Photons Interactions With Matter.

Selected chapter of lecture notes on Quantum Mechanics

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Contents

This Chapter is the continuation of the Chapter "Quantized EM Field". We will use the quantum description of the EM field discussed there to provide several simple examples of how photons are emitted and absorbed by quantum matter systems.

1 Interaction Hamiltonian

1.1 Separating the interaction terms

As was shown in the Chapter "Quantized EM Field" the Hamiltonian operator of the EM field interacting with (non relativistic) matter is

$$\hat{H} = \sum_{a=1}^{N} \frac{1}{2m_a}[\hat{\mathbf{p}}_a - q_a\hat{\mathbf{A}}_T(\mathbf{r}_a)]^2 + V_{Coul} + \frac{\epsilon_0}{2}\int \left[\hat{\mathbf{E}}_T(\mathbf{r})^2 + c^2(\nabla \times \hat{\mathbf{A}}_T(\mathbf{r}))^2\right] d^3r \quad (1)$$

with

$$\hat{\mathbf{A}}_T(\mathbf{r}) = \sum_{\mathbf{k}\alpha}\left(\frac{\hbar}{2\epsilon_0\omega_k\Omega}\right)^{1/2}\left[\hat{a}_{\mathbf{k}\alpha}\boldsymbol{\lambda}_{\mathbf{k}\alpha}e^{i\mathbf{k}\cdot\mathbf{r}} + \hat{a}^\dagger_{\mathbf{k}\alpha}\boldsymbol{\lambda}_{\mathbf{k}\alpha}e^{-i\mathbf{k}\cdot\mathbf{r}}\right] \quad (2)$$

$$\hat{\mathbf{E}}_T(\mathbf{r}) = \sum_{\mathbf{k}\alpha} i\left(\frac{\hbar\omega_k}{2\epsilon_0\Omega}\right)^{1/2}\left[\hat{a}_{\mathbf{k}\alpha}\boldsymbol{\lambda}_{\mathbf{k}\alpha}e^{i\mathbf{k}\cdot\mathbf{r}} - \hat{a}^\dagger_{\mathbf{k}\alpha}\boldsymbol{\lambda}_{\mathbf{k}\alpha}e^{-i\mathbf{k}\cdot\mathbf{r}}\right] \quad (3)$$

and

$$V_{Coul} = \frac{1}{8\pi\epsilon_0}\sum_{a\neq b}^{N}\frac{q_aq_b}{|\mathbf{r}_a - \mathbf{r}_b|}$$

This expression can be written as

$$\hat{H} = \hat{H}_{matter} + \hat{H}_r + \hat{H}_{matter-radiation\ interaction} \quad (4)$$

with

$$\begin{aligned}
\hat{H}_{matter} &= \sum_{a=1}^{N}\frac{\hat{\mathbf{p}}_a^2}{2m_a} + V_{Coul}(\mathbf{r}_1, ..., \mathbf{r}_n) \\
\hat{H}_r &= \frac{\epsilon_0}{2}\int \left[\hat{\mathbf{E}}_T(\mathbf{r})^2 + c^2(\nabla \times \hat{\mathbf{A}}_T(\mathbf{r}))^2\right] d^3r \\
\hat{H}_{matter-radiation\ interaction} &= \hat{H}_{I1} + \hat{H}_{I2}
\end{aligned} \quad (5)$$

and

$$\hat{H}_{I1} = -\sum_{a=1}^{N} \frac{q_a}{2m_a} \left[\hat{\mathbf{p}}_a \cdot \hat{\mathbf{A}}_T(\mathbf{r}_a) + \hat{\mathbf{A}}_T(\mathbf{r}_a) \cdot \hat{\mathbf{p}}_a \right] \tag{6}$$

$$\hat{H}_{I2} = \sum_{a=1}^{N} \frac{q_a^2}{2m_a} [\hat{\mathbf{A}}_T(\mathbf{r}_a)]^2 \tag{7}$$

