems makes it impossible to obtain exact analytical solutions. We are thus forced to seek numerical solutions based on perturbation or approximation methods that will reduce the complexity. Among these methods, time-dependent perturbation theory is the most widely used approach for calculations in spectroscopy, relaxation, and other rate processes. In this section we will work on classifying approximation methods and work out the details of time-dependent perturbation theory.

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