9 Perturbation Theory II: Time Dependent Case

In this chapter we'll study perturbation theory in the case that the perturbation varies in time. Unlike the time–independent case, where we mostly wanted to know the bound state energy levels of the system including the perturbation, in the time–dependent case our interest is usually in the *rate* at which a quantum system changes its state in response to the presence of the perturbation.

9.1 The Interaction Picture

Consider the Hamiltonian

$$H(t) = H_0 + \Delta_{\mathrm{S}}(t) \tag{9.1}$$

where H_0 is a time-independent Hamiltonian whose spectrum and eigenstates we understand, and $\Delta_{\mathrm{S}}(t)$ is a perturbation that we now allow to depend on time. (The footnote on $\Delta_{\mathrm{S}}(t)$ is to remind us that this operator has genuine, explicit time dependence even in the Schrödinger picture.) The idea is that H_0 models a system in quiescent state, and we want to understand how eigenstates of H_0 respond as they start to notice the perturbation. In the absence of the time-dependent perturbation, the time evolution operator would be $U_0(t) = \mathrm{e}^{-\mathrm{i}H_0 t/\hbar}$ as appropriate for the model Hamiltonian H_0. We define the *interaction picture* state $|\psi_{\mathrm{I}}(t)\rangle$ as

$$|\psi_{\mathrm{I}}(t)\rangle = U_0^{-1}(t)|\psi_{\mathrm{S}}(t)\rangle\,, \tag{9.2}$$

where $|\psi_{\mathrm{S}}(t)\rangle$ is the Schrödinger picture state evolving in accordance with the TDSE for the full Hamiltonian (9.1). Thus, in the absence of $\Delta_{\mathrm{S}}(t)$, we'd simply have $|\psi_{\mathrm{I}}(t)\rangle = U_0^{-1}(t)\,U_0(t)|\psi(0)\rangle = |\psi(0)\rangle$ so the state $|\psi_{\mathrm{I}}(0)\rangle$ would in fact be independent of time. The presence of the perturbation means that our states do *not* evolve purely according to $U_0(t)$, so $|\psi_{\mathrm{I}}(t)\rangle$ has non-trivial time dependence.

To calculate the evolution of $|\psi_{\mathrm{I}}(t)\rangle$, we differentiate

$$\begin{aligned}
\mathrm{i}\hbar\frac{\partial}{\partial t}|\psi_{\mathrm{I}}(t)\rangle &= -H_0\,\mathrm{e}^{\mathrm{i}H_0 t/\hbar}|\psi_{\mathrm{S}}(t)\rangle + \mathrm{e}^{\mathrm{i}H_0 t/\hbar}\,\mathrm{i}\hbar\frac{\partial}{\partial t}|\psi_{\mathrm{S}}(t)\rangle \\
&= -H_0\,\mathrm{e}^{\mathrm{i}H_0 t/\hbar}|\psi_{\mathrm{S}}(t)\rangle + \mathrm{e}^{\mathrm{i}H_0 t/\hbar}\,(H_0 + \Delta(t))|\psi_{\mathrm{S}}(t)\rangle \\
&= U_0^{-1}(t)\,\Delta(t)\,U_0(t)|\psi_{\mathrm{I}}(t)\rangle\,,
\end{aligned} \tag{9.3}$$

where we've used the full TDSE to evaluate $\partial|\psi_{\mathrm{S}}\rangle/\partial t$, and in the last line we've written our state back in terms of the interaction picture. Similarly, the expectation value of an operator A_{S} in the Schrödinger picture becomes

$$\langle\psi_{\mathrm{S}}(t)|A_{\mathrm{S}}|\psi_{\mathrm{S}}(t)\rangle = \langle\psi_{\mathrm{I}}(t)|U_0^{-1}(t)A_{\mathrm{S}}U_0(t)|\psi_{\mathrm{I}}(t)\rangle \tag{9.4}$$

in terms of the interaction picture states, so we define the interaction picture operator $A_{\mathrm{I}}(t)$ by

$$A_{\mathrm{I}}(t) = U_0^{-1}(t)A_{\mathrm{S}}U_0(t) \tag{9.5}$$

again using just the evolution operators of the unperturbed, rather than full, Hamiltonian. Infinitesimally, this is

$$\frac{d}{dt}A_{\mathrm{I}}(t) = \frac{\mathrm{i}}{\hbar}[H_0, A_{\mathrm{I}}(t)] + U_0^{-1}(t)\frac{\partial A_{\mathrm{I}}(t)}{\partial t}U_0(t) \tag{9.6}$$

where the final term comes from the explicit time dependence present even in the Schrödinger picture operator. In this sense, the interaction picture is 'halfway between' the Schrödinger picture, in which states evolve and operators are time independent, and the Heisenberg picture, in which states are always taken at their initial value $|\psi(0)\rangle$, but operators evolve according to the full Hamiltonian. In the interaction picture, states evolve by just the time-dependent perturbation as

$$\mathrm{i}\hbar\frac{\partial}{\partial t}|\psi_{\mathrm{I}}(t)\rangle = \Delta_{\mathrm{I}}(t)|\psi_{\mathrm{I}}(t)\rangle \tag{9.7}$$

where $\Delta_{\mathrm{I}}(t) = U_0^{-1}(t)\Delta(t)U_0(t)$ is the perturbation in the interaction picture, whilst operators also evolve, but only via the model Hamiltonian.

It will turn out to be useful to introduce an interaction picture time evolution operator $U_{\mathrm{I}}(t)$ defined so that

$$|\psi_{\mathrm{I}}(t)\rangle = U_{\mathrm{I}}(t)|\psi_{\mathrm{I}}(0)\rangle \qquad \text{for any initial state } |\psi_{\mathrm{I}}(0)\rangle \in \mathcal{H}\,. \tag{9.8}$$

From (9.3) we find that $U_{\mathrm{I}}(t)$ satisfies the differential equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}U_{\mathrm{I}}(t) = \Delta_{\mathrm{I}}(t)\,U_{\mathrm{I}}(t)\,. \tag{9.9}$$

Note that since the operator $\Delta_{\mathrm{I}}(t)$ itself depends on time, we cannot immediately integrate this to write $U_{\mathrm{I}}(t)$ in terms of the exponential of $\Delta_{\mathrm{I}}(t)$: in particular it is generally *not* correct to claim

$$U_{\mathrm{I}}(t) \overset{?}{=} \exp\left(-\frac{\mathrm{i}}{\hbar}\int_0^t \Delta_{\mathrm{I}}(t')\,dt'\right)\,, \tag{9.10}$$

because since the operator $\Delta_{\mathrm{I}}(t)$ itself now depends on time, in general

$$[\Delta_{\mathrm{I}}(t), \Delta_{\mathrm{I}}(t')] \neq 0\,.$$

Thus, when expanding the exponential as a power series, we'd have to commute the operators at different times through one another.

