Interaction of Molecules with Light

1 Characterization of the radiation field and molecular field from Maxwell equations

In this Section we want to describe how a quantum mechanical particle, e.g., an electron in a hydrogen atom, is affected by electromagnetic fields. For this purpose we need to establish a suitable description of this field, then state the Hamiltonian which describes the resulting interaction.

It turns out that the proper description of the electromagnetic field requires a little bit of effort. We will describe the electromagnetic field classically. Such description should be sufficient for high quantum numbers, i.e., for situations in which the photons absorbed or emitted by the quantum system do not alter the energy content of the field. We will later introduce a simple rule which allows one to account to some limited degree for the quantum nature of the electromagnetic field, i.e., for the existence of discrete photons. More detailed derivations are provided in the Chapter 8 of "Notes on Quantum Mechanics" (qmbook.pdf) posted on the BioCoRe website.

1.1 Description of the Classical Electromagnetic Field / Separation of Longitudinal and Transverse Components

The aim of the following derivation is to provide a description of the electromagnetic field which is most suitable for deriving later a perturbation expansion which yields the effect of electromagnetic radiation on a bound charged particle, e.g., on an electron in a hydrogen atom. The problem is that the latter electron, or other charged particles, are affected by the Coulomb interaction $V(\vec{r})$ which is part of the forces which produce the bound state, and are affected by the external electromagnetic field. However, both the Coulomb interaction due to charges contributing to binding the particle, e.g., the attractive Coulomb force between proton and electron in case of the hydrogen atom, and the external electromagnetic field are of electromagnetic origin and, hence, must be described consistently. This is achieved in the following derivation.

The classical electromagnetic field is governed by the Maxwell equations. We assume that the system considered is in vacuum in which charge and current sources described by the densities $\rho(\vec{r},t)$ and $\vec{J}(\vec{r},t)$ are present. These sources enter the two inhomogeneous Maxwell

equations[1]

$$\nabla \cdot \vec{E}(\vec{r},t) \;=\; 4\,\pi\,\rho(\vec{r},t) \tag{1}$$

$$\nabla \times \vec{B}(\vec{r},t) \;-\; \partial_t \vec{E}(\vec{r},t) \;=\; 4\,\pi\,\vec{J}(\vec{r},t)\;. \tag{2}$$

In addition, the two homogeneous Maxwell equations hold

$$\nabla \times \vec{E}(\vec{r},t) \;+\; \partial_t \vec{B}(\vec{r},t) \;=\; 0 \tag{3}$$

$$\nabla \cdot \vec{B}(\vec{r},t) \;=\; 0\;. \tag{4}$$

Scalar and Vector Potential Setting

$$\vec{B}(\vec{r},t) \;=\; \nabla \times \vec{A}(\vec{r},t) \tag{5}$$

for some vector-valued function $\vec{A}(\vec{r},t)$, called the *vector potential*, solves implicitly (4). Equation (3) reads then

$$\nabla \times \Big(\vec{E}(\vec{r},t) \;+\; \partial_t \vec{A}(\vec{r},t) \Big) \;=\; 0 \tag{6}$$

which is solved by

$$\vec{E}(\vec{r},t) \;+\; \partial_t \vec{A}(\vec{r},t) \;=\; -\nabla V(\vec{r},t) \tag{7}$$

where $V(\vec{r},t)$ is a scalar function, called the *scalar potential*. From this follows

$$\vec{E}(\vec{r},t) \;=\; -\nabla V(\vec{r},t) \;-\; \partial_t \vec{A}(\vec{r},t)\;. \tag{8}$$

Gauge Transformations We have expressed now the electric and magnetic fields $\vec{E}(\vec{r},t)$ and $\vec{B}(\vec{r},t)$ through the scalar and vector potentials $V(\vec{r},t)$ and $\vec{A}(\vec{r},t)$. As is well known, the relationship between fields and potentials is not unique. The following substitutions, called gauge transformations, alter the potentials, but leave the fields unaltered:

$$\vec{A}(\vec{r},t) \;\longrightarrow\; \vec{A}(\vec{r},t) \;+\; \nabla\chi(\vec{r},t) \tag{9}$$

$$V(\vec{r},t) \;\longrightarrow\; V(\vec{r},t) \;-\; \partial_t \chi(\vec{r},t)\;. \tag{10}$$

This gauge freedom will be exploited now to introduce potentials which are most suitable for the purpose of separating the electromagnetic field into a component arising from the Coulomb potential connected with the charge distribution $\rho(\vec{r},t)$ and the current due to moving net charges, and a component due to the remaining currents. In fact, the gauge freedom allows us to impose on the vector potential $\vec{A}(\vec{r},t)$ the condition

$$\nabla \cdot \vec{A}(\vec{r},t) \;=\; 0\;. \tag{11}$$

[1] We assume so-called Gaussian units. The reader is referred to the well-known textbook "Classical Electrodynamics", 2nd Edition, by J. D. Jackson (John Wiley & Sons, New York, 1975) for a discussion of these and other conventional units.

The corresponding gauge is referred to as the *Coulomb gauge*, a name which is due to the form of the resulting scalar potential $V(\vec{r},t)$. In fact, this potential results from inserting (8) into (1)

$$\nabla \cdot \Big(-\nabla V(\vec{r},t) \; - \; \partial_t \vec{A}(\vec{r},t) \Big) \; = \; 4\,\pi\,\rho(\vec{r},t)\;. \tag{12}$$

Using $\nabla \cdot \partial_t \vec{A}(\vec{r},t) \; = \; \partial_t \nabla \cdot \vec{A}(\vec{r},t)$ together with (11) yields then the Poisson equation

$$\nabla^2 V(\vec{r},t) \; = \; -\,4\,\pi\,\rho(\vec{r},t)\;. \tag{13}$$

In case of the boundary condition

$$V(\vec{r},t) \; = \; 0 \quad \text{for } \vec{r} \in \partial\Omega_\infty \tag{14}$$

the solution is given by the Coulomb integral

$$V(\vec{r},t) \; = \; \int_{\Omega_\infty} d^3r' \, \frac{\rho(\vec{r}\,',t)}{|\vec{r} \; - \; \vec{r}\,'|} \tag{15}$$

This is the potential commonly employed in quantum mechanical calculations for the description of Coulomb interactions between charged particles.

