1 Time-dependent perturbations

1.1 Transitions

In this section: What we mean by transition and by transition probability; the importance of time-dependent perturbation theory in Quantum Physics.

Suppose that we expose an atom of hydrogen to a time-dependent electric field, the field being turned on at some time t_0 and turned off at some later time t_1. Suppose also that the atom was in its ground state before the field was turned on, and that one checks whether the atom is, say, in the $2p_{m=0}$ state after the field is turned off. If the atom is found to be in the $2p_{m=0}$ state at a time $t > t_1$, then one says that the atom has made a transition from the ground state to the $2p_{m=0}$ state. The probability that upon measurement the atom is found to be in the $2p_{m=0}$ state is the corresponding transition probability. Calculating transition probabilities exactly is a problem of formidable difficulty in most cases of practical interest. Time-dependent perturbation theory offers a relatively simple way of calculating these probabilities approximately. (Approximately, but in many cases accurately enough.)

Before continuing, let us revisit the above paragraph point by point and clarify what we are talking about.

- Atom of hydrogen: As the atom is electrically neutral, the position of its centre of mass is not changed by the electric field. We only need to consider the effect of the field on the relative motion of the electron and the proton.

- Electric field: A time-dependent electric field is normally associated with a magnetic field. Here we ignore the latter. The action of the electric field on the atom can then be taken into account by adding a potential energy term $e\boldsymbol{\mathcal{E}}(\mathbf{r}, t) \cdot \mathbf{r}$ to the Hamiltonian of the field-free atom, H_0. The latter is given by Eq. (102) of the QM Primer, namely

$$H_0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}. \tag{1.1}$$

  Recall that $\mathbf{r}$ is the position vector of the electron respective to the proton, e is the charge of the electron in absolute value ($e > 0$), μ is the reduced mass of the system ($\mu \approx m$, the mass of the electron) and ϵ_0 is the permittivity of free space. Here $\boldsymbol{\mathcal{E}}(\mathbf{r}, t)$ is the electric field at position $\mathbf{r}$ and time t (the electric field the atom is exposed to, not the electric field of the proton or the electron).

- The initial state of the atom: "The atom was in its ground state before the field was turned on" means that at times $t < t_0$ the atom was in the

state described by the time-dependent wave function

$$\Psi_{100}(\mathbf{r}, t) \equiv \psi_{100}(\mathbf{r}) \exp(-iE_1 t/\hbar), \qquad (1.2)$$

where E_1 is the ground state energy and $\psi_{100}(\mathbf{r})$ is the corresponding eigen-function of the field free Hamiltonian (see Section 5.1 of the QM Primer). As noted above, the complete Hamiltonian of the problem, H, is the sum of the field free Hamiltonian, H_0, and the potential energy term $e\boldsymbol{\mathcal{E}}(\mathbf{r}, t) \cdot \mathbf{r}$:

$$H = H_0 + e\boldsymbol{\mathcal{E}}(\mathbf{r}, t) \cdot \mathbf{r}, \qquad (1.3)$$

where H_0 is given by Eq. (1.1). Since $H = H_0$ before the field is turned on, $\Psi_{100}(\mathbf{r}, t)$ is an eigenfunction of H for as long as the field has not started acting. Hence, once in that state, the atom remains in that state until $t = t_0$ (see Section 3.11 of the QM Primer).

- The $2\mathrm{p}_{m=0}$ state: I used the spectroscopic notation mentioned in Section 5.1 of the QM primer. The $2\mathrm{p}_{m=0}$ state is the state with principal quantum number $n = 2$, the orbital angular momentum quantum number $l = 1$ and the magnetic quantum number $m = 0$.

- The final state of the atom: Once the field is on, H differs from H_0, and therefore the wave function $\Psi_{100}(\mathbf{r}, t)$ can no longer be a solution of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi(\mathbf{r}, t) \qquad (1.4)$$

for $t_0 < t < t_1$. Instead, the state of the atom evolves in a complicated way between t_0 and t_1, and is no longer a well defined eigenstate of H_0 at t_1, when the electric field is off again.

- The atom is found to be in the $2\mathrm{p}_{m=0}$ state upon measurement: If at the time of the measurement the atom is in a state orthogonal to the $2\mathrm{p}_{m=0}$ state, then there is zero probability that it is found in that state. Otherwise, this probability is non-zero. That the atom is found to be in the $2\mathrm{p}_{m=0}$ state does not imply that it *was* in that particular state; rather, finding it in that state means that at the time of the measurement the atom was not in a state orthogonal to the $2\mathrm{p}_{m=0}$ state (see Section 1.3 of the QM Primer).

This example should not make you think that time-dependent perturbation theory is something relevant only for obscure problems of little practical interest. To the contrary, it is an essential tool for developing an understanding of the physical world. Time-*in*dependent perturbation theory is about making

sense of how energy levels shift and split under the effect of a weak perturbation. Time-dependent perturbation theory is about understanding why quantum states evolve in the way they do under the effect of a weak perturbation, and why certain changes are more probable than others. In this course, time-dependent perturbation theory will be primarily used to develop a formulation of how matter (atoms, molecules, nuclei, condensed matter, etc.) interacts with light, a topic of fundamental importance in Physics. In this context, a "measurement" is not necessarily something done in a lab using some sophisticated equipment: for example, someone noticing the arrival of a bunch of photons in their eyes also makes a measurement.

Understanding what happens when this hydrogen atom interacts with an external electric is an example of the much more general problem we concentrate on in this part of the course: Suppose that a weak perturbation starts to act on certain quantum system at a time t_0, so that the Hamiltonian of the system changes from a time-independent Hamiltonian H_0 at $t < t_0$ to a time-dependent Hamiltonian $H_0 + H'(t)$ at $t > t_0$. Suppose, moreover, that the system was in a given, well defined eigenstate of H_0 before the perturbation started, state a say, and that at some time $t > t_0$ one checks whether it is in another eigenstate of H_0, state b say. What can one say about the probability of a transition to state b (i.e., about the probability that at time t this system is found to be in state b)?

1.2 Transition probability

In this section: Writing a transition probability in terms of wave functions.

We thus look at the case where a quantum system is governed by a Hamiltonian $H(t)$ which at a time t_0 changes from a time-independent Hamiltonian H_0 to a time-dependent Hamiltonian $H_0 + H'(t)$. (In the example of Section 1.1, H_0 was the Hamiltonian of a field-free hydrogen atom and $H'(t)$ was the potential energy term $e\boldsymbol{\mathcal{E}}(\mathbf{r}, t) \cdot \mathbf{r}$). We will denote the wave function of this system by $\Psi(\mathbf{r}, t)$. Let us assume that the system is in a certain eigenstate of H_0 for $t < t_0$, a bound tate a say, so that

$$\Psi(\mathbf{r}, t) \equiv \psi_a^{(0)}(\mathbf{r}) \exp(-iE_a^{(0)}t/\hbar) \quad \text{for} \quad t < t_0. \tag{1.5}$$

The time-independent wave function $\psi_a^{(0)}(\mathbf{r})$ and the energy E_a are such that

$$H_0\psi_a^{(0)}(\mathbf{r}) = E_a^{(0)}\psi_a^{(0)}(\mathbf{r}). \tag{1.6}$$

The superscript (0) emphasizes that $\psi_a^{(0)}(\mathbf{r})$ and $E_a^{(0)}$ are, respectively, an eigenfunction and an eigenenergy of the "unperturbed" Hamiltonian H_0.

Note 1: In general, the wave functions depend on several sets of coordinates, which can collectively be referred to by the symbol τ. A more general form of Eq. (1.6) would read $H_0\psi_a^{(0)}(\tau) = E_a^{(0)}\psi_a^{(0)}(\tau)$, or, in Dirac notation, $H_0|\psi_a^{(0)}\rangle = E_a^{(0)}|\psi_a^{(0)}\rangle$, and similarly for Eq. (1.5). Here, for simplicity, we work in terms of wave functions depending only on the vector $\mathbf{r}$. No lack of generality is intended.

For $t > t_0$, H is no longer the same as H_0 at all times and $\Psi(\mathbf{r}, t)$ is no longer given by Eq. (1.6). Solving the time-dependent Schrödinger equation analytically to find $\Psi(\mathbf{r}, t)$ in closed form would be impossible for any case of practical interest. However, this wave function can often be calculated approximately, e.g., by using the perturbative method described in Section 1.3.

Having $\Psi(\mathbf{r}, t)$ for $t > t_0$, one can, in principle, calculate the required transition probabilities. We denote by $P_{ba}(t)$ the probability that in a measurement at time t the system is found to be in a bound eigenstate b of the Hamiltonian H_0 rather than in the initial state a. To use the vocabulary introduced at the beginning of Section 1.1, $P_{ba}(t)$ is the probability for a transition from state a to state b. This quantity is given by the following equation, according to the general principles of Quantum Mechanics:

$$P_{ba}(t) = \left| \int \psi_b^{(0)*}(\mathbf{r})\, \Psi(\mathbf{r}, t)\, \mathrm{d}^3r \right|^2, \tag{1.7}$$

where $\psi_b^{(0)}(\mathbf{r})$ is the wave function of state b. (See Section 2.4 of the QM Primer. Here as in the rest of this part of the course we assume that the wave functions $\psi_a^{(0)}(\mathbf{r})$, $\psi_b^{(0)}(\mathbf{r})$ and $\Psi(\mathbf{r}, t)$ are normalized.)

