

Klaus Schulten
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PHYS550 - Module 1 - Photobiology

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 the “Notes on Quantum Mechanics” textbook.

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 equations¹

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

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

¹We 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.

In addition, the two homogeneous Maxwell equations hold

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

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

Scalar and Vector Potential

Setting

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

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

$$\nabla \times \left(\vec{E}(\vec{r}, t) + \partial_t \vec{A}(\vec{r}, t) \right) = 0 \quad (6)$$

which is solved by

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

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

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

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:

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

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

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

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

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)

$$\nabla \cdot \left(-\nabla V(\vec{r}, t) - \partial_t \vec{A}(\vec{r}, t) \right) = 4\pi \rho(\vec{r}, t). \quad (12)$$

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

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

In case of the boundary condition

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

the solution is given by the Coulomb integral

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

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

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

The identity

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

together with condition (11) leads us to

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

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

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

For the curl of \vec{J}_ℓ holds

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

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

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

or

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

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

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

and from this follows

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

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

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

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

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

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

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

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

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

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

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

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

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

where the dispersion relationship

$$|\vec{k}| = \omega \quad (31)$$

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

$$\hat{u} \cdot \vec{k} = 0. \quad (32)$$

\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

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

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

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

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

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

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

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

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

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

$$\langle \epsilon \rangle = \frac{\omega^2}{8\pi} A_o^2 \quad (38)$$

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)

²The definition *incoming waves* and *outgoing waves* is rationalized below in the discussion following Eq. (77); see also the comment below Eqs. (37, 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}_ω the energy density is obviously

$$\langle \epsilon \rangle = \frac{\mathcal{N}_\omega \hbar \omega}{\mathcal{V}}. \quad (39)$$

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

$$A_o = \sqrt{\frac{8\pi\mathcal{N}_\omega\hbar}{\omega\mathcal{V}}}. \quad (40)$$

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

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

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

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

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 longitudinal 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

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

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

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

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

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

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

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

where $((\dots))$ 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

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

For this purpose one notes

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

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

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 densities³.

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

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

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.

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

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

$$H = \frac{\hat{p}^2}{2m} - \frac{q}{2m} (\hat{p}\cdot\vec{A} + \vec{A}\cdot\hat{p}) + \frac{q^2}{2m} A^2 + qV \quad (51)$$

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

$$(\hat{p}\cdot\vec{A} - \vec{A}\cdot\hat{p})f(\vec{r}) = \frac{\hbar}{i} (\vec{A}\cdot\nabla f + f\nabla\cdot\vec{A} - \vec{A}\cdot\nabla f) = \frac{\hbar}{i} f\nabla\cdot\vec{A}. \quad (52)$$

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

$$\hat{p}\cdot\vec{A}f = \vec{A}\cdot\hat{p}f \quad (53)$$

and, consequently,

$$H = \frac{\hat{p}^2}{2m} - \frac{q}{m} \hat{p}\cdot\vec{A} + \frac{q^2}{2m} A^2 + qV. \quad (54)$$

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 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

$$H = H_o + \mathcal{V}_S \quad (55)$$

$$H_o = \frac{\hat{p}^2}{2m} + qV \quad (56)$$

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

where $\vec{A}(\vec{r},t)$ is given by (41). Here the so-called unperturbed system is governed by the Hamilto-

nian H_o with stationary states defined through the eigenvalue problem

$$H_o |n\rangle = \epsilon_n |n\rangle \quad , \quad n = 0, 1, 2 \dots \quad (58)$$

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

$$\langle n|m\rangle = \delta_{nm} \quad (59)$$

and for the identity

$$\mathbb{1} = \sum_{n=0}^{\infty} |n\rangle\langle n| . \quad (60)$$

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 follows⁴. We first note, using (40)

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

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

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

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., $\lambda = 2\pi c/\omega$, one obtains for (61) using $\mathcal{V} = \lambda^3 = 8\pi^3 c^3/\omega^3$

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

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

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

500 keV

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

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

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

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

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

For the same assumptions as above one obtains

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

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

$$\left| \frac{e^2}{2m_e} A^2 \right| \sim 10 \text{ eV} \cdot 10^{-8} = 10^{-7} \text{ eV} . \quad (68)$$

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

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

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

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

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 elliptically 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 simultaneously interact with an electronic system, such that the combined radiation field is described by the vector potential

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

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

$$\mathcal{V}_S = \left[\hat{V}_1 \exp(-i\omega_1 t) + \hat{V}_2 \exp(\mp i\omega_2 t) \right] e^{\lambda t}, \lambda \rightarrow 0+, t_o \rightarrow -\infty \quad (72)$$

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

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

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 $\exp(\lambda t)$, $\lambda \rightarrow 0+$ has been introduced which describes that at time $t_o \rightarrow -\infty$ 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 $|n\rangle$, $n = 1, 2, \dots$. 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

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

subject to the initial condition

$$|\Psi_S(t_o)\rangle = |0\rangle . \quad (75)$$

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

$$p_{0 \rightarrow n}(t) = |\langle n | \Psi_S(t) \rangle|^2 . \quad (76)$$

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

$$k = \left\langle \frac{d}{dt} p_{0 \rightarrow n}(t) \right\rangle_t = \frac{2\pi}{\hbar} \left[|\langle n | \hat{V}_1 | 0 \rangle|^2 \delta(\epsilon_n - \epsilon_o - \hbar\omega_1) + |\langle n | \hat{V}_2 | 0 \rangle|^2 \delta(\epsilon_n - \epsilon_o \mp \hbar\omega_2) \right] \quad (77)$$

Obviously, the two terms appearing 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

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

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

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

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

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

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

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

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

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

where

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

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

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

Dipole Approximation

We seek to evaluate the matrix element

$$\vec{M} = \langle n | \hat{\vec{p}} e^{i\vec{k} \cdot \vec{r}} | 0 \rangle. \quad (85)$$

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)

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

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

and the integral is

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

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

$$e^{i\vec{k}\cdot\vec{r}} \approx 1 + i\vec{k}\cdot\vec{r} + \dots \quad (89)$$

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

$$\lambda = \frac{2\pi\hbar c}{\Delta E_{2p-1s}} = 1216 \text{ \AA} \quad (90)$$

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

$$e^{i\vec{k}\cdot\vec{r}} \approx 1. \quad (91)$$

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 $\hat{p} = \frac{\hbar}{i}\nabla$ replaced by the simpler multiplicative operator \vec{r} . This simplification results from the identity

$$\hat{p} = \frac{m}{i\hbar} [\vec{r}, H_o] \quad (92)$$

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

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

For the commutator in (92) one finds

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

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

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

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

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

Insertion into (84) yields

$$k_{\text{abs}} = \frac{4\pi^2 e^2 \mathcal{N} \omega}{\mathcal{V}} \left| \hat{u} \cdot \langle n | \hat{\vec{r}} | 0 \rangle \right|^2 \delta(\epsilon_n - \epsilon_o - \hbar\omega) \quad (97)$$

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.

