8. Atoms in Electromagnetic Fields

Our goal in this chapter is to understand how atoms interact with electromagnetic fields.

There will be several stages to our understanding. We start by looking at atoms in constant, background electromagnetic fields. Because these fields break various symmetries of the problem, we expect to see a splitting in the degeneracies of states. The splitting of the atomic spectrum due to an electric field is called the *Stark effect*. The splitting due to a magnetic field is called the *Zeeman effect*. We deal with each in turn.

We then move on to look at what happens when we shine light on atoms. Here the physics is more dramatic: the atom can absorb a photon, causing the electron to jump from one state to a higher one. Alternatively the electron can decay to lower state, emitting a photon as it falls. We will begin with a classical treatment of the light but, ultimately, we will need to treat both light and atoms in a quantum framework.

8.1 The Stark Effect

Consider the hydrogen atom, where the electron also experience a constant, background electric field. We'll take the electric field to lie in the z direction, $\mathbf{E} = \mathcal{E}\hat{\mathbf{z}}$. The Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + e\mathcal{E}z \tag{8.1}$$

The total potential energy, $V(z) = e\mathcal{E}z - e^2/4\pi\epsilon_0 r$ is sketched in the diagram.

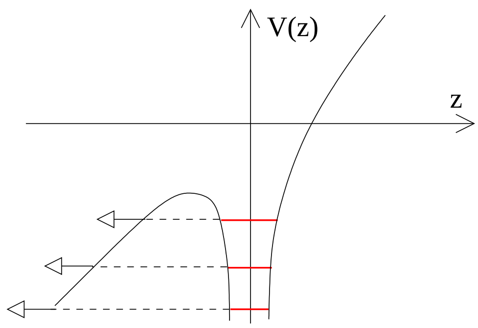

Figure 81:

The first thing to note is that the potential is unbounded below as $z \to -\infty$. This means that all electron bound states, with wavefunctions localised near the origin, are now unstable. Any electron can tunnel through the barrier to the left, and then be accelerated by the electric field to $z \to -\infty$. However, we know from our WKB analysis in Section 6.2.5 that the probability rate for tunnelling is exponentially suppressed by the height of the barrier (see, for example, (6.30)). This means that the lowest lying energy levels will have an extremely long lifetime.

If you want some numbers, the strength of a typical electric field is around $\mathcal{E} \sim 10\ eV\,cm^{-1}$. We know that the ground state of hydrogen is $E_0 \sim -13.6\ eV$ and the Bohr radius is $a_0 \sim 5 \times 10^{-9}\ cm$, which suggests that the typical electric field inside the atom is around $\mathcal{E}_{\rm atom} \sim 10^9\ eV\,cm^{-1}$, which is eight orders of magnitude greater than the applied electric field. On general, ground we expect that the tunnelling probability is suppressed by a factor of e^{-10^8}. At this point is doesn't really matter what our units are, this is going to be a very small number. The states which are well bound are stable for a very long time. Only those states very close to threshold are in danger of being destabilised by the electric field. For this reason, we'll proceed by ignoring the instability.

8.1.1 The Linear Stark Effect

We're going to work in perturbation theory. Before we look at the hydrogen atom, here's a general comment about what happens when you perturb by electric fields. Suppose that we have a non-degenerate energy eigenstate $|\psi\rangle$. Then adding a background, constant electric field will shift the energy levels by

$$\Delta E = \langle\psi|e\mathbf{E}\cdot\mathbf{x}|\psi\rangle = -\mathbf{P}\cdot\mathbf{E} \tag{8.2}$$

where we have introduced the *electric dipole*

$$\mathbf{P} = -e\langle\psi|\mathbf{x}|\psi\rangle = -e\int d^3x\ \mathbf{x}\,|\psi(\mathbf{x})|^2 \tag{8.3}$$

The shift in energies is first order in the electric field and is known as the *linear Stark effect*.

For the hydrogen atom, there is an extra complication: the states $|n,l,m\rangle$ are degenerate. The energy levels

$$(E_0)_n = -\frac{Ry}{n^2}$$

with $Ry \approx -13.6\ eV$ have degeneracy n^2 (ignoring spin). This means that we will have to work with degenerate perturbation theory. For the electric field $\mathbf{E} = \mathcal{E}\hat{\mathbf{z}}$, we must compute the matrix elements

$$\langle n,l',m'|z|n,l,m\rangle$$

With a large degeneracy of n^2, this looks like it becomes increasingly complicated as we go up in energy levels. Fortunately, there is a drastic simplification.

The first simplification follows from using the parity operator π. Recall from Section 5.1 that the states of the hydrogen atom transform as (5.10)

$$\pi|n,l,m\rangle = (-1)^l|n,l,m\rangle$$

from which we have

$$\begin{aligned}\langle n,l',m'|z|n,l,m\rangle &= (-1)^{l+l'}\langle n,l',m'|\pi z\pi|n,l,m\rangle \\ &= (-1)^{l+l'+1}\langle n,l',m'|z|n,l,m\rangle\end{aligned}$$

This means that the matrix element is non-vanishing only if $l+l'$ is odd. From this, we immediately learn that the unique ground state $|n=1,0,0\rangle$ does not change its energy at leading order.

We can also use the fact that the perturbation commutes with L_z. This means that

$$\begin{aligned}m\hbar\langle n,l',m'|z|n,l,m\rangle &= \langle n,l',m'|zL_z|n,l,m\rangle \\ &= \langle n,l',m'|L_z z|n,l,m\rangle = m'\hbar\langle n,l',m'|z|n,l,m\rangle\end{aligned}$$

So the perturbation is non-vanishing only if $m=m'$. (In Section 8.3.3, we'll see that electric fields in the x or y direction have non-vanishing matrix elements only if $m'=m\pm 1$.)

This is enough to determine the corrections to the $n=2$ states. The $|2,1,\pm1\rangle$ states remain unaffected at leading order. Meanwhile, the $|2,0,0\rangle$ state mixes with the $|2,1,0\rangle$ state. The integrals over the hydrogen wavefunctions are straightforward to evaluate and yield

$$U = \langle 2,0,0|z|2,1,0\rangle = -3e\mathcal{E}a_0$$

The first corrections to the energy are then given by the eigenvalues of the matrix

$$3e\mathcal{E}a_0\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$$

We learn that, to first order in perturbation theory, the $n=2$ energy eigenstates and eigenvalues are given by

$$|2,1,\pm1\rangle \quad \text{with} \quad E=(E_0)_{n=2} \tag{8.4}$$

and

$$|2,\pm\rangle = \frac{1}{\sqrt{2}}(|2,0,0\rangle \pm |2,1,0\rangle) \quad \text{with} \quad E=(E_0)_{n=2}\pm 3e\mathcal{E}a_0 \tag{8.5}$$

From our general discussion above, we learn that the eigenstates $|2,\pm\rangle$ can be thought of as having a permanent electric dipole moment (8.3).

For higher energy levels $n \geq 3$, we need to look at the different l quantum numbers more carefully. In Section 8.3.3, we will show that $\langle n, l', m'|z|n, l, m\rangle$ is non-vanishing only if $l' = l \pm 1$.

8.1.2 The Quadratic Stark Effect

We saw above that the vast majority of states do not receive corrections at first order in perturbation theory. This is because these states do not have a permanent dipole moment $\mathbf{P}$, a fact which showed up above as the vanishing of matrix elements due to parity.

However, at second order in perturbation theory all states will receive corrections. As we now see, this can be understood as the formation of an *induced* dipole moment.

Here we focus on the ground state $|1, 0, 0\rangle$. A standard application of second order perturbation theory tells us that the shift of the ground state energy level is

$$\Delta E = e^2 \mathcal{E}^2 \sum_{n=2}^{\infty} \sum_{l,m} \frac{|\langle 1, 0, 0|z|n, l, m\rangle|^2}{E_1 - E_n} \tag{8.6}$$

In fact, strictly speaking, we should also include an integral over the continuum states, as well as the bound states above. However, it turns out that these are negligible. Moreover, the summand above turns out to scale as $1/n^3$ for large n, so only the first few n contribute significantly.

The exact result is not so important for our purposes. More interesting is the parametric dependence which follows from (8.6)

$$\Delta E = -4\pi\epsilon_0 C \mathcal{E}^2 a_0^3$$

where C is a number of order 1 that you get from doing the sum. For what it's worth, $C = \frac{9}{4}$.

The polarisation is given by

$$\mathbf{P} = -\nabla_{\mathbf{E}} E \tag{8.7}$$

where $\nabla_{\mathbf{E}}$ means "differentiate with respect to the components of the electric field" and the thing we're differentiating, which is a non-bold E, is the energy. Note that for states with a permanent dipole, this definition agrees with the energy (8.2) which is linear in the electric field. However, for states with an induced dipole, the energy is typically proportional to $\mathbf{E} \cdot \mathbf{E}$, and the definition (8.7) means that it can be written as

$$\Delta E = -\frac{1}{2} \mathbf{P} \cdot \mathbf{E}$$

From our expression above, we see that the ground state of hydrogen has an induced polarisation of this kind, given by

$$\mathbf{P} = 2C \times 4\pi\epsilon_0 a_0^3\, \mathbf{E} \tag{8.8}$$

W've actually seen the result (8.8) before: in the lectures on Electromagnetism we discussed Maxwell's equations in matter and started with a simple classical model of the polarisation of an atom that gave the expression (8.8) with $2C = 1$ (see the start of Section 7.1 of those lectures.). The quantum calculation above, with $2C = \frac{9}{2}$, is the right way to do things.

Degeneracies in the Presence of an Electric Field

As we've seen above, only degenerate states $|n, l', m'\rangle$ and $|n, l, m\rangle$ with $l = l'$ and $m = m'$ are affected at leading order in perturbation theory. All states are affected at second order. When the dust settles, what does the spectrum look like?

On general grounds, we expect that the large degeneracy of the hydrogen atom is lifted. The addition of an electric field breaks both the hidden $SO(4)$ symmetry of the hydrogen atom — which was responsible for the degeneracy in l — and the rotational symmetry which was responsible for the degeneracy in m. We therefore expect these degeneracies to be lifted and, indeed, this is what we find. We retain the spin degeneracy, $m_s = \pm\frac{1}{2}$, since the electric field is blind to the spin.