The vector potential $\vec{A}(\vec{r},t)$ can be obtained employing (2), the second inhomogeneous Maxwell equation. Using the expressions (5) and (8) for the fields results in

$$\nabla \times \Big(\nabla \times \vec{A}(\vec{r},t) \Big) \; + \; \partial_t \Big(\nabla V(\vec{r},t) \; + \; \partial_t \vec{A}(\vec{r},t \Big) \; = \; 4\,\pi\,\vec{J}(\vec{r},t)\;. \tag{16}$$

The identity

$$\nabla \times \Big(\nabla \times \vec{A}(\vec{r},t) \Big) \; = \; \nabla \Big(\nabla \cdot \vec{A}(\vec{r},t) \Big) \; - \; \nabla^2 \vec{A}(\vec{r},t) \tag{17}$$

together with condition (11) leads us to

$$\nabla^2 \vec{A}(\vec{r},t) \; - \; \partial_t^2 \vec{A}(\vec{r},t) \; - \; \partial_t \nabla V(\vec{r},t) \; = \; -\,4\,\pi\,\vec{J}(\vec{r},t)\;. \tag{18}$$

Unfortunately, equation (18) couples the vector potential $\vec{A}(\vec{r},t)$ and $V(\vec{r},t)$. One would prefer a description in which the Coulomb potential (15) and the vector potential are uncoupled, such that the latter describes the electromagnetic radiation, and the former the Coulomb interactions in the unperturbed bound particle system. Such description can, in fact, be achieved. For this purpose we examine the offending term $\partial_t \nabla V(\vec{r},t)$ in (18) and define

$$\vec{J}_\ell(\vec{r},t) \; = \; \frac{1}{4\pi}\,\partial_t \nabla V(\vec{r},t)\;. \tag{19}$$

For the curl of $\vec{J}_\ell$ holds

$$\nabla \times \vec{J}_\ell(\vec{r},t) \; = \; 0\;. \tag{20}$$

For the divergence of $\vec{J}_\ell(\vec{r},t)$ holds, using $\partial_t\nabla = \nabla\partial_t$ and the Poisson equation (13),

$$\nabla\cdot\vec{J}_\ell(\vec{r},t) \;=\; \frac{1}{4\pi}\,\partial_t\nabla^2 V(\vec{r},t) \;=\; -\,\partial_t\rho(\vec{r},t) \tag{21}$$

or

$$\nabla\cdot\vec{J}_\ell(\vec{r},t) \;+\; \partial_t\rho(\vec{r},t) \;=\; 0\,. \tag{22}$$

This continuity equation identifies $\vec{J}_\ell(\vec{r},t)$ as the current due to the time-dependence of the charge distribution $\rho(\vec{r},t)$. Let $\vec{J}(\vec{r},t)$ be the total current of the system under investigation and let $\vec{J}_t = \vec{J} - \vec{J}_\ell$. For $\vec{J}$ also holds the continuity equation

$$\nabla\cdot\vec{J}(\vec{r},t) \;+\; \partial_t\rho(\vec{r},t) \;=\; 0 \tag{23}$$

and from this follows

$$\nabla\cdot\vec{J}_t(\vec{r},t) \;=\; 0\,. \tag{24}$$

Because of properties (20) and (24) one refers to $\vec{J}_\ell$ and $\vec{J}_t$ as the *longitudinal* and the *transverse* currents, respectively.

The definitions of $\vec{J}_\ell$ and $\vec{J}_t$ applied to (18) yield

$$\nabla^2\vec{A}(\vec{r},t) \;-\; \partial_t^2\vec{A}(\vec{r},t) \;=\; -\,4\,\pi\,\vec{J}_t(\vec{r},t)\,. \tag{25}$$

This equation does not couple anymore scalar and vector potentials. The vector potential determined through (25) and (11) and the Coulomb potential (15) yield finally the electric and magnetic fields. $V(\vec{r},t)$ contributes solely an electric field component

$$\vec{E}_\ell(\vec{r},t) \;=\; -\,\nabla V(\vec{r},t) \tag{26}$$

which is obviously curl-free ($\nabla\times\vec{E}_\ell(\vec{r},t) \;=\; 0$), hence, the name *longitudinal electric field*. $\vec{A}(\vec{r},t)$ contributes an electrical field component as well as the total magnetic field

$$\vec{E}_t(\vec{r},t) \;=\; -\,\partial_t\vec{A}(\vec{r},t) \tag{27}$$

$$\vec{B}_t(\vec{r},t) \;=\; \nabla\times\vec{A}(\vec{r},t)\,. \tag{28}$$

These fields are obviously divergence -free (e.g., $\nabla\cdot\vec{E}_t(\vec{r},t) \;=\; 0$), hence, the name *transverse fields*.

1.2 Planar Electromagnetic Waves

The current density $\vec{J}_t$ describes ring-type currents in the space under consideration; such current densities exist, for example, in a ring-shaped antenna which exhibits no net charge, yet a current. Presently, we want to assume that no ring-type currents, i.e., no divergence-free currents, exist in the space considered. In this case (25) turns into the well-known wave

equation

$$\nabla^2 \vec{A}(\vec{r},t) \;-\; \partial_t^2 \vec{A}(\vec{r},t) \;=\; 0 \tag{29}$$

which describes electromagnetic fields in vacuum. A complete set of solutions is given by the so-called plane waves

$$\vec{A}(\vec{r},t) \;=\; A_o\, \hat{u} \exp\Big[\, i(\vec{k}\cdot\vec{r} \mp \omega t)\Big] \tag{30}$$

where the dispersion relationship

$$|\vec{k}| \;=\; \omega \tag{31}$$

holds. Note that in the units chosen the velocity of light is $c = 1$. Here the "-" sign corresponds to so-called *incoming waves* and the "+" sign to *outgoing waves*[2], the constant $\vec{k}$ is referred to as the *wave vector*. The Coulomb gauge condition (11) yields

$$\hat{u}\cdot\vec{k} \;=\; 0\,. \tag{32}$$

$\hat{u}$ is a unit vector ($|\hat{u}| = 1$) which, obviously, is orthogonal to $\vec{k}$; accordingly, there exist two linearly independent orientations for $\hat{u}$ corresponding to two independent planes of polarization.

