

## 9. Time-dependent Perturbation Theory

Until this point, we have confined our attention to those situations in which the potential, and, by implication, the Hamiltonian, is not an explicit function of time. This allowed us to solve the time-dependent Schrödinger equation by separation of variables, *i.e.*,  $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-iEt/\hbar}$ .

We now want to treat *transitions* between quantum states, which are driven by a *time-dependent* Hamiltonian. This moves us from the realm of *statics* to *dynamics*.

### 9.1 Two-level systems

Consider a time-independent  $H_0$  for which two e.s. form a complete set:  $H_0|a\rangle = E_a|a\rangle$  and  $H_0|b\rangle = E_b|b\rangle$ ,  $\exists \langle a|b\rangle = \delta_{ab}$ .

Any state can be expressed as a linear combination of these e.s.:

$\Psi(t) = c_a|a\rangle e^{-iE_a t/\hbar} + c_b|b\rangle e^{-iE_b t/\hbar}$ , where  $c_a$  and  $c_b$  are constants and  $|c_a|^2 + |c_b|^2 = 1$ .

Suppose we add a time-dependent  $H'(t)$ . The form of the general  $\Psi$  is still the same, except that  $c_a$  and  $c_b$  are now explicit functions of  $t$ . Determining these  $c_a(t)$  and  $c_b(t)$  is somewhat more complicated than it was when the perturbing term was time-independent.

Substituting  $H = H_0 + H'(t)$  into  $H\Psi = i\hbar\frac{\partial\Psi}{\partial t}$  and eliminating equivalent terms, we get

$$c_a H' |a\rangle e^{-iE_a t/\hbar} + c_b H' |b\rangle e^{-iE_b t/\hbar} \\ = i\hbar \dot{c}_a |a\rangle e^{-iE_a t/\hbar} + i\hbar \dot{c}_b |b\rangle e^{-iE_b t/\hbar}.$$

Operate on this equation with  $\langle a|$  to obtain:

$$\dot{c}_a = -\frac{i}{\hbar} [c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar}], \text{ where} \\ H'_{ij} \equiv \langle i|H'|j\rangle \text{ and } H'_{ij} = (H'_{ji})^* \text{ due to} \\ \text{Hermiticity.}$$

$$\text{Similarly, } \dot{c}_b = -\frac{i}{\hbar} [c_b H'_{bb} + c_a H'_{ba} e^{+i(E_b - E_a)t/\hbar}].$$

It is often the case that the diagonal matrix elements of  $H'$  vanish naturally, or can be handled in other ways. If  $H'_{aa} = 0 = H'_{bb}$ , then

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b \text{ and } \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{+i\omega_0 t} c_a,$$

where  $\omega_0 \equiv \frac{E_b - E_a}{\hbar}$  and  $E_b > E_a \Rightarrow \omega_0 > 0$ .

## Small perturbations

So far, the general equation for  $\dot{c}_a$  and  $\dot{c}_b$  have involved no approximations. Let us now assume that  $H'$  is 'small' enough that we can solve Schrödinger's equation by a process of successive approximations.

Suppose that the particle starts out in state  $a$  ( $c_a(0) = 1$ ,  $c_b(0) = 0$ ) and that the perturbing  $H'$  has no diagonal elements.

To zeroth order, the particle remains in that state:  $c_a^{(0)}(t) = 1$ ,  $c_b^{(0)}(t) = 0$ .

To first order, insert the zeroth-order expressions on the right side of the equations for  $\dot{c}_a$  and  $\dot{c}_b$ :

$$\dot{c}_a = 0 \Rightarrow c_a(t) = 1$$

$$\dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{+i\omega_0 t}$$

$$\Rightarrow c_b(t) = -\frac{i}{\hbar} \int_0^t dt' H'_{ba}(t') e^{+i\omega_0 t'}$$

Note that each expression contains *both* zeroth- and first-order terms.