There is, however, one further small degeneracy that remains. This follows from the existence of two surviving symmetries of the Hamiltonian (8.1). The first is rotations in the (x, y)-plane, perpendicular to the electric field. This ensures that $[H, L_z] = 0$ and energy eigenstates can be labeled by the quantum number m. We'll call these states $|a; m\rangle$, where a is a label, not associated to a symmetry, which specifies the state. We have $L_z|a, m\rangle = m\hbar|a; m\rangle$.

The second symmetry is time-reversal invariance discussed in Section 5.2. The anti-unitary operator Θ acts on angular momentum as (5.24),

$$\Theta\mathbf{L}\Theta^{-1} = -\mathbf{L}$$

This means that $\Theta|a; m\rangle = |a; -m\rangle$. Because $[\Theta, H] = 0$, the states $|a; m\rangle$ and $|a; -m\rangle$ must have the same energy. This means that most states are two-fold degenerate. The exception is the $m = 0$ states. These can be loners.

8.1.3 A Little Nazi-Physics History

The Stark effect was discovered by Johannes Stark in 1913. For this he was awarded the 1922 Nobel prize.

Stark was a deeply unpleasant man. He was an early adopter of the Nazi agenda and a leading light in the Deutsche Physik movement of the early 1930s whose primary goal was to discredit the Jüdische Physik of Einstein's relativity. Stark's motivation was to win approval from the party and become the Führer of German physics.

Stark's plans backfired when he tangled with Heisenberg who had the temerity to explain that, regardless of its origin, relativity was still correct. In retaliation, Stark branded Heisenberg a "white Jew" and had him investigated by the SS. Things came to a head when – and I'm not making this up – Heisenberg's mum called Himmler's mum and asked the Nazi party to leave her poor boy alone. Apparently the Nazi's realised that they were better off with Heisenberg's genius than Stark's bitterness, and House Stark fell from grace.

8.2 The Zeeman Effect

The splitting of energy levels due to a background magnetic field is called the *Zeeman effect*. It was discovered in 1896 by Pieter Zeeman who, like many great scientists, ignored what his boss told him to do and instead followed his nose. For this, he was fired. The award of the Nobel prize six years later may have gone some way towards making amends.

The addition of a magnetic field results in two extra terms in the Hamiltonian. The first arises because the electron is charged and so, as explained in more detail in Section 1, the kinetic terms in the Hamiltonian become

$$H = \frac{1}{2m}(\mathbf{p} + e\mathbf{A})^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} \tag{8.9}$$

where $\mathbf{A}$ is the vector potential and the magnetic field is given by $\mathbf{B} = \nabla \times \mathbf{A}$. We take the magnetic field to lie in the z-direction: $\mathbf{B} = B\hat{\mathbf{z}}$ and work in symmetric gauge

$$\mathbf{A} = \frac{B}{2}(-y, x, 0)$$

We can now expand out the square in (8.9). The cross terms are $\mathbf{p} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{p} = B(xp_y - yp_x)/2$. Note that, even when viewed as quantum operators, there is no ordering ambiguity. Moreover, we recognise the combination in brackets as the component of the angular momentum in the z-direction: $L_z = xp_y - yp_x$. We can then write the Hamiltonian as

$$H = \frac{1}{2m}\left(\mathbf{p}^2 + e\mathbf{B} \cdot \mathbf{L} + e^2B^2(x^2 + y^2)\right) - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} \tag{8.10}$$

Note that the $\mathbf{B} \cdot \mathbf{L}$ term takes the characteristic form of the energy of a magnetic dipole moment $\boldsymbol{\mu}$ in a magnetic field. Here

$$\boldsymbol{\mu}_L = -\frac{e}{2m}\mathbf{L}$$

is the dipole moment that arises from the orbital angular momentum of the electron.

The second term that arises from a magnetic field is the coupling to the spin. We already saw this in Section 1.5 and again in Section 7.1.3

$$\Delta H = g\frac{e}{2m}\mathbf{B} \cdot \mathbf{S}$$

where the g-factor is very close to $g \approx 2$. Combining the two terms linear in B gives the so-called *Zeeman Hamiltonian*

$$H_Z = \frac{e}{2m}\mathbf{B} \cdot (\mathbf{L} + 2\mathbf{S}) \tag{8.11}$$

Note that it's not quite the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ that couples to the magnetic field. There is an extra factor of $g = 2$ for the spin. This means that the appropriate dipole moment is

$$\boldsymbol{\mu}_{\text{total}} = -\frac{e}{2m}(\mathbf{L} + 2\mathbf{S}) \tag{8.12}$$

The terms linear in $\mathbf{B}$ given in (8.11) are sometimes called the *paramagnetic terms*; these are responsible for the phenomenon of Pauli paramagnetism that we met in the Statistical Physics lectures. The term in (8.10) that is quadratic in B is sometimes called the *diamagnetic tem*; it is related to Landau diamagnetism that we saw in Statistical Physics.

In what follows, we will work with magnetic fields that are small enough so that we can neglect the diamagnetic B^2 term. In terms of dimensionless quantities, we require that $eBa_0^2/\hbar \ll 1$ where a_0, the Bohr radius, is the characteristic size of the atom. In practical terms, this means $B \lesssim 10\ T$ or so.

8.2.1 Strong(ish) Magnetic Fields

We work with the Zeeman Hamiltonian (8.11). It turns out that for the kinds of magnetic fields we typically create in a lab — say $B \lesssim 5\ T$ or so — the shift in energy levels from H_Z is smaller than the fine-structure shift of energy levels that we discussed in Section 7.1. Nonetheless, to gain some intuition for the effect of the Zeeman Hamiltonian, we will first ignore the fine-structure of the hydrogen atom. We'll then include the fine structure and do a more realistic calculation.

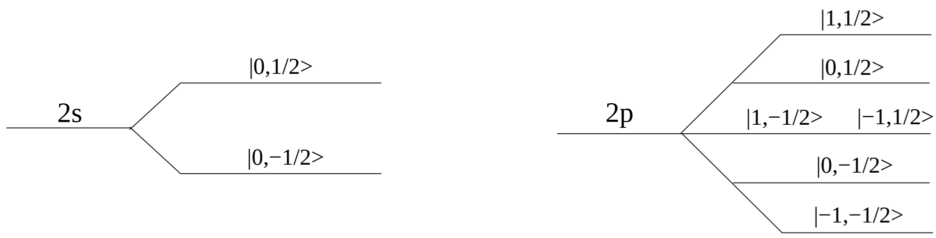

Figure 82: Splitting of the $2s$ and $2p$ energy levels in a magnetic field. The quantum numbers $|m_l, m_s\rangle$ are shown.

We want to solve the Hamiltonian

$$H = H_0 + H_Z = \frac{1}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} + \frac{e}{2m}\mathbf{B}\cdot(\mathbf{L}+2\mathbf{S}) \tag{8.13}$$

We start from the standard states of the hydrogen atom, $|n, l, m_l, m_s\rangle$ where now we include both orbital angular momentum and spin quantum numbers. The energy of these states from H_0 is $E_0 = -Ry/n^2$ and each level has degeneracy $2n^2$.

Happily, each of the states $|n, l, m_l, m_s\rangle$ remains an eigenstate of the full Hamiltonian H. The total energy is therefore $E = E_0 + E_Z$, where the Zeeman contribution depends only on the m_l and m_s quantum numbers

$$(E_Z)_{m_l,m_s} = \langle n, l, m_l, m_s|H_Z|n, l, m_l, m_s\rangle = \frac{e\hbar}{2m}(m_l + 2m_s)B \tag{8.14}$$

This gives our desired splitting. The two $1s$ states are no longer degenerate. For the $n = 2$ states, the splitting is shown in the figure. The $2s$ states split into two energy levels, while the six $2p$ states split into five. Note that the $m_l = 0$ states from $2p$ are degenerate with the $2s$ states.

As we mentioned above, the energy spectrum (8.14) holds only when we can neglect both the fine-structure of the hydrogen atom and the quadratic B^2 terms. This restricts us to a window of relatively large magnetic fields $5\ T \lesssim B \lesssim 10\ T$. The result (8.14) is sometimes called the *Paschen-Back effect* to distinguish it from the weak field Zeeman effect that we will study below.

The states $|n, l, m_l, m_s\rangle$ are eigenstates of the full Hamiltonian (8.13). This means that we could now consider perturbing these by the fine-structure corrections we met in Section 7.1 to find additional splitting.

8.2.2 Weak Magnetic Fields

When the magnetic fields are small, we have to face up to the fact that the fine-structure corrections of Section 7.1 are larger than the Zeeman splitting. In this case, the correct way to proceed is to start with the fine structure Hamiltonian and then perturb by H_Z.

Because of the spin-orbit coupling, the eigenstates of the fine structure Hamiltonian are *not* labelled by $|n, l, m_l, m_s\rangle$. Instead, as we saw in Section 7.1.3, the eigenstates are

$$|n, j, m_j; l\rangle$$

where $j = |l \pm \frac{1}{2}|$ is the total angular momentum, and the final label l is not a quantum number, but is there to remind us whether the state arose from $j = l + \frac{1}{2}$ or $j = l - \frac{1}{2}$. The upshot of our calculations in Sections 7.1.2 - 7.1.4 is that the energies depend only on n and j and, to leading order, are given by

$$E_{n,j} = (Z\alpha)^2 mc^2 \left(-\frac{1}{2n^2} + (Z\alpha)^2 \left(\frac{3}{4n} - \frac{2}{2j+1} \right) \frac{1}{2n^3} \right)$$

We now perturb by the Zeeman Hamiltonian H_Z given in (8.11) to find, at leading order, the shifts of the energy levels given by

$$\Delta E = \frac{eB}{2m} \langle n, j, m_j; l | L_z + 2S_z | n, j, m_j; l \rangle \tag{8.15}$$

You might think that we need to work with degenerate perturbation theory here. Indeed, the existence of degenerate states with energy $E_{n,j}$ means that we should allow for the possibility of different quantum numbers m_j' and l' on the state $\langle n, j, m_j'; l'|$. However, since both $[\mathbf{L}^2, H_Z] = 0$ and $[J_z, H_Z] = 0$, the matrix elements vanish unless $l = l'$ and $m_j = m_j'$. Fortunately, we again find ourselves in a situation where, despite a large degneracy, we naturally work in the diagonal basis.

