

# Chapter 4

# Time Dependent Perturbation Theory

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## 4.1 Time dependent perturbations

We will assume that, as before, we have a Hamiltonian  $H^{(0)}$  that is known and is *time independent*. Known means we know the spectrum of energy eigenstates and the energy eigenvalues. This time the perturbation to the Hamiltonian, denoted as  $\delta H(t)$  will be time dependent and, as a result, the full Hamiltonian  $H(t)$  is also time dependent

$$H(t) = H^{(0)} + \delta H(t). \quad (4.1.1)$$

While  $H^{(0)}$  has a well-defined spectrum,  $H(t)$  does not. Being time dependent,  $H(t)$  does not have energy eigenstates. It is important to remember that the existence of energy eigenstates was predicated on the factorization of solutions  $\Psi(x, t)$  of the full Schrödinger equation into a space-dependent part  $\psi(x)$  and a time dependent part that turned out to be  $e^{-iEt/\hbar}$ , with  $E$  the energy. Such factorization is not possible when the Hamiltonian is time dependent. Since  $H(t)$  does not have energy eigenstates the goal is to find the solutions  $|\Psi(x, t)\rangle$  directly. Since we are going to focus on the time dependence, we will suppress the labels associated with space. We simply say we are trying to find the solution  $|\Psi(t)\rangle$  to the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = (H^{(0)} + \delta H(t)) |\Psi(t)\rangle. \quad (4.1.2)$$

In typical situations the perturbation  $\delta H(t)$  vanishes for  $t < t_0$ , it exists for some finite time, and then vanishes for  $t > t_f$  (see Figure 4.1). The system starts in an eigenstate of  $H^{(0)}$  at  $t < t_0$  or a linear combination thereof. We usually ask: What is the state of the system for  $t > t_f$ ? Note that both initial and final states are nicely described in terms of eigenstates of  $H^{(0)}$  since this *is* the Hamiltonian for  $t < t_0$  and  $t > t_f$ . Even during the

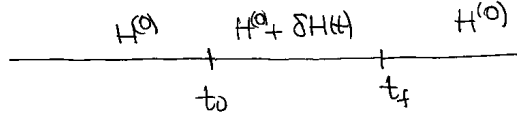


Figure 4.1: Time dependent perturbations typically exist for some time interval, here from  $t_0$  to  $t_f$ .

time when the perturbation is on we can use the eigenstates of  $H^{(0)}$  to describe the system, since these eigenstates form a complete basis, but the time dependence is very nontrivial.

Many physical questions can be couched in this language. For example, assume we have a hydrogen atom in its ground state. We turn on EM fields for some time interval. We can then ask: What are the probabilities to find the atom in each of the various excited states after the perturbation turned off?

#### 4.1.1 The interaction picture

In order to solve efficiently for the state  $|\Psi(t)\rangle$  we will introduce the *Interaction Picture* of Quantum Mechanics. This picture uses some elements of the Heisenberg picture and some elements of the Schrödinger picture. We will use the known Hamiltonian  $H^{(0)}$  to define some Heisenberg operators and the perturbation  $\delta H$  will be used to write a Schrödinger equation.

We begin by recalling some facts from the Heisenberg picture. For *any* Hamiltonian, time dependent or not, one can determine the unitary operator  $\mathcal{U}(t)$  that generates time evolution:

$$|\Psi(t)\rangle = \mathcal{U}(t)|\Psi(0)\rangle. \quad (4.1.3)$$

The Heisenberg operator  $\hat{A}_H$  associated with a Schrödinger operator  $\hat{A}_s$  is obtained by considering a rewriting of expectation values:

$$\langle \Psi(t) | \hat{A}_s | \Psi(t) \rangle = \langle \Psi(0) | \mathcal{U}^\dagger(t) \hat{A}_s \mathcal{U}(t) | \Psi(0) \rangle = \langle \Psi(0) | \hat{A}_H | \Psi(0) \rangle, \quad (4.1.4)$$

where

$$\hat{A}_H \equiv \mathcal{U}^\dagger(t) \hat{A}_s \mathcal{U}(t). \quad (4.1.5)$$

This definition applies even for time dependent Schrödinger operators. Note that the operator  $\mathcal{U}^\dagger$  brings states to rest:

$$\mathcal{U}^\dagger(t) |\Psi(t)\rangle = \mathcal{U}^\dagger(t) \mathcal{U}(t) |\Psi(0)\rangle = |\Psi(0)\rangle. \quad (4.1.6)$$

In our problem the known Hamiltonian  $H^{(0)}$  is time independent and the associated unitary time evolution operator  $\mathcal{U}_0(t)$  takes the simple form

$$\mathcal{U}_0(t) = \exp\left(-\frac{iH^{(0)}t}{\hbar}\right). \quad (4.1.7)$$

The state  $|\Psi(t)\rangle$  in our problem evolves through the effects of  $H^{(0)}$  plus  $\delta H$ . Motivated by (4.1.6) we define the auxiliary ket  $|\tilde{\Psi}(t)\rangle$  as the ket  $|\Psi(t)\rangle$  partially brought to rest through  $H^{(0)}$ :

$$|\tilde{\Psi}(t)\rangle \equiv \exp\left(\frac{iH^{(0)}t}{\hbar}\right)|\Psi(t)\rangle. \quad (4.1.8)$$

Expect that Schrödinger equation for  $|\tilde{\Psi}(t)\rangle$  will be simpler, as the above must have taken care of the time dependence generated by  $H^{(0)}$ . Of course, if we can determine  $|\tilde{\Psi}(t)\rangle$  we can easily get back the desired state  $|\Psi(t)\rangle$  inverting the above relation to find

$$|\Psi(t)\rangle = \exp\left(-\frac{iH^{(0)}t}{\hbar}\right)|\tilde{\Psi}(t)\rangle. \quad (4.1.9)$$

Our objective now is to find the Schrödinger equation for  $|\tilde{\Psi}(t)\rangle$ . Taking the time derivative of (4.1.8) and using (4.1.2)

$$\begin{aligned} i\hbar \frac{d}{dt}|\tilde{\Psi}(t)\rangle &= -H^{(0)}|\tilde{\Psi}(t)\rangle + \exp\left(\frac{iH^{(0)}t}{\hbar}\right)(H^{(0)} + \delta H(t))|\Psi(t)\rangle \\ &= \left[-H^{(0)} + \exp\left(\frac{iH^{(0)}t}{\hbar}\right)(H^{(0)} + \delta H(t))\exp\left(-\frac{iH^{(0)}t}{\hbar}\right)\right]|\tilde{\Psi}(t)\rangle \\ &= \exp\left(\frac{iH^{(0)}t}{\hbar}\right)\delta H(t)\exp\left(-\frac{iH^{(0)}t}{\hbar}\right)|\tilde{\Psi}(t)\rangle, \end{aligned} \quad (4.1.10)$$

where the dependence on  $H^{(0)}$  cancelled out. We have thus found the Schrödinger equation

$$i\hbar \frac{d}{dt}|\tilde{\Psi}(t)\rangle = \delta\tilde{H}(t)|\tilde{\Psi}(t)\rangle. \quad (4.1.11)$$

where the operator  $\delta\tilde{H}(t)$  is defined as

$$\delta\tilde{H}(t) \equiv \exp\left(\frac{iH^{(0)}t}{\hbar}\right)\delta H(t)\exp\left(-\frac{iH^{(0)}t}{\hbar}\right). \quad (4.1.12)$$

Note that as expected the time evolution left in  $|\tilde{\Psi}(t)\rangle$  is generated by  $\delta\tilde{H}(t)$  via a Schrödinger equation. The operator  $\delta\tilde{H}(t)$  is nothing else but the Heisenberg version of  $\delta H$  generated using  $H^{(0)}$ ! This is an *interaction picture*, a mixture of Heisenberg's and Schrödinger picture. While we have some Heisenberg<sup>(0)</sup> operators there is still a time dependent state  $|\tilde{\Psi}(t)\rangle$  and a Schrödinger equation for it.

How does it all look in an orthonormal basis? Let  $|n\rangle$  be the complete orthonormal basis of states for  $H^{(0)}$ :

$$H^{(0)}|n\rangle = E_n|n\rangle. \quad (4.1.13)$$

This time there is no need for a (0) superscript, since neither the states nor their energies will be corrected (there are no energy eigenstates in the time-dependent theory). We then write an ansatz for our unknown ket:

$$|\tilde{\Psi}(t)\rangle = \sum_n c_n(t)|n\rangle. \quad (4.1.14)$$

Here the functions  $c_n(t)$  are unknown. This expansion is justified since the states  $|n\rangle$  form a basis, and thus at all times they can be used to describe the state of the system. The original wavefunction is then:

$$|\Psi(t)\rangle = \exp\left(-\frac{iH^{(0)}t}{\hbar}\right)|\tilde{\Psi}(t)\rangle = \sum_n c_n(t) \exp\left(-\frac{iE_n t}{\hbar}\right)|n\rangle. \quad (4.1.15)$$

Note that the time dependence due to  $H^{(0)}$  is present here. If we had  $\delta H = 0$  the state  $|\tilde{\Psi}(t)\rangle$  would be a constant, as demanded by the Schrödinger equation (4.1.11) and the  $c_n(t)$  would be constants. The solution above would give the expected time evolution of the states under  $H^{(0)}$ .

To see what the Schrödinger equation tells us about the functions  $c_n(t)$  we plug the ansatz (4.1.14) into (4.1.11):

$$i\hbar \frac{d}{dt} \sum_m c_m(t)|m\rangle = \delta\tilde{H}(t) \sum_n c_n(t)|n\rangle \quad (4.1.16)$$

Using dots for time derivatives and introducing a resolution of the identity on the right-hand side we find

$$\begin{aligned} \sum_m i\hbar \dot{c}_m(t)|m\rangle &= \sum_m |m\rangle \langle m| \delta\tilde{H}(t) \sum_n c_n(t)|n\rangle \\ &= \sum_m |m\rangle \sum_n \langle m| \delta\tilde{H}(t)|n\rangle c_n(t) \\ &= \sum_{m,n} \delta\tilde{H}_{mn}(t) c_n(t)|m\rangle. \end{aligned} \quad (4.1.17)$$

Here we have used the familiar matrix element notation

$$\delta\tilde{H}_{mn}(t) \equiv \langle m| \delta\tilde{H}(t)|n\rangle. \quad (4.1.18)$$

Equating the coefficients of the basis kets  $|m\rangle$  in (4.1.17) we get the equations

$$i\hbar \dot{c}_m(t) = \sum_n \delta\tilde{H}_{mn}(t) c_n(t). \quad (4.1.19)$$

The Schrödinger equation has become an infinite set of coupled first-order differential equations. The matrix elements in the equation can be simplified a bit by passing to un-tilde variables:

$$\begin{aligned}\widetilde{\delta H}_{mn}(t) &= \langle m | \exp\left(\frac{iH^{(0)}t}{\hbar}\right) \delta H(t) \exp\left(-\frac{iH^{(0)}t}{\hbar}\right) | n \rangle \\ &= \exp\left[\frac{i}{\hbar}(E_m - E_n)t\right] \langle m | \delta H(t) | n \rangle.\end{aligned}\quad (4.1.20)$$

If we define

$$\omega_{mn} \equiv \frac{E_m - E_n}{\hbar}, \quad (4.1.21)$$

we then have

$$\widetilde{\delta H}_{mn}(t) = e^{i\omega_{mn}t} \delta H_{mn}(t). \quad (4.1.22)$$

The coupled equations (4.1.19) for the functions  $c_n(t)$  then become

$$\boxed{i\hbar \dot{c}_m(t) = \sum_n e^{i\omega_{mn}t} \delta H_{mn}(t) c_n(t).} \quad (4.1.23)$$

### 4.1.2 Example (based on Griffiths Problem 9.3)

Consider a two-state system with basis states  $|a\rangle$  and  $|b\rangle$ , eigenstates of  $H^{(0)}$  with energies  $E_a$  and  $E_b$ , respectively. Call

$$\omega_{ab} \equiv (E_a - E_b)/\hbar. \quad (4.1.24)$$

Now take the perturbation to be a matrix times a delta function at time equal zero. Thus the perturbation only exists for time equal zero:

$$\delta H(t) = \begin{pmatrix} 0 & \alpha \\ \alpha^* & 0 \end{pmatrix} \delta(t) \equiv U \delta(t), \quad (4.1.25)$$

where  $\alpha$  is a complex number. With the basis vectors ordered as  $|1\rangle = |a\rangle$  and  $|2\rangle = |b\rangle$  we have

$$U = \begin{pmatrix} U_{aa} & U_{ab} \\ U_{ba} & U_{bb} \end{pmatrix}, \quad \text{with } U_{aa} = U_{bb} = 0 \text{ and } U_{ab} = U_{ba}^* = \alpha. \quad (4.1.26)$$

There is a sudden violent perturbation at  $t = 0$  with off-diagonal elements that should produce transition. Take the system to be in  $|a\rangle$  for  $t = -\infty$ , what is the probability that it is in  $|b\rangle$  for  $t = +\infty$ ?

