

CHAPTER OVERVIEW

6: Adiabatic Approximation

In quantum mechanics, the adiabatic approximation refers to those solutions to the Schrödinger equation that make use of a time-scale separation between fast and slow degrees of freedom, and use this to find approximate solutions as product states in the fast and slow degrees of freedom. Perhaps the most fundamental and commonly used version is the Born–Oppenheimer (BO) approximation, which underlies much of how we conceive of molecular electronic structure and is the basis of potential energy surfaces. The BO approximation assumes that the motion of electrons is much faster than nuclei due to their large difference in mass, and therefore electrons adapt very rapidly to any changes in nuclear geometry. That is, the electrons “adiabatically follow” the nuclei. As a result, we can solve for the electronic state of a molecule for fixed nuclear configurations. Gradually stepping nuclear configurations and solving for the energy leads to a potential energy surface, or adiabatic state. Much of our descriptions of chemical reaction dynamics is presented in terms of propagation on these potential energy surfaces. The barriers on these surfaces are how we describe the rates of chemical reactions and transition state. The trajectories along these surfaces are used to describe mechanism.

More generally, the adiabatic approximation can be applied in other contexts in which there is a time-scale separation between fast and slow degrees of freedom. For instance, in the study of vibrational dynamics when the bond vibrations of molecules occur much faster than the intermolecular motions of a liquid or solid. It is also generally implicit in a separation of the Hamiltonian into a system and a bath, a method we will often use to solve condensed matter problems. As widely used as the adiabatic approximation is, there are times when it breaks down, and it is important to understand when this approximation is valid, and the consequences of when it is not. This will be particularly important for describing time-dependent quantum mechanical processes involving transitions between potential energy sources.

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