Chapter 4
Atoms and Energy

In this chapter, we look at the energy of electrons in an atom and determine how the quantum state of the atom changes over time. This leads us to introduce the energy operator, or Hamiltonian, and the Schrödinger equation that governs the behaviour of quantum systems. We show how light can interact with an atom, and as a demonstration of the quantum theory developed so far we explain how atomic clocks work.

4.1 The Energy Spectrum of Atoms

Atoms consist of electrons in orbits around a nucleus made of protons and neutrons. The negatively charged electrons are attracted to the positively charged protons in the nucleus by the Coulomb force, and this is how atoms are held together. It is very tempting to think of an atom as a mini solar system, with the nucleus in place of the sun and the electrons as planets, but this is a misleading picture. As in the previous chapters, we again consider a simple experiment to guide our investigations.

We fill a transparent container with hydrogen gas, and heat it in order to break up the hydrogen molecules into hydrogen atoms. White light is sent first through the container and second through a diffraction grating that separates the different frequencies of the white light into a spectrum. This is a technique called *spectroscopy* (see Fig. 4.1). When we inspect the spectrum, we will see the familiar rainbow pattern. In addition, we observe dark lines at specific colours in the spectrum. These are absorption lines, shown in Fig. 4.2. Somehow, the hydrogen interacts strongly with

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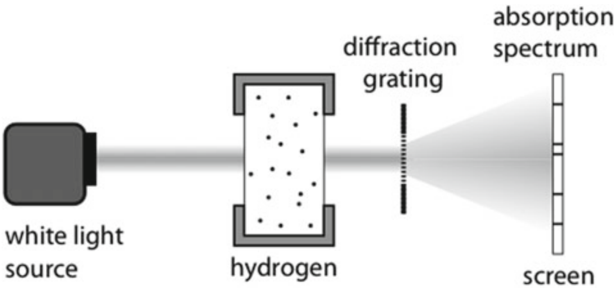

Fig. 4.1 Spectroscopy

light of these particular wavelengths (the absorption lines are not there if there isn't any hydrogen in the container).

The explanation of this phenomenon, first given by Niels Bohr (1913) in 1913 and based on Einstein's explanation of the photoelectric effect (Einstein 1905) from 1905, is simple: photons of a particular wavelength λ carry an energy $E = hc/\lambda$, with h Planck's constant and c the speed of light. We often write this in terms of the (angular) frequency ω:

$$E = \frac{hc}{\lambda} = \hbar\omega\,. \tag{4.1}$$

The angular frequency is measured in radians per second (rad s^{-1}), and is related to the frequency f via $\omega = 2\pi f$. The photon is a packet of electromagnetic energy that can be absorbed by the electron in a hydrogen atom. This leads to a more energetic electron, and the disappearance of the photon. When lots of hydrogen atoms are placed in the path of a beam of light, many photons are absorbed, leading to a reduced intensity of the light. The experimental fact that the reduced intensity happens for very specific frequencies (the absorption lines) indicates that electrons can absorb only photons of these frequencies. Bohr argued that the electrons in the hydrogen atom can exist only in very specific energy states, and the frequency lines in the absorption spectrum correspond to the energy it takes to go from one energy state to another. Moreover, the electrons have a lowest possible energy state called the ground state, which is why the electrons do not crash into the nucleus (see Fig. 4.3). This is related to the uncertainty in position and momentum of the electron, and we will explore this further in Chap. 9.

We can now identify the energy states of an electron in a hydrogen atom by carefully studying the absorption lines. An electron with energy E will be in the energy state $|E\rangle$. We can enumerate the energy states $|E_n\rangle$ with $n = 1, 2, 3, \ldots$, where E_1 is the energy of the ground state, E_2 is the energy of the first excited state, and so on. From the absorption spectrum of hydrogen we find that

Fig. 4.2 Spectral lines. The interactive figure is available online (see supplementary material 1)

$$E_n = \frac{E_0}{n^2}\,, \tag{4.2}$$

with $E_0 = -13.6\,\text{eV}$ a constant energy that is specific to hydrogen. Since only energy *differences* are recorded in the absorption spectrum, we can choose the energy of the ground state as we like by adding a constant to E_n. Here, $E_0 = -13.6$ eV is chosen such that if an electron in the ground state absorbs more than 13.6 eV it will no longer be bound to the nucleus. This number will be different for other types of atoms, and also the exact dependence on n will change.

In the previous chapters, we considered systems with two distinct states, such as a photon in two arms of an interferometer, and an electron with two spin states. Here, an electron bound to a proton in a hydrogen atom has infinitely many energy states, one for each value of n. Clearly, we cannot write this as a column vector, since it has infinitely many elements. In the remainder of this chapter, we will consider simplified atoms with only a few energy levels in order to keep the mathematics simple. However, the full theory of quantum mechanics has no problem dealing with these infinite vectors.

