CHAPTER OVERVIEW

14: Fluctuations in Spectroscopy

Here we will describe how fluctuations are observed in experimental observables, as is common to experiments in molecular condensed phases. As our example, we will focus on absorption spectroscopy and how environmentally induced dephasing influences the absorption lineshape. Our approach will be to calculate a dipole correlation function for transition dipole interacting with a fluctuating environment, and show how the time scale and amplitude of fluctuations are encoded in the lineshape. Although the description here is for the case of a spectroscopic observable, the approach can be applied to any such problems in which the deterministic motions of an internal variable of a quantum system are influenced by a fluctuating environment.

We also aim to establish a connection between this problem and the Displaced Harmonic Oscillator model. Specifically, we will show that a frequency-domain representation of the coupling between a transition and a continuous distribution of harmonic modes is equivalent to a time-domain picture in which the transition energy gap fluctuates about an average frequency with a statistical time scale and amplitude given by the distribution of coupled modes. Thus an absorption spectrum is merely a spectral representation of the dynamics experienced by a experimentally probed transition.
