Advanced Quantum Physics
Week 9

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Time evolution of quantum systems

Until now we have mainly been interested in systems that were described by a time-independent Hamiltonian. This framework is very well suited to discuss the physics of closed systems with a conserved energy. Any eigenstate the Hamiltonian with eigenenergy E_n would simply evolve according to $|\Psi(t)\rangle = e^{-iE_nt/\hbar}|\Psi(t=0)\rangle$. But truly closed systems do not exist. In a realistic description of a hydrogen atom, if the electron is in one of the excited states, it is expected that it will eventually return to the ground state. The reason this happens is that the hydrogen atom is not isolated: It is always interacting with the external environment such as the electromagnetic field. Indeed, in the process of returning to the ground state, the electron emits a photon that modifies the state of the external environment.

In order to discuss phenomena such as this radiative transition in the hydrogen atom, it is useful to describe the system as an isolated system with a time-independent Hamiltonian $\hat{\mathcal{H}}_0$ (whose eigenstates and eigenenergies we know) and a time-dependent perturbation $\hat{W}(t)$. The full Hamiltonian is therefore given by

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_0 + \hat{W}(t)$$

The evolution of the system is determined by the solution of the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{\mathcal{H}}(t)|\Psi(t)\rangle$$

Interaction picture

Because of the way we decompose the Hamiltonian, it is useful to work in a modified basis of states that evolves according to $\hat{\mathcal{H}}_0$. This *interaction representation* is defined by

$$|\widetilde{\Psi}(t)\rangle = e^{i\hat{\mathcal{H}}_0t/\hbar}|\Psi(t)\rangle,$$

where the tilde indicates that the state is expressed in the interaction representation. One can think of $|\widetilde{\Psi}(t)\rangle$ as the expression of the state in a rotating reference frame. It is easy to verify that the time evolution of $|\widetilde{\Psi}(t)\rangle$ is described by the equation

$$i\hbar\frac{\partial}{\partial t}|\widetilde{\Psi}(t)\rangle = \widetilde{W}(t)|\widetilde{\Psi}(t)\rangle,$$

where the time-dependent perturbation is expressed in the interaction representation as well

$$\widetilde{W}(t) = e^{i\hat{\mathcal{H}}_0 t/\hbar}\hat{W}e^{-i\hat{\mathcal{H}}_0 t/\hbar}$$

Time-evolution equations

Let $\{|n\rangle\}$ be the eigenstates of $\hat{\mathcal{H}}_0$ with eigenvalue E_n

$$\hat{\mathcal{H}}_0|n\rangle = E_n|n\rangle$$

If we express $|\widetilde{\Psi}(t)\rangle$ in this basis

$$|\widetilde{\Psi}(t)\rangle = \sum_n \gamma_n(t)|n\rangle,$$

we can rewrite the time evolution equation of $|\widetilde{\Psi}(t)\rangle$ as

$$i\hbar\frac{\partial}{\partial t}\sum_n \gamma_n(t)|n\rangle = \widetilde{W}(t)\sum_n \gamma_n(t)|n\rangle$$

Multiplying on both sides by $\langle m|$, we see that the coefficients $\gamma_n(t)$ obey

$$i\hbar\dot{\gamma}_m(t) = \sum_n \langle m|\widetilde{W}(t)|n\rangle\gamma_n(t)$$

Reintroducing the expression of $\widetilde{W}$ in this equation and using the fact that $|\Psi(t)\rangle = \exp(-i\hat{\mathcal{H}}_0 t/\hbar)|\widetilde{\Psi}(t)\rangle$, we find that the eigenstates of $\hat{\mathcal{H}}(t)$ are given by the solution of

$$|\Psi(t)\rangle = \sum_n \gamma_n(t)e^{-i\omega_n t}|n\rangle$$
$$i\hbar\,\dot{\gamma}_m(t) = \sum_n e^{i(\omega_m-\omega_n)t}\,\langle m|\hat{W}(t)|n\rangle\,\gamma_n(t),$$

where we have introduced $\omega_k = E_k/\hbar$. In order to find the solution for the time evolution of the system one must therefore solve the above set of coupled equations for all $\gamma_k(t)$.