We would like to have a device that can perform a measurement of the energy of the electron in an atom. However, this is impossible since only energy *differences* are physically meaningful. We will have to settle for something slightly more modest. We will create a procedure that will tell us if the electron is in a specific energy state or not, via the physical phenomenon of *resonance fluorescence*. In this process, we send light into the atom with a frequency that corresponds to the energy difference between the energy level of interest E_n and a higher energy level E_m. If the electron is in the state $|E_n\rangle$, it will absorb a photon and jump to energy level $|E_m\rangle$. After some time, the electron will jump back[1] to the state $|E_n\rangle$ and emit a photon with energy $E_m - E_n$. We can measure this photon if it is emitted in a direction that differs from the incoming light. Repeating this procedure will produce a lot of photons that are unlikely to be all missed, and detecting some of these photons means that the electron was in the state $|E_n\rangle$. If we do not measure any photons it is overwhelmingly likely that the electron was not in the state $|E_n\rangle$.

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[1] This is a bit of an over-simplification, but it is good enough for our purpose right now.

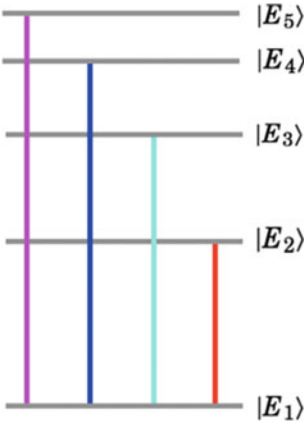

Fig. 4.3 The origin of spectral lines due to energy levels of the hydrogen atom. The interactive figure is available online (see supplementary material 2)

4.2 Changes Over Time

So far we have described how to calculate probabilities of measurement outcomes and averages of physical quantities (such as the expectation value of the electron spin). We have considered simple transformations in the form of a beam splitter, and in this chapter we will study in more detail how quantum states change over time. We can gain some insight into how this works by considering the parallels between photon and electron energy states.

Classically, light is an electromagnetic wave, and the time behaviour of such a wave can be written as $\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega t)$, where $\mathbf{E}$ is the electric field and ω is the angular frequency of the wave. We can also write this as $\mathbf{E}(t) = \mathbf{E}_0 \, e^{-i\omega t}$ and take the real part of $\mathbf{E}(t)$ as the physical value (see the complex numbers intermezzo in Chap. 2). The quantity ωt is the phase of the light (but we will also call $e^{-i\omega t}$ a phase, or sometimes a phase factor). Since a photon is a quantum of light, the natural time evolution of a photon with frequency ω is given by

$$|\text{photon}\rangle \to e^{-i\omega t}|\text{photon}\rangle \,, \tag{4.3}$$

exactly the same as for the electric field $\mathbf{E}(t)$. The photon with frequency ω is a quantum of energy of the electromagnetic field wave of the same frequency, and its energy is $E = \hbar\omega$. The phase can therefore be rewritten as

$$e^{-i\omega t} = e^{-iEt/\hbar} \tag{4.4}$$

In other words, the energy state $|\text{photon}\rangle$ accumulates a phase $e^{-iEt/\hbar}$ over time.

Energy is a very general concept that applies to all systems. It is therefore tempting to assume that the energy state of an electron in an atom behaves in a similar way:

$$|E_n\rangle \to e^{-iE_nt/\hbar}|E_n\rangle\,. \tag{4.5}$$

Indeed, this assumption leads to behaviour that is observed in experiments, as we will now show.

Consider a (simplified) atom with a ground state $|g\rangle = |E_g\rangle$ and an excited state $|e\rangle = |E_e\rangle$. Furthermore, we will assume that we can measure whether the atom is in the state $|g\rangle$ or $|e\rangle$ via resonance fluorescence with some higher energy level. First, at time $t = 0$ we prepare the atom in an equal superposition of the ground state and the excited state

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}|g\rangle + \frac{1}{\sqrt{2}}|e\rangle\,. \tag{4.6}$$

After a time t, the ground state $|g\rangle$ and the excited state $|e\rangle$ will each have accumulated a phase that is proportional to their energies:

$$|\psi(0)\rangle \to |\psi(t)\rangle = \frac{e^{-iE_gt/\hbar}}{\sqrt{2}}|g\rangle + \frac{e^{-iE_et/\hbar}}{\sqrt{2}}|e\rangle\,. \tag{4.7}$$

We can take out $e^{-iE_gt/\hbar}$ as a global unobservable phase (see Exercise 15 in Chap. 2), and obtain

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}|g\rangle + \frac{e^{-i(E_e-E_g)t/\hbar}}{\sqrt{2}}|e\rangle\,. \tag{4.8}$$

In vector notation, this becomes

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ e^{-i(E_e-E_g)t/\hbar} \end{pmatrix}, \tag{4.9}$$

with

$$|g\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{and} \qquad |e\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{4.10}$$

The relative phase is proportional to the energy difference. We could have guessed this beforehand, because the absolute value of the ground state energy is a matter of convention, and if the relative phase depended on individual energies we would be able to measure the value of the ground state energy.