Note 2: Thus defined, $P_{ba}(t)$ is the probability for a transition to a certain eigenstate of H_0. Since the Hamiltonian of the system, $H(t)$, is not identical to H_0 at all times $t > t_0$, one may wonder whether it would not make more sense to look at the probability for a transition to a certain eigenstate of $H(t)$ (an "instantaneous" eigenstate, that is: when $H(t)$ is time-dependent, its eigenstates change all the time). In many applications, however, these eigenstates hardly differ from those of H_0, which are normally easier to calculate. Eq. (1.7) is thus relevant. The case where one looks instead at transitions to specific eigenstates of $H(t)$ is considered in Section 1.5.

1.3 Time-dependent perturbation theory

In this section: How to calculate transition probabilities in first order time-dependent perturbation theory.

As in the previous sections, we write the Hamiltonian in the following form:

$$H(t) = H_0 + H'(t), \tag{1.8}$$

where H_0 is a time-independent Hamiltonian and $H'(t)$ is a Hermitian operator with the physical dimensions of an energy. However, we now concentrate on the case where the interaction described by $H'(t)$ is weak enough that the time-dependent Schrödinger equation for $H(t)$ is amenable to a perturbative calculation. In this context, $H'(t)$ is often called the "perturbation Hamiltonian".

As in the case of time-independent perturbation theory, which you studied at level 2, it is useful to introduce a parameter λ and work with the more general Hamiltonian

$$H(t; \lambda) = H_0 + \lambda H'(t). \tag{1.9}$$

Clearly, $H(t)$ of Eq. (1.8) is simply $H(t; \lambda)$ for $\lambda = 1$. The wave function of the system can then be sought in the form of a power series in λ:

$$\Psi(\mathbf{r}, t) = \Psi^{(0)}(\mathbf{r}, t) + \lambda \Psi^{(1)}(\mathbf{r}, t) + \lambda^2 \Psi^{(2)}(\mathbf{r}, t) + \cdots \tag{1.10}$$

The idea is to calculate the different terms in this series order by order, starting with $\Psi^{(0)}(\mathbf{r}, t)$.

Let us assume, as we have done in the previous sections, that $H(t) = H_0$ before a certain time t_0. In other words, that

$$H'(t) \equiv 0, \quad t < t_0. \tag{1.11}$$

Let us also assume that the system is initially in a certain state a of the unperturbed Hamiltonian H_0, so that Eq. (1.5) applies. Therefore

$$\Psi^{(0)}(\mathbf{r}, t) = \psi_a^{(0)}(\mathbf{r}) \exp(-iE_a^{(0)}t/\hbar) \tag{1.12}$$

for all values of t. (This is so because $\Psi^{(0)}(\mathbf{r}, t)$ describes the state in which the system would be in the absence of the perturbation $H'(t)$, and the system would remain in state a if it is not perturbed.)

Having $\Psi^{(0)}(\mathbf{r}, t)$, it is possible to obtain $\Psi^{(1)}(\mathbf{r}, t)$, and having done this write down a general expression for the transition probabilities. We will skip the details of the calculation and go straight to the result, which is remarkably simple: For the Hamiltonian $H(t)$ of Eq. (1.8), the probability of transition from a bound state a to a bound state b other than a is given by the equation

$$P_{ba}^{(1)}(t) = \frac{1}{\hbar^2} \left| \int_{t_0}^t H'_{ba}(t) \exp(i\omega_{ba}t) \, \mathrm{d}t \right|^2. \tag{1.13}$$

Here $H'_{ba}(t)$ is the "matrix element" (as such integrals are called)

$$H'_{ba}(t) = \int \psi_b^{(0)*}(\mathbf{r}) H'(t) \psi_a^{(0)}(\mathbf{r}) \, \mathrm{d}^3 r, \tag{1.14}$$

and ω_{ba} is the Bohr angular frequency for the transition from state a to state b:

$$\omega_{ba} = \frac{E_b^{(0)} - E_a^{(0)}}{\hbar}. \tag{1.15}$$

The superscript (1) specified in $P_{ba}^{(1)}(t)$ is a reminder that this quantity is the transition probability obtained when only the terms of zero and first order in λ are retained in the perturbative expansion of the wave function. Eq. (1.13) is an important result and forms the basis of a large part of this course.

Note 1: One can write down similar expressions for transition probabilities based on the second order wave function, third order wave function, etc. However, these expressions are considerably more complicated.

Note 2: Here is a proof of Eq. (1.13). Although we do not know the wave function $\Psi(\mathbf{r}, t)$, we know that it can be written in the form of a linear combination of all the eigenfunctions of H_0 (that's because these eigenfunctions form a complete basis set). As is explained in Appendix A, the eigenstates of H_0 normally include bound eigenstates, corresponding to discrete energy levels, and may also include unbound eigenstates, corresponding to a continuum of energy levels. (It is recommended that you read through this appendix before continuing if you are unfamiliar with the concept of continuum states.) We thus write

$$\Psi(\mathbf{r}, t) = \sum_n c_n(t)\psi_n^{(0)}(\mathbf{r})\exp(-iE_n^{(0)}t/\hbar) +$$

$$\int c_{\mathbf{k}}(t)\psi_{\mathbf{k}}^{(0)}(\mathbf{r})\exp(-iE_{\mathbf{k}}^{(0)}t/\hbar)\,\mathrm{d}^3k. \quad (1.16)$$

The discrete sum runs over all the bound eigenstates of H_0, with the index k standing for the set of the quantum numbers identifying each of these states. For example, if H_0 is the non-relativistic Hamiltonian of a field-free hydrogen atom, n would refer to the set formed by the principal quantum number, the orbital angular momentum quantum number and the magnetic quantum number. Similarly, the integral runs over all the continuum eigenstates of H_0, and it is assumed that each of these states can be identified uniquely by a certain wave vector $\mathbf{k}$.

Next, we write that $\Psi(\mathbf{r}, t)$ satisfies the Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t} = [H_0 + \lambda H'(t)]\Psi(\mathbf{r}, t), \quad (1.17)$$

and in this equation we replace $\Psi(\mathbf{r}, t)$ by the right-hand side of Eq. (1.16). We then multiply the equation on the left by the complex conjugate of the wave function of the bound state b and integrate over space. The calculation is made easier by the facts that

$$\int \psi_b^{(0)*}(\mathbf{r})\psi_n^{(0)}(\mathbf{r})\,\mathrm{d}^3r = \delta_{bn} \quad (1.18)$$

(the bound state eigenfunctions $\psi_n^{(0)}(\mathbf{r})$ are orthonormal), that

$$\int \psi_b^{(0)*}(\mathbf{r})\psi_{\mathbf{k}}^{(0)}(\mathbf{r})\,\mathrm{d}^3 r = 0 \tag{1.19}$$

(bound eigenstates are orthogonal to continuum eigenstates) and that

$$H_0\psi_n^{(0)}(\mathbf{r}) = E_n^{(0)}\psi_n^{(0)}(\mathbf{r}) \quad \text{and} \quad H_0\psi_{\mathbf{k}}^{(0)}(\mathbf{r}) = E_{\mathbf{k}}^{(0)}\psi_{\mathbf{k}}^{(0)}(\mathbf{r}) \tag{1.20}$$

(these functions are eigenfunctions of H_0). This yields

$$i\hbar\frac{\mathrm{d}c_b}{\mathrm{d}t} = \lambda\sum_n H'_{bn}(t)\exp(i\omega_{bn}t)c_n(t)+$$

$$\lambda\int H'_{b\mathbf{k}}(t)\exp(i\omega_{b\mathbf{k}}t)c_{\mathbf{k}}(t)\,\mathrm{d}^3 k, \tag{1.21}$$

where the matrix elements $H'_{bn}(t)$ and $H'_{b\mathbf{k}}(t)$ and the Bohr angular frequencies ω_{bn} and $\omega_{b\mathbf{k}}$ are defined in the same way as the matrix element $H'_{ba}(t)$ and the Bohr angular frequency ω_{ba} introduced previously. We are particularly interested in the coefficient $c_b(t)$ because Eqs. (1.7), (1.16), (1.18) and (1.19) show that $P_{ba}(t) = |c_b(t)|^2$.