2.5 Absorption of Thermal Radiation

We want to assume now that the hydrogen atom is placed in an environment which is sufficiently hot, i.e., a very hot oven, such that the thermal radiation present supplies a continuum of frequencies, directions, and all polarizations of the radiation. We have demonstrated in our derivation of the rate of one-photon processes that in first order the contributions of all components of the radiation field add. We can, hence, obtain the transition rate in the present case by adding the individual transition rates of all planar waves present in the oven. Instead of adding the components of all possible \vec{k} values we integrate over all \vec{k} using the following rule

$$\sum_{\vec{k}} \sum_{\hat{u}} \implies \mathcal{V} \int_{-\infty}^{+\infty} \frac{k^2 dk}{(2\pi)^3} \int d\hat{k} \sum_{\hat{u}} \quad (98)$$

Here $\int d\hat{k}$ is the integral over all orientations of \vec{k} . Integrating and summing accordingly over all contributions as given by

$$k_{\text{abs}} = \frac{4\pi^2 e^2 \mathcal{N} \omega}{\mathcal{V}} \left| \hat{u} \cdot \langle n | \hat{\vec{r}} | 0 \rangle \right|^2 \delta(\epsilon_n - \epsilon_o - \hbar\omega) \quad (99)$$

and using $kc = \omega$ results in the total absorption rate

$$k_{\text{abs}}^{(\text{tot})} = \frac{e^2 \mathcal{N} \omega^3}{2\pi c^3 \hbar} \int d\hat{k} \sum_{\hat{u}} \left| \hat{u} \cdot \langle n | \hat{\vec{r}} | 0 \rangle \right|^2 \quad (100)$$

where the factor $1/\hbar$ arose from the integral over the δ -function.

In order to carry out the integral $\int d\hat{k}$ we note that \hat{u} describes the possible polarizations of the planar waves as defined in Eqs. 30-34 of previous lecture notes (Section 1.2 Planar Electromagnetic Waves). \hat{k} and \hat{u} , according to Eq. 32 (in section 1.2) are orthogonal to each other. As a result, there are only two linearly independent directions of \hat{u} possible, say \hat{u}_1 and \hat{u}_2 . The unit vectors \hat{u}_1 , \hat{u}_2 and \hat{k} can be chosen to point along the x_1 , x_2 , x_3 -axes of a right-handed cartesian coordinate system.

Let us assume that the wave functions describing states $|n\rangle$ and $|0\rangle$ have been chosen real such that $\vec{\rho} = \langle n|\vec{r}|0\rangle$ is a real, three-dimensional vector. The direction of this vector in the $\hat{u}_1, \hat{u}_2, \hat{k}$ frame is described by the angles ϑ, φ , the direction of \hat{u}_1 is described by the angles $\vartheta_1 = \pi/2, \varphi_1 = 0$ and of \hat{u}_2 by $\vartheta_2 = \pi/2, \varphi_2 = \pi/2$. For the two angles $\alpha = \angle(\hat{u}_1, \vec{\rho})$ and $\beta = \angle(\hat{u}_2, \vec{\rho})$ holds then

$$\cos\alpha = \cos\vartheta_1 \cos\vartheta + \sin\vartheta_1 \sin\vartheta \cos(\varphi_1 - \varphi) = \sin\vartheta \cos\varphi \quad (101)$$

and

$$\cos\beta = \cos\vartheta_2 \cos\vartheta + \sin\vartheta_2 \sin\vartheta \cos(\varphi_2 - \varphi) = \sin\vartheta \sin\varphi. \quad (102)$$

Accordingly, one can express

$$\sum_{\hat{u}} |\hat{u} \cdot \langle n|\vec{r}|0\rangle|^2 = |\rho|^2 (\cos^2\alpha + \cos^2\beta) = \sin^2\vartheta. \quad (103)$$

and obtain

$$\int d\hat{k} \sum_{\hat{u}} |\hat{u} \cdot \langle n|\vec{r}|0\rangle|^2 = |\rho|^2 \int_0^{2\pi} \int_{-1}^1 d\cos\vartheta (1 - \cos^2\vartheta) = \frac{8\pi}{3} \quad (104)$$

This geometrical average, finally, can be inserted into (100) to yield the total absorption rate

$$k_{\text{abs}}^{(\text{tot})} = \mathcal{N}_\omega \frac{4e^2\omega^3}{3c^3\hbar} |\langle n|\vec{r}|0\rangle|^2, \quad \mathcal{N}_\omega \text{ photons before absorption.} \quad (105)$$

For absorption processes involving the electronic degrees of freedom of atoms and molecules this radiation rate is typically of the order of 10^9 s^{-1} . For practical evaluations we provide an expression which eliminates the physical constants and allows one to determine numerical values readily. For this purpose we use $\omega/c = 2\pi/\lambda$ and obtain

$$\frac{4e^2\omega^3}{3c^3\hbar} = \frac{32\pi^3}{3} \frac{e^2}{a_o\hbar} \frac{a_o}{\lambda^3} = 1.37 \times 10^{19} \frac{1}{\text{s}} \times \frac{a_o}{\lambda^3} \quad (106)$$

and

$$k_{\text{abs}}^{(\text{tot})} = \mathcal{N}_\omega 1.37 \times 10^{19} \frac{1}{\text{s}} \times \frac{a_o}{\lambda} \frac{|\langle n|\vec{r}|0\rangle|^2}{\lambda^2}, \quad (107)$$

where

$$\lambda = \frac{2\pi c\hbar}{\epsilon_n - \epsilon_o} \quad (108)$$

The last two factors in (105) combined are typically somewhat smaller than $(1 \text{ \AA}/1000 \text{ \AA})^3 = 10^{-9}$. Accordingly, the absorption rate is of the order of 10^9 s^{-1} or 1/nanosecond.

