# CHAPTER OVERVIEW

## 2: Diagrammatic Perturbation Theory

In practice, the nonlinear response functions as written above provide little insight into what the molecular origin of particular nonlinear signals is. These multiply nested terms are difficult to understand when faced the numerous light-matter interactions, which can take on huge range of permutations when performing experiments on a system with multiple quantum states. The different terms in the response function can lead to an array of different nonlinear signals that vary not only microscopically by the time-evolution of the molecular system, but also differ macroscopically in terms of the frequency and wavevector of the emitted radiation.

Diagrammatic perturbation theory (DPT) is a simplified way of keeping track of the contributions to a particular nonlinear signal given a particular set of states in $H_0$ that are probed in an experiment. It uses a series of simple diagrams to represent the evolution of the density matrix for $H_0$, showing repeated interaction of ρ with the fields followed by time-propagation under $H_0$. From a practical sense, DPT allows us to interpret the microscopic origin of a signal with a particular frequency and wavevector of detection, given the specifics of the quantum system we are studying and the details of the incident radiation. It provides a shorthand form of the correlation functions contributing to a particular nonlinear signal, which can be used to understand the microscopic information content of particular experiments. It is also a bookkeeping method that allows us to keep track of the contributions of the incident fields to the frequency and wavevector of the nonlinear polarization.

There are two types of diagrams we will discuss, Feynman and ladder diagrams, each of which has certain advantages and disadvantages. For both types of diagrams, the first step in drawing a diagram is to identify the states of $H_0$ that will be interrogated by the light-fields. The diagrams show an explicit series of absorption or stimulated emission events induced by the incident fields which appear as action of the dipole operator on the *bra* or *ket* side of the density matrix. They also symbolize the coherence or population state in which the density matrix evolves during a given time interval. The trace taken at the end following the action of the final dipole operator, i.e. the signal emission, is represented by a final wavy line connecting dipole coupled states.