Chapter 1

The interaction of radiation with matter

1.1 Reading

In preparing this lecture I have closely followed the following literature:

1. J. D. Jackson, *Classical Electrodynamics*, second edition, John Wiley & Sons, New York, 1975, section 12.1, pages 572 - 575.
2. C. Cohen-Tannoudji, B. Diu, and F. Laloë, *Quantum Mechanics*, vol. 2, John Wiley & Sons, New York, 1970, Complement $\mathrm{A}_{\mathrm{XIII}}$.
3. J. J. Sakurai, *Advanced Quantum Mechanics*, Addison-Wesley, Reading, Massachusetts, 1967, chapter 2.

1.2 Spectroscopy

Spectroscopy is concerned with investigating the properties of matter by studying the matter's *absorption* and *emission spectra*. In the case of emission a particle is emitted, and this could be, e.g., a photon, electron, α-particle, muon, etc. Both absorption and emission necessitate a transition between two quantum mechanical states, from a lower-energy state to a higher-energy state in absorption and vice versa in emission. In the emission case it is necessary to first prepare the quantum mechanical system in an excited state. Thus, in both emission and absorption spectroscopy a transition is needed from a lower-energy to a higher-energy state, and this transition is induced the interaction of the quantum mechanical system with an elementary particle such as a photon or an electron. More exotic particles – such as positrons or muons – also may play an important role, for example in the emission and absorption spectra observed in astronomy. Sometimes they are also used in man-made spectroscopy.

In a spectroscopy experiment a *spectrum* is recorded. Spectrum is Latin for *appearance* or *apparition* and came into use in the 17th century for describing what is observed when white light is shone onto a prism as in Figure 1.1. Since then the term has become used in a more general sense. In the physical sciences it is used for describing the outcome of a measurement in which one investigates, which (eigen)values an observable can assume as a result of an interaction. The most commonly measured observable is energy (which is equivalent to measuring a wavelength or wave number), but also other observables, such as momentum or mass, play an important role. A couple of examples for different spectra are provided in Figure 1.2.

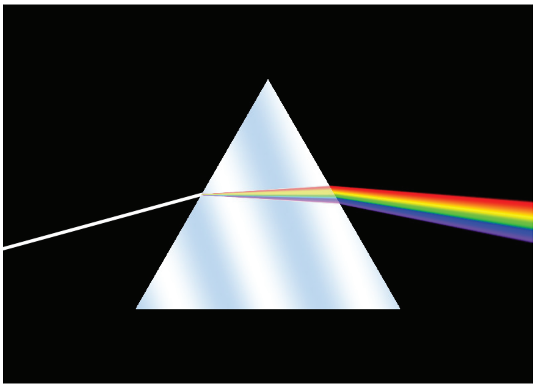

Figure 1.1: The spectrum of white light observed with a prism. The image is fetched from the article on *Spectrum Analysis* on www.wikipedia.org.

1.3 The interaction of radiation with matter

Essentially, radiation can interact with matter in two ways: it can be scattered (and diffracted), and it can induce quantum mechanical transitions in the particles, nuclei, atoms, and molecules it interacts with. Diffraction is extremely important for the determination of the structural properties of matter; however, we are not concerned with it here. What we are interested in is light-induced transition from one eigenstate of the investigated system to another (and possibly further subsequent transitions given rise to by the first transition). A very simple (and unrealistic) such system with only two eigenstates is depicted in Figure 1.3. In the simplest approximation, the initial state and the final state are considered to be eigenstates of the same Hamiltonian; in general, this is not correct for other processes than purely scattering processes: normally, the Hamiltonian of the system in the final state is different from that of the initial state. Luckily, one most often can expand the eigenstates of the new Hamiltonian in terms of those of the old Hamiltonian, and, typically, there is a strong correlation between a particular eigenstate of the old Hamiltonian and one of the new Hamiltonian. During the course we will consider more explicitly the expansion of the eigenstates of the new Hamiltonian in terms of the eigentstates of the old Hamiltonian for the case of photoemission.

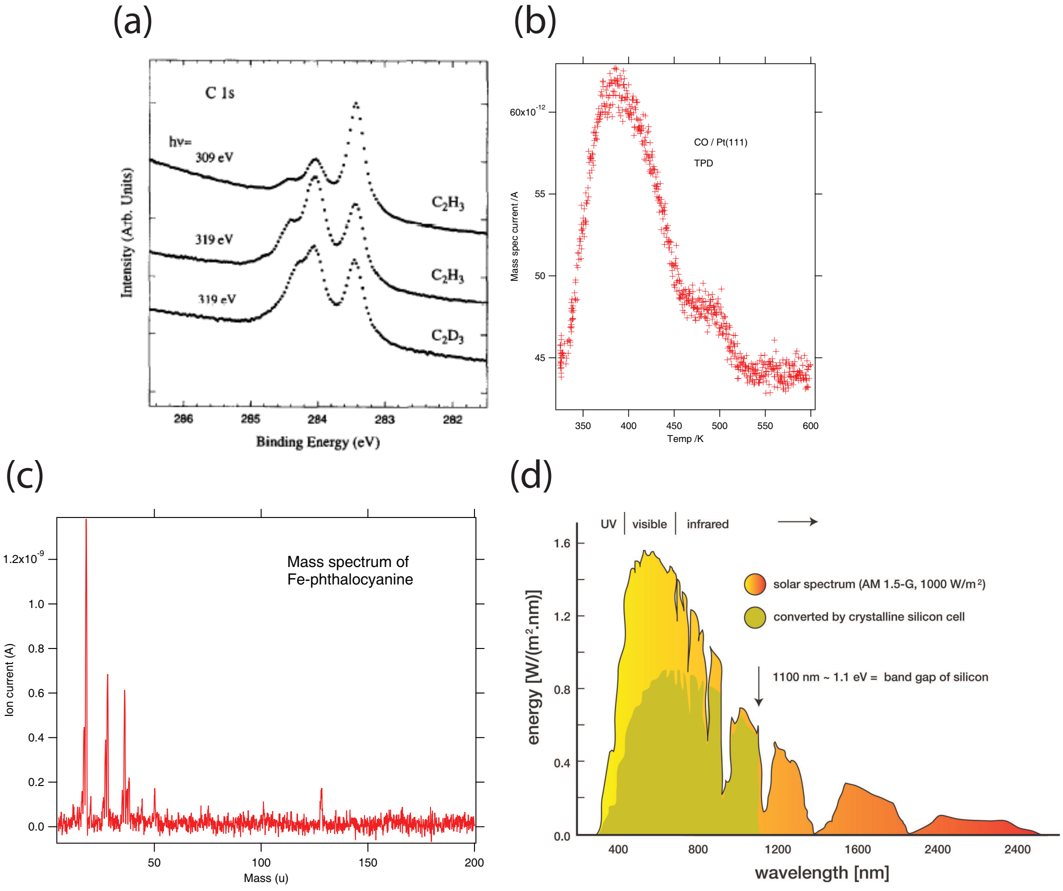

Figure 1.2: Some examples of spectra: (a) photoelectron spectrum (from J. N. Andersen, A. Beutler, S. L. Sorensen, R. Nyholm, B. Setlik and D. Heskett, Chem. Phys. Lett. **269** 371 (1997)), (b) thermal desorption spectrum for carbon monoxide on Pt(111), (c) mass spectrum of iron-phthalocyanine, (d) solar emission spectrum (from American Institute of Physics, http://www.vicphysics.org/events/stav2005.html).

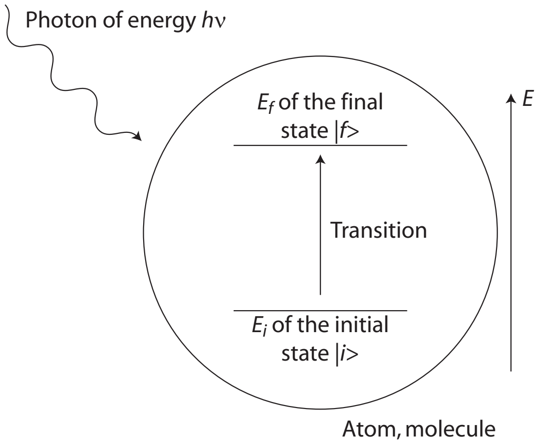

Figure 1.3: Highly idealised atomic system with only two eigenstates interacting with light, which induces a transition between these eigenstates. Note that the transition also could be from the high to the low energy state accompanied by the emission of a particle (photon, electron).

1.4 The Hamiltonian of a particle interacting with radiation

What we are interested in is the quantum mechanics of a charged particle interacting with radiation. What we will do is to first formulate a description of the electromagnetic field (section 1.4.1), then to describe a free charged particle (section 1.4.2), and finally put these two together in order to describe the interaction of the charged particle with the electromagnetic field (section 1.4.3).

1.4.1 Description of the electromagnetic field

The simplest assumption that we can make for the nature of the electromagnetic wave is that it is a plane wave, and in many experiments this is a very good approximation. In this section we will have a look at how the assumption of a plane wave is motivated by classical electrodynamics.

The starting point for describing the electromagnetic field are Maxwell's equations, and here I give them for radiation in vacuum:

$$\nabla \times \boldsymbol{B} = \mu_0 \varepsilon_0 \frac{\partial \boldsymbol{E}}{\partial t} + \mu_0 \boldsymbol{j} \text{ (Ampère's law)} \tag{1.1}$$

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \text{ (Faraday's law)} \tag{1.2}$$

$$\nabla \boldsymbol{B} = 0 \text{ (Solenoidality of the B-field)} \tag{1.3}$$

$$\nabla \boldsymbol{E} = \frac{\varrho}{\varepsilon_0} \text{ (Coulomb's law),} \tag{1.4}$$

where, of course, j and ϱ are the electrical current and charge densities, respectively.

Mathematically, things can be made easier by the introduction of a vector potential $\boldsymbol{A}$:

$$\boldsymbol{B} = \nabla \times \boldsymbol{A}. \tag{1.5}$$

The existence of such a vector potential is implied by equation (1.3), since $\nabla(\nabla \times \boldsymbol{A}) = (\nabla \times \nabla)\boldsymbol{A} = 0$. Faraday's law (1.2) then leads to

$$\nabla \times \boldsymbol{E} = -\frac{\partial}{\partial t}(\nabla \times \boldsymbol{A}) \Leftrightarrow \nabla \times \left\{ \boldsymbol{E} + \frac{\partial}{\partial t}\boldsymbol{A} \right\} = 0. \tag{1.6}$$

The last equation in turn implies that there exists a scalar potential U (essentially in the same way as for the vector potential) so that

$$\boldsymbol{E} + \frac{\partial}{\partial t}\boldsymbol{A} = -\nabla U, \tag{1.7}$$

and hence one ends up with the following expressions for the $\boldsymbol{B}$ and $\boldsymbol{E}$ fields[1]:

$$\boldsymbol{B} = \nabla \times \boldsymbol{A}, \tag{1.8}$$

$$\boldsymbol{E} = -\nabla U - \frac{\partial \boldsymbol{A}}{\partial t}. \tag{1.9}$$

Instead of the potential pair $(\boldsymbol{A}, U)$ consider now the pair

$$\boldsymbol{A}' = \boldsymbol{A} + \nabla \chi, \tag{1.10}$$

$$U' = U - \frac{\partial \chi}{\partial t}. \tag{1.11}$$

First of all, this pair fulfills equations (1.8) and (1.9) equally well as the original pair. Second, there are some particularly useful choice of χ. One such choice is

$$\frac{\partial \chi}{\partial t} = U, \tag{1.12}$$

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[1] In Gaussian units equation (1.9) becomes $\boldsymbol{E} = -\nabla U - \frac{1}{c}\frac{\partial \boldsymbol{A}}{\partial t}$.

which means that $U' = 0$. Another very useful choice is

$$U = \frac{\varepsilon_0}{4\pi} \int \frac{\rho(\boldsymbol{x}', t)}{|\boldsymbol{x} - \boldsymbol{x}'|} d^3x', \tag{1.13}$$

which implies

$$\nabla^2 U = -\varepsilon_0 \rho \tag{1.14}$$

and thus, due to equation (1.9) together with Coulomb's law (1.4),

$$\nabla \boldsymbol{A} = 0. \tag{1.15}$$

This is the so-called transversality condition.