Transition Dipole Moment

The expression (105) for the absorption rate shows that the essential property of a molecule which determines the absorption rate is the so-called transition dipole moment $|\langle n|\vec{r}|0\rangle|$. The transition dipole moment can vanish for many transitions between stationary states of a quantum system, in particular, for atoms or symmetric molecules. The value of $|\langle n|\vec{r}|0\rangle|$ determines the strength of an

optical transition. The most intensely absorbing molecules are long, linear molecules.

2.6 Emission of Radiation

We now consider the rate of emission of a photon. The radiation field is described, as for the absorption process, by planar waves with vector potential

$$\vec{A}(\vec{r}, t) = \sqrt{\frac{2\pi\mathcal{N}\hbar}{\omega\mathcal{V}}} \hat{u} \exp\left[\frac{1}{\hbar}(\vec{k} \cdot \vec{r} - \omega t)\right] + \sqrt{\frac{2\pi\mathcal{N}\hbar}{\omega\mathcal{V}}} \hat{u} \exp\left[\frac{1}{\hbar}(-\vec{k} \cdot \vec{r} + \omega t)\right]. \quad (109)$$

and perturbation

$$\mathcal{V}_S = \left[\hat{V}_1 \exp(-i\omega t) + \hat{V}_2 \exp(+i\omega t) \right] e^{\lambda t}, \quad \lambda \rightarrow 0+, \quad t_o \rightarrow -\infty \quad (110)$$

where

$$\hat{V}_{1,2} = \frac{e}{m} \sqrt{\frac{2\pi\mathcal{N}\hbar}{\omega\mathcal{V}}} \hat{\vec{p}} \cdot \hat{u} e^{\pm i\vec{k} \cdot \vec{r}}. \quad (111)$$

In case of emission only the second term $\hat{V}_2 \exp(+i\omega t)$ in (111) contributes. Otherwise, the calculation of the emission rate proceeds as in the case of absorption. However, the resulting total rate of emission bears a different dependence on the number of photons present in the environment. This difference between emission and absorption is due to the quantum nature of the radiation field.

The quantum nature of radiation manifests itself in that the number of photons \mathcal{N}_ω must be an integer, i.e., $\mathcal{N}_\omega = 0, 1, 2, \dots$. This poses, however, a problem in case of emission by quantum systems in complete darkness, i.e., for $\mathcal{N}_\omega = 0$. In case of a classical radiation field one would expect that emission cannot occur. However, a quantum mechanical treatment of the radiation field leads to a total emission rate which is proportional to $\mathcal{N}_\omega + 1$ where \mathcal{N}_ω is the number of photons *before* emission. This dependence predicts, in agreement with observations, that emission occurs even if no photon is present in the environment. The corresponding process is termed *spontaneous emission*. However, there is also a contribution to the emission rate which is proportional to \mathcal{N}_ω which is termed *induced emission* since it can be induced through radiation provided, e.g., in lasers. The total rate of emission, accordingly, is

$$\begin{aligned} k_{\text{em}}^{(\text{tot})} &= \frac{4e^2\omega^3}{3c^3\hbar} |\langle n|\vec{r}|0\rangle|^2 \quad (\text{spontaneous emission}) \\ &+ \mathcal{N}_\omega \frac{4e^2\omega^3}{3c^3\hbar} |\langle n|\vec{r}|0\rangle|^2 \quad (\text{induced emission}) \\ &= (\mathcal{N}_\omega + 1) \frac{4e^2\omega^3}{3c^3\hbar} |\langle n|\vec{r}|0\rangle|^2 \end{aligned} \quad (112)$$

$$\mathcal{N}_\omega \text{ photons before emission.} \quad (113)$$

2.7 Planck's Radiation Law

The postulate of the $\mathcal{N}_\omega + 1$ dependence of the rate of emission as given in (112) is consistent with Planck's radiation law which reflects the (boson) quantum nature of the radiation field. To demonstrate this property we apply the transition rates (106) and (112) to determine the stationary

distribution of photons $\hbar\omega$ in an oven of temperature T . Let N_o and N_n denote the number of atoms in state $|0\rangle$ and $|n\rangle$, respectively. For these numbers holds

$$N_n / N_o = \exp[-(\epsilon_n - \epsilon_o)/k_B T] \quad (114)$$

where k_B is the Boltzmann constant. We assume $\epsilon_n - \epsilon_o = \hbar\omega$. Under stationary conditions the number of hydrogen atoms undergoing an absorption process $|0\rangle \rightarrow |n\rangle$ must be the same as the number of atoms undergoing an emission process $|n\rangle \rightarrow |0\rangle$. Defining the rate of spontaneous emission

$$k_{sp} = \frac{4 e^2 \omega^3}{3 c^3 \hbar} |\langle n | \vec{r} | 0 \rangle|^2 \quad (115)$$

the rates of absorption and emission are $\mathcal{N}_\omega k_{sp}$ and $(\mathcal{N}_\omega + 1)k_{sp}$, respectively. The number of atoms undergoing absorption in unit time are $\mathcal{N}_\omega k_{sp} N_o$ and undergoing emission are $(\mathcal{N}_\omega + 1)k_{sp} N_n$. Hence, it must hold

$$\mathcal{N}_\omega k_{sp} N_o = (\mathcal{N}_\omega + 1) k_{sp} N_n \quad (116)$$

It follows, using (114),

$$\exp[-\hbar\omega/k_B T] = \frac{\mathcal{N}_\omega}{\mathcal{N}_\omega + 1}. \quad (117)$$

This equation yields

$$\mathcal{N}_\omega = \frac{1}{\exp[\hbar\omega/k_B T] - 1}, \quad (118)$$

i.e., the well-known Planck radiation formula.

In many important processes induced by interactions between radiation and matter two or more photons participate. Examples are radiative transitions in which two photons are absorbed or emitted or scattering of radiation by matter in which a photon is absorbed and another re-emitted. In the following we discuss several examples.

2.8 Two-Photon Absorption

The interaction of electrons with radiation, under ordinary circumstances, induce single photon absorption processes as described by the transition rate Eq. 97 of Section 2.4. The transition requires that the transition dipole moment $\langle n | \vec{r} | 0 \rangle$ does not vanish for two states $|0\rangle$ and $|n\rangle$. However, a transition between the states $|0\rangle$ and $|n\rangle$ may be possible, even if $\langle n | \vec{r} | 0 \rangle$ vanishes, but then requires the absorption of two photons. In this case one needs to choose the energy of the photons to obey

$$\epsilon_n = \epsilon_o + 2\hbar\omega. \quad (119)$$

The respective radiative transition is of 2nd order. The resulting rate of the transition depends on \mathcal{N}_ω^2 . The intense radiation fields of lasers allow one to increase transition rates to levels which can readily be observed in the laboratory.