**Solution:** First note that if the system is in  $|a\rangle$  at  $t = -\infty$  it will remain in state  $|a\rangle$  until  $t = 0^-$ , that is, just before the perturbation turns on. This is because  $|a\rangle$  is an energy eigenstate of  $H^{(0)}$ . In fact we have, up to a constant phase,

$$|\Psi(t)\rangle = e^{-iE_a t/\hbar} |a\rangle, \quad \text{for } -\infty < t \leq 0^-. \quad (4.1.27)$$

We are asked what will be the probability to find the state in  $|b\rangle$  at  $t = \infty$ , but in fact, the answer is the same as the probability to find the state in  $|b\rangle$  at  $t = 0^+$ . This is because the perturbation does not exist anymore and if the state at  $t = 0^+$  is

$$|\Psi(0^+)\rangle = \gamma_a|a\rangle + \gamma_b|b\rangle, \quad (4.1.28)$$

with  $\gamma_1$  and  $\gamma_2$  constants, then the state for any time  $t > 0$  will be

$$|\Psi(t)\rangle = \gamma_a|a\rangle e^{-iE_a t/\hbar} + \gamma_b|b\rangle e^{-iE_b t/\hbar}. \quad (4.1.29)$$

The probability  $p_b(t)$  to find the state  $|b\rangle$  at time  $t$  will be

$$p_b(t) = |\langle b|\Psi(t)\rangle|^2 = \left| \gamma_b e^{-iE_b t/\hbar} \right|^2 = |\gamma_b|^2, \quad (4.1.30)$$

and, as expected, this is time independent. It follows that to solve this problem we must just find the state at  $t = 0^+$  and determine the constants  $\gamma_1$  and  $\gamma_2$ .

Since we have two basis states the unknown tilde state is

$$|\tilde{\Psi}(t)\rangle = c_a(t)|a\rangle + c_b(t)|b\rangle, \quad (4.1.31)$$

and the initial conditions are stating that the system begins in the state  $|a\rangle$  are

$$c_a(0^-) = 1, \quad c_b(0^-) = 0. \quad (4.1.32)$$

The differential equations (4.1.23) take the form

$$\begin{aligned} i\hbar \dot{c}_a(t) &= e^{i\omega_{ab}t} \delta H_{ab}(t) c_b(t), \\ i\hbar \dot{c}_b(t) &= e^{i\omega_{ba}t} \delta H_{ba}(t) c_a(t). \end{aligned} \quad (4.1.33)$$

The couplings are off-diagonal because  $\delta H_{aa} = \delta H_{bb} = 0$ . Using the form of the  $\delta H$  matrix elements,

$$\begin{aligned} i\hbar \dot{c}_a(t) &= e^{i\omega_{ab}t} \alpha \delta(t) c_b(t), \\ i\hbar \dot{c}_b(t) &= e^{-i\omega_{ab}t} \alpha^* \delta(t) c_a(t). \end{aligned} \quad (4.1.34)$$

We know that for functions  $f$  continuous at  $t = 0$  we have  $f(t)\delta(t) = f(0)\delta(t)$ . We now ask if we are allowed to use such identity for the right-hand side of the above equations. In fact we can use the identity for  $e^{\pm i\omega_{ab}t}$  but not for the functions  $c_a(t)$  and  $c_b(t)$  that, are expected to be discontinuous at  $t = 0$ . They must be so, because they can only change at  $t = 0$ , when the delta function exists. Evaluating the exponentials at  $t = 0$  we then get the simpler equations

$$\begin{aligned} i\hbar \dot{c}_a(t) &= \alpha \delta(t) c_b(t), \\ i\hbar \dot{c}_b(t) &= \alpha^* \delta(t) c_a(t). \end{aligned} \quad (4.1.35)$$

With such singular right-hand sides, the solution of these equations needs regulation. We will regulate the delta function and solve the problem. A consistency check is that the solution has a well-defined limit as the regulator is removed. We will replace the  $\delta(t)$  by the function  $\Delta_{t_0}(t)$ , with  $t_0 > 0$ , defined as follows:

$$\delta(t) \rightarrow \Delta_{t_0}(t) = \begin{cases} 1/t_0, & \text{for } t \in [0, t_0], \\ 0, & \text{otherwise.} \end{cases} \quad (4.1.36)$$

Note that as appropriate,  $\int dt \Delta_{t_0}(t) = 1$ , and that  $\Delta_{t_0}(t)$  in the limit as  $t_0 \rightarrow 0$  approaches a delta function. If we replace the delta functions in (4.1.37) by the regulator we find, for  $t \in [0, t_0]$

$$\begin{aligned} \text{For } t \in [0, t_0]: \quad i\hbar \dot{c}_a(t) &= \frac{\alpha}{t_0} c_b(t), \\ i\hbar \dot{c}_b(t) &= \frac{\alpha^*}{t_0} c_a(t). \end{aligned} \quad (4.1.37)$$

For any other times the right-hand side vanishes. By taking a time derivative of the first equation and using the second one we find that

$$\ddot{c}_a(t) = \frac{1}{i\hbar} \frac{\alpha}{t_0} \frac{1}{i\hbar} \frac{\alpha^*}{t_0} c_a(t) = - \left( \frac{|\alpha|}{\hbar t_0} \right)^2 c_a(t). \quad (4.1.38)$$

This is a simple second order differential equation and its general solution is

$$c_a(t) = \beta_0 \cos\left(\frac{|\alpha|t}{\hbar t_0}\right) + \beta_1 \sin\left(\frac{|\alpha|t}{\hbar t_0}\right). \quad (4.1.39)$$

This is accompanied with  $c_b(t)$  which is readily obtained from the first line in (4.1.37):

$$c_b(t) = \frac{i\hbar t_0}{\alpha} \dot{c}_a(t) = \frac{i|\alpha|}{\alpha} \left( -\beta_0 \sin\left(\frac{|\alpha|t}{\hbar t_0}\right) + \beta_1 \cos\left(\frac{|\alpha|t}{\hbar t_0}\right) \right). \quad (4.1.40)$$

The initial conditions (4.1.32) tell us that in this regulated problem  $c_a(0) = 1$  and  $c_b(0) = 0$ . Given the solutions above, the first condition fixes  $\beta_0 = 1$  and the second fixes  $\beta_1 = 0$ . Thus, our solutions are:

$$\text{For } t \in [0, t_0]: \quad c_a(t) = \cos\left(\frac{|\alpha|t}{\hbar t_0}\right), \quad (4.1.41)$$

$$c_b(t) = -i \frac{|\alpha|}{\alpha} \sin\left(\frac{|\alpha|t}{\hbar t_0}\right). \quad (4.1.42)$$

When the (regulated) perturbation is turned off ( $t = t_0$ ),  $c_a$  and  $c_b$  stop varying and the constant value they take is their values at  $t = t_0$ . Hence

$$c_a(t > t_0) = c_a(t_0) = \cos\left(\frac{|\alpha|}{\hbar}\right), \quad (4.1.43)$$

$$c_b(t > t_0) = c_b(t_0) = -i \frac{|\alpha|}{\alpha} \sin\left(\frac{|\alpha|}{\hbar}\right). \quad (4.1.44)$$

Note that these values are  $t_0$  independent. Being regulator independent, we can safely take the limit  $t_0 \rightarrow 0$  to get

$$c_a(t > 0) = \cos\left(\frac{|\alpha|}{\hbar}\right), \quad (4.1.45)$$

$$c_b(t > 0) = -i\frac{|\alpha|}{\alpha} \sin\left(\frac{|\alpha|}{\hbar}\right). \quad (4.1.46)$$

Our calculation above shows that at  $t = 0^+$  the state will be

$$|\Psi(0^+)\rangle = |\tilde{\Psi}(0^+)\rangle = \cos\left(\frac{|\alpha|}{\hbar}\right)|a\rangle - i\frac{|\alpha|}{\alpha} \sin\left(\frac{|\alpha|}{\hbar}\right)|b\rangle. \quad (4.1.47)$$

With only free evolution ensuing for  $t > 0$  we have (as anticipated in (4.1.29))

$$|\Psi(t)\rangle = \cos\left(\frac{|\alpha|}{\hbar}\right)|a\rangle e^{-iE_a t/\hbar} - i\frac{|\alpha|}{\alpha} \sin\left(\frac{|\alpha|}{\hbar}\right)|b\rangle e^{-iE_b t/\hbar}. \quad (4.1.48)$$

The probabilities to be found in  $|a\rangle$  or in  $|b\rangle$  are time-independent, we are in a superposition of energy eigenstates! We can now easily calculate the probability  $p_b(t)$  to find the system in  $|b\rangle$  for  $t > 0$  as well as the probability  $p_a(t)$  to find the system in  $|a\rangle$  for  $t > 0$ :

$$\begin{aligned} p_b(t) &= |\langle b|\Psi(t)\rangle|^2 = \sin^2\left(\frac{|\alpha|}{\hbar}\right), \\ p_a(t) &= |\langle a|\Psi(t)\rangle|^2 = \cos^2\left(\frac{|\alpha|}{\hbar}\right). \end{aligned} \quad (4.1.49)$$

Note that  $p_a(t) + p_b(t) = 1$ , as required. The above is the exact solution of this system. If we had worked in perturbation theory, we would be taking the strength  $|\alpha|$  of the interaction to be small. The answers we would obtain would form the power series expansion of the above formulas in the limit as  $|\alpha|/\hbar$  is small.

## 4.2 Perturbative solution

In order to set up the perturbative expansion properly we include a unit-free small parameter  $\lambda$  multiplying the perturbation  $\delta H$  in the time-dependent Hamiltonian (4.1.1):

$$H(t) = H^{(0)} + \lambda\delta H(t). \quad (4.2.1)$$

With such a replacement the interaction picture Schrödinger equation for  $|\tilde{\Psi}(t)\rangle$  in (4.1.11) now becomes

$$i\hbar\frac{d}{dt}|\tilde{\Psi}(t)\rangle = \lambda\tilde{\delta H}(t)|\tilde{\Psi}(t)\rangle. \quad (4.2.2)$$

As we did in time-independent perturbation theory we start by expanding  $|\tilde{\Psi}(t)\rangle$  in powers of the parameter  $\lambda$ :

$$|\tilde{\Psi}(t)\rangle = |\tilde{\Psi}^{(0)}(t)\rangle + \lambda|\tilde{\Psi}^{(1)}(t)\rangle + \lambda^2|\tilde{\Psi}^{(2)}(t)\rangle + \mathcal{O}(\lambda^3). \quad (4.2.3)$$



We now insert this into both sides of the Schrödinger equation (4.2.2), and using  $\partial_t$  for time derivatives, we find

$$\begin{aligned} i\hbar\partial_t|\tilde{\Psi}^{(0)}(t)\rangle + \lambda i\hbar\partial_t|\tilde{\Psi}^{(1)}(t)\rangle + \lambda^2 i\hbar\partial_t|\tilde{\Psi}^{(2)}(t)\rangle + \lambda^3 i\hbar\partial_t|\tilde{\Psi}^{(2)}(t)\rangle + \mathcal{O}(\lambda^4) \\ = \lambda \widetilde{\delta H}|\tilde{\Psi}^{(0)}(t)\rangle + \lambda^2 \widetilde{\delta H}|\tilde{\Psi}^{(1)}(t)\rangle + \lambda^3 \widetilde{\delta H}|\tilde{\Psi}^{(2)}(t)\rangle + \mathcal{O}(\lambda^4). \end{aligned} \quad (4.2.4)$$

The coefficient of each power of  $\lambda$  must vanish, giving us

$$\begin{aligned} i\hbar\partial_t|\tilde{\Psi}^{(0)}(t)\rangle &= 0, \\ i\hbar\partial_t|\tilde{\Psi}^{(1)}(t)\rangle &= \widetilde{\delta H}|\tilde{\Psi}^{(0)}(t)\rangle, \\ i\hbar\partial_t|\tilde{\Psi}^{(2)}(t)\rangle &= \widetilde{\delta H}|\tilde{\Psi}^{(1)}(t)\rangle, \\ \vdots &= \vdots \\ i\hbar\partial_t|\tilde{\Psi}^{(n+1)}(t)\rangle &= \widetilde{\delta H}|\tilde{\Psi}^{(n)}(t)\rangle. \end{aligned} \quad (4.2.5)$$

The origin of the pattern is clear. Since the Schrödinger equation has an explicit  $\lambda$  multiplying the right-hand side, the time derivative of the  $n$ -th component is coupled to the  $\widetilde{\delta H}$  perturbation acting on the  $(n-1)$ -th component.

Let us consider the initial condition in detail. We will assume that the perturbation turns on at  $t=0$ , so that the initial condition is given in terms of  $|\Psi(0)\rangle$ . Since our Schrödinger equation is in terms of  $|\tilde{\Psi}(t)\rangle$  we use the relation ((4.1.8)) between them to conclude that both tilde and un-tilde wavefunctions are equal at  $t=0$ :

$$|\tilde{\Psi}(0)\rangle = |\Psi(0)\rangle. \quad (4.2.6)$$

Given this, the expansion (4.2.3) evaluated at  $t=0$  implies that:

$$|\tilde{\Psi}(0)\rangle = |\Psi(0)\rangle = |\tilde{\Psi}^{(0)}(0)\rangle + \lambda|\tilde{\Psi}^{(1)}(0)\rangle + \lambda^2|\tilde{\Psi}^{(2)}(0)\rangle + \mathcal{O}(\lambda^3). \quad (4.2.7)$$

This must be viewed, again, as an equation that holds for all values of  $\lambda$ . As a result, the coefficient of each power of  $\lambda$  must vanish and we have

$$\begin{aligned} |\tilde{\Psi}^{(0)}(0)\rangle &= |\Psi(0)\rangle, \\ |\tilde{\Psi}^{(n)}(0)\rangle &= 0, \quad n = 1, 2, 3, \dots \end{aligned} \quad (4.2.8)$$

These are the relevant initial conditions.