Already here I want to point out that the vector potential $\boldsymbol{A}$ and the scalar potential U together form a relativistic four-vector potential

$$A^\alpha = (U, \boldsymbol{A}) \,. \tag{1.16}$$

Now we choose $U = 0$ (since we know that there exists a χ that allows us to do so) and

$$\boldsymbol{A} = \frac{E_0}{2i\omega} \boldsymbol{e_z} e^{i(ky-\omega t)} + i \frac{E_0}{2\omega} \boldsymbol{e_z} e^{-i(ky-\omega t)}. \tag{1.17}$$

Note that this particular vector field also fulfills the transversality condition $\nabla \boldsymbol{A} = 0$. If we require

$$\frac{E_0}{B_0} = \frac{\omega}{k} = c, \tag{1.18}$$

and use equations (1.8) and (1.9) we end up with the situation depicted in Figure 1.4, i.e.,

$$\boldsymbol{E} = E_0 \boldsymbol{e_z} \cos(ky - \omega t), \tag{1.19}$$

$$\boldsymbol{B} = B_0 \boldsymbol{e_x} \cos(ky - \omega t). \tag{1.20}$$

1.4.2 The classical Hamiltonian of a charged particle

While we described the electromagnetic field in the last section, we now turn to the description of a particle with charge q. We start out with the free particle, which will be inserted into an electromagnetic field in section 1.4.3. The easiest way towards formulating the Hamiltonian is via Lagrangian dynamics. If you are not familiar with this formulation of mechanics or with the four-vector formulation of special relativity, you just may accept the results.

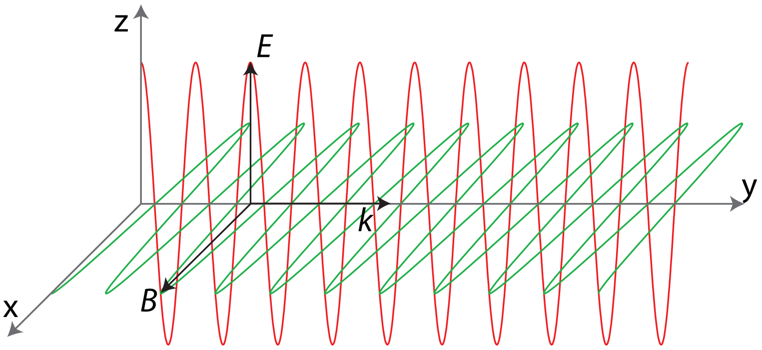

Figure 1.4: Coordinate system for the plane electromagnetic wave.

The equations of motion for a particle with charge q in and external electromagnetic field ($\boldsymbol{E}$,$\boldsymbol{B}$) are

$$\frac{d\boldsymbol{p}}{dt} = q\left\{\boldsymbol{E} + \frac{1}{c}\boldsymbol{v} \times \boldsymbol{B}\right\}, \tag{1.21}$$

$$\frac{d\mathcal{E}}{dt} = q\boldsymbol{v}\boldsymbol{E} \tag{1.22}$$

($\mathcal{E}$ is the energy and not the absolute value of the E-field; note that I here used Gaussian units instead of SI ones as in the preceding section). These equations we now want to write in a covariant (relativistic) form using four-vectors. To this end, I'll first recall a couple of definitions, starting with the contravariant four-velocity vector of the charged particle[2]:

$$V^\alpha = (\gamma c, \gamma\boldsymbol{v}) = \left(\frac{\mathcal{E}}{mc}, \frac{\boldsymbol{p}}{m}\right) = \frac{p^\alpha}{m}. \tag{1.23}$$

This implies

$$V_\alpha = (\gamma c, -\gamma\boldsymbol{v}) \tag{1.24}$$

for the covariant four-velocity. Furthermore, the field tensor combining the $\boldsymbol{E}$- and $\boldsymbol{B}$- fields is

$$F^{\alpha\beta} = \begin{pmatrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & -B_z & B_y \\ E_y & B_z & 0 & -B_x \\ E_z & -B_y & B_x & 0 \end{pmatrix}. \tag{1.25}$$

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[2] In special relativity one works with two forms of four-vectors, the contravariant and covariant four-vectors. If a contravariant four-vector is given by $A^\alpha = (A_0, A_1, A_2, A_3)$, then its covariant counterpart is given by $A_\alpha = (A_0, -A_1, -A_2, -A_3)$. The scalar product of two four-vectors is given by $A^\alpha B_\alpha \equiv \sum_\alpha A^\alpha B_\alpha$, and you see that it is convention to omit the sum symbol.

We also need the differential of the "proper" time τ

$$d\tau = \frac{dt}{\gamma}, \tag{1.26}$$

where

$$\gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}. \tag{1.27}$$

Finally recall that

$$\mathcal{E} = \gamma mc^2 \tag{1.28}$$

(probably the best-known physical formula, although it normally is written combining γ and the rest mass m into the relativistic mass m_r and hence $\mathcal{E} = m_r c^2$). Using these formulas one can arrive at

$$\frac{dV^\alpha}{d\tau} = \frac{q}{mc} F^{\alpha\beta} V_\beta. \tag{1.29}$$

Remember that $A^\alpha B_\alpha \equiv \sum_\alpha A^\alpha B_\alpha$ when you have the same index once in the top (contravariant vector) and once in the bottom position (covariant vector). Likewise, $F^{\alpha\beta}V_\beta \equiv \sum_\beta F^{\alpha\beta}V_\beta$. The equation of motion (1.29) describes the motion of a charged particle in an external electromagnetic field, i.e., in a radiation field. In principle, the Hamiltonian can be derived directly from it; however, it is much easier to take the route via Lagrangian dynamics.

The motion of the particle is determined by the principle of least action, which means that the action

$$A = \int_{t_1}^{t_2} L dt = \int_{\tau_1}^{\tau_2} \gamma L d\tau \tag{1.30}$$

should be an extremum. Here $L = \varepsilon_{kin} - \varepsilon_{pot}$ is the Lagrangian. ε_{kin} and ε_{pot} are the kinetic and potential energies, respectively. The Lagrangian is a functional of the generalised co-ordinates q and their derivatives $\dot{q}$. A has to be invariant under a Lorentz transformation (in other words, it must be a Lorentz scalar). From (1.30) one sees that if A is a invariant under a Lorentz transformation, also γL must be invariant due to the invariance of $d\tau$.

Starting with a free particle, the Lagrangian L_{free} cannot depend on the particle's position, but it may be a function of the velocity and the mass. Thinking about which function of the velocity V_α is invariant under Lorentz transformations, there is only one possibility, namely $V_\alpha V^\alpha = c^2$. Thus $\gamma L_{\text{free}} \propto V_\alpha V^\alpha$ or $L_{\text{free}} \propto V_\alpha V^\alpha/\gamma = c^2/\gamma$. We now make an educated guess for the Lorentzian of the free particle and afterwards we check its validity by using the Euler-Lagrange equations of motion

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0. \tag{1.31}$$

In our case of a free charged particle the generalised coordinates $(q_i, \dot{q}_i)$ can be identified with $((x, y, z), (v_x, v_y, v_z))$. Now the guess is

$$L_{\text{free}} = -mc^2\sqrt{1 - \frac{v^2}{c^2}}. \tag{1.32}$$

Since L_{free} does not explicitly depend on x, y, z, it is clear that $\frac{\partial L}{\partial x} = 0$ and the same for the other co-ordinates. Furthermore $\frac{\partial L}{\partial v_x} = \gamma m v_x c^2$ and hence

$$\frac{d}{dt}\frac{\partial L}{\partial v_x} = c^2\frac{d}{dt}\gamma m v_x = 0,$$

which leads to

$$\frac{d}{dt}\gamma m\boldsymbol{v} = 0. \tag{1.33}$$

This is entirely correct, since $\gamma m v$ is the mechanical momentum p of the free particle (remember that γm is the relativistic mass), and hence (1.32) was the right guess for the Lagrangian of the free particle.

1.4.3 Description of the charged particle interacting with an electromagnetic field

Now we can turn from the free particle to the particle in an electromagnetic field. The Lagrangian will contain two terms: the free particle Lagrangian from equation (1.32) plus an particle – electromagnetic field interaction term L_{int}, and the latter will have to be related to the potential energy of the particle, since the non-relativistic Lagrangian is composed of the kinetic energy T and the potential energy V as $L = T - V$. Of course we know that the potential energy of the only slowly moving particle in the electromagnetic field is qU, and in the non-relativistic limit L_{int} will reduce to $-qU$. In connection with equation (1.16) I mentioned that U is the zeroth component of the four-potential A^α. Hence we expect γL_{int} to involve A^α. We also know that it must be a scalar and thus we should multiply it with either the momentum or position vector of the particle, since these are the only ones at hand for describing the particle[3]. One more educated guess leads to

$$L_{\text{int}} = -\frac{q}{\gamma c} V_\alpha A^\alpha = -qU + \frac{q}{c}\boldsymbol{vA}. \tag{1.34}$$

The total Lagrangian is thus

$$L = L_{\text{free}} + L_{\text{int}} = -mc^2\sqrt{1-\frac{v^2}{c^2}} + \frac{q}{c}\boldsymbol{vA} - qU. \tag{1.35}$$

Let us check, using (1.31), that this indeed leads to the Lorentz force equation (1.21). We have to calculate $\frac{\partial L}{\partial x_i}$ and $\frac{d}{dt}\frac{\partial L}{\partial x_i}$ for $i = x, y, z$ and find the following:

$$\frac{\partial L}{\partial x_i} = \frac{q}{c}\boldsymbol{v}\frac{\partial \boldsymbol{A}}{\partial x_i} - q\frac{\partial U}{\partial x_i}, \tag{1.36}$$

$$\frac{\partial L}{\partial v_i} = \gamma m v_i + \frac{q}{c}A_i = p_i + \frac{q}{c}A_i \equiv P_i. \tag{1.37}$$

Note that in the last equation the $\gamma m v_i$ is the *mechanical* momentum, which is different from the *conjugate* (or canonical) momentum P.[4] We have to calculate the time derivative of $\frac{\partial L}{\partial v_i}$. In this calculation we will need

$$\boldsymbol{v}\times\boldsymbol{B} = \boldsymbol{v}\times(\nabla\times\boldsymbol{A}) = \begin{pmatrix} v_y\partial_x A_y - v_y\partial_y A_x - v_z\partial_z A_x + v_z\partial_x A_z \\ v_z\partial_y A_z - v_z\partial_z A_y - v_x\partial_x A_y + v_x\partial_y A_x \\ v_x\partial_z A_x - v_x\partial_x A_z - v_y\partial_y A_z + v_y\partial_z A_y \end{pmatrix}, \tag{1.38}$$

where I have used ∂_i $(i = x, y, z)$ as abbreviation for $\frac{\partial}{\partial x_i}$. You also should recall equations (1.8) and (1.9), the expressions for the $\boldsymbol{B}$- and $\boldsymbol{E}$-fields in terms of $\boldsymbol{A}$ and U, as well as

$$\frac{d}{dt} = dt\frac{\partial}{\partial t} + \sum_i \frac{dx_i}{dt}\frac{\partial}{\partial x_i} = dt\frac{\partial}{\partial t} + \sum_i v_i\frac{\partial}{\partial x_i}. \tag{1.39}$$

Altogether, this gives

$$\frac{d}{dt}\frac{\partial L}{\partial v_i} = \frac{dp_i}{dt} + \frac{q}{c}\left\{\frac{\partial A_i}{\partial t} + \sum_j \frac{\partial A_i}{\partial x_j}v_j\right\}, \tag{1.40}$$

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[3] Jackson argues that the Lagrangian must be Lorentz- and translationally invariant and that thus the Lagrangian cannot involve the co-ordinates explicitly. However, A^α *must* be explicitly position-dependent, since otherwise $\nabla\times\boldsymbol{A} = 0$ and hence $\boldsymbol{B} = 0$. In contrast, $\boldsymbol{A}$ cannot be explicitly dependent on the velocity of the particle.

[4] As a little side remark: the fact that $\frac{\partial L}{\partial \dot{q}_i} = P$ together with the form of the Euler-Lagrange equations (1.31) reveals that those equations are nothing else than generalised equations of motion with a generalised force $\frac{d}{dt}\frac{\partial L}{\partial q_i}$ and generalised co-ordinates and velocities q_i and $\dot{q}_i$.

and hence using the Euler-Lagrange equations (1.31)

$$\frac{d}{dt}\left(\frac{\partial L}{\partial v_i}\right)-\frac{\partial L}{\partial x_i}=\frac{dp_i}{dt}+\frac{q}{c}\left\{\frac{\partial A_i}{\partial t}+\sum_j\left(\frac{\partial A_i}{\partial x_j}v_j-\frac{\partial A_j}{\partial x_i}v_j\right)\right\}+q\frac{\partial U}{\partial x_i}=0. \tag{1.41}$$

Bringing the latter two terms onto the right-hand side of the equation and reordering leads to

$$\frac{dp_i}{dt}=q\left\{-\frac{1}{c}\frac{\partial A_i}{\partial t}-\frac{\partial U}{\partial x_i}\right\}-\frac{q}{c}\left\{\sum_j\left(\frac{\partial A_i}{\partial x_j}v_j-\frac{\partial A_j}{\partial x_i}v_j\right)\right\} \tag{1.42}$$

According to equation (1.9) the first term is the i-th component of $e\boldsymbol{E}$. Concerning the second term you either see with an eagle's eye that it indeed corresponds to the magnetic field part of the Lorentz force (1.21) or you calculate the components of this vector and use equation (1.38) to find the equality.