The perturbation which accounts for the coupling of the electronic system and the radiation field is the same as in case of 1st order absorption processes and given by (Eqs. 82-83 ; however, in case of absorption only \hat{V}_1 contributes. One obtains, dropping the index 1 characterizing the

radiation,

$$k = \frac{2\pi}{\hbar} \left(\frac{e^2}{m_e^2} \frac{2\pi\mathcal{N}_\omega\hbar}{\omega\mathcal{V}} \right)^2 \left| \sum_{m=0}^{\infty} \frac{\langle n|\hat{u} \cdot \hat{\vec{p}} e^{i\vec{k}\cdot\vec{r}}|m\rangle \langle m|\hat{u} \cdot \hat{\vec{p}} e^{i\vec{k}\cdot\vec{r}}|0\rangle}{\epsilon_m - \epsilon_o - \hbar\omega_1 - i\hbar\lambda} \right|^2 \times \delta(\epsilon_m - \epsilon_o - 2\hbar\omega). \quad (120)$$

Employing the dipole approximation (91) and using (92) from Section 2.4 yields, finally,

$$k = \left(\frac{\mathcal{N}_\omega}{\mathcal{V}} \right)^2 \frac{8\pi^3 e^4}{\hbar} \left| \sum_{m=0}^{\infty} \frac{(\epsilon_n - \epsilon_m) \hat{u} \cdot \langle n|\hat{\vec{r}}|m\rangle (\epsilon_m - \epsilon_o) \hat{u} \cdot \langle m|\hat{\vec{r}}|0\rangle}{\hbar\omega (\epsilon_m - \epsilon_o - \hbar\omega - i\hbar\lambda)} \right|^2 \times \delta(\epsilon_m - \epsilon_o - 2\hbar\omega). \quad (121)$$

Expression (121) for the rate of 2-photon transitions shows that the transition $|0\rangle \rightarrow |n\rangle$ becomes possible through intermediate states $|m\rangle$ which become virtually excited through absorption of a single photon. In applying (121) one is, however, faced with the dilemma of having to sum over all intermediate states $|m\rangle$ of the system. If the sum in (121) does not converge rapidly, which is not necessarily the case, then expression (121) does not provide a suitable avenue of computing the rates of 2-photon transitions.

2.9 Rayleigh Scattering

We turn first to an example of so-called elastic scattering, i.e., a process in which the electronic state remains unaltered after the scattering. Rayleigh scattering is defined as the limit in which the wave length of the scattered radiation is so long that none of the quantum states of the electronic system can be excited; in fact, one assumes the even stronger condition

$$\hbar\omega_1 \ll |\epsilon_o - \epsilon_m|, \text{ for all states } |m\rangle \text{ of the electronic system} \quad (122)$$

Using $|n\rangle = |0\rangle$ and, consequently, $\omega_1 = \omega_2$, it follows

$$d\sigma = r_o^2 (\mathcal{N}_2 + 1) d\Omega_2 |\hat{u}_1 \cdot \hat{u}_2 - S(\hbar\omega)|^2 \quad (123)$$

where

$$S(\hbar\omega) = \frac{1}{m_e} \sum_m \left(\frac{\langle 0|\hat{u}_1 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_2 \cdot \hat{\vec{p}}|0\rangle}{\epsilon_m - \epsilon_o + \hbar\omega} + \frac{\langle 0|\hat{u}_2 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_1 \cdot \hat{\vec{p}}|0\rangle}{\epsilon_m - \epsilon_o - \hbar\omega} \right). \quad (124)$$

Condition (122) suggests to expand $S(\hbar\omega)$

$$S(\hbar\omega) = S(0) + S'(0) \hbar\omega + \frac{1}{2} S''(0) (\hbar\omega)^2 + \dots \quad (125)$$

Using

$$\frac{1}{\epsilon_m - \epsilon_o \pm \hbar\omega} = \frac{1}{\epsilon_m - \epsilon_o} \mp \frac{\hbar\omega}{(\epsilon_m - \epsilon_o)^2} + \frac{(\hbar\omega)^2}{(\epsilon_m - \epsilon_o)^3} + \dots \quad (126)$$

one can readily determine

$$S(0) = \sum_m \left(\frac{\langle 0|\hat{u}_1 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_2 \cdot \hat{\vec{p}}|0\rangle}{m_e (\epsilon_m - \epsilon_o)} + \frac{\langle 0|\hat{u}_2 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_1 \cdot \hat{\vec{p}}|0\rangle}{m_e (\epsilon_m - \epsilon_o)} \right) \quad (127)$$

$$S'(0) = \sum_m \left(\frac{\langle 0|\hat{u}_2 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_1 \cdot \hat{\vec{p}}|0\rangle}{m_e (\epsilon_m - \epsilon_o)^2} - \frac{\langle 0|\hat{u}_1 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_2 \cdot \hat{\vec{p}}|0\rangle}{m_e (\epsilon_m - \epsilon_o)^2} \right) \quad (128)$$

$$S''(0) = 2 \sum_m \left(\frac{\langle 0|\hat{u}_1 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_2 \cdot \hat{\vec{p}}|0\rangle}{m_e (\epsilon_m - \epsilon_o)^3} + \frac{\langle 0|\hat{u}_2 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_1 \cdot \hat{\vec{p}}|0\rangle}{m_e (\epsilon_m - \epsilon_o)^3} \right) \quad (129)$$

These three expressions can be simplified using the expression (92) for $\hat{\vec{p}}$ and the expression (60) for the identity operator from Section.2.2 and 2.4 respectively.