So far our considerations have been exact, but to make progress we must now approximate. To do so, it'll be convenient to rewrite (9.9) as an integral equation[77]

$$U_{\mathrm{I}}(t) = 1 - \frac{\mathrm{i}}{\hbar}\int_0^t \Delta_{\mathrm{I}}(t')\,U_{\mathrm{I}}(t')\,dt' \tag{9.11}$$

in which the operator $U_{\mathrm{I}}(t)$ we wish to understand also appears on the *rhs* inside the integral. We now replace the $U_{\mathrm{I}}(t')$ in the integral (9.11) by its value according to its own equation, obtaining

$$U_{\mathrm{I}}(t) = 1 - \frac{\mathrm{i}}{\hbar}\int_0^t \Delta_{\mathrm{I}}(t_1)\,dt_1 + \left(-\frac{\mathrm{i}}{\hbar}\right)^2\int_0^t \Delta_{\mathrm{I}}(t_1)\left[\int_0^{t_1}\Delta_{\mathrm{I}}(t_2)\,U_{\mathrm{I}}(t_2)\,dt_2\right]dt_1\,. \tag{9.12}$$

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[77] To obtain this equation, we've just integrated (9.9) using the initial condition $U_{\mathrm{I}}(0) = 1$.

The term containing $U_{\rm I}(t)$ on the *rhs* now has two explicit powers of the perturbation $\Delta(t)$, so may be hoped to be of lower order in our perturbative treatment. Iterating this procedure gives

$$U_{\rm I}(t) = \sum_{n=0}^{\infty}\left(-\frac{\rm i}{\hbar}\right)^n \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n\, \Delta_{\rm I}(t_1)\,\Delta_{\rm I}(t_2)\cdots\Delta_{\rm I}(t_n) \tag{9.13}$$

in general. Note that the operators $\Delta(t_i)$ at different times do not necessarily commute — they appear in this expression in a time–ordered sequence, with the integrals taken over the range

$$0 \le t_n \le t_{n-1} \le \cdots \le t_1 \le t\,.$$

Instead of the naïve expression (9.10), we often write the series (9.13) as

$$U_{\rm I}(t) = {\rm T}\exp\left(-\frac{\rm i}{\hbar}\int_0^t \Delta_{\rm I}(t')\,dt'\right) \tag{9.14}$$

for short, where the *time–ordered exponential*[78] $\mathrm{T}\exp(\cdots)$ is defined by the series (9.13). It's a good exercise to check that this time–ordered exponential is equal to the usual exponential in the case that $[\Delta(t_1),\Delta(t_2)] = 0$ for all t_1 and t_2.

The interaction picture perturbation is $\Delta_{\rm I}(t) = U_0^{-1}(t)\Delta_{\rm S}(t)\,U_0(t)$, so we can also write (9.13) as

$$U_{\rm I}(t) = \sum_{n=0}^{\infty}\left(-\frac{\rm i}{\hbar}\right)^n \int\limits_0^t dt_1 \cdots \int\limits_0^{t_{n-1}} dt_n\, U_0^{-1}(t_1)\Delta_{\rm S}(t_1)\,U_0(t_1{-}t_2)\,\Delta_{\rm S}(t_2)\cdots U_0(t_{n-1}{-}t_n)\,\Delta_{\rm S}(t_n)\,U_0(t_n) \tag{9.15}$$

using the fact that $U_0^{-1}(t_i)U_0(t_{i-1}) = U_0(t_{i-1}-t_i)$. In this form we see that the perturbative expansion of $U_{\rm I}(t)$ treats the effect of the perturbation as a sequence of impulses: we evolve according to H_0 for some time $t_n \ge 0$ then feel the effect $\Delta_{\rm S}(t_n)$ of the perturbation just at this time, before evolving according to H_0 for a further time $(t_{n-1}-t_n) \ge 0$ and feeling the next impulse from the perturbation, and so on. Finally, we integrate over all the possible intermediate times at which the effects of the perturbation were felt, and sum over how many times it acted. This method, closely related to Green's functions in pdes, is also the basis of Feynman diagrams in QFT, where H_0 is usually taken to be a free Hamiltonian.

Now let's put these ideas to work. Suppose that at some initial time t_0 we're in the state $|\psi(t_0)\rangle = \sum_n a_n(t_0)|n\rangle$, described in terms of some superposition of the basis $\{|n\rangle\}$ of eigenstates of the unperturbed Hamiltonian. Then a later time t the interaction picture state will be $|\psi_{\rm I}(t)\rangle = U_{\rm I}(t-t_0)|\psi(t_0)\rangle$ and can again be described by a superposition $\sum_n a_n(t)|n\rangle$. Contracting with a state $\langle k|$ gives

$$a_k(t) = \langle k|\,U_{\rm I}(t-t_0)|\psi_{\rm I}(t_0)\rangle \tag{9.16}$$

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[78] Time–ordered exponentials were introduced by Freeman Dyson and play a prominent role in QFT. They're also familiar in differential geometry in the context of computing the holonomy of a connection around a closed path. (This is not a coincidence, but it would take us too far afield to explain here.)

in the interaction picture. Thus, using (9.13) we have

$$\begin{aligned} a_k(t) &\approx a_k(t_0) - \frac{\mathrm{i}}{\hbar}\sum_n a_n(t_0)\int_{t_0}^t \langle k|\,\Delta_{\mathrm{I}}(t')\,|n\rangle\,dt' \\ &= a_k(t_0) - \frac{\mathrm{i}}{\hbar}\sum_n a_n(t_0)\int_{t_0}^t \langle k|\,U_0^{-1}(t')\Delta_{\mathrm{S}}(t')\,U_0(t')\,|n\rangle\,dt' \\ &= a_k(t_0) - \frac{\mathrm{i}}{\hbar}\sum_n a_n(t_0)\int_{t_0}^t \mathrm{e}^{\mathrm{i}(E_k-E_n)t'/\hbar}\,\langle k|\Delta_{\mathrm{S}}(t')|n\rangle\,dt'\,, \end{aligned} \tag{9.17}$$

to first non-trivial order in Δ, where we used the fact that $H_0|n\rangle = E_n|n\rangle$. In particular, if at $t = t_0$ we begin in an eigenstate $|m\rangle$ of H_0, so that

$$a_n(t_0) = \begin{cases} 1 & \text{if } n = m \\ 0 & \text{else} \end{cases}\,, \tag{9.18}$$

then the amplitude for our perturbation to caused the system to make a transition into a different H_0 eigenstate $|k\rangle \neq |m\rangle$ is

$$a_k(t) = -\frac{\mathrm{i}}{\hbar}\int_{t_0}^t \mathrm{e}^{\mathrm{i}(E_k-E_m)t'/\hbar}\,\langle k|\Delta_{\mathrm{S}}(t')|m\rangle\,dt' \tag{9.19}$$

to first order in the perturbation. Henceforth, we'll drop the subscript on the Schrödinger picture perturbation – note that this is the form in which the perturbation enters the original Hamiltonian.