As we will now see, evaluating (8.15) gives a different result from (8.14). Before proceeding, it's worth pausing to ask why we get different results. When the magnetic field is weak, the physics is dominated by the spin-orbit coupling $\mathbf{L} \cdot \mathbf{S}$ that we met in Section 7.1.3. This locks the orbital angular momentum and spin, so that only the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ sees the magnetic field. Mathematically, this means that we use the states $|n, j, m_j; l\rangle$ to compute the energy shifts in (8.15). In contrast, when the magnetic field is strong, the orbital angular momentum and spin both couple to the magnetic field. In a (semi-)classical picture, each would precess independently around the $\mathbf{B}$ axis. Mathematically, this means that we use the states $|n, l, m_l, m_s\rangle$ to compute the energy shifts in (8.14).

Let's now compute (8.15). It's a little trickier because we want the z-components of $\mathbf{L}$ and $\mathbf{S}$ while the states are specified only by the quantum numbers of $\mathbf{J}$. We'll need some algebraic gymnastics. First note the identity

$$i\hbar\,\mathbf{S}\times\mathbf{L} = (\mathbf{L}\cdot\mathbf{S})\mathbf{S} - \mathbf{S}(\mathbf{L}\cdot\mathbf{S}) \tag{8.16}$$

which follows from the commutators $[S_i, S_j] = i\hbar\epsilon_{ijk}S_k$ and $[L_i, S_j] = 0$. Further, since $2\mathbf{L}\cdot\mathbf{S} = \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2$, we have $[\mathbf{L}\cdot\mathbf{S}, \mathbf{J}] = 0$, which means that we can take the cross product of (8.16) to find

$$i\hbar\,(\mathbf{S}\times\mathbf{L})\times\mathbf{J} = (\mathbf{L}\cdot\mathbf{S})\,\mathbf{S}\times\mathbf{J} - \mathbf{S}\times\mathbf{J}\,(\mathbf{L}\cdot\mathbf{S})$$

But, by standard vector identities, we also have

$$\begin{aligned}(\mathbf{S}\times\mathbf{L})\times\mathbf{J} &= \mathbf{L}(\mathbf{S}\cdot\mathbf{J}) - \mathbf{S}(\mathbf{L}\cdot\mathbf{J})\\ &= \mathbf{J}(\mathbf{S}\cdot\mathbf{J}) - \mathbf{S}(\mathbf{J}^2)\end{aligned}$$

where, in the second line, we have simply used $\mathbf{L} = \mathbf{J} - \mathbf{S}$. Putting these two together gives the identity

$$(\mathbf{L}\cdot\mathbf{S})\,\mathbf{S}\times\mathbf{J} - \mathbf{S}\times\mathbf{J}\,(\mathbf{L}\cdot\mathbf{S}) = i\hbar\Big(\mathbf{J}(\mathbf{S}\cdot\mathbf{J}) - \mathbf{S}(\mathbf{J}^2)\Big) \tag{8.17}$$

Finally, we again use the fact that $2\mathbf{L}\cdot\mathbf{S} = \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2$ to tell us that $\mathbf{L}\cdot\mathbf{S}$ is diagonal in the basis $|n, j, m_j; l\rangle$. This means that the expectation value of the left-hand side of (8.17) vanishes in the states $|n, j, m_j; l\rangle$. Obviously the same must be true of the right-hand side. This gives us the expression

$$\langle n, j, m_j; l|\mathbf{S}(\mathbf{J}^2)|n, j, m_j; l\rangle = \langle n, j, m_j; l|\mathbf{J}(\mathbf{S}\cdot\mathbf{J})|n, j, m_j; l\rangle$$

Using $2(\mathbf{S}\cdot\mathbf{J}) = \mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2$, we then find that

$$\langle n, j, m_j; l|\mathbf{S}|n, j, m_j; l\rangle = \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}\,\langle n, j, m_j; l|\mathbf{J}|n, j, m_j; l\rangle$$

This is the result we need. Using $\mathbf{L} = \mathbf{J} - \mathbf{S}$, the shift in energy levels (8.15) can be written as

$$\begin{aligned}\Delta E &= \frac{eB}{2m}\langle n, j, m_j; l|J_z + S_z|n, j, m_j; l\rangle\\ &= \frac{eB}{2m}\Big(m_j\hbar + \langle n, j, m_j; l|S_z|n, j, m_j; l\rangle\Big) = \frac{e\hbar B}{2m}m_j g_J \end{aligned}\tag{8.18}$$

where g_J is known as the *Landé g-factor*, and is the ratio of angular momentum quantum numbers given by

$$g_J = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

It is a number which lies between 1 and 2.

We see that our final answer (8.18) for the Zeeman splitting is rather simple. Indeed, it's the answer we would expect for a magnetic dipole of the form,

$$\boldsymbol{\mu}_J = \frac{eg_J}{2m}\mathbf{J} \tag{8.19}$$

We see here the effect of the spin-orbit interaction. As explained above, it locks the spin and angular momentum together into the total angular momentum $\mathbf{J}$. This changes the dipole moment from (8.12) to this result.

The splitting of atomic energy levels allows us to see magnetic fields from afar. For example, we know the strength of magnetic fields in sunspots through the Zeeman splitting of the spectral lines of iron.

As the magnetic field is increased, the Zeeman interaction becomes increasingly competitive with the spin orbit coupling, and we must interpolate between (8.19) and the Paschen-Back effect (8.12). With no hierarchy of scales, life is more complicated and we must treat both H_Z and the fine-structure Hamiltonian separately. In practice, it is difficult to reach magnetic fields which dominate the spin-orbit interaction.

However, the discussion above also holds for the hyperfine interaction, whose energy splitting is comparable with magnetic fields that we can achieve in the lab. In this case, the total angular momentum is $\mathbf{F} = \mathbf{J} + \mathbf{I}$ with $\mathbf{I}$ the spin of the nucleus. Including the hyperfine interaction between the electron and nuclear spins, it is not hard to show that the magnetic moment of the atom becomes

$$\boldsymbol{\mu}_F = \frac{eg_F}{2m}\mathbf{F}$$

where

$$g_F = g_J\,\frac{F(F+1) + j(j+1) - I(I+1)}{2f(f+1)}$$

8.2.3 The Discovery of Spin

The suggestion that the electron carries an intrinsic angular momentum – which we now call spin – was first made by the Dutch physicists Samuel Goudsmit and George Uhlenbeck in 1925. At the time, both were students of Ehrenfest.

With hindsight, there was plenty of evidence pointing to the existence of spin. As we've seen in these lectures, the electron spin affects the atomic energy levels and resulting spectral lines in two different ways:

- Spin-Orbit Coupling: This is particularly prominent in sodium, where the existence of electron spin gives rise to a splitting of the $3p$ states. The transition of these states back to the $3s$ ground state results in the familiar yellow colour emitted by sodium street lights, and was long known to consist of two distinct lines rather than one.

- Zeeman Effect: The magnetic field couples to both the orbital angular momentum and to the electron spin. If the angular momentum is quantised as $l \in \mathbf{Z}$, we would expect to see a splitting into $(2l + 1)$ states, which is always an odd number. However, it was known that there are atoms – such as hydrogen – where the splitting results in an even number of states. Historically this was referred to as the *anomalous Zeeman effect*, reflecting the fact that no one could make sense of it. We now know that it arises because the electron spin is quantised as a half-integer.

On the more theoretical level, in early 1925 Pauli proposed his famous exclusion principle for the first time. He employed this to explain the structure of the periodic table, but it only worked if the electrons had four quantum numbers rather than three — what we now call n, l, m and m_s.

Despite these many hints, the proposal of Goudsmit and Uhlenbeck was not greeted with unanimous enthusiasm. Pauli was particularly dismissive. Lorentz, mired in a classical worldview, argued that if the electron was spinning like the Earth then its surface would have to be travelling faster than light. Indeed, a few months previously Kronig had privately considered the possibility of an electron spin, but had been talked out of it by these great minds.

One key reason for the skepticism lay in the initial difficulty of reconciling the spin-orbit and Zeeman effects: if you get the Zeeman splitting right, then the fine-structure splitting is off by a factor of 2. Here is what Goudsmit had to say[10]

> "*The next day, I received a letter from Heisenberg and he refers to our "mutige Note" (courageous note). I did not even know we needed courage to publish that. I wasn't courageous at all.... He says: "What have you done with the factor 2?" Which factor? Not the slightest notion.*
>
> *Of course, we ought to have made a quantitative calculation of the size of the splittings...We did not do that because we imagined it would be very difficult...We didn't know how to do it, and therefore we had not done it*

[10]You can read the full, charming, speech at http://lorentz.leidenuniv.nl/history/spin/goudsmit.html.

Luckily we did not know, because if we had done it, then we would have run into an error by a factor of 2"

This was only resolved a year later when Thomas discovered the relativistic effect that we now call Thomas precession. As we saw in Section 7.1.3, this changes the magnitude of the spin-orbit coupling by the necessary factor of 2. It was only with this addition to the theory that everything fitted and the spin of the electron became generally accepted.

The intrinsic spin of the electron is one of the most important discoveries in atomic and particle physics. It was ultimately explained by Dirac as a consequence of special relativity. For this Dirac was awarded the Nobel prize. For Goudsmit and Uhlenbeck, there was no such luck. Instead, in 1927, they were awarded their PhDs.

8.3 Shine a Light

In this section we look at what happens if you take an atom and shine a light on it. We'll continue to treat the electromagnetic field as classical. Ultimately we'll see that this approach has shortcomings and in later sections we'll consider both the atom and the light to be quantum.

A monochromatic light wave is described by oscillating electric and magnetic fields,

$$\mathbf{E} = \mathbf{E}_0\, e^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)} \quad \text{and} \quad \mathbf{B} = \frac{1}{c}(\hat{\mathbf{k}} \times \mathbf{E}_0)\, e^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)}$$

with $\omega^2 = c^2k^2$. The wavelength of the light is $\lambda = 2\pi/k = 2\pi c/\omega$. We will require that:

- The wavelength is much larger than the size of the atom: $\lambda \gg a_0$. This means that the electron does not experience a spatial gradient in the electric and magnetic fields; only a temporal change.