Compare Eq. (4.8) with Eq. (3.36) and identify $|\uparrow\rangle$ with $|g\rangle$ and $|\downarrow\rangle$ with $|e\rangle$. The state of the two-level atom (consisting of $|g\rangle$ and $|e\rangle$) we consider here can then also be described by a vector in the Bloch sphere, and the time evolution is equivalent to a counter-clockwise rotation of the state vector around the vertical (z) axis. Similarly, if $E_e - E_g = \hbar\omega$, that is, the transition frequency from energy state $|g\rangle$ to $|e\rangle$ is ω, the time evolution of a general state of the atom is given by

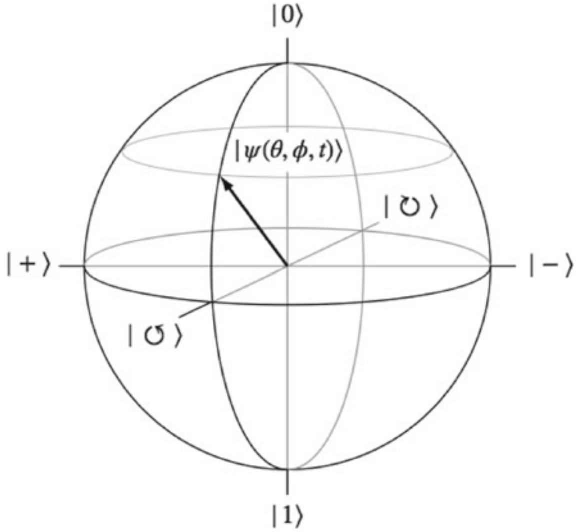

Fig. 4.4 Time evolution as a rotation of the state vector in the Bloch sphere. The interactive figure is available online (see supplementary material 3)

$$|\psi(\theta, \phi, t)\rangle = \cos\left(\frac{\theta}{2}\right)|g\rangle + e^{i\phi - i\omega t}\sin\left(\frac{\theta}{2}\right)|e\rangle\,. \tag{4.11}$$

This corresponds to circular paths around the vertical axis in the Bloch sphere as shown in Fig. 4.4. In other words, the state precesses around the z-axis. When there are more than two energy levels to consider, the Bloch sphere is no longer the correct state space, and the time evolution is not quite as simple.

4.3 The Hamiltonian

Let's consider a general quantum state of our two-level atom $|\psi\rangle = a|g\rangle + b|e\rangle$ with $|a|^2 + |b|^2 = 1$. As usual, we can write this in vector form:

$$|\psi\rangle = a\begin{pmatrix}1\\0\end{pmatrix} + b\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}a\\b\end{pmatrix}\,. \tag{4.12}$$

The probability of finding the atom in the ground state is given by $p_g = |\langle g|\psi\rangle|^2$, and the probability of finding the atom in the excited state is given by $p_e = |\langle e|\psi\rangle|^2$. The average energy in the atom is then given by

$$\begin{aligned}\langle E\rangle &= p_g E_g + p_e E_e \\ &= |\langle g|\psi\rangle|^2 E_g + |\langle e|\psi\rangle|^2 E_e\,. \end{aligned} \tag{4.13}$$

We can expand the modulus-squared to find the energy observable, just like we did with the spin observable in the previous chapter:

$$\begin{aligned}\langle E\rangle &= E_g\langle\psi|g\rangle\langle g|\psi\rangle + E_e\langle\psi|e\rangle\langle e|\psi\rangle \\ &= \langle\psi|\left(E_g|g\rangle\langle g| + E_e|e\rangle\langle e|\right)|\psi\rangle\,. \end{aligned} \tag{4.14}$$

We can then define an energy operator

$$H = E_g|g\rangle\langle g| + E_e|e\rangle\langle e|\,. \tag{4.15}$$

In matrix form, this is given by

$$H = \begin{pmatrix} E_g & 0 \\ 0 & E_e \end{pmatrix}\,. \tag{4.16}$$

This is such an important operator in quantum mechanics that it has a special name: the Hamiltonian (hence the symbol H instead of E). We thus found that the average energy $\langle E\rangle$ is given by the expectation value of the Hamiltonian $\langle\psi|H|\psi\rangle$.