Consider now the first equation in (4.2.5). It states that  $|\tilde{\Psi}^{(0)}(t)\rangle$  is time independent. This is reasonable: if the perturbation vanishes, this is the only equation we get and we should expect  $|\tilde{\Psi}(t)\rangle$  constant. Using the time-independence of  $|\tilde{\Psi}^{(0)}(t)\rangle$  and the initial condition we have

$$|\tilde{\Psi}^{(0)}(t)\rangle = |\tilde{\Psi}^{(0)}(0)\rangle = |\Psi(0)\rangle, \quad (4.2.9)$$

and we have solved the first equation completely:

$$\boxed{|\tilde{\Psi}^{(0)}\rangle = |\Psi(0)\rangle.} \quad (4.2.10)$$

Using this result, the  $\mathcal{O}(\lambda)$  equation reads:

$$i\hbar\partial_t|\tilde{\Psi}^{(1)}(t)\rangle = \widetilde{\delta H}|\tilde{\Psi}^{(0)}(t)\rangle = \widetilde{\delta H}(t)|\Psi(0)\rangle. \quad (4.2.11)$$

The solution can be written as an integral:

$$\boxed{|\tilde{\Psi}^{(1)}(t)\rangle = \int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar} |\Psi(0)\rangle dt'.} \quad (4.2.12)$$

Note that by setting the lower limit of integration at  $t = 0$  we have implemented correctly the initial condition  $|\tilde{\Psi}^{(1)}(0)\rangle = 0$ . The next equation, of order  $\lambda^2$  reads:

$$i\hbar\partial_t|\tilde{\Psi}^{(2)}(t)\rangle = \widetilde{\delta H}|\tilde{\Psi}^{(1)}(t)\rangle, \quad (4.2.13)$$

and its solution is

$$|\tilde{\Psi}^{(2)}(t)\rangle = \int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar} |\tilde{\Psi}^{(1)}(t')\rangle dt', \quad (4.2.14)$$

consistent with the initial condition. Using our previous result to write  $|\tilde{\Psi}^{(1)}(t')\rangle$  we now have an iterated integral expression:

$$\boxed{|\tilde{\Psi}^{(2)}(t)\rangle = \int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar} dt' \int_0^{t'} \frac{\widetilde{\delta H}(t'')}{i\hbar} |\Psi(0)\rangle dt''} \quad (4.2.15)$$

It should be clear from this discussion how to write the iterated integral expression for  $|\tilde{\Psi}^{(k)}(t)\rangle$ , with  $k > 2$ . The solution, setting  $\lambda = 1$  and summarizing is then

$$|\Psi(t)\rangle = \exp\left(-\frac{iH^{(0)}t}{\hbar}\right) \left( |\Psi(0)\rangle + |\tilde{\Psi}^{(1)}(t)\rangle + |\tilde{\Psi}^{(2)}(t)\rangle + \dots \right) \quad (4.2.16)$$

Let us use our perturbation theory to calculate the probability  $P_{m \leftarrow n}(t)$  to transition from  $|n\rangle$  at  $t = 0$  to  $|m\rangle$ , with  $m \neq n$ , at time  $t$ , under the effect of the perturbation. By definition

$$P_{m \leftarrow n}(t) = |\langle m|\Psi(t)\rangle|^2. \quad (4.2.17)$$

Using the tilde wavefunction, for which we know how to write the perturbation, we have

$$P_{m \leftarrow n}(t) = |\langle m|e^{-iH^{(0)}t/\hbar}|\tilde{\Psi}(t)\rangle|^2 = |\langle m|\tilde{\Psi}(t)\rangle|^2, \quad (4.2.18)$$

since the phase that arises from the action on the bra vanishes upon the calculation of the norm squared. Now using the perturbation expression for  $|\tilde{\Psi}(t)\rangle$  (setting  $\lambda = 1$ ) we have

$$P_{m \leftarrow n}(t) = \left| \langle m | \left( |\Psi^{(0)}\rangle + |\tilde{\Psi}^{(1)}(t)\rangle + |\tilde{\Psi}^{(2)}(t)\rangle + \dots \right) \right|^2. \quad (4.2.19)$$

Since we are told that  $|\Psi(0)\rangle = |n\rangle$  and  $|n\rangle$  is orthogonal to  $|m\rangle$  we find

$$P_{m \leftarrow n}(t) = \left| \langle m | \tilde{\Psi}^{(1)}(t) \rangle + \langle m | \tilde{\Psi}^{(2)}(t) \rangle + \dots \right|^2. \quad (4.2.20)$$

To first order in perturbation theory we only keep the first term in the sum and using our result for  $|\tilde{\Psi}^{(1)}(t)\rangle$  we find

$$P_{m \leftarrow n}^{(1)}(t) = \left| \langle m | \int_0^t \frac{\delta \tilde{H}(t')}{i\hbar} |n\rangle dt' \right|^2 = \left| \int_0^t \frac{\langle m | \delta \tilde{H}(t') |n\rangle}{i\hbar} dt' \right|^2. \quad (4.2.21)$$

Recalling the relation between the matrix elements of  $\delta \tilde{H}$  and those of  $\delta H$  we finally have our result for the transition probability to first order in perturbation theory:

$$\boxed{P_{m \leftarrow n}^{(1)}(t) = \left| \int_0^t e^{i\omega_{mn}t'} \frac{\delta H_{mn}(t')}{i\hbar} dt' \right|^2}. \quad (4.2.22)$$

This is a key result and will be very useful in the applications we will consider.

**Exercise:** Prove the remarkable equality of transition probabilities

$$\boxed{P_{m \leftarrow n}^{(1)}(t) = P_{n \leftarrow m}^{(1)}(t)}, \quad (4.2.23)$$

valid to first order in perturbation theory.

It will also be useful to have our results in terms of the time-dependent coefficients  $c_n(t)$  introduced earlier through the expansion

$$|\tilde{\Psi}(t)\rangle = \sum_n c_n(t) |n\rangle. \quad (4.2.24)$$

Since  $|\Psi(0)\rangle = |\tilde{\Psi}(0)\rangle$  the initial condition reads

$$|\Psi(0)\rangle = \sum_n c_n(0) |n\rangle = |\tilde{\Psi}^{(0)}(0)\rangle, \quad (4.2.25)$$

where we also used (4.2.9). In this notation, the  $c_n(t)$  functions also have a  $\lambda$  expansion, because we write

$$|\tilde{\Psi}^{(k)}(t)\rangle = \sum_n c_n^{(k)}(t) |n\rangle, \quad k = 0, 1, 2, \dots \quad (4.2.26)$$

and therefore the earlier relation

$$|\tilde{\Psi}(t)\rangle = |\tilde{\Psi}^{(0)}(t)\rangle + \lambda|\tilde{\Psi}^{(1)}(t)\rangle + \lambda^2|\tilde{\Psi}^{(2)}(t)\rangle + \mathcal{O}(\lambda^3). \quad (4.2.27)$$

now gives

$$c_n(t) = c_n^{(0)}(t) + \lambda c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \dots \quad (4.2.28)$$

Since  $|\tilde{\Psi}^{(0)}(t)\rangle$  is in fact constant we have

$$c_n^{(0)}(t) = c_n^{(0)}(0) = c_n(0), \quad (4.2.29)$$

where we used (4.2.25). The other initial conditions given earlier in (4.2.8) imply that

$$c_n^{(k)}(0) = 0, \quad k = 1, 2, 3, \dots \quad (4.2.30)$$

Therefore, using our result (4.2.12) for  $|\tilde{\Psi}^{(1)}(t)\rangle$  we have

$$|\tilde{\Psi}^{(1)}(t)\rangle = \sum_n c_n^{(1)}(t)|n\rangle = \int_0^t \frac{\delta\tilde{H}(t')}{i\hbar} dt' \sum_n c_n(0)|n\rangle, \quad (4.2.31)$$

and as a result,

$$c_m^{(1)}(t) \equiv \langle m|\tilde{\Psi}^{(1)}(t)\rangle = \sum_n \int_0^t \frac{\langle m|\delta\tilde{H}(t')|n\rangle}{i\hbar} c_n(0) dt'. \quad (4.2.32)$$

We therefore have

$$\boxed{c_m^{(1)}(t) = \sum_n \int_0^t dt' e^{i\omega_{mn}t'} \frac{\delta H_{mn}(t')}{i\hbar} c_n(0)}. \quad (4.2.33)$$

The probability  $P_m(t)$  to be found in the state  $|m\rangle$  at time  $t$  is

$$P_m(t) = |\langle m|\Psi(t)\rangle|^2 = \left| \langle m|\tilde{\Psi}(t)\rangle \right|^2 = |c_m(t)|^2. \quad (4.2.34)$$

To first order in perturbation theory the answer would be (with  $\lambda = 1$ )

$$\begin{aligned} P_m^{(1)}(t) &= |c_m(0) + c_m^{(1)}(t)|^2 \\ &= |c_m(0)|^2 + c_m(0)^* c_m^{(1)}(t) + c_m^{(1)}(t)^* c_m(0) + \mathcal{O}(\delta H^2). \end{aligned} \quad (4.2.35)$$

Note that the  $|c_m^{(1)}(t)|^2$  term cannot be kept to this order of approximation, since it is of the same order as contributions that would arise from  $c_m^{(2)}(t)$ .

### 4.2.1 Example NMR

The Hamiltonian for a particle with a magnetic moment inside a magnetic field can be written in the form

$$H = \boldsymbol{\omega} \cdot \mathbf{S}, \quad (4.2.36)$$

where  $\mathbf{S}$  is the spin operator and  $\boldsymbol{\omega}$  is precession angular velocity vector, itself a function of the magnetic field. Note that the Hamiltonian has properly units of energy ( $\omega\hbar$ ). Let us take the unperturbed Hamiltonian to be

$$H^{(0)} = \omega_0 S_z = \frac{\hbar}{2} \omega_0 \sigma_z. \quad (4.2.37)$$

For NMR applications one has  $\omega_0 \approx 500$  Hz and this represents the physics of a magnetic field along the  $z$  axis. Let us now consider some possible perturbations.

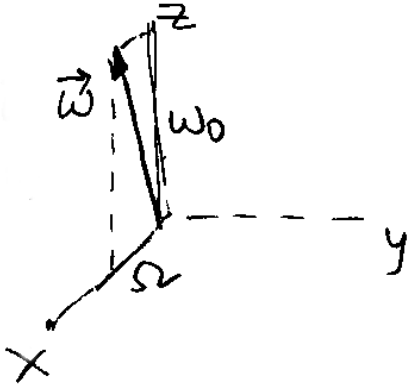
**Case 1: Time independent perturbation** Let us consider adding at  $t = 0$  a constant perturbation associated with an additional small uniform magnetic field along the  $x$  axis:

$$H = H^{(0)} + \delta H, \quad \text{with } \delta H = \Omega S_x, \quad (4.2.38)$$

For this to be a small perturbation we will take

$$\Omega \ll \omega_0. \quad (4.2.39)$$

Hence, for the full Hamiltonian  $H$  we have  $\boldsymbol{\omega} = (\Omega, 0, \omega_0)$

$$H = \underbrace{(\Omega, 0, \omega_0)}_{\boldsymbol{\omega}} \cdot (S_x, S_y, S_z) \quad (4.2.40)$$


The problem is simple enough that an exact solution is possible. The perturbed Hamiltonian  $H$  has energy eigenstates  $|\mathbf{n}; \pm\rangle$ , spin states that point with  $\mathbf{n} = \frac{\boldsymbol{\omega}}{|\boldsymbol{\omega}|}$  with energies  $\pm \frac{\hbar}{2} |\boldsymbol{\omega}|$ . These eigenstates could be recovered using time-independent non-degenerate perturbation theory using  $\Omega/\omega_0$  as a small parameter and starting with the eigenstates  $|\pm\rangle$  of  $H^{(0)}$ .

In *time-dependent* perturbation theory we obtain the time-dependent evolution of initial states as they are affected by the perturbation. Recalling (4.2.12) we have

$$|\tilde{\Psi}^{(1)}(t)\rangle = \int_0^t \frac{\delta \tilde{H}(t')}{i\hbar} |\Psi(0)\rangle dt' \quad (4.2.41)$$

The calculation of  $\widetilde{\delta H}$  requires a bit of computation. One quickly finds that

$$\widetilde{\delta H}(t) = \exp \left[ i\omega_0 t \frac{\sigma_z}{2} \right] \Omega \hat{S}_x \exp \left[ -i\omega_0 t \frac{\sigma_z}{2} \right] = \Omega \left( \hat{S}_x \cos \omega_0 t - \hat{S}_y \sin \omega_0 t \right). \quad (4.2.42)$$

As a result we set:

$$\begin{aligned} |\widetilde{\Psi}^{(1)}(t)\rangle &= \frac{\Omega}{i\hbar} \int_0^t \left( \hat{S}_x \cos \omega_0 t' - \hat{S}_y \sin \omega_0 t' \right) |\Psi(0)\rangle dt' \\ &= \frac{1}{i\hbar} \frac{\Omega}{\omega_0} \left[ \hat{S}_x \sin \omega_0 t + (\cos(\omega_0 t) - 1) \hat{S}_y \right] |\Psi(0)\rangle. \end{aligned} \quad (4.2.43)$$

As expected, the result is first order in the small parameter  $\Omega/\omega_0$ . Following (4.2.16) the time-dependent state is, to first approximation

$$\begin{aligned} |\Psi(t)\rangle &= \exp \left[ -i\omega_0 t \frac{\sigma_z}{2} \right] \left( 1 + \frac{1}{i\hbar} \frac{\Omega}{\omega_0} \left[ \hat{S}_x \sin \omega_0 t + (\cos(\omega_0 t) - 1) \hat{S}_y \right] \right) |\Psi(0)\rangle \\ &\quad + \mathcal{O}((\Omega/\omega_0)^2). \end{aligned} \quad (4.2.44)$$

Physically the solution is clear. The original spin state  $|\Psi(0)\rangle$  precesses about the direction of  $\boldsymbol{\omega}$  with angular velocity  $\omega$ .