- The wavelength is tuned to be close to the energy transition between two atom states. For simplicity, we will focus on the ground state and first excited state. We then require $\omega \approx \omega_0$ where $\hbar\omega_0 = (E_2 - E_1)$. This condition will allow us to restrict our attention to just these two states, ignoring the others.

  Note that the second condition is compatible with the first. A typical energy level of hydrogen corresponds to a wavelength $\lambda \approx 2\pi a_0/\alpha$, so the factor of $\alpha \approx 1/137$ gives us a leeway of couple of orders of magnitude.

Shining a light means that we perturb the atom by both an electric and magnetic field. We know from Sections 8.1 and 8.2 that the typical energy shift in the linear Stark effect is $\Delta E \sim e\mathcal{E}a_0 \sim e\mathcal{E}\hbar/mc\alpha$, while the typical energy shift in the Zeeman effect is $\Delta E \sim eB\hbar/2m \sim e\mathcal{E}\hbar/2mc$. We see that the effects of the electric field are larger by a factor of $1/\alpha$. For this reason, we neglect the oscillating magnetic field in our discussion and focus only on the electric field.

Because $\lambda \gg a_0$, we can treat the electric field a time-dependent, but spatially uniform. We describe such a field by a potential $\phi = \mathbf{E} \cdot \mathbf{x}$, with $\mathbf{A} = 0$. This means that the full Hamiltonian is $H = H_0 + \Delta H(t)$, where the time-dependent perturbation is given by

$$\Delta H(t) = e\mathbf{E}_0 \cdot \mathbf{x} \cos(\omega t)$$

Our goal is to find the eigenstates of the time-dependent Hamiltonian. This is a straightforward exercise.

8.3.1 Rabi Oscillations

By construction, we will only consider two states, $|\psi_1\rangle$ and $|\psi_2\rangle$, obeying

$$H_0|\psi_i\rangle = E_i|\psi_i\rangle$$

Within the space spanned by these two states, the most general ansatz is

$$|\Psi(t)\rangle = c_1(t)e^{-iE_1t/\hbar}|\psi_1\rangle + c_2(t)e^{-iE_2t/\hbar}|\psi_2\rangle$$

with $|c_1|^2 + |c_2|^2 = 1$. We substitute this into the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial|\Psi\rangle}{\partial t} = (H_0 + \Delta H(t))|\Psi\rangle$$

to get

$$i\hbar\dot{c}_1 e^{-iE_1t/\hbar}|\psi_1\rangle + i\hbar\dot{c}_2 e^{-iE_2t/\hbar}|\psi_2\rangle = c_1 e^{-iE_1t/\hbar}\Delta H|\psi_1\rangle + c_2 e^{-iE_2t/\hbar}\Delta H|\psi_2\rangle$$

Now we take the overlap with $\langle\psi_1|$ and $\langle\psi_2|$ to find two, coupled differential equations

$$\begin{aligned} i\hbar\dot{c}_1 &= c_1\langle\psi_1|\Delta H|\psi_1\rangle + c_2\langle\psi_1|\Delta H|\psi_2\rangle e^{-i\omega_0 t} \\ i\hbar\dot{c}_2 &= c_1\langle\psi_1|\Delta H|\psi_2\rangle e^{i\omega_0 t} + c_2\langle\psi_2|\Delta H|\psi_2\rangle \end{aligned}$$

where

$$\hbar\omega_0 = E_2 - E_1$$

Our next task is to compute the matrix elements $\langle\psi_i|\Delta H|\psi_j\rangle$. The diagonal matrix elements are particularly simple

$$\langle\psi_i|\Delta H|\psi_i\rangle = e\mathbf{E}_0 \cdot \langle\psi_i|\mathbf{x}|\psi_i\rangle \cos(\omega t) = 0$$

These vanish because each $|\psi_i\rangle$ is a parity eigenstate and these are sandwiched between the parity-odd operator $\mathbf{x}$. This is the same argument that we used in Section 8.1 to show that the linear Stark effect vanishes for nearly all states.

The off-diagonal matrix elements are non-vanishing as long as $|\psi_1\rangle$ has opposite parity to $|\psi_2\rangle$. We define the *Rabi frequency* Ω as

$$\hbar\Omega = e\mathbf{E}_0 \cdot \langle\psi_1|\mathbf{x}|\psi_2\rangle \tag{8.20}$$

Note in particular that the Rabi frequency is proportional to the amplitude of the electric field. We're left having to solve the coupled differential equations

$$\begin{aligned} i\dot{c}_1 &= \Omega\cos(\omega t)\, e^{-i\omega_0 t} c_2 \\ i\dot{c}_2 &= \Omega\cos(\omega t)\, e^{+i\omega_0 t} c_1 \end{aligned}$$

In fact, there is one further simplification that we make. We write these as

$$\begin{aligned} i\dot{c}_1 &= \frac{\Omega}{2}\left(e^{i(\omega-\omega_0)t} + e^{i(\omega+\omega_0)t}\right) c_2 \\ i\dot{c}_2 &= \frac{\Omega}{2}\left(e^{-i(\omega-\omega_0)t} + e^{i(\omega+\omega_0)t}\right) c_1 \end{aligned} \tag{8.21}$$

The right-hand side of each of these equations has two oscillatory terms. Recall, however, that we required our frequency of light to be close to the atomic energy splitting ω_0. This means, in particular, that

$$|\omega-\omega_0| \ll \omega+\omega_0$$

So the second terms in (8.21) oscillate much faster than the first. We are interested only in the behaviour on long time scales – comparable to $|\omega-\omega_0|^{-1}$ — over which the fast oscillations simply average out. For this reason, we neglect the terms proportional to $e^{i(\omega+\omega_0)t}$. This is known as the *rotating wave approximation*, even though it's not obvious that it has anything to do with rotating waves! (For what it's worth, the name comes from nuclear magnetic resonance where a similar approximation means that you keep the wave which rotates in the same way as a spin and throw away the wave which rotates in the opposite direction.)

Invoking the rotating wave approximation, our equations simplify to

$$i\dot{c}_1 = \frac{\Omega}{2}e^{i\delta t}c_2 \quad \text{and} \quad i\dot{c}_2 = \frac{\Omega}{2}e^{-i\delta t}c_1 \tag{8.22}$$

where $\delta = \omega - \omega_0$ tells us how much the frequency of light ω differs from the natural frequency of the atomic energy levels ω_0.

Resonance

We start by considering the case $\delta = 0$, so that energy of light coincides with that of the level splitting. In this case the equations (8.22) are particularly simple: they are equivalent to the familiar second order differential equation

$$\ddot{c}_1 = -\frac{\Omega^2}{4}c_1 \quad \Rightarrow \quad c_1 = \cos\left(\frac{\Omega t}{2}\right) \quad \text{and} \quad c_2 = -i\sin\left(\frac{\Omega t}{2}\right)$$

where we picked initial conditions so that we sit in the ground state $|\Psi\rangle = |\psi_1\rangle$ at time $t = 0$.

We see that something lovely happens. The atom oscillates between the ground state and the first excited state with frequency Ω. This phenomena is known as *Rabi oscillations* or, sometimes, *Rabi flopping*.

The probability that the atom sits in the excited state at time t is given by $P_2(t) = |c_2|^2 = \sin^2(\Omega t/2)$. This means that if we start with the atom in the ground state and shine a pulse of resonant light for a time $T = \pi/\Omega$ then the atom will definitely be in the first excited state. This is known as a *π-pulse*.

Alternatively, we could act with a "$\frac{\pi}{2}$-pulse", shining resonant light for a time $T = \pi/2\Omega$. This leaves the atom in the superposition $|\Psi\rangle = (|\psi_1\rangle - i|\psi_2\rangle)/\sqrt{2}$. This allows us to experimentally create superpositions of states.

Off-Resonance

When the incident light is detuned from resonance, so $\delta \neq 0$, the first order equations (8.22) can be combined into the second order differential equation for c_1

$$\begin{aligned} &\frac{d^2c_1}{dt^2} - i\delta\frac{dc_1}{dt} + \frac{\Omega^2}{4}c_1 = 0 \\ \Rightarrow \quad &\left(\frac{d}{dt} - \frac{i\delta}{2} + \frac{i\sqrt{\Omega^2+\delta^2}}{2}\right)\left(\frac{d}{dt} - \frac{i\delta}{2} - \frac{i\sqrt{\Omega^2+\delta^2}}{2}\right)c_1 = 0 \end{aligned}$$

This has the solution

$$c_1(t) = e^{i\delta t/2}\left[A\cos\left(\frac{\sqrt{\Omega^2+\delta^2}}{2}t\right) + B\sin\left(\frac{\sqrt{\Omega^2+\delta^2}}{2}t\right)\right]$$

We'll again require that all the particles sit in the ground state $|\psi_1\rangle$ at time $t = 0$. This fixes $A = 1$ but this time we don't have $B = 0$. Instead, we use the first of the equations (8.22) to determine c_2 and require that $c_2(t = 0) = 0$. This gives the solution

$$c_1 = e^{i\delta t/2}\left[\cos\left(\frac{\sqrt{\Omega^2+\delta^2}}{2}t\right) - \frac{i\delta}{\sqrt{\Omega^2+\delta^2}}\sin\left(\frac{\sqrt{\Omega^2+\delta^2}}{2}t\right)\right]$$

and

$$c_2 = -ie^{-i\delta t/2}\frac{\Omega}{\sqrt{\Omega^2+\delta^2}}\sin\left(\frac{\sqrt{\Omega^2+\delta^2}}{2}t\right)$$

We see that the oscillations now occur at the *generalised Rabi frequency* $\sqrt{\Omega^2+\delta^2}$. This means that as we detune away from resonance, the oscillation rate increases. The probability of sitting in the excited state is now

$$P_2(t) = |c_2(t)|^2 = \frac{\Omega^2}{\Omega^2+\delta^2}\sin^2\left(\frac{\sqrt{\Omega^2+\delta^2}}{2}t\right) \tag{8.23}$$

We see that, for $\delta \neq 0$, this probability never reaches one: we can no longer be certain that we have excited the atom. However, the Rabi frequency Ω is proportional to the amplitude of the electric field (8.20). This means that as we increase the intensity of the electric field, the probability of excitation increases. In contrast, for very weak electric fields we have $\delta \gg \Omega$ and the probability never gets above Ω^2/δ^2,

$$P_2(t) \approx \frac{\Omega^2}{\delta^2}\sin^2\left(\frac{\delta\, t}{2}\right) \tag{8.24}$$

Electric Dipoles vs Magnetic Dipoles

Our discussion above describes transitions between states that are driven by the oscillating electric field. These are called *electric dipole transitions*.