We now come to the final step in assembling the Hamiltonian of the particle in an electromagnetic field. In this step we insert the Lagrangian (1.35) into the expression for the Hamiltonian

$$H=\boldsymbol{P}\boldsymbol{v}-L \tag{1.43}$$

(note that we use the conjugate momentum P!) and make a transition to the independent variables $(\boldsymbol{P},\boldsymbol{x})$ instead of $(\boldsymbol{v},\boldsymbol{x})$ as in the Lagrangian. From (1.37) it can be shown that

$$\boldsymbol{v}=\frac{c\boldsymbol{P}-q\boldsymbol{A}}{\sqrt{\left(\boldsymbol{P}-\frac{q\boldsymbol{A}}{c}\right)+m^2c^2}}. \tag{1.44}$$

It is not straightforward to derive this expression; however, the validity is, however, easily shown by substituting (1.44) into (1.37). We go on by replacing $\boldsymbol{v}$ in (1.43):

$$\begin{aligned}H=&\frac{c\boldsymbol{P}^2-q\boldsymbol{A}\boldsymbol{P}}{\sqrt{\left(\boldsymbol{P}-\frac{q}{c}\boldsymbol{A}\right)^2+m^2c^2}}+mc^2\sqrt{1-\frac{(c\boldsymbol{P}-q\boldsymbol{A})^2}{c^2\left(\boldsymbol{P}-\frac{q}{c}\boldsymbol{A}\right)^2+m^2c^4}}-\\&-\frac{q\boldsymbol{A}\boldsymbol{P}-\frac{q^2}{c}\boldsymbol{A}^2}{\sqrt{\left(\boldsymbol{P}-\frac{q}{c}\boldsymbol{A}\right)^2+m^2c^4}}+qU.\end{aligned} \tag{1.45}$$

The first and the third term together yield

$$\frac{c\left(\boldsymbol{P} - \frac{q}{c}\boldsymbol{A}\right)^2}{\sqrt{\left(\boldsymbol{P} - \frac{q}{c}\boldsymbol{A}^2\right)^2 + m^2c^2}},$$

while the second term can be rewritten to

$$\frac{m^2c^3}{\sqrt{\left(\boldsymbol{P} - \frac{q}{c}\boldsymbol{A}\right)^2 + m^2c^2}}.$$

Putting these terms and the potential together leads to

$$H = \sqrt{\left(c\boldsymbol{P} - q\boldsymbol{A}\right)^2 + m^2c^4} + qU = \sqrt{c^2\boldsymbol{p}^2 + m^2c^4} + qU. \tag{1.46}$$

This is nothing else than the relativistic energy! So if we beforehand had known that we have to replace the mechanical momentum $\boldsymbol{p}$ by an expression containing the canonical momentum $\boldsymbol{P} = \boldsymbol{p} + \frac{q}{c}\boldsymbol{A}$ than we could have arrived much faster at equation (1.46).

We have to make one further step, however, in order to fully derive the commonly used Hamiltonian for a non-relativistic particle interacting with an electromagnetic field. In the non-relativistic limit $\left(c\boldsymbol{P} - q\boldsymbol{A}\right)^2 \ll m^2c^4$. A taylor expansion of $\sqrt{x+y}$ around $x = 0$ gives $\sqrt{y} + \frac{1}{2\sqrt{y}}x$ and hence

$$H = mc^2 + \frac{1}{2m}\left(\boldsymbol{P} - \frac{q\boldsymbol{A}}{c}\right)^2 + qU.$$

We are just interested in the energy related to the interaction of the particle with the electromagnetic field and hence we skip the mc^2 term to yield the interaction Hamiltonian

$$H = \frac{1}{2m}\left(\boldsymbol{P} - \frac{q\boldsymbol{A}}{c}\right)^2 + qU. \tag{1.47}$$

What we are interested in is an (atomic) electron interacting with a plane electromagnetic wave. The description of the electromagnetic wave was derived in section 1.4.1. The electron will carry a spin and we thus have to include another term in the Hamiltonian, which describes the interaction of the spin magnetic moment of the electron with the magnetic field of the radiation. This we do in an *ad hoc* fashion knowing from classical mechanics that the magnetic field will try to align the magnetic moment with the field. Hence we have to introduce a scalar product $-\boldsymbol{SB}$ into the Hamiltonian. In addition, we have to introduce the central potential $V(r)$ of the atom, and we set the previous term qU to zero, as proposed in section 1.4.1 before equation (1.17). The Hamiltonian then becomes (note that I am back in the SI)

$$H = \frac{1}{2m}\left(\boldsymbol{P} - q\boldsymbol{A}\right)^2 + V(r) - \frac{q}{m}\boldsymbol{SB}. \tag{1.48}$$

This is the full Hamiltonian of a charged particle interacting with an electromagnetic field. It is quite complicated and in the following we'll now introduce different approximations which allow to extract useful information from the expression.

1.5 Electric dipole transitions

In the following we will regard the interaction of the electron (of charge q) with the electromagnetic field as a perturbation of the Hamiltonian of the electron in the central potential of the nucleus, i.e.,

$$H = H_0 + H_{\text{int}}, \tag{1.49}$$

where

$$H_0 = \frac{P^2}{2m} + V(r). \tag{1.50}$$

The separation is straightforward for the electromagnetic field described in section 1.4.1, since we have chosen $\boldsymbol{A}$ to be parallel to the z-axis and the Poynting ($\boldsymbol{k}$) vector along the y-axis. Then the only coupling terms between $\boldsymbol{P}$ and $\boldsymbol{A}$ (i.e., scalar products of $\boldsymbol{P}$ and $\boldsymbol{A}$) in an expansion of the first term in (1.48) are those between p_z and A_z, and A_z does not contain z, but only the y co-ordinate. p_z and y commute (i.e., $p_z y = y p_z$, while, e.g., $p_z z \neq z p_z$), and the expansion does not pose any problem:

$$H_{\text{int}} = -\frac{q}{m}\boldsymbol{PA} - \frac{q}{m}\boldsymbol{SB} + \frac{q^2}{2m}\boldsymbol{A}^2. \tag{1.51}$$

The very last term is quadratic in $\frac{E_0}{2\omega}$ (the amplitude occurring in (1.17)), while the first term terms are linear in $\frac{E_0}{2\omega}$. Assuming that the light intensity is sufficiently low, we skip the last term and write H_{int} as a sum of two terms

$$H_{\text{int}} = H^{I}_{\text{int}} + H^{II}_{\text{int}} \equiv -\frac{q}{m}\boldsymbol{PA} - \frac{q}{m}\boldsymbol{SB}. \tag{1.52}$$

Let's have a look at the orders of magnitude of the matrix elements $\langle\phi_1| H_{\text{int}} |\phi_2\rangle$ of the two interactions terms. We find

$$\frac{H^{II}_{\text{int}}}{H^{I}_{\text{int}}} \approx \frac{\frac{q}{m}\hbar k \frac{E_0}{\omega}}{\frac{q}{m}P\frac{E_0}{\omega}} = \frac{\hbar k}{P}, \tag{1.53}$$

since S will give a contribution of the order of $\hbar$ and the magnitude of B_0 was estimated from equation (1.18). The extension of the molecular orbitals is approximately given by the Bohr radius a_0, and the Heisenberg position – momentum uncertainty relationship then means that $\hbar/P$ is of the order of a_0. k can be calculated from the wavelength λ by virtue of $k = 2\pi/\lambda$. Typically

$$\frac{H^{II}_{\text{int}}}{H^{I}_{\text{int}}} \approx \frac{a_0}{\lambda} \ll 1. \tag{1.54}$$

$H^{II}_{\text{int}} \ll H^{I}_{\text{int}}$ is used in the so-called *electric dipole approximation* (which often is just called the *dipole approximation*). Only H^{I}_{int} is retained in the interaction Hamiltonian, and it is actually further simplified by expanding $\boldsymbol{A}$ in equation (1.17) in terms of ky, which also is much smaller than one ($ky \approx \frac{1}{\lambda}a_0$). Then $e^{iky} \approx e^{-iky} \approx 1$ and

$$\textit{Electric dipole Hamiltonian: } H^{I}_{\text{int,DA}} \equiv \left\{-\tfrac{q}{m}\boldsymbol{PA}\right\}_{\text{lowest order}} =$$

$$= \left\{-\tfrac{q}{m}P_z\left\{\tfrac{E_0}{2i\omega}e^{i(ky-\omega t)} + \tfrac{iE_0}{2\omega}e^{-i(ky-\omega t)}\right\}\right\}_{\text{lowest order}} = \tag{1.55}$$

$$= \tfrac{qE_0}{m}P_z \sin\omega t,$$

since $\sin\omega t = 1/(2i)\,(e^{i\omega t} - e^{-i\omega t})$. You might find this formulation of the *dipole* approximation strange, since the electric dipole moment of the electron $\boldsymbol{d} = q\boldsymbol{r}$ does not appear in H_{int}. One would rather expect

$$H^{I}_{\text{int,DA}} = -\boldsymbol{dE} = -E_0 qz\cos\omega t, \tag{1.56}$$

for an electric field $\boldsymbol{E} = E_0\boldsymbol{e}_z\cos\omega t$. Indeed, both formulations (1.55) and (1.56) are equivalent. One way to see the equivalency of P_z and Z (or more generally speaking of the $\boldsymbol{P}$ and $\boldsymbol{r}$ operators) in the dipole approximation can be derived from the expression for the commutator of z with the non-interacting Hamiltonian:

$$[z, H_0] = \frac{i\hbar}{m}\boldsymbol{P_z}, \tag{1.57}$$

where $H_0 = \boldsymbol{P}^2/(2m)$ and the square brackets indicate the commutator ($[A,B] \equiv AB - BA$).

$$\begin{gathered}
\langle f| P_z |i\rangle = \tfrac{m}{i\hbar} \langle f| [z, H_0] |i\rangle = \\
= \tfrac{m}{i\hbar}(\langle f| zH_0 |i\rangle - \langle f| H_0 z |i\rangle) = \tfrac{m}{i\hbar}(\langle f| zH_0 |i\rangle - \langle f| H_0^\dagger z |i\rangle) = \\
= \langle f| z |i\rangle \tfrac{m}{i\hbar}(E_i - E_f).
\end{gathered} \tag{1.58}$$

In this equation we implicitly assumed that $|f\rangle$ and $|i\rangle$ are eigenstates of the non-interacting Hamiltonian H_0. This makes senses since we finally are interested in light-induced transitions between eigenstates of our atomic or molecular system.

The same commutator appears in Ehrenfest's theorem, which relates the time development of the expectation value $\langle O\rangle \equiv \langle a| O |a\rangle$ of an operator O to the commutator of the operator with the Hamiltonian. In the special cases for the position and momentum vectors the theorem states

$$\begin{aligned}
\tfrac{d}{dt}\langle \boldsymbol{r}\rangle &= \tfrac{1}{i\hbar}\langle [\boldsymbol{r}, H]\rangle \\
\tfrac{d}{dt}\langle \boldsymbol{P}\rangle &= \tfrac{1}{i\hbar}\langle [\boldsymbol{P}, H]\rangle .
\end{aligned} . \tag{1.59}$$

In the special case of our Hamiltonian (1.49) with $H^I_{\text{int,DA}}$ given by equation (1.55) (and neglecting all other terms of H_{int}) we find

$$\begin{aligned}
\tfrac{d}{dt}\langle \boldsymbol{r}\rangle &= \tfrac{1}{i\hbar}\left\langle \left[\boldsymbol{r}, H_0 + H^I_{\text{int,DA}}\right]\right\rangle = \frac{\langle \boldsymbol{P}\rangle}{m} + \tfrac{qE_0}{m\omega}\boldsymbol{e}_z \sin\omega t \\
\tfrac{d}{dt}\langle \boldsymbol{P}\rangle &= \tfrac{1}{i\hbar}\left\langle \left[\boldsymbol{P}, H_0 + H^I_{\text{int,DA}}\right]\right\rangle = -\langle \nabla V(r)\rangle .
\end{aligned} \tag{1.60}$$

Taking the time derivative of the first of these two equations and combining with the second leads to

$$m\frac{d^2}{dt^2}\langle r\rangle = -\langle \nabla V(r)\rangle + qE_0\boldsymbol{e}_z \cos\omega t. \tag{1.61}$$

Thus the centre of the wave packet of the electron moves like a particle of mass m and charge q in the central potential of the atom (first term) and under the influence of an oscillating electric field (second term).