To go further, we must specify how the perturbation $\Delta(t)$ actually depends on time.

9.2 Prodding the Harmonic Oscillator

As a simple example, let's consider a $d = 1$ harmonic oscillator that receives a gentle 'prod' described by the time-dependent force $F_{\mathrm{pr}}(t) = F_0\,\mathrm{e}^{-t^2/\tau^2}$, in addition to the force $F = -kX$ from the spring constant. We can describe the kick using the potential $V(X) = -F_0 X \mathrm{e}^{-t^2/\tau^2}$ which we will treat as a perturbation. Now suppose that, long before the kick, the oscillator was in its ground state $|0\rangle$. Then to first order in the perturbation, the amplitude for the oscillator to have made a transition into the k^{th} excited state as $t \to \infty$ is

$$\lim_{t\to\infty} a_k(t) = -\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{\infty} -F_0\langle k|X|0\rangle\,\mathrm{e}^{\mathrm{i}k\omega t - t^2/\tau^2}\,dt \tag{9.20}$$

Recalling that $X = \sqrt{\frac{\hbar}{2m\omega}}(A + A^\dagger)$, we see that $a_k(t) = 0$ for $k \neq 1$, while

$$\lim_{t\to\infty} a_1(t) = F_0\sqrt{\frac{\pi\hbar}{2m\omega}}\,\tau\,\mathrm{e}^{-\omega^2\tau^2/4} \tag{9.21}$$

where the Gaussian integral is performed by completing the square in the exponent. Thus the probability of the kick causing a transition is

$$\mathrm{Prob}(|0\rangle \to |1\rangle) = F_0^2\,\frac{\pi\hbar}{2m}\,\frac{\tau^2}{\omega}\,\mathrm{e}^{-\omega^2\tau^2/4} \tag{9.22}$$

Figure 18: *As $t \to \infty$, the function $\sin^2(xt)/x^2 t \to \pi\delta(x)$.*

to first order in perturbation theory. This grows like τ^2 for small τ, then falls as $\mathrm{e}^{-\omega^2\tau^2/4}$ for $\tau \gg \omega^{-1}$. For an oscillator of fixed (classical) frequency ω, the maximum probability occurs when $\tau \sim \omega^{-1}$. Transitions to higher excited states are possible at higher order in perturbation theory, but if we really kick the oscillator, then perturbation theory will cease to be appropriate.

9.3 A Constant Perturbation Turned On at $t = 0$

As a further example, consider the case that

$$\Delta(t) = \begin{cases} 0 & \text{for } t < 0 \\ \Delta & \text{for } t > 0\,, \end{cases} \tag{9.23}$$

where $\Delta(X, P, \cdots)$ is a time-independent operator. Let's start our system so that it's in the m^{th} eigenstate $|m\rangle$ of H_0 at $t = 0$. Then from (9.19) with $t_0 = 0$ we have

$$a_k(t) = -\frac{\mathrm{i}}{\hbar}\int_0^t \langle k|\Delta|m\rangle\, \mathrm{e}^{\mathrm{i}\omega_{km}t'}\, dt' = \frac{\Delta_{km}}{E_k - E_m}\left(1 - \mathrm{e}^{\mathrm{i}\omega_{km}t}\right)\,, \tag{9.24}$$

where $\Delta_{km} = \langle k|\Delta|m\rangle$ and $\omega_{km} = (E_k - E_m)/\hbar$. Thus the probability of the perturbation causes the system to be in the k^{th} state at time t is

$$|a_k(t)|^2 = \frac{4|\Delta_{km}|^2}{\hbar^2\omega_{km}^2}\sin^2(\omega_{km}t/2)\,. \tag{9.25}$$

We see that the transition probability depends on the energy difference $\hbar\omega_{km}$ as well as the matrix element Δ_{km}.

Consider the graph of $(1/\Omega^2)\sin^2(\Omega t/2)$ as a function of Ω for fixed t, shown in figure 18. The height of the central peak is $\propto t^2$ while its width is $\sim 1/t$, where we recall that t is the time over which the perturbation acted. For large t, $|a_k(t)|^2$ is only appreciable for states $|k\rangle$ whose energies obey

$$t \sim \frac{2\pi}{|\omega_{km}|} = \frac{2\pi\hbar}{|E_k - E_m|} \tag{9.26}$$

In other words, if Δt is the time for which the perturbation has been switched on and ΔE the energy difference between states which have an appreciable probability of a transition, then we require

$$\Delta t\,\Delta E \sim \hbar\,.$$

For small Δt, the central peak in figure 18 is broad and we can have appreciable probability of a transition even between states with $\Delta E \neq 0$. However, if the constant perturbation has been switched on for a long time, we will only obtain transitions to states $|k\rangle$ that are (very nearly) degenerate with the original states $|m\rangle$. In fact as $t \to \infty$, for $\Omega \neq 0$ we have

$$\lim_{t\to\infty} \frac{\sin^2(\Omega t/2)}{\Omega^2 t} \leq \lim_{t\to\infty} \frac{1}{\Omega^2 t} = 0\,, \qquad \text{whilst} \qquad \lim_{\Omega\to 0} \frac{\sin^2(\Omega t/2)}{\Omega^2 t} = \frac{t}{4}\,,$$

which diverges if we then send $t \to \infty$. Furthermore, the integral of this function is

$$\int_{-\infty}^{\infty} \frac{\sin^2(\Omega t/2)}{\Omega^2 t}\, d\Omega = \frac{\pi}{2}\,,$$

independent of t. This shows that we can replace

$$\lim_{t\to\infty} \frac{\sin^2(\Omega t/2)}{\Omega^2 t} = \frac{\pi}{2}\,\delta(\Omega)\,, \tag{9.27}$$

so that as $t \to \infty$, the transition probability (9.25) behaves as

$$|a_k(t)|^2 \sim \frac{2\pi}{\hbar^2} |\langle k|\Delta|m\rangle|^2\; \delta(\omega_{km})\; t\,. \tag{9.28}$$

We define the *transition rate* $\Gamma(m \to k)$ by

$$\Gamma(m \to k) = \lim_{t\to\infty} \frac{\partial}{\partial t} |a_k(t)|^2\,. \tag{9.29}$$

In the case of a constant perturbation switched on at $t = 0$, we thus have

$$\Gamma(m \to k) = \frac{2\pi}{\hbar}\, |\langle k|\Delta|m\rangle|^2\, \delta(E_k - E_m) \tag{9.30}$$

where we have written the argument of the δ-function in terms of energies, pulling out a factor of $\hbar$. As claimed, for this constant perturbation we only have a non-zero transition rate to states which are degenerate with our initial state.