However, there are also situations where the oscillating magnetic field dominates the physics. This occurs, for example, in fine structure and hyperfine structure transitions, both of which involve flipping a spin degree of freedom. The theory underlying these transitions is the same as we described above, now with a Rabi frequency given by

$$\hbar\Omega = \mathbf{B}\cdot\langle\psi_1|\boldsymbol{\mu}|\psi_2\rangle$$

where $\boldsymbol{\mu}$ is the atomic magnetic moment. Such transitions are called *magnetic dipole transitions*.

The oscillatory behaviour described above was first observed in hyperfine transitions. For this Isador Rabi won the 1944 Nobel prize.

8.3.2 Spontaneous Emission

Take an atom in an excited state, place it in a vacuum, and leave it alone. What happens? If we model the atom using the usual quantum mechanical Hamiltonian for the electrons orbiting a nucleus, then we get a simple prediction: nothing happens. Any quantum system when placed in an energy eigenstate will stay there, with only its phase oscillating as $e^{-iEt/\hbar}$.

Yet in the real world, something does happen. An atom in an excited state will decay, dropping down to a lower state and emitting a photon in the process. This is called *spontaneous emission*. This is not a process which happens deterministically. We cannot predict when a given atom will decay. We can only say that, on average, a given excited state has a lifetime τ. We would like to know how to calculate this lifetime.

How can we describe spontaneous emission in quantum mechanics? It is difficult because we need a framework in which the number of particles changes: before the decay, we have just the atom; after the decay we have both the atom and the photon. To model this properly we need to understand how to treat the electromagnetic field in a manner consistent with quantum mechanics. This is the subject of *quantum field theory*. We will make baby steps towards this in Section 8.4.

However, it turns out that there is a clever statistical mechanics argument, originally due to Einstein, that allows us to compute the lifetime τ of excited states without using the full framework of quantum field theory. We now describe this argument.

Rate Equations

Consider a large number of atoms. We start with N_1 in the ground state and N_2 in the excited state. Each of these excited atoms will spontaneously decay to the ground state with a rate that we call A_{21}. We model this with the rate equation

$$\frac{dN_2}{dt} = -A_{21}N_2 \tag{8.25}$$

The solution tells us that the population of excited atoms decays with a characteristic exponential behaviour, with lifetime τ defined as

$$N_2(t) = N_2(0)\, e^{-t/\tau} \qquad \text{with} \quad \tau = \frac{1}{A_{21}} \tag{8.26}$$

Our ultimate goal is to compute A_{21}. To do this, we will take the unusual step of making the situation more complicated: we choose to bathe the atoms in light.

The light gives rise to two further processes. First, the ground state atoms absorb light and are promoted to excited states. This happens at a rate which is proportional to the intensity of light, $\rho(\omega)$. Furthermore, as we saw above, the dominant effect comes from the light which is resonant with the energy difference of the atomic states,

$$\omega = \omega_0 \equiv \frac{E_2 - E_1}{\hbar}$$

We call the total rate for the ground state to be excited to the excited state $\rho(\omega_0)B_{12}$. (There is a slight subtlety here: the rate actually gets contributions from all frequencies, but these are absorbed into the definition of B_{12}. We'll see this in more detail below.)

The second process is a little counter-intuitive: the excited states can receive extra encouragement to decay to the ground state from the incident light. This process, known as *stimulated emission*. It too is proportional to the intensity of light. We denote the rate as $\rho(\omega_0)B_{21}$. If you're suspicious about this effect, you can alway view B_{21} as an extra parameter which could plausibly vanish. However, we'll see that one outcome of the argument is that $B_{21} \neq 0$: the phenomenon of stimulated emission is necessary on consistency grounds.

The net effect of bathing the atoms in light is that the rate equation (8.25) becomes

$$\frac{dN_2}{dt} = \rho(\omega_0)(B_{12}N_1 - B_{21}N_2) - A_{21}N_2$$

There is a similar equation for the population of ground state atoms

$$\frac{dN_1}{dt} = -\rho(\omega_0)(B_{12}N_1 - B_{21}N_2) + A_{21}N_2$$

The coefficients A_{21}, B_{21} and B_{12} are called the *Einstein A and B coefficients.*

In equilibrium, the populations are unchanging. In this case, the density of light of frequency ω_0 must be given by

$$\rho(\omega_0) = \frac{A_{21}N_2}{B_{12}N_1 - B_{21}N_2} \tag{8.27}$$

Throwing in Some Thermodynamics

At this point, we look at the problem from the more microscopic perspective of statistical mechanics. (See the lecture notes on Statistical Physics for the necessary background.) Before we proceed, we need to specify more information about the atom. We denote the degeneracy of the ground states, with energy E_1, and g_1 and the degeneracy of excited states, with energy E_2, as g_2.

We now assume that the whole atom/light mix sits in thermal equilibrium at a temperature T. Then the Boltzmann distribution tells us that the relative population of atomic states is given by

$$\frac{N_2}{N_1} = \frac{g_2 e^{-E_2/k_BT}}{g_1 e^{-E_1/k_BT}} = \frac{g_2}{g_1}\, e^{-\hbar\omega_0/k_BT}$$

Furthermore, the energy density of light is given by the Planck distribution,

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_BT} - 1} \tag{8.28}$$

Combining these formulae with our previous result (8.27), we find the result

$$\rho(\omega_0) = \frac{\hbar}{\pi^2 c^3} \frac{\omega_0^3}{e^{\hbar\omega_0/k_BT} - 1} = \frac{A_{21}}{B_{12}(g_1/g_2) e^{\hbar\omega_0/k_BT} - B_{21}}$$

We want this equation to hold for any temperature T. This is a strong requirement. First, it relates the absorption and stimulated emission coefficients

$$g_1 B_{12} = g_2 B_{21} \tag{8.29}$$

We see that, as promised, it is a thermodynamic requirement that stimulated emission occurs if absorption can occur. More surprisingly, we also get a relationship between the rates for stimulated emission and spontaneous emission

$$A_{21} = \frac{\hbar\omega_0^3}{\pi^2 c^3}\, B_{21} \tag{8.30}$$

This is a remarkable result. All information about the temperature of the background light bath has dropped out. Instead, we are left with a relationship that only depends on the inherent properties of the atom itself. Furthermore, the probability for an atom to decay in vacuum is related to the probability for it to decay when bombarded by light.

Computing the Einstein Coefficients

If we know one of the three Einstein coefficients, then the relations (8.29) and (8.30) immediately give us the other two. But we have already computed the probability for an atom to be excited in Section 8.3.1 in the context of Rabi oscillations.

We still need to do a little work to translate between the two results. In the limit of weak electromagnetic fields, the probability to excite the ground state by shining light of frequency ω was given in (8.24)

$$P_2(t) = \frac{\Omega^2}{(\omega-\omega_0)^2}\,\sin^2\left(\frac{(\omega-\omega_0)t}{2}\right)$$

If we take the electric field to be $\mathbf{E}_0 = (0,0,\mathcal{E})$, then the (square of the) Rabi frequency given by (8.20)

$$\Omega^2 = \frac{e^2\mathcal{E}^2}{\hbar^2}\,|\langle\psi_1|z|\psi_2\rangle|^2$$

In thermal equilibrium we have photons of all frequencies ω, whose energy distribution is governed by the blackbody formula (8.28). This means that we have electric fields $\mathcal{E}$ of all frequencies. Recall that the energy density $\rho(\omega)$ stored in an electric field is $\epsilon_0\mathcal{E}^2/2$. Integrating over frequencies, the probability to sit in the excited state is

$$P_2(t) = \frac{2e^2}{\epsilon_0\hbar^2}|\langle\psi_1|z|\psi_2\rangle|^2 \int d\omega\,\frac{\rho(\omega)}{(\omega-\omega_0)^2}\,\sin^2\left(\frac{(\omega-\omega_0)t}{2}\right)$$

This integral is dominated by the region near $\omega = \omega_0$. We therefore replace $\rho(\omega)$ by $\rho(\omega_0)$ and bring it outside the integral,

$$P_2(t) \approx \frac{2e^2}{\epsilon_0\hbar^2}\,\rho(\omega_0)|\langle\psi_1|z|\psi_2\rangle|^2 \int d\omega\,\frac{1}{(\omega-\omega_0)^2}\,\sin^2\left(\frac{(\omega-\omega_0)t}{2}\right)$$

Note that this step ensures that the rate is indeed proportional to $\rho(\omega_0)$, which was an assumption in deriving our rate equations above. Finally, to do the integral we write $x = (\omega-\omega_0)t/2$ and extend the range from $-\infty$ to ∞,

$$\begin{aligned} P_2(t) &\approx \frac{2e^2}{\epsilon_0\hbar^2}\,\rho(\omega_0)|\langle\psi_1|z|\psi_2\rangle|^2\,\frac{t}{2}\int_{-\infty}^{+\infty} dx\,\frac{\sin^2 x}{x^2} \\ &= \frac{e^2\pi}{\epsilon_0\hbar^2}\,\rho(\omega_0)|\langle\psi_1|z|\psi_2\rangle|^2\;t \end{aligned}$$

The fact that the probability grows linearly with t is an artefact of the approximation above. The answer is correct only for small t. The real lesson to take from this is that the rate $\dot{P}_2(t)$ is given by

$$\text{Rate of Absorption} = \dot{P}_2(t) = \frac{e^2\pi}{\epsilon_0\hbar^2}\,\rho(\omega_0)|\langle\psi_1|z|\psi_2\rangle|^2$$

from which we get the Einstein coefficient

$$B_{12} = \frac{e^2\pi}{\epsilon_0\hbar^2}\,|\langle\psi_1|z|\psi_2\rangle|^2$$

Finally, since the light is bombarding the atom from all directions, this is often written using rotationally invariant matrix elements,

$$B_{12} = \frac{e^2\pi}{3\epsilon_0\hbar^2}\,|\langle\psi_1|\mathbf{x}|\psi_2\rangle|^2 \tag{8.31}$$

Using the Einstein relations (8.29) and (8.30), we see that the smaller the matrix element, the longer lived the particle.