In Chap. 2 we saw that the beam splitter operator could be applied to the state of a photon before it entered the beam splitter. This gave us the state of the photon after the beam splitter. The Hamiltonian works differently because it is an observable, but since it is an operator, we can also apply it to a state. If we apply H to an energy state we obtain the following:

$$H|g\rangle = \begin{pmatrix} E_g & 0 \\ 0 & E_e \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} E_g \\ 0 \end{pmatrix} = E_g|g\rangle\,. \tag{4.17}$$

Similarly,

$$H|e\rangle = \begin{pmatrix} E_g & 0 \\ 0 & E_e \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ E_e \end{pmatrix} = E_e|e\rangle\,. \tag{4.18}$$

In other words, the Hamiltonian H does not change the energy states but multiplies it with the energy value. This is not true in general. Consider the general state $|\psi\rangle$:

$$\begin{aligned} H|\psi\rangle &= \begin{pmatrix} E_g & 0 \\ 0 & E_e \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} aE_g \\ bE_e \end{pmatrix} \\ &= aE_g|g\rangle + bE_e|e\rangle\,. \end{aligned} \tag{4.19}$$

Since generally $E_e \neq E_g$ they do not factor out and $H|\psi\rangle$ is *not* the same as the state $|\psi\rangle$ multiplied by some number. In general, H will change the state it operates on. The energy states are special because they do not change when acted on by the Hamiltonian. They are called *eigenstates* (or eigenvectors) of the Hamiltonian matrix. The energies E_g and E_e are called the *eigenvalues* of the states $|g\rangle$ and $|e\rangle$, respectively. Equations (4.17) and (4.18) are eigenvalue equations for the Hamiltonian.

Since the Hamiltonian is the energy operator of a system, it is often fairly straightforward to find from general principles. The problem is then to find the eigenvalues (the allowed energy values of the system, or spectrum) and the eigenstates. There is a whole area of mathematics devoted to finding the eigenvalues and eigenvectors of matrices, and we will briefly touch upon this in the next chapter.

The Hamiltonian is so important because it is related in a very fundamental way to the time evolution of a quantum system. Consider again the quantum state of the atom $|\psi(0)\rangle = a|g\rangle + b|e\rangle$ at time $t = 0$. According to Eq. (4.7), the time-evolved state can be written as

$$|\psi(t)\rangle = ae^{-iE_gt/\hbar}|g\rangle + be^{-iE_et/\hbar}|e\rangle\,. \tag{4.20}$$

You should check that this state is still properly normalised. But what if we know only the Hamiltonian, and not the energy eigenstates and eigenvalues? We need some procedure to find $|\psi(t)\rangle$ based only on the Hamiltonian.

The change of a state over time is related to the time derivative. You are already familiar with this: if we are interested in the change of position of a particle, then we take the time derivative of the position, which gives the velocity, or change in position over time. Similarly, we can take the time derivative of the state $|\psi(t)\rangle$:

$$\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\hbar}E_gae^{-iE_gt/\hbar}|g\rangle - \frac{i}{\hbar}E_ebe^{-iE_et/\hbar}|e\rangle\,. \tag{4.21}$$

We can re-write this using Eqs. (4.17) and (4.18) as

$$\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\hbar}Hae^{-iE_gt/\hbar}|g\rangle - \frac{i}{\hbar}Hbe^{-iE_et/\hbar}|e\rangle\,, \tag{4.22}$$

or more compactly,

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = H|\psi(t)\rangle\,. \tag{4.23}$$

This is the famous *Schrödinger equation* (Schrödinger 1926), which describes how the state of a system evolves over time. It is a differential equation that must be solved for $|\psi(t)\rangle$ given our knowledge of H and initial condition $|\psi(0)\rangle$. A large part of mastering quantum mechanics is to find solutions of the Schrödinger equation for various forms of H.

Sometimes it is convenient to look at a different way to find the time evolution of a quantum state. Consider again the time evolution of the energy states

$$|g\rangle \to e^{-iE_gt/\hbar}|g\rangle \qquad \text{and} \qquad |e\rangle \to e^{-iE_et/\hbar}|e\rangle\,. \tag{4.24}$$

Each time-dependent phase has the form of an exponential, which we can write as

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots, \tag{4.25}$$

with $x = -itE_g/\hbar$ or $x = -itE_e/\hbar$. Let's consider E_g. The phase factor can then be written as

$$e^{-itE_g/\hbar}|g\rangle = \left[1 + \frac{-it}{\hbar}E_g + \frac{(-it)^2}{2\hbar^2}E_g^2 + \dots\right]|g\rangle\,. \tag{4.26}$$