Example: A driven two-level system

Let us consider the example of a driven two-level system described by the Hamiltonian $\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_0 + \hat{W}(t)$ with

$$\hat{\mathcal{H}}_0 = \frac{\hbar}{2}\begin{pmatrix}\omega_0 & 0\\ 0 & -\omega_0\end{pmatrix} \qquad \hat{W}(t) = \frac{\hbar}{2}\begin{pmatrix}0 & \omega_1 e^{-i\omega t}\\ \omega_1 e^{i\omega t} & 0\end{pmatrix}$$

We have already met this Hamiltonian in the description of a spin-1/2 placed in the sum of a uniform static field in the z direction and a rotating field in the xy plane. But it is also relevant for other systems, such as the ammonia maser, where the two levels are related to two possible states of the ammonia molecule. For these systems, we need to solve the following equation for the coefficients $\gamma_k(t)$

$$i\hbar\dot{\vec{\gamma}} = \frac{\hbar\omega_1}{2}\begin{pmatrix} 0 & e^{i(\omega_0-\omega)t} \\ e^{-i(\omega_0-\omega)t} & 0 \end{pmatrix}\vec{\gamma}(t),$$

where $\vec{\gamma}(t) = (\gamma_1(t), \gamma_2(t))$. We suppose that the state at $t = 0$ has $\gamma_1(t = 0) = 1$ and $\gamma_2(t = 0) = 0$. Then, the solution of the equation for $\vec{\gamma}(t)$ is

$$\gamma_1(t) = e^{-i\omega t/2}\left[\cos\left(\frac{\Omega t}{2}\right) + i\frac{\omega-\omega_0}{\Omega}\sin\left(\frac{\Omega t}{2}\right)\right]$$
$$\gamma_2(t) = -e^{i\omega t/2}\frac{i\omega_1}{\Omega}\sin\left(\frac{\Omega t}{2}\right),$$

where the Rabi frequency Ω is given by $\Omega^2 = (\omega-\omega_0)^2 + \omega_1^2$. The probability to find the system in the second state at time t is

$$|\gamma_2(t)|^2 = \left(\frac{\omega_1}{\Omega}\right)^2 \sin^2\left(\frac{\Omega t}{2}\right)$$

Time-dependent perturbation theory

It is in general not possible to solve the equations for the time evolution of a quantum system exactly. Even the simple example of a driven two-level system is already not that easy to solve. This motivates the construction of an approximate solution to the problem where we suppose that $\hat{W}(t)$ can be treated as a small perturbation of the time-independent Hamiltonian $\hat{\mathcal{H}}_0$. We want to solve

$$\begin{aligned} i\hbar\,\dot{\gamma}_k(t) &= \sum_n e^{i(\omega_k-\omega_n)t}\,\langle k|\hat{W}(t)|n\rangle\,\gamma_n(t) \\ \dot{\gamma}_k(t) &= -\frac{i}{\hbar}\sum_n \gamma_n(t) e^{i\omega_{kn}t}\,W_{kn}(t), \end{aligned}$$

where we have introduced the matrix elements $W_{kn}(t)$ and $\omega_{kn} = \omega_k - \omega_n$. At time $t = 0$, we suppose that the system is in state $|i\rangle$. Now let us write a perturbative series for $\gamma_k(t)$ in powers of the interaction $\hat{W}$

$$\gamma_k(t) = \gamma_k^{(0)}(t) + \gamma_k^{(1)}(t) + \gamma_k^{(2)}(t) + \cdots$$

At order 0, we have

$$\dot{\gamma}_k^{(0)}(t) = 0 \quad \Rightarrow \quad \gamma_k^{(0)}(t) = \gamma_k^{(0)}(t=0) = \delta_{k,i}$$

At order $p+1$, we see that the equation will be

$$\dot{\gamma}_k^{(p+1)}(t) = -\frac{i}{\hbar}\sum_n \gamma_n^{(p)}(t) e^{i\omega_{kn}t}\,W_{kn}(t)$$

If we stop at first order, we obtain what is often called the *Born approximation*, with

$$\begin{aligned} \dot{\gamma}_k^{(1)}(t) &= -\frac{i}{\hbar}\sum_n \gamma_n^{(0)}(t) e^{i\omega_{kn}t}\,W_{kn}(t) \\ &= -\frac{i}{\hbar}\sum_n \delta_{n,i} e^{i\omega_{kn}t}\,W_{kn}(t) \\ &= -\frac{i}{\hbar} e^{i\omega_{ki}t}\,W_{ki}(t) \end{aligned}$$