We want to characterize now the radiation field connected with the plane wave solutions (30). The corresponding electric and magnetic fields, according to (27, 28), are

$$\vec{E}_t(\vec{r},t) \;=\; \pm i\,\omega\,\vec{A}(\vec{r},t) \tag{33}$$

$$\vec{B}_t(\vec{r},t) \;=\; i\,\vec{k}\times\vec{A}(\vec{r},t)\,. \tag{34}$$

The vector potential in (30) and the resulting fields (33, 34) are complex-valued quantities. In applying the potential and fields to physical observables and processes we will only employ the real parts.

Obviously, $\vec{E}_t(\vec{r},t)$ and $\vec{B}_t(\vec{r},t)$ in (33, 34), at each point $\vec{r}$ and moment t, are orthogonal to each other and are both orthogonal to the wave vector $\vec{k}$. The latter vector describes the direction of propagation of the energy flux connected with the plane wave electromagnetic radiation. This flux is given by

$$\vec{S}(\vec{r},t) \;=\; \frac{1}{4\pi}\,\mathrm{Re}\,\vec{E}_t(\vec{r},t)\times \mathrm{Re}\,\vec{B}(\vec{r},t)\,. \tag{35}$$

Using the identity $\vec{a}\times(\vec{b}\times\vec{c}) = \vec{b}\,(\vec{a}\cdot\vec{c}) - \vec{c}\,(\vec{a}\cdot\vec{b})$ and (30, 31, 33, 34) one obtains

$$\vec{S}(\vec{r},t) \;=\; \pm\frac{\omega^2}{4\pi}\,A_o^2\,\hat{k}\,\sin^2(\,\vec{k}\cdot\vec{r}\mp\omega t\,) \tag{36}$$

[2]The definition *incoming waves* and *outgoing waves* is rationalized below in the discussion following Eq. (77); see also the comment below Eqs. (37, 38).

where $\hat{k}$ is the unit vector $\hat{k} = \vec{k}/|\vec{k}|$. Time average over one period $2\pi/\omega$ yields

$$\langle \vec{S}(\vec{r},t) \rangle \;=\; \pm\frac{\omega^2}{8\pi}\, A_o^2\, \hat{k}\;. \tag{37}$$

In this expression for the energy flux one can interprete $\hat{k}$ as the propagation velocity (note $c = 1$) and, hence,

$$\langle \epsilon \rangle \;=\; \frac{\omega^2}{8\pi}\, A_o^2 \tag{38}$$

as the energy density. The sign in (37) implies that for *incoming waves*, defined below Eqs. (30,31), the energy of the plane wave is transported in the direction of $-\vec{k}$, whereas in the case of *outgoing* waves the energy is transported in the direction of $\vec{k}$.

A correct description of the electromagnetic field requires that the field be quantized. A 'poor man's' quantization of the field is possible at this point by expressing the energy density (38) through the density of photons connected with the planar waves (30). These photons each carry the energy $\hbar\omega$. If we consider a volume $\mathcal{V}$ with a number of photons $\mathcal{N}_\omega$ the energy density is obviously

$$\langle \epsilon \rangle \;=\; \frac{\mathcal{N}_\omega \hbar\omega}{\mathcal{V}}\;. \tag{39}$$

It should be pointed out that $\mathcal{N}_\omega$ represents the number of photons for a specific frequency ω, a specific $\hat{k}$ and a specific $\hat{u}$. Comparision of (38) and (39) allows one to express then the field amplitudes

$$A_o \;=\; \sqrt{\frac{8\pi\mathcal{N}_\omega\hbar}{\omega\mathcal{V}}}\;. \tag{40}$$

Inserting this into (30) allows one finally to state for the planar wave vector potential

$$\vec{A}(\vec{r},t) \;=\; \sqrt{\frac{8\pi\mathcal{N}_\omega\hbar}{\omega\mathcal{V}}}\;\hat{u}\exp\Big[\,i(\vec{k}\cdot\vec{r}-\omega t)\Big] \quad ,\; |\vec{k}| \,=\, \omega\;,\; \hat{u}\cdot\vec{k} \,=\, 0\;. \tag{41}$$

2 Characterization of the interaction of the radiation field and molecules

2.1 Hamilton Operator

The classical Hamiltonian for a particle of charge q in a scalar and vector potential $V(\vec{r})$ and $\vec{A}(\vec{r},t)$, respectively, is

$$\begin{aligned} H \;=\; & \frac{\Big[\,\vec{p}\,-\,q\vec{A}(\vec{r},t)\,\Big]^2}{2\,m} \;+\; qV(\vec{r}) \\ & +\,\frac{1}{8\pi}\int_{\Omega_\infty} d^3r'\,E_\ell^2 \;+\; \frac{1}{16\pi}\int_{\Omega_\infty} d^3r\,\Big(\,|E_t|^2\,+\,|B_t|^2\,\Big)\;. \end{aligned} \tag{42}$$

Here the fields are defined through Eqs. (26, 27, 28) together with the potentials (15, 30). The integrals express the integration over the energy density of the fields. Note that $\vec{E}_\ell(\vec{r},t)$ is real and that $\vec{E}_t(\vec{r},t)$, $\vec{B}_t(\vec{r},t)$ are complex leading to the difference of a factor $\frac{1}{2}$ in the energy densities of the lontitudinal and transverse components of the fields.