What have we achieved so far? We have formulated the Hamiltonian in the electric dipole approximation (1.55) and seen that it indeed is related to the electric dipole associated with the electron. In addition, we have seen that the wave packet of the electron moves as (classically) expected. Now we want to see what kind of transitions such an electric dipole Hamiltonian, i.e., the interaction of the atomic electron with radiation, can introduce between two different electron states. First, we realise that the probability density for such a transition (apart from pre-factors) is given by the *matrix element* of the interaction Hamiltonian $H^I_{\text{int,DA}}$ between the two states $|i\rangle$ and $|f\rangle$. In equation (1.58) we already were close to calculating this matrix element. From the appearance of the interaction Hamiltonian (1.55) it is clear that

$$\langle f|\, H^I_{\text{int,DA}}\, |i\rangle = \frac{qE_0}{m\omega}\sin\omega t\,\langle f|\, P_z\, |i\rangle\,. \tag{1.62}$$

By virtue of (1.58) this turns into

$$\langle f|\, H^I_{\text{int,DA}}\, |i\rangle = iq\frac{E_f - E_i}{\hbar\omega}E_0\sin\omega t\,\langle f|\, z\, |i\rangle\,. \tag{1.63}$$

If this matrix element is non-zero, the (light-induced) transition from the initial state $|i\rangle$ to the initial state $|f\rangle$ is called an *electric dipole transition* (often it is also called a *dipole-allowed transition*). Remember that $|i\rangle$ and $|f\rangle$ are eigenstates of the non-perturbed Hamiltonian, i.e., the Hamiltonian without the influence of radiation. These eigenstates can be written in terms of radial functions and spherical harmonics:

$$\begin{array}{c}\Phi_{n_i,l_i,m_i}(\boldsymbol{r}) = R_{n_i,l_i}(r)Y^{m_i}_{l_i}(\theta,\phi)\\ \Phi_{n_f,l_f,m_f}(\boldsymbol{r}) = R_{n_f,l_f}(r)Y^{m_f}_{l_f}(\theta,\phi)\end{array}, \tag{1.64}$$

where the n's are the principal quantum numbers of the initial and final states, respectively, the l's the orbital quantum numbers, and the m's the magnetic quantum numbers (since we are working with a central potential). Also the operator z occurring in the matrix element can be expressed in terms of a spherical harmonic:

$$z = r\cos\theta = \sqrt{\frac{4\pi}{3}}rY^0_1(\theta). \tag{1.65}$$

Taken together this yields for the matrix element

$$\begin{aligned}\langle f|\, H^I_{\text{int}}\, |i\rangle &= iq\tfrac{E_f-E_i}{\hbar\omega}E_0\sin\omega t\,\langle f|\, z\, |i\rangle = \\ &= iq\tfrac{E_f-E_i}{\hbar\omega}E_0\sin\omega t\int d\Omega\; Y^{m_f\,*}_{l_f}(\theta,\phi)Y^0_1(\theta)Y^{m_i}_{l_f}\int dr\;\sqrt{\tfrac{4\pi}{3}}rR^*_{n_f,l_f}R_{n_i,l_i}(r).\end{aligned} \tag{1.66}$$

It can be shown that the angular integral in the middle is different from zero if and only if[5]

$$\begin{aligned} l_f &= l_i \pm 1 \\ & \qquad . \\ m_f &= m_i \end{aligned} \tag{1.67}$$

These are the *electric dipole transition selection rules.*

The operator z occurred in the matrix element since we chose to have the polarisation of the electromagnetic wave to be parallel to the $\boldsymbol{z}$-axis. In general, this is not the case, and the polarisation may also have components in the $\boldsymbol{x}$- and $\boldsymbol{y}$-directions. Then we have to deal with a matrix element of the form $\langle f|Ax + By + Cz|i\rangle$. Since

$$x = \frac{1}{2}\sqrt{\frac{8\pi}{3}} ir \left(Y_1^2 + Y_1^{-1}\right)$$

$$y = \frac{1}{2}\sqrt{\frac{8\pi}{3}} ir \left(Y_1^2 - Y_1^{-1}\right)$$

the angular integral in (1.66) becomes

$$\int d\Omega\, Y_{l_f}^{m_f\,*}(\theta,\phi) Y_1^0(\theta) Y_{l_f}^{m_i} + (A{+}B)\int d\Omega\, Y_{l_f}^{m_f\,*}(\theta,\phi) Y_1^1(\theta) Y_{l_f}^{m_i} + (A{-}B)\int d\Omega\, Y_{l_f}^{m_f\,*}(\theta,\phi) Y_1^{-}1(\tag{1.68}$$

The first integral is different from zero only if $m_f = m_i$, the second only if $m_f = m_i + 1$, and the third if $m_f = m_i - 1$. Altogether the set of electric dipole transition selection rules becomes

$$\begin{aligned} \Delta l &= \pm 1 \\ \Delta m &= 0, \pm 1. \end{aligned} \tag{1.69}$$

As a side remark one can note that the relationship between the orientation of the polarisation and the selection rule for the magnetic quantum number m is expected, since m describes the spatial orientation of the angular momentum $\boldsymbol{L}$.

1.5.1 Higher order transitions

In the last section we completely ignored the second part of the interaction Hamiltonian H_{int}^{II} in equation (1.52) and, furthermore, we only expanded H_{int}^{I}

---

[5] In fact, $\Delta l = 1$ can be seen as the conservation of angular momentum, since the photon carries an angular momentum ±$\hbar$.

to the linear terms in E_0. Of course we can go on and retain the next smaller terms in H^I_{int} and H^{II}_{int}. For H^I_{int} this means that we take $e^{\pm iky} \approx 1 \pm iky$ or, alternatively (remember for $H^I_{\text{int,DA}}$ we took $e^{\pm iky} \approx 1$)

$$\begin{aligned} H^I_{\text{int}} - H^I_{\text{int,DA}} &= -\tfrac{q}{m} P_z \left\{ \tfrac{E_0}{2i\omega} e^{i(ky-\omega t)} + \tfrac{iE_0}{2\omega} e^{-i(ky-\omega t)} \right\} - \\ &- \tfrac{q}{m} P_z \left\{ \tfrac{E_0}{2i\omega} e^{-i\omega t} + \tfrac{iE_0}{2\omega} e^{i\omega t} \right\} \approx \\ &\approx -\tfrac{q}{n} P_z \left\{ \tfrac{E_0}{2\omega} kye^{-i\omega t} + \tfrac{E_0}{2\omega} kye^{i\omega t} \right\} = \\ &= -\tfrac{q}{m} P_z \left\{ \tfrac{B_0}{2} ye^{-i\omega t} + \tfrac{B_0}{2} ye^{i\omega t} \right\} = -\tfrac{q}{m} B_0 y \cos\omega t P_z, \end{aligned} \tag{1.70}$$

where (1.18) was used. Rewriting $P_z y$ yields

$$P_z y = \frac{1}{2}(P_z y - zPy) + \frac{1}{2}(P_z y + zp_y) = \frac{1}{2} L_x + \frac{1}{2}(P_z y + zP_y), \tag{1.71}$$

and thus

$$H^I_{\text{int}} - H^I_{\text{int,DA}} \approx -\frac{q}{2m} L_x \cos\omega t - \frac{q}{2m} B_0 (yP_z + zP_y). \tag{1.72}$$

$H^{II}_{\text{int}} = -\frac{q}{m}\boldsymbol{SB} = -\frac{q}{m} S_x B_x = -\frac{q}{m} S_x B_0 \cos{(ky - \omega t)}$ is even smaller and we just keep it to lowest order in ky, so that

$$H^{II}_{\text{int}} \approx -\frac{q}{m} S_x B_0 \cos\omega t. \tag{1.73}$$

Putting everything together we get

$$\begin{aligned} H_{\text{int}} &= H^I_{\text{int}} + H^{II}_{\text{int}} \approx \\ &\approx H^I_{\text{int,DA}} - \tfrac{q}{2m}(L_x + 2S_x) B_0 \cos\omega t - \tfrac{q}{2mc}(yP_z + zP_y) E_0 \cos\omega t \equiv \\ &\equiv H^I_{\text{int,DA}} + H^{II}_{\text{int,DM}} + H^{II}_{\text{int,QE}}, \end{aligned} \tag{1.74}$$

where DM and QE indicate that these Hamiltonians induce magnetic dipole and electric quadrupole transitions, respectively. For these one can show that the following selection rules are valid:

$$\begin{gathered}\textit{Selection rules magnetic dipole transitions:}\\ \Delta l = 0\\ \Delta m_l = 0, \pm 1\\ \Delta m_s = 0, \pm 1\\ \textit{Selection rules electric quadrupole transitions:}\\ \Delta l = 0\\ \Delta m = 0, \pm 1, \pm 2.\end{gathered} \tag{1.75}$$

1.5.2 Fermi's Golden Rule

Before we go on with the investigation of transitions in the electric dipole approximation, we need to develop a formalism for calculating the transition probabilities in the perturbation limit, i.e., for a perturbation that is small compared to the magnitude of the original Hamiltonian. In the case for a discrete state coupled to a continuum of states this will lead to an expression called "Fermi's Golden Rule".

Quite as in equation (1.49) we consider a Hamiltonian, which consists of an unperturbed part H_0 and the (generally time-dependent) interaction Hamiltonian H_{int}. We assume that H_0 has the eigenstates $|\phi_n\rangle$, i.e.,

$$H_0 |\phi_n\rangle = E_n |\phi_n\rangle \,, \tag{1.76}$$

which implies

$$\langle\phi_n|H_0|\phi_k\rangle = 0. \tag{1.77}$$

The total Hamiltonian is

$$H(t) = H_0 + H_{\text{int}}(t), \tag{1.78}$$

and we furthermore assume

$$H_{\text{int}} = \lambda W(t) \text{ with } \lambda \ll 1. \tag{1.79}$$

The matrix elements of W in the basis of the eigenstates of H_0 are then written

$$W_{nk}(t) = \langle \phi_n | W(t) | \phi_k \rangle \,. \tag{1.80}$$

The time-dependent Schrödinger equation becomes

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \{H_0 + \lambda W(t)\} |\psi(t)\rangle \,, \tag{1.81}$$

and we assume that the system shall be in the eigenstate $|\phi_i\rangle$ of H_0 prior to and at $t = 0$, i.e.,

$$|\psi(t=0)\rangle = |\phi_i\rangle \,. \tag{1.82}$$

The probability of finding the system in another eigenstate $|\phi_f\rangle$ of H_0 at time t is then

$$P_{if}(t) = |\langle \phi_f | \psi(t) \rangle|^2 \,. \tag{1.83}$$

We expand the state of the system $|\psi(t)\rangle$ in terms of the eigenstates of H_0:

$$|\psi(t)\rangle = \sum_n c_n(t) \, |\phi_n\rangle \,, \tag{1.84}$$

where

$$c_n(t) = \langle \phi_n | \psi(t) \rangle \,. \tag{1.85}$$

The Schrödinger equation can be rewritten in terms of the coefficients c_n:

$$\begin{gathered}
i\hbar \tfrac{d}{dt} |\psi\rangle = \{H_0 + \lambda W\} |\psi\rangle \Leftrightarrow \\
\Leftrightarrow i\hbar \tfrac{d}{dt} \langle \phi_n | \psi \rangle = \langle \phi_n | H_0 | \psi \rangle + \langle \phi_n | \lambda W | \psi \rangle \Leftrightarrow \\
\Leftrightarrow i\hbar \tfrac{d}{dt} c_n(t) = E_n c_n(t) + \textstyle\sum_k \langle \phi_n | \lambda W | \phi_k \rangle \langle \phi_k | \psi \rangle \Leftrightarrow \\
\Leftrightarrow i\hbar \tfrac{d}{dt} c_n(t) = E_n c_n(t) + \textstyle\sum_k \lambda W_{nk}(t) c_k(t),
\end{gathered} \tag{1.86}$$

where use was made of the closure relation $\sum_k |\phi_k\rangle\langle\phi_k| = 1$.

The simplest case of equation (1.86) is $\lambda = 0$ for all times t, i.e., the interaction stays switched off. Then the solution to the differential equations is

$$c_n(t) = b_n e^{-iE_n t/\hbar}, \tag{1.87}$$

where b_n is a constant which depends on the initial conditions. Note that (1.87) implies that the system remains in state $|\phi\rangle$ for all t, since the exponential phase term leaves the probability of finding the system in $|\phi\rangle$ unchanged.