This equation is easily solved and we find the first-order time-dependent perturbation theory

$$\begin{aligned} |\Psi(t)\rangle &= e^{-i\omega_i t}|i\rangle + \sum_k \gamma_k^{(1)}(t) e^{-i\omega_k t}|k\rangle \\ \gamma_k^{(1)}(t) &= -\frac{i}{\hbar}\int_0^t e^{i\omega_{ki}t'}\,\langle k|\hat{W}(t')|i\rangle\,dt' \end{aligned}$$

From this equation, we see that the probability to be in the final state $|f\rangle$ at time t if the system was in the state $|i\rangle$ at $t = 0$ is given by the following expression at first-order

$$\mathcal{P}_{i\to f}(t) = |\gamma_f(t)|^2 = \left|\frac{1}{\hbar}\int_0^t e^{i\omega_{fi}t'}\,\langle f|\hat{W}(t')|i\rangle\,dt'\right|^2$$

It is also interesting to write the full expression for the state in first-order perturbation theory in the following way

$$|\Psi(t)\rangle = e^{-i\omega_i t}|i\rangle - \frac{i}{\hbar}\sum_k \int_0^t e^{-i\omega_k(t-t')}\,\langle k|\hat{W}(t')|i\rangle e^{-i\omega_i t'}\,dt'\,|k\rangle$$

This shows that the wavefunction is a sum of two terms. The first term is just the evolution of the original $|i\rangle$ state. The second term is a sum over all possible states $|k\rangle$. For each state there is a quantum superposition of all possible ways to reach the state $|k\rangle$ at time t. It has a part that describes the evolution of the original state $|i\rangle$ until time t'. Then, the perturbation scatters this state on the $|k\rangle$ state and evolves during a time $(t-t')$ until the final time t.

Let us now investigate some special cases for the perturbation $\hat{W}(t)$ that are often met in quantum mechanics.

Constant perturbation

We can start to consider a constant perturbation of the form

$$\hat{W}(t) = \hat{W}$$

The expression from the first-order perturbation theory is simply

$$\begin{aligned}\gamma_k^{(1)}(t) &= -\frac{i}{\hbar}\int_0^t e^{i\omega_{ki}t'}\,W_{ki}\,dt' \\ &= -\frac{i}{\hbar}W_{ki}\frac{e^{i\omega_{fi}t}-1}{i\omega_{fi}} \\ &= -\frac{i}{\hbar}W_{ki}e^{i\omega_{fi}t/2}\frac{\sin\omega_{fi}t/2}{\omega_{fi}/2}\end{aligned}$$

The probability to be in state $|f\rangle$ at time t, starting from the initial state $|i\rangle$ is then

$$\mathcal{P}_{i\to f}(t) = |\gamma_f(t)|^2 = \frac{|W_{ki}|^2}{\hbar^2}\frac{\sin^2\omega_{fi}t/2}{(\omega_{fi}/2)^2}$$

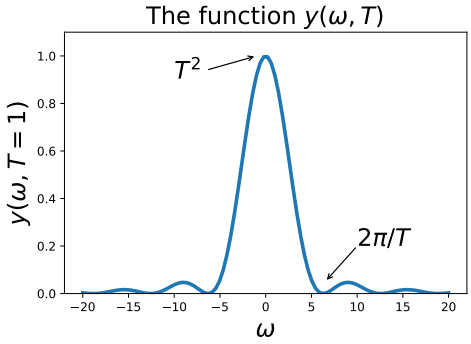
We see that a transition to the state $|f\rangle$ is only possible if the matrix element $W_{ki} \neq 0$. This is called a *selection rule*. If some matrix elements are vanishing the corresponding transitions are forbidden within first-order perturbation theory. Note that the transition probability is a periodic function in time, with period $2\pi/\omega_{fi}$. It is also often written as

$$\mathcal{P}_{i\to f}(t) = \frac{\Omega_0^2}{4}\,y(\omega_{fi},t),$$

where

$$\frac{\Omega_0}{2} = \frac{|W_{fi}|}{\hbar} \qquad y(\omega,t) = \frac{\sin^2\omega t/2}{(\omega/2)^2}$$

The function $y(\omega,t)$ is shown below for fixed time $t=T$ as a function of ω



We see that the function is very concentrated around zero. Most of the weight of the function is in the interval $[-2\pi/T, 2\pi/T]$. We can conclude that the transition to a state $|f\rangle$ will be more likely only if $|\omega_{fi}| < 2\pi/T$ or written differently

$$\Delta E \times T < 2\pi\hbar$$

This is very reminiscent of the time-energy uncertainty relation. A consequence is that at long times, energies have very small uncertainties and transitions happen only if the energy of the final state is very close to the energy of the initial state.