The expressions for $\hat{H}_{I1}$ and $\hat{H}_{I2}$ depend on the coordinates and momenta of the particles and on the "coordinates" $\hat{\mathbf{A}}_T(\mathbf{r})$ of the field. It is worth noting that the transversality of $\mathbf{A}_T$ means that $\mathbf{p}_a$ and $\hat{\mathbf{A}}_T(\mathbf{r}_a)$ commute

$$\sum_{i=1}^{3} \left[\hat{p}_{a,i}, \hat{A}_{T,i}(\mathbf{r}_a) \right] = -i\hbar \nabla_a \cdot \hat{\mathbf{A}}_T(\mathbf{r}_a) = 0$$

so that the interaction $\hat{H}_{I1}$ can be written as one term

$$\hat{H}_{I1} = -\sum_{a=1}^{N} \frac{q_a}{m_a} \hat{\mathbf{A}}_T(\mathbf{r}_a) \cdot \hat{\mathbf{p}}_a \tag{8}$$

1.2 Adding spin and external fields

When matter particles have spins one must add spin degrees of freedom $\mathbf{s}_a$ to the particle coordinates $\mathbf{r}_a$. As a rule spinning particles have non zero magnetic moment $\boldsymbol{\mu}_a$[1] which is parallel to the spin and follows its dynamics. The proportionality relation between the corresponding operators is conventionally written

$$\hat{\boldsymbol{\mu}}_a = g_a \frac{q_a}{2m_a} \hat{\mathbf{s}_a} \tag{9}$$

where g_a is the so called Lande factor or g-factor (see e.g. the appropriate section in the Chapter "Motion in External Electromagnetic Field").

Particle magnetic moments interact with the magnetic field so one must add a new term to the interaction Hamiltonian $\hat{H}_{matter-radiation\ interaction}$,

$$\hat{H}_{I3} = -\sum_{a=1}^{N} \hat{\boldsymbol{\mu}}_a \cdot \hat{\mathbf{B}}(\mathbf{r}_a) \tag{10}$$

[1]This is obvious for charged particles but in fact also neutral particles with spin, e.g. molecules, atoms, neutrons, etc, may have non zero $\boldsymbol{\mu}$ due to the "spinning" charges inside the overall neutral system. Charged quarks in a neutron is an obvious example.

with the operator of the magnetic field (cf., the Chapter "Quantized EM Field")

$$\hat{\mathbf{B}}(\mathbf{r}) = \sum_{\mathbf{k}\alpha} i \left(\frac{\hbar}{2\epsilon_0 \omega_k \Omega} \right)^{1/2} \left[\hat{a}_{\mathbf{k}\alpha} (\mathbf{k} \times \boldsymbol{\lambda}_{\mathbf{k}\alpha}) e^{i\mathbf{k}\cdot\mathbf{r}} - \hat{a}^\dagger_{\mathbf{k}\alpha} (\mathbf{k} \times \boldsymbol{\lambda}_{\mathbf{k}\alpha}) e^{-i\mathbf{k}\cdot\mathbf{r}} \right] \tag{11}$$

We have up to now considered a closed matter-EM field system. One often encounters a situation in which in addition there are external fields acting on the matter particles. Examples are Coulomb potential of a heavy nucleus acting on atomic electrons or external magnetic field acting on electrons in Landau levels. Such external fields are to a good approximation classical with prescribed space and time dependence. In their presence the Hamiltonian (1) should be modified by adding external classical vector potential, external scalar potential and external magnetic field. The full Hamiltonian will then have the form [2]

$$\begin{aligned} \hat{H} &= \sum_{a=1}^{N} \frac{1}{2m_a} \left[\hat{\mathbf{p}}_a - q_a \mathbf{A}^{external}(\mathbf{r}_a, t) - q_a \hat{\mathbf{A}}_T(\mathbf{r}_a \right]^2 + V_{Coul} + \\ &+ \sum_{a=1}^{N} U^{external}(\mathbf{r}_a, t) - \sum_{a=1}^{N} \hat{\boldsymbol{\mu}}_a \cdot \mathbf{B}^{external}(\mathbf{r}_a, t) - \\ &- \sum_{a=1}^{N} \hat{\boldsymbol{\mu}}_a \cdot \hat{\mathbf{B}}(\mathbf{r}_a) + \frac{\epsilon_0}{2} \int \left[\hat{\mathbf{E}}_T(\mathbf{r})^2 + c^2 \nabla \times \hat{\mathbf{A}}_T(\mathbf{r}) \right] d^3 r \\ V_{Coul} &= \frac{1}{8\pi\epsilon_0} \sum_{a \neq b}^{N} \frac{q_a q_b}{|\mathbf{r}_a - \mathbf{r}_b|} \end{aligned} \tag{12}$$

where we have also added the spin degrees of freedom interacting with external magnetic fields via the particles magnetic moments.