**Case 2: Time dependent perturbation.** Suppose that to the original Hamiltonian we add the effect of a rotating magnetic field, rotating with the same angular velocity  $\omega_0$  that corresponds to the Larmor frequency of the original Hamiltonian:

$$\delta H(t) = \Omega \left( \hat{S}_x \cos \omega_0 t + \hat{S}_y \sin \omega_0 t \right). \quad (4.2.45)$$

To compute the perturbation  $\widetilde{\delta H}$  we can use (4.2.42) with  $t$  replaced by  $-t$  so that the right-hand side of this equation is proportional to  $\delta H$ :

$$\exp \left[ -i\omega_0 t \frac{\sigma_z}{2} \right] \Omega \hat{S}_x \exp \left[ i\omega_0 t \frac{\sigma_z}{2} \right] = \Omega \left( \hat{S}_x \cos \omega_0 t + \hat{S}_y \sin \omega_0 t \right). \quad (4.2.46)$$

Moving the exponentials on the left-hand side to the right-hand side we find

$$\Omega \hat{S}_x = \exp \left[ i\omega_0 t \frac{\sigma_z}{2} \right] \Omega \left( \hat{S}_x \cos \omega_0 t + \hat{S}_y \sin \omega_0 t \right) \exp \left[ -i\omega_0 t \frac{\sigma_z}{2} \right]. \quad (4.2.47)$$

The right-hand side is, by definition,  $\widetilde{\delta H}$ . Thus we have shown that

$$\widetilde{\delta H}(t) = \Omega \hat{S}_x, \quad (4.2.48)$$

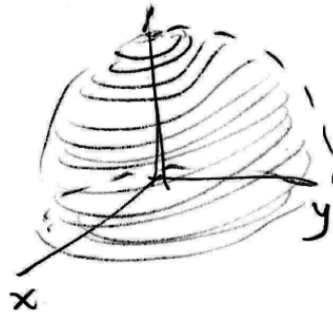
is in fact a time-independent Hamiltonian. This means that the Schrödinger equation for  $|\widetilde{\Psi}\rangle$  is immediately solved

$$|\widetilde{\Psi}(t)\rangle = \exp \left[ -i \frac{\widetilde{\delta H} t}{\hbar} \right] |\widetilde{\Psi}(0)\rangle = \exp \left[ -i \frac{\Omega \hat{S}_x t}{\hbar} \right] |\Psi(0)\rangle. \quad (4.2.49)$$

The complete and exact answer is therefore

$$|\Psi(t)\rangle = \exp\left[-\frac{iH^{(0)}t}{\hbar}\right] |\tilde{\Psi}(t)\rangle = \exp\left[-i\omega_0 t \frac{\sigma_z}{2}\right] \exp\left[-i\Omega t \frac{\sigma_x}{2}\right] |\Psi(0)\rangle. \quad (4.2.50)$$

This is a much more non trivial motion! A spin originally aligned along  $\hat{z}$  will spiral into the  $x, y$  plane with angular velocity  $\Omega$ .



### 4.3 Fermi's Golden Rule

Let us now consider transitions where the initial state is part of a discrete spectrum but the final state is part of a continuum. The ionization of an atom is perhaps the most familiar example: the initial state may be one of the discrete bound states of the atom while the final state includes a free electron a momentum eigenstate that is part of a continuum of non-normalizable states.

As we will see, while the probability of transition between discrete states exhibits periodic dependence in time, if the final state is part of a continuum an integral over final states is needed and the result is a transition probability *linear* in time. To such probability function we will be able to associate a transition *rate*. The final answer for the transition rate is given by Fermi's Golden Rule.

We will consider two different cases in full detail:

1. Constant perturbations. In this case the perturbation, called  $V$  turns on at  $t = 0$  but it is otherwise time independent:

$$H = \begin{cases} H^{(0)}, & \text{for } t \leq 0, \\ H^{(0)} + V & \text{for } t > 0. \end{cases} \quad (4.3.1)$$

This situation is relevant for the phenomenon of auto-ionization, where an internal transition in the atom is accompanied by the ejection of an electron.

2. Harmonic perturbations. In this case the time dependence of the perturbation  $\delta H$  is periodic, namely,

$$H(t) = H^{(0)} + \delta H(t), \quad (4.3.2)$$

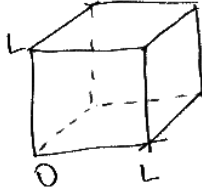
with

$$\delta H(t) = \begin{cases} 0, & \text{for } t \leq 0, \\ 2H' \cos \omega t, & \text{for } t > 0. \end{cases} \quad (4.3.3)$$

Note the factor of two entering the definition of  $\delta H$  in terms of the time independent  $H'$ . This situation is relevant to the interaction of electromagnetic fields with atoms.

Before starting with the analysis of these two cases let us consider the way to deal with continuum states, as the final states in the transition will belong to a continuum. The fact is that we need to be able to count the states in the continuum, so we will replace infinite space by a very large cubic box of side length  $L$  and we will impose periodic boundary conditions on the wavefunctions. The result will be a discrete spectrum where the separation between the states can be made arbitrarily small, thus simulating accurately a continuum in the limit  $L \rightarrow \infty$ . If the states are energetic enough and the potential is short range, momentum eigenstates are a good representation of the continuum.

To count states use a large box, which can be taken to be a cube of side  $L$ :



We call  $L$  a regulator as it allows us to deal with infinite quantities (like the volume of space or the number of continuum states). At the end of our calculations the value of  $L$  must drop out. This is a consistency check. The momentum eigenstates  $\psi(\mathbf{x})$  take the form

$$\psi(\mathbf{x}) = \frac{1}{\sqrt{L^3}} e^{ik_x x} e^{ik_y y} e^{ik_z z}, \quad (4.3.4)$$

with constant  $\mathbf{k} = (k_x, k_y, k_z)$ . It is clear that the states are normalized correctly

$$\int_{\text{box}} |\psi(\mathbf{x})|^2 d^3x = \frac{1}{L^3} \int d^3x = 1. \quad (4.3.5)$$

The  $k$ 's are quantized by the periodicity condition on the wavefunction:

$$\psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L) = \psi(x, y, z). \quad (4.3.6)$$

The quantization gives

$$\begin{aligned} k_x L = 2\pi n_x &\rightarrow L dk_x = 2\pi dn_x, \\ k_y L = 2\pi n_y &\rightarrow L dk_y = 2\pi dn_y, \\ k_z L = 2\pi n_z &\rightarrow L dk_z = 2\pi dn_z. \end{aligned} \quad (4.3.7)$$



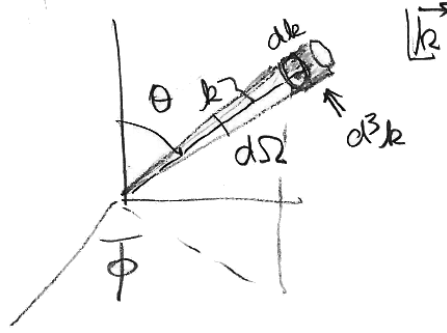
Define  $\Delta N$  as the total number of states within the little cubic volume element  $d^3k$ . It follows from (4.3.7) that we have

$$\Delta N \equiv dn_x dn_y dn_z = \left(\frac{L}{2\pi}\right)^3 d^3k. \quad (4.3.8)$$

Note that  $\Delta N$  only depends on  $d^3k$  and not on  $\mathbf{k}$  itself: the density of states is constant in momentum space.

Now let  $d^3k$  be a volume element determined in spherical coordinates  $k, \theta, \phi$  and by ranges  $dk, d\theta, d\phi$ . Therefore

$$d^3k = k^2 dk \sin \theta d\theta d\phi = k^2 dk d\Omega \quad (4.3.9)$$



We now want to express the density of states as a function of energy. For this we take differentials of the relation between the wavenumber  $k$  and the energy  $E$ :

$$E = \frac{\hbar^2 k^2}{2m} \quad \rightarrow \quad k dk = \frac{m}{\hbar^2} dE. \quad (4.3.10)$$

Back in (4.3.9) we have

$$d^3k = k \frac{m}{\hbar^2} dE d\Omega, \quad (4.3.11)$$

hence

$$\Delta N = \left(\frac{L}{2\pi}\right)^3 k \frac{m}{\hbar^2} d\Omega dE. \quad (4.3.12)$$

We now equate

$$\Delta N = \rho(E) dE, \quad (4.3.13)$$

where  $\rho(E)$  is a *density* of states, more precisely, it is the number of states per unit energy at around energy  $E$  and with momentum pointing within the solid angle  $d\Omega$ . The last two equations determine for us this density:

$$\rho(E) = \frac{L^3}{8\pi^3} \frac{m}{\hbar^2} k d\Omega. \quad (4.3.14)$$

With a very large box, a sum over states can be replaced by an integral as follows

$$\sum_{\text{states}} \dots \rightarrow \int \dots \rho(E) dE \quad (4.3.15)$$

where the dots denote an arbitrary function of the momenta  $\mathbf{k}$  of the states.

### 4.3.1 Constant transitions.

The Hamiltonian, as given in (4.3.1) takes the form

$$H = \begin{cases} H^{(0)} & \text{for } t \leq 0 \\ H^{(0)} + V & \text{for } t > 0. \end{cases} \quad (4.3.16)$$

We thus identify  $\delta H(t) = V$  for  $t \geq 0$ . Recalling the formula (4.2.33) for transition amplitudes to first order in perturbation theory we have

$$c_m^{(1)}(t) = \sum_n \int_0^t dt' e^{i\omega_{mn}t'} \frac{V_{mn}}{i\hbar} c_n(0). \quad (4.3.17)$$

To represent an initial state  $i$  at  $t = 0$  we take  $c_n(0) = \delta_{n,i}$ . For a transition to a final state  $f$  at time  $t_0$  we set  $m = f$  and we have an integral that is easily performed:

$$c_f^{(1)}(t_0) = \frac{1}{i\hbar} \int_0^{t_0} V_{fi} e^{i\omega_{fi}t'} dt' = \frac{V_{fi}}{i\hbar} \left. \frac{e^{i\omega_{fi}t'}}{i\omega_{fi}} \right|_0^{t_0} \quad (4.3.18)$$

Evaluating the limits and simplifying

$$c_f^{(1)}(t_0) = \frac{V_{fi}}{E_f - E_i} \left(1 - e^{i\omega_{fi}t_0}\right) = \frac{V_{fi} e^{i\omega_{fi}t_0/2}}{E_f - E_i} (-2i) \sin\left(\frac{\omega_{fi}t_0}{2}\right). \quad (4.3.19)$$

The transition probability to go from  $i$  at  $t = 0$  to  $f$  at  $t = t_0$  is then  $|c_f^{(1)}(t_0)|^2$  and is therefore

$$P_{f \leftarrow i}(t_0) = |V_{fi}|^2 \frac{4 \sin^2\left(\frac{\omega_{fi}t_0}{2}\right)}{(E_f - E_i)^2}. \quad (4.3.20)$$

This first order result in perturbation theory is expected to be accurate at time  $t_0$  if  $P_{f \leftarrow i}(t_0) \ll 1$ . Certainly a large transition probability at first order could not be trusted and would require examination of higher orders.

To understand the main features of the result for the transition probability we examine how it behaves for different values of the final energy  $E_f$ . If  $E_f \neq E_i$  the transition is said to be energy non-conserving. Of course, energy is conserved overall, as it would be supplied by the perturbation. If  $E_f = E_i$  we have an energy conserving transition. Both are possible and let us consider them in turn.

1.  $E_f \neq E_i$ . In this case the transition probability  $P_{f \leftarrow i}(t_0)$  as a function of  $t_0$  is shown in Figure 4.2. The behavior is oscillatory with frequency  $|\omega_{fi}|$ . If the amplitude of the oscillation is much less than one

$$\frac{4|V_{fi}|^2}{(E_f - E_i)^2} \ll 1 \quad (4.3.21)$$

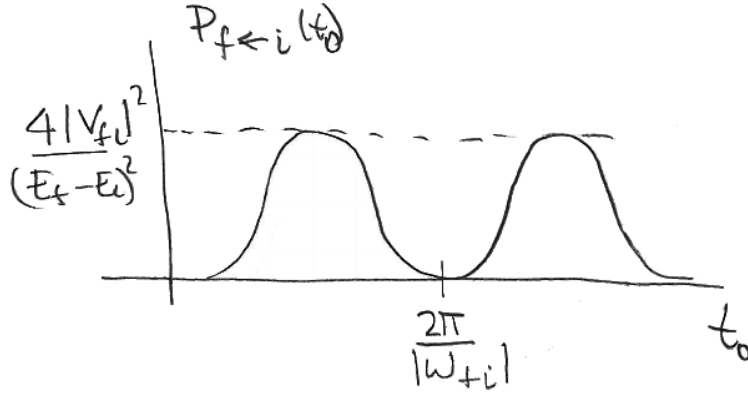


Figure 4.2: The transition probability as a function of time for constant perturbations.

then this first order transition probability  $P_{f \leftarrow i}(t_0)$  is accurate for all times  $t_0$  as it is always small. The amplitude is suppressed as  $|E_f - E_i|$  grows, due to the factor in the denominator. This indicates that the larger the energy ‘violation’ the smaller the probability of transition. This is happening because a perturbation that turns on and then remains constant is not an efficient supply of energy.

2.  $E_f \rightarrow E_i$ . In this limit  $\omega_{fi}$  approaches zero and therefore

$$\sin^2\left(\frac{\omega_{fi} t_0}{2}\right) \simeq \frac{(E_f - E_i)^2}{4\hbar^2} t_0^2. \quad (4.3.22)$$

It follows from (4.3.20) that

$$\lim_{E_f \rightarrow E_i} P_{f \leftarrow i}(t_0) = \frac{|V_{fi}|^2}{\hbar^2} t_0^2. \quad (4.3.23)$$

The probability for an energy-conserving transition grows quadratically in time, and does so without bound! This result, however, can only be trusted for small enough  $t_0$  such that  $P_{f \leftarrow i}(t_0) \ll 1$ .