We can use Eq. (4.17) to replace $E_g|g\rangle$ with $H|g\rangle$, $E_g^2|g\rangle$ with $H^2|g\rangle$, and so on. When we collapse the series again into an exponential, we obtain

$$|g\rangle \to e^{-iHt/\hbar}|g\rangle\,, \tag{4.27}$$

where the phase factor is now an operator. The crucial observation is that we can do exactly the same for the energy eigenstate $|e\rangle$:

$$|e\rangle \to e^{-iHt/\hbar}|e\rangle\,. \tag{4.28}$$

The phase operators in Eqs. (4.27) and (4.28) are the same, so we can take *any* state $|\psi\rangle = a|g\rangle + b|e\rangle$ and find the time evolution by applying the phase operator $\exp(-iHt/\hbar)$:

$$|\psi(t)\rangle = e^{-iHt/\hbar}|\psi(0)\rangle\,. \tag{4.29}$$

Note that because H is an operator, this is not the same as a global phase. It is a so-called *formal* solution of the Schrödinger equation (4.23): we have removed the derivative from the equation, but we don't quite have an explicit form of $|\psi(t)\rangle$, because the exponential may be hard to calculate. However, for the two-level atom we consider here the exponential is often quite easy to find.

We have essentially already solved the Schrödinger equation in (4.23) for the case where H is given by Eq. (4.16). The solution is given by Eq. (4.11). This represents the physical situation where the atom is prepared in some superposition of $|g\rangle$ and $|e\rangle$ and left isolated. The mere passing of time will change the state. This is called the *free* evolution of the atom, since we are not doing anything to it by, for example, shining lasers on the atom.

4.4 Interactions

The Hamiltonian in the previous section gives rise to the simple time evolution when the atom is left to its own. But often we are interested in situations where the atom interacts with other physical systems. For example, we can shine a laser onto the atom with a frequency ω that matches the energy transition between $|g\rangle$ and $|e\rangle$. How do we describe such interactions?

The effect of the laser will be to drive the atom from the ground state $|g\rangle$ into the excited state $|e\rangle$. In addition, it will drive the atom from the excited state $|e\rangle$ into the ground state $|g\rangle$ (this may surprise you, but it is true. It is called *stimulated emission* (Einstein 1916) and lies at the heart of how lasers operate: Light Amplification by Stimulated Emission of Radiation). This interaction of the atom with the laser is also part of the time evolution, and there is indeed a Hamiltonian that describes this mechanism. It is called an *interaction Hamiltonian*, and it can be constructed as

$$H_{\text{int}} = \gamma |e\rangle\langle g| + \gamma^* |g\rangle\langle e| \,, \tag{4.30}$$

with an interaction strength γ that may be a complex number. In matrix form, this is given by

$$H_{\text{int}} = \begin{pmatrix} 0 & \gamma^* \\ \gamma & 0 \end{pmatrix} . \tag{4.31}$$

Typically, the total Hamiltonian for the atom is the Hamiltonian of the free evolution H plus the interaction Hamiltonian H_{int}, which can be expressed as

$$H_{\text{total}} = H + H_{\text{int}} = \begin{pmatrix} E_g & \gamma^* \\ \gamma & E_e \end{pmatrix} . \tag{4.32}$$

Let's break the interaction Hamiltonian down into its components and see what it does. First of all, the factor γ is the strength of the interaction. It can be complex, since it is directly related to the amplitude of the laser light (which has a complex phase factor), and for reasons that we will explore in the next chapter, we must include both γ and its complex conjugate γ^*. When the strength of the interaction goes to zero ($\gamma \to 0$) we retrieve the free evolution, as we should.

The term $|e\rangle\langle g|$ represents the physical transition from the ground state to the excited state, since

$$|e\rangle\langle g| \times |g\rangle = |e\rangle\langle g|g\rangle = |e\rangle \,, \tag{4.33}$$

and $\langle g|g\rangle = 1$. Similarly, applying $|e\rangle\langle g|$ to $|e\rangle$ will be zero, since $\langle g|e\rangle = 0$. The last term in the interaction Hamiltonian does exactly the opposite, it gives the transition from the excited state to the ground state:

$$|g\rangle\langle e| \times |e\rangle = |g\rangle\langle e|e\rangle = |g\rangle\,. \tag{4.34}$$

This is the time reversal of the first term in H_{int}. Every properly constructed Hamiltonian must have terms for both the physical process and its time-reversed process. This is a consequence of the fact that the physical laws at the microscopic level have no preferred direction in time. It is only when we consider larger systems that the arrow of time becomes apparent.

We can study the effect of the interaction Hamiltonian H_{int} separately from H. In particular, we want to calculate the matrix form of the phase operator in Eq. (4.31). We start by calculating the square of H_{int}:

$$H_{\text{int}}^2 = \begin{pmatrix} 0 & \gamma^* \\ \gamma & 0 \end{pmatrix}\begin{pmatrix} 0 & \gamma^* \\ \gamma & 0 \end{pmatrix} = |\gamma|^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{4.35}$$

In other words, H_{int}^2 is proportional to the identity, which means that H_{int}^3 will be proportional to H_{int}, and so on. At this point it is convenient to choose γ as a real number (i.e., the imaginary component is zero) and independent of time in order to keep the formulas reasonably short. We will also use the following abbreviations:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{and} \quad \mathbb{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{4.36}$$