Now assume that $\lambda \neq 0$, but $\lambda \ll 1$. It makes senses to look for solutions of (1.86) that are similar to those in (1.87),

$$c_n(t) = b_n(t) e^{-iE_n t/\hbar}. \tag{1.88}$$

We get a new Schrödinger equation for the coefficients $b_n(t)$:

$$i\hbar e^{-iE_n t/\hbar} \frac{d}{dt} b_n(t) = \sum_k \lambda W_{nk}(t) b_k(t) e^{-iE_k t\hbar}. \tag{1.89}$$

Both sides of the equation can be divided by $e^{-E_n t/\hbar}$ and this gives, after introduction of the Bohr angular frequency $\omega_{nk} = \frac{E_n - E_k}{\hbar}$,

$$i\hbar \frac{d}{dt} b_n(t) = \lambda \sum_k e^{i\omega_{nk} t} W_{nk}(t) b_k(t). \tag{1.90}$$

Since λ is small it now makes sense to expand the $b_n(t)$ in a power series in λ, i.e.

$$b_n(t) = \sum_{k=0}^{\infty} \lambda^k b_n^{(k)}(t) \approx b_n^{(0)}(t) + \lambda b_n^{(1)}(t), \tag{1.91}$$

where I have retained the zeroth and first order terms only. This is put into equation (1.90) and then the the coefficients of λ^r on both sides of the equation are set equal (we can do this since λ now is regarded as an independent variable):

$$\begin{gathered} r = 0 : \\ i\hbar \tfrac{d}{dt} b_n^{(0)}(t) = 0 \\ r \neq 0 : \\ i\hbar \tfrac{d}{dt} b_n^{(r)}(t) = \textstyle\sum_k e^{i\omega_{nk} t} W_{nk}(t) b_k^{(r-1)}(t), \end{gathered} \tag{1.92}$$

since

$$i\hbar \sum_{r=0}^{\infty} \lambda^r \frac{db_n^{(r)}}{dt} = \sum_k \sum_r e^{i\omega_{nk} t} W_{nk}(t) \lambda^{r+1} b_k^{(r)},$$

where the right-hand side does not contain a zeroth term in λ^r. Note that this equation gives a recursive solution for the $b_k^{(r)}$.

We have said before that the system shall be in state $|\phi_i\rangle$ prior to and at $t = 0$. At this point the interaction is switched on. Since the interaction remains finite, the system has time to adjust to the new Hamiltonian and the solution of the Schrödinger equation is continuous. This means that

$$\begin{aligned} & b_n(t=0)=\delta_{ni} \Rightarrow \\ & \Rightarrow b_n^{(0)}(t=0)=\delta_{ni}, b_n^{(r)}(t=0)=0(r \geq 1). \end{aligned} \tag{1.93}$$

From (1.92) one then necessarily finds

$$b_n^{(0)}(t)=\delta_{ni} \tag{1.94}$$

and, using the recursive formula,

$$i\hbar \frac{d}{dt} b_n^{(1)}(t)=\sum_k e^{i\omega_{nk}t} W_{nk}(t)\delta_{ki}=e^{i\omega_{ni}t} W_{ni}(t). \tag{1.95}$$

Integration yields

$$b_n^{(1)}(t)=\frac{1}{i\hbar}\int_0^t e^{i\omega_{ni}t'} W_{ni}(t')\, dt'. \tag{1.96}$$

The transition probability between the states $|\phi_i\rangle$ and $|\phi_f\rangle$ is (cf. (1.83), (1.87), (1.85), and (1.91))

$$\begin{aligned} P_{if}(t) &= \left|\langle\phi_f|\psi(t)\rangle\right|^2=\left|c_f(t)\right|^2=\left|b_f(t)\right|^2=\lambda^2\left|b_f^{(1)}(t)\right|^2= \\ &= \tfrac{1}{\hbar^2}\left|\int_0^t e^{i\omega_{fi}t'} H_{int,fi}(t')\, dt'\right|^2, \end{aligned} \tag{1.97}$$

where $H_{int,fi}=\lambda W_{fi}$.

The goal is to treat the interaction of a charged particle with light, and as we have seen previously an electromagnetic wave can be described by a sinus function. Thus we introduce a sinusoidal perturbation

$$H_{\text{int}}(t)=W_0 \sin \omega t, \tag{1.98}$$

where the amplitude W_0 is time-independent. Then the matrix elements of H_{int} take the form

$$H_{\text{int,fi}}(t)=W_{0,fi}\sin \omega t=\frac{W_{0,fi}}{2i}\left(e^{i\omega t}-e^{-i\omega t}\right), \tag{1.99}$$

which, using (1.96), yields

$$\begin{aligned} b_n^{(1)}(t) &= -\tfrac{W_{0,ni}}{2\hbar}\int_0^t\left\{e^{i(\omega_{ni}+\omega)t'}-e^{i(\omega_{ni}-\omega)t'}\right\} dt' = \\ &= \tfrac{W_{0,ni}}{2\hbar}\left\{\tfrac{1-e^{i(\omega_{ni}+\omega)t}}{\omega_{ni}+\omega}-\tfrac{1-e^{i(\omega_{ni}-\omega)t}}{\omega_{ni}-\omega}\right\}. \end{aligned} \tag{1.100}$$

Hence, the transition probability between the states $|\phi_i\rangle$ and $|\phi_f\rangle$ under the influence of the sinusoidal perturbation $H_{\text{int}}(t)$ is

$$P_{if}(t) = \lambda^2 \left|b_f^{(1)}(t)\right|^2 = \frac{|W_{0,fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i\left(\omega_{fi}+\omega\right)t}}{\omega_{fi}+\omega} - \frac{1 - e^{i\left(\omega_{fi}-\omega\right)t}}{\omega_{fi}-\omega} \right|^2 . \qquad (1.101)$$

Assume that

$$\omega \approx \omega_{fi},$$

i.e., the system is at resonance. In that case the denominator of the second term in (1.101) becomes very small and the term very large and much more important than the first term, which we thus can neglect. Thus

$$\begin{aligned} P_{if}(t,\omega) &= \frac{\left|W_{0,fi}\right|^2}{4\hbar^2} \left| \frac{1-e^{i\left(\omega_{fi}-\omega\right)t}}{\omega_{fi}-\omega} \right|^2 = \\ &= \frac{\left|W_{0,fi}\right|^2}{4\hbar^2} \left| -ie^{i\frac{\left(\omega_{fi}-\omega\right)t}{2}} \frac{\sin\left\{\left(\omega_{fi}-\omega\right)t/2\right\}}{\frac{\left(\omega_{fi}-\omega\right)}{2}} \right|^2 = \qquad (1.102) \\ &= \frac{\left|W_{0,fi}\right|^2}{4\hbar^2} \left\{ \frac{\sin\frac{\left(\omega_{fi}-\omega\right)t}{2}}{\frac{\left(\omega_{fi}-\omega\right)}{2}} \right\}^2 \equiv \frac{\left|W_{0,fi}\right|^2}{4\hbar^2} F(t, \omega - \omega_{fi}), \end{aligned}$$

where the ω in the arguments of P_{if} indicate that ω is the other independent variable next to t.

We are now coming close to the final step in developing Fermi's Golden Rule. Imagine that a part of the spectrum of the Hamiltonian is continuous rather than discrete (however, we assume that there also is a discrete part of the spectrum, and we will investigate transitions between a discrete state and the continuum). For example, the continuous part might be the vacuum states in the photoelectric effect, or, much simpler, the states above a quantum well of finite depth. Then $|\langle\phi_f|\psi(t)\rangle|^2$ is a probability density rather than a probability. Let's say that we can label the eigenstates of the continuous spectrum part of the Hamiltonian by an index α. We require orthogonality in α:

$$\langle\alpha|\alpha'\rangle = \delta(\alpha - \alpha'). \qquad (1.103)$$

The probability of finding the system (described by $|\psi(t)\rangle$) in a group of final states $\alpha_f \pm \Delta\alpha$ is

$$\delta P(\alpha_f, t) = \int_{\alpha-\Delta\alpha\leq\alpha\leq\alpha+\Delta\alpha} |\langle\alpha|\psi(t)\rangle|^2 \; d\alpha. \qquad (1.104)$$

Physically, instead of one index α one will often have to use a couple of indices (one for each independent observable) such as the energy E and the crystal momentum $\boldsymbol{k}$. Thus, we make a change of variable to E and another parameter β so that the total differential of α reads

$$d\alpha = \rho(\beta, E)\ d\beta\ dE. \tag{1.105}$$

ρ is a density of (final) states. Then

$$\delta P(\alpha_f, t) = \int_{\beta-\Delta\beta\le\beta\le\beta+\Delta\beta, E-\Delta E\le E\le E+\Delta E} \rho(\beta, E)\, |\langle\beta, E|\psi(t)\rangle|^2\ d\beta\ dE. \tag{1.106}$$

As written above, the system was initially in the (discrete) eigenstate ϕ_i of the unperturbed Hamiltonian. We then introduced the sinusoidal perturbation (1.98) and calculated the matrix elements $P_{if}(t) = |\langle\phi_f|\psi(t)\rangle|^2$ in equation (1.102). This expression is still valid in the present case of a transition between a discrete state and a continuum. We just have to change labels:

$$|\langle\beta, E|\psi(t)\rangle|^2 = \frac{1}{4\hbar^2}\, |\langle\beta, E|W_0|\phi_i\rangle|^2\, F\left(t, \omega - \frac{E - E_i}{\hbar}\right), \tag{1.107}$$

where I used the continuous (final state) energy E rather than the discrete final state energy E_f. Putting this into equation (1.106) one derives for the probability density of a transition from the discrete state ϕ_i to the continuum

$$\delta P(\phi_i, \alpha_f, t) = \frac{1}{4\hbar^2} \int \rho(\beta, E)\, |\langle\beta, E|W_0|\phi_i\rangle|^2\ F\left(t, \omega - \frac{E - E_i}{\hbar}\right)\ d\beta\ dE, \tag{1.108}$$

with the integration over the relevant parts of the Hamiltonian's spectrum in energy and β space.

It can be shown that

$$\lim_{\varepsilon\to 0} \frac{\varepsilon}{\pi} \frac{\sin^2 \frac{x}{\varepsilon}}{x^2} = \delta(x). \tag{1.109}$$

Hence

$$\lim_{t\to\infty} \frac{\pi t}{\pi t} F\left(t, \omega - \frac{E - E_i}{\hbar}\right) = t\pi\ \delta\left(\frac{\hbar\omega}{2\hbar} - \frac{E - E_i}{2\hbar}\right) = 2t\pi\hbar\ \delta(\hbar\omega - (E - E_i)), \tag{1.110}$$

which can be used in (1.108). The integration over E can be performed using $\int \delta(x - x_0)\ f(x)\ dx = f(x_0)$. Often the $\Delta\beta$ is sufficiently small so that the integration over β becomes unnecessary. The result for $\delta P(\phi_i, \alpha_f, t)$ thus becomes

$$
\begin{gathered}
E - \Delta E \leq E_i + \hbar\omega \leq E + \Delta E : \\
\delta P(\phi_i, \alpha_f, t) = \delta\beta_f \ \tfrac{\pi}{2\hbar} t \left|\langle \beta_f, E_f = E_i + \hbar\omega | W_0 | \phi_i\rangle\right|^2 \ \rho(\beta_f, E_f = E_i + \hbar\omega) \\
E_i \text{ not within these limits:} \\
\delta P(\phi_i, \alpha_f, t) = 0.
\end{gathered}
\tag{1.111}
$$

The transition probability per unit time and per unit interval of β_f is defined as

$$
w(\phi_i, \alpha_f) = \frac{\delta(\frac{d}{dt}\delta P(\phi_i, \alpha_f, t))}{\delta\beta_f}. \tag{1.112}
$$

This leads to the final expression for *Fermi's Golden Rule* in the case of a sinusoidal perturbation:

$$
w(\phi_i, \alpha_f) = \frac{\pi}{2\hbar} \left|\langle \beta_f, E_f = E_i + \hbar\omega | W_0 | \phi_i\rangle\right|^2 \ \rho(\beta_f, E_f = E_i + \hbar\omega). \tag{1.113}
$$

1.5.3 Resonant excitation

We have said that our system is in state $|i\rangle = |\phi_i\rangle$ up to $t = 0$. At this point we put it into an electromagnetic field with an angular frequency close to that of a transition between $|i\rangle$ and $|f\rangle$, i.e., close to a Bohr frequency. In the dipole approximation we found (cf. equation (1.55))

$$
H_{\text{int}} = H^I_{\text{int,DA}} = \frac{qE_0}{m} P_z \sin\omega t. \tag{1.114}
$$

Remember that the matrix elements of H_{int} then are given by equations (1.62) and (1.63):

$$
\langle f | H_{\text{int}} | i\rangle = \left\langle f \middle| H^I_{\text{int,DA}} \middle| i \right\rangle = \frac{qE_0}{m\omega} \sin\omega t \, \langle f | P_z | i\rangle = iq\frac{\omega_{fi}}{\omega} E_0 \sin\omega t \, \langle f | z | i\rangle . \tag{1.115}
$$

Using equation (1.98) we identify

$$
W_0 = \frac{qE_0}{m} P_z = iq\frac{\omega_{fi} E_0}{\omega} z. \tag{1.116}
$$

The time-dependent transition probability between $|i\rangle$ and $|f\rangle$ is, according to equation (1.102) and using the preceding equations,

$$\begin{aligned} P_{if}(t,\omega) &= \frac{\left|W_{0,fi}\right|^2}{4\hbar^2} F(t,\omega-\omega_{fi}) = \\ &= \frac{\left|\langle f|\frac{q\omega_{fi}}{\omega}E_0 z|i\rangle\right|^2}{4\hbar^2} F(t,\omega-\omega_{fi}) = \\ &= \frac{q^2E_0^2}{4\hbar^2}\left(\frac{\omega_{fi}}{\omega}\right)^2 \left|\langle f|z|i\rangle\right|^2 F(t,\omega-\omega_{fi}) \end{aligned} \tag{1.117}$$

with

$$F(t,\omega-\omega_{fi}) = \left(\frac{\sin\frac{(\omega_{fi}-\omega)t}{2}}{\frac{(\omega_{fi}-\omega)}{2}}\right)^2 . \tag{1.118}$$