8.3.3 Selection Rules

What happens if the matrix element (8.31) vanishes? In this case the excited state does not decay when subjected to oscillating electric fields: it is stable against electric dipole transitions. The fact that some transitions are forbidden is referred to as *selection rules*. This doesn't mean that these excited atomic states are fully stable because there can still be other decay channels as we explain below.

We have already seen situations where $\langle\psi_1|\mathbf{x}|\psi_2\rangle$ vanishes when discussing the Stark effect. Because $\mathbf{x}$ is parity odd, the two states must differ in parity. However, there are more stringent selection rules than those that follow from parity alone. Here we recapitulate and extend these results.

First, an obvious point. The operator $\mathbf{x}$ knows nothing about the spin of the states, so $|\psi_1\rangle$ and $|\psi_2\rangle$ must have the same spin. We write this as the requirement

$$\Delta s = \Delta m_s = 0$$

More powerful selection rules come from looking at the other angular momentum quantum numbers. Neglecting spin, the atomic states $|\psi\rangle$ are labelled by $|n, l, m\rangle$. Using $[L_z, z] = 0$, we have

$$\langle n', l', m'|[L_z, z]|n, l, m\rangle = \hbar(m' - m)\langle n', l', m'|z|n, l, m\rangle = 0$$

This tells us that electric fields which oscillate in the z-direction can only effect a transition if $m = m'$, or

$$\Delta m = 0 \quad \text{for light polarised in the } z \text{ direction}$$

However, we also have $[L_z, x \pm iy] = \pm\hbar(x \pm iy)$ which tells us

$$\begin{aligned} \langle n', l', m'|[L_z, x \pm iy]|n, l, m\rangle &= \hbar(m' - m)\langle n', l', m'|x \pm iy|n, l, m\rangle \\ &= \pm\hbar\langle n', l', m'|x \pm iy|n, l, m\rangle \end{aligned}$$

This tells us that electric fields oscillating perpendicular to the z-direction can only effect a transition when $m' - m = \pm 1$, or

$$\Delta m = \pm 1 \quad \text{for light polarised transverse to the } z \text{ direction}$$

To determine the allowed transitions between l quantum numbers, we use the identity $[L^2, [L^2, \mathbf{x}]] = 2\hbar^2(\mathbf{x}L^2 + L^2\mathbf{x})$, which gives us

$$\begin{aligned} \langle n', l', m'|L^2, [L^2, \mathbf{x}]]|n, l, m\rangle &= \hbar^2(l'(l'+1) - l(l+1))^2\langle n', l', m'|\mathbf{x}|n, l, m\rangle \\ &= 2\hbar^2(l'(l'+1) + l(l+1))\langle n', l', m'|\mathbf{x}|n, l, m\rangle \end{aligned}$$

Rearranging and factorising, we have

$$(l + l')(l + l' + 2)((l - l')^2 - 1)\langle n', l', m'|\mathbf{x}|n, l, m\rangle = 0$$

Since $l, l' > 0$, we learn that this matrix element is non-vanishing only if $l - l' = \pm 1$, or

$$\Delta l = \pm 1$$

We've derived each of these selection rules by pulling a commutation relation identity out of thin air and then seeing that it happens to give the right answer. This feels a little like a trick. A much more systematic approach is to invoke the Wigner-Eckart theorem, which tells us what matrix elements are non-vanishing based on the representation theory of the rotation group.

An example of an electric dipole transition consistent with these selection rules is the $2p \to 1s$ decay of hydrogen. It is a simple matter to compute this using the formulae above: one finds a lifetime $\tau \approx 10^{-9}$ seconds. In contrast, the $2s \to 1s$ transition is forbidden by the selection rule $\Delta l = \pm 1$. The decay does eventually happen, but has to find another route. (It turns out that it primarily emits two photons rather than one). Correspondingly, the lifetime is much longer, $\tau \approx 10^{-1}$ seconds.

There's a cute piece of physics here related to the Stark effect. Recall from Section 8.1 that a constant background electric field causes the $2s$ state of hydrogen to mix with the $2p$ state. (See equation (8.5).) But, when combined with the phenomena of spontaneous emission, this state immediately becomes more unstable. This means that we can create a gas of hydrogen atoms in the $2s$ state, comfortable in the knowledge that they will last a relatively long time (around a tenth of a second). But when subjected to a constant electric field, they will immediately decay to the ground state, releasing a burst of light.

Magnetic Dipole Transitions

The selection rules described above hold for electric dipole transitions. However, if the matrix elements vanish it does not mean that the excited state of the atom is absolutely stable. To paraphrase Jeff Goldblum, Nature will find a way. There are other channels through which the atom can decay. Indeed, we already briefly described the magnetic dipole transition, in which the relevant matrix element is

$$\langle\psi_1|\boldsymbol{\mu}|\psi_2\rangle$$

Here the selection rules are different. In particular, $\boldsymbol{\mu}$ is related to the angular momentum operator and is parity even. This means that, in contrast to the electric dipole transition, the matrix element above is non-vanishing only if $|\psi_1\rangle$ and $|\psi_2\rangle$ have the same parity. For example, transitions between levels spit by fine structure or hyperfine structure have the same parity and so occur through magnetic dipole effects.

The lifetime of any excited state is determined by the largest matrix element. Sometimes, even the largest matrix element can be very small in which case the atomic state is long lived. An extreme example occurs for the hyperfine structure of hydrogen, which gives rise to the 21 cm line: its lifetime is around 10 million years.

8.4 Photons

The relationship (8.29) and (8.30) have allowed us to determine the rate of spontaneous emission of a photon. But it's clear the argument relied on the magic of thermodynamics. To go beyond this description, we need a way to incorporate both the quantum state of the atom and the quantum state of the electromagnetic field. This is the framework of *Quantum Field Theory*. We will see how to quantise the electromagnetic field in next year's *Quantum Field Theory* lectures. Here we offer a baby version.

8.4.1 The Hilbert Space of Photons

The quantum state of the electromagnetic field is described by how many *photons* it contains. Each photon is a particle of light. Its properties are described by two quantum numbers. The first is the momentum, which is given by $\mathbf{p} = \hbar\mathbf{k}$. Here $\mathbf{k}$ is the wavevector and its magnitude, $k = |\mathbf{k}|$, is the wavenumber; it is related to the wavelength by $\lambda = 2\pi/k$ and to the frequency by $\omega(k) = kc$. . The energy of a photon is given by the famous formula

$$E = \hbar\omega \tag{8.32}$$

Note that, when combined with the definition of momentum, this is simply the relativistic dispersion relation for a massless particle: $E = pc$.

The second property of the photon is its polarisation. This is described by a vector which is orthogonal to $\mathbf{k}$. For each $\mathbf{k}$, we define a two-dimensional basis of polarisation vectors $\mathbf{e}^\lambda_{\mathbf{k}}$, with $\lambda = 1, 2$, obeying

$$\mathbf{e}^\lambda_{\mathbf{k}} \cdot \mathbf{k} = 0$$

To specify the state of the electromagnetic field, we need to say how many photons it contains, together with the information $\mathbf{k}$ and $\mathbf{e}^\lambda_{\mathbf{k}}$ for each photon. The states are therefore labelled by a list of non-negative integers,

$$|\{n_{\mathbf{k}\,\lambda}\}\rangle$$

where $n_{\mathbf{k}\,\lambda} \in \mathbf{Z}$ tells us how many photons we have with momentum $\mathbf{k}$ and polarisation λ.

We start with the state with no photons. This is the vacuum state and is denoted as $|0\rangle$. The key to quantum field theory is to view the particles – in this case, the photons – as excitations of the underlying field, in much the same way that the states of the harmonic oscillator arise from exciting the vacuum. For each type of photon, we introduce annihilation and creation operators, $a_{\mathbf{k}\,\lambda}$ and $a^\dagger_{\mathbf{k}\,\lambda}$. These obey the familiar commutation relations of the harmonic oscillator,

$$[a_{\mathbf{k}\,\lambda}, a^\dagger_{\mathbf{k}\,\lambda'}] = \delta_{\mathbf{k},\mathbf{k}'}\delta_{\lambda,\lambda'}$$

The annihilation operators have the property that $a_{\mathbf{k}\,\lambda}|0\rangle = 0$. The quantum state of a single photon with momentum $\mathbf{k}$ and polarisation λ is described by $a^\dagger_{\mathbf{k}\,\lambda}|0\rangle$. The general state of the quantum field is given by

$$|\{n_{\mathbf{k}\,\lambda}\}\rangle = \prod_{\mathbf{k},\lambda} = \frac{(a^\dagger_{\mathbf{k}\,\lambda})^{n_{\mathbf{k}\,\lambda}}}{\sqrt{n_{\mathbf{k}\,\lambda}!}}|0\rangle \tag{8.33}$$

This is the same kind of set-up that we saw in Section 4.1.4 when discussing the quantisation of phonons.

So far we have only described the Hilbert space of the electromagnetic field. It consists of an infinite number of harmonic oscillators, one for each $\mathbf{k}$ and λ. Note that already here we're dealing with something unfamiliar from the quantum mechanics perspective. Usually in quantum mechanics we fix the number of particles and then look at the Hilbert space. But here our Hilbert space contains states with different numbers of photons. Such Hilbert spaces are sometimes referred to as *Fock spaces*.