Let us briefly examine when perturbation theory is valid. The transition probability $\mathcal{P}_{i\to f}(t)$ is given by $|\gamma_f^{(1)}(t)|^2$. Its amplitude is therefore an indication of how big the perturbation is. If we want perturbation theory to be valid, we must make sure that the probability $\mathcal{P}_{i\to f}(t)$ remains much smaller than 1. There are two ways to ensure this condition is fulfilled. Because $y(\omega_{fi}, t) \leq (2/\omega_{fi})^2$, we have that $\mathcal{P}_{i\to f}(t) \leq (\Omega_0/\omega_{fi})^2$. So the probability will be small if $\Omega_0 \ll |\omega_{fi}|$. If Ω_0 is not small, the perturbation theory will still be valid if the times considered are small enough. Indeed, the function y has the property $y(\omega_{fi}, t) \leq t^2$ as can be seen from a Taylor expansion. Therefore $\mathcal{P}_{i\to f}(t) \leq \Omega_0^2 t^2/4$ and we can make it small for times such that $\Omega_0 t \ll 1$. To summarize, perturbation theory is valid in the two following cases

$$\Omega_0 \ll |\omega_{fi}| \qquad \text{or} \qquad \Omega_0 t \ll 1$$

The first condition basically expresses that the matrix elements $|W_{fi}|$ should be much smaller than the distance between the energies E_i and E_f. We have encountered this condition in time-independent perturbation theory already. The second condition only exists in time-dependent perturbation theory and shows that there is always a short-time regime that can be described perturbatively.

Sinusoidal perturbation

The second example we will discuss is a perturbation with a sinusoidal variation in the time interval $0 < t < T$. It has the general form

$$\hat{W}(t) = e^{-i\omega t}\hat{W} \qquad \text{for} \qquad 0 < t < T$$

We will be interested in the probability to go from the initial state $|i\rangle$ to the final state $|f\rangle$ at time $t = T$. We therefore need to compute

$$\gamma_k^{(1)}(T) = -\frac{i}{\hbar}\int_0^T e^{i\omega_{ki}t'}\, e^{-i\omega t'}\, \langle k|\hat{W}|i\rangle\, dt'$$

This is exactly the same integral as we computed just above, with the difference that the frequency in the integral has been shifted $\omega_{fi} \to \omega_{fi} - \omega$. So transition probability is

$$\mathcal{P}_{i\to f}(T) = \frac{\Omega_0^2}{4}\, y(\omega_{fi} - \omega, T),$$

where we recall that

$$\frac{\Omega_0}{2} = \frac{|W_{fi}|}{\hbar} \qquad y(\omega, t) = \frac{\sin^2 \omega t/2}{(\omega/2)^2}$$

We see that there is a value for ω that maximizes the transition probability. When $\omega = \omega_{fi}$ there is a *resonance* and the system is more likely to make a transition. According to the sign of $E_f - E_i$ one can associate this transition as an absorption (e.g. of a photon) that excites the system to a higher energy level, or a stimulated emission where the system has a transition to a lower energy state and emits, e.g. a photon.

It is useful to come back to the exact solution that we calculated above for the driven two-level system. In that example, the transition probability from one level to the other was given by

$$\mathcal{P}_{i\to f}(T) = \frac{\omega_1^2}{\Omega^2}\, \sin^2\left(\frac{\Omega T}{2}\right),$$

where the Rabi oscillation is given by $\Omega^2 = (\omega - \omega_0)^2 + \omega_1^2$, $\hbar\omega_0 = \hbar\omega_{fi}$ is the energy difference between the two levels, ω is the frequency of the perturbation and $\hbar\omega_1/2 = |W_{fi}| = \hbar\Omega_0/2$. We can compare this expression with the approximate expression from first-order perturbation theory, which reads

$$\mathcal{P}_{i\to f}(T) = \frac{\omega_1^2}{4}\, \frac{\sin^2(\omega_0 - \omega)T/2}{((\omega_0 - \omega)/2)^2} = \frac{\omega_1^2}{(\omega_0 - \omega)^2}\, \sin^2\left(\frac{(\omega_0 - \omega)T}{2}\right)$$

One can see that the perturbative approach gives a good estimate of the exact result for all times when the frequency of the perturbation is far from the resonance, more specifically when $\omega_1 \ll |\omega - \omega_0|$. If one is close to the resonance, one can consider the Taylor expansion of the sine and both expressions give $\mathcal{P}_{i\to f}(T) = \omega_1^2 T^2/2$, which is valid only as long as it remains much smaller than one, namely if the interaction time is short enough $\omega_1 T/2 \ll 1$.