We now expand the coefficients $c_n(t)$ and $c_{\mathbf{k}}(t)$ in powers of λ:

$$\begin{aligned} c_n(t) &= c_n^{(0)}(t) + \lambda c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \cdots \tag{1.22}\\ c_{\mathbf{k}}(t) &= c_{\mathbf{k}}^{(0)}(t) + \lambda c_{\mathbf{k}}^{(1)}(t) + \lambda^2 c_{\mathbf{k}}^{(2)}(t) + \cdots \tag{1.23} \end{aligned}$$

Substituting $c_n(t)$ and $c_{\mathbf{k}}(t)$ by their expansions in Eq. (1.21) and equating terms of same order in λ yields the following equation, to first order in this parameter:

$$i\hbar\frac{\mathrm{d}c_b^{(1)}}{\mathrm{d}t} = \sum_n H'_{bn}(t)\exp(i\omega_{bn}t)c_n^{(0)}(t)+$$

$$\int H'_{b\mathbf{k}}(t)\exp(i\omega_{b\mathbf{k}}t)c_{\mathbf{k}}^{(0)}(t)\,\mathrm{d}^3 k. \tag{1.24}$$

However, $c_a^{(0)}(t) \equiv 1$, $c_{n\neq a}^{(0)}(t) \equiv 0$ and $c_{\mathbf{k}}^{(0)}(t) \equiv 0$ in view of Eq. (1.12). Hence, only one term is non-zero in the right-hand of Eq. (1.24) and we simply have

$$i\hbar\frac{\mathrm{d}c_b^{(1)}}{\mathrm{d}t} = H'_{ba}(t)\exp(i\omega_{ba}t). \tag{1.25}$$

This first order differential equation must be solved subject to the initial condition imposed by Eq. (1.5), namely $c_b^{(1)}(t = t_0) = 0$. The solution is

$$c_b^{(1)}(t) = \frac{1}{i\hbar}\int_{t_0}^t H'_{ba}(t)\exp(i\omega_{ba}t)\,\mathrm{d}t. \tag{1.26}$$

The corresponding transition probability for $\lambda = 1$ is $|c_b^{(1)}(t)|^2$ since $c_b^{(0)}(t) \equiv 0$. Eq. (1.13) follows.

Note 3: Transitions from a bound state to a continuum state or between continuum states can be treated in a similar way. We will come to this issue in Section 1.8.

Eq. (1.13) provides a simple "recipe" for calculating the probability for a transition from a bound eigenstate of the unperturbed Hamiltonian H_0 to another bound eigenstate of this Hamiltonian:

1. Find the wave functions $\psi_a^{(0)}(\mathbf{r})$ and $\psi_b^{(0)}(\mathbf{r})$ of these two states, and the corresponding energies $E_a^{(0)}$ and $E_b^{(0)}$.

2. Calculate the matrix element of the perturbation between states a and state b, $H_{ba}'(t)$.

3. Integrate the product $H_{ba}'(t)\exp(i\omega_{ba}t)$ over time and use Eq. (1.13) to calculate $P_{ba}^{(1)}(t)$.

It should be noted that this approach is valid only if the perturbed wave function $\Psi(\mathbf{r}, t)$ does not differ much from the initial wave function, $\psi_a^{(0)}(\mathbf{r})\exp(-iE_a^{(0)}t/\hbar)$. The probabilities predicted by Eq. (1.13) are likely to be wrong if the perturbation is so strong that $\sum_{b\neq a} P_{ba}^{(1)}(t) \gtrsim 1$.

In applications to actual problems, some of these steps may involve a long and arduous numerical computation. Even then, though, the perturbative approach is usually advantageous compared to solving the time-dependent Schrödinger equation in its full complexity.

Note 4: The following is worth noting in regards to Eq. (1.13). First, in the case where the perturbation ceases at a time t_1, so that $H'(t) \equiv 0$ for $t > t_1$, then Eq. (1.13) gives a constant $P_{ba}^{(1)}(t)$ for $t > t_1$,

$$P_{ba}^{(1)}(t > t_1) = \frac{1}{\hbar^2}\left|\int_{t_0}^{t_1} H_{ba}'(t)\exp(i\omega_{ba}t)\,dt\right|^2. \qquad (1.27)$$

This means that the probability of a particular outcome in a measurement of the state of the system does not depend on the time at which this measurement is made as long as it is made after the perturbation has stopped acting.

Second, Eq. (1.13) should not be used to calculate the probability $P_{aa}^{(1)}(t)$ that at time t the system is still in the initial state a. This equation applies only if state b is orthogonal to state a. Instead, $P_{aa}^{(1)}(t)$ can be calculated (in principle) from the following equation:

$$P_{aa}^{(1)}(t) = 1 - \sum_{b\neq a} P_{ba}^{(1)}(t), \qquad (1.28)$$

where the sum runs over *all* the eigenstates of H_0 (except state a). (Exercise: can you make sense of this last equation?)

1.4 An example

In this section: An example of calculation of a transition probability; the case a perturbation constant in time.

To illustrate this general formalism, let us come back to the example we started with in Section 1.1. The problem was to calculate the probability that a hydrogen atom is found in the excited $2\mathrm{p}_{m=0}$ state if the measurement is made after the atom has been exposed to an electric field $\boldsymbol{\mathcal{E}}(\mathbf{r}, t)$, given that the field acted only from $t = t_0$ to $t = t_1$ and that the atom was in its ground state before t_0. The first step when applying the equations seen above to this problem is to identify what the unperturbed Hamiltonian H_0 is in the present case, what the perturbation Hamiltonian $H'(t)$ is and what states a and b are.

- Clearly, H_0 is the Hamiltonian of the field-free atom, which is given by Eq. (1.1).

- $H'(t) = e\boldsymbol{\mathcal{E}}(\mathbf{r}, t) \cdot \mathbf{r}$, the potential energy arising from the interaction of the atom with the electric field.

- State a is the ground state of the field free atom. Correspondingly, the unperturbed wave function $\psi_a^{(0)}(\mathbf{r})$ is the ground state wave function, $\psi_{100}(\mathbf{r})$, and the unperturbed energy $E_a^{(0)}$ is the ground state energy, E_1 (that's the eigenenergy E_n, where n is the principal quantum number, for $n = 1$).

- State b is the $2\mathrm{p}_{m=0}$ state. Hence $\psi_b^{(0)}(\mathbf{r}) \equiv \psi_{210}(\mathbf{r})$ and $E_b^{(0)} = E_2$.

Let us first imagine that the electric field is turned on abruptly at a time t_0, turned off abruptly at a time t_1, and kept constant between t_0 and t_1. We also assume, which is realistic, that the field varies so little in space over the size of the atom that it can be considered to be constant in $\mathbf{r}$ for the purpose of this calculation. Turning a field on and off can never be done instantly, but to keep the maths simple we model these changes by step functions. That is, we set

$$\boldsymbol{\mathcal{E}}(\mathbf{r}, t) = \boldsymbol{\mathcal{E}}_0 f(t) \tag{1.29}$$

where $\boldsymbol{\mathcal{E}}_0$ is a constant vector and

$$f(t) = \begin{cases} 0 & t < t_0, \\ 1 & t_0 < t < t_1, \\ 0 & t_1 < t. \end{cases} \tag{1.30}$$

Therefore $H'(t) = \hat{H}' f(t)$ with

$$\hat{H}' = e\boldsymbol{\mathcal{E}}_0 \cdot \mathbf{r}. \tag{1.31}$$

Hence $H'_{ba}(t) = \hat{H}'_{ba} f(t)$ with

$$\hat{H}'_{ba} = \int \psi^*_{210}(\mathbf{r}) \, e\boldsymbol{\mathcal{E}}_0 \cdot \mathbf{r} \, \psi_{100}(\mathbf{r}) \, \mathrm{d}^3 r. \tag{1.32}$$

The integral appearing in this last equation can be worked out using known expressions for the wave functions $\psi_{100}(\mathbf{r})$ and $\psi_{210}(\mathbf{r})$ (see workshops and homework questions).

Eq. (1.27) then reduces to

$$P^{(1)}_{ba}(t) = \frac{1}{\hbar^2} \left| \int_{t_0}^{t_1} \hat{H}'_{ba} f(t) \exp(i\omega_{ba} t) \, \mathrm{d}t \right|^2, \quad t > t_1, \tag{1.33}$$

with $\omega_{ba} = (E_2 - E_1)/\hbar$. Taking the constant matrix element $\hat{H}'_{ba}$ out of the integral yields

$$P^{(1)}_{ba}(t) = \frac{1}{\hbar^2} |\hat{H}'_{ba}|^2 \left| \int_{t_0}^{t_1} f(t) \exp(i\omega_{ba} t) \, \mathrm{d}t \right|^2, \quad t > t_1. \tag{1.34}$$

Moreover, since $f(t) = 1$ over the interval $t_0 < t < t_1$,

$$\left| \int_{t_0}^{t_1} f(t) \exp(i\omega_{ba} t) \, \mathrm{d}t \right|^2 = \left| \int_{t_0}^{t_1} \exp(i\omega_{ba} t) \, \mathrm{d}t \right|^2 = 4 \frac{\sin^2[\omega_{ba}(t_1 - t_0)/2]}{\omega_{ba}^2}. \tag{1.35}$$

(The calculation is done step by step in Appendix B.) Therefore, in the present case,

$$P^{(1)}_{ba}(t) = \frac{4}{\hbar^2} |\hat{H}'_{ba}|^2 \frac{\sin^2[\omega_{ba}(t_1 - t_0)/2]}{\omega_{ba}^2}, \quad t > t_1. \tag{1.36}$$

We see that this transition probability oscillates as a function of $t_1 - t_0$, the duration of the time interval during which the atom is exposed to the field. In particular, it is zero for certain values of $t_1 - t_0$. The theory predicts that at these values the atom cannot be left in the $2\mathrm{p}_{m=0}$ state at $t = t_1$, no matter how strong the field was between t_0 and t_1. (One should bear in mind, however, that this result is only a first order approximation. A small but non-zero probability would be found if the calculation was carried out to higher orders of perturbation theory.)