9.4 Fermi's Golden Rule

Just a small extension of the above gives us one of the most important cases of time-dependent perturbation theory. Suppose our perturbation takes the form

$$\Delta(t) = \begin{cases} 0 & \text{for } t < 0 \\ \Delta\, \mathrm{e}^{-\mathrm{i}\omega t} + \Delta^\dagger\, \mathrm{e}^{+\mathrm{i}\omega t} & \text{for } t > 0 \end{cases} \tag{9.31}$$

where again $\Delta = \Delta(X, P, \cdots)$ is some time–independent operator. Thus, as before our Schrödinger picture perturbation $\Delta(t)$ is turned on at $t = 0$, but thereafter it now oscillates with fixed frequency ω. Since $\Delta(t)$ appears as a term in the Hamiltonian, it must be Hermitian, so we've included both an $\mathrm{e}^{-\mathrm{i}\omega t}$ and $\mathrm{e}^{+\mathrm{i}\omega t}$ term and without loss we may take $\omega > 0$. We'll see below that these two terms are responsible for different physics. We call such perturbations *monochromatic* in anticipation of the case that they describe an applied electromagnetic field, corresponding to light of frequency ω.

We'll again consider the case where our system is initially in the m^{th} eigenstate of the unperturbed H_0, so that $a_n(0) = \delta_{nm}$. Performing the time integral in (9.19) in this monochromatic case is again trivial and yields

$$a_k(t) = \frac{\langle k|\Delta|m\rangle}{\hbar(\omega_{km}-\omega)}\left[\mathrm{e}^{\mathrm{i}(\omega_{km}-\omega)t} - 1\right] + \frac{\langle k|\Delta^\dagger|m\rangle}{\hbar(\omega_{km}+\omega)}\left[\mathrm{e}^{\mathrm{i}(\omega_{km}+\omega)t} - 1\right] . \tag{9.32}$$

This is very similar to our result (9.24), with the time–dependence of the perturbation just causing ω_{km} to be replaced by $\omega_{km} - \omega$ in the first term and $\omega_{km} + \omega$ in the second. Consequently, as $t \to \infty$, we will obtain significant transition amplitudes only to states $|m\rangle$ for which $E_k - E_m \approx \hbar\omega$, or else for which $E_k - E_m \approx -\hbar\omega$ to high accuracy. The first situation, where $E_k > E_m$ corresponds to our system *absorbing* energy from the perturbation, whilst the second is *stimulated emissions*, where the system is prompted to release energy by the perturbation. In this way, the time–dependent monochromatic perturbation can be regarded as an enormous source and sink of energy that can be exchanged with the system.

In the case of absorption, the first term dominates at late times. Thus the probability that the perturbation excites the system from $|m\rangle \to |k\rangle$ is

$$|a_k(t)|^2 \approx \frac{4\,|\langle k|\Delta|m\rangle|^2}{\hbar^2(\omega_{km}-\omega)^2}\,\sin^2\left(\frac{\omega_{km}-\omega}{2}t\right) . \tag{9.33}$$

with $E_k > E_m$, correct to order $|\Delta|^2$. Replacing the late–time behaviour of $|a_k(t)|^2$ by a δ-function as before shows that the transition rate is

$$\Gamma(m \to k) = \lim_{t\to\infty} \frac{\partial}{\partial t}|a_k(t)|^2 = \frac{2\pi}{\hbar}\,|\langle k|\Delta|m\rangle|^2\,\delta(E_k - E_m - \hbar\omega) \tag{9.34a}$$

in the case that the system absorbs energy from the perturbation. In the opposite case that the system loses energy back into the perturbation, we have $E_k < E_m$ and the corresponding transition rate is

$$\Gamma(m \to k) = \frac{2\pi}{\hbar}\,|\langle m|\Delta|k\rangle|^2\,\delta(E_k - E_m + \hbar\omega) . \tag{9.34b}$$

with an opposite sign in the δ-function. These results were first obtained by Dirac. They proved to be so useful in describing atomic transitions that Fermi dubbed them 'golden rules'. The name stuck and now (9.34a) & (9.34b) are known as *Fermi's golden rule.*

In practice, a truly monochromatic perturbation never actually causes transitions between two discrete energy levels, such as two bound states of an atom, because we cannot hope to tune its frequency precisely enough so that the δ-functions in (9.34a) or(9.34b) can be satisfied. There are thus two different classes of circumstances in which Fermi's golden rule is useful.

On the one hand, we may be interested not in transitions to some *specific* final state $|k\rangle$, but to any one of a range of continuum eigenstates of H_0. A typical example here would be transitions between an initial bound state of an atom to any of the continuum of positive-energy (non-bound) states. In these circumstances, we let $n(E_k)\,\delta E_k$ denote the number of (final) states with energy in the interval $(E_k, E_k + \delta E_k)$. The function $n(E_k)$ — which needs to be calculated in each case — is known as the *density of states*; note that it must have dimensions of 1/(energy) in order for $n(E_k)\,\delta E_k$ to be a *number* of states. The total transition probability from $|m\rangle$ is then $\int |a_k(t)|^2\, n(E_k)\, dE_k$, generalizing the sum $\sum_k |a_k(t)|^2$ in the discrete case. In particular, in the case of absorption the total transition rate from our initial eigenstate $|m\rangle$ is given by

$$\begin{aligned}\int \Gamma(m\to k)\,\rho(E_k)\,dE_k &= \frac{2\pi}{\hbar}\int |\langle k|\Delta|m\rangle|^2\,\delta(E_k - E_m - \hbar\omega)\,\rho(E_k)\,dE_k \\ &= \frac{2\pi}{\hbar}|\langle k|\Delta|m\rangle|^2\,\rho(E_k)\bigg|_{E_k=E_m+\hbar\omega}\end{aligned} \tag{9.35}$$

to lowest non-trivial order in perturbation theory. We see that we always make transitions through an energy of exactly $\hbar\omega$, with the density of states telling us how many states of energy $E_m + \hbar\omega$ there actually are.

On the other hand, Fermi's golden rule is also useful when our perturbation itself contains a continuum of different frequencies, perhaps thought of as a Laplace or Fourier transform of some a perturbation with generic time dependence. In this case, transitions between discrete bound states are possible, because there will always be some perturbation at exactly the right frequency $\omega = \omega_{km} = (E_k - E_m)/\hbar$, even though the *rhs* takes discrete values as k varies over different bound states as the final state.

Let's now consider an example of each of these two cases.

9.4.1 The Photoelectric Effect

First, we'll use Fermi's golden rule to calculate the rate at which an applied monochromatic electromagnetic field can ionize an atom, say hydrogen, stripping off the electron from a bound state into the continuum of ionized states. We'll assume that the electromagnetic field itself may be treated classically – this assumption is valid *e.g.* in a laser, or at the focus of the antenna of a radio telescope where the field is large. Of course, if we wish perturbation theory to produce reliable results, we'll still need this applied electromagnetic field to be small compared to the Coulomb fields binding the electron(s) to the nucleus of the atom.