A similar substitution yields the expression for  $c_a$  to second order:

$$c_a(t) = 1 - \frac{1}{\hbar^2} \int_0^t dt' H'_{ab}(t') e^{-i\omega_0 t'} \left[ \int_0^{t'} dt'' H'_{ba}(t'') e^{+i\omega_0 t''} \right].$$

The second-order expression for  $c_b$  is unchanged from first order.

If we continued this process, we would find that  $c_a$  is modified with every *even* order and  $c_b$  with every *odd*.

## Small sinusoidal perturbations

Suppose further that the perturbation is sinusoidal:  $H'(\mathbf{r}, t) = V(\mathbf{r}) \cos(\omega t)$ . Then,  $H'_{ab} = V_{ab} \cos(\omega t)$ , where  $V_{ab} \equiv \langle a|V|b \rangle$  and the diagonal matrix elements are assumed to vanish.

$$\begin{aligned} \text{To first order, } c_b(t) &\cong -\frac{i}{\hbar} V_{ba} \int_0^t dt' \cos(\omega t') e^{i\omega_0 t'} \\ &= -\frac{iV_{ba}}{2\hbar} \int_0^t dt' [e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'}] \\ &= -\frac{V_{ba}}{2\hbar} \left[ \frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega} \right]. \end{aligned}$$

This result can be simplified by letting the driving frequency  $\omega$  be close to the natural transition frequency  $\omega_0$ ,  
*i.e.*,  $|\omega_0 - \omega| \ll (\omega_0 + \omega)$ .

Then the second term in  $c_b(t)$  is much larger than the first, so that  $c_b(t)$  can be rewritten as  $c_b(t) \cong -i \frac{V_{ba}}{\hbar} \frac{\sin [(\omega_0 - \omega)t/2]}{\omega_0 - \omega} e^{i(\omega_0 - \omega)t/2}$ .

One can now find the probability that a particle which started out in  $|a\rangle$  will be found in  $|b\rangle$  at  $t$ , called the transition probability:

$$P_{a \rightarrow b}(t) \equiv |c_b(t)|^2 \cong \frac{|V_{ba}|^2 \sin^2 [(\omega_0 - \omega)t/2]}{\hbar^2 (\omega_0 - \omega)^2}.$$

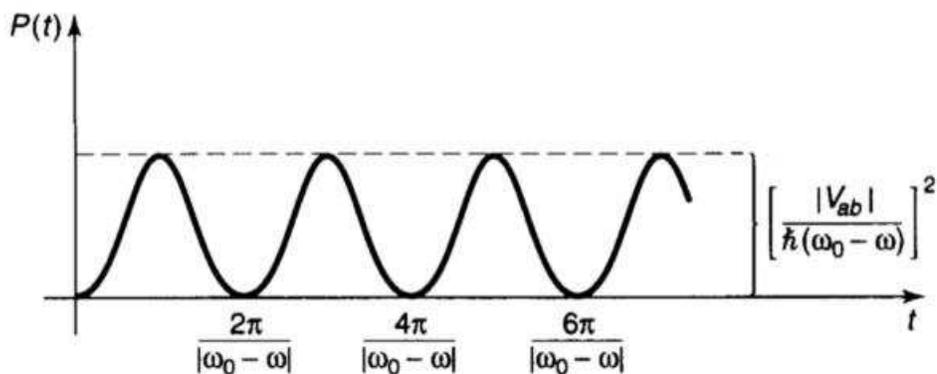


Figure 9.1 - Transition probability as a function of time for a sinusoidal perturbation.

The most surprising aspect of this result is that  $P_{a \rightarrow b}$  oscillates between zero and a maximum value (which depends on  $V_{ab}$ ). In other words, the probability of a transition drops to zero periodically. This is *not* an artifact of perturbation theory.

The strong effect of  $\omega \approx \omega_0$  on  $P_{a \rightarrow b}(t)$  is easily illustrated by plotting  $P_{a \rightarrow b}$  as a function of  $\omega$  for fixed  $t$ , yielding a function which falls off rapidly for  $\omega \neq \omega_0$ .