We assume that the energy content of the fields is not altered significantly in the processes described and, hence, we will neglect the respective terms in the Hamiltonian (42). We are left with a classical Hamiltonian function which has an obvious quantum mechanical analogue

$$\hat{H} \;=\; \frac{\left[\hat{\vec{p}} \,-\, q\vec{A}(\vec{r},t)\right]^2}{2\,m} \;+\; qV(\vec{r})\;. \tag{43}$$

replacing the classical momentum $\vec{p}$ by the differential operator $\hat{\vec{p}} = \frac{\hbar}{i}\nabla$. The wave function $\Psi(\vec{r},t)$ of the particle is then described by the Schrödinger equation

$$i\,\hbar\,\partial_t\,\Psi(\vec{r},t) \;=\; \hat{H}\,\Psi(\vec{r},t)\;. \tag{44}$$

Gauge Transformations It is interesting to note that in the quantum mechanical description of a charged particle the potentials $V(\vec{r},t)$ and $\vec{A}(\vec{r},t)$ enter whereas in the classical equations of motion

$$m\ddot{\vec{r}} \;=\; q\,\vec{E}(\vec{r},t) \;+\; q\,\dot{\vec{r}} \times \vec{B}(\vec{r},t) \tag{45}$$

the fields enter. This leads to the question in how far the gauge transformations (9, 10) affect the quantum mechanical description. In the classical case such question is mute since the gauge transformations do not alter the fields and, hence, have no effect on the motion of the particle described by (45).

Applying the gauge transformations (9, 10) to (43, 44) leads to the Schrödinger equation

$$i\hbar\partial_t\Psi(\vec{r},t) \;=\; \left[\frac{\left[\hat{\vec{p}} \,-\, q\vec{A} \,-\, q((\nabla\chi))\right]^2}{2\,m} \;+\; qV \;-\; q((\partial_t\chi))\right]\Psi(\vec{r},t) \tag{46}$$

where $((\cdots))$ denotes derivatives in $((\nabla\chi))$ and $((\partial_t\chi))$ which are confined to the function $\chi(\vec{r},t)$ inside the double brackets. One can show that (46) is equivalent to

$$i\hbar\partial_t e^{iq\chi(\vec{r},t)/\hbar}\Psi(\vec{r},t) \;=\; \left[\frac{\left[\hat{\vec{p}} \,-\, q\vec{A}\right]^2}{2\,m} \;+\; qV\right] e^{iq\chi(\vec{r},t)/\hbar}\Psi(\vec{r},t)\;. \tag{47}$$

For this purpose one notes

$$i\hbar\partial_t\, e^{iq\chi(\vec{r},t)/\hbar}\Psi(\vec{r},t) \;=\; e^{iq\chi(\vec{r},t)/\hbar}\,\left[\,i\hbar\partial_t \;-\; q((\partial_t\chi))\,\right]\Psi(\vec{r},t) \tag{48}$$

$$\hat{\vec{p}}\,e^{iq\chi(\vec{r},t)/\hbar}\Psi(\vec{r},t) \;=\; e^{iq\chi(\vec{r},t)/\hbar}\,\left[\hat{\vec{p}} \;+\; q((\nabla\chi))\right]\Psi(\vec{r},t)\;. \tag{49}$$

The equivalence of (46, 47) implies that the gauge transformation (9, 10) of the potentials is equivalent to multiplying the wave function $\Psi(\vec{r},t)$ by a local and time-dependent phase factor $e^{iq\chi(\vec{r},t)/\hbar}$. Obviously, such phase factor does not change the probability density $|\Psi(\vec{r},t)|^2$ and, hence, does not change expectation values which contain the probability densities[3].

An important conceptual step of modern physics has been to turn the derivation given around and to state that introduction of a local phase factor $e^{iq\chi(\vec{r},t)/\hbar}$ should not affect a system and that, accordingly, in the Schrödinger equation

$$i\hbar\partial_t\Psi(\vec{r},t) \;=\; \left[\frac{\left[\hat{\vec{p}} \,-\, q\vec{A}\right]^2}{2\,m} \;+\; qV\right]\Psi(\vec{r},t)\;. \tag{50}$$

the potentials $\vec{A}(\vec{r},t)$ and $V(\vec{r},t)$ are necessary to compensate terms which arise through the phase factor. It should be noted, however, that this principle applies only to fundamental interactions, not to phenomenological interactions like the molecular van der Waals interaction.

The idea just stated can be generalized by noting that multiplication by a phase factor $e^{iq\chi(\vec{r},t)/\hbar}$ constitutes a unitary transformation of a scalar quantity, i.e., an element of the group U(1). Elementary constituents of matter which are governed by other symmetry groups, e.g., by the group SU(2), likewise can demand the existence of fields which compensate local transformations described by $e^{i\vec{\sigma}\cdot\vec{\chi}(\vec{r},t)}$ where $\vec{\sigma}$ is the vector of Pauli matrices, the generators of SU(2). The resulting fields are called Yang-Mills fields.