The way $P^{(1)}_{ba}(t)$ varies with $t_1 - t_0$ depends, of course, on how the electric field varies in time. The probability would not be given by Eq. (1.36) for a different time function $f(t)$. Irrespective of how this function varies, however, $P^{(1)}_{ba}(t)$ is zero at all times if $\hat{H}'_{ba}$ happens to be zero. (In fact, in our case $\hat{H}'_{ba}$ is zero for certain orientations of the field and non-zero for others, see the first homework of the course). More generally, the transition probability predicted by Eq. (1.13) is always zero if $H'_{ba}(t) \equiv 0$ for the initial and final states considered.

Note 1: Being complicated integrals, transition matrix elements rarely vanish by accident. There are usually well defined reasons, having to do with the symmetry of the problem, for a matrix element $H'_{ba}(t)$ to be zero at all times for certain transitions. We will come back to this issue in the second part of these notes.

We also note that since $\hat{H}'$ is proportional to $|\boldsymbol{\mathcal{E}}_0|$, the transition probability predicted by Eq. (1.36) is proportional to $|\boldsymbol{\mathcal{E}}_0|^2$ and could therefore be close to or even exceed 1 if the field is strong enough. The transition probability would need to be calculated otherwise in this case, e.g., by carrying the calculation to a higher order of perturbation theory or by following a non-perturbative approach.

1.5 Aside: The sudden approximation

In this section: A non-perturbative formalism applicable to situations where the Hamiltonian changes suddenly, at one instant, rather than smoothly over an extended period of time.

The time-dependent electric field considered in the previous section was taken to jump instantaneously from zero to a non-zero value and back to zero again, leading to a Hamiltonian $H(t)$ discontinuous in time. As already mentioned, such discontinuous changes never occur in real systems. Nonetheless, in some systems the Hamiltonian changes so rapidly that the change can indeed be treated as being instantaneous, in excellent approximation. In this section we focus on the case where the Hamiltonian $H(t)$ changes suddenly from a time-independent Hamiltonian H_0 to another time-independent Hamiltonian H_1, so that

$$H(t) = \begin{cases} H_0 & t < 0, \\ H_1 & t > 0, \end{cases} \tag{1.37}$$

assuming that the change happens at $t = 0$.

A good example of such systems is offered by the beta-decay of the nucleus of a tritium atom, the heaviest form of atomic hydrogen. This atom is composed of an atomic electron and a nucleus. The latter contains one proton and two neutrons and is unstable against beta-decay: it may change into a helium-3 nucleus (two protons and one neutron) upon emitting an antineutrino and an electron. In most cases the speed of the emitted electron is to the speed of light. This electron thus disappears from the vicinity of the atom almost instantaneously on the time scale over which the wave function of the atomic electron normally varies. As a result, and if one ignores the recoil of the nucleus, the effect of the decay on the atomic electron is limited to an abrupt change of its potential energy (the electric charge of the nucleus

increases from e to $2e$ in the reaction). The system can thus be modelled by the Hamiltonian of Eq. (1.37) with

$$H_0 = -\frac{\hbar^2}{2\mu_0}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r} \tag{1.38}$$

and

$$H_1 = -\frac{\hbar^2}{2\mu_1}\nabla^2 - \frac{2}{4\pi\epsilon_0}\frac{e^2}{r} \tag{1.39}$$

Here μ_0 and μ_1 are the reduced mass of the system, respectively before and after the decay. Both are almost equal to the mass of the electron, m. The main difference between H_0 and H_1 in the present case is the factor of two change in the potential energy term. This change is very far from small, and perturbation theory would not appropriate to calculate how the decay affects the atomic electron.

More generally, we assume that the two operators H_0 and H_1 appearing in Eq. (1.37) are both time-independent. We will denote their eigenfunctions by $\psi_n(\mathbf{r})$ and $\phi_n(\mathbf{r})$ and the corresponding eigenenergies by E_n and ϵ_n:

$$H_0\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}), \quad H_1\phi_n(\mathbf{r}) = \epsilon_n\phi_n(\mathbf{r}). \tag{1.40}$$

To keep the notation simple, we write these entities in terms of a single position vector, $\mathbf{r}$, and represent all the relevant quantum numbers identifying each eigenstate by a single index n, as we have done in previous sections. We also represent the state of the system by a wave function $\Psi(\mathbf{r}, t)$.

We will assume that the system described by the Hamiltonian $H(t)$ is initially in a certain bound eigenstate a of H_0. That is,

$$\Psi(\mathbf{r}, t) = \psi_a(\mathbf{r})\exp(-iE_at/\hbar), \quad t < 0. \tag{1.41}$$

The changeover from H_0 to H_1 normally modifies the state of the system in a complicated way. However, since the eigenstates of H_1 form a complete basis set, we know that $\Psi(\mathbf{r}, t)$ can be expressed in the following form for $t > 0$:

$$\Psi(\mathbf{r}, t) = \sum_n c_n\phi_n(\mathbf{r})\exp(-i\epsilon_nt/\hbar), \quad t > 0, \tag{1.42}$$

the coefficients c_n being time-independent.

Note 1: More pedantically, this last equation should be written

$$\Psi(\mathbf{r}, t) = \sum_n c_n\phi_n(\mathbf{r})\exp(-i\epsilon_nt/\hbar) +$$

$$\int c_{\mathbf{k}}\phi_{\mathbf{k}}(\mathbf{r})\exp(-i\epsilon_{\mathbf{k}}t/\hbar)\,\mathrm{d}^3k, \tag{1.43}$$

where the summation over n runs over the bound eigenstates of H_1 and the integral over $\mathbf{k}$ runs over this continuum eigenstates — see Note 2 of Section 1.3. The coefficients c_n and $c_{\mathbf{k}}$ are constant, here, because H_1 is time-independent. Thus

$$i\hbar\frac{\partial\Psi}{\partial t} = \sum_n c_n\epsilon_n\phi_n(\mathbf{r})\exp(-i\epsilon_n t/\hbar)+$$

$$\int c_{\mathbf{k}}\epsilon_{\mathbf{k}}\phi_{\mathbf{k}}(\mathbf{r})\exp(-i\epsilon_{\mathbf{k}}t/\hbar)\,\mathrm{d}^3k$$

$$= \sum_n c_n H_1\phi_n(\mathbf{r})\exp(-i\epsilon_n t/\hbar)+$$

$$\int c_{\mathbf{k}}H_1\phi_{\mathbf{k}}(\mathbf{r})\exp(-i\epsilon_{\mathbf{k}}t/\hbar)\,\mathrm{d}^3k$$

$$= H_1\psi(\mathbf{r},t), \tag{1.44}$$

which shows that the wave function defined by Eq. (1.43) is indeed a solution of the time-dependent Schrödinger equation. This would not be the case if H_1 was time-dependent, as in this case its eigenfunctions and eigenenergies would also vary with t, and the first lines of Eq. (1.44) would then be incorrect.

An important advantage of representing $H(t)$ by Eq. (1.37) is that the coefficients c_n are given by a simple formula. The key observation leading to this result is that although the Hamiltonian $H(t)$ is discontinuous at $t = 0$, the wave function $\Psi(\mathbf{r},t)$ must continuous (this is a mathematical consequence that the wave function must be a solution of the time-dependent Schrödinger equation, which is first order in time). Hence

$$\lim_{t\to 0,\,t>0}\Psi(\mathbf{r},t) = \lim_{t\to 0,\,t<0}\Psi(\mathbf{r},t), \tag{1.45}$$

which means, in view of Eqs. (1.41) and (1.42), that $\sum_n c_n\phi_n(\mathbf{r}) = \psi_a(\mathbf{r})$. Therefore

$$c_n = \int \phi_n^*(\mathbf{r})\,\psi_a(\mathbf{r})\,\mathrm{d}^3r, \tag{1.46}$$

if we assume (which is not restrictive) that the eigenfunctions $\phi_n(\mathbf{r})$ are orthonormal.

We stress that Eq. (1.46) is valid only to the extent that the Hamiltonian can be taken to jump discontinuously from H_0 to H_1. For any real system the Hamiltonian would vary continuously from H_0 to H_1, over a non-zero time interval T. Calculating the final wave function according to Eq. (1.46) on account that T is short enough is an approximation, called the sudden approximation.

Suppose that one checks in an experiment whether the system is in a certain bound eigenstate of H_1, state b say, after the change over from H_0 to H_1. We will use the same symbol to denote this probability than in the previous sections, P_{ba}; however, note that here P_{ba} is the probability for finding

the system in a particular eigenstate of the *final* Hamiltonian, not a particular eigenstate of the *initial* Hamiltonian. As a consequence of Eq. (1.42), $P_{ba} = |c_b|^2$. Hence, within the sudden approximation,

$$P_{ba} = \left| \int \phi_b^*(\mathbf{r})\, \psi_a(\mathbf{r})\, \mathrm{d}^3 r \right|^2. \tag{1.47}$$

Note that this result for the transition probability is non-perturbative. It applies even if the change from the Hamiltonian H_0 to the Hamiltonian H_1 has a large effect on the system, as long as this change is rapid enough.

Note 2: Although at $t = 0$ the system is still in state a of the Hamiltonian H_0, it does not remain in that state at later times since $\psi_a(\mathbf{r})$ is not an eigenstate of H_1. In particular, it could be found in a state of an energy much higher than E_a.