1.3 Disentangling radiation from the matter degrees of freedom

The objects like $\hat{\mathbf{A}}_T(\mathbf{r}_a)$ and $\hat{\mathbf{B}}(\mathbf{r}_a)$ in the expressions (6), (7) and (10) are operator valued functions (fields) of operators (particle coordinates). It is easy and convenient

[2] Note that external fields influence the radiation only via matter. There is no direct effect on the dynamics of the radiation. This is a consequence of the linearity of the Maxwell equations.

to disentangle this complicated dependence using the identities

$$\hat{\mathbf{A}}_T(\mathbf{r}_a) = \int \delta(\mathbf{r}-\mathbf{r}_a)\hat{\mathbf{A}}_T(\mathbf{r})\, d^3r \ , \ \hat{\mathbf{A}}_T^2(\mathbf{r}_a) = \int \delta(\mathbf{r}-\mathbf{r}_a)\hat{\mathbf{A}}_T^2(\mathbf{r})\, d^3r$$

and

$$\hat{\mathbf{B}}(\mathbf{r}_a) = \int \delta(\mathbf{r}-\mathbf{r}_a)\hat{\mathbf{B}}(\mathbf{r})\, d^3r$$

Using these one can write the interactions (6), (7) and (10) as

$$\hat{H}_{I1} = -\int d^3r \sum_{a=1}^{N} \frac{q_a}{2m_a} [\hat{\mathbf{p}}_a\delta(\mathbf{r}-\mathbf{r}_a) + \delta(\mathbf{r}-\mathbf{r}_a)\hat{\mathbf{p}}_a] \cdot \hat{\mathbf{A}}_T(\mathbf{r}) \tag{13}$$

$$\hat{H}_{I2} = \int d^3r \sum_{a=1}^{N} \frac{q_a^2}{2m_a}\delta(\mathbf{r}-\mathbf{r}_a)[\hat{\mathbf{A}}_T(\mathbf{r})]^2 \tag{14}$$

$$\hat{H}_{I3} = -\int d^3r \sum_{a=1}^{N} \hat{\boldsymbol{\mu}}_a\delta(\mathbf{r}-\mathbf{r}_a) \cdot \hat{\mathbf{B}}(\mathbf{r}) \tag{15}$$

The 1st and the 3rd of these expressions have a simple form

$$\hat{H}_{I1} = -\int \hat{\mathbf{j}}(\mathbf{r}) \cdot \hat{\mathbf{A}}_T(\mathbf{r})\, d^3r \tag{16}$$

and

$$\hat{H}_{I3} = -\int \hat{\mathbf{m}}(\mathbf{r}) \cdot \hat{\mathbf{B}}(\mathbf{r})\, d^3r \tag{17}$$

with current operator

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2}\sum_{a=1}^{N} \frac{q_a}{m_a} [\hat{\mathbf{p}}_a\delta(\mathbf{r}-\mathbf{r}_a)) + \delta(\mathbf{r}-\mathbf{r}_a)\hat{\mathbf{p}}_a]$$

and magnetization operator

$$\hat{\mathbf{m}}(\mathbf{r}) = \sum_{a=1}^{N} \hat{\boldsymbol{\mu}}_a\delta(\mathbf{r}-\mathbf{r}_a)$$

