Harmonic Perturbations

We now consider perturbations which depend upon time. Usually we can Fourier analyze the time dependence and view the perturbation as a superposition of many perturbations that each depend harmonically on the time. Therefore, the next thing to consider is a perturbation harmonically varying in time. As a good example, which we shall consider later, consider the effect of an electromagnetic wave incident upon an atomic electron. If the wave is nearly monochromatic then one can model the time dependence of the associated perturbation as harmonic.

Suppose, then, that the perturbation is of the form

\[ V(t) = V e^{i\omega t} + V^\dagger e^{-i\omega t}, \quad \omega \geq 0 \]

where \( V \) is some time-independent operator and \( \omega \) is a given frequency. (Note that when considering transitions between former stationary states there are now two time scales in the problem: that associated with the perturbation, and that defined by the difference in unperturbed energies.) We again suppose that at the initial time \( t = 0 \) the system is in an eigenstate \( |i\rangle \) of \( H_0 \). We ask what is the probability for finding the system in the state \( |n\rangle \) at time \( t \) \( (n \neq i) \). Using our previous results we have that (exercise)

\[
P(i \rightarrow n; i \neq n) = \left| \frac{1}{\hbar} \int_0^t dt' (V_{ni} e^{i\omega t'} + V^\dagger_{ni} e^{-i\omega t'}) e^{i\omega_{ni} t} \right|^2, \quad \omega_{ni} := \frac{E_n - E_i}{\hbar}.
\]

The integral is the sum of two terms, where each is of the form encountered in the time-independent perturbation case, except that now the frequency in the exponents is shifted via

\[
\omega_{ni} \rightarrow \omega_{ni} \pm \omega.
\]

This allows us to use our previous analysis for the late time transition rates, provided the frequencies are modified as shown above in order to handle the current situation.

In detail, after taking the absolute-square in the above formula for the probability, we have 3 terms: two “direct terms” and a cross term. Each has a vanishing denominator “on resonance”, that is, when the initial and final states are such that \( \omega_{ni} \pm \omega = 0 \). As before, the limit as the denominator vanishes for each of these terms is finite and grows with time. Thus, as before, the principal transitions at “late times” are such that one of these frequency combinations vanishes. The direct terms have the square of the growing probability, while the cross term only involves this quantity linearly. The cross term can therefore be ignored compared to the direct terms.
In summary, at large enough times, the only transitions with appreciable probability will be those for which either

\[ \omega_{ni} + \omega = 0 \]

or

\[ \omega_{ni} - \omega = 0. \]

Of course, only one of these two situations can occur for a given choice of frequency \( \omega \) and for a given initial and final state. In the first case we have

\[ \omega_{ni} + \omega = 0 \iff E_n = E_i - \hbar \omega, \]

and in the second case we have

\[ \omega_{ni} - \omega = 0 \iff E_n = E_i + \hbar \omega. \]

So, using the unperturbed energy \( H_0 \) to interpret these results, we have the following situation. When \( E_n = E_i - \hbar \omega \) we speak of stimulated emission, since the perturbation has (from the unperturbed point of view) caused the system to “emit” a quantum of energy \( \hbar \omega \). When \( E_n = E_i + \hbar \omega \) we speak of stimulated absorption, since the perturbation has (from the unperturbed point of view) caused the system to “absorb” a quantum of energy \( \hbar \omega \).

To get a formula for the late time transition rates we simply have to make the appropriate shift

\[ \omega_{ni} \rightarrow \omega_{ni} \pm \omega \]

in our previous formulas. In the case of a (quasi-)continuum of final states we get

\[ \frac{d}{dt} P(i \rightarrow n, i \neq n) = \frac{2\pi}{\hbar} \left[ |V_{ni}|^2 \delta(E_n - E_i + \hbar \omega) + |V_{ni}^\dagger|^2 \delta(E_n - E_i - \hbar \omega) \right]. \]

This is yet another version of Fermi’s Golden Rule. Note that, since

\[ |V_{ni}|^2 = V_{ni}^* V_{ni} = V_{in}^\dagger (V_{in}^\dagger)^* = |V_{in}^\dagger|^2 \]

the transition rate (per unit energy) for \( i \rightarrow n \) is the same as that for \( n \rightarrow i \), a phenomenon often called “detailed balancing”.