Note that a quadratic growth of  $P_{f \leftarrow i}$  is also visible in the energy non-conserving  $E_f \neq E_i$  case for very small times  $t_0$ . Indeed, (4.3.20) leads again to  $\lim_{t_0 \rightarrow 0} P_{f \leftarrow i}(t_0) = |V_{fi}|^2 t_0^2 / \hbar^2$ , while  $E_f \neq E_i$ . This behavior can be noted near the origin in Figure 4.2.

Our next step is to integrate the transition probability over the now discretized continuum of final states. Remarkably, upon integration the oscillatory and quadratic behaviors of the transition probability as a function of time will conspire to create a linear behavior!

The sum of transition probabilities over final states is approximated by an integral, as explained in (4.3.15). We thus have

$$\sum_f P_{f \leftarrow i}(t_0) = \int P_{f \leftarrow i}(t_0) \rho(E_f) dE_f = 4 \int |V_{fi}|^2 \frac{\sin^2\left(\frac{\omega_{fi} t_0}{2}\right)}{(E_f - E_i)^2} \rho(E_f) dE_f. \quad (4.3.24)$$

We have noted that  $P_{f \leftarrow i}$  in the above integrand is suppressed as  $|E_f - E_i|$  becomes large. We therefore expect that the bulk of the contribution to the integral will occur for a narrow range  $\Delta E_f$  of  $E_f$  near  $E_i$ . Let us assume now that  $|V_{fi}|^2$  and  $\rho(E_f)$  are slow varying and therefore approximately constant over the narrow interval  $E_f$  (we will re-examine this assumption below). If this is the case we can evaluate them for  $E_f$  set equal to  $E_i$  and take them out of the integrand to find

$$\sum_f P_{f \leftarrow i}(t_0) = \frac{4|V_{fi}|^2}{\hbar^2} \rho(E_f = E_i) \cdot I(t_0), \quad (4.3.25)$$

where the integral  $I(t_0)$  is given by

$$I(t_0) \equiv \int \frac{1}{\omega_{fi}^2} \sin^2 \left( \frac{\omega_{fi} t_0}{2} \right) dE_f = \hbar \int \sin^2 \left( \frac{\omega_{fi} t_0}{2} \right) \frac{d\omega_{fi}}{\omega_{fi}^2}. \quad (4.3.26)$$

As it stands, the integral extends from minus infinity to plus infinity. It is useful to plot the final integrand for  $I(t_0)$  as a function of the integration variable  $\omega_{fi}$ . The result is shown in Figure 4.3 and exhibits a main central lobe followed by symmetrically arranged lobes of decreasing amplitude. The lobes are separated by zeroes occurring for  $\omega_{fi} = 2\pi k/t_0$ , with  $k$  integer. Note that for

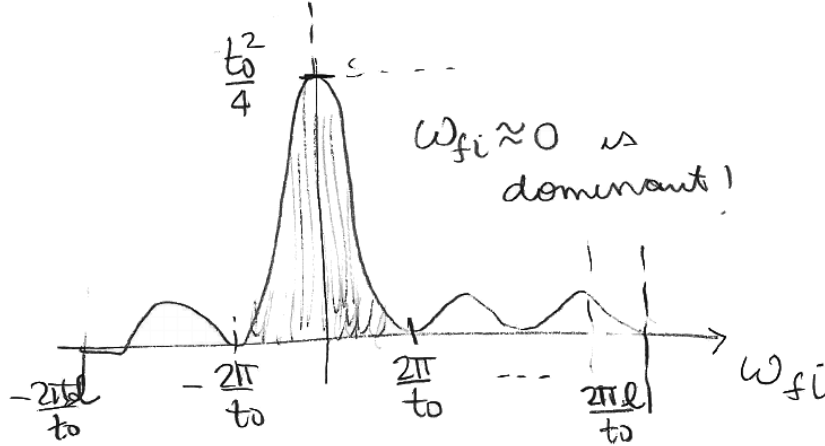


Figure 4.3: Plot of  $\frac{1}{\omega_{fi}^2} \sin^2 \left( \frac{\omega_{fi} t_0}{2} \right)$ , the integrand of  $I$ .

The largest contribution to  $I(t_0)$  arises from the main lobe

$$-\frac{2\pi}{t_0} < \omega_{fi} < \frac{2\pi}{t_0}. \quad (4.3.27)$$

In terms of energies this corresponds to the range

$$E_i - \frac{2\pi\hbar}{t_0} < E_f < E_i + \frac{2\pi\hbar}{t_0}. \quad (4.3.28)$$

We need this range to be a narrow, thus  $t_0$  **must be sufficiently large**. The narrowness is required to justify our taking of the density of states  $\rho(E)$  and the matrix element  $|V_{fi}|^2$  out of the integral. If we want to include more lobes this can be made consistent with a narrow range of energies by making  $t_0$  larger.

The linear dependence of  $I(t_0)$  as a function of  $t_0$  is intuitively appreciated by noticing that the height of the main lobe is proportional to  $t_0^2$  and its width is proportional to  $1/t_0$ . In fact, the linear dependence is a simple mathematical fact made manifest by a change of variables. Letting

$$u = \frac{\omega_{fi}t_0}{2} \implies du = \frac{t_0}{2}d\omega_{fi}, \quad (4.3.29)$$

so that

$$I(t_0) = \frac{2\hbar}{t_0} \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2 \cdot \frac{4}{t_0^2}} = \frac{\hbar t_0}{2} \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2}, \quad (4.3.30)$$

making the linear dependence in  $t_0$  manifest. The remaining integral evaluates to  $\pi$  and we thus get

$$I(t_0) = \frac{\pi}{2} \hbar t_0. \quad (4.3.31)$$

Had restricted the integral to the main lobe, concerned that the density of states and matrix elements would vary over larger ranges, we would have gotten 90% of the total contribution. Including the next two lobes, one to the left and one to the right, brings the result up to 95% of the total contribution. By the time we include ten or more lobes on each side we are getting 99% of the answer. For sufficiently large  $t_0$  is still a narrow range.

Having determined the value of the integral  $I(t_0)$  we can substitute back into our expression for the transition probability (4.3.26). Replacing  $t_0$  by  $t$

$$\sum_k P_{k \leftarrow i}(t) = \frac{4|V_{fi}|^2}{\hbar^2} \rho(E_f) \frac{\pi}{2} \hbar t = \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_f) t. \quad (4.3.32)$$

This holds, as discussed before, for sufficiently large  $t$ . Of course  $t$  cannot be too large as it would make the transition probability large and unreliable. The linear dependence of the transition probability implies we can define a transition rate  $w$ , or probability of transition per unit time, by dividing the transition probability by  $t$ :

$$w \equiv \frac{1}{t} \sum_f P_{f \leftarrow i}(t). \quad (4.3.33)$$

This finally gives us Fermi's golden rule for constant perturbations:

Fermi's golden rule:  $w = \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_f), \quad E_f = E_i.$

(4.3.34)

Not only is the density of states evaluated at the energy  $E_i$ , the matrix element  $V_{fi}$  is also evaluated at the energy  $E_i$  and other observables of the final state, like the momentum. In

this version of the golden rule the integration over final states has been performed. The units are manifestly right:  $|V_{fi}|^2$  has units of energy squared,  $\rho$  has units of one over energy, and with an  $\hbar$  in the denominator the whole expression has units of one over time, as appropriate for a rate. We can also see that the dependence of  $w$  on the size-of-the-box regulator  $L$  disappears: The matrix element

$$V_{fi} = \langle f|V|i\rangle \sim L^{-3/2}, \quad (4.3.35)$$

because the final state wavefunction has such dependence (see (4.3.4)). Then the  $L$  dependence in  $|V_{fi}|^2 \sim L^{-3}$  cancels with the  $L$  dependence of the density of states  $\rho \sim L^3$ , noted in (4.3.14).

Let us summarize the approximations used to derive the golden rule. We have two conditions that must hold simultaneously:

1. We assumed that  $t_0$  is large enough so that the energy range

$$E_i - k \frac{2\pi\hbar}{t_0} < E_f < E_i + k \frac{2\pi\hbar}{t_0}, \quad (4.3.36)$$

with  $k$  some small integer, is narrow enough that  $\rho(E)$  and  $|V_{fi}|^2$  are approximately constant over this range. This allowed us to take them out of the integral simplifying greatly the problem and making a complete evaluation possible.

2. We cannot allow  $t_0$  to be arbitrarily large. As we have

$$\sum_f P_{f \leftarrow i}(t_0) = w t_0, \quad (4.3.37)$$

we must keep  $w t_0 \ll 1$  for our first order calculation to be accurate.

Can the two conditions on  $t_0$  be satisfied? There is no problem if the perturbation can be made small enough: indeed, suppose condition 1 is satisfied for some suitable  $t_0$  but condition 2 is not. Then we can make the perturbation  $V$  smaller making  $w$  small enough that the second condition is satisfied. In practice, in specific problems, one could do the following check. First compute  $w$  assuming the golden rule. Then fix  $t_0$  such that  $w t_0$  is very small, say equal to 0.01. Then check that over the range  $\sim \hbar/t_0$  the density of states and the matrix elements are roughly constant. If this works out the approximation should be very good!

**Helium atom and autoionization.** The helium has two protons ( $Z = 2$ ) and two electrons. Let  $H^{(0)}$  be the Hamiltonian for this system ignoring the the Coulomb repulsion between the electrons:

$$H^{(0)} = \frac{\mathbf{p}_1^2}{2m} - \frac{e^2}{r_1} + \frac{\mathbf{p}_2^2}{2m} - \frac{e^2}{r_2}. \quad (4.3.38)$$

Here the labels 1 and 2 refer to each one of the two electrons. The spectrum of this Hamiltonian consists of *hydrogenic states*, with  $n_1, n_2$  the principal quantum numbers for the electrons. The energies are then

$$E_{n_1, n_2} = -(13.6 \text{ eV})Z^2 \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) = -(54.4 \text{ eV}) \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right). \quad (4.3.39)$$

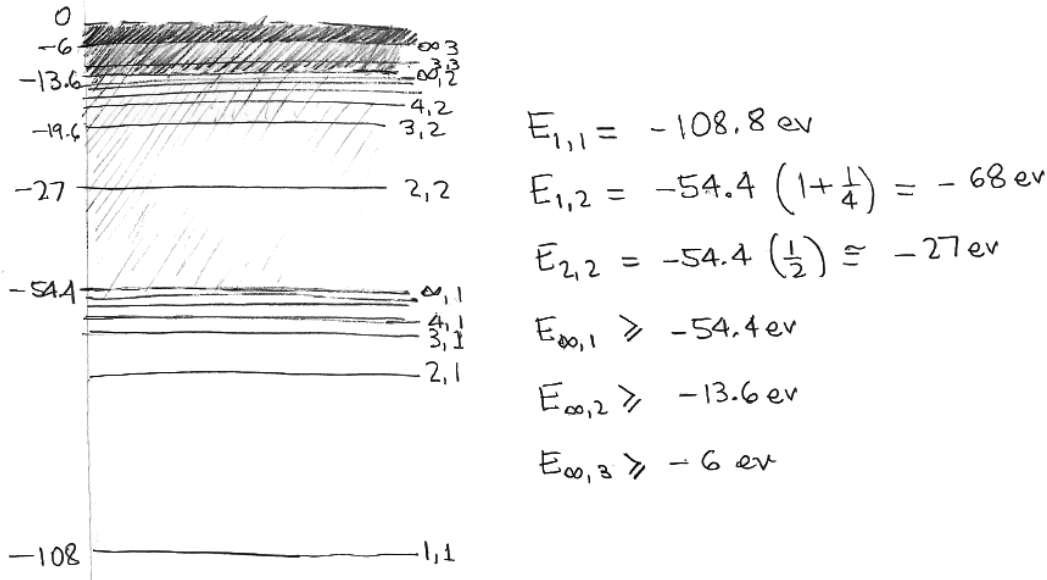


Figure 4.4: Hydrogenic states in helium and continuum states of negative total energy.

For the hydrogen atom we have bound states of negative energy and continuum states of positive energy that can be described to a good approximation as momentum eigenstates of the electron which is no longer bound to the proton. Since we have two electrons in the case of helium, there are continuum states in the spectrum with *negative* energy.

This first happens for  $n_1 = 1$  in the limit as  $n_2 \rightarrow \infty$ . For  $n_1 = 1$  and  $n_2 = \infty$  the second electron is essentially free and contributes no energy. Thus a continuum appears for energy  $E_{1,\infty} = -54.4 \text{ eV}$ . This  $(1S)(\infty)$  continuum extends for all  $E \geq -54.4 \text{ eV}$  as the free electron can have arbitrary positive kinetic energy. The state  $(2S)(\infty)$  is the beginning of a second continuum, also including states of negative energy. In general the state  $(nS)(\infty)$  with  $n \geq 1$  marks the beginning of the  $n$ -th continuum. In each of these continua one electron is still bound and the other is free. A diagram showing some discrete states and a couple of continua is given in Figure 4.4.

Self-ionizing energy-conserving transitions can occur because discrete states can find themselves in the middle of a continuum. The state  $(2S)^2$ , for example, with two electrons on the  $2S$  configuration and with energy  $E_{2,2} = -27 \text{ eV}$  is in the middle of the  $(1S)(\infty)$  continuum. We can view the original  $(2S)^2$  hydrogenic state as a  $t = 0$  eigenstate of  $H^{(0)}$  and treat the Coulomb repulsion as a perturbation. We thus have a total Hamiltonian  $H$

that takes the form

$$H = H^{(0)} + V, \quad V = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (4.3.40)$$

The perturbation  $V$  produces “auto-ionizing” *Auger transitions* to the continuum. We have a transition from a state with energy  $E_{2,2} = -27\text{eV}$  to a state of one bound electron with energy  $-54.4\text{eV}$  and one free electron with kinetic energy of  $27\text{eV}$ . That final state is part of a continuum. Radiative transitions from  $(2S)^2$  to  $1S2S$ , with photo-emission, are in fact a lot less likely than auto-ionizing transitions!