The second term $\hat{H}_{I2}$ simplifies when all the charges and masses of the particles are equal $q_1 = q_2 = ... = q_N = q$, $m_1 = m_2 = ... = m_N = m$. Then

$$\hat{H}_{I2} = \frac{q}{m}\int \hat{\rho}(\mathbf{r})[\hat{\mathbf{A}}_T(\mathbf{r})]^2\, d^3r \tag{18}$$

with charge density operator

$$\hat{\rho}(\mathbf{r}) = \sum_{a=1}^{N} q\delta(\mathbf{r} - \mathbf{r}_a)$$

1.4 Resulting insights

1.4.1 Matter creates, annihilates, scatters photons

Qualitative insights into the nature of the interaction terms is gained if the expressions for the fields $\hat{\mathbf{A}}_T(\mathbf{r})$ and $\hat{\mathbf{B}}(\mathbf{r})$ in terms of the photon creation and annihilation operators written in the form[3]

$$\hat{\mathbf{A}}_T(\mathbf{r}) = \sum_{\mathbf{k}\alpha} \left(\frac{\hbar}{2\epsilon_0\omega_k\Omega}\right)^{1/2} \boldsymbol{\lambda}_{\mathbf{k}\alpha} e^{i\mathbf{k}\cdot\mathbf{r}} (\hat{a}_{\mathbf{k}\alpha} + \hat{a}^\dagger_{-\mathbf{k}\alpha}) \tag{19}$$

$$\hat{\mathbf{B}}(\mathbf{r}) = \sum_{\mathbf{k}\alpha} i\left(\frac{\hbar}{2\epsilon_0\omega_k\Omega}\right)^{1/2} (\mathbf{k} \times \boldsymbol{\lambda}_{\mathbf{k}\alpha}) e^{i\mathbf{k}\cdot\mathbf{r}} \left(\hat{a}_{\mathbf{k}\alpha} + \hat{a}^\dagger_{-\mathbf{k}\alpha}\right) \tag{20}$$

are inserted in Eqs. (13 - 15). The interaction term $\hat{H}_{I1}$ takes the form

$$\hat{H}_{I1} = -\sum_{\mathbf{k}\alpha} \left(\frac{\hbar}{2\epsilon_0\omega_k\Omega}\right)^{1/2} (\hat{\mathbf{j}}_{-\mathbf{k}} \cdot \boldsymbol{\lambda}_{\mathbf{k}\alpha})(\hat{a}_{\mathbf{k}\alpha} + \hat{a}^\dagger_{-\mathbf{k}\alpha}) \tag{21}$$

with

$$\hat{\mathbf{j}}_{\mathbf{k}} = \int \hat{\mathbf{j}}(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}\, d^3r = \sum_{a=1}^{N} \frac{q_a}{2m_a} \left[\hat{\mathbf{p}}_a e^{-i\mathbf{k}\cdot\mathbf{r}_a} + e^{-i\mathbf{k}\cdot\mathbf{r}_a}\hat{\mathbf{p}}_a\right] \tag{22}$$

It is seen that to 1st order [4] this interaction acts by creating or annihilating single photons with (not surprising but worth noting) opposite signs of the momentum $\hbar\mathbf{k}$.

[3] To simplify expressions we assume here and in the following that the polarization vectors for $\mathbf{k}$ and $-\mathbf{k}$ modes are chosen to be the same $\boldsymbol{\lambda}_{\mathbf{k}\alpha} = \boldsymbol{\lambda}_{-\mathbf{k}\alpha}$.

[4] By "to 1st order" here and in the following we mean that the interaction acts one time on a wave function. Note that in solving the Schrödinger equation the Hamiltonian acts "infinitely many times" so to speak. This can be seen by viewing the time evolution

$$\psi(t) = \exp[-(i/\hbar)\hat{H}(t-t_0)]\psi(t_0) = [1 + (-i/\hbar)\hat{H}(t-t_0) + (-i/\hbar)^2\hat{H}^2(t-t_0)^2 + ...]\psi(t_0)$$

It is also important to note that (as will become clearer later and especially in the chapter on Second Quantization) the expression

$$\boldsymbol{\lambda}_{\mathbf{k}\alpha} e^{i\mathbf{k}\cdot\mathbf{r}}$$

can often be regarded as a photon wave function having definite momentum $\mathbf{p} = \hbar\mathbf{k}$ and polarization $\boldsymbol{\lambda}_\alpha$.