We want to simplify first (127). For this purpose we replace $\hat{\vec{p}}$ using (92)

$$\frac{\langle 0|\hat{u}_1 \cdot \hat{\vec{p}}|m\rangle}{m_e (\epsilon_m - \epsilon_o)} = \frac{1}{i\hbar} \langle 0|\hat{u}_1 \cdot \vec{r}|m\rangle \quad , \quad \frac{\langle m|\hat{u}_1 \cdot \hat{\vec{p}}|0\rangle}{m_e (\epsilon_m - \epsilon_o)} = -\frac{1}{i\hbar} \langle m|\hat{u}_1 \cdot \vec{r}|0\rangle \quad (130)$$

This transforms (127) into

$$S(0) = \frac{1}{i\hbar} \sum_m (\langle 0|\hat{u}_1 \cdot \vec{r}|m\rangle \langle m|\hat{u}_2 \cdot \hat{\vec{p}}|0\rangle - \langle 0|\hat{u}_2 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_1 \cdot \vec{r}|0\rangle) \quad (131)$$

According to (60) this is

$$S(0) = \frac{1}{i\hbar} \langle 0|\hat{u}_1 \cdot \vec{r} \hat{u}_2 \cdot \hat{\vec{p}} - \hat{u}_2 \cdot \hat{\vec{p}} \hat{u}_1 \cdot \vec{r}|0\rangle . \quad (132)$$

The commutator property $[x_j, \hat{p}_k] = i\hbar \delta_{jk}$ yields finally

$$S(0) = \frac{1}{i\hbar} \sum_{j,k=1}^3 (\hat{u}_1)_j (\hat{u}_2)_k \langle 0|[x_j, \hat{p}_k]|0\rangle = \sum_{j,k=1}^3 (\hat{u}_1)_j (\hat{u}_2)_k \delta_{jk} = \hat{u}_1 \cdot \hat{u}_2 \quad (133)$$

Obviously, this term cancels the $\hat{u}_1 \cdot \hat{u}_2$ term in (123).

We want to prove now that expression (128) vanishes. For this purpose we apply (130) both to $\hat{u}_1 \cdot \hat{\vec{p}}$ and to $\hat{u}_2 \cdot \hat{\vec{p}}$ which results in

$$S'(0) = \frac{m_e}{\hbar^2} \sum_m (\langle 0|\hat{u}_2 \cdot \vec{r}|m\rangle \langle m|\hat{u}_1 \cdot \vec{r}|0\rangle - \langle 0|\hat{u}_1 \cdot \vec{r}|m\rangle \langle m|\hat{u}_2 \cdot \vec{r}|0\rangle) . \quad (134)$$

Employing again (60) yields

$$S'(0) = \frac{m_e}{\hbar^2} \langle 0|[\hat{u}_2 \cdot \vec{r}, \hat{u}_1 \cdot \vec{r}]|0\rangle = 0 \quad (135)$$

where we used for the second identity the fact that $\hat{u}_1 \cdot \vec{r}$ and $\hat{u}_2 \cdot \vec{r}$ commute.

$S''(0)$ given in (129) provides then the first non-vanishing contribution to the scattering cross section (123). Using again (130) both for the $\hat{u}_1 \cdot \hat{\vec{p}}$ and the $\hat{u}_2 \cdot \hat{\vec{p}}$ terms in (129) we obtain

$$S''(0) = \frac{2m_e}{\hbar^2} \sum_m \left(\frac{\langle 0 | \hat{u}_1 \cdot \vec{r} | m \rangle \langle m | \hat{u}_2 \cdot \vec{r} | 0 \rangle}{\epsilon_m - \epsilon_o} + \frac{\langle 0 | \hat{u}_2 \cdot \vec{r} | m \rangle \langle m | \hat{u}_1 \cdot \vec{r} | 0 \rangle}{\epsilon_m - \epsilon_o} \right) \quad (136)$$

We can now combine eqs. (125, 133, 135, 136) and obtain the leading contribution to the expression (123) of the cross section for Rayleigh scattering

$$d\sigma = r_o^2 m_e^2 \omega^4 (\mathcal{N}_2 + 1) d\Omega_2 \times \left| \sum_m \left(\frac{\langle 0 | \hat{u}_1^* \cdot \vec{r} | m \rangle \langle m | \hat{u}_2 \cdot \vec{r} | 0 \rangle}{\epsilon_m - \epsilon_o} + \frac{\langle 0 | \hat{u}_2^* \cdot \vec{r} | m \rangle \langle m | \hat{u}_1 \cdot \vec{r} | 0 \rangle}{\epsilon_m - \epsilon_o} \right) \right|^2 \quad (137)$$

We have applied here a modification which arises in case of complex polarization vectors \hat{u} which describe circular and elliptical polarizaed light.

Expression (137) is of great practical importance. It explains, for example, the blue color of the sky and the polarization pattern in the sky which serves many animals, i.e., honey bees, as a compass.

2.10 Raman Scattering and Brillouin Scattering

We now consider inelastic scattering described by the Kramers-Heisenberg formula. In the case of such scattering an electron system absorbs and re-emits radiation without ending up in the initial state. The energy deficit is used to excite the system. The excitation can be electronic, but most often involves other degrees of freedom. For electronic systems in molecules or crystals the degrees of freedom excited are nuclear motions, i.e., molecular vibrations or crystal vibrational modes. Such scattering is called *Raman scattering*. If energy is absorbed by the system, one speaks of *Stokes scattering*, if energy is released, one speaks of *anti-Stokes scattering*. In case that the nuclear degrees of freedom excited absorb very little energy, as in the case of excitations of accustical modes of crystals, or in case of translational motion of molecules in liquids, the scattering is termed *Brillouin scattering*.

In the case that the scattering excites other than electronic degrees of freedom, the states $|n\rangle$ etc. defined below in (153) represent actually electronic as well as nuclear motions, e.g., in case of a diatomic molecule $|n\rangle = |\phi(elect.)_n, \phi(vibr.)_n\rangle$. Since the scattering is inelastic, the first term in (153) vanishes and one obtains in case of Raman scattering

$$d\sigma = r_o^2 (\mathcal{N}_2 + 1) \frac{\omega_2}{\omega_1} d\Omega_2 |\hat{u}_2 \cdot \mathbf{R} \cdot \hat{u}_1|^2 \quad (138)$$

where \mathbf{R} represents a 3×3 -matrix with elements

$$R_{jk} = \frac{1}{m_e} \sum_m \left(\frac{\langle n | \hat{p}_j | m \rangle \langle m | \hat{p}_k | 0 \rangle}{\epsilon_m - \epsilon_o + \hbar\omega_2} + \frac{\langle n | \hat{p}_k | m \rangle \langle m | \hat{p}_j | 0 \rangle}{\epsilon_m - \epsilon_o - \hbar\omega_1} \right) \quad (139)$$

$$\omega_2 = \omega_1 - (\epsilon_n - \epsilon_o)/\hbar \quad (140)$$

We define $\vec{x} \cdot \mathbf{R} \cdot \vec{y} = \sum_{j,k} x_j R_{jk} y_k$.