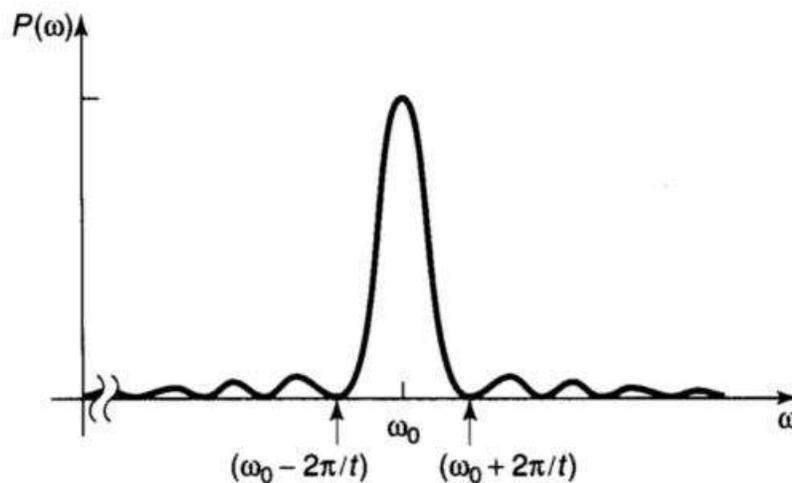


Figure 9.2 - Transition probability as a function of driving frequency for a sinusoidal perturbation.

## 9.2 Emission and absorption of radiation

An electromagnetic wave consists of transverse and mutually perpendicular electric and magnetic fields which oscillate with  $t$ , of which principally  $\mathbf{E}$  interacts with an atom.

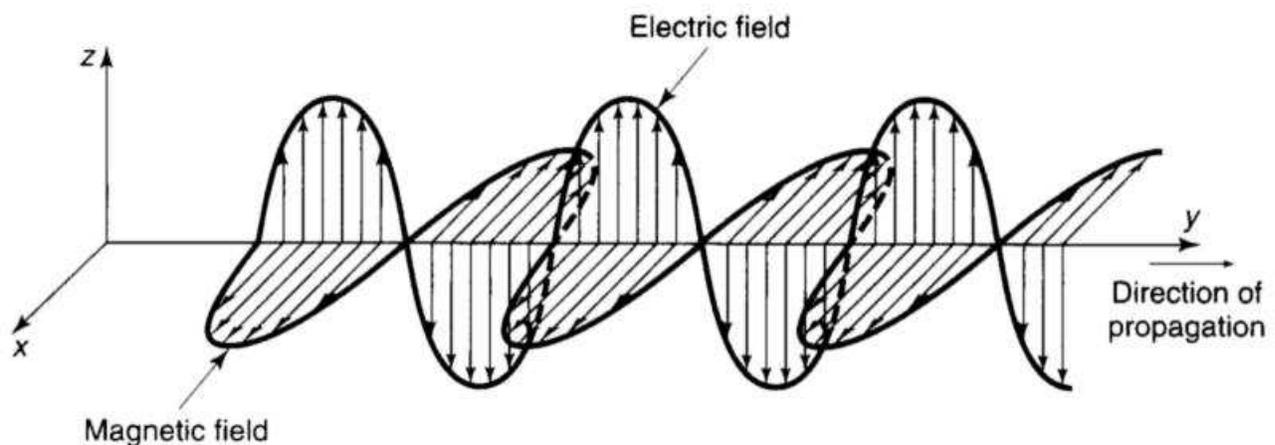


Figure 9.3 - An electromagnetic wave.

If the wavelength is long compared with the size of an atom (which is the case for all light less energetic than x rays), we can ignore the spatial variation of the field.

It is therefore reasonable to approximate the interaction between an atom and a light wave with the interaction between an electron and an oscillating spatially-uniform electric field:

$$H' = -q \int d\mathbf{r} \cdot \mathbf{E} = -qzE_0 \cos(\omega t).$$

$\therefore H'_{ba} = -\wp E_0 \cos(\omega t)$ , where  $\wp \equiv q\langle b|z|a\rangle$ , or, simply,  $V_{ba} = -\wp E_0$ .