Inserting the expression for $\hat{\mathbf{B}}(\mathbf{r})$ into the interaction $\hat{H}_{I3}$, Eq.(15), one obtains

$$\hat{H}_{I3} = -\sum_{\mathbf{k}\alpha} i \left(\frac{\hbar}{2\epsilon_0 \omega_k \Omega}\right)^{1/2} [\hat{\mathbf{m}}_{-\mathbf{k}} \cdot (\mathbf{k} \times \boldsymbol{\lambda}_{\mathbf{k}\alpha})] \, (\hat{a}_{\mathbf{k}\alpha} + \hat{a}^\dagger_{-\mathbf{k}\alpha}) \tag{23}$$

with

$$\hat{\mathbf{m}}_{\mathbf{k}} = \int \hat{\mathbf{m}}(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} \, d^3r = \sum_{a=1}^{N} \hat{\boldsymbol{\mu}}_a e^{-i\mathbf{k}\cdot\mathbf{r}_a} \tag{24}$$

One observes that this interaction term also creates or annihilates one photon in 1st order. The difference with $\hat{H}_{I1}$ is that in the former case the photon creation or annihilation was "accompanied" with the "action" on the matter variables of the corresponding component $\hat{\mathbf{j}}_{-\mathbf{k}}$ of the current operator projected on the photon polarization $\boldsymbol{\lambda}_{\mathbf{k}\alpha}$. In $\hat{H}_{I3}$ this action is replaced with $\hat{\mathbf{m}}_{-\mathbf{k}}$ component of the magnetization density $\hat{\mathbf{m}}(\mathbf{r})$ projected on $\mathbf{k} \times \boldsymbol{\lambda}_{\mathbf{k}\alpha}$.

Turning now to the $\hat{H}_{I2}$, Eq. (14), we note that the presence of the square $[\hat{\mathbf{A}}_T(\mathbf{r})]^2$ means that the creation and annihilation operators will appear in this expression in the products

$$\hat{a}_{\mathbf{k}\alpha}\hat{a}_{\mathbf{k}'\alpha'} \quad , \quad \hat{a}^\dagger_{\mathbf{k}\alpha}\hat{a}^\dagger_{\mathbf{k}'\alpha'} \quad , \quad \hat{a}^\dagger_{\mathbf{k}\alpha}\hat{a}_{\mathbf{k}'\alpha'} \quad , \quad \hat{a}_{\mathbf{k}\alpha}\hat{a}^\dagger_{\mathbf{k}'\alpha'}$$

which shows that these interaction terms in the 1st order either create or destroy two photons or simultaneously create and destroy a photon with different momentum and polarization.

1.4.2 Matter "shifts", "mixes" the radiation oscillators

Let us recall that $\hat{\mathbf{A}}_T(\mathbf{r})$ is written in terms of the running plane waves as

$$\mathbf{A}_T(\mathbf{r}) = \frac{1}{\sqrt{\Omega\epsilon_0}} \sum_{\mathbf{k}} \left(\mathbf{Q}_{\mathbf{k}} \cos(\mathbf{k}\cdot\mathbf{r}) - \frac{1}{\omega_k} \mathbf{P}_{\mathbf{k}} \sin(\mathbf{k}\cdot\mathbf{r}) \right)$$

where $\boldsymbol{\lambda}_{\mathbf{k}\alpha}$'s are fixed polarization vectors orthogonal to $\mathbf{k}$. Recalling also that $\hat{H}_r$ is the sum of the normal modes oscillators

$$\hat{H}_r = \frac{1}{2}\sum_{\mathbf{k}\alpha}\left(\hat{P}^2_{\mathbf{k}\alpha} + \omega_k^2 \hat{Q}^2_{\mathbf{k}\alpha}\right) \tag{25}$$

we find that in terms of $\hat{P}_{\mathbf{k},\alpha}$'s and $\hat{Q}_{\mathbf{k}\alpha}$ the Hamiltonian is written

$$\hat{H} = \hat{H}_{matter} + \frac{1}{2}\sum_{\mathbf{k}\alpha}\left(\hat{P}^2_{\mathbf{k}\alpha} + \omega_k^2 \hat{Q}^2_{\mathbf{k}\alpha}\right) + \sum_{\mathbf{k}\alpha}\left(\hat{S}_{\mathbf{k}\alpha}\hat{Q}_{\mathbf{k}\alpha} + \hat{C}_{\mathbf{k}\alpha}\hat{P}_{\mathbf{k}\alpha}\right) + \hat{H}_{I2} + \hat{H}_{I3} \tag{26}$$