Where does the difference in energy come from, given that H_1 is time-independent and therefore conserves energy? The answer is that although H_1 is indeed time-indepedent, $H(t)$ isn't. The change from H_0 to H_1 can transfer energy to the system. For instance, in the example of the tritium atom, the nuclear electron does not leave instantly: it is during its transit from close to the nucleus to far away from the atom that the charge of the nucleus "seen" by the atomic electron increases from e to $2e$. The nuclear electron can transfer some of its kinetic energy to the atomic electron as it moves away.

1.6   Harmonic perturbations

In this section: The transition probability for a perturbation varying in time like a sine or cosine function; conservation of energy; resonances.

In this section we come back to time-dependent perturbation theory and address the important case of a weak perturbation oscillating harmonically (i.e., like a sine or cosine function). Specifically, we assume that the Hamiltonian is given by Eq. (1.8) with

$$H'(t) = \begin{cases} 0 & t < 0 \\ \hat{H}' \sin \omega t & t \geq 0. \end{cases} \tag{1.48}$$

Here $\hat{H}'$ is a certain time-independent energy operator and ω is a constant angular frequency. When applying this formalism to the case of a hydrogen atom exposed to a linearly polarized beam of light, later in the course, we will see that for this system $H'(t)$ can be taken to be $e\mathcal{E}_0 \hat{\boldsymbol{\epsilon}} \cdot \mathbf{r} \sin(2\pi\nu t)$ for $t \geq 0$, where $\mathcal{E}_0$ is the amplitude of the electric field component of the corresponding

electromagnetic field, $\hat{\boldsymbol{\epsilon}}$ is a constant unit vector and ν is the frequency of the light. In this case, $\hat{H}' = e\mathcal{E}_0\hat{\boldsymbol{\epsilon}} \cdot \mathbf{r}$ and $\omega = 2\pi\nu$. However, for the time being $\hat{H}'$ just represents an unspecified time-independent Hermitian operator with the physical dimensions of an energy.

As in sections 1.2, 1.3 and 1.4, we assume that the system is initially in the eigenstate a of the unperturbed Hamiltonian H_0, and we are interested in the transition probability $P_{ba}(t)$ that it is found in the eigenstate b of that Hamiltonian after the perturbation has acted for a time t. Given the form of $H'(t)$, this probability is here given by Eq. (1.13) as

$$P_{ba}^{(1)}(t) = \frac{1}{\hbar^2}\left|\int_0^t \hat{H}'_{ba}\sin(\omega t)\exp(i\omega_{ba}t)\,\mathrm{d}t\right|^2 \tag{1.49}$$

with

$$\hat{H}'_{ba} = \int \psi_b^{(0)*}(\mathbf{r})\hat{H}'\psi_a^{(0)}(\mathbf{r})\,\mathrm{d}^3r. \tag{1.50}$$

(Note that $t_0 = 0$ here.) We continue to use the same notation as previously: $\psi_a^{(0)}(\mathbf{r})$ and $\psi_b^{(0)}(\mathbf{r})$ represent the wave functions of state a and state b, and, as in Eq. (1.15),

$$\omega_{ba} = \frac{E_b^{(0)} - E_a^{(0)}}{\hbar}. \tag{1.51}$$

Recall that $E_a^{(0)}$ and $E_b^{(0)}$ are the energies of these two unperturbed states.

In order to progress further, we rewrite Eq. (1.48) in terms of the complex exponentials $\exp(i\omega t)$ and $\exp(-i\omega t)$:

$$H'(t) = \begin{cases} 0 & t < 0 \\ A\exp(i\omega t) + A^\dagger\exp(-i\omega t) & t \geq 0, \end{cases} \tag{1.52}$$

where A and $A^\dagger$ are time-independent operators related to $\hat{H}'$ by the equations $A = \hat{H}'/(2i)$ and $A^\dagger = -\hat{H}'/(2i)$. (The symbol $A^\dagger$ reads "A-dagger".) Using this form of the perturbation Hamiltonian in Eq. (1.49) yields

$$P_{ba}^{(1)}(t) = \frac{1}{\hbar^2}\left|\int_0^t A_{ba}\exp[i(\omega_{ba} + \omega)t]\,\mathrm{d}t + \right.$$
$$\left.\int_0^t A_{ba}^\dagger\exp[i(\omega_{ba} - \omega)t]\,\mathrm{d}t\right|^2 \tag{1.53}$$

with

$$A_{ba} = \int \psi_b^{(0)*}(\mathbf{r})A\,\psi_a^{(0)}(\mathbf{r})\,\mathrm{d}^3r, \tag{1.54}$$

$$A_{ba}^\dagger = \int \psi_b^{(0)*}(\mathbf{r})A^\dagger\psi_a^{(0)}(\mathbf{r})\,\mathrm{d}^3r. \tag{1.55}$$

The integrals appearing in Eq. (1.53) are easily worked out. The result is

$$P_{ba}^{(1)}(t) = \frac{1}{\hbar^2} \left| A_{ba} \frac{\exp[i(\omega_{ba} + \omega)t] - 1}{\omega_{ba} + \omega} + \right.$$
$$\left. A_{ba}^\dagger \frac{\exp[i(\omega_{ba} - \omega)t] - 1}{\omega_{ba} - \omega} \right|^2. \qquad (1.56)$$

> Note 1: Mathematical note, only for those who have studied adjoint operators in another course: You may have recognized that the operator $-\hat{H}'/(2i)$ is the adjoint of the operator $\hat{H}'/(2i)$ since $\hat{H}'$ is assumed to be Hermitian. This is why we use a † superscript to distinguish the former from the latter (this superscript is traditionally used to denote the adjoint). Eq. (1.52) is more general than Eq. (1.48). For example, we will see in a workshop that
>
> $$H'(t) = \begin{cases} 0 & t < 0 \\ e\mathcal{E}_0[\hat{\boldsymbol{\epsilon}} \cdot \mathbf{r} \exp(-i\omega t) + \hat{\boldsymbol{\epsilon}}^* \cdot \mathbf{r} \exp(i\omega t)] & t \geq 0 \end{cases} \qquad (1.57)$$
>
> in the case of a hydrogen atom exposed to a *circularly* polarized laser beam (here $\hat{\boldsymbol{\epsilon}}$ is a *complex* unit vector). This perturbation Hamiltonian can be written in the form of Eq. (1.52) but not in the form of Eq. (1.48).

The angular frequency of the perturbation, ω, is always positive. However, the Bohr angular frequency ω_{ba} can be positive or negative, depending on whether state b is higher or lower in energy than state a. In the case where $E_b^{(0)} > E_a^{(0)}$, both ω and ω_{ba} are positive, and $\omega_{ba} - \omega \approx 0$ when

$$E_b^{(0)} \approx E_a^{(0)} + \hbar\omega. \qquad (1.58)$$

If instead state b is lower in energy than state a, then $\omega_{ba} + \omega \approx 0$ when

$$E_b^{(0)} \approx E_a^{(0)} - \hbar\omega. \qquad (1.59)$$

In either case, one of the two terms in Eq. (1.56) can be neglected compared to the other one if ω is sufficiently close to $|\omega_{ba}|$.

We first consider the case where $E_b^{(0)} \approx E_a^{(0)} + \hbar\omega$. Since the denominator of the second term in Eq. (1.56) becomes much smaller (in absolute magnitude) than the denominator of the first term when $\omega_{ba} - \omega$ approaches zero, one can neglect the first term when ω is sufficiently close to ω_{ba}. Then

$$P_{ba}^{(1)}(t) \approx \frac{1}{\hbar^2} |A_{ba}^\dagger|^2 \left| \frac{\exp[i(\omega_{ba} - \omega)t] - 1}{\omega_{ba} - \omega} \right|^2. \qquad (1.60)$$

This result can also be written in the alternative form

$$P_{ba}^{(1)}(t) \approx \frac{2}{\hbar^2} |A_{ba}^\dagger|^2 F(t, \omega_{ba} - \omega), \tag{1.61}$$

where

$$
\begin{aligned}
F(t, \omega_{ba} - \omega) &= \frac{1}{2} \left| \frac{\exp[i(\omega_{ba} - \omega)t] - 1}{\omega_{ba} - \omega} \right|^2 \\
&= 2 \frac{\sin^2[(\omega_{ba} - \omega)t/2]}{(\omega_{ba} - \omega)^2}.
\end{aligned}
\tag{1.62}
$$

(The calculation is done step by step in Appendix B.)

How the function $F(t, \omega_{ba} - \omega)$ varies with t, ω and ω_{ba} is of very important for the rest of the discussion. A quick analysis reveals that for increasing values of t, the graph of this function is more and more dominated by a tall and narrow peak centered at $\omega = \omega_{ba}$, and that the width of this peak is of the order of $2\pi/t$ and therefore shrinks to 0 as $t \to \infty$ (see Note 3 below for details). The upshot is that the range of values of ω over which the transition probability $P_{ba}^{(1)}(t)$ is largest tends to reduce to a small band extending from about $\omega_{ba} - \pi/t$ to about $\omega_{ba} + \pi/t$ when t increases. In other words, the probability that the system is in state b a time t after the perturbation has started to act is much more probable if $|\omega - \omega_{ba}| \lesssim \pi/t$ than if $|\omega - \omega_{ba}| > \pi/t$. Since $\hbar(\omega - \omega_{ba}) = E_a^{(0)} + \hbar\omega - E_b^{(0)}$, we also see that for a given angular frequency ω, it is unlikely that the system would be found in a state whose energy differs from $E_a^{(0)} + \hbar\omega$ by more than $\pi\hbar/t$ (assuming, of course, that the detector has a sufficient energy resolution).