In the vacuum, the electromagnetic field is divergence free and is entirely generated by Faraday's Law $\nabla\times\mathbf{E} = -\partial\mathbf{B}/\partial t$. The whole electromagnetic field can be described by a vector potential $\mathbf{A}$ via

$$\mathbf{B} = \nabla\times\mathbf{A} \qquad \text{and} \qquad \mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}\,. \tag{9.36}$$

In the monochromatic case, Faraday's equation is solved by

$$\mathbf{A}(\mathbf{x},t) = \boldsymbol{\epsilon}\cos(\mathbf{k}'\cdot\mathbf{x} - \omega t)\,, \tag{9.37}$$

where $\boldsymbol{\epsilon}$ is a constant vector describing the polarization of the wave and $\mathbf{k}'$ is the wavevector. (We call the wavevector $\mathbf{k}'$, reserving $\mathbf{k}$ for later use.) From the vacuum Maxwell equation $\boldsymbol{\nabla}\cdot\mathbf{E}=0$, we learn that

$$\mathbf{k}'\cdot\boldsymbol{\epsilon}=0\,, \tag{9.38}$$

saying that the wave is transverse. Faraday's law then reduces to the statement that $\omega=c|\mathbf{k}'|$ so that the wave travels at the speed of light.

The coupling of an elementary particle of charge q to such a vector potential is given by the *minimal coupling* rule, replacing

$$\mathbf{P}\mapsto\mathbf{P}-q\mathbf{A}(\mathbf{X},t) \tag{9.39}$$

in the Hamiltonian[79], so

$$H=\frac{(\mathbf{P}-q\mathbf{A})^2}{2\mu}+V(\mathbf{X})=H_0-\frac{q}{2\mu}\left(\mathbf{P}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{P}\right)+\frac{q^2\mathbf{A}^2}{2\mu}\,, \tag{9.40}$$

where H_0 contains the original potential term $V(\mathbf{X})$ as well as the kinetic term. In our case of atomic transitions, an electron has charge $q=-e$ so to first–order in e the perturbing Hamiltonian is

$$\Delta(t)=\frac{e}{2\mu}\left(\mathbf{P}\cdot\boldsymbol{\epsilon}\cos(\mathbf{k}'\cdot\mathbf{X}-\omega t)+\cos(\mathbf{k}'\cdot\mathbf{X}-\omega t)\,\boldsymbol{\epsilon}\cdot\mathbf{P}\right)\,. \tag{9.41}$$

The component $\boldsymbol{\epsilon}\cdot\mathbf{P}$ of the momentum operator in the direction of the polarization of the electromagnetic wave commutes with $\cos(\mathbf{k}'\cdot\mathbf{X}-\omega t)$ by the transversality condition (9.38) (recall that $\boldsymbol{\epsilon}$ itself is a constant vector). Thus

$$\begin{aligned}\Delta(t)&=\frac{e}{\mu}\cos(\mathbf{k}'\cdot\mathbf{X}-\omega t)\,\boldsymbol{\epsilon}\cdot\mathbf{P}\\&=\frac{e}{2\mu}\left(\mathrm{e}^{\mathrm{i}(\mathbf{k}'\cdot\mathbf{X}-\omega t)}+\mathrm{e}^{-\mathrm{i}(\mathbf{k}'\cdot\mathbf{X}-\omega t)}\right)\boldsymbol{\epsilon}\cdot\mathbf{P}\,,\end{aligned} \tag{9.42}$$

simplifying the perturbation.

Having found the form of our perturbation, we now need calculate its matrix element between our initial and final states. We'll consider the case where the hydrogen atom is initially in its ground state, so that $|m\rangle=|100\rangle$ with position space wavefunction

$$\psi_0(\mathbf{x})=\langle\mathbf{x}|100\rangle=\frac{1}{\sqrt{\pi a_0^3}}\,\mathrm{e}^{-r/a_0}\,,$$

where a_0 is the Bohr radius. For the final state, we're interested in the case where the electron has been liberated from the proton. If the energy of the ejected electron is sufficiently great, we can ignore its Coulomb attraction back to the ion and treat the final electron as a free particle of momentum $\hbar\mathbf{k}$, so we take our final state $|\mathbf{k}\rangle$ to be the plane-wave

$$\psi_{\mathbf{k}}(\mathbf{x})=\langle\mathbf{x}|\mathbf{k}\rangle=\frac{1}{(2\pi\hbar)^{3/2}}\,\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}\,.$$

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[79] This is called *minimal* coupling because more complicated modifications are possible if the charged particle is not elementary, or in other more complicated circumstances. You'll learn more about this in the Part II Classical Dynamics course, or if you take AQM next term.

This transition requires that the electron absorbs energy from the radiation, so the matrix element we seek comes from the first term on the *rhs* of (9.42). We have

$$\begin{aligned}\langle\mathbf{k}|\Delta|100\rangle &= \frac{e}{2\mu}\langle\mathbf{k}|\,\mathrm{e}^{\mathrm{i}\mathbf{k}'\cdot\mathbf{X}}\,\boldsymbol{\epsilon}\cdot\mathbf{P}\,|100\rangle \\ &= -\frac{\mathrm{i}\hbar e}{2\mu}\frac{1}{(2\pi\hbar)^{3/2}(\pi a_0^3)^{1/2}}\int_{\mathbb{R}^3}\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{x}}\,\mathrm{e}^{\mathrm{i}\mathbf{k}'\cdot\mathbf{x}}\,\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}(\mathrm{e}^{-r/a_0})\,d^3x\,.\end{aligned} \tag{9.43}$$

Integrating by parts and using the fact that the bound state wavefunction decays exponentially as $|\mathbf{x}|\to\infty$, this is

$$\langle\mathbf{k}|\Delta|100\rangle = \frac{e\hbar}{2\mu}\frac{\boldsymbol{\epsilon}\cdot\mathbf{k}}{(2\pi\hbar)^{3/2}(\pi a_0^3)^{1/2}}\int_{\mathbb{R}^3}\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{x}}\,\mathrm{e}^{-r/a_0}\,d^3x\,, \tag{9.44}$$

where $\mathbf{q}=\mathbf{k}-\mathbf{k}'$ is the momentum transfer and we recall that the polarization vector is transverse, $\boldsymbol{\epsilon}\cdot\mathbf{k}'=0$. We're left with just the Fourier transform of the ground state wavefunction. Choosing the z-axis to lie along the direction of $\mathbf{q}$ and working in polar coordinates, this is

$$\int \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{x}}\,\mathrm{e}^{-r/a_0}\,d^3x = \frac{4\pi}{q}\int_0^\infty r\,\mathrm{e}^{-r/a_0}\,\sin(qr)\,dr = \frac{8\pi a_0^3}{(1+a_0^2q^2)^2} \tag{9.45}$$

where $q=|\mathbf{q}|$.