We can write the series expansion of $\exp(-iH_{\text{int}}t/\hbar)$ as

$$e^{-iH_{\text{int}}t/\hbar} = \mathbb{I} + \frac{-i\gamma t}{\hbar}\sigma_x + \frac{(-i\gamma t)^2}{2\hbar^2}\mathbb{I} + \frac{(-i\gamma t)^3}{6\hbar^3}\sigma_x + \ldots \tag{4.37}$$

Next, we collect the even and odd powers of $-i\gamma t/\hbar$, and note the following mathematical identities:

$$\cos x = 1 - \frac{x^2}{2} + \frac{x^4}{4!} + \ldots \tag{4.38}$$

and

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} + \ldots \tag{4.39}$$

This leads to

$$e^{-iH_{\text{int}}t/\hbar} = \cos\left(\frac{\gamma t}{\hbar}\right)\mathbb{I} - i\sin\left(\frac{\gamma t}{\hbar}\right)\sigma_x\,. \tag{4.40}$$

Setting $\Omega = \gamma/\hbar$, this becomes in matrix form

$$e^{-iH_{\text{int}}t/\hbar} = \begin{pmatrix} \cos(\Omega t) & -i\sin(\Omega t) \\ -i\sin(\Omega t) & \cos(\Omega t) \end{pmatrix} . \tag{4.41}$$

When we apply this operator to the ground state $|g\rangle$ we obtain

$$\begin{aligned} |\psi(t)\rangle = e^{-iH_{\text{int}}t/\hbar}|g\rangle &= \begin{pmatrix} \cos(\Omega t) & -i\sin(\Omega t) \\ -i\sin(\Omega t) & \cos(\Omega t) \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \cos(\Omega t)|g\rangle - i\sin(\Omega t)|e\rangle . \end{aligned} \tag{4.42}$$

We can draw the path of the evolving quantum state again in the Bloch sphere and see that this interaction Hamiltonian generates a rotation around the x-axis. In the special case where $\Omega t = \pi/2$, we have

$$|\psi(t)\rangle = -i \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -i \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |e\rangle , \tag{4.43}$$

where we ignored the global phase factor $-i$ in the last term. Clearly the interaction term drives the atom from the ground state $|g\rangle$ to the excited state $|e\rangle$.

However, you also see that it is easy to over- or undershoot: A slightly weaker or stronger interaction or a slightly shorter or longer interaction time will leave the atom not in the excited state, but in a superposition of mostly excited state and a small amount of ground state. The magnitude of γ (or Ω) gives the speed, or frequency, of the rotation. When $\gamma \gg E_e$, the rotation from $|g\rangle$ to $|e\rangle$ occurs much faster than the free evolution. Therefore, with a sufficiently strong and short laser pulse we can excite the atom almost instantly from $|g\rangle$ to $|e\rangle$.

4.5 ❧ The Atomic Clock

One of the most fundamental and important measuring devices in physics is the atomic clock (Essen and Parry 1955). Using the theory we have developed so far we can now explain the basic principle of such devices. To do this, we will need to know a little bit about the background of clocks. First, a clock measures time, so we better have a good definition of the unit of time, the second. According to the *Bureau International des Poids et Mesures*, which maintains the standards of the SI units, the definition of the second is:

> *The duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium 133 atom.*

Here, hyperfine means that the nucleus of the caesium atom has a spin that interacts with the spin of the outer electron. This interaction will cause a splitting of the energy levels, because it is energetically more favourable for the electron and nuclear spin vectors to be parallel rather than anti-parallel. We call the two hyperfine levels of the ground state $|g\rangle$ and $|e\rangle$, which have spin values of $-\hbar/2$ and $+\hbar/2$, respectively. The fact that the two levels have different electron spin values means that we can manipulate the atoms using the Stern–Gerlach apparatus introduced in the previous chapter. The 133 refers to the fact that the particular isotope of caesium has 55 protons + 78 neutrons = 133 nucleons.

In its most general description, a clock is a device made of a physical system that naturally oscillates with a very regular frequency, coupled to a mechanism that counts the number of cycles in the oscillation. The higher the frequency, the shorter the counting steps, and the more accurate the clock is. For example, a grandfather clock has a pendulum (the *oscillator*) that swings back and forth with regular intervals, and a mechanism called an *escapement* that pushes the hands of the clock a tiny bit forward with each swing of the pendulum. The escapement also pushes the pendulum a little at each swing, which overcomes the natural drag of the pendulum and prevents it from coming to a halt after a few minutes.

Another example is the quartz clock used in computers and digital wrist watches. In these clocks a quartz crystal is cut to a specific shape (typically the shape of a tuning fork), and made to vibrate at its resonance frequency. Quartz is a piezo-electric material, which means that deformations of the crystal cause an electric signal. This signal is used both to drive the oscillation and to measure the number of periods. The quartz crystal is the oscillator, and the electronics serve as the escapement.