Normally, one deals with broad-band excitation, i.e., with a flux of more or less non-monochromatised electromagnetic radiation. Let $I(\omega)\,d\omega$ represent the flux of electromagnetic energy per unit surface within ω and $\omega+d\omega$. The energy flux across a unit surface in the xz-plane connected with the wave depicted in Figure 1.4 is then[6]

$$G\,dS = \varepsilon_0 c\frac{E_0^2}{2}\,dS. \tag{1.119}$$

Here, we identify G with $I(\omega)\,d\omega$ and solve for E_0^2, i.e.,

$$E_0^2\,d\omega = \frac{2I(\omega)\,d\omega}{\varepsilon_0 c}. \tag{1.120}$$

Using this in (1.117) and integrating over ω yields

$$P_{if}(t) = \frac{q^2}{2\varepsilon_0 c\hbar^2}\left|\langle f|z|i\rangle\right|^2 \int d\omega\,\left(\frac{\omega_{fi}}{\omega}\right)^2 I(\omega)F(t,\omega-\omega_{fi}). \tag{1.121}$$

We already saw that in equation (1.110) that F can be approximated by

$$F(t,\omega-\omega_{fi}) \approx 2\pi t\hbar\,\delta(E_f-E_i) = 2\pi t\,\delta(\omega-\omega_{fi}) \tag{1.122}$$

(note that I went back to the discrete case and replaced E by E_f). The integration can thus easily be carried out to give

$$P_{if}(t) = \frac{\pi q^2}{\varepsilon_0 c\hbar^2}\left|\langle f|z|i\rangle\right|^2\, I(\omega_{fi})\,t \equiv C_{if}\,I(\omega_{fi})\,t. \tag{1.123}$$

---

[6] This is derived (after time-averaging) from the poynting vector $\boldsymbol{G} = \varepsilon_0 c^2 \boldsymbol{E}\times\boldsymbol{B}$ and the finding that the energy flux across a surface element dS perpendicular to the unit vector $\boldsymbol{n}$ is $\boldsymbol{G}\boldsymbol{n}\,dS$.

Hence, $P_{if}(t)$ increases linearly with time and the transition probability per unit time is equal to $W_{if} = C_{if}\ I(\omega_{fi})$.

Here we treated the special case of light propagation in the y-direction with the polarisation along the z-axis. By including all other possibilities for the propagation direction and polarisation orientations one could define coefficients B_{if} similar to the C_{if}. The B_{if} are the absorption and induced emission coefficients introduced by Einstein.

1.6 The Kramers-Heisenberg formula

The purpose of this section is to look at the scattering of a photon by atomic electrons. This is the problem typically encountered at low and moderate photon energies, while the nuclear field plays a role at high photon energies only, as can be seen from Figure 1.5. The treatment will lead to the Kramers-Heisenberg formula (1.144) and (1.145), which describes the differential cross section for photon scattering[7]. This first requires to express the vector field of the electromagnetic radiation in a quantum mechanical formulation (section 1.6.1) as opposed to the classical treatment used so far.

1.6.1 Quantum treatment of the electromagnetic wave

The Hamiltonian (1.48)

$$\begin{aligned} H &= \tfrac{1}{2m}\left(\boldsymbol{P} - \tfrac{q\boldsymbol{A}}{c}\right)^2 + V(r) - \tfrac{q}{m}\boldsymbol{S}\boldsymbol{B} = \\ &= \tfrac{\boldsymbol{P}^2}{2m} - \tfrac{q}{2mc}\boldsymbol{P}\boldsymbol{A} - \tfrac{q}{2mc}\boldsymbol{A}\boldsymbol{P} + \tfrac{q^2}{2mc^2}\boldsymbol{A}^2 + V(r) - \tfrac{q}{m}\boldsymbol{S}\boldsymbol{B} \end{aligned} \tag{1.124}$$

is semi-classical since the vector field was treated in a purely classical way. This is not satisfying since quantum mechanics clearly postulates the quantum nature of photons, and since, indeed, a quantum treatment is necessary in order to correctly describe the absorption, emission, and scattering of photons by matter. A good starting point is the Fourier series of the vector field (note that I here assume the point of view of many different possible propagation directions $\boldsymbol{k}/k$ as well as a polarisation of the light described by the orthogonal vectors $\boldsymbol{\varepsilon}_1$ and $\boldsymbol{\varepsilon}_2$, which both are perpendicular to $\boldsymbol{k}$; this is

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[7] The formula was derived by Kramers and Heisenberg prior to the development of both the non-relativistic and relativistic formulations of quantum mechanics (Z. Phys. **31** (1925) 681.

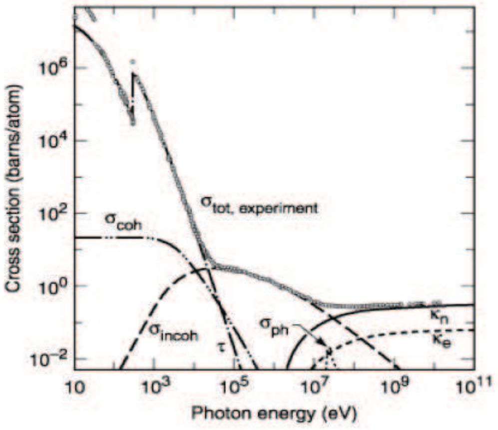

Figure 1.5: Photon cross sections in carbon as a function of energy. σ_{tot} is the the sum of the cross sections of the different processes. τ is the photoionisation cross section, σ_{coh} the coherent (Rayleigh) scattering cross section, σ_{incoh} the incoherent (Compton) scattering cross section, κ_n the cross section for pair production in the nuclear field, κ_e the cross section for pair production in the electron field, and σ_{ph} the cross section for photonuclear absorption. From J.H. Hubbell *et al.*, J. Phys. Chem. Ref. Data **9**, (1980) 1023.

different from the above assumption (1.17) of a single-energy electromagnetic wave propagating in a single direction):

$$\boldsymbol{A}(\boldsymbol{x},t) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \sum_{\alpha=1,2} \left(c_{\boldsymbol{k}\alpha}(0) \boldsymbol{\varepsilon}_\alpha e^{i(\boldsymbol{kx}-\omega t)} + c^*_{\boldsymbol{k}\alpha}(0) \boldsymbol{\varepsilon}_\alpha e^{-i(\boldsymbol{kx}-\omega t)} \right), \quad (1.125)$$

where

$$\begin{aligned} c_{\boldsymbol{k}\alpha}(t) &= c_{\boldsymbol{k}\alpha}(0)\ e^{-i\omega t} \\ c^*_{\boldsymbol{k}\alpha}(0) &= c^*_{\boldsymbol{k}\alpha}(0)\ e^{i\omega t} \end{aligned} \quad (1.126)$$

are the time-dependent Fourier coefficients in the classical field description. These obviously satisfy

$$\begin{aligned} \partial_t^2 c_{\boldsymbol{k}\alpha}(t) &= -\omega^2 c_{\boldsymbol{k}\alpha}(t), \\ \partial_t^2 c^*_{\boldsymbol{k}\alpha}(t) &= -\omega^2 c^*_{\boldsymbol{k}\alpha}(t), \end{aligned} \quad (1.127)$$

which has the same form as the equations for the momentum P and position Q for an harmonic oscillator. In analogy, P and Q are introduced for the photon field:

$$\begin{aligned} c_{\boldsymbol{k}\alpha}(t) &= -\tfrac{c}{2i\omega} P_{\boldsymbol{k}\alpha} + \tfrac{c}{2} Q_{\boldsymbol{k}\alpha} \\ c^*_{\boldsymbol{k}\alpha}(t) &= \tfrac{c}{2i\omega} P_{\boldsymbol{k}\alpha} + \tfrac{c}{2} Q_{\boldsymbol{k}\alpha}. \end{aligned} \quad (1.128)$$

Observe that in (1.128) P and Q are variables, while in the following expressions they are quantum mechanical operators. This means that we take the transition to quantum mechanics in the very next step. As usual for the operators P and Q they have to fulfill the typical commutation rules:

$$\begin{aligned} [Q_{\boldsymbol{k}\alpha}, P_{\boldsymbol{k}'\alpha'}] &= i\hbar \delta_{\boldsymbol{kk}'} \delta_{\alpha\alpha'}, \\ [Q_{\boldsymbol{k}\alpha}, Q_{\boldsymbol{k}'\alpha'}] &= 0, \\ [P_{\boldsymbol{k}\alpha}, P_{\boldsymbol{k}'\alpha'}] &= 0. \end{aligned} \quad (1.129)$$

Now define

$$\begin{aligned} a_{\boldsymbol{k}\alpha} &\equiv \tfrac{1}{\sqrt{2\hbar\omega}} \left(\omega Q_{\boldsymbol{k}\alpha} + i P_{\boldsymbol{k}\alpha} \right) \\ a^\dagger_{\boldsymbol{k}\alpha} &\equiv \tfrac{1}{\sqrt{2\hbar\omega}} \left(\omega Q_{\boldsymbol{k}\alpha} - i P_{\boldsymbol{k}\alpha} \right). \end{aligned} \quad (1.130)$$

These expressions have have the same form as

$$\begin{aligned} \tfrac{\sqrt{2\omega} c_{\boldsymbol{k}\alpha}}{c} &= \tfrac{1}{\sqrt{2\hbar\omega}} \left(i P_{\boldsymbol{k}\alpha} + \omega Q_{\boldsymbol{k}\alpha} \right) \\ \tfrac{\sqrt{2\omega} c^*_{\boldsymbol{k}\alpha}}{c} &= \tfrac{1}{\sqrt{2\hbar\omega}} \left(-i P_{\boldsymbol{k}\alpha} + \omega Q_{\boldsymbol{k}\alpha} \right), \end{aligned} \quad (1.131)$$

and thus the $a_{\boldsymbol{k}\alpha}$ and $a^\dagger_{\boldsymbol{k}\alpha}$ are the quantum mechanical equivalents of the classical Fourier coefficients $c_{\boldsymbol{k}\alpha}$ and $c^*_{\boldsymbol{k}\alpha}$. When acting on a multi-photon state

$$\left|n_{\boldsymbol{k}_1\alpha_1}; n_{\boldsymbol{k}_2\alpha_2}; \ldots; n_{\boldsymbol{k}_x\alpha_x}; \ldots\right\rangle = \left|n_{\boldsymbol{k}_1\alpha_1}\right\rangle \left|n_{\boldsymbol{k}_2\alpha_2}\right\rangle \ldots \left|n_{\boldsymbol{k}_x\alpha_x}\right\rangle \ldots$$

with $n_{\boldsymbol{k}_x\alpha_x}$ photons in the state characterised by the wavevector/polarisation pair $(\boldsymbol{k}_x/\alpha_x)$, $a_{\boldsymbol{k}\alpha}$ and $a^\dagger_{\boldsymbol{k}\alpha}$ have the following properties:

$$\begin{gathered} a^\dagger_{\boldsymbol{k}_x\alpha_x} \left|n_{\boldsymbol{k}_1\alpha_1}; n_{\boldsymbol{k}_2\alpha_2}; \ldots; n_{\boldsymbol{k}_x\alpha_x}; \ldots\right\rangle = \\ = \sqrt{n_{\boldsymbol{k}_x\alpha_x}+1} \left|n_{\boldsymbol{k}_1\alpha_1}; n_{\boldsymbol{k}_2\alpha_2}; \ldots; n_{\boldsymbol{k}_x\alpha_x}+1; \ldots\right\rangle \\ a_{\boldsymbol{k}_x\alpha_x} \left|n_{\boldsymbol{k}_1\alpha_1}; n_{\boldsymbol{k}_2\alpha_2}; \ldots; n_{\boldsymbol{k}_x\alpha_x}; \ldots\right\rangle = \\ = \sqrt{n_{\boldsymbol{k}_x\alpha_x}} \left|n_{\boldsymbol{k}_1\alpha_1}; n_{\boldsymbol{k}_2\alpha_2}; \ldots; n_{\boldsymbol{k}_x\alpha_x}-1; \ldots\right\rangle \\ a^\dagger_{\boldsymbol{k}_x\alpha_x} a_{\boldsymbol{k}_x\alpha_x} \left|n_{\boldsymbol{k}_1\alpha_1}; n_{\boldsymbol{k}_2\alpha_2}; \ldots; n_{\boldsymbol{k}_x\alpha_x}; \ldots\right\rangle = \\ = n_{\boldsymbol{k}_x\alpha_x} \left|n_{\boldsymbol{k}_1\alpha_1}; n_{\boldsymbol{k}_2\alpha_2}; \ldots; n_{\boldsymbol{k}_x\alpha_x}; \ldots\right\rangle . \end{gathered} \tag{1.132}$$

Thus $a_{\boldsymbol{k}\alpha}$, $a^\dagger_{\boldsymbol{k}\alpha}$, and $N_{\boldsymbol{k}\alpha} \equiv a^\dagger_{\boldsymbol{k}_x\alpha_x} a_{\boldsymbol{k}_x\alpha_x}$ are the photon annihilation, creation, and number operators, respectively. They are time-dependent and can be shown to fulfill the same equations of motion (1.127) as the Fourier coefficients from the analysis of the classical vector field.