We now wish to use this matrix element in Fermi's golden rule for the transition rate. Since there are a range of possible final momenta, we define the *differential rate* $\delta\Gamma_{|100\rangle\to|\mathbf{k}\rangle}$ to be the rate at which the radiation ionizes an atom so that the momentum of the ejected electron lies in the range $\hbar(\mathbf{k},\mathbf{k}+\delta\mathbf{k})$, so

$$\begin{aligned}d\Gamma_{|100\rangle\to|\mathbf{k}\rangle} &= \frac{2\pi}{\hbar}\,|\langle\mathbf{k}|\Delta|100\rangle|^2\,\delta(E_{\mathbf{k}}-E_{100}-\hbar\omega)\;\hbar^3\,d^3k \\ &= 2\pi\hbar^2\,|\langle\mathbf{k}|\Delta|100\rangle|^2\,\delta(E_p-E_{100}-\hbar\omega)\,d\phi\,\sin\theta\,d\theta\,k^2dk\end{aligned} \tag{9.46}$$

where $d\Omega=\sin\theta\,d\theta\,d\phi$. To relate this differential rate to our previous expression for the rate of transition into states of particular *energy*, recall that we're treating the final electron as a free particle, so it's energy is $E_{\mathbf{k}}=\hbar^2\mathbf{k}^2/2\mu$. Thus we have

$$k^2dk = k^2(dE_k/dk)^{-1}dE_k = (\mu k/\hbar^2)\,dE_k\,,$$

so for a free particle, the density of states $n(E_k)=\mu k/\hbar^2=\mu\sqrt{2\mu E_k}/\hbar^3$. Putting all the pieces together and integrating over the final state energy, the transition rate for electrons to be emitted into the direction $d\Omega$ of solid angle is

$$\frac{d\Gamma_{|100\rangle\to|\mathbf{k}\rangle}}{d\Omega} = \frac{4e^2(ka_0)^3}{\pi\mu\hbar}\frac{|\boldsymbol{\epsilon}\cdot\hat{\mathbf{k}}|^2}{(1+a_0^2q^2)^4} \tag{9.47}$$

where $\hbar k=\sqrt{2\mu E_k}$ is frozen to $\sqrt{2\mu(\hbar\omega+E_{100})}\approx\sqrt{2\mu\hbar\omega}$ and we recall that $\mathbf{q}=\mathbf{k}-\mathbf{k}'$ is the momentum transfer.

9.4.2 Absorption and Stimulated Emission

Now let's consider the case where instead of being illuminated by monochromatic light such as from a laser, our atom is immersed in a bath of thermal radiation. This radiation bath supplies us with a continuous range of different frequencies, so transitions between different (discrete) bound states of the atom are now possible.

The problem simplifies if we assume that the typical electromagnetic wavelength $1/k'$ in the thermal bath is much larger than the Bohr radius of the atom. This is a good approximation provided the atomic transition occurs between states that are separated in energy by much less than $\alpha\mu c^2$, as will be the case for transitions between highly excited energy levels, perhaps by the valence electrons in a heavy atom. Such wavelengths correspond to radiation with frequencies that are less than those of soft X-rays. In this approximation, $\mathbf{k}'\cdot\mathbf{X} \ll 1$ for all locations in the atom or molecule at which there is significant probability of finding the electron. To lowest order, we can thus approximate the electric field as being constant over the scale of the atom. The Hamiltonian for the atom is then

$$H = H_0 + e\sum_r \mathbf{E}(t)\cdot\mathbf{X}_r\,, \tag{9.48}$$

where H_0 is the Hamiltonian of the unperturbed atom, $\mathbf{E}(t)$ is the fluctuating electric field due to the radiation and $\mathbf{X}_r$ is the position operator for the r^{th} electron in the atom. This is known as the *dipole approximation* since the operator $e\sum_r \mathbf{X}_r$ represents the atom's dipole moment. We interpret the transition as occurring due to the interaction between the applied electric field and this dipole.

Whilst roughly constant over the atom, the electric field $\mathbf{E}(t)$ fluctuates rapidly in time as the atom is jostled by radiation of different frequencies in the thermal bath. In particular, on average $\overline{\mathbf{E}(t)} = 0$ since the electric field is equally likely to point in any direction at any given moment. We take $\mathbf{E}(t)$ to be correlated as

$$\overline{\mathrm{E}_i(t_1)\,\mathrm{E}_j(t_2)} = \delta_{ij}\int_{\mathbb{R}} \mathcal{P}(\omega)\,\mathrm{e}^{-\mathrm{i}\omega(t_1-t_2)}\,d\omega\,. \tag{9.49}$$

The presence of δ_{ij} on the *rhs* means that fluctuations in different directions are uncorrelated, whilst fluctuations that are aligned are correlated equally no matter their direction. This just says that there is no preferred direction for the electric field and holds *e.g.* for a thermal bath of radiation.

We can understand the meaning of the function $\mathcal{P}(\omega)$ as follows. First, note that if the electric fields are real, then we must have

$$\mathcal{P}(-\omega) = \mathcal{P}(\omega) \qquad \text{and} \qquad \mathcal{P}(\omega)^* = \mathcal{P}(\omega) \tag{9.50}$$

so that $\mathcal{P}(\omega)$ is a real, even function of ω. Recall from IB Electromagnetism (or looking ahead to Part II Electrodynamics) that the energy density of an electromagnetic field is

$$\frac{\varepsilon_0}{2}\left(\mathbf{E}^2(\mathbf{x},t) + c^2\mathbf{B}^2(\mathbf{x},t)\right)$$

and in a purely radiative (source–free) field $\mathbf{E}^2 = c^2\mathbf{B}^2$. In our case, equation (9.49) shows that the average energy density we expect to find in the radiation at time t is

$$\epsilon_0\overline{\mathrm{E}_i(t)\mathrm{E}_i(t)} = 3\varepsilon_0\int_{-\infty}^{\infty}\mathcal{P}(\omega)\,d\omega = 6\varepsilon_0\int_0^{\infty}\mathcal{P}(\omega)\,d\omega\,, \tag{9.51}$$

so $\rho(\omega) = 6\varepsilon_0\mathcal{P}(\omega)$ represents the average energy density in the radiation (at any time) due to frequencies in the range $(\omega, \omega + d\omega)$. (If the radiation is truly thermal at temperature T, then $\rho(\omega)$ would be given by Planck's blackbody formula

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^3c^2}\frac{1}{\mathrm{e}^{-\hbar\omega/k_\mathrm{B}T} - 1} \tag{9.52}$$

coming from the Bose–Einstein distribution. You'll learn about this if you take next term's Statistical Physics lectures.)