The final step is to determine that Hamiltonian that governs the evolution of these states. This too is lifted from the harmonic oscillator: it is

$$H = \sum_{\mathbf{k},\lambda} \left(\hbar\omega(k)\, a^\dagger_{\mathbf{k}\,\lambda} a_{\mathbf{k}\,\lambda} + \frac{1}{2} \right)$$

Acting on our states (8.33) we have

$$H|\{n_{\mathbf{k}\,\lambda}\}\rangle = E|\{n_{\mathbf{k}\,\lambda}\}\rangle \quad \text{with} \quad E = \sum_{\mathbf{k},\lambda} n_{\mathbf{k}\,\lambda}\, \hbar\omega(k)$$

which agrees with the formula (8.32), now generalised to a large number of photons.

Above, we have simply stated the Hilbert space and Hamiltonian for the electromagnetic field. Of course, ultimately we should derive these results starting from the Maxwell equations. This will be done in the *Quantum Field Theory* course.

8.4.2 Coherent States

Recall from our earlier lectures on the harmonic oscillator that there is a special state which most closely mimics a classical state. This is the *coherent state*. In the present context a coherent state is parameterised by $\alpha \in \mathbf{C}$ and consists of a sum of photons, each with the same wavevector and polarisation. We write $a \equiv a_{\mathbf{k}\,\lambda}$. The coherent state can then be expressed as

$$|\alpha\rangle = e^{\alpha a^\dagger - \alpha^\star a}|0\rangle = e^{-|\alpha|^2/2} e^{\alpha a^\dagger}|0\rangle$$

where the equality follows from some standard manipulations of creation and annihilation operators. States of this kind are the closest that a quantum state gets to a classical plane wave. In particular, the classical expectation values of the electric and magnetic fields can be shown to oscillate back and forth with frequency $\omega = kc$.

The coherent states are eigenstates of the annihilation operator, meaning that they are unchanged by the removal of a photon. The parameter α determines the mean number of photons in the state,

$$\langle n\rangle = \langle\alpha|a^\dagger a|\alpha\rangle = |\alpha|^2$$

Coherent states play a particularly important role in quantum optics. In this context, they are sometimes referred to as *Glauber states*. (Roy Glauber was award the 2005 Nobel prize for pioneering the use of these states.)

Making a Coherent State

The light emitted by a laser is described by a coherent state. I'm not going to try to explain how a laser works here. (It's to do with stimulated emission of a bunch of atoms.) But there is a simple model which explains how coherent states naturally arise: it is the *driven harmonic oscillator*,

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) + \hbar\Big(f^\star(t)a + f(t)a^\dagger\Big)$$

Here $f(t)$ is a forcing function which excites the harmonic oscillator. In the context of electrodynamics, we think of $a^\dagger$ as creating photons of frequency ω (and some unspecified polarisation). We will now show that the forcing term creates photons.

We solve the Hamiltonian in the interaction picture, taking $H_0 = \hbar\omega(a^\dagger a + \frac{1}{2})$. Recall that states in the interaction picture are related to those in the Schrödinger picture by $|\psi\rangle_I = e^{iH_0t/\hbar}|\psi\rangle_S$. The interaction picture for the interaction Hamiltonian is

$$H_I = \hbar e^{iH_0t/\hbar}\Big(f^\star(t)a + f(t)a^\dagger\Big)e^{-iH_0t/\hbar} = \hbar\Big(e^{-i\omega t}f^\star(t)a + e^{i\omega t}f(t)a^\dagger\Big)$$

The states then evolve as $|\psi(t)\rangle_I = U_I(t)|\psi(0)\rangle_I$, where the unitary operator U_I obeys

$$i\hbar\frac{\partial U_I}{\partial t} = H_I U_I$$

You can check that the solution is given by

$$U_I(t) = \exp\Big(\alpha(t)a^\dagger - \alpha^\star(t)a + i\varphi(t)\Big)$$

where $\alpha(t) = -i\int^t dt'\, f(t')e^{i\omega t'}$ and $\varphi(t) = \frac{1}{2}\int^t dt'\,\mathrm{Im}(\dot{\alpha}^\star\alpha)$. (To check this, you'll need to use some commutation relations, in particular $[e^{\alpha a^\dagger}, a]e^{-\alpha a^\dagger} = -\alpha$.)

Now suppose that we drive the oscillator at its natural frequency, so that $f(t) = f_0e^{-i\omega t}$. In this case, $\alpha(t) = -if_0t$ and the states in the interaction picture are given by

$$|\psi(t)\rangle_I = e^{-if_0(a^\dagger + a)t}|0\rangle_I = e^{-(f_0t)^2/2}e^{-if_0a^\dagger t}|0\rangle_I$$

This is the coherent state $|\alpha\rangle$. Equivalently, if we transform back to the Schrödinger picture, we have the coherent state

$$|\psi(t)\rangle_S = e^{-iH_0t/\hbar}|\psi(t)\rangle_I = e^{-(f_0t)^2/2}e^{-if_0e^{-i\omega t}a^\dagger t}|0\rangle$$

The upshot of this discussion is that adding a forcing term to the harmonic oscillator drives the ground state to a coherent state. While this doesn't explain the importance of coherent states in, say, laser physics, hopefully it at least provides some motivation.

8.4.3 The Jaynes-Cummings Model

Now that we have a description of the quantised electromagnetic field, we would like to understand how it interacts with atoms. Here we construct a simple, toy model that captures the physics.

The first simplification is that we consider the atom to have just two states. This is essentially the same approximation that we made in Section 8.3 when discussing Rabi oscillations. Here we change notation slightly: we call the ground state of the system $|\downarrow\rangle$ and the excited state of the system $|\uparrow\rangle$. (These names are adopted from the notation for spin, but that's not the meaning here. For example, $|\downarrow\rangle$ may describe the $1s$ state of hydrogen, and $|\uparrow\rangle$ the 2p state.)

As in our discussion of Rabi oscillations, we take the energy splitting between the two states to be $\hbar\omega_0$. This means that, in the absence of any coupling to the electromagnetic field, our two-state "atom" is simply described by the Hamiltonian

$$H_{\text{atom}} = \frac{1}{2}\begin{pmatrix} \hbar\omega_0 & 0 \\ 0 & -\hbar\omega_0 \end{pmatrix} \tag{8.34}$$

This atom will interact with photons of frequency ω. We will only include photons with this frequency and no others. In reality, this is achieved by placing the atom in a box which can only accommodate photons of wavelength $\lambda = 2\pi c/\omega$. For this reason, the restriction to a single frequency of photon is usually referred to as *cavity quantum electrodynamics.*

We will ignore the polarisation of the photon. Following our discussion above, we introduce the creation operator $a^\dagger$. The Hilbert space of photons is then spanned by the states $|n\rangle = (a^\dagger)^n/\sqrt{n!}|0\rangle$, with Hamiltonian

$$H_{\text{photon}} = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \tag{8.35}$$

We often omit the zero-point energy $\hbar\omega/2$ since it only contributes a constant.

Combining the two, the Hilbert space is $\mathcal{H} = \mathcal{H}_{\text{atom}} \otimes \mathcal{H}_{\text{photon}}$ and is spanned by the states $|n;\uparrow\rangle$ and $|n;\downarrow\rangle$, with $n \geq 0$. The Hamiltonian includes both (8.34) and (8.35), but also has an interaction term. We want this interaction term to have the property that if the excited state $|\uparrow\rangle$ decays to the ground state $|\downarrow\rangle$ then it emits a photon. Similarly, the ground state $|\downarrow\rangle$ may absorb a photon to become excited to $|\uparrow\rangle$. This physics is captured by the following Hamiltonian

$$H_{JC} = \frac{\hbar}{2}\begin{pmatrix} \omega_0 & ga \\ ga^\dagger & -\omega_0 \end{pmatrix} + \hbar\omega a^\dagger a$$

This is the *Jaynes-Cummings model.* The constant g characterises the coupling between the atom and the photons.

As we'll see, the Jaynes-Cummings model captures many of the features that we've seen already, including Rabi oscillations and spontaneous emission. However, you shouldn't think of the photons in this model as little wavepackets which, when emitted, disappear off into the cosmos, never to be seen again. Instead, the photons are momentum eigenstates, spread throughout the cavity in which the atom sits. When emitted, they hang around. This will be important to understand the physics.

We now look at the dynamics of the Jaynes-Cummings model. The state $|0,\downarrow\rangle$ describes an atom in the ground state with no photons around. This state is an eigenstate of H_{JC} with energy $H_{JC}|0,\downarrow\rangle = -\frac{1}{2}\epsilon|0,\downarrow\rangle$.

However, the state $|0,\uparrow\rangle$, describing an excited atom in the vacuum is not an eigenstate. It can evolve into $|1,\downarrow\rangle$, describing an atom in the ground state with one photon. More generally, the Hilbert space splits into sectors with the $|n-1,\uparrow\rangle$ state mixing with the $|n,\downarrow\rangle$ state. Restricted to these two states, the Hamiltonian is a 2×2 matrix given by

$$H_n = \left(n - \frac{1}{2}\right)\omega \mathbf{1}_2 + \frac{1}{2}(\omega_0 - \omega)\sigma^3 + \frac{1}{2}g\sqrt{n}\sigma^1$$

where σ^i are the Pauli matrices. The two eigenstates are

$$\begin{aligned} |n_+\rangle &= \sin\theta|n-1,\uparrow\rangle - \cos\theta|n,\downarrow\rangle \\ |n_-\rangle &= \cos\theta|n-1,\uparrow\rangle + \sin\theta|n,\downarrow\rangle \end{aligned}$$

where

$$\tan(2\theta) = \frac{g\sqrt{n}}{\delta} \quad , \quad \delta = \omega_0 - \omega \tag{8.36}$$

δ is the same detuning parameter we used before. When $\delta = 0$, we are on resonance, with the energy of the photon coinciding with the energy splitting of the atom. In general, two energy eigenvalues are

$$E_\pm = \left(n + \frac{1}{2}\right)\hbar\omega \pm \frac{1}{2}\hbar\sqrt{g^2 n + \delta^2}$$

Let's now extract some physics from these solutions.