with

$$\begin{aligned} \hat{S}_{\mathbf{k}\alpha} &= -\frac{1}{\sqrt{\Omega\epsilon_0}}\int \boldsymbol{\lambda}_{\mathbf{k}\alpha}\cdot\hat{\mathbf{j}}(\mathbf{r})\cos(\mathbf{k}\cdot\mathbf{r})\,d^3r \\ \hat{C}_{\mathbf{k}\alpha} &= \frac{1}{\sqrt{\Omega\epsilon_0\omega^2}}\int \boldsymbol{\lambda}_{\mathbf{k}\alpha}\cdot\hat{\mathbf{j}}(\mathbf{r})\sin(\mathbf{k}\cdot\mathbf{r})d^3r \end{aligned} \tag{27}$$

Schematically one can say that via the $\hat{H}_{I1}$ interaction the matter causes shifts of the oscillators of the radiation normal modes. The shift is in both the coordinates $Q_{\mathbf{k}\alpha}$ and momenta $P_{\mathbf{k}\alpha}$. For fixed classical $S_{\mathbf{k}\alpha}$ and $C_{\mathbf{k}\alpha}$ each oscillator gets shifted

$$\frac{1}{2}\left(\hat{P}^2_{\mathbf{k}\alpha} + \omega^2\hat{Q}^2_{\mathbf{k}\alpha}\right) \to \frac{1}{2}\left[\left(\hat{P}_{\mathbf{k}\alpha} - P^{(0)}_{\mathbf{k}\alpha}\right)^2 + \omega_k^2\left(\hat{Q}_{\mathbf{k}\alpha} - Q^{(0)}_{\mathbf{k}\alpha}\right)^2\right] + E^{(0)}_{\mathbf{k}\alpha} \tag{28}$$

with $P^{(0)}_{\mathbf{k}\alpha}$, $Q^{(0)}_{\mathbf{k}\alpha}$ and $E^{(0)}_{\mathbf{k}\alpha}$ determined by $S_{\mathbf{k}\alpha}$ and $C_{\mathbf{k}\alpha}$ in an obvious way. Of course in a real situation $S_{\mathbf{k}\alpha}$ and $C_{\mathbf{k}\alpha}$ are dynamical and quantized.

Let us also note that the interaction term $\hat{H}_{I3}$ may schematically be viewed in a similar way as we outlined above for $\hat{H}_{I1}$ since it is linear in $\hat{\mathbf{B}}(\mathbf{r}) = \nabla\times\hat{\mathbf{A}}_T(\mathbf{r})$ and therefore in $Q_{\mathbf{k}\alpha}$ and $P_{\mathbf{k}\alpha}$ variables.

The interaction term $\hat{H}_{I2}$ on the other hand is quadratic in $\hat{\mathbf{A}}_T(\mathbf{r})$. Its dependence on the field normal modes variables is therefore quadratic depending on products $Q_{\mathbf{k}\alpha}Q_{\mathbf{k}'\alpha'}$, $P_{\mathbf{k}\alpha}P_{\mathbf{k}'\alpha'}$ and $Q_{\mathbf{k}\alpha}P_{\mathbf{k}'\alpha'}$ mixing the normal modes $\mathbf{k}\alpha$'s already in the 1st order.

1.4.3 Generation of coherent states. Schematic model of a laser

Let us recall the properties of the coherent states which were discussed in the Section 6.1.3. of the Quantized EM Field chapter. It was shown there that such states

can be viewed as ground states of a shifted harmonic oscillator. Turning to the expression (28) we notice that if just one photon mode $\mathbf{k}\alpha$ is selected and the current which "feeds" this mode is external, constant in time and classical then the lowest eigenstate of the corresponding Hamiltonian will be a coherent state.

Such a Hamiltonian can actually be used as a simplest schematic model to begin understanding the quantum mechanics of the light emitted by a laser. Selecting a single mode is modeling (in the simplest way) of the laser resonator. The classical external current is (a very much simplified description of) the source of excitations of the electric charges which de-excite by emitting photons into the resonator mode. This shifted harmonic oscillator model obviously is extremely schematic and misses many important laser features and details. It nevertheless correctly indicates that a simple reasonable approximation to the state of light which (one mode) laser emits is a coherent state.