One says that a resonance occurs when $\omega = \omega_{ba}$, i.e., when the angular frequency of the perturbation exactly matches the Bohr angular frequency for the transition. The transition probability is usually very much larger when $\omega = \omega_{ba}$ than when $\omega \gg \omega_{ba}$ or $\omega \ll \omega_{ba}$.

> Note 2: Resonances in quantum systems submitted to a periodic perturbation have much in common with the resonances in oscillating electronic circuits or in driven classical oscillators (see, e.g., Chapters 14 and 31 of Young and Freedman). Here the transition probability is particularly large at the resonance frequency, whereas in these classical systems it is the amplitude of oscillation which is particularly large. In either case, the perturbation has its strongest effect when its frequency matches one of the system's natural frequencies of oscillation.

Note 3: Let us look at the variation of $F(t, \omega_{ba} - \omega)$ more in detail. We can note the following:

- When $\omega \neq \omega_{ba}$, the function $F(t, \omega_{ba} - \omega)$ oscillates between 0 and a maximum value of $2/(\omega_{ba} - \omega)^2$ when t increases. However, at $\omega = \omega_{ba}$ there is a rapid, monotonic increase, not an oscillation, as $F(t, \omega_{ba} - \omega) = t^2/2$ when $\omega_{ba} - \omega = 0$.

- For a fixed value of t, the graph of $F(t, \omega_{ba} - \omega)$ vs. ω is a central peak of height $t^2/2$ at $\omega = \omega_{ba}$ surrounded on each side by an oscillatory pattern of secondary maxima with zeros at $\omega = \omega_{ba} \pm 2\pi/t$, $\pm 4\pi/t$, $\pm 6\pi/t$, etc.

- The secondary maxima separating these zeros rapidly decrease in height and are always much lower than the central peak. For example, at its first secondary maximum on the right of this peak, which occurs at $\omega \approx \omega_{ba} + 3\pi/t$, $F(t, \omega_{ba} - \omega) \approx 0.0225\,t^2$, which is less than 5% of the height of the central peak.

- The width of this oscillatory pattern shrinks as t increases, as can be seen from the fact that the successive zeros are separated by a distance $2\pi/t$, which is inversely proportional to t. The width of the central peak at its "basis", i.e., the distance between the zeros at $\omega_{ba} \pm 2\pi/t$, is $4\pi/t$, and its full width at half maximum is approximately $2\pi/t$. This peak thus becomes narrower and narrower and higher and higher as t increases.

Note 4: Since $F(t, \omega - \omega_{ba}) = t^2/2$ for $\omega = \omega_{ba}$, $P_{ba}^{(1)}(t) \approx |A_{ba}^\dagger|^2 t^2/\hbar^2$ at the resonance. Clearly, the monotonic increase of the transition probability predicted by this equation cannot continue indefinitely, as a probability cannot be larger than 1. First order perturbation theory is valid only to the extent that $P_{ba}^{(1)}(t) \ll 1$. This equation thus represents the exact transition probability only for $t \ll \hbar/|A_{ba}^\dagger|$. How to deal with longer interaction times is addressed in Section 1.7.

So far we have looked at the case case where state b is higher in energy than state a and $E_b^{(0)} \approx E_a^{(0)} + \hbar\omega$. The case where instead state b is lower in energy and $E_b^{(0)} \approx E_a^{(0)} - \hbar\omega$ is almost identical, apart that the Bohr angular frequency ω_{ba} is negative and it is the first term in Eq. (1.56), not the second, which becomes dominant when $|\omega_{ba}| - \omega$ approaches zero. Instead of Eq. (1.61), the first order transition probability is thus given by[1]

$$P_{ba}^{(1)}(t) \approx \frac{2}{\hbar^2}\,|A_{ba}|^2\,F(t, |\omega_{ba}| - \omega) \tag{1.63}$$

---

[1] $F(t, \omega_{ba} + \omega) \equiv F(t, |\omega_{ba}| - \omega)$ when $\omega_{ba} < 0$.

when $E_b^{(0)} \approx E_a^{(0)} - \hbar\omega$. All what we have seen for the case where $E_b^{(0)} \approx E_a^{(0)} + \hbar\omega$ still applies, except that ω_{ba} should be replaced by $|\omega_{ba}|$ and $A_{ba}^\dagger$ by A_{ba}. In particular, one still finds that the probability of a transition from state a to state b is particularly large when $\hbar\omega$ matches the difference in energy between the two states, i.e., when the resonance condition $\omega = |\omega_{ba}|$ is fulfilled.

1.7 Rabi oscillations

In this section: The non-perturbative dynamics of two-state quantum systems driven by a harmonic interaction (e.g., an atom or molecule interacting with a resonant laser field); Rabi oscillations.

In the previous section we examined the case of a weak harmonic perturbation coupling two states of a quantum system. We saw that the transition probability calculated to first order in the perturbation had a particularly simple form when the angular frequency of the perturbation matched or nearly matched the difference in energy between the two states. However, this result was valid only for perturbations weak enough that the transition probability remained much smaller than 1. As it turns out, it is possible to calculate the wave function and the transition probability non-perturbatively when two states of a quantum system are coupled by an oscillating interaction, even if this interaction is so strong that perturbation theory would not be applicable. The results of this calculation are important in a number of areas — e.g., in Atomic Physics, to describe how a cloud of atoms interacts with a resonant laser beam, and in Nuclear Magnetic Resonance Spectroscopy, to describe how nuclear spins interact with an oscillating magnetic field.

As in Section 1.6, we write the total Hamiltonian $H(t)$ as $H_0 + H'(t)$ with $H'(t)$ given by Eq. (1.48), the operators H_0 and $\hat{H}'$ being both time-independent. We also assume that initially the system is a bound eigenstate a of H_0 and that the angular frequency ω matches, or nearly matches, the Bohr angular frequency ω_{ba} for a transition to another bound eigenstate of H_0, state b (we take state b to be higher in energy than state a, so that $\omega_{ba} > 0$). However, we do not longer restrict the analysis to the case where the interaction represented by $H'(t)$ is a weak perturbation.

In principle, the wave function of the system, $\Psi(\mathbf{r}, t)$, can be written as

$$\Psi(\mathbf{r}, t) = \sum_n c_n(t) \psi_n^{(0)}(\mathbf{r}) \exp(-iE_n^{(0)} t/\hbar), \qquad (1.64)$$

where the sum is meant to run over *all* the eigenstates of H_0. As initially the system is in state a, $c_a(t) = 1$ and $c_{n \neq a}(t) = 0$ for $t \leq 0$. The coefficients $c_n(t)$ for $n \neq a$ may differ from 0 and vary in a complicated way for $t > 0$. However, we have seen in Section 1.6 that when $\omega \approx \omega_{ba}$ the probability that

the system makes a transition to state b is much larger than the probability that it makes a transition to any another state (assuming that $E_b^{(0)}$ is not degenerate). Although this result was based on a calculation carried out only to first order in the perturbation, it indicates that close to resonance only the coefficients $c_a(t)$ and $c_b(t)$ may differ significantly from zero as t increases. This suggests to simplify the problem by retaining only state a and state b in the expansion, effectively setting all the coefficients $c_n(t)$ equal to zero apart from $c_a(t)$ and $c_b(t)$. Within this approximation,

$$\Psi(\mathbf{r}, t) = c_a(t)\psi_a^{(0)}(\mathbf{r}) \exp(-iE_a^{(0)}t/\hbar) + c_b(t)\psi_b^{(0)}(\mathbf{r}) \exp(-iE_b^{(0)}t/\hbar). \quad (1.65)$$

It is then possible to solve the time-dependent Schrödinger equation to obtain approximate expressions for $c_a(t)$ and $c_b(t)$. The calculation is proposed as an exercise in one of the workshops associated with the course.

Note 1: The calculation leads to equations containing two types of terms, namely terms proportional to the oscillating exponentials $\exp[\pm i(\omega_{ba} - \omega)t]$, and terms proportional to the oscillating exponentials $\exp(\pm i\omega t)$ or $\exp[\pm i(\omega_{ba} + \omega)t]$. As $\omega \approx \omega_{ba}$ here, the terms in $\omega_{ba} + \omega$ oscillate much more rapidly than those in $\omega_{ba} - \omega$. It therefore makes sense to neglect the former and keep only the latter. This approximation is often referred to as the "rotating wave approximation", for historical reasons. We made the same approximation when we neglected the term in $\omega + \omega_{ba}$ in Eq. (1.56).

Note 2: Mathematical note, following Note 1 of Section 1.6: The calculation also makes use of the identity $A_{ba}^\dagger = A_{ab}^*$, where $A_{ba}^\dagger$ is defined by Eq. (1.55) and A_{ab} by the equation

$$A_{ab} = \int \psi_a^{(0)*}(\mathbf{r}) \, A \, \psi_b^{(0)}(\mathbf{r}) \, \mathrm{d}^3 r. \quad (1.66)$$

This identity always holds, by definition of the adjoint operator.