Rabi Oscillations Revisited

Consider an atom in the ground state, surrounded by a fixed number of photons n. The initial state is $|\Psi(t=0)\rangle = |n, \downarrow\rangle = \sin\theta|n_-\rangle - \cos\theta|n_+\rangle$. The state subsequently evolves as

$$|\Psi(t)\rangle = \left[e^{-iE_- t/\hbar}\sin\theta|n_-\rangle - e^{-iE_+ t/\hbar}\cos\theta|n_+\rangle\right]$$

From this, we can extract the probability of sitting in the excited state

$$P_\uparrow(t) = \frac{g^2 n}{g^2 n + \delta^2}\,\sin^2\left(\frac{\sqrt{g^2 n + \delta^2}}{2}t\right)$$

This agrees with our earlier result (8.23) which was derived for an atom sitting in a classical electric field. Note that the Rabi frequency (8.20) should be equated with $\Omega = g\sqrt{n}$. This makes sense: the coupling g is capturing the matrix element, while the number of photons n is proportional to the energy stored in the electromagnetic field, so $\sqrt{n}$ is proportional to the amplitude of the electric field.

Death and Resurrection

The Jaynes-Cummings model captures also new physics, not seen when we treat the electromagnetic field classically. This is simplest to see if we tune the photons to resonance, setting $\delta = 0$. With this choice, (8.36) tells us that $\cos\theta = \sin\theta = 1/\sqrt{2}$.

We again place the atom in its ground state, but this time we do not surround it with a fixed number of photons. Instead, we place the electromagnetic field in a *coherent state*

$$|\Psi\rangle = e^{-|\alpha|^2/2}e^{\alpha a^\dagger}|0,\downarrow\rangle = e^{-|\lambda|^2/2}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n,\downarrow\rangle$$

We will take the average number of photons in this state to be macroscopically large. This means $|\alpha| \gg 1$. Now the evolution is given by

$$|\Psi(t)\rangle = e^{-(|\alpha|^2 - i\omega t)/2}\sum_{n=0}^{\infty}\frac{(\alpha e^{-i\omega t})^n}{\sqrt{n!}}\left[\cos\left(\frac{g\sqrt{n}t}{2}\right)|n,\downarrow\rangle) + i\sin\left(\frac{g\sqrt{n}t}{2}\right)|n-1,\uparrow\rangle\right]$$

The probability to find the atom in its excited state is

$$P_\uparrow(t) = e^{-|\alpha|^2}\sum_{n=0}^{\infty}\frac{|\alpha|^{2n}}{n!}\sin^2\left(\frac{g\sqrt{n}t}{2}\right)$$

Now there are many oscillatory contributions to the probability, each with a different frequency. We would expect these to wash each other out, so that there are no coherent oscillations in the probability. Indeed, we we will now see, this is what happens. But there is also a surprise in store.

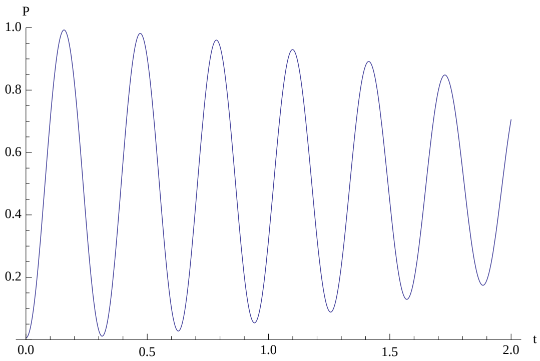

Figure 83: Rabi Oscillations at short times...

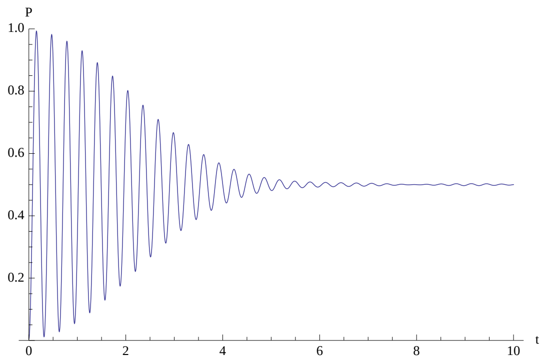

Figure 84: ...and their decay at longer times.

To analyse the sum over different frequencies, we first rewrite the probability as

$$P_\uparrow(t) = e^{-|\alpha|^2} \sum_{n=0}^{\infty} \frac{|\alpha|^{2n}}{n!} \left(\frac{1}{2} - \frac{1}{2}\cos(g\sqrt{n}t) \right) = \frac{1}{2} - \frac{1}{2} e^{-|\alpha|^2} \sum_{n=0}^{\infty} \frac{|\alpha|^{2n}}{n!} \cos(g\sqrt{n}t)$$

where, in the second equality, we have used the Taylor expansion of the exponential. The sum is sharply peaked at the value $n \approx |\alpha|^2$. To see this, we use Stirlings formula to write

$$\frac{|\alpha|^{2n}}{n!} \approx \frac{1}{\sqrt{2\pi n}} e^{n\log|\alpha|^2 - n\log n + n}$$

The exponent $f(n) = 2n\alpha|\alpha| - n\log n + n$ has a maximum at $f'(n) = \log|\alpha|^2 - \log n = 0$, or $n = |\alpha|^2$. We then use $f''(n) = -1/n$. Taylor expanding around the maximum, we have

$$\frac{|\alpha|^{2n}}{n!} \approx \frac{1}{\sqrt{2\pi|\alpha|^2}} e^{|\alpha|^2 - m^2/2|\alpha|^2}$$

where $m = n - |\alpha|^2$. With $|\alpha|^2$ sufficiently large, the sum over m effectively ranges from $-\infty$ to $+\infty$. We have

$$P_\uparrow(t) \approx \frac{1}{2} - \frac{1}{2} \sum_{m=-\infty}^{\infty} \frac{1}{\sqrt{2\pi|\alpha|^2}} e^{-m^2/2|\alpha|^2} \cos\left(gt\sqrt{|\alpha|^2 + m}\right) \tag{8.37}$$

Let's now try to build some intuition for this sum. First note that for very short time periods, there will be the familiar Rabi oscillations. A single cycle occurs with period $gT|\alpha| = 2\pi$, or

$$T_{\text{Rabi}} \approx \frac{2\pi}{g|\alpha|}$$

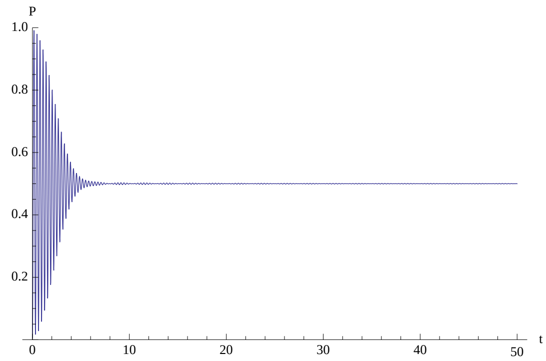

Figure 85: Once decayed, they stay decayed...

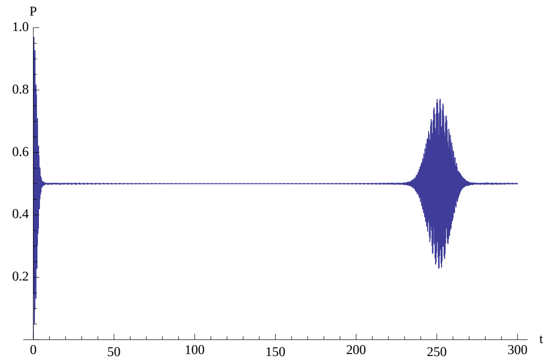

Figure 86: ...until they don't!

These oscillations occur at a Rabi frequency determined by the average number of photons $\langle n\rangle = |\alpha|^2$. In the first figure, we've plotted the function (8.37) for $|\alpha| = 20$ and times $gt \leq 2$. We clearly see the Rabi oscillations at these time scales

There are other features that occur on longer time scales. The exponential suppression means that only the terms up to $|m| \approx |\alpha|$ will contribute in a significant way. If, over the range of these terms, we get a change of phase by 2π then we expect destructive interference among the different oscillations. This occurs when $gT(\sqrt{|\alpha|^2 + |\alpha|} - |\alpha|) \approx 2\pi$, or

$$T_{\text{collapse}} \approx \frac{4\pi}{g}$$

This tells us that after approximately $|\alpha|$ Rabi oscillations, the probability asymptotes to $P_\uparrow = \frac{1}{2}$. This is the expected behaviour if the atom is subjected to lots of different frequencies. This collapse is clearly seen in the first right-hand figure, which plots the function (8.37) for $|\alpha| = 20$ and time scales up to $gt \leq 10$. Indeed, the left-hand plot of the next diptych extends the timescale to $gt \approx 50$, where we clearly see that the probability settles to $P_\uparrow = \frac{1}{2}$.

However, there is a surprise in store! At much longer timescales, each term in the sum picks up the same phase from the cos factor: i.e. $\cos(gT|\alpha|) = \cos(gT\sqrt{|\alpha|^2 + 1})$, or $gT(\sqrt{|\alpha|^2 + 1} - |\alpha|) = 2\pi$. This occurs when

$$T_{\text{revival}} \approx \frac{4\pi|\alpha|}{g}$$

On these time scales, the terms in the sum once again add coherently and we can find the particle in the excited state with an enhanced probability. This is called *quantum* *revival* and is clearly seen in the second right-hand plot. Note that the probability in the revival never reaches one, nor dips to zero.

Revival is a novel effect that arises from the quantisation of the electromagnetic field; it has no classical analog. Note that this effect does not occur because of any coherence between the individual photon states. Rather, it occurs because of the discreteness of the electromagnetic field

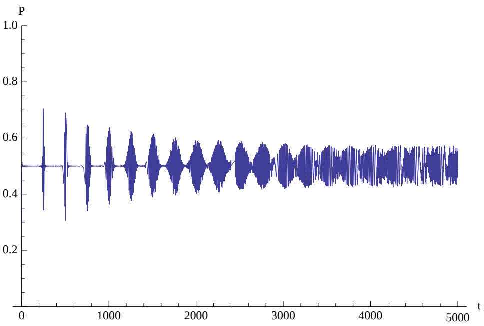

Figure 87:

Finally, we can ask what the probability looks like on extremely long time scales $t \gg T_{\text{revival}}$. On the right, we continue our plots to $gt = 5000$. We see a number of collapses and revivals, until the system becomes noisy and fluctuating at large times.