**What happens when you shine light on an atom?**

We shall study the perturbative dynamics of an atomic electron when exposed to a (weak) plane electromagnetic wave. This is a simple model which can be used to answer (at least in part) the question posed in the title of this section. The story is a little long, but I think it is useful and instructive.
We are principally interested in the case where the electron is, in the absence of the perturbation, in a “bound stationary state” of some potential, with the electromagnetic field serving to stimulate transitions between the bound or ionized states. Our strategy is as follows. We model the atom as a spinless particle bound by some potential $V_0$. Of course, more sophisticated models of the atom are available. We could specialize $V_0$ to be a central potential, or even the Coulomb potential, but we won’t have to make any such choices for a while. Thus, the unperturbed Hamiltonian is of the form

$$H_0 = \frac{p^2}{2m} + V_0(\vec{X}).$$

The unperturbed stationary states are just the energy eigenstates of $H_0$ — these are the “energy levels” of the atom.

Now we want to introduce the electromagnetic radiation. The total electromagnetic field that the particle interacts with will then be the superposition of the field represented by $V_0$ (e.g., an electrostatic field) with the field of the incident radiation. Let us describe the radiation using the vector potentials $(\phi(\vec{r},t), \vec{A}(\vec{r},t))$. It is a standard result of electromagnetic theory that, in regions of space free of electromagnetic sources, it is always possible to choose the electromagnetic potentials so that they are in the “radiation gauge”:

$$\phi = 0, \quad \nabla \cdot \vec{A} = 0.$$

In this gauge the electric and magnetic fields are determined by the potentials according to

$$\vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t}, \quad \vec{B} = \nabla \times \vec{A}.$$ 

We wish to use this description to incorporate the electromagnetic perturbation only. We could, if desired, use this description also to include the $V_0$ contribution to the total electromagnetic field. In this case, though, one is not easily able to make the split between the unperturbed system and the perturbation.

Note that we are using a physical model in which the EM radiation is specified once and for all, ignoring all electromagnetic sources in our system. Of course, the atomic electron itself also serves as a source of an EM field. Thus we are in an approximation where this effect can be ignored. Nonetheless, at the end of the day we will interpret the dynamics as energy level transitions accompanied by absorption or emission of radiation by the electron! This is a typical “physical” analysis in which we make suitable approximations but use our knowledge of physical behavior to interpret the results, even if our interpretation goes beyond the validity of the mathematical model. In physics, this kind of reasoning is something akin to an art form.

Next, I remind you of the form of the Hamiltonian for a particle of charge $q$ and mass $m$ moving in a given electromagnetic field. We have

$$H = \frac{1}{2m} (\vec{P} - \frac{q}{c} \vec{A})^2 + q\phi,$$
where \((\phi, \vec{A})\) are operators, possibly depending upon time, obtained by taking the scalar and vector potentials \((\phi(\vec{r}, t), \vec{A}(\vec{r}, t))\) and viewing them as operators via
\[
\phi = \phi(\vec{X}, t), \quad \vec{A} = \vec{A}(\vec{X}, t).
\]
The radiation field has \(\phi = 0\). If you like, you can think of \(V_0\) as being obtained from the \(q\phi\) contribution to \(H\). In any case, the perturbation comes from the terms involving \(\vec{A}\). We are, of course, assuming that the components of the vector potential are suitably small so that their contribution to the matrix elements of \(H\) are small compared to the matrix elements of \(H_0\). Since the vector potential is to be “small”, in a first approximation we can neglect the term quadratic in \(\vec{A}\) in the above Hamiltonian. We are left with the following (approximate) Hamiltonian:
\[
H = H_0 + V,
\]
where
\[
V = -\frac{q}{mc} \vec{A} \cdot \vec{P}.
\]
We will use this Hamiltonian, in the context of perturbation theory, to investigate the behavior of an atomic electron in the presence of an electromagnetic wave.

**The radiation field**

We have seen that we can describe the radiation field by a vector potential. The Maxwell equations determine the vector potential, in the radiation gauge, according to
\[
\nabla^2 \vec{A} - \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} = 0, \quad \nabla \cdot \vec{A} = 0.
\]
It is easy to write down the general solution to this equation. We will specialize to a solution representing a plane-polarized electromagnetic wave traveling in the direction of the unit vector \(\hat{n}\):
\[
\vec{A}(\vec{r}, t) = \hat{e} \int_{-\infty}^{\infty} d\omega A(\omega) e^{-i\omega(t - \frac{1}{c} \hat{n} \cdot \vec{r})},
\]
where \(A(\omega) = A^*(\omega)\) determines the frequency composition of the wave. Because the vector potential is “transverse”, \(\nabla \cdot \vec{A} = 0\), we have that
\[
\hat{e} \cdot \hat{n} = 0.
\]
Evidently, the vector \(\hat{e}\) determines the polarization.

A general radiation field can be viewed as a superposition of plane waves of the type shown above. The superposition is over the propagation directions and polarizations. If we have time, later we will consider this case. For now we will stick with plane waves of a fixed polarization and propagation direction.