In case that the incoming photon energy $\hbar\omega_1$ is chosen to match one of the electronic excitations, e.g., $\hbar\omega_1 \approx \epsilon_m - \epsilon_o$ for a particular state $|m\rangle$, the Raman scattering cross section will be much enhanced, a case called *resonant Raman scattering*. Of course, no singularity develops in such case due to the finite life time of the state $|m\rangle$. Nevertheless, the cross section for resonant Raman scattering can be several orders of magnitude larger than that of ordinary Raman scattering, a property which can be exploited to selectively probe suitable molecules of low concentration in bulk matter.

Scattering of Photons at Electrons – Kramers-Heisenberg Cross Section

We consider in the following the scattering of a photon at an electron governed by the Hamiltonian H_o as given in (56) with stationary states $|n\rangle$ defined through (58). We assume that a planar wave with wave vector \vec{k}_1 and polarization \hat{u}_1 , as described through the vector potential

$$\vec{A}(\vec{r}, t) = A_{o1} \hat{u}_1 \cos(\vec{k}_1 \cdot \vec{r} - \omega_1 t), \quad (141)$$

has been prepared. The electron absorbs the radiation and emits immediately a second photon. We wish to describe an observation in which a detector is placed at a solid angle element $d\Omega_2 = \sin\theta_2 d\theta_2 d\phi_2$ with respect to the origin of the coordinate system in which the electron is described. We assume that the experimental set-up also includes a polarizer which selects only radiation with a certain polarization \hat{u}_2 . Let us assume for the present that the emitted photon has a wave vector \vec{k}_2 with cartesian components

$$\vec{k}_2 = k_2 \begin{pmatrix} \sin\theta_2 \cos\phi_2 \\ \sin\theta_2 \sin\phi_2 \\ \cos\theta_2 \end{pmatrix} \quad (142)$$

where the value of k_2 has been fixed; however, later we will allow the quantum system to select appropriate values. The vector potential describing the emitted plane wave is then

$$\vec{A}(\vec{r}, t) = A_{o2} \hat{u}_2 \cos(\vec{k}_2 \cdot \vec{r} - \omega_2 t). \quad (143)$$

The vector potential which describes both incoming wave and outgoing wave is a superposition of the potentials in (141, 143). We know already from our description in Section 2.3 above that the absorption of the radiation in (141) and the emission of the radiation in (143) is accounted for by the following contributions of (141, 143)

$$\vec{A}(\vec{r}, t) = A_{o1}^+ \hat{u}_1 \exp[i(\vec{k}_1 \cdot \vec{r} - \omega_1 t)] + A_{o2}^- \hat{u}_2 \exp[i(\vec{k}_2 \cdot \vec{r} - \omega_2 t)]. \quad (144)$$

The first term describes the absorption of a photon and, hence, the amplitude A_{o1}^+ is given by

$$A_{o1}^+ = \sqrt{\frac{8\pi\mathcal{N}_1\hbar}{\omega_1\mathcal{V}}} \quad (145)$$

where $\mathcal{N}_1/\mathcal{V}$ is the density of photons for the wave described by (141), i.e., the wave characterized through \vec{k}_1, \hat{u}_1 . The second term in (144) accounts for the emitted wave and, according to the description of emission processes on page 3 of the Emission of Radiation, the amplitude A_{o2}^- defined in (144) is

$$A_{o2}^- = \sqrt{\frac{8\pi(\mathcal{N}_2 + 1)\hbar}{\omega_1\mathcal{V}}} \quad (146)$$

where $\mathcal{N}_2/\mathcal{V}$ is the density of photons characterized through \vec{k}_2, \hat{u}_2 .

The perturbation which arises due to the vector potential (144) is stated in Eq.(57). In the present case we consider only scattering processes which absorb radiation corresponding to the vector potential (141) and emit radiation corresponding to the vector potential (143). The relevant terms of the perturbation (57) using the vector potential (144) are given by

$$\begin{aligned} \mathcal{V}_S(t) = & \underbrace{\frac{e}{2m_e} \hat{\vec{p}} \cdot \left\{ A_{o1}^+ \hat{u}_1 \exp[i(\vec{k}_1 \cdot \vec{r} - \omega_1 t)] + A_{o2}^- \hat{u}_2 \exp[-i(\vec{k}_2 \cdot \vec{r} - \omega_2 t)] \right\}}_{\text{contributes in 2nd order}} \\ & + \underbrace{\frac{e^2}{4m_e} A_{o1}^+ A_{o2}^- \hat{u}_1 \cdot \hat{u}_2 \exp\{i[(\vec{k}_1 - \vec{k}_2) \cdot \vec{r} - (\omega_1 - \omega_2)t]\}}_{\text{contributes in 1st order}} \end{aligned} \quad (147)$$

This expansion yields, in the present case, for the components of the wave function accounting for absorption and re-emission of a photon

$$\begin{aligned} \langle n | \Psi_D(t) \rangle = & \langle n | 0 \rangle + \quad (148) \\ & + \frac{1}{i\hbar} \frac{e^2}{4m_e} A_{o1}^+ A_{o2}^- \hat{u}_1 \cdot \hat{u}_2 \langle n | 0 \rangle \int_{t_o}^t dt' e^{i(\epsilon_n - \epsilon_o - \hbar\omega_1 + \hbar\omega_2 + i\hbar\lambda)t'} \\ & + \sum_{m=0}^{\infty} \left(\frac{1}{i\hbar} \right)^2 \frac{e^2}{4m_e^2} A_{o1}^+ A_{o2}^- \times \\ & \times \left\{ \hat{u}_1 \cdot \langle n | \hat{\vec{p}} | m \rangle \hat{u}_2 \cdot \langle m | \hat{\vec{p}} | 0 \rangle \times \right. \\ & \quad \times \int_{t_o}^t dt' \int_{t_o}^{t'} dt'' e^{i(\epsilon_n - \epsilon_m - \hbar\omega_1 + i\hbar\lambda)t'} e^{i(\epsilon_m - \epsilon_o + \hbar\omega_2 + i\hbar\lambda)t''} \\ & \quad + \hat{u}_2 \cdot \langle n | \hat{\vec{p}} | m \rangle \hat{u}_1 \cdot \langle m | \hat{\vec{p}} | 0 \rangle \times \\ & \quad \times \left. \int_{t_o}^t dt' \int_{t_o}^{t'} dt'' e^{i(\epsilon_n - \epsilon_m + \hbar\omega_2 + i\hbar\lambda)t'} e^{i(\epsilon_m - \epsilon_o - \hbar\omega_1 + i\hbar\lambda)t''} \right\} \end{aligned}$$

We have adopted the dipole approximation (91) in stating this result.