Transitions to a continuum of final states

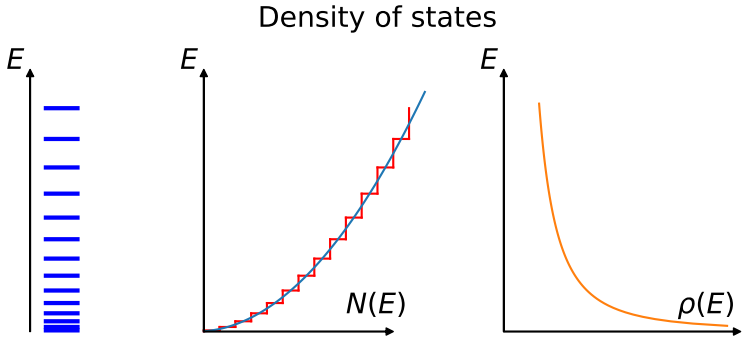
In this section, we will investigate systems where the initial state is part of a discrete spectrum but coupled to a continuum of final states. There are many examples of such transition, such as the ionization of an atom, where the initial state has an electron in one of the bound states of the atom and the final state is a free electron in one of its continuous momentum eigenstates. Another example is the decay of a radioactive nucleus, etc. One of the important results we will obtain is that while the transition probability is periodic in time for discrete spectra, it becomes linear in time when the final states are in a continuum. In practice, this means that once a particle has left its initial state, it will never come back.

The density of final states

We will see that the transition to the continuum is controlled by the number of available states. Because these states form a continuum, it is useful to use the notion of *density of states* which quantifies how many states are available in an infinitesimal energy window. The density of states $\rho(E)$ is defined by

$$\rho(E) = \frac{dN}{dE}$$

The density of states $\rho(E)$ is the derivative of the total number $N(E)$ of states with an energy smaller than E. This means that the number of states in the interval $[E, E+\delta E]$ is given by $\int_E^{E+\delta E} \rho(E)dE = N(E+\delta E) - N(E)$. For an infinitesimal interval δE, this gives $\rho(E)\delta E$. The figure below is an illustration of the density of states



The plot on the left shown the energy levels of the system. In this example, we chose $E_n = n^2 E_1$. The middle panel shows the number of states $N(E)$ with energies below E. In the limit of a continuous spectrum $N(E) = \sqrt{E/E_1}$. Finally, the panel on the right is the density of states $\rho(E) = dN/dE = 1/2\sqrt{EE_1}$. Let us consider one more example with the one-dimensional harmonic oscillator. The eigenenergies are given by $E_n = (n+1/2)\hbar\omega_0$. The total number of states with energies smaller than E is $N(E) \simeq 1/2 + E/(\hbar\omega_0)$. From this equation one finds the density of states $\rho(E) = 1/(\hbar\omega_0)$.

The density of states allows to simplify expression that involve sums over all final states. The latter can be replaced by integrals over the density of states

$$\sum_k f(E_k) \simeq \int_{-\infty}^{\infty} \rho(E) f(E) dE,$$

where f is an arbitrary function of only the energy of the final states.

Fermi's golden rule

Let us consider again a perturbation that is constant in time. We want to compute the probability that the system has left the initial state $|i\rangle$. This can be expressed as the sum over all final states $|f\rangle$ of the probability to have a transition to $|f\rangle$

$$\mathcal{P}(t) = \sum_f \mathcal{P}_{i\to f}(t) = \sum_f \frac{|W_{fi}(E_f)|^2}{\hbar^2}\, y\left(\frac{E_f - E_i}{\hbar}, t\right)$$

In this formula, we have made the assumption that the matrix elements $W_{fi}(E_f)$ only depend on the energy of the final state $|f\rangle$. This allows to rewrite the sum over final states as an integral

$$\mathcal{P}(t) = \int_{-\infty}^{\infty} \frac{|W_{fi}(E_f)|^2}{\hbar^2}\, y\left(\frac{E_f - E_i}{\hbar}, t\right)\, \rho(E_f) dE_f$$