Putting this all together, we get an expression for 'photoabsorption':

$$P_{a \rightarrow b}(t) \cong \left( \frac{|\wp| E_0}{\hbar} \right)^2 \frac{\sin^2 [(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}.$$

In this process, the atom absorbs energy

$E_b - E_a = \hbar\omega_0$  from the electromagnetic field by the promotion of an electron from state  $a$  to  $b$ . We refer to this as 'absorbing a photon', even though we are treating the field classically and the concept of *photon* properly belongs to quantum electrodynamics.

Of course, there is a companion process in which the electron undergoes a transition from state  $b$  to state  $a$ , giving up energy  $E_b - E_a = \hbar\omega_0$  in the process.

We can calculate the probability for this process by assuming that  $c_a(0) = 0$ ,  $c_b(0) = 1$ , and following the above derivation, yielding *exactly* the above result for  $P_{b \rightarrow a}(t)$ . In other words, the absorption and emission of a photon have exactly the same probability, a remarkable result.

If  $E_0$  is due to applied light, then we call the resulting emission 'stimulated emission'. Together with 'population inversion' to augment the numbers of electrons in the excited states, this leads to the possibility of light amplification and lasing.

Even in the absence of applied light, however, quantum statistics requires that  $E_0 > 0$ , leading to so-called 'spontaneous' emission.

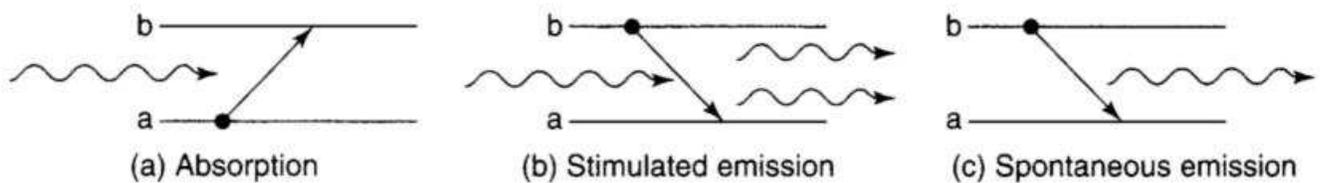


Figure 9.4 - Three ways in which light interacts with atoms: (a) absorption; (b) stimulated emission; (c) spontaneous emission.

# Incoherent perturbations

Since the energy density in an electromagnetic wave is given by  $u = \frac{\epsilon_0}{2} E_0^2$ , the transition probabilities we have calculated are proportional to the energy density of the incoming radiation. Suppose we now consider a situation in which the incoming radiation is electromagnetic waves of many frequencies. It is best then to replace  $u$  with the energy density in the range  $d\omega$  (i.e.,  $u \rightarrow d\omega\rho(\omega)$ ) and integrate over the frequency spectrum:

$$P_{b \rightarrow a}(t) \cong \frac{2|\mathcal{E}|^2}{\epsilon_0 \hbar^2} \int_0^\infty d\omega \rho(\omega) \left\{ \frac{\sin^2 [(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \right\}.$$

Note that this expression assumes that the waves at different frequencies are independent, so that we can add transition probabilities. If, instead, the waves were phase correlated (coherent), we would need to add amplitudes ( $c_b(t)$ ) instead of probabilities ( $|c_b(t)|^2$ ), resulting in additional cross terms.

Since usually the term in braces is sharply peaked about  $\omega \approx \omega_0$  while  $\rho(\omega)$  is slowly varying, we can move  $\rho$  outside the integral:

$$P_{b \rightarrow a}(t) \cong \frac{2|\wp|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) \int_0^\infty d\omega \frac{\sin^2 [(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}.$$

The integral is handled by extending the range to  $x \equiv (\omega_0 - \omega)t/2 = \pm\infty$  (since the integrand is 'very small' out there anyway) and using the definite integral:

$$\int_{-\infty}^{\infty} dx \frac{\sin^2 x}{x^2} = \pi, \text{ so that } P_{b \rightarrow a}(t) \cong \frac{\pi |\wp|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) t.$$

Notice that the transition probability is no longer oscillating with time, but is instead increasing monotonically. Thus we can think of a 'transition rate' ( $R \equiv \frac{dP}{dt}$ ) for the emission of light:  $R_{b \rightarrow a} = \frac{\pi}{\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0)$ .

