7.1: Introduction to Light-Matter Interactions

The term “spectroscopy” comes from the Latin “spectron” for spirit or ghost and the Greek "σκοπιεν" for to see. These roots are telling because in molecular spectroscopy you use light to interrogate matter, but you actually never see the molecules, only their influence on the light. Different types of spectroscopy give you different perspectives. This indirect contact with the microscopic targets means that the interpretation of spectroscopy requires a model, whether it is stated or not. Modeling and laboratory practice of spectroscopy are dependent on one another, and spectroscopy is only as useful as its ability to distinguish different models. This makes an accurate theoretical description of the underlying physical process governing the interaction of light and matter important.

Quantum mechanically, we will treat spectroscopy as a perturbation induced by the light which acts to couple quantum states of the charged particles in the matter, as we have discussed earlier. Our starting point is to write a Hamiltonian for the light–matter interaction, which in the most general sense would be of the form

$$H = H_M + H_L + H_{LM} \tag{7.1.1}$$

Although the Hamiltonian for the matter may be time-dependent, we will treat the Hamiltonian for the matter H_M as time-independent, whereas the electromagnetic field H_L and its interaction with the matter H_{LM} are time-dependent. A quantum mechanical treatment of the light would describe the light in terms of photons for different modes of electromagnetic radiation, which we will describe later. We begin with a semiclassical treatment of the problem, which describes the matter quantum mechanically and the light field classically. We assume that a light field described by a time-dependent vector potential acts on the matter, but the matter does not influence the light. (Strictly, energy conservation requires that any change in energy of the matter be matched with an equal and opposite change in the light field.) For the moment, we are just interested in the effect that the light has on the matter. In that case, we can really ignore H_L, and we have a Hamiltonian for the system that is

$$\begin{aligned} H &\approx H_M + H_{LM}(t) \\ &= H_0 + V(t) \end{aligned}$$

which we can solve in the interaction picture. We will derive an explicit expression for the Hamiltonian H_{LM} in the Electric Dipole Approximation. Here, we will derive a Hamiltonian for the light–matter interaction, starting with the force experienced by a charged particle in an electromagnetic field, developing a classical Hamiltonian for this interaction, and then substituting quantum operators for the matter:

$$\begin{aligned} p &\rightarrow -i\hbar\hat{\nabla} \\ x &\rightarrow \hat{x} \end{aligned} \tag{7.1.2}$$

In order to get the classical Hamiltonian, we need to work through two steps:

1. describe electromagnetic fields, specifically in terms of a vector potential, and
2. describe how the electromagnetic field interacts with charged particles.