Only the second (1st order) and the third (2nd order) terms in (148) correspond to scattering processes in which the radiation field 'looses' a photon $\hbar\omega_1$ and 'gains' a photon $\hbar\omega_2$. Hence, only these two terms contribute to the scattering amplitude. Following closely the procedures adopted in evaluating the rates of 1st order and 2nd order radiative transitions, i.e., evaluating the time

integrals in (148) and taking the limits $\lim_{t_o \rightarrow -\infty}$ and $\lim_{\lambda \rightarrow 0^+}$ yields the transition rate

$$k = \frac{2\pi}{\hbar} \delta(\epsilon_n - \epsilon_o - \hbar\omega_1 + \hbar\omega_2) \left| \frac{e^2}{4m_e^2} A_{o1}^+ A_{o2}^- \hat{u}_1 \cdot \hat{u}_2 \langle n|0\rangle \right. \quad (149)$$

$$\left. - \sum_m \frac{e^2}{4m_e} A_{o1}^+ A_{o2}^- \left(\frac{\langle n|\hat{u}_1 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_2 \cdot \hat{\vec{p}}|0\rangle}{\epsilon_m - \epsilon_o + \hbar\omega_2} + \frac{\langle n|\hat{u}_2 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_1 \cdot \hat{\vec{p}}|0\rangle}{\epsilon_m - \epsilon_o - \hbar\omega_1} \right) \right|^2$$

We now note that the quantum system has the freedom to interact with any component of the radiation field to produce the emitted photon $\hbar\omega_2$. Accordingly, one needs to integrate the rate as given by (149) over all available modes of the field, i.e., one needs to carry out the integration $\mathcal{V}(2\pi)^{-3} \int k_2^2 dk_2 \dots$. Inserting also the values (145, 146) for the amplitudes A_{o1}^+ and A_{o2}^- results in the *Kramers-Heisenberg* formula for the scattering rate

$$k = \frac{\mathcal{N}_1 c}{\mathcal{V}} r_o^2 \frac{\omega_2}{\omega_1} (\mathcal{N}_2 + 1) d\Omega_2 \left| \hat{u}_1 \cdot \hat{u}_2 \langle n|0\rangle \right. \quad (150)$$

$$\left. - \frac{1}{m_e} \sum_m \left(\frac{\langle n|\hat{u}_1 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_2 \cdot \hat{\vec{p}}|0\rangle}{\epsilon_m - \epsilon_o + \hbar\omega_2} + \frac{\langle n|\hat{u}_2 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_1 \cdot \hat{\vec{p}}|0\rangle}{\epsilon_m - \epsilon_o - \hbar\omega_1} \right) \right|^2$$

Here r_o denotes the classical electron radius

$$r_o = \frac{e^2}{m_e c^2} = 2.8 \cdot 10^{-15} \text{ m} . \quad (151)$$

The factor $\mathcal{N}_1 c / \mathcal{V}$ can be interpreted as the flux of incoming photons. Accordingly, one can relate (150) to the scattering cross section defined through

$$d\sigma = \frac{\text{rate of photons arriving in the the solid angle element } d\Omega_2}{\text{flux of incoming photons}} \quad (152)$$

It holds then

$$d\sigma = r_o^2 \frac{\omega_2}{\omega_1} (\mathcal{N}_2 + 1) d\Omega_2 \left| \hat{u}_1 \cdot \hat{u}_2 \langle n|0\rangle \right. \quad (153)$$

$$\left. - \frac{1}{m_e} \sum_m \left(\frac{\langle n|\hat{u}_1 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_2 \cdot \hat{\vec{p}}|0\rangle}{\epsilon_m - \epsilon_o + \hbar\omega_2} + \frac{\langle n|\hat{u}_2 \cdot \hat{\vec{p}}|m\rangle \langle m|\hat{u}_1 \cdot \hat{\vec{p}}|0\rangle}{\epsilon_m - \epsilon_o - \hbar\omega_1} \right) \right|^2$$

3 A first look at electronic excitation: Polyene molecules

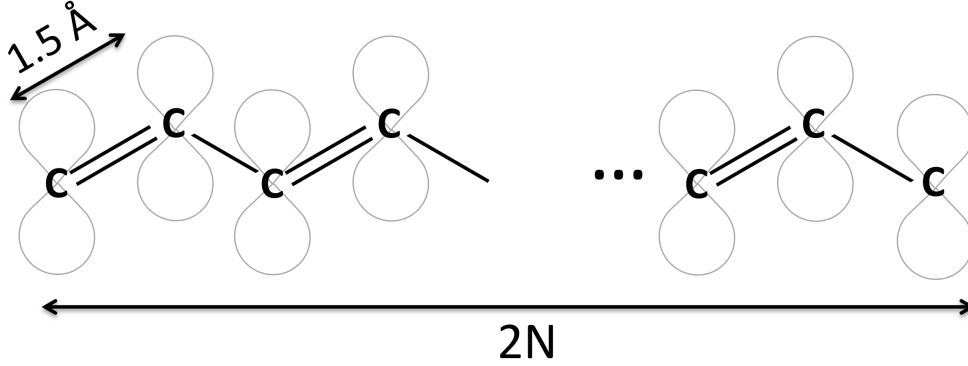


Figure 1: Polyene molecule model. Carbon nuclei form the planar frame of the molecule. The shown orbitals are perpendicular to the plane of the molecule. N marks the number of double bonds in the molecule.

In Fig. 1, we show a model polyene molecule. We assume that electrons occupying the orbitals shown in Fig. 1 are non-interacting (independent) particles. Then, the wavefunction of each electron can be written as a linear combination of basis functions Φ_j

$$\Psi_n = \sum_{j=1}^{2N} C_{nj} \Phi_j \quad (154)$$

where n labels the electronic state, and j labels the atom index (site).