While the details of this calculation are not essential for us, the final result is interesting: One finds that the probability that the system is in state b at a time $t > 0$ is given by the following equation:

$$P_{ba}(t) = \frac{4}{\hbar^2} \frac{|A_{ba}^\dagger|^2}{\omega_{\mathrm{R}}^2} \sin^2(\omega_{\mathrm{R}} t/2), \quad (1.67)$$

where

$$\omega_{\mathrm{R}} = \left(\Delta^2 + \frac{4|A_{ba}^\dagger|^2}{\hbar^2} \right)^{1/2} \quad (1.68)$$

with
$$\Delta = \omega - \omega_{ba}. \tag{1.69}$$

The angular frequency Δ is called the detuning ($\Delta = 0$ when the resonance condition $\omega = \omega_{ba}$ is fulfilled). The angular frequency ω_{R}, which is always positive, is called the Rabi frequency, or sometimes the generalized Rabi frequency.

We see that this transition probability oscillates between 0 and a maximum value of $4|A_{ba}^{\dagger}|^2/\hbar^2\omega_{\mathrm{R}}^2$ when t increases, a variation often referred to as a Rabi oscillation (named after Isidor Rabi, who applied this formalism to ground breaking work on nuclear magnetic resonance; the word "Rabi flopping" is also used to refer to this dynamics). The period of this oscillation is $2\pi/\omega_{\mathrm{R}}$. It depends on the detuning and on the strength of the interaction, but is usually much longer than the period of the oscillation of $H'(t)$, $2\pi/\omega$. Note that the maximum value of $P_{ba}(t)$ is 1 when $\Delta = 0$, which means that exactly on resonance the system really oscillates between state a and state b rather than between state a and some linear combination of states a and b.

Note 3: An example of Rabi oscillation observed in an actual experiment can be found on DUO, in the Course Documents > Quantum Mechanics 3 > Handouts and Other Documents folder.

Note 4: The first order transition probability we found in Section 1.6 for $\omega \approx \omega_{ba}$ was
$$P_{ba}^{(1)}(t) \approx \frac{4}{\hbar^2} \frac{|A_{ba}^{\dagger}|^2}{\Delta^2} \sin^2(\Delta t/2), \tag{1.70}$$

if we write the result in terms of the detuning Δ. Although obtained perturbatively and valid only when $P_{ba}^{(1)}(t) \ll 1$, this equation is similar to Eq. (1.67), which results from a non-perturbative calculation and is valid even when $P_{ba} \approx 1$. In fact, the first order expression of the probability given by Eq. (1.70) is the leading term in the expansion of $P_{ba}(t)$ in powers of the perturbation, as it is not difficult to see. Eq. (1.70) is thus consistent with Eq. (1.67).

Note 5: The transition probability predicted by Eq. (1.67) never exceeds 1, as befits a probability. In particular, $P_{ba}(t) = \sin^2(|A_{ba}^{\dagger}|t/\hbar)$ when $\omega = \omega_{ba}$. By contrast, the probability predicted by the first order theory is arbitrarily large when the interaction is resonant with the transition. Indeed, $P_{ba}^{(1)}(t) \approx |A_{ba}^{\dagger}|^2 t^2/\hbar^2$ when $\omega = \omega_{ba}$. This fact was already highlighted in Note 3 of Section 1.6 and it was pointed out that this first order result should not be expected to be correct unless $t \ll \hbar|A_{ba}^{\dagger}|$. This result is in fact consistent with Eq. (1.67), since $\sin^2(|A_{ba}^{\dagger}|t/\hbar) \approx |A_{ba}^{\dagger}|^2 t^2/\hbar^2$ when $t \ll \hbar|A_{ba}^{\dagger}|$.

1.8   Fermi's Golden Rule

In this section: How to calculate the probability for a transition from a bound state to a group of unbound states distributed continuously in energy.

It is recommended that you read through Appendix A before you study this section, as you will not be able to make sense of the material covered below if you are not sufficiently familiar with the concept of continuum states.

As is explained in Appendix A, many quantum systems have both bound states and unbound (or continuum) states. A time-dependent perturbation may thus induce a transition from one of the former to one of the latter, which would correspond to a break-up of the system. For example, a hydrogen atom initially in the ground state can break into a proton and an electron when exposed to a beam of XUV light, a process called ionization (the atom is transformed into a positive ion, here a single proton, upon the loss of the electron). Since its fragments are free to go to arbitrarilty large distances from each other when the system is in an unbound state, a transition of this kind is often referred to as a "bound-free" transition. Such transitions are very common in Physics: ionization is just one example, as is the emission of photoelectrons by a piece of metal exposed to light or the disintegration or an atomic nucleus exposed to gamma rays. Other examples of bound-free transitions are the beta-decay of a neutron (the neutron "breaks apart" into a proton, an electron and an antineutrino), and the spontaneous decay to the ground state of a hydrogen atom initially in a 2p state (the electron and proton do not separate from each other in this transition, but the decay is accompanied by the emission of a photon which is free to go arbitrarily far away). Fermi's Golden Rule, which this section is about, is an extension of Eq. (1.13) applicable to such cases.

Eq. (1.13) cannot be directly used to calculate the probability for a bound-free transition because it refers to a transition to a single, well defined energy eigenstate belonging to a discrete energy level. It makes sense to talk about the probability of finding the system in a state b if the energy resolution of

the detector makes it possible to tell whether the system is in that state and not in a different state, close in energy. Bound states belong to discrete energy levels, i.e., energy levels separated from each other by a non-zero energy gap. Distinguishing between two bound states belonging to different energy levels is possible, in principle, if the measurement is made for long enough (recall the energy - time uncertainty relation: the duration of the measurement, Δ, should not be much smaller than about $\hbar/\Delta E$, where ΔE is the different in energy between the two states). However, for bound-free transitions the final state belongs to a continuum of energy levels (see Appendix A). As there is no gap between adjacent energy levels in this case, a detector would only record whether the system has made a transition to a certain *group* of states close in energy.

In the interest of simplicity, we only consider the case where a perturbation oscillating harmonically in time couples the initial state of a 1D system to continuum states higher in energy. As previously, we assume that the Hamiltonian is the sum of an unperturbed Hamiltonian H_0 and a perturbation Hamiltonian $H'(t)$ given by Eq. (1.52). The initial and final states are described by eigenfunctions of H_0, the initial state by a bound state eigenfunction $\psi_a(x)$ and the final states by continuum eigenfunctions $\psi_k(x)$ labelled by a wave number k. The corresponding eigenenergies are E_a and E_k, respectively. (We stress that $\psi_a(x)$, $\psi_k(x)$, E_a and E_k are eigenfunctions and eigenenergies of the unperturbed Hamiltonian H_0. To simplify the notation, we no longer write the superscript (0) used to identify the eigenfunctions and eigenenergies of this Hamiltonian in previous sections.)

As usual, we describe the state of the system by a time-dependent wave function $\Psi(x,t)$. According to the general principles summarized in Appendix A,

$$P_{ka}(t) = \left| \int_{-\infty}^{\infty} \psi_k^*(x)\, \Psi(x,t)\, \mathrm{d}x \right|^2 \tag{1.71}$$

is the *density of probability* that at time t the system is in a continuum state of wave number k. The *probability* $P(t)$ of a transition to a group of continuum states with wave numbers distributed between a certain value k_1 and a certain value k_2 is therefore obtained by integrating $P_{ka}(t)$ over k:

$$P(t) = \int_{k_1}^{k_2} P_{ka}(t)\, \mathrm{d}k. \tag{1.72}$$

Note 1:   In many applications, the relation between the eigenenergy E_k and the wave number k is the same as for a free particle,

$$E_k = \hbar^2 k^2 / (2m), \tag{1.73}$$

where m is the mass of the particle (see Appendix A). Note that the relation between the wave number and the energy of the state is not a one-to-one relation. In 1D, a continuum state of energy E_k can be the eigenstate of H_0 with the positive wave number $k = (2mE_k/\hbar^2)^{-1/2}$, or the eigenstate with the negative wave number $k = -(2mE_k/\hbar^2)^{-1/2}$, or a linear combination of these two eigenstates. To avoid ambiguities, we consider a transition to a state of specific *wave number* (or wave vector), not to a state of specific *energy*.

Note 2:   In 1D, positive and negative wave numbers correspond to opposite directions of propagation of the particle. In 3D, this direction is defined by the polar angles of the wave vector characterizing the state, not by the sign of the wave number (in 3D the wave number is the norm of the wave vector and is always positive).

Note 3:   We assume here that the continuum eigenfunctions $\psi_k(x)$ are normalized in such a way that

$$\int_{-\infty}^{\infty} \psi_{k'}^*(x)\,\psi_k(x)\,\mathrm{d}x = \delta(k - k'), \tag{1.74}$$

as is explained in Appendix A.