We will not do the quantitative analysis required to determine lifetime of the  $(2S)^2$  state. In general auto-ionization is a process in which an atom or a molecule in an excited state spontaneously emits one of the outer-shell electrons. Auto-ionizing states are in general short lived. *Auger transitions* are auto-ionization processes in which the filling of an inner shell vacancy is accompanied by the emission of an electron. Our example of the  $(2S)^2$  state is an Auger transition. Molecules can have auto ionizing Rydberg states, in which the little energy needed to remove the Rydberg electron is supplied by a vibrational excitation of the molecule.

### 4.3.2 Harmonic Perturbation

It is now time to consider the case when the perturbation is harmonic. We will be able to derive a similar looking Fermi golden rule for the transition rate. The most important difference is that now the transitions are of two types. They involve either absorption of energy or a release of energy. In both cases that energy (absorbed or released) is equal to  $\hbar\omega$  where  $\omega$  is the frequency of the perturbation.

As indicated in (4.3.3) we have

$$H(t) = H^{(0)} + \delta H(t), \quad (4.3.41)$$

where the perturbation  $\delta H(t)$  takes the form

$$\delta H(t) = \begin{cases} 0, & \text{for } t \leq 0, \\ 2H' \cos \omega t, & \text{for } t > 0. \end{cases} \quad (4.3.42)$$

Here  $\omega > 0$  and  $H'$  is some time independent Hamiltonian. The inclusion of an extra factor of two in the relation between  $\delta H$  and  $H'$  is convenient because it results in a golden rule does not have additional factors of two compared to the case of constant transitions.

We again consider transitions from an initial state  $i$  to a final state  $f$ . The transition amplitude this time From (4.2.33)

$$c_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^{t_0} dt' e^{i\omega_{fi}t'} \delta H_{fi}(t'). \quad (4.3.43)$$



Using the explicit form of  $\delta H$  the integral can be done explicitly

$$\begin{aligned}
c_f^{(1)}(t_0) &= \frac{1}{i\hbar} \int_0^{t_0} e^{i\omega_{fi}t'} 2H'_{fi} \cos \omega t' dt' \\
&= \frac{H'_{fi}}{i\hbar} \int_0^{t_0} \left( e^{i(\omega_{fi}+\omega)t'} + e^{i(\omega_{fi}-\omega)t'} \right) dt' \\
&= -\frac{H'_{fi}}{\hbar} \left[ \frac{e^{i(\omega_{fi}+\omega)t_0} - 1}{\omega_{fi} + \omega} + \frac{e^{i(\omega_{fi}-\omega)t_0} - 1}{\omega_{fi} - \omega} \right].
\end{aligned} \tag{4.3.44}$$

Comments:

- The amplitude takes the form of a factor multiplying the sum of two terms, each one a fraction. As  $t_0 \rightarrow 0$  each fraction goes to  $it_0$ . For finite  $t_0$ , which is our case of interest, each numerator is a complex number of bounded absolute value that oscillates in time from zero up to two. In comparing the two terms the relevant one is the one with the smallest denominator.<sup>1</sup>
- The first term is relevant as  $\omega_{fi} + \omega \approx 0$ , that is, when there are states at energy  $E_f = E_i - \hbar\omega$ . This is “stimulated emission”, the source has stimulated a transition in which energy  $\hbar\omega$  is released.
- The second term relevant if  $\omega_{fi} - \omega \approx 0$ , that is, when there are states at energy  $E_f = E_i + \hbar\omega$ . Energy is transferred from the perturbation to the system, and we have a process of “absorption”.

Both cases are of interest. Let us do the calculations for the case of absorption; the answer for the case of spontaneous emission will be completely analogous. We take  $i$  to be a discrete state, possibly bound, and  $f$  to be a state in the continuum at the higher energy  $E_f \approx E_i + \hbar\omega$ . Since  $\omega_{fi} \simeq \omega$ , the second term in the last line of (4.3.44) is much more important than the first. Keeping only the second term we have

$$c_f^{(1)}(t_0) = -\frac{H'_{fi}}{\hbar} \frac{e^{\frac{i}{2}(\omega_{fi}-\omega)t_0}}{\omega_{fi} - \omega} 2i \sin\left(\frac{\omega_{fi} - \omega}{2} t_0\right), \tag{4.3.45}$$

and the transition probability is

$$P_{f \leftarrow i}(t_0) = |c_f^{(1)}(t_0)|^2 = \frac{4|H'_{fi}|^2 \sin^2\left(\frac{\omega_{fi}-\omega}{2} t_0\right)}{\hbar^2 (\omega_{fi} - \omega)^2} \tag{4.3.46}$$

The transition probability is exactly the same as that for constant perturbations (see (4.3.20)) with  $V$  replaced by  $H'$  and  $\omega_{fi}$  replaced by  $\omega_{fi} - \omega$ . The analysis that follows is

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<sup>1</sup>This is like comparing two waves that are being superposed. The one with larger amplitude is more relevant even though at some special times, as it crosses the value of zero, it is smaller than the other wave.

completely analogous to the previous one so we shall be brief. Summing over final states we have

$$\sum_k P_{k \leftarrow i}(t_0) = \int P_{f \leftarrow i} \rho(E_f) dE_f = \int \frac{4|H'_{fi}|^2 \sin^2\left(\frac{\omega_{fi}-\omega}{2}t_0\right)}{\hbar^2 (\omega_{fi}-\omega)^2} \rho(E_f) dE_f. \quad (4.3.47)$$

This time the main contribution comes from the region

$$-\frac{2\pi}{t_0} < \omega_{fi} - \omega < \frac{2\pi}{t_0} \quad (4.3.48)$$

In terms of the final energy this is the band

$$E_i + \hbar\omega - \frac{2\pi\hbar}{t_0} < E_f < E_i + \hbar\omega + \frac{2\pi\hbar}{t_0} \quad (4.3.49)$$

For sufficiently large  $t_0$  this is the narrow band of states illustrated in Figure 4.5. Assume

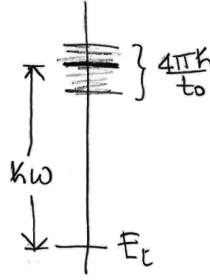


Figure 4.5: In the absorption process we must integrate over a narrow band of states about the final energy  $E_i + \hbar\omega$ .

that over the band  $H'_{fi}$  and the density of states is constant so that we get

$$\sum_k P_{k \leftarrow i}(t_0) = \frac{4}{\hbar} |H'_{fi}|^2 \rho(E_i + \hbar\omega) \int \frac{\sin^2\left(\frac{\omega_{fi}-\omega}{2}t_0\right)}{(\omega_{fi}-\omega)^2} d\omega_{fi}. \quad (4.3.50)$$

Defining

$$u \equiv \frac{1}{2}(\omega_{fi} - \omega) t_0 \quad \rightarrow \quad du = \frac{1}{2} d\omega_{fi} t_0, \quad (4.3.51)$$

the integral in (4.3.50) becomes

$$\int_{-\infty}^{\infty} \frac{\sin^2 u}{\left(\frac{2u}{t_0}\right)^2} \frac{2}{t_0} du = \frac{t_0}{2} \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2} du = \frac{t_0}{2} \pi. \quad (4.3.52)$$

Finally, the transition probability is

$$\sum_k P_{k \leftarrow i}(t_0) = \frac{2\pi}{\hbar} |H'_{fi}|^2 \rho(E_i + \hbar\omega) t_0. \quad (4.3.53)$$

The transition rate  $w$  is finally given by

Fermi's golden rule:  $w = \frac{2\pi}{\hbar} \rho(E_f) |H'_{fi}|^2, \quad E_f = E_i + \hbar\omega.$

(4.3.54)

Here  $H'(t) = 2H' \cos \omega t$ . Equation (4.3.54) is known as Fermi's golden rule for the case of harmonic perturbations. For the case of spontaneous emission the only change required in the above formula is  $E_f = E_i - \hbar\omega$ .

## 4.4 Ionization of hydrogen

We aim to find the ionization rate for hydrogen when hit by the harmonically varying electric field of an electromagnetic wave. We assume the hydrogen atom has its electron on the ground state. In this ionization process a photon ejects the bound electron, which becomes free.

Let us first do a few estimates to understand the validity of the approximations that will be required. If the electromagnetic field has frequency  $\omega$  the incident photons have energy

$$E_\gamma = \hbar\omega. \quad (4.4.1)$$

The energy  $E_e$  and the magnitude  $k$  of the momentum of the ejected electron are given by

$$E_e = \frac{\hbar^2 k^2}{2m} = E_\gamma - R_y, \quad (4.4.2)$$

where the Rydberg  $R_y$  is the magnitude of the energy of the ground state:

$$2R_y = \frac{e^2}{a_0} = \frac{\hbar^2}{ma_0^2} = \alpha \frac{\hbar c}{a_0}, \quad R_y \simeq 13.6 \text{ eV}. \quad (4.4.3)$$

### Inequalities

1. Any electromagnetic wave has spatial dependence. We can ignore the spatial dependence of the wave if the wavelength  $\lambda$  of the photon is much bigger than the Bohr radius  $a_0$ :

$$\frac{\lambda}{a_0} \gg 1. \quad (4.4.4)$$

Such a condition puts an *upper* bound on the photon energy, since the more energetic photon the smaller its wavelength. To bound the energy we first write

$$\lambda = \frac{2\pi}{k_\gamma} = \frac{2\pi c}{\omega} = \frac{2\pi \hbar c}{\hbar\omega}, \quad (4.4.5)$$

and then find

$$\frac{\lambda}{a_0} = \frac{2\pi \hbar c}{\hbar\omega a_0} = \frac{4\pi R_y}{\alpha \hbar\omega} \simeq 1722 \frac{R_y}{\hbar\omega} \quad (4.4.6)$$

The inequality (4.4.4) then gives

$$\hbar\omega \ll 1722 R_y \simeq 23 \text{ keV} \quad (4.4.7)$$

2. For final states we would like to use free particle momentum eigenstates. This requires the ejected electron to be energetic enough not to be much effected by the Coulomb field. As a result, the photon to be energetic enough, and this constraint provides a *lower* bound for its energy. We have

$$E_e = E_\gamma - R_y \gg R_y \quad \rightarrow \quad \hbar\omega \gg R_y. \quad (4.4.8)$$

The two inequalities above imply

$$R_y \ll \hbar\omega \ll 1722 R_y. \quad (4.4.9)$$

If consider that  $1 \ll 10$  we could take

$$140\text{eV} \leq \hbar\omega \leq 2.3 \text{ keV}. \quad (4.4.10)$$

Note that even for the upper limit the electron is non relativistic:  $2.3 \text{ keV} \ll m_e c^2 \simeq 511\text{keV}$ .

**Exercise:** Determine  $ka_0$  in terms of  $\hbar\omega$  and  $R_y$ .

*Solution:*

$$\frac{\hbar^2 k^2}{2m} = \hbar\omega - R_y = R_y \left( \frac{\hbar\omega}{R_y} - 1 \right) = \frac{\hbar^2}{2ma_0^2} \left( \frac{\hbar\omega}{R_y} - 1 \right) \quad (4.4.11)$$

$$k^2 a_0^2 = \frac{\hbar\omega}{R_y} - 1 \quad \rightarrow \quad ka_0 = \sqrt{\frac{\hbar\omega}{R_y} - 1}. \quad (4.4.12)$$

This is the desired result. In the range of (4.4.10) we have

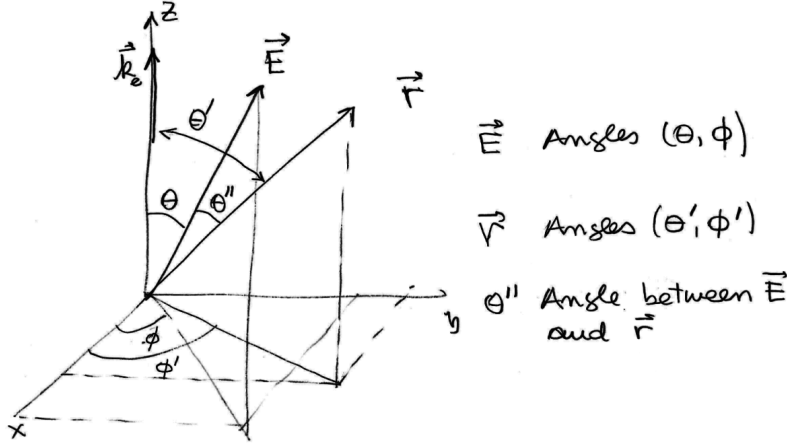
$$3 \leq ka_0 \leq 13. \quad (4.4.13)$$

**Calculating the matrix element.** Our perturbation Hamiltonian is

$$\delta H = -e\Phi, \quad (4.4.14)$$

where  $\Phi$  is the electric scalar potential. Let the electric field at the atom be polarized in the  $\hat{z}$  direction

$$\mathbf{E}(t) = E(t)\hat{z} = 2E_0 \cos \omega t \hat{z} \quad (4.4.15)$$



The associated scalar potential is

$$\Phi = -E(t)z, \quad (4.4.16)$$

and therefore

$$\delta H = eE(t)z = eE(t)r \cos \theta = 2 \underbrace{eE_0 r \cos \theta}_{H'} \cos \omega t \equiv 2H' \cos \omega t \quad (4.4.17)$$