Next, we can define the Hamiltonian for the polyene system as

$$H = \begin{pmatrix} \varepsilon_0 & \beta & 0 & & \\ \beta & \varepsilon_0 & \beta & & \\ 0 & \beta & \varepsilon_0 & & \\ & & & \dots & \\ & & & & \varepsilon_0 \end{pmatrix}$$

where ε_0 is the energy of the electron at site j and β is the energy associated with the electron jumping from site j to the neighboring site $j \pm 1$. We neglect the other off-diagonal terms, since we assume that energy associated with electron jumping to non-neighboring atoms is much larger than β . The energy ε_0 is the energy of the electron in the $2p_z$ orbital of carbon atom

$$\varepsilon_0 = -\frac{\hbar^2}{2m_e a_0^2} \frac{Z^2}{n^2}, \quad n = 2, \quad Z = 6 \quad (155)$$

where m_e is mass of the electron, a_0 is Bohr radius, n is the principal quantum number for hydrogen-like atoms ($n = 2$ for p orbitals), and Z is the atomic number ($Z = 6$ for carbon atom). In subsequent calculations we assume that $\beta = -2.5$ eV.

To obtain stationary states of individual electrons, one needs to solve:

$$H\Psi_n = E_n\Psi_n \quad (156)$$

The solutions of Eq. 156 are

$$\Psi_n = \sum_{j=1}^{2N} A_n \sin \frac{j\pi n}{2N+1} \Phi_j \quad (157)$$

For each electron, Eq. 156 can be written as

$$A_n \left(\beta \sin \frac{(j-1)\pi n}{2N+1} + \varepsilon_0 \sin \frac{j\pi n}{2N+1} + \beta \sin \frac{(j+1)\pi n}{2N+1} \right) = E_n A_n \sin \frac{j\pi n}{2N+1} \quad (158)$$

Using the identity $\sin(A \pm B) = \sin A \cos B \pm \cos A \sin B$, we can write

$$\sin \frac{(j \pm 1)\pi n}{2N+1} = \sin \frac{j\pi n}{2N+1} \cos \frac{\pi n}{2N+1} \pm \cos \frac{j\pi n}{2N+1} \sin \frac{\pi n}{2N+1}. \quad (159)$$

Since the second term in Eq. 159 cancels, Eq. 158 reduces to

$$2\beta \cos \frac{\pi n}{2N+1} + \varepsilon_0 = E_n \quad (160)$$

and the solution for E_n is

$$E_n = \varepsilon_0 + 2\beta \sin \frac{\pi n}{2N+1} \quad (161)$$

The energy difference between subsequent electronic states, i.e. the energy of the absorbed photon is:

$$\Delta E = 2\beta \left(\cos \frac{(n+1)\pi}{2N+1} - \cos \frac{n\pi}{2N+1} \right) = \beta \frac{4\pi}{2N+1} \quad (162)$$

Therefore, for molecules with $N = 5 - 10$ double bonds, and assuming that $\beta = -2.5$ eV, $\Delta E \approx 1.5 - 3$ eV.

Now, to calculate the absorption rate

$$k_{\text{abs}}^{(\text{tot})} = \mathcal{N}_\omega 1.37 \times 10^{19} \frac{1}{\text{s}} \times \frac{a_o}{\lambda} \frac{|\langle n | \vec{r} | 0 \rangle|^2}{\lambda^2}, \quad (163)$$

one needs to determine $\langle n | \vec{r} | 0 \rangle$

$$\langle n | \vec{r} | 0 \rangle = \langle n | \Delta \vec{r} | 0 \rangle + \langle n | \vec{r}_{\text{center}} | 0 \rangle \quad (164)$$

Since the second term in Eq. 164 vanishes, one can write

$$\langle n | \vec{r} | 0 \rangle = \sum_{j,j'} C_{bj} C_{aj'} \langle j | \Delta \vec{r} | j' \rangle \approx \sum_j C_{bj} C_{aj} \Delta \vec{r}_j \delta_{jj'}. \quad (165)$$

Finally, for the transition dipole moment, $\langle n | \vec{r} | 0 \rangle$, to be nonzero, the product $C_{bj} C_{aj} \Delta \vec{r}_j$ needs to be of even symmetry. $\Delta \vec{r}_j$ has odd symmetry, therefore (b, a) pair needs to have (even, odd) or (odd, even) symmetry, for the product to be of even symmetry. The requirement leads to the selection rules for electronic transitions.

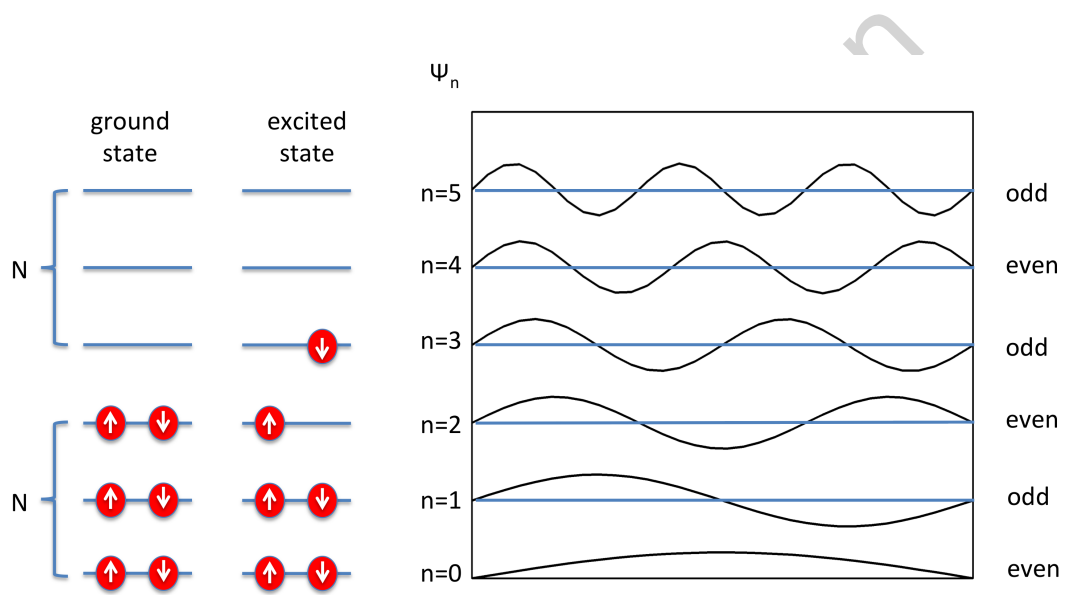


Figure 2: Solution of the polyene model described in the text for $2N = 6$.