For our most accurate clocks, we need an extremely accurate oscillator. As we have seen in the definition of the second, the radiation between the lowest energy states $|g\rangle$ and $|e\rangle$ of caesium 133 can be used as the oscillator, since it can be described as a wave and therefore has a periodic behaviour. The question is: how do we get a practical clock read-out from this oscillator? In other words, how do we build the escapement? The answer is that we use a feedback mechanism to lock the atomic transition to the frequency of a quartz crystal that we can read out electronically. This mechanism relies critically on the interaction of the caesium atoms with an external laser, as studied in the previous section.

First, as shown in Fig. 4.5, we set up a vacuum tube with a source of caesium 133 on one side and atom detectors on the other side. The source is often called an oven, since it heats the caesium and lets it escape into the tube towards the detectors. Immediately after the oven, the atoms pass through a Stern Gerlach apparatus that deflects the atoms in the state $|e\rangle$. Only caesium atoms in the state $|g\rangle$ pass through the tube. This is called a state separator. At the other end, before the detectors, the caesium atoms pass through another Stern–Gerlach apparatus separating atoms in states $|g\rangle$ and $|e\rangle$ into different beams. Each beam is sent into a detector that counts the number of atoms. Clearly, when the atoms pass through the vacuum tube from the first Stern–Gerlach to the second, their state should not change and all atoms should be detected in the ground state $|g\rangle$.

Second, we aim a microwave laser (or *maser*, generated by a magnetron, the active component in your microwave oven) into the path of the caesium atoms between the two state separators. While the atoms are in the beam of the maser, they experience the interaction described in Eq. (4.29). If the maser is on resonance with the transition between $|g\rangle$ and $|e\rangle$ the atoms entering the second state separator are in the state

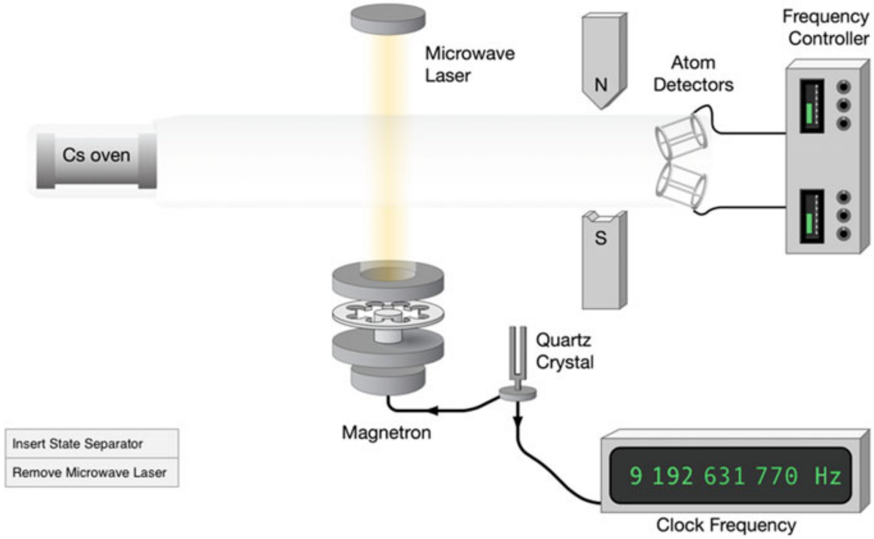

Fig. 4.5 Working principle of the atomic clock. The interactive figure is available online (see supplementary material 4)

$$|\psi(t)\rangle = \cos\Omega t|g\rangle - i\sin\Omega t|e\rangle\,, \tag{4.44}$$

where t is the time the atoms spent in the maser beam and Ω is the coupling strength of the interaction. The probability that such an atom is detected in the state $|e\rangle$ is given by

$$p_e = |\langle e|\psi(t)\rangle|^2 = \sin^2\Omega t\,. \tag{4.45}$$

When the maser is off resonance, meaning that the frequency of the maser does not match the transition frequency between $|g\rangle$ and $|e\rangle$, the coupling Ω' is much reduced. As a consequence, $\sin\Omega' t$ is much closer to 0, and the probability of finding an atom in the state $|e\rangle$ is suppressed.

Finally, we can control the frequency of the maser using a quartz crystal. This crystal is cut into the shape of a tuning fork such that the frequency is centred around the transition between $|g\rangle$ and $|e\rangle$ at 9 192 631 770 Hz. However, it is not nearly this precise, for if it was we would not need the atomic transition. As a result, the frequency of the maser will drift away from the resonance frequency, and the coupling strength of the interaction will drop. This means that fewer atoms will be detected in the state $|e\rangle$. A frequency counter monitors the relative number of atoms detected in the state $|e\rangle$, and when it drops the controller applies a small voltage to the quartz crystal, nudging it back to the resonance frequency. This feedback mechanism will keep the quartz crystal locked at 9 192 631 770 Hz, and the frequency is much more stable than the quartz crystal can maintain on its own. By counting the oscillations of the—now stabilised—quartz crystal (which can be done electronically due to the piezo-electric effect), we can mark the passage of time with great accuracy. This is how an atomic clock works.