Putting everything together, thus one arrives at the following quantised expression for the vector potential:

$$\boldsymbol{A}(\boldsymbol{x},t) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \sum_{\alpha=1,2} c\sqrt{\frac{\hbar}{2\omega}} \left(a_{\boldsymbol{k}\alpha}(0)\boldsymbol{\varepsilon}_\alpha e^{i\boldsymbol{k}\boldsymbol{x}-i\omega t} + a^\dagger_{\boldsymbol{k}\alpha}(0)\boldsymbol{\varepsilon}_\alpha e^{-i\boldsymbol{k}\boldsymbol{x}+i\omega t}\right) . \tag{1.133}$$

From this expression it is already seen that an interaction of the electromagnetic radiation with matter will lead to the creation and annihilation of photons (absorption and emission!), since the vector potentials contains the photon creation and annihilation operators.

1.6.2 Derivation of the Kramers-Heisenberg formula in the non-resonant case

The situation which to be investigated is depicted in Figure 1.6. Of interest is what happens in the middle of the figure, and this we want to describe

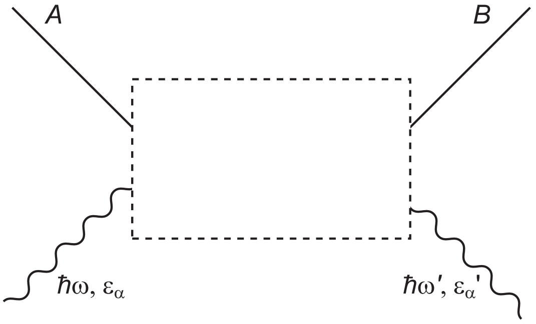

Figure 1.6: Description of the starting point for the treatment of the photon scattering process. The initial state consists of an atomic in state A and a photon with wave vector $\boldsymbol{k}$ and polarisation $\boldsymbol{\varepsilon}_\alpha$, while the final state is composed of an atom in state B and a photon characterised by $(\boldsymbol{k}, \boldsymbol{\varepsilon}_\alpha)$.

now. The Hamiltonian which describes the interaction is the same as that of the classical expression (1.48)/(1.124), although it is kept in mind that $\boldsymbol{A}$ now is an operator, which we have expressed in terms of the creation and annihilation operators. Here we also skip the spin-orbit interaction term $\boldsymbol{SB}$ and note that neither the kinetic energy $\boldsymbol{P}^2/2m$ nor the radial potential $V(r)$ are relevant for the interaction between the electrons and the light. The interaction Hamiltonian is thus[8]

$$H_{\text{int}} = -\frac{q}{2mc}\boldsymbol{PA} - \frac{q}{2mc}\boldsymbol{AP} + \frac{q^2}{2mc^2}\boldsymbol{A}^2. \tag{1.134}$$

First-order interaction

The Hamiltonian contains two linear and one quadratic term in $\boldsymbol{A}$. Equation (1.133) shows that $\boldsymbol{A}$ changes the number of photons by one (up or down). The overall process does not change the number of photons, and hence, to first order, $\boldsymbol{Ap}$ and $\boldsymbol{pA}$ do not give any contribution to the scattering process. In contrast, $\boldsymbol{A}^2$ does, since it contains $aa^\dagger$ and $a^\dagger a$, which leave the number of photons unchanged[9]. More specifically, we are interested in combinations of $a^\dagger_{\boldsymbol{k}'\alpha'}$ and $a_{\boldsymbol{k}\alpha}$, since these operators corresponded to the situation depicted in Figure 1.6 with the creation of the final photon state ($\boldsymbol{k}'$, $\boldsymbol{\varepsilon}_{\alpha'}$) and the annihilation of the initial photon state ($\boldsymbol{k}$, $\boldsymbol{\varepsilon}_\alpha$). Thus, in first order, we are

---

[8] $\boldsymbol{A}$ and $\boldsymbol{P}$ do not commute. Nevertheless it is possible to replace $\boldsymbol{PA}\ldots = (\boldsymbol{PA}) + \boldsymbol{AP}\ldots$ by $\boldsymbol{AP}$ due to the transversality condition (1.15), which zeroes the first term in the sum.

[9] $\boldsymbol{A}^2$ also contains aa and $a^\dagger a^\dagger$, which would change the number of photons by two.

looking for

$$\begin{gathered}
\langle B; \boldsymbol{k'}, \boldsymbol{\varepsilon}_{\alpha'} | H_{\text{int}} | A; \boldsymbol{k}, \boldsymbol{\varepsilon}_{\alpha} \rangle = \\
= \left\langle B; \boldsymbol{k'}, \boldsymbol{\varepsilon}_{\alpha'} \middle| \tfrac{q^2}{2mc^2} \boldsymbol{A}^2 \middle| A; \boldsymbol{k}, \boldsymbol{\varepsilon}_{\alpha} \right\rangle = \\
= \left\langle B; \boldsymbol{k'}, \boldsymbol{\varepsilon}_{\alpha'} \middle| \tfrac{q^2}{2mc^2} \left(a_{\boldsymbol{k}\alpha} a^{\dagger}_{\boldsymbol{k'}\alpha'} + a^{\dagger}_{\boldsymbol{k'}\alpha'} a_{\boldsymbol{k}\alpha} \right) \tfrac{c^2 \hbar}{2V\sqrt{\omega\omega'}} \; \boldsymbol{\varepsilon}_{\alpha} \boldsymbol{\varepsilon}_{\alpha'} \; e^{i(\boldsymbol{k}-\boldsymbol{k'})\boldsymbol{x} - i(\omega-\omega')t} \middle| A; \boldsymbol{k}, \boldsymbol{\varepsilon}_{\alpha} \right\rangle = \\
= \tfrac{q^2}{2mc^2} \tfrac{c^2 \hbar}{2V\sqrt{\omega\omega'}} 2 \boldsymbol{\varepsilon}_{\alpha} \boldsymbol{\varepsilon}_{\alpha'} \; e^{-i(\omega-\omega')t} \, \langle B | A \rangle \, .
\end{gathered} \tag{1.135}$$

Here, it has been used that (a) $e^{i\boldsymbol{kx}} \approx e^{i\boldsymbol{kx}} \approx 1$ since $|\boldsymbol{k}| \ll |\boldsymbol{x}|$ as also in the dipole approximation and (b)

$$\left\langle \boldsymbol{k'}, \alpha' \middle| a_{\boldsymbol{k}\alpha} a^{\dagger}_{\boldsymbol{k'}\alpha'} \middle| \boldsymbol{k}, \alpha \right\rangle = \left\langle \boldsymbol{k'}, \alpha' \middle| a^{\dagger}_{\boldsymbol{k'}\alpha'} a_{\boldsymbol{k}\alpha} \middle| \boldsymbol{k}, \alpha \right\rangle = 1.$$

In section 1.5.2 it was seen that for a Hamiltonian $H(t) = H_0 + H_{\text{int}}(t)$ the wave function solution of the time-dependent Schrödinger equation can be written

$$|\psi(t)\rangle = \sum_n b_n(t) e^{-iE_n t/\hbar} \, |\phi_n\rangle \, ,$$

where $|\phi_n\rangle$ is an eigenstate of the unperturbed Hamiltonian H_0. When it is assumed that the system initially is in a state $|\phi_i\rangle$ with energy E_i then the coefficient $b_n(t)$ related to the probability of at time t finding the system in state $|\phi_n\rangle$ with energy E_n can in first order be determined to (cf. equation (1.96) for the derivation)

$$b_n^{(1)}(t) = \frac{1}{i\hbar} \int_0^t e^{i(E_n - E_i)t'/\hbar} \; \langle \phi_n | H_{\text{int}}(t') | \phi_i \rangle \; dt'. \tag{1.136}$$

In the present case $|\phi_i\rangle$ and $|\phi_n\rangle$ are identified with $|A\rangle$ and $|B\rangle$, respectively, and it is noted that $\langle B|A\rangle = \delta_{AB}$. Using the first order photon scattering matrix element just calculated in equation (1.135), $b^{(1)}$ (where I skipped the index) is found to be

$$b^{(1)}(t) = \frac{1}{i\hbar} \frac{q^2}{2mc^2} \frac{c^2 \hbar}{2V\sqrt{\omega\omega'}} \, 2\delta_{AB} \; \boldsymbol{\varepsilon}_{\alpha} \boldsymbol{\varepsilon}_{\alpha'} \int_0^t e^{i(\hbar\omega' + E_B - \hbar\omega - E_A)t_x/\hbar} \, dt_x. \tag{1.137}$$

This expression is the first-order transition amplitude for the process shown in Figure 1.7.

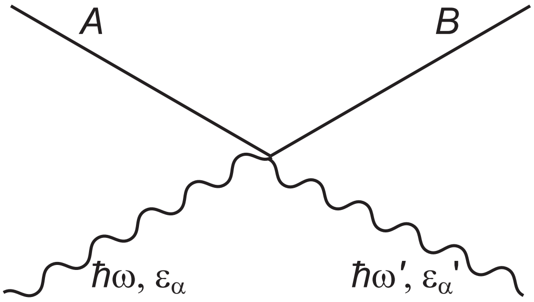

Figure 1.7: Feynman diagram for the first-order transition in an interaction of a photon with an atom (molecule etc.) initially in state A and in state B after the interaction. The relevant interaction is given rise to by the $\boldsymbol{A}^2$ operator in the interaction Hamiltonian.

Second-order interaction

In order to evaluate the second-order interaction one needs the second-order transition amplitude $b^{(2)}$. Time-dependent perturbation theory provides a general expression[10]:

$$\begin{aligned} b_n^{(2)}(t) = \tfrac{1}{(i\hbar)^2}\sum_m \int_0^t dt'' \int_0^{t''} dt' \; &\langle\phi_n|H_{\text{int}}(t'')|\phi_m\rangle \; e^{i(E_n-E_m)t''/\hbar} \times \\ &\times \; \langle\phi_m|H_{\text{int}}(t')|\phi_i\rangle \, e^{i(E_m-E_i)t'/\hbar}. \end{aligned} \tag{1.138}$$

Here, the sum is over all possible states $|\phi_m\rangle$ (m for inter*m*ediate).

The second order transition has to contain contributions from the double application of $\boldsymbol{AP}$, since such a double application can leave the net number of photons unchanged (as did the application of the $\boldsymbol{A}^2$ operator). However, it will put the system into an intermediate state, in which the number of photons has been changed as compared to the total initial state (which consists of the atom (molecule, etc.) and one photon). There are two possibilities:

1. First annihilation of a photon, then creation of a photon, and thus with an overall intermediate state containing no photons.
2. First creation of a photon, then annihilation of a photon, and thus with an overall intermediate state containing two photons.

These possibilities are depicted in Figure 1.8. In order to now calculate

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[10] A derivation is given in, e.g., J. J. Sakuari, San Fu Tuan (Ed.), *Modern Quantum Mechanics*, Revised edition, Addison-Wesley, New York, 1994.