Now let's put these results to work. For a transition $|m\rangle \to |k\rangle$, we have from (9.19) and (9.48) that

$$a_k(t) = -\frac{\mathrm{i}e}{\hbar}\int_0^t\sum_r\langle k|\mathbf{E}(t')\cdot\mathbf{X}_r|m\rangle\,\mathrm{e}^{\mathrm{i}\omega_{km}t'}\,dt'\,. \tag{9.53}$$

We write the probability that the atom is found in state $|k\rangle$ at time t as a double integral

$$|a_k(t)|^2 = \frac{e^2}{\hbar^2}\int_0^t\int_0^t\sum_{r,r'}\langle k|\mathbf{E}(t_1)\cdot\mathbf{X}_{r'}|m\rangle\,\langle m|\mathbf{E}(t_2)\cdot\mathbf{X}_r|k\rangle\,\mathrm{e}^{\mathrm{i}\omega_{km}(t_1-t_2)}\,dt_1\,dt_2\,. \tag{9.54}$$

The correlations (9.49) in our thermal bath shows that, on average,

$$\begin{aligned}\overline{|a_k(t)|^2} &= \frac{e^2}{\hbar^2}\int_0^t\int_0^t\overline{\mathrm{E}_i(t_1)\mathrm{E}_j(t_2)}\sum_{r,r'}\langle k|(X_{r'})_i|m\rangle\,\langle m(X_r)_j|k\rangle\,\mathrm{e}^{\mathrm{i}\omega_{km}(t_1-t_2)}\,dt_1\,dt_2\\ &= \frac{e^2}{\hbar^2}\left|\sum_r\langle k|\mathbf{X}_r|m\rangle\right|^2\times\int_{-\infty}^{\infty}\mathcal{P}(\omega)\left[\int_0^t\int_0^t\mathrm{e}^{\mathrm{i}(\omega_{km}-\omega)(t_1-t_2)}\,dt_1\,dt_2\right]d\omega\\ &= \frac{e^2}{\hbar^2}\left|\sum_r\langle k|\mathbf{X}_r|m\rangle\right|^2\times\int_{-\infty}^{\infty}\mathcal{P}(\omega)\left|\int_0^t\mathrm{e}^{\mathrm{i}(\omega_{km}-\omega)t_1}\,dt_1\right|^2\,d\omega\\ &= \frac{4e^2}{\hbar^2}\left|\sum_r\langle k|\mathbf{X}_r|m\rangle\right|^2\times\int_{-\infty}^{\infty}\mathcal{P}(\omega)\,\frac{\sin^2((\omega_{km}-\omega)t/2)}{(\omega_{km}-\omega)^2}\,d\omega\,,\end{aligned} \tag{9.55}$$

where the mod-square includes the Euclidean inner product (dot product) of the two $\langle k|\mathbf{X}_r|m\rangle$ matrix elements. This form is again familiar, except that instead of a density of final states, we have $\mathcal{P}(\omega)$, representing the average energy density $\rho(\omega)$ of the frequency ω component of the radiation. Making our familiar replacement, and performing the integral over ω using the resulting δ-function, we have the transition rate

$$\Gamma(|m\rangle \to |k\rangle) = \frac{\pi e^2}{3\epsilon_0\hbar^2}\left|\sum_r\langle k|\mathbf{X}_r|m\rangle\right|^2\rho(\omega_{km}) \tag{9.56}$$

in the case that the states $|m\rangle$ and $|k\rangle$ are discrete but we have a continuous range of perturbing frequencies. Again we recall that $\omega_{km} = (E_k - E_m)/\hbar$ is the fixed difference between the initial and final bound state energy levels.

This result is very intuitive: the rate of transition depends on the probability that the dipole moment transition can link states $|m\rangle$ and $|k\rangle$, together with the energy density in the radiation bath at the right frequency to match this transition. For hydrogenic states of the atom, we recall from section 6.2.2 that the matrix element vanishes unless the selection rules

$$|\ell - \ell'| = 1 \qquad \text{and} \qquad |m - m'| \leq 1$$

are obeyed. These selection rules were derived under the assumption that the transition is just due to the dipole approximation where the perturbation involves matrix elements of the dipole moment operator $e\mathbf{X}$. The effects of both higher orders in perturbation theory, and inclusion of interactions beyond those of an electric field with wavelength $\lambda \gg a_0$ mean that transitions that are 'forbidden' according to the above selection rules may in fact occur. They will typically do so, however, at a much smaller rate.

Now, whether or not the radiation bath is thermal, the reality conditions (9.50) show that the rate $\Gamma(|m\rangle \to |k\rangle)$ in (9.56) is an even function of ω_{km}. Consequently, for fixed $|E_k - E_m|$, *this rate is the same whether* $E_k > E_m$ *or* $E_k < E_m$. For $E_k > E_m$, the atom *absorbs* energy from the radiation, exciting to a higher energy level, whilst if $E_k < E_m$ the atom *emits* energy back into the radiation as it decays to a lower energy state. The important result we've obtained is that the rate for stimulated emission is the same as the rate of absorption.

9.4.3 Spontaneous Emission

Our treatment above calculated the rate at which an atom would decay (or excite) due to being immersed in a bath of radiation. However, we currently cannot understand decays of an *isolated* atom: if the atom is prepared in any eigenstate of H_0, quantum mechanics says that in the absence of a perturbation it will just stay there. Remarkably, Einstein was able to relate the rate of spontaneous decay of an atom to the rate of stimulated decay that we calculated above.

Suppose our atom is immersed in a bath of radiations where the energy density of photons with frequency in the range $(\omega, \omega + d\omega)$ is $\rho(\omega)\, d\omega$. Einstein defined $A_{m\to k}(\omega_{mk})$ as the rate at which an atom would spontaneously decay from a state of energy E_m to a state of *lower* energy E_k, where $\omega_{mk} = (E_m - E_k)/\hbar$ is the frequency of the emitted photon. We let $\rho(\omega_{km})\, B_{k\to m}(\omega_{km})$ denote the rate at which energy is absorbed from the radiation bath, exciting the atom from $|k\rangle \to |m\rangle$. Similarly, let $\rho(\omega_{km})\, B_{m\to k}(\omega_{km})$ denote the rate of decay of the excited atom due to stimulation by the presence of the radiation bath. We calculated $B_{m\to k}$ and $B_{k\to m}$ in the dipole approximation above, finding they were the same, but let's pretend that (like Einstein) we don't know this yet.