We have thus identified, in our notation,

$$H' = eE_0 r \cos \theta. \quad (4.4.18)$$

We want to compute the matrix element between an initial state  $|i\rangle$  that is the ground state of hydrogen, and a final state  $|f\rangle$  which is an electron plane wave with momentum  $\mathbf{k}_e$ . The associated wavefunctions are

$$\text{Final state:} \quad u_{\mathbf{k}}(x) = \frac{1}{L^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (4.4.19)$$

$$\text{Initial state:} \quad \psi_0(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}} \quad (4.4.20)$$

The only physical angle here is that between the ejected electron momentum  $\mathbf{k}_e$  and the electric field polarization  $\mathbf{E}$ . We expect electron to be ejected maximally along  $\mathbf{E}$ . This suggests rearranging the axes to have the electron momentum along the  $z$  axis and letting  $\theta$  be the angle between the electron momentum and the electric field. The integration variable  $\mathbf{r}$  will have angles  $\theta', \phi'$ , and the angle between the electric field and  $\mathbf{r}$  is now called  $\theta''$  as shown in the figure, so that  $H' = eE_0 r \cos \theta''$ :

$$\begin{aligned} \langle f|H'|i\rangle &= \int d^3x \frac{1}{L^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}} eE_0 r \cos \theta'' \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}} \\ &= \frac{eE_0}{\sqrt{\pi a_0^3} L^3} \int r^2 dr \sin \theta' d\theta' d\phi' e^{ikr \cos \theta'} r \cos \theta'' e^{-\frac{r}{a_0}} \end{aligned} \quad (4.4.21)$$

The main complication with doing the integral is the factor  $\cos \theta''$ . The dot product of unit vectors along  $\mathbf{E}$  and  $\mathbf{n}$  is  $\cos \theta''$ :

$$\begin{aligned}\cos \theta'' &= (\sin \theta \cos \phi)(\sin \theta' \cos \phi') + (\sin \theta \sin \phi)(\sin \theta' \sin \phi') + \cos \theta \cos \theta' \\ &= \sin \theta \sin \theta' \cos(\phi - \phi') + \cos \theta \cos \theta'\end{aligned}\quad (4.4.22)$$

Since the following integral vanishes

$$\int d\phi' \cos(\phi - \phi') = 0 \quad (4.4.23)$$

the first term in the expression for  $\cos \theta''$  will vanish upon  $\phi'$  integration. We therefore can replace  $\cos \theta'' \rightarrow \cos \theta \cos \theta'$  to find

$$\begin{aligned}\langle f|H'|i\rangle &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}} \int r^3 dr \sin \theta' d\theta' d\phi' e^{ikr \cos \theta'} \cos \theta \cos \theta' e^{-\frac{r}{a_0}} \\ &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}} (\cos \theta)(2\pi) \int r^3 dr e^{-\frac{r}{a_0}} \int_{-1}^1 d(\cos \theta') \cos \theta' e^{ikr \cos \theta'}\end{aligned}\quad (4.4.24)$$

Now let  $r = a_0 u$  and do the radial integration:

$$\begin{aligned}\langle f|H'|i\rangle &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}} 2\pi \cos \theta a_0^4 \int_{-1}^1 d(\cos \theta') \cos \theta' \int u^3 du e^{-u(1+ika_0 \cos \theta')} \\ &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}} 2\pi \cos \theta a_0^4 \int_{-1}^1 d(\cos \theta') \cos \theta' \frac{3!}{(1 + ika_0 \cos \theta')^4}.\end{aligned}\quad (4.4.25)$$

Writing  $x = \cos \theta'$  the angular integral is not complicated:

$$\begin{aligned}\langle f|H'|i\rangle &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}} 2\pi \cos \theta a_0^4 \frac{3!}{(ika_0)^4} \int_{-1}^1 \frac{x}{\left(x + \frac{1}{ika_0}\right)^4} dx \\ &= \frac{eE_0}{\sqrt{\pi a_0^3 L^3}} 2\pi \cos \theta a_0^4 \frac{3!}{(ika_0)^4} \frac{8 \left(\frac{1}{ika_0}\right)}{3 \left(1 + \frac{1}{k^2 a_0^2}\right)^3} \\ &= -i \frac{32\pi eE_0 a_0}{\sqrt{\pi a_0^3 L^3}} \frac{ka_0^4}{(1 + k^2 a_0^2)^3} \cos \theta\end{aligned}\quad (4.4.26)$$

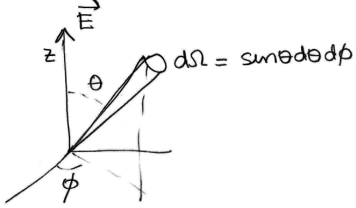
Hence, with a little rearrangement

$$\boxed{\langle f|H'|i\rangle = -i32\sqrt{\pi} (eE_0 a_0) \frac{ka_0^4}{\sqrt{a_0^3 L^3}} \frac{1}{(1 + k^2 a_0^2)^3} \cos \theta.} \quad (4.4.27)$$

The above matrix element has the units of  $(eE_0 a)$ , which is energy. This is as expected. Squaring we find

$$|H'_{fi}|^2 = 1024 \pi (eE_0 a)^2 \frac{k^2 a_0^5}{L^3} \frac{\cos^2 \theta}{(1 + k^2 a_0^2)^6} \quad (4.4.28)$$

At this point, with  $\theta$  the angle between  $\mathbf{k}_e$  and  $\mathbf{E}$ , it is more convenient to align  $\mathbf{E}$  along the z-axis and let  $\mathbf{k}_e$  be defined by the polar angles  $\theta, \phi$ . The density of states was given in (4.3.14)

$$\rho(E_e) = \frac{L^3 m}{8\pi^3 \hbar^2} k d\Omega$$


$$(4.4.29)$$

so that using Fermi's Golden rule, the rate  $dw$  to go into final states in the solid angle  $d\Omega$  is

$$\begin{aligned} dw &= \frac{2\pi}{\hbar} \rho(E_e) |H'_{fi}|^2 \\ &= \frac{2\pi}{\hbar} \frac{L^3 m}{8\pi^3 \hbar^2} k d\Omega 1024\pi (eE_0 a_0)^2 \frac{k^2 a_0^5}{L^3} \frac{\cos^2 \theta}{(1 + k^2 a_0^2)^6}. \end{aligned} \quad (4.4.30)$$

It follows that

$$\boxed{\frac{dw}{d\Omega} = \frac{256}{\pi} \frac{m a_0^2}{\hbar^2} \frac{(eE_0 a_0)^2}{\hbar} \frac{k^3 a_0^3}{(1 + k^2 a_0^2)^6} \cos^2 \theta.} \quad (4.4.31)$$

$\frac{dw}{d\Omega}$  is the probability of ionization per unit time and per unit solid angle. All the ejected electrons will have the same momentum  $\hbar k$ . Note that the units have worked out:  $w \sim \frac{[E]^2}{\hbar} \cdot \frac{1}{[E]} \sim \frac{1}{T}$  as expected. In here  $2E_0$  is the peak amplitude of the electric field in the wave. The  $\cos^2 \theta$  implies that the electron tends to be ejected in the direction of the electric field.

The total ionization probability per unit time is obtained by integration over solid angle. Using

$$\int \cos^2 \theta d\Omega = \frac{1}{3} 4\pi, \quad (4.4.32)$$

and recalling that  $\frac{\hbar^2}{m a_0^2} = 2R_y$

$$w = \int d\Omega \frac{dw}{d\Omega} = \frac{512}{3} \frac{(eE_0 a_0)^2}{\hbar R_y} \frac{k^3 a_0^3}{(1 + k^2 a_0^2)^6}. \quad (4.4.33)$$

For the window of validity (4.4.13) we have  $9 \leq (ka_0)^2 \leq 169$ , and we neglect the "one" in the denominator to get

$$w = \frac{512}{3} \frac{(eE_0 a_0)^2}{\hbar R_y} \frac{1}{(ka_0)^9}. \quad (4.4.34)$$

This is our final answer. For numerical calculations it is useful to note the atomic units in which the answer takes the form

$$w = \frac{256}{3} \left( \frac{E_p}{E_*} \right)^2 \frac{1}{t_*} \frac{1}{(ka_0)^9}. \quad (4.4.35)$$

Here  $E_p = 2E_0$  is the peak amplitude of the electric field. Moreover, the atomic electric field  $E_*$  and the atomic time  $t_*$  are given by

$$\begin{aligned} E_* &= \frac{2R_y}{ea_0} = \frac{e}{a_0^2} = 5.14 \times 10^{11} \text{V/m} \\ t_* &= \frac{a_0}{\alpha c} = 2.42 \times 10^{-17} \text{ sec.} \end{aligned} \quad (4.4.36)$$

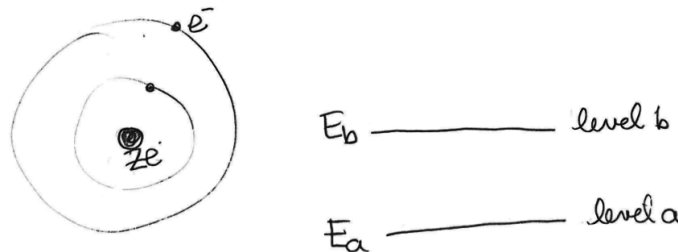
Note that  $E_*$  is the electric field of a proton at a distance  $a_0$  while  $t_*$  is the time it takes the electron to travel a distance  $a_0$  at the velocity  $\alpha c$  in the ground state. A laser intensity of  $3.55 \times 10^{16} \text{W/cm}^2$  has an peak electric field of magnitude  $E_*$ .

## 4.5 Light and atoms

### 4.5.1 Absorption and stimulated emission

The physical problem we are trying to solve consists of a collection of atoms with two possible energy levels interacting with light at a temperature  $T$ . We want to understand the processes of absorption and emission of radiation and how they can produce thermal equilibrium.

Let us first consider a single atom and the possible processes. Consider two possible levels of an electron in an atom



Define

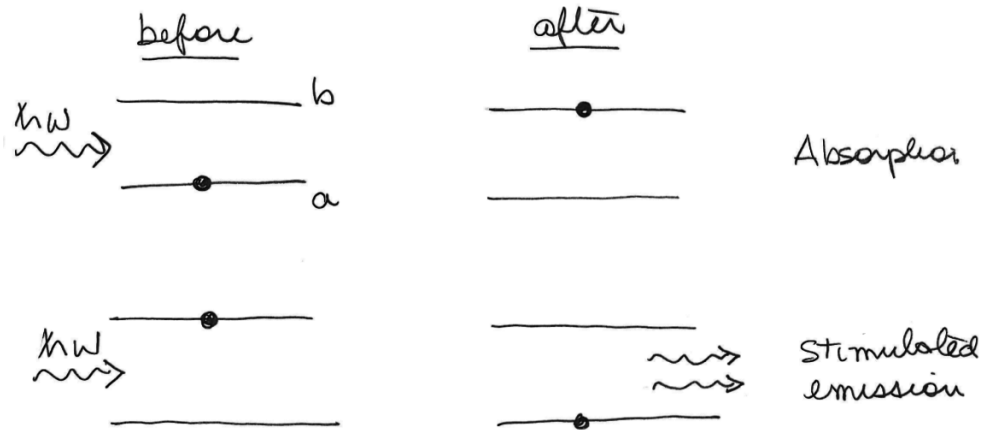
$$\omega_{ab} \equiv \frac{E_b - E_a}{\hbar}.$$

Imagine now shining light into the atom at a frequency  $\omega_{ab}$ . There are two possibilities depending on the initial state of the atom:

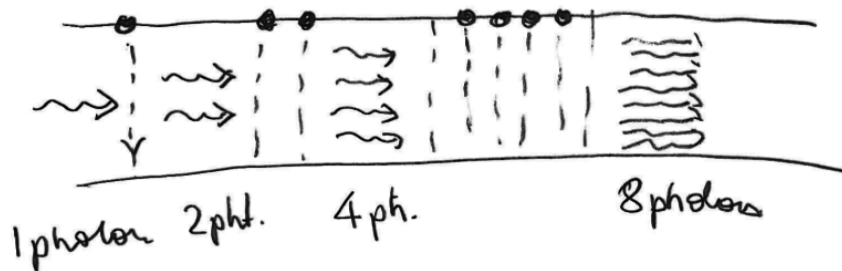
- (i) Electron initially in  $|a\rangle$ : there will be an *absorption rate* at which a photon is absorbed and the electron goes from  $|a\rangle \rightarrow |b\rangle$ .
- (ii) Electron initially in  $|b\rangle$ : there will be a *stimulated emission rate* at which the photon field stimulates an electronic transition  $|b\rangle \rightarrow |a\rangle$  with the release of an additional photon.



These processes are illustrated in the figure below:

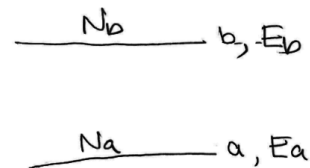


A LASER, *Light Amplification by Stimulated Emission of Radiation*, works by having population inversion, namely most of the atoms are in the excited energy level. Then any small number of photons can trigger larger and larger numbers of stimulated emission processes!



### 4.5.2 Einstein's Argument

Atoms in states  $a$  or  $b$  with  $E_b > E_a$ , with populations  $N_a$  and  $N_b$  respectively. The atoms are in equilibrium with a bath of photons all at temperature  $T$ . Einstein discovered a number of relations from the condition of equilibrium.