Clocks like this have a typical precision of one part in 10^{13}. Modern atomic clocks are still an area of active research, and can achieve precisions as high as one part in 10^{18}. They are used for all sorts of applications, from GPS to measuring the spectrum of anti-hydrogen.

Exercises

1. Normalise the state $3|g\rangle - i|e\rangle$.
2. An atomic state
$$|\psi\rangle = \frac{1}{\sqrt{3}}|g\rangle + \sqrt{\frac{2}{3}}|e\rangle$$
evolves with an evolution matrix $\begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix}$. Calculate the state $|\psi(t)\rangle$ at time t. Calculate the probability of finding $|+\rangle = (|g\rangle + |e\rangle)/\sqrt{2}$ at time t.
3. A two-level atom with ground state $|g\rangle$ and excited state $|e\rangle$ is prepared in the state
$$|+\rangle = \frac{1}{\sqrt{2}}|g\rangle + \frac{1}{\sqrt{2}}|e\rangle$$
at time $t = 0$. The energy difference between $|g\rangle$ and $|e\rangle$ is $\hbar\omega$.
   (a) Calculate the probability of finding the atom in the state
$$|R\rangle = \frac{1}{\sqrt{2}}|g\rangle + \frac{i}{\sqrt{2}}|e\rangle\,.$$
   (b) The atom evolves according to the Schrödinger equation with the Hamiltonian
$$H = \frac{\hbar\omega}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$
   Calculate the probability of finding the atom in the state $|R\rangle$ at time t.
   (c) Sketch this probability as a function of time.
   (d) Sketch the trajectory of the quantum state over time in the Bloch sphere.
4. An electron with spin $1/2$ is prepared in the state $|\uparrow\rangle$ in the z-direction. A magnetic field is pointing 45° away from the z-axis and towards the x-axis.
   (a) Using Eq. (3.63), construct the matrix form of the Hamiltonian H in the Schrödinger equation.

(b) Show that the states

$$|+45\rangle = \cos\left(\frac{\pi}{8}\right)|\uparrow\rangle + \sin\left(\frac{\pi}{8}\right)|\downarrow\rangle$$
$$|+135\rangle = -\sin\left(\frac{\pi}{8}\right)|\uparrow\rangle + \cos\left(\frac{\pi}{8}\right)|\downarrow\rangle$$

are eigenstates of the matrix H. What are the corresponding eigenvalues?

(c) The eigenstates form the poles of the rotation axis determined by H. Sketch the time trajectory of the electron spin in the Bloch sphere.

(d) Does the electron spin ever reach the state $|\downarrow\rangle$?

5. At time $t = 0$ an atom is prepared in the state

$$|\psi\rangle = \frac{|g\rangle - i\sqrt{2}|e\rangle}{\sqrt{3}} .$$

(a) Calculate the probability of finding the measurement outcome "+" and "–", associated with the states $|\pm\rangle = (|g\rangle \pm |e\rangle)/\sqrt{2}$.

The free evolution of the atom is determined by the Hamiltonian

$$H = -\frac{1}{2}\hbar\omega\,(|g\rangle\langle g| - |e\rangle\langle e|) .$$

(b) Calculate the state at time t.

(c) Sketch the rotation axis of the evolution due to H' on the Bloch sphere.

6. (a) A photon in a polarisation state $|\psi\rangle = \alpha|H\rangle + \beta|V\rangle$ with $|\alpha|^2 + |\beta|^2 = 1$ is measured in the polarisation basis $\{|H\rangle, |V\rangle\}$. What are the possible measurement outcomes and their corresponding probabilities?

(b) If we measure an identically prepared photon in the *circular* polarisation basis $(|H\rangle \pm i|V\rangle)/\sqrt{2}$, what will be the measurement outcomes and their corresponding probabilities?

(c) The free evolution of the photon is governed by the Hamiltonian

$$H = i\hbar\omega(|H\rangle\langle V| - |V\rangle\langle H|) ,$$

with ω the angular frequency of the light. Find the state of the photon at time $t = T$ given that the state at $t = 0$ is given by $|\psi\rangle = \alpha|H\rangle + \beta|V\rangle$.

(d) Calculate and sketch the probability of finding the outcomes of a measurement in the polarisation basis $\{|H\rangle, |V\rangle\}$ in the time interval $0 \le t \le T$ when $\alpha = \beta = 1/\sqrt{2}$.

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