So far we have been assuming that the perturbing wave is traveling in the  $+y$  direction with polarization in the  $z$  direction. But in fact we are interested in situations where the radiation comes in from all directions, and is polarized in all directions (allowed by its propagation direction). In order to take care of this variation, we must replace  $|\wp|^2$  above with the *average* of  $|\wp \cdot \hat{n}|^2$ , where  $\wp \equiv q\langle b|\mathbf{r}|a\rangle$  and  $\hat{n}$  is the direction of polarization. This can be done choosing the  $z$  axis for the direction of propagation, so that  $\hat{n}$  is in the  $xy$  plane and the vector  $\wp$  is in the  $yz$  plane:

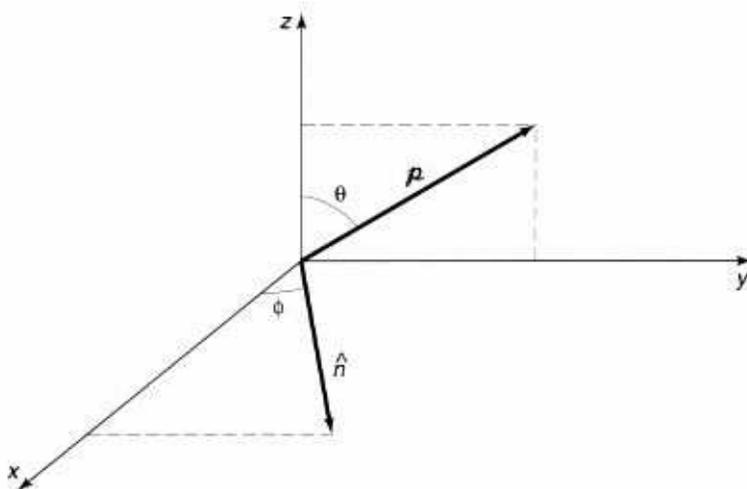


Figure 9.5 - Axes for averaging of  $|\wp \cdot \hat{n}|^2$ .

Averaging over  $\theta$  and  $\phi$  leads to

$$R_{b \rightarrow a} = \frac{\pi}{\epsilon_0 \hbar^2} \frac{|\wp|^2}{3} \rho(\omega_0).$$

## 9.3 Spontaneous emission

In order to ascertain the rate for spontaneous emission, let's follow Einstein's argument regarding the Planck blackbody radiation formula.

Consider a box containing  $N_a$  atoms in the  $a$  state and  $N_b$  atoms in the  $b$  state. Let  $B_{ba}\rho(\omega_0)$  and  $B_{ab}\rho(\omega_0)$  be the transition rates for stimulated emission and absorption into the radiation bath, and  $A$  be the transition rate for 'spontaneous' emission. The net rate of change of  $N_b$  can then be written as

$$\frac{dN_b}{dt} = -N_b A - N_b B_{ba}\rho(\omega_0) + N_a B_{ab}\rho(\omega_0).$$

Suppose that these atoms are in thermal equilibrium with the ambient field. Then,  $\frac{dN_b}{dt} = 0$ , so that one can solve the rhs of that equation to obtain  $\rho(\omega_0) = \frac{A}{(N_a/N_b)B_{ab} - B_{ba}}$ .