As we have discussed above, the function $y((E_f - E_i)/\hbar, t)$ takes non-negligible values over a typical interval of final energies $-2\pi\hbar/t < E_f - E_i < 2\pi\hbar/t$. For long times t, this will filter energies E_f that are close to E_i. It is often reasonable to suppose that $W_{fi}(E_f)$ and $\rho(E_f)$ are very slowly varying over the energy interval $-2\pi\hbar/t < E_f - E_i < 2\pi\hbar/t$. With this assumption, the matrix elements and the density of states can be taken away from the integral and we have

$$\mathcal{P}(t) = \frac{|W_{fi}(E_i)|^2}{\hbar^2}\rho(E_i) \int_{-\infty}^{\infty} y\left(\frac{E_f - E_i}{\hbar}, t\right)\, dE_f,$$

where we have approximated W_{fi} and ρ by their value at the energy E_i. The integral is easy to compute and yields $2\pi\hbar t$. The probability then reduces to

$$\mathcal{P}(t) = \frac{2\pi}{\hbar}|W_{fi}(E_i)|^2 \rho(E_i)\, t$$

It appears that the probability to have a transition is *linear* with the time t. This is very different from the situation with a discrete spectrum where the probability was periodic in time. We can write the probability as $\mathcal{P}(t) = \Gamma t$, where

$$\Gamma = \frac{d\mathcal{P}}{dt} = \frac{2\pi}{\hbar}|W_{fi}(E_i)|^2 \rho(E_i)$$

is the *transmission rate*. This result is known as *Fermi's golden rule*. As a consequence, the probability to remain in the original state $|i\rangle$ is given by

$$\mathcal{P}_i(t) = 1 - \Gamma t$$

Fermi's golden rule is justified only if the probability remains much smaller than 1, i.e. for a time $t \ll 1/\Gamma$. On the other hand, we have also supposed that the variation of $W_{fi}(E)$ and $\rho(E)$ is small in an interval $\pm 2\pi\hbar/t$ around E_i which means that t should not be too small either. A treatment of the long time limit shows that $\mathcal{P}_i(t)$ decreases exponentially

$$\mathcal{P}_i(t) = e^{-\Gamma t} \qquad \Gamma = \frac{2\pi}{\hbar}|W_{fi}(E_i)|^2\rho(E_i)$$

The decay is controlled by Γ. We can see that the lifetime of the original state $|i\rangle$ is of the order of $1/\Gamma$.

Example: spontaneous emission in atoms

Let us illustrate Fermi's golden rule in a practical situation. We consider an atom in one of its excited eigenstates. It could for example be a hydrogen atom with its electron in the $2s$ orbital. If the atom was truly isolated the electron would remain in that state forever with a trivial evolution of its wavefunction with a phase $\exp(-iE_{2s}t/\hbar)$. However, an atom is never truly isolated. It is always in contact with its environment. Even if is very far from other atoms, it would still be coupled to the electromagnetic field. Therefore, if we want a realistic description of the atom, we need to include the electromagnetic field as well. One can then think of the initial excited state as a tensor product $|i\rangle = |2s\rangle \otimes |0\rangle$, where the state on the right describes the electromagnetic vacuum. The possible final states are described by a continuum $|f\rangle = |1s\rangle \otimes |1_{\vec{\epsilon},\vec{k}}\rangle$. Here $|1_{\vec{\epsilon},\vec{k}}\rangle$ is a photon with wavevector $\vec{k}$ and polarization $\vec{\epsilon}$. The atomic spectrum is discrete, but the photon spectrum is continuous. If the energy of the final state is close to the original state, i.e. when $\hbar kc \sim E_{2s} - E_{1s}$, we can expect that there is a relevant coupling between the inital and final state. Using Fermi's golden rule, we conclude that the probability that the electron remains in the excited state decays exponentially $e^{-\Gamma t}$. Therefore, on a typical time scale $1/\Gamma$, we will have a spontaneous emission of a photon as the electron returns to the ground state. In the framework of quantum electrodynamics, it is possible to compute the matrix elements that couple the inital and final states. These calculations show that the typical lifetime of such an excited atomic state is of the order of $1 - 10$ ns.