The Hamiltonian (43) can be expanded

$$H \;=\; \frac{\hat{\vec{p}}^{\,2}}{2m} \;-\; \frac{q}{2m}\left(\hat{\vec{p}}\cdot\vec{A} \;+\; \vec{A}\cdot\hat{\vec{p}}\right) \;+\; \frac{q^2}{2m}A^2 \;+\; qV \tag{51}$$

For any function $f(\vec{r})$ holds

$$\left(\hat{\vec{p}}\cdot\vec{A} \;-\; \vec{A}\cdot\hat{\vec{p}}\right)f(\vec{r}) \;=\; \frac{\hbar}{i}\left(\vec{A}\cdot\nabla f \;+\; f\,\nabla\cdot\vec{A} \;-\; \vec{A}\cdot\nabla f\right) \;=\; \frac{\hbar}{i}\,f\,\nabla\cdot\vec{A}\,. \tag{52}$$

This expression vanishes in the present case since since $\nabla\cdot A \;=\; 0$ [cf. (11)]. Accordingly, holds

$$\hat{\vec{p}}\cdot A\,f \;=\; \vec{A}\cdot\hat{\vec{p}}\,f \tag{53}$$

and, consequently,

$$H \;=\; \frac{\hat{\vec{p}}^{\,2}}{2m} \;-\; \frac{q}{m}\,\hat{\vec{p}}\cdot\vec{A} \;+\; \frac{q^2}{2m}A^2 \;+\; qV\;. \tag{54}$$

2.2 Time-Dependent Perturbation Theory

We want to consider now a quantum system involving a charged particle in a bound state perturbed by an external radiation field described through the Hamiltonian (54). We assume

[3]The effect on other expectation values is not discussed here.

that the scalar potential V in (54) confines the particle to stationary bound states; an example is the Coulomb potential $V(\vec{r},t) = 1/4\pi r$ confining an electron with energy $E < 0$ to move in the well known orbitals of the hydrogen atom. The external radiation field is accounted for by the vector potential $\vec{A}(\vec{r},t)$ introduced above. In the simplest case the radiation field consists of a single planar electromagnetic wave described through the potential (30). Other radiation fields can be expanded through Fourier analysis in terms of such plane waves. We will see below that the perturbation resulting from a 'pure' plane wave radiation field will serve us to describe also the perturbation resulting from a radiation field made up of a superposition of many planar waves.

The Hamiltonian of the particle in the radiation field is then described through the Hamiltonian

$$H = H_o + \mathcal{V}_S \tag{55}$$

$$H_o = \frac{\hat{\vec{p}}^2}{2m} + qV \tag{56}$$

$$\mathcal{V}_S = -\frac{q}{m}\hat{\vec{p}}\cdot\vec{A}(\vec{r},t) + \frac{q^2}{2m}A^2(\vec{r},t) \tag{57}$$

where $\vec{A}(\vec{r},t)$ is given by (41). Here the so-called unperturbed system is governed by the Hamiltonian H_o with stationary states defined through the eigenvalue problem

$$H_o|n\rangle = \epsilon_n|n\rangle \quad , n = 0, 1, 2 \ldots \tag{58}$$

where we adopted the Dirac notation for the states of the quantum system. The states $|n\rangle$ are thought to form a complete, orthonormal basis, i.e., we assume

$$\langle n|m\rangle = \delta_{nm} \tag{59}$$

and for the identity

$$\mathbb{1} = \sum_{n=0}^{\infty} |n\rangle\langle n| \, . \tag{60}$$

We assume for the sake of simplicity that the eigenstates of H_o can be labeled through integers, i.e., we discount the possibility of a continuum of eigenstates. However, this assumption can be waved as our results below will not depend on it.

Estimate of the Magnitude of $\mathcal{V}_S$

We want to demonstrate now that the interaction $\mathcal{V}_S(t)$, as given in (57) for the case of radiation-induced transitions in atomic systems, can be considered a weak perturbation. In fact, one can estimate that the perturbation, in this case, is much smaller than the eigenvalue differences near typical atomic bound states, and that the first term in (57), i.e., the term $\sim \hat{\vec{p}}\cdot\vec{A}(\vec{r},t)$, is much larger than the second term, i.e., the term $\sim A^2(\vec{r},t)$. This result will

allow us to neglect the second term in (57) in further calculations and to expand the wave function in terms of powers of $\mathcal{V}_S(t)$ in a perturbation calculation.

For an electron charge $q = -e$ and an electron mass $m = m_e$ one can provide the estimate for the first term of (57) as follows[4]. We first note, using (40)

$$\left| \frac{e}{m_e} \hat{\vec{p}} \cdot \vec{A} \right| \sim \frac{e}{m_e} \left| 2m_e \frac{p^2}{2m_e} \right|^{\frac{1}{2}} \sqrt{\frac{8\pi \mathcal{N}_\omega \hbar}{\omega \mathcal{V}}} . \tag{61}$$

The virial theorem for the Coulomb problem provides the estimate for the case of a hydrogen atom

$$\left| \frac{p^2}{2m_e} \right| \sim \frac{1}{2} \frac{e^2}{a_o} \tag{62}$$

where a_o is the Bohr radius. Assuming a single photon, i.e., $\mathcal{N}_\omega = 1$, a volume $\mathcal{V} = \lambda^3$ where λ is the wave length corresponding to a plane wave with frequency ω, i.e., $\lambda = 2\pi c/\lambda$, one obtains for (61) using $\mathcal{V} = \lambda 4\pi^2 c^2/\omega^2$

$$\left| \frac{e}{m_e} \hat{\vec{p}} \cdot \vec{A} \right| \sim \frac{e^2}{4\pi a_o} \left| \frac{2}{\pi} \frac{a_o}{\lambda} \frac{\hbar\omega}{m_e c^2} \right|^{\frac{1}{2}} \tag{63}$$

For $\hbar\omega = 3$ eV and a corresponding $\lambda = 4000$ Å one obtains, with $a_o \approx 0.5$ Å, and $m_e c^2 \approx 500$ keV

$$\left| \frac{2}{\pi} \frac{a_o}{\lambda} \frac{\hbar\omega}{m_e c^2} \right| \approx 10^{-8} \tag{64}$$

and with $e^2/a_o \approx 27$ eV, altogether,

$$\left| \frac{e}{m_e} \hat{\vec{p}} \cdot \vec{A} \right| \sim 10\,\text{eV} \cdot 10^{-4} = 10^{-3}\,\text{eV} . \tag{65}$$

This magnitude is much less than the differences of the typical eigenvalues of the lowest states of the hydrogen atom which are of the order of 1 eV. Hence, the first term in (57) for radiation fields can be considered a small perturbation.