In thermodynamic equilibrium these rates must balance, so if there are n_k atoms in state $|k\rangle$ and n_m in state $|m\rangle$ we must have

$$n_m \left(A_{m\to k}(\omega_{mk}) + \rho(\omega_{km})\, B_{m\to k}(\omega_{km})\right) = n_k\, \rho(\omega_{km})\, B_{k\to m}(\omega_{km})\,. \tag{9.57}$$

We now borrow two results you'll derive in the Part II Statistical Mechanics course, next term. First, when a gas of atoms is in equilibrium at temperature T, the relative numbers of atoms in states with energies E_m and E_k is given by the *Boltzmann distribution*

$$\frac{n_k}{n_m} = \frac{\mathrm{e}^{-E_k/k_\mathrm{B}T}}{\mathrm{e}^{-E_m/k_\mathrm{B}T}} = \mathrm{e}^{\hbar\omega_{mk}/k_\mathrm{B}T}\,, \tag{9.58}$$

where $k_\mathrm{B} \approx 1.38 \times 10^{-23}\,\mathrm{JK}^{-1}$ is Boltzmann's constant. Furthermore, if radiation is in equilibrium at the same temperature then the density of states at frequency ω is

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\,\frac{1}{\mathrm{e}^{\hbar\omega/k_\mathrm{B}T}-1}\,, \tag{9.59}$$

which is essentially the *Bose–Einstein distribution.* Using these in (9.57) gives

$$A_{m\to k}(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\,\frac{1}{\mathrm{e}^{\hbar\omega/k_\mathrm{B}T}-1}\left(\mathrm{e}^{\hbar\omega/k_\mathrm{B}T}\,B_{k\to m}(\omega) - B_{m\to k}(\omega)\right)\,. \tag{9.60}$$

where $\omega = \omega_{mk}$. However, $A_{m\to k}$ is supposed to be the rate of *spontaneous* emission of radiation from the atom, so it cannot depend on any properties of the radiation bath. In particular, it must be independent of the temperature T. This is possible iff

$$B_{k\to m}(\omega) = B_{m\to k}(\omega) \tag{9.61}$$

so that the rates of stimulated emission and absorption agree. In this case, we have

$$A_{m\to k}(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} B_{m\to k}(\omega) \tag{9.62}$$

so that knowing the rate $B_{k\to m}(\omega)$ at which a classical electromagnetic wave of frequency $\omega = (E_m - E_k)/\hbar$ is absorbed by an atom, we can also calculate the rate $A_{m\to k}(\omega)$ at which the atom spontaneously decays, even in the absence of radiation.

Now, in equation (9.56) we found from a first–principles calculation that

$$\Gamma(|m\rangle \to |k\rangle) = \frac{\pi e^2}{3\epsilon_0\hbar^2}\left|\sum_r \langle k|\mathbf{X}_r|m\rangle\right|^2 \rho(\omega_{km}) \tag{9.63}$$

in the dipole approximation, to first-order in perturbation theory. Consequently, for our atom Einstein's B coefficient is

$$B_{k\to m}(\omega_{km}) = B_{m\to k}(\omega_{mk}) = \frac{\pi e^2}{3\epsilon_0\hbar^2}\left|\sum_r \langle k|\mathbf{X}_r|m\rangle\right|^2\,. \tag{9.64}$$

for stimulated emission or absorption. From Einstein's statistical argument we thus learn that

$$A_{m\to k}(\omega) = \frac{e^2\omega^3}{3\epsilon_0\pi\hbar c^3}\left|\sum_r \langle k|\mathbf{X}_r|m\rangle\right|^2 \tag{9.65}$$

is the rate at which an excited atom must spontaneously decay, even in the absence of any applied radiation.

Ingenious though it is, there's something puzzling about this calculation of the rate of spontaneous decay. Where does our quantum mechanical calculation – stating that isolated excited atoms do not decay – go wrong? The answer is that while we treated the energy levels of the atom fully quantum mechanically, the electromagnetic field itself was treated classically. Spontaneous emission is only possible once one also quantizes the electromagnetic field, since it is fluctuations in the zero–point value of this field that allow the atom to emit a photon and decay; heuristically, the fluctuating value of the quantum electromagnetic field – even in the vacuum – 'tickles' the excited atom prompting the decay. Treating the EM field classically is appropriate if the radiation comes from a high–intensity laser, where the energy density of the field is so high that the terms $B(\omega)\rho(\omega)$ dominate in (9.57). By contrast, emission of light from the atoms in a humble candle is an inherently quantum phenomenon, occurring purely by spontaneous emission once the flame is lit — candlelight shines even in ambient darkness.

Einstein gave his statistical argument in 1916, when Bohr's model of the atom (the first thing you met in IB QM) was still the deepest understanding physicists had of quantum theory. This was at the same time as he was revolutionising our understanding of gravity, space and time, which obviously wasn't enough to keep him fully occupied. The quantum treatment of stimulated emission given in the previous section is due to Dirac in 1926, the same year as Schrödinger first published his famous equation. A first–principles calculation of the spontaneous emission rate $A_{m\to k}$, requiring the quantization of the electromagnetic field, was also given by Dirac just one year later. Things move fast. Dirac's 1927 results agreed with those we've found via Einstein's argument. The necessity also to quantize the electromagnetic field heralded the arrival of Quantum Field Theory.

Let's use these results to calculate the typical lifetime of an excited state of an isolated atom. When the radiation density $\rho(\omega)$ is very small, the number of atoms n_m in the excited state obeys

$$\frac{\partial n_m}{\partial t} = -A_{m\to k}\, n_m \tag{9.66}$$

so the atom decays exponentially with a characteristic timescale $\sim A^{-1}_{m\to k}$. For hydrogen or an alkali atom, typically the outermost electron changes its energy level in the transition, so we can drop the sum in (9.65) to find

$$A_{m\to k}(\omega) = \frac{e^2\omega^3}{3\pi\epsilon_0\hbar c^3}\,|\langle k|\mathbf{X}|m\rangle|^2 \tag{9.67}$$

where $\mathbf{X}$ is the position of the outermost electron. Unless $\langle k|\mathbf{X}|m\rangle$ vanishes due to some selection rule, we'd expect this matrix element to be of the typical size $a_0 = 4\pi\epsilon_0\hbar^2/\mu e^2$ characteristic of the atom, so $|\langle k|\mathbf{X}|m\rangle|^2 \sim a_0^2$. Hence the characteristic lifetime of the excited atomic state is roughly

$$\tau = A^{-1}_{m\to k} \sim \frac{3\pi\epsilon_0\hbar c^3}{e^2\omega^3 a_0^2} = \frac{3\mu c^3}{4\hbar\omega^3 a_0} \tag{9.68}$$

where μ is the mass of the electron. Optical light has a frequency of order $\omega \sim 10^{15}\,$Hz, so the timescale τ is around 10^7 times longer than the timescale $\hbar/E_{200}$ associated to the energy E_{200} of the first excited state of hydrogen. Thus around 10^7 oscillations of the hydrogen atom occur before it radiates a photon, decaying down into the ground state.