Fact 1: Equilibrium values for populations:

$$\dot{N}_a = \dot{N}_b = 0 \tag{4.5.1}$$

Fact 2: Equilibrium populations governed by thermal distribution

$$\frac{N_a}{N_b} = \frac{e^{-\beta E_b}}{e^{-\beta E_a}} = e^{-\beta \hbar \omega_{ab}}, \quad \beta \equiv \frac{1}{k_b T} \tag{4.5.2}$$

Fact 3: For a thermal blackbody, the energy  $U(\omega)d\omega$  per unit volume in the frequency range  $d\omega$  is known to be

$$U(\omega)d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{e^{\beta\hbar\omega} - 1} \quad (4.5.3)$$

Process		Rate
Absorption:	$ a\rangle \rightarrow  b\rangle$ photon absorbed	$B_{ab}U(\omega_{ba})N_a$
Stimulated emission:	$ b\rangle \rightarrow  a\rangle$ photon released	$B_{ba}U(\omega_{ba})N_b$

In the table above we have indicated the two obvious processes: absorption and stimulated emission. The rate indicated is the number of transitions per unit time. For absorption, this rate is proportional to the number  $N_a$  of atoms in the ground state, capable of absorbing a photon, times  $U(\omega_{ab})$  which captures the information about the number of photons available, times a  $B$  coefficient  $B_{ab}$  that we want to determine. For stimulated emission, the rate is proportional to the number  $N_b$  of atoms in the excited state, thus capable of emitting a photon, times  $U(\omega_{ab})$  times a  $B$  coefficient  $B_{ba}$ . The inclusion of  $U(\omega_{ab})$  reflects the “stimulated” character of the transition.

Can we make this work, that is, can we achieve equilibrium? We will see that we *cannot*. With the two processes above, the rate of change of  $N_b$  is

$$\dot{N}_b = \text{rate absorption} - \text{rate stimulated emission} \quad (4.5.4)$$

At equilibrium  $\dot{N}_b = 0$ , hence

$$\begin{aligned} 0 = \dot{N}_b &= B_{ab}U(\omega_{ba})N_a - B_{ba}U(\omega_{ba})N_b \\ &= (B_{ab}N_a - B_{ba}N_b)U(\omega_{ba}) \\ 0 &= N_a \left( B_{ab} - B_{ba}e^{-\beta\hbar\omega_{ba}} \right) U(\omega_{ba}) \end{aligned} \quad (4.5.5)$$

This is a strange result: in order to have equilibrium we need  $B_{ab} - B_{ba}e^{-\beta\hbar\omega_{ba}} = 0$ . The  $B$  coefficients, however, depend on the electronic configurations in the atom and *not* on the temperature  $T$ . Thus this cancellation is not possible for arbitrary temperature. We also note that the photon energy density does not feature in the equilibrium condition. In conclusion, equilibrium is not possible.

What are we missing? Another process: *spontaneous emission!!*, an emission rate that does not depend on the thermal photons. The rate is proportional to the number of atoms  $N_b$  in the excited state, with a coefficient of proportionality called  $A$ :

Process		Rate
Spontaneous emission:	$ b\rangle \rightarrow  a\rangle$ photon released	$AN_b$

Reconsider now the equilibrium condition with this extra contribution to  $\dot{N}_b$ :

$$\begin{aligned}
 0 &= \dot{N}_b = B_{ab}U(\omega_{ba})N_a - B_{ba}U(\omega_{ba})N_b - AN_b \\
 \implies A &= \left( B_{ab} \frac{N_a}{N_b} - B_{ba} \right) U(\omega_{ba}) \\
 \implies U(\omega_{ba}) &= \frac{A}{B_{ab}} \frac{1}{e^{\beta\hbar\omega_{ba}} - \frac{B_{ba}}{B_{ab}}}
 \end{aligned} \tag{4.5.6}$$

The equilibrium condition indeed gives some important constraint on  $U(\omega_{ab})$ . But from Eq. (4.5.3) we know

$$U(\omega_{ba}) = \frac{\hbar\omega_{ba}^3}{\pi^2c^3} \frac{1}{e^{\beta\hbar\omega_{ba}} - 1} \tag{4.5.7}$$

Hence comparing the two equations we get

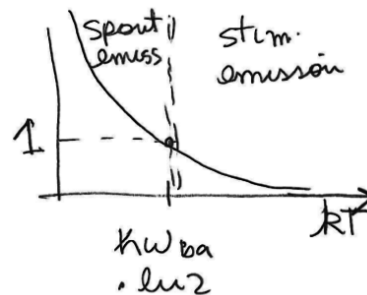
$$B_{ab} = B_{ba} \quad \text{and} \quad \frac{A}{B_{ab}} = \frac{\hbar\omega_{ba}^3}{\pi^2c^3} \tag{4.5.8}$$

As we'll see, we'll be able to calculate  $B_{ab}$ , but  $A$  is harder. Happily, thanks to (4.5.8), we can obtain  $A$  from  $B_{ab}$ .

Spontaneous emission does not care about  $U(\omega_{ba})$ ; the photons flying around. At a deep level one can think of spontaneous emission as stimulated emission due to vacuum fluctuation of the EM field.

For a given atomic transition expect stimulated emission rate to dominate at higher temperature, the there are more photons around. Spontaneous emission should dominate at very low temperature. Indeed from (4.5.6)

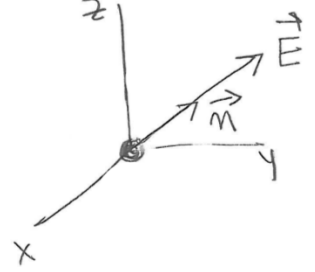
$$\frac{A}{B_{ab}U(\omega_{ba})} = \exp\left(\frac{\hbar\omega_{ba}}{k_bT}\right) - 1$$



### 4.5.3 Atom/light interaction

Focus on  $\vec{E}$  field. Effects of  $\vec{B}$  are weaker by  $\mathcal{O}(\frac{v}{c}) \sim \alpha$ . For optical frequencies  $\lambda \sim 4000 - 8000 \text{ \AA}$  and since  $a_0 \simeq 0.5 \text{ \AA}$ , we can ignore the spatial dependence of the field (even for ionization frequencies  $\frac{\lambda}{a_0} \sim 1700$ )  
Electric field at the atom

$$\mathbf{E}(t) = E(t)\mathbf{n} = 2E_0 \cos(\omega t)\mathbf{n}$$



where  $\mathbf{n}$  is the direction of the field.

$$\Phi(\mathbf{r}, t) = -\mathbf{r} \cdot \mathbf{E}(t), \quad \nabla\Phi = -\mathbf{E} \quad (4.5.9)$$

as expected. The perturbation is therefore

$$\delta H = +q\Phi(\mathbf{r}) = -q\mathbf{r} \cdot \mathbf{E}(t) \quad (4.5.10)$$

By defining the dipole moment  $\mathbf{d}$  as  $\mathbf{d} \equiv q\mathbf{r}$ , we can rewrite the perturbation as

$$\delta H = -\mathbf{d} \cdot \mathbf{E}(t) = -\mathbf{d} \cdot \mathbf{n} 2E_0 \cos(\omega t) = 2(-\mathbf{d} \cdot \mathbf{n} E_0) \cos(\omega t). \quad (4.5.11)$$

Since we defined  $\delta H = 2H' \cos \omega t$  we can read

$$H' = -\mathbf{d} \cdot \mathbf{n} E_0. \quad (4.5.12)$$

Recall that to first order in perturbation theory  $P_{b \leftarrow a}(t) = P_{a \leftarrow b}(t)$  so let's consider just  $P_{a \leftarrow b}(t)$ , the stimulated emission process, from (4.3.46)

$$P_{a \leftarrow b}(t) = \frac{4|H'_{ab}|^2 \sin^2\left(\frac{\omega_{ba} - \omega}{2}t\right)}{\hbar^2 (\omega_{ba} - \omega)^2} = \frac{4E_0^2 |(\mathbf{d} \cdot \mathbf{n})_{ab}|^2 \sin^2\left(\frac{\omega_{ba} - \omega}{2}t\right)}{\hbar^2 (\omega_{ba} - \omega)^2} \quad (4.5.13)$$


Now think in terms of energy. The energy density  $u_E$  in the electric field  $E(t) = 2E_0 \cos(\omega t)\mathbf{n}$  is

$$u_E = \frac{|E(t)|^2}{8\pi} = \frac{4E_0^2}{8\pi} \cos^2 \omega t \implies \langle u_E \rangle_{\text{time}} = \frac{4E_0^2}{8\pi} \cdot \frac{1}{2} = \frac{E_0^2}{4\pi}. \quad (4.5.14)$$

In a wave the electric and magnetic energy are the same and therefore

$$\langle u \rangle_{\text{time}} = 2\langle u_E \rangle_{\text{time}} = \frac{E_0^2}{2\pi} \implies E_0^2 = 2\pi \langle u \rangle \quad (4.5.15)$$

The superposition of light is incoherent, so we will add probabilities of transition due to each component of light. For this we must turn a sum of electric field intensities into an integral.



$$\sum_i E_0^2(\omega_i) = 2\pi \int U(\omega) d\omega \quad (4.5.16)$$

where  $U(\omega)$  is the energy density per unit frequency. In this way the transition rate in terms of energy reads

$$\begin{aligned} P_{a \leftarrow b}(t) &= \frac{|\mathbf{d} \cdot \mathbf{n}|_{ab}^2}{\hbar^2} 2\pi \int U(\omega) d\omega \frac{\sin^2\left(\frac{\omega_{ba} - \omega}{2} t\right)}{(\omega_{ba} - \omega)^2} \\ &= \frac{|\mathbf{d} \cdot \mathbf{n}|_{ab}^2}{\hbar^2} (2\pi) U(\omega_{ab}) \int d\omega \frac{\sin^2\left(\frac{\omega_{ba} - \omega}{2} t\right)}{(\omega_{ba} - \omega)^2} \end{aligned} \quad (4.5.17)$$

As usual, take  $x \equiv \left(\frac{\omega_{ba} - \omega}{2} t\right) \implies d\omega = 2\frac{dx}{t}$ , so that (4.5.17) is

$$\frac{2}{t} \cdot t^2 \int \frac{\sin^2 x}{x^2} dx = 2t\pi \quad (4.5.18)$$

$$\boxed{R_{a \leftarrow b} = \frac{4\pi^2}{\hbar^2} |\mathbf{d} \cdot \mathbf{n}|_{ab}^2 U(\omega_{ba})} \quad (4.5.19)$$

So far we have two vectors:  $\mathbf{d}$  which depends on the atom geometry and  $\mathbf{n}$  which is the direction of the electric field. Since light comes in all possible polarization, this amounts to averaging over all possible directions of  $\mathbf{n}$

$$\langle |\mathbf{d}_{ab} \cdot \mathbf{n}|^2 \rangle = \langle \left| \sum_i d_{ab}^i n_i \right|^2 \rangle = \left\langle \left( \sum_i d_{ab}^i n_i \right)^* \left( \sum_j d_{ab}^j n_j \right) \right\rangle = \sum_{i,j} (d_{ab}^i)^* (d_{ab}^j) \langle n_i n_j \rangle \quad (4.5.20)$$

Expect

$$\langle n_x n_x \rangle = \langle n_y n_y \rangle = \langle n_z n_z \rangle \quad (4.5.21)$$

Since

$$\left\langle \sum_i n_i n_i \right\rangle = \langle n^2 \rangle = 1 \quad (4.5.22)$$

then

$$\langle n_i n_j \rangle = \frac{1}{3} \delta_{ij} \quad (4.5.23)$$

$$\langle |\mathbf{d}_{ab} \cdot \mathbf{n}|^2 \rangle = \frac{1}{3} \mathbf{d}_{ab}^* \cdot \mathbf{d}_{ab} \equiv \frac{1}{3} |\mathbf{d}_{ab}|^2 \quad (4.5.24)$$

This is the magnitude of a complex vector!

$$R_{a \leftarrow b} = \frac{4\pi^2}{3\hbar^2} |\mathbf{d}_{ab}|^2 U(\omega_{ba}) \quad (4.5.25)$$

This is the transition probability per unit time for a single atom

$$B_{ab} = \frac{4\pi^2}{3\hbar^2} |\mathbf{d}_{ab}|^2 \quad (4.5.26)$$

thus recalling (4.5.8)

$$A = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} B_{ab} = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} \frac{4\pi^2}{3\hbar^2} |\mathbf{d}_{ab}|^2 \quad (4.5.27)$$

hence we have that  $A$ , the transition probability per unit time for an atom to go from  $|b\rangle \rightarrow |a\rangle$ , is

$$A = \frac{4}{3} \frac{\omega_{ba}^3}{\hbar c^3} |\mathbf{d}_{ab}|^2. \quad (4.5.28)$$

The lifetime for the state is  $\tau = \frac{1}{A}$ . The number  $N$  of particles decays exponentially in time

$$\frac{dN}{dt} = -AN \implies N(t) = e^{-At} = N_0 e^{-t/\tau} \quad (4.5.29)$$

If there are various decay possibilities  $A_1, A_2, \dots$ , the transition rates add

$$A_{\text{tot.}} = A_1 + A_2 + \dots \quad \text{and} \quad \tau = \frac{1}{A_{\text{tot.}}} \quad (4.5.30)$$

#### 4.5.4 Selection rules

(to be covered in recitation) Given two states  $|n\ell m\rangle$  and  $|n'\ell'm'\rangle$ , when  $\langle n\ell m | \mathbf{r} | n'\ell'm'\rangle \neq 0$ ? One can learn that

$$\langle n\ell m | z | n'\ell'm'\rangle = 0 \quad \text{for } m' \neq m \quad (4.5.31)$$

$$\langle n\ell m | x | n'\ell'm'\rangle = \langle n\ell m | y | n'\ell'm'\rangle = 0 \quad \text{for } m' \neq m \pm 1 \quad (4.5.32)$$

Hence no transition unless

$$\Delta m \equiv m' - m = 0, \pm 1 \quad (4.5.33)$$

Additionally

$$\Delta \ell \equiv \ell' - \ell = \pm 1 \quad (4.5.34)$$

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