We want to estimate now the second term in (57). Using again (40) one can state

$$\left| \frac{e^2}{2m_e} A^2 \right| \sim \frac{e^2}{2m_e} \frac{1}{\omega^2} \frac{8\pi \mathcal{N}_\omega \hbar\omega}{\mathcal{V}} \tag{66}$$

For the same assumptions as above one obtains

$$\left| \frac{e^2}{2m_e} A^2 \right| \sim \frac{e^2}{8\pi a_o} \cdot \left(\frac{a_o}{\lambda} \frac{4\hbar\omega}{m_e c^2} \right) . \tag{67}$$

[4]The reader should note that the estimates are very crude since we are establishing an order of magnitude estimate only.

Employing for the second factor the estimate as stated in (64) yields

$$\left| \frac{e^2}{2m_e} A^2 \right| \sim 10\,\mathrm{eV} \cdot 10^{-8} = 10^{-7}\,\mathrm{eV} . \tag{68}$$

This term is obviously much smaller than the first term. Consequently, one can neglect this term as long as the first term gives non-vanishing contributions, and as long as the photon densities $\mathcal{N}_\omega/\mathcal{V}$ are small. We can, hence, replace the perturbation (57) due to a radiation field by

$$\mathcal{V}_S = -\frac{q}{m} \hat{\vec{p}} \cdot \vec{A}(\vec{r}, t) . \tag{69}$$

In case that such perturbation acts on an electron and is due to superpositions of planar waves described through the vector potential (41) it holds

$$\mathcal{V}_S \approx \frac{e}{m} \sum_{\vec{k},\hat{u}} \sqrt{\frac{4\pi \mathcal{N}_k \hbar}{k\mathcal{V}}}\, \alpha(\vec{k}, \hat{u})\, \hat{\vec{p}} \cdot \hat{u} \exp\left[i(\vec{k} \cdot \vec{r} - \omega t) \right] . \tag{70}$$

where we have replaced ω in (41) through $k = |\vec{k}| = \omega$. The sum runs over all possible $\vec{k}$ vectors and might actually be an integral, the sum over $\hat{u}$ involves the two possible polarizations of planar electromagnetic waves. A factor $\alpha(\vec{k}, \hat{u})$ has been added to describe eliptically or circularly polarized waves. Equation (70) is the form of the perturbation which, under ordinary circumstances, describes the effect of a radiation field on an electron system and which will be assumed below to describe radiative transitions.

2.3 Perturbations due to Electromagnetic Radiation

We had identified in Eq. (70) above that the effect of a radiation field on an electronic system is accounted for by perturbations with a so-called harmonic time dependence $\sim \exp(-i\omega t)$. A perturbation expansion for the transition amplitude is derived on page 218 of Chapter 8 of qmbook.pdf. We want to apply now the perturbation expansion to such perturbations. For the sake of including the effect of superpositions of plane waves we will assume, however, that two planar waves simulataneously interact with an electronic system, such that the combined radiation field is decribed by the vector potential

$$\begin{aligned} \vec{A}(\vec{r}, t) &= A_1\, \hat{u}_1 \exp\left[i\,(\vec{k}_1 \cdot \vec{r} - \omega_1\, t) \right] \quad \text{incoming wave} \\ &+ A_2\, \hat{u}_2 \exp\left[i\,(\vec{k}_2 \cdot \vec{r} \mp \omega_2\, t) \right] \quad \text{incoming or outgoing wave} \end{aligned} \tag{71}$$

combining an incoming and an incoming or outgoing wave. The coefficients A_1, A_2 are defined through (40).

The resulting perturbation on an electron system, according to (70), is

$$\mathcal{V}_S \;=\; \Big[\, \hat{V}_1 \exp(-i\omega_1 t) \;+\; \hat{V}_2 \exp(\mp i\omega_2 t) \Big]\; e^{\lambda t} \;,\; \lambda \,\to\, 0+ \;,\; t_o \,\to\, -\infty \tag{72}$$

where $\hat{V}_1$ and $\hat{V}_2$ are time-independent operators defined as

$$\hat{V}_j \;=\; \underbrace{\frac{e}{m}\sqrt{\frac{8\pi\mathcal{N}_j\hbar}{\omega_j\mathcal{V}}}}_{\text{I}}\;\underbrace{\hat{\vec{p}}\cdot\hat{u}_j}_{\text{II}}\;\underbrace{e^{i\vec{k}\cdot\vec{r}}}_{\text{III}} \;. \tag{73}$$

Here the factor I describes the strength of the radiation field (for the specified planar wave) as determined through the photon density $\mathcal{N}_j/\mathcal{V}$ and the factor II describes the polarization of the planar wave; note that $\hat{u}_j$, according to (33, 71), defines the direction of the $\vec{E}$-field of the radiation. The factor III in (73) describes the propagation of the planar wave, the direction of the propagation being determined by $\hat{k} \,=\, \vec{k}/|\vec{k}|$. We will demonstrate below that the the sign of $\mp i\omega t$ determines if the energy of the planar wave is absorbed ("-" sign) or emitted ("+" sign) by the quantum system. In (73) $\vec{r}$ is the position of the electron and $\hat{\vec{p}} \,=\, (\hbar/i)\nabla$ is the momentum operator of the electron. A factor $\exp(\lambda t)$, $\lambda \,\to\, 0+$ has been introduced which describes that at time $t_o \,\to\, -\infty$ the perturbation is turned on gradually. This factor will serve mainly the purpose of keeping in the following derivation all mathematical quantities properly behaved, i.e., non-singular.