But, in thermal equilibrium, we know that the relative occupancy of these states is determined by the Boltzmann factor,

$$\frac{N_a}{N_b} = e^{\hbar\omega_0/k_B T}, \text{ so that } \rho(\omega_0) = \frac{A}{e^{\hbar\omega_0/k_B T} B_{ab} - B_{ba}}.$$

On the other hand, according to Planck's blackbody radiation formula, the energy density of thermal radiation is given by

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}.$$

Comparing these two expressions for  $\rho$ , we conclude that  $B_{ab} = B_{ba}$  and  $A = \frac{\omega^3 \hbar}{\pi^2 c^3} B_{ba}$ .

The first of these equations tells us that the rates of absorption and stimulated emission are equal, which we had already found out.

The second equation tells us the rate for spontaneous emission in terms of that for stimulated emission, which we already know.

$$\text{Thus, } A = \frac{\omega^3 |\rho|^2}{3\pi\epsilon_0 \hbar c^3}.$$

The calculation of spontaneous emission rates has been reduced to the evaluation of matrix elements of the form  $\langle b | \mathbf{r} | a \rangle$ .

Given the rate for spontaneous emission, we can determine the rate at which atoms in an excited state will decay *even in the absence of fields*:  $dN_b = -AN_b dt \Rightarrow N_b(t) = N_b(0)e^{-t/\tau}$ , where  $\tau = 1/A$ .

If there are several lower energy states to which an excited state can decay, then the lifetimes add in reciprocal:  $\tau = \frac{1}{A_1 + A_2 + A_3 + \dots}$ .

Finally, it should be noted that conditions can be derived for which the transition rate/photon emission vanishes. These are known as 'selection rules' for electric-dipole transitions (the case we have been considering).

For the usual situation, in which the atom is spherically symmetric, manipulation shows that electric-dipole radiation cannot occur unless:  $\Delta m = 0, \pm 1$ ;  $\Delta l = \pm 1$ .

The selection rules for these transitions can be attributed to conservation of angular momentum: the atom must give up whatever angular momentum the photon takes away.

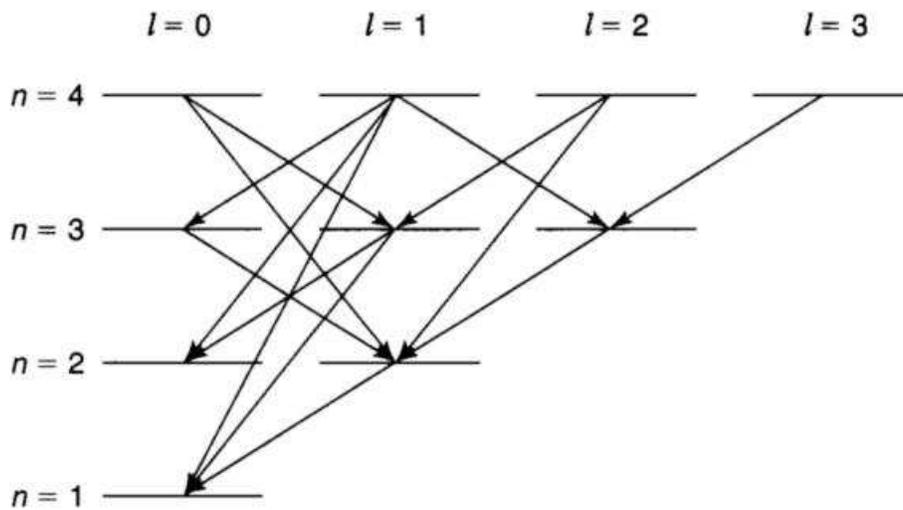


Figure 9.6 - Allowed decays for the first four Bohr levels in hydrogen.

Evidently, not all transitions to lower-energy states can proceed by spontaneous emission. Some are forbidden by the selection rules. Note that the  $2S$  state ( $\psi_{200}$ ) is 'stuck'. It cannot decay because there is no lower-energy state with  $l = 1$ . It is called a *metastable* state, and its lifetime is indeed much longer than that of, for example, the  $2P$  states ( $\psi_{211}, \psi_{210}, \psi_{21-1}$ ). Metastable states do eventually decay, either by collisions or by what are (misleadingly) called *forbidden* transitions, or by multiphoton emission.