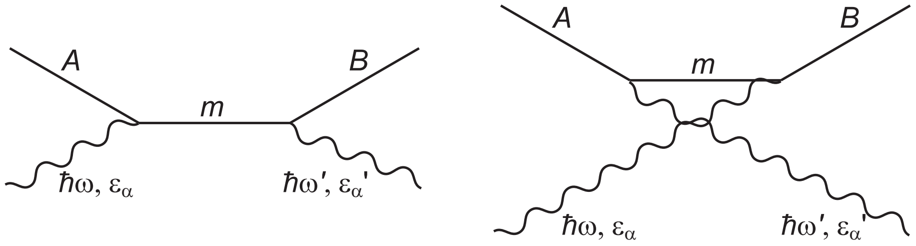

Figure 1.8: Feynman diagrams for the second-order transitions in an interaction of a photon with an atom (molecule etc.) initially in state A and in state B after the interaction. The relevant interactions are given rise to by the $\boldsymbol{AP}$ operator in the interaction Hamiltonian.

the corresponding second-order transition amplitude one has to evaluate the matrix elements of the form $\langle \phi_y; n \pm 1 | {-q/(mc)} \boldsymbol{P}\boldsymbol{A} | \phi_x; n \rangle$. If we start with the annihilation of a photon (i.e., absorption), $|\phi_y; n-1\rangle$ has to contain one less photon than $|\phi_x; n\rangle$. Denoting the number of photons as above by $n_{\boldsymbol{k}\alpha}$ and using the expression (1.133) for the vector potential $\boldsymbol{A}$ it is found that

$$
\begin{aligned}
&\left\langle \phi_y; n_{\boldsymbol{k}\alpha} - 1 \middle| -\tfrac{q}{mc}\boldsymbol{P}\boldsymbol{A} \middle| \phi_x; n_{\boldsymbol{k}\alpha} \right\rangle = \\
&= \left\langle \phi_y; n_{\boldsymbol{k}\alpha} - 1 \middle| -\tfrac{q}{mc}\boldsymbol{P}\tfrac{1}{\sqrt{V}}\, c\, \sqrt{\tfrac{\hbar}{2\omega}}\; a_{\boldsymbol{k}\alpha}(0)\boldsymbol{\varepsilon}_\alpha e^{i\boldsymbol{k}\boldsymbol{x}-i\omega t} \middle| \phi_x; n_{\boldsymbol{k}\alpha} \right\rangle = \\
&= \tfrac{q}{m}\sqrt{\tfrac{\hbar}{2V\omega}} \left\langle \phi_y; n_{\boldsymbol{k}\alpha} - 1 \middle| \boldsymbol{P}\sqrt{n_{\boldsymbol{k}\alpha}}\; \varepsilon_\alpha \middle| \phi_x; n_{\boldsymbol{k}\alpha} - 1 \right\rangle e^{i\boldsymbol{k}\boldsymbol{x}-i\omega t} \approx \qquad (1.139) \\
&\approx \tfrac{q}{m}\sqrt{\tfrac{\hbar}{2V\omega}} \left\langle \phi_y; n_{\boldsymbol{k}\alpha} - 1 \middle| \boldsymbol{P}\sqrt{n_{\boldsymbol{k}\alpha}}\; \varepsilon_\alpha \middle| \phi_x; n_{\boldsymbol{k}\alpha} - 1 \right\rangle e^{-i\omega t} = \\
&= \tfrac{q}{m}\sqrt{\tfrac{\hbar}{2V\omega}} \left\langle \phi_y \middle| \sqrt{n_{\boldsymbol{k}\alpha}}\; \boldsymbol{P}\, \boldsymbol{\varepsilon}_\alpha \middle| \phi_x \right\rangle e^{-i\omega t},
\end{aligned}
$$

where, once more, the dipole approximation was applied and $\langle n_{\boldsymbol{k}'\alpha'} | n_{\boldsymbol{k}'\alpha'} \rangle = \delta_{\boldsymbol{k}'\boldsymbol{k}}\, \delta_{\alpha'\alpha}$ was used. In the derivation $a^\dagger$ does not play any role, since it would create a photon, in contrast to the assumption of absorption.

In a similar manner one finds the matrix element for photon creation (i.e., emission):

$$
\begin{aligned}
&\left\langle \phi_y; n_{\boldsymbol{k}\alpha}+1 \middle| -\tfrac{q}{mc}\boldsymbol{P}\boldsymbol{A} \middle| \phi_x; n_{\boldsymbol{k}\alpha} \right\rangle = \\
&= \left\langle \phi_y; n_{\boldsymbol{k}\alpha}+1 \middle| -\tfrac{q}{mc}\boldsymbol{P}\tfrac{1}{\sqrt{V}}\; c\; \sqrt{\tfrac{\hbar}{2\omega}}\; a^{\dagger}_{\boldsymbol{k}\alpha}(0)\boldsymbol{\varepsilon}_{\alpha} e^{-i\boldsymbol{k}\boldsymbol{x}+i\omega t} \middle| \phi_x; n_{\boldsymbol{k}\alpha} \right\rangle = \\
&= \tfrac{q}{m}\sqrt{\tfrac{\hbar}{2V\omega}} \left\langle \phi_y; n_{\boldsymbol{k}\alpha}+1 \middle| \boldsymbol{P}\sqrt{n_{\boldsymbol{k}\alpha}+1}\; \boldsymbol{\varepsilon}_{\alpha} \middle| \phi_x; n_{\boldsymbol{k}\alpha}+1 \right\rangle e^{-i\boldsymbol{k}\boldsymbol{x}+i\omega t} \approx \\
&\approx \tfrac{q}{m}\sqrt{\tfrac{\hbar}{2V\omega}} \left\langle \phi_y; n_{\boldsymbol{k}\alpha}+1 \middle| \boldsymbol{P}\sqrt{n_{\boldsymbol{k}\alpha}+1}\; \boldsymbol{\varepsilon}_{\alpha} \middle| \phi_x; n_{\boldsymbol{k}\alpha}+1 \right\rangle e^{i\omega t} = \\
&\tfrac{q}{m}\sqrt{\tfrac{\hbar}{2V\omega}} \left\langle \phi_y \middle| \sqrt{n_{\boldsymbol{k}\alpha}+1}\; \boldsymbol{P}\,\boldsymbol{\varepsilon}_{\alpha} \middle| \phi_x \right\rangle e^{i\omega t}.
\end{aligned}
\tag{1.140}
$$

In the case that we are interested in, $n = 1$ before the first photon-atom interaction, $n = 0$ or $n = 2$ in the intermediate state, and $n = 1$ in the final state of the total system.

These expressions can now – in the combinations corresponding to the two points listed above – be introduced in the expression for the second-order transition amplitude:

$$
\begin{aligned}
b^{(2)}(t) &= \tfrac{1}{(i\hbar)^2}\sum_m \int_0^t dt_y \int_0^{t_y} dt_x \times \\
&\times e^{\frac{i(E_B-E_m)t_y}{\hbar}} e^{\frac{i(E_m-E_A)t_x}{\hbar}} \times \\
&\times \Big\{ \tfrac{q}{m}\sqrt{\tfrac{\hbar}{2V\omega'}} \left\langle B \middle| \sqrt{1}\; \boldsymbol{P}\,\boldsymbol{\varepsilon}_{\alpha'} \middle| m \right\rangle e^{i\omega' t_y} \times \\
&\times \tfrac{q}{m}\sqrt{\tfrac{\hbar}{2V\omega}} \left\langle m \middle| \sqrt{1}\; \boldsymbol{P}\,\boldsymbol{\varepsilon}_{\alpha} \middle| A \right\rangle e^{-i\omega t_x} + \\
&+ \Big\{ \tfrac{q}{m}\sqrt{\tfrac{\hbar}{2V\omega}} \left\langle B \middle| \sqrt{1}\; \boldsymbol{P}\,\boldsymbol{\varepsilon}_{\alpha} \middle| m \right\rangle e^{-i\omega t_y} \times \\
&\times \tfrac{q}{m}\sqrt{\tfrac{\hbar}{2V\omega'}} \left\langle m \middle| \sqrt{1}\; \boldsymbol{P}\,\boldsymbol{\varepsilon}_{\alpha'} \middle| A \right\rangle e^{i\omega' t_x} \Big\} =
\end{aligned}
\tag{1.141}
$$

$$
\begin{aligned}
&= -\tfrac{q^2}{i2Vm^2\sqrt{\omega\omega'}}\sum_m \left(\tfrac{\langle B|\boldsymbol{P}\,\boldsymbol{\varepsilon}_{\alpha'}|m\rangle\langle m|\boldsymbol{P}\,\boldsymbol{\varepsilon}_{\alpha}|A\rangle}{E_m-E_A-\hbar\omega}\right) + \left(\tfrac{\langle B|\boldsymbol{P}\,\boldsymbol{\varepsilon}_{\alpha}|m\rangle\langle m|\boldsymbol{P}\,\boldsymbol{\varepsilon}_{\alpha'}|A\rangle}{E_m-E_A-\hbar\omega'}\right) \times \\
&\times \int_0^t dt_x\; e^{i(E_B-E_A+\hbar\omega'-\hbar\omega)t_x/\hbar}.
\end{aligned}
$$

When evaluated over *all* times, i.e., when $t_x = 0$ is replaced by by $t_0 \to -\infty$ and $t \to +\infty$, the last integral results in a δ-function for the energy, thus 'merely' expresses energy conservation and is not taken into account anymore.

The overall transition probability and the differential cross section

Now we are close! All we have to do is to sum the first- and second-order contributions (1.137) and (1.141), square them, and multiply with the photon density of final states into account, which is known from the treatment of blackbody radiation,

$$\rho(\hbar\omega') = \frac{8\pi}{(hc)^3}(\hbar\omega')^2. \tag{1.142}$$

The procedure then yields the transition probability $d\sigma$ into a solid angle $d\Omega$ (not normalised for the incident photon flux, though):

$$\begin{aligned} d\sigma &= \left| c^{(1)} + c^{(2)} \right|^2 \rho(\hbar\omega') d\Omega = \\ &= \tfrac{2\pi}{\hbar} \left(\tfrac{c^2\hbar}{2V\sqrt{\omega\omega'}}\right)^2 \left(\tfrac{q^2}{mc^2}\right)^2 \tfrac{V}{(2\pi)^3} \tfrac{\omega'^2}{\hbar c^3} \, d\Omega \times \\ &\times \left| \delta_{AB} \, \boldsymbol{\varepsilon}_\alpha \, \boldsymbol{\varepsilon}_{\alpha'} - \tfrac{1}{m} \sum_m \left\{ \tfrac{\langle B|\boldsymbol{P}\boldsymbol{\varepsilon}_{\alpha'}|m\rangle\langle m|\boldsymbol{P}\boldsymbol{\varepsilon}_\alpha|A\rangle}{E_m - E_A - \hbar\omega} + \tfrac{\langle B|\boldsymbol{P}\boldsymbol{\varepsilon}_\alpha|m\rangle\langle m|\boldsymbol{P}\boldsymbol{\varepsilon}_{\alpha'}|A\rangle}{E_m - E_A + \hbar\omega'} \right\} \right|^2 . \end{aligned} \tag{1.143}$$

For the differential cross section it is thus found that

$$\frac{d\sigma}{d\Omega} \propto \frac{\omega'}{\omega} \left| \delta_{AB} \, \boldsymbol{\varepsilon}_\alpha \, \boldsymbol{\varepsilon}_{\alpha'} - \frac{1}{m} \sum_m \left(\frac{\langle B|\boldsymbol{P}\boldsymbol{\varepsilon}_{\alpha'}|m\rangle \, \langle m|\boldsymbol{P}\boldsymbol{\varepsilon}_\alpha|A\rangle}{E_m - E_A - \hbar\omega} + \frac{\langle B|\boldsymbol{P}\boldsymbol{\varepsilon}_\alpha|m\rangle \, \langle m|\boldsymbol{P}\boldsymbol{\varepsilon}_{\alpha'}|A\rangle}{E_m - E_A - \hbar\omega'} \right) \right|^2 . \tag{1.144}$$

This is the Kramers-Heisenberg formula, which provides a first- and second-order description of the photon scattering process and simultaneous promotion of the interacting atom (molecule, etc.) from a state A to a state B. Its three terms correspond to the direct transition, the absorption and then emission of a photon (photon-free intermediate state), and the emission and then absorption of a photon (two-photon intermediate state). Observe (a) that all three processes can interfere, and (b) that you can construct similar equations for the case of processes with a net change of charge in the atomic system.

1.6.3 The Kramers-Heisenberg formula for the resonant case

Equation (1.144) obviously does not work for the resonant case, when $E_m - E_A \approx \hbar\omega$. Then the second term goes to infinity. Experimentally, an enhancement is certainly seen, but of course the differential cross section cannot become infinitely large. To understand what is wrong, consider the an atom is brought into an intermediate state m by absorption of a photon (that is the first process of the second term). The intermediate state is not a stable state, and thus the probability amplitude of finding the atom in state m, $c_m(t)$, will change *even when it does not interact with any photon.* Spontaneous emission will lead to a damping of $c_m(t)$, and the amplitude will vary like $e^{\Gamma t/2\hbar}$, where $\Gamma = \hbar/\tau$ is defined by the intermediate state lifetime τ. When evaluated, it is seen that this leads to an introduction of a term $-i\Gamma/2$ in the energy of the intermediate state E_m, i.e. $E_m \rightarrow E_m - i\Gamma/2$. The Kramers-Heisenberg formula thus becomes

$$\frac{d\sigma}{d\Omega} \propto \frac{\omega'}{\omega} \left| \delta_{AB}\, \boldsymbol{\varepsilon}_\alpha\, \boldsymbol{\varepsilon}_{\alpha'} - \frac{1}{m} \sum_m \left(\frac{\langle B|\boldsymbol{P}\boldsymbol{\varepsilon}_{\alpha'}|m\rangle \langle m|\boldsymbol{P}\boldsymbol{\varepsilon}_\alpha|A\rangle}{E_m - E_A - \hbar\omega - i\Gamma/2} + \frac{\langle B|\boldsymbol{P}\boldsymbol{\varepsilon}_\alpha|m\rangle \langle m|\boldsymbol{P}\boldsymbol{\varepsilon}_{\alpha'}|A\rangle}{E_m - E_A - \hbar\omega'} \right) \right|^2 . \tag{1.145}$$