The generic situation we attempt to describe entails a particle at time $t \,=\, t_o$ in a state $|0\rangle$ and a radiation field beginning to act at $t \,=\, t_o$ on the particle promoting it into some of the other states $|n\rangle$, $n = 1, 2, \ldots$. The states $|0\rangle$, $|n\rangle$ are defined in (58–60) as the eigenstates of the unperturbed Hamiltonian H_o. One seeks to predict the probability to observe the particle in one of the states $|n\rangle$, $n \,\neq\, 0$ at some later time $t \,\geq\, t_o$. For this purpose one needs to determine the state $|\Psi_S(t)\rangle$ of the particle. This state obeys the Schrödinger equation

$$i\hbar\,\partial_t|\Psi_S(t)\rangle \;=\; [\,H_o \;+\; \mathcal{V}_S(t)\,]\,|\Psi_S(t)\rangle \tag{74}$$

subject to the initial condition

$$|\Psi_S(t_o)\rangle \;=\; |0\rangle \;. \tag{75}$$

The probability to find the particle in the state $|n\rangle$ at time t is then

$$p_{0\to n}(t) \;=\; |\langle n|\Psi_S(t)\rangle|^2 \;. \tag{76}$$

Using derivations in Eqs. (8.145-8.157) of Chapter 8, one can conclude for the average transition rate

$$\begin{aligned} k \;=\; \langle\, \frac{d}{dt}\, p_{0\to n}(t)\,\rangle_t \quad &=\quad \frac{2\pi}{\hbar}\,\Big[\; |\langle n|\hat{V}_1|0\rangle|^2\,\delta(\epsilon_n \,-\, \epsilon_o \,-\, \hbar\omega_1) \\ &\qquad +\quad |\langle n|\hat{V}_2|0\rangle|^2\,\delta(\epsilon_n \,-\, \epsilon_o \,\mp\, \hbar\omega_2)\;\Big] \end{aligned} \tag{77}$$

Obviously, the two terms apearing on the rhs. of this expression describe the individual effects of the two planar wave contributions of the perturbation (71–73). The δ-functions appearing in this expression reflect energy conservation: the incoming plane wave contribution of (72, 73), due to the vector potential

$$A_1 \, \hat{u}_1 \exp\left[i \, (\vec{k}_1 \cdot \vec{r} \, - \, \omega_1 \, t) \right] \; , \tag{78}$$

leads to final states $|n\rangle$ with energy $\epsilon_n \, = \, \epsilon_o + \hbar\omega_1$. The second contribution to (77), describing either an incoming or an outgoing plane wave due to the vector potential

$$A_2 \, \hat{u}_2 \exp\left[i \, (\vec{k}_1 \cdot \vec{r} \, \mp \, \omega_2 \, t) \right] \; , \tag{79}$$

leads to final states $|n\rangle$ with energy $\epsilon_n \, = \, \epsilon_o \, \pm \, \hbar\omega_2$. The result supports our definition of *incoming* and *outgoing* waves in (30) and (71)

The matrix elements $\langle n|\hat{V}_1|0\rangle$ and $\langle n|\hat{V}_2|0\rangle$ in (77) play an essential role for the transition rates of radiative transitions. First, these matrix elements determine the so-called *selection rules* for the transition: the matrix elements vanish for many states $|n\rangle$ and $|0\rangle$ on the ground of symmetry and geometrical properties. In case the matrix elements are non-zero, the matrix elements can vary strongly for different states $|n\rangle$ of the system, a property, which is observed through the so-called spectral intensities of transitions $|0\rangle \, \rightarrow \, |n\rangle$.

2.4 One-Photon Absorption and Emission in Atoms

We finally can apply the results derived to describe transition processes which involve the absorption or emission of a single photon. For this purpose we will employ the transition rate as given in Eq. (77) which accounts for such transitions.

Absorption of a Plane Polarized Wave

We consider first the case of absorption of a monochromatic, plane polarized wave described through the complex vector potential

$$\vec{A}(\vec{r},t) \; = \; \sqrt{\frac{8\pi\mathcal{N}\hbar}{\omega\mathcal{V}}} \; \hat{u} \, \exp\left[\frac{1}{\hbar}(\vec{k} \cdot \vec{r} \, - \, \omega t) \right] \; . \tag{80}$$

We will employ only the real part of this potential, i.e., the vector potential actually assumed is

$$\vec{A}(\vec{r},t) \; = \; \sqrt{\frac{2\pi\mathcal{N}\hbar}{\omega\mathcal{V}}} \; \hat{u} \, \exp\left[\frac{1}{\hbar}(\vec{k} \cdot \vec{r} \, - \, \omega t) \right] \; + \; \sqrt{\frac{2\pi\mathcal{N}\hbar}{\omega\mathcal{V}}} \; \hat{u} \, \exp\left[\frac{1}{\hbar}(-\vec{k} \cdot \vec{r} \, + \, \omega t) \right] \; . \tag{81}$$

The perturbation on an atomic electron system is then according to (72, 73)

$$\mathcal{V}_S \; = \; \left[\hat{V}_1 \, \exp(-i\omega t) \; + \; \hat{V}_2 \, \exp(+i\omega t) \right] \, e^{\lambda t} \; , \, \lambda \, \rightarrow \, 0+ \; , \, t_o \, \rightarrow \, -\infty \tag{82}$$

where

$$\hat{V}_{1,2} \;=\; \frac{e}{m}\sqrt{\frac{2\pi\mathcal{N}\hbar}{\omega\mathcal{V}}}\;\hat{\vec{p}}\cdot\hat{u}\;e^{\pm i\vec{k}\cdot\vec{r}}\;. \tag{83}$$

Only the first term of (72) will contribute to the absorption process, the second term can be discounted in case of absorption. The absorption rate, according to (77), is then

$$k_{\rm abs} \;=\; \frac{2\pi}{\hbar}\,\frac{e^2}{m_e^2}\,\frac{2\pi\mathcal{N}\hbar}{\omega\mathcal{V}}\;\left|\,\hat{u}\cdot\langle n|\,\hat{\vec{p}}\,e^{i\vec{k}\cdot\vec{r}}\,|0\rangle\,\right|^2\;\delta(\epsilon_n\,-\,\epsilon_o\,-\,\hbar\omega) \tag{84}$$