We had seen in Section 1.6 that for a harmonic perturbation of angular frequency ω, the probability of transition from a bound state a to a bound state b is particularly large when the energies of these two states differ exactly, or almost exactly, by $\hbar\omega$. In terms of maths, the reason for this large probability was the tall and narrow peak the function $F(t, \omega_{ba} - \omega)$ develops at $\omega = \omega_{ba}$ for increasing values of t. As the behaviour of this function does not depend on whether b is a bound state or a continuum state, we should expect that the density of probability $P_{ka}(t)$ is also strongly peaked around the value(s) of k at which $E_k \approx E_\mathrm{f}$, where

$$E_\mathrm{f} = E_a + \hbar\omega. \tag{1.75}$$

If so, the transition probability $P(t)$ may be significant only if the energy E_f does match the energy of some of the continuum states with wave number in the interval (k_1, k_2). Let us suppose that it does, i.e., that there is a wave number $k_\mathrm{f} \in (k_1, k_2)$ such that $E_k = E_\mathrm{f}$ at $k = k_\mathrm{f}$. Then, to first order in the perturbation, one finds that for t large enough,

$$P(t) \approx \frac{2\pi}{\hbar}\,\rho_{1\mathrm{D}}(E_\mathrm{f})\,|A_{k_\mathrm{f}a}^\dagger|^2\,t \tag{1.76}$$

for t large enough (the calculation is done in Note 5 below.) In this equation,

$$A^{\dagger}_{k_{\mathrm{f}}a} = \int_{-\infty}^{\infty} \psi^{*}_{k_{\mathrm{f}}}(x) A^{\dagger} \psi_{a}(x)\, \mathrm{d}x \qquad (1.77)$$

and

$$\rho_{\mathrm{1D}}(E_{\mathrm{f}}) = \left. \frac{\mathrm{d}k}{\mathrm{d}E_{k}} \right|_{E_{k}=E_{\mathrm{f}}}. \qquad (1.78)$$

The function $\rho_{\mathrm{1D}}(E_{k}) = \mathrm{d}k/\mathrm{d}E_{k}$ is called the density of states. If the wave number k and the energy E_{k} are related through Eq. (1.73), then, as a function of E_{k}, $k = (2mE_{k}/\hbar^{2})^{1/2}$ and $\rho_{\mathrm{1D}}(E_{k}) = [m/(2\hbar^{2}E_{k})]^{1/2}$.

Note 4: The reason for the name "density of states" can be more easily understood if one remembers that the continuum eigenfunctions $\psi_{k}(x)$ are uniquely identified by the wave number k. In a sense, the faster k varies with E, the denser the continuum states are on the energy scale. The relation between $\rho_{\mathrm{1D}}(E)$ and the concept of a density of states is clarified in Appendix C, where Eq. 1.76) is derived using box-normalized wave functions.

The subscript 1D emphasizes that Eq. (1.78) applies only to the 1D case. The equation defining the corresponding density of states in 3D is similar but different. See Appendix D for more information about this point.

Note 5: Here is a derivation of Eq. (1.76). We start by calculating the wave function $\Psi(x, t)$ to first order in H', proceeding in the same way as in Section 1.6. In view of Eqs. (1.15), (1.55) and (1.61), this yields

$$P^{(1)}(t) \approx \frac{2}{\hbar^{2}} \int_{k_{1}}^{k_{2}} |A^{\dagger}_{ka}|^{2}\, F(t, \omega_{ka} - \omega)\, \mathrm{d}k, \qquad (1.79)$$

with

$$A^{\dagger}_{ka} = \int_{-\infty}^{\infty} \psi^{*}_{k}(x) A^{\dagger} \psi_{a}(x)\, \mathrm{d}x. \qquad (1.80)$$

and

$$\omega_{ka} = \frac{E_{k} - E_{a}}{\hbar}. \qquad (1.81)$$

We now make use of the fact that when t is large enough the function $F(t, \omega_{ka} - \omega)$ is strongly peaked at $\omega_{ka} - \omega = 0$. Therefore, (i) only the wave numbers k close to k_{f} significantly contribute to the integral (we assume that $k_{1} < k_{\mathrm{f}} < k_{2}$, and, by definition of k_{f}, $\omega_{ka} - \omega \approx 0$ when $k \approx k_{\mathrm{f}}$); and (ii) as a function of k the matrix element $A^{\dagger}_{ka}$ varies more slowly than the function $F(t, \omega_{ka} - \omega)$ when $k \approx k_{\mathrm{f}}$. Hence, for t large enough,

$$P(t) \approx \frac{2}{\hbar^2} |A_{k_\mathrm{f}a}|^2 \int_{k_1}^{k_2} F(t, \omega_{ka} - \omega) \, \mathrm{d}k. \tag{1.82}$$

As $F(t, \omega_{ka} - \omega)$ depends on k only through the energy E_k, we transform the integral over k into an integral over E_k. Since $\mathrm{d}k = \rho_{1\mathrm{D}}(E_k) \, \mathrm{d}E_k$,

$$P(t) \approx \frac{2}{\hbar^2} |A_{k_\mathrm{f}a}^\dagger|^2 \int_{E_{k_1}}^{E_{k_2}} F(t, \omega_{ka} - \omega) \, \rho_{1\mathrm{D}}(E_k) \, \mathrm{d}E_k \tag{1.83}$$

if we assume that k is a monotonical function of E_k over the interval (k_1, k_2). Like $|A_{ka}^\dagger|^2$, $\rho_{1\mathrm{D}}(E_k)$ is almost constant in the range of energies which significantly contributes to the integral. Hence

$$P(t) \approx \frac{2}{\hbar^2} |A_{k_\mathrm{f}a}^\dagger|^2 \, \rho_{1\mathrm{D}}(E_\mathrm{f}) \int_{E_{k_1}}^{E_{k_2}} F(t, \omega_{ka} - \omega) \, \mathrm{d}E_k. \tag{1.84}$$

Now, we recognize that because $F(t, \omega_{ka} - \omega) \approx 0$ unless $E_k \approx E_\mathrm{f}$, we can replace the integral

$$\int_{E_{k_1}}^{E_{k_2}} F(t, \omega_{ka} - \omega) \, \mathrm{d}E_k$$

by the integral

$$\int_{-\infty}^{\infty} F(t, \omega_{ka} - \omega) \, \mathrm{d}E_k.$$

This substitution is a mere mathematical trick. Although it extends the range of integration to unphysical values of E_k, it has not implication for the Physics of the problem. However, it makes it possible to use the fact that

$$\int_{-\infty}^{\infty} F(t, \omega_{ka} - \omega) \, \mathrm{d}E_k = \pi \hbar t \tag{1.85}$$

to complete the calculation. (This integral cannot be worked out by elementary methods. The result quoted can be established by contour integration, a method of Complex Analysis taught in the Maths Workshops module and in some modules offered by the Maths Department. The proof is outside the scope of the course).

Eq. (1.76) is a statement of Fermi's Golden Rule for these 1D systems. This important result calls for several comments:

- The "rule" set by this equation is a recipe for calculating a transition probability: In order to calculate the probability of a transition from the initial bound state a to a final unbound state with wave vector close or equal to k_f, (1) calculate the relevant transition matrix element $A_{k_\mathrm{f}a}^\dagger$, (2) multiply $|A_{k_\mathrm{f}a}^\dagger|^2$ by the density of states $\rho_{1D}(E_k)$ at $E_k = E_\mathrm{f}$, and (3) multiply this product by $2\pi t/\hbar$.

- Eq. (1.76) is the rule for a 1D system. The rule for a 3D system is similar but is not covered in the course. More details about the 3D rule and an example of application can be found in Appendix D, which is not examinable.

- As Eq. (1.76) results from a perturbative calculation, it is valid only to the extent that $P(t) \ll 1$. In particular, it does not hold when the time t is so large that $P(t) \approx 1$. Eq. (1.76) is not accurate either for very short times (i.e., immediately after the perturbation has started acting).

- For t large enough, the density of probability $P_{ka}(t)$ is so strongly peaked at $k = k_{\mathrm{f}}$ that only wave numbers $k \approx k_{\mathrm{f}}$ contribute significantly to the integral over k defining the probability $P(t)$. This is why the probability given by Eq. (1.76) does not depend on the width of the integration interval (k_1, k_2). However, Eq. (1.76) holds only if $k_1 < k_{\mathrm{f}} < k_2$. In the condition where this equation applies, a transition to continuum states with energy differing much from E_{f} would be very improbable.

- Eq. (1.76) predicts that the probability $P(t)$ varies linearly in time, not like t^2 or a $\sin^2$ function as we found in Section 1.6 for bound-bound transitions.[2] Owing to this linear dependence, the rate of transition,

$$R \equiv \frac{\mathrm{d}P}{\mathrm{d}t}, \tag{1.86}$$

is constant when Eq. (1.76) holds. (A rate of transition is the probability of transition per unit time.)

Note 6:   An alternative formulation of the Golden Rule is to say that

$$R_{ka} \approx \frac{2\pi}{\hbar} \rho_{1\mathrm{D}}(E_k) \, |A^{\dagger}_{ka}|^2 \, \delta(E_k - E_{\mathrm{f}}) \tag{1.87}$$

is the rate of transition from state a to a final state of wave number k and energy E_k.

Note 7:   An example of application of this formalism is provided in Appendix D, where the Born approximation for the scattering cross section is derived from Fermi's Golden Rule.

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[2]Mathematically, the difference arises from the fact that the probability for a transition to a *bound state b* is proportional to the *function $F(t, \omega_{ba} - \omega)$*, whereas the probability $P(t)$ for a transition to a *range of continuum states* is proportional to the *integral* of this function.