2 Emission and Absorption of Photons

In this section we discuss the details of quantum mechanical description of photon emission and absorption. We will do this treating the radiation-matter interaction using the perturbation theory and will limit ourselves to the leading 1st order terms. As should be clear from our discussion above the relevant terms for such 1st order processes are $\hat{H}_{I1}$ and $\hat{H}_{I3}$. We will begin by considering only the effect of $\hat{H}_{I1}$ i.e. photon emission and absorption resulting from the change of the state of the electric current of the matter system. Classically this would correspond to emission of radiation by an alternating current (like e.g. in a simple antenna). The treatment of the photon emission by changing the spin states of matter, i.e. the effect of the $\hat{H}_{I3}$ interaction term will fit naturally in the discussion of these processes in relation to the changes of the states of magnetic moments, cf., Section 2.6.4.

Following this introduction we will begin by considering the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_{I1} \tag{29}$$

where the unperturbed part is

$$\hat{H}_0 = \hat{H}_{matter} + \sum_{\mathbf{k}\alpha} \hbar\omega_k \, \hat{a}^\dagger_{\mathbf{k}\alpha} \hat{a}_{\mathbf{k}\alpha} \tag{30}$$

and where we dropped the constant vacuum energy term $E_{vacuum} = (1/2)\sum_{\mathbf{k}\alpha} \hbar\omega_k$.

2.1 Paradigm of spontaneous emission of radiation - discrete matter level coupled to a photon continuum

2.1.1 Unperturbed energies

We assume that we know how to solve the matter Hamiltonian i.e. that we know its eigenstates and the corresponding eigenvalues

$$\hat{H}_{matter}|n\rangle = E_n|n\rangle \tag{31}$$

We therefore know the eigenstates of the unperturbed $\hat{H}_0$, Eq. (30), i.e.

$$|n\rangle|\{N_{\mathbf{k},\alpha}\}\rangle \quad \text{with eigenenergies} \quad E(n,\{N_{\mathbf{k}\alpha}\}) = E_n + \sum_{\mathbf{k},\alpha} N_{\mathbf{k}\alpha}\,\hbar\omega_k \tag{32}$$

We assume that (as is typical for atomic, molecular or nuclear systems) the low lying matter eigenenergies in (32) form discrete system of levels following by higher lying continuum states (like e.g. simplest hydrogen atom at rest[5]). Let us consider the sector of unperturbed levels with zero photons

$$E_n + 0 \text{ photons}$$

and compare to the corresponding levels in the one photon sector

$$E_n + 1 \text{ photon} = E_n + \hbar\omega_k$$

It is important to note that

$$\hbar\omega_k = \hbar ck$$

form a continuum of levels because of essentially continuum values of k (for a large quantisation volume).

Plotting these energies, cf. Fig. 1, one can see discrete levels of the matter without photons "embedded" in the continuum of matter + one or more photon levels. The simplest is e.g. the first excited matter level with no photons

$$|n=1\rangle|\{0_{\mathbf{k}\alpha}\}\rangle \quad \text{with} \quad E(1,\{0_{\mathbf{k}\alpha}\}) = E_1 + 0 \text{ photons}$$

vs the ground state E_0 plus one photon

$$|n=0\rangle|1_{\mathbf{k}\alpha},\{0_{\mathbf{k}'\alpha'}\}\rangle \quad \text{with} \quad E(0,1_{\mathbf{k}\alpha},\{0_{\mathbf{k}'\alpha'}\}) = E_0 + \hbar\omega_k$$

[5] We ignore at the moment the center of mass motion of the emitting system. Its effects will be discussed below.

continuum of levels.

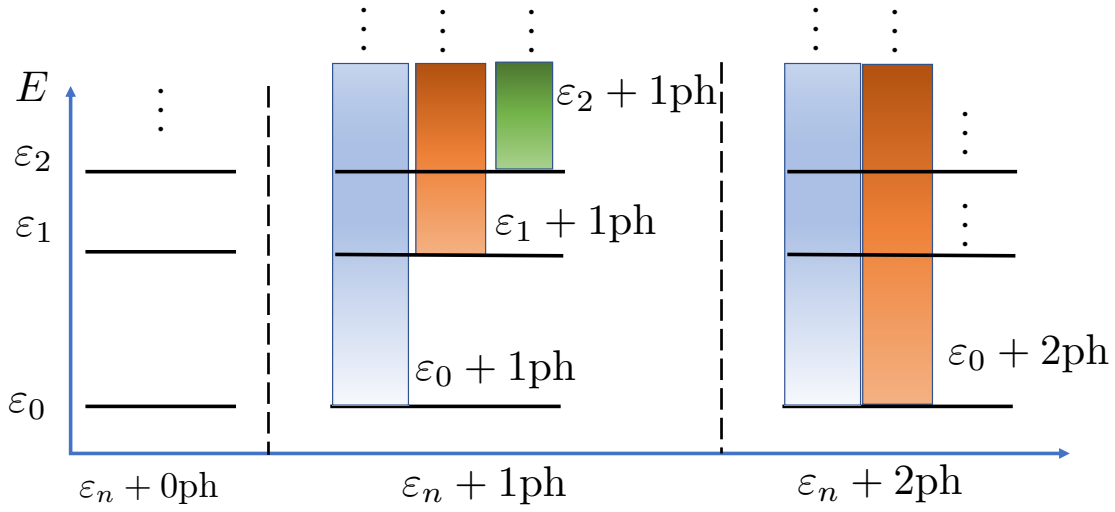

Figure 1: The presence of the continuum of the photonic levels i.e. of photons in the continuum of the EM field modes (represented schematically as colored bands in the figure) means that the discrete excited levels of matter are embedded in this continuum. As explained in this section the coupling of the matter to the EM field means in turn that the discrete matter levels get "smeared" over the nearby continuum of photonic levels. The result is that their energy position gets shifted and they acquire a width becoming somewhat analogous to classical resonances.

2.1.2 Coupling to the continuum - time domain. Exponential decay

We now turn to the discussion of what will the perturbation $\hat{H}_{I1}$ which has matrix elements connecting such levels cause. We will do this in the framework of a simple model - a single discrete state coupled to a continuum of states. This is known as Weisskopf-Wigner model. We present here the main results for this model. Details are found in the Appendix of this chapter, as well as in Ch.I-C3 and Complement C_I of Ref.[1].

We will use simplified notations. Consider a quantum state with energy $\mathcal{E}_0$ and wave function ψ_0 imbedded into a broad continuum of levels with energies $\mathcal{E}_\nu$ and

wavefunctions ψ_ν. In the notation of the previous section $\mathcal{E}_0$ stands for $E(1,\{0_{\mathbf{k}\alpha}\})$ while $\mathcal{E}_\nu$ for $E(0;1_{\mathbf{k}\alpha},\{0_{\mathbf{k}'\alpha'}\})$ with the corresponding wave functions.

Let V be the interaction between the levels with matrix elements

$$V_{0\nu} = V^*_{\nu 0} \quad , \quad V_{\nu\mu} = V^*_{\mu\nu}$$

We want to consider how the system develops in time if it was initially (say at $t = 0$) prepared in the discrete state ψ_0. Formally we need to solve the Schrödinger equation of this system

$$i\hbar\frac{\partial\Psi(t)}{\partial t} = (\hat{H}_0 + \hat{V})\Psi(t) \tag{33}$$

with the initial condition

$$\Psi(t=0) = \psi_0 \tag{34}$$

Let us write $\Psi(t)$ as an expansion in the basis of the unperturbed states $\{\psi_0, \psi_\nu\}$

$$\Psi(t) = c_0(t)\psi_0 e^{-i\mathcal{E}_0 t/\hbar} + \int c_\nu(t)\psi_\nu e^{-i\mathcal{E}_\nu t/\hbar}\, d\nu \tag{35}$$

where for convenience we "pull out" the factors $e^{-i\mathcal{E}_0 t/\hbar}$ and $e^{-i\mathcal{E}_\nu t/\hbar}$ from the (yet undetermined) time dependent coefficients $c_0(t)$ and $c_\nu(t)$. We note that the coefficient $c_0(t)e^{-i\mathcal{E}_0 t/\hbar}$ determines the time dependence of the "persistence amplitude" of the initial state ψ_0

$$\langle\psi_0|\Psi(t)\rangle = c_0