Dipole Approximation We seek to evaluate the matrix element

$$\vec{M} \;=\; \langle n|\,\hat{\vec{p}}\,e^{i\vec{k}\cdot\vec{r}}\,|0\rangle\;. \tag{85}$$

The matrix element involves a spatial integral over the electronic wave functions associated with states $|n\rangle$ and $|0\rangle$. For example, in case of a radiative transition from the 1s state of hydrogen to one of its three 2p states, the wave functions are (n,ℓ,m denote the relevant quantum numbers)

$$\psi_{n=1,\ell=0,m=0}(r,\theta,\phi) \;\;=\;\; 2\sqrt{\frac{1}{a_o^3}}\;e^{-r/a_o}\,Y_{00}(\theta,\phi)\quad 1{\rm s} \tag{86}$$

$$\psi_{n=2,\ell=1,m}(r,\theta,\phi) \;\;=\;\; -\frac{1}{2}\sqrt{\frac{6}{a_o^3}}\;\frac{r}{a_o}\;e^{-r/2a_o}\,Y_{1m}(\theta,\phi)\quad 2{\rm p} \tag{87}$$

and the integral is

$$\begin{aligned}\vec{M} \;\;=\;\; \frac{\hbar\sqrt{6}}{ia_o^4}\int_0^\infty r^2dr\int_{-1}^1 d\cos\theta\int_0^{2\pi}d\phi\;r\,e^{-r/2a_o}\,Y^*_{1m}(\theta,\phi)\;\times\\ \times\nabla e^{i\vec{k}\cdot\vec{r}}e^{-r/a_o}\,Y_{00}(\theta,\phi)\end{aligned} \tag{88}$$

These wave functions make significant contributions to this integral only for r-values in the range $r\,<\,10\,a_o$. However, in this range one can expand

$$e^{i\vec{k}\cdot\vec{r}} \;\approx\; 1\;+\;i\vec{k}\cdot\vec{r}\;+\;\ldots \tag{89}$$

One can estimate that the absolute magnitude of the second term in (89) and other terms are never larger than $20\pi\,a_o/\lambda$. Using $|\vec{k}|\;=\;2\pi/\lambda$, the value of the wave length for the 1s $\rightarrow$ 2p transition

$$\lambda \;=\; \frac{2\pi\hbar c}{\Delta E_{2p-1s}} \;=\; 1216\ \text{Å} \tag{90}$$

and $a_o\;=\;0.529$ Å one concludes that in the significant integration range in (88) holds $e^{i\vec{k}\cdot\vec{r}}\;\approx$ $1\;+\;{\rm O}(\frac{1}{50})$ such that one can approximate

$$e^{i\vec{k}\cdot\vec{r}} \;\approx\; 1\;. \tag{91}$$

One refers to this approximation as the *dipole approximation*.

Transition Dipole Moment A further simplification of the matrix element (85) can then be achieved and the differential operator $\hat{\vec{p}} = \frac{\hbar}{i}\nabla$ replaced by by the simpler multiplicative operator $\vec{r}$. This simplification results from the identity

$$\hat{\vec{p}} \;=\; \frac{m}{i\hbar}\,[\,\vec{r},\,H_o\,] \tag{92}$$

where H_o is the Hamiltonian given by (56) and, in case of the hydrogen atom, is

$$H_o \;=\; \frac{(\hat{\vec{p}})^2}{2m_e} \;+\; V(\vec{r}) \quad ,\; V(\vec{r}) \;=-\;\frac{e^2}{r}\;. \tag{93}$$

For the commutator in (92) one finds

$$\begin{aligned}
[\,\vec{r},\,H_o\,] \;&=\; [\,\vec{r},\,\frac{\hat{\vec{p}}^2}{2m_e}\,] \;+\; \underbrace{[\,\vec{r},\,V(\vec{r})\,]}_{=\,0} \\
&=\; \frac{1}{2m_e}\sum_{k=1}^{3}\hat{p}_k\,[\,\vec{r},\,\hat{p}_k\,] \;+\; \frac{1}{2m_e}\sum_{k=1}^{3}[\,\vec{r},\,\hat{p}_k\,]\,p_k
\end{aligned} \tag{94}$$

Using $\vec{r} = \sum_{j=1}^{3} x_j\hat{e}_j$ and the commutation property $[x_k,\,\hat{p}_j] \;=\; i\hbar\,\delta_{kj}$ one obtains

$$[\,\vec{r},\,H_o\,] \;=\; \frac{i\hbar}{m}\sum_{j,k=1}^{3} p_k\;\hat{e}_j\,\delta_{jk} \;=\; \frac{i\hbar}{m}\sum_{j,k=1}^{3} p_k\;\hat{e}_k \;=\; \frac{i\hbar}{m}\;\hat{\vec{p}} \tag{95}$$

from which follows (92).

We are now in a position to obtain an alternative expression for the matrix element (85). Using (91) and (92) one obtains

$$\vec{M} \;\approx\; \frac{m}{i\hbar}\,\langle n|\,[\vec{r},\,H_o]\,|0\rangle \;=\; \frac{m\,(\epsilon_o \,-\, \epsilon_n)}{i\hbar}\,\langle n|\vec{r}\,|0\rangle\;. \tag{96}$$

Insertion into (84) yields

$$k_{\rm abs} \;=\; \frac{4\pi^2\,e^2\,\mathcal{N}\,\omega}{\mathcal{V}}\;\Big|\;\hat{u}\cdot\langle n|\,\hat{\vec{r}}\,|0\rangle\;\Big|^2\;\delta(\epsilon_n - \epsilon_o - \hbar\omega) \tag{97}$$

where we used the fact that due to the δ-function factor in (84) one can replace $\epsilon_n - \epsilon_o$ by $\hbar\omega$. The δ-function appearing in this expression, in practical situations, will actually be replaced by a distribution function which reflects (1) the finite life time of the states $|n\rangle$, $|0\rangle$, and (2) the fact that strictly monochromatic radiation cannot be prepared such that any radiation source provides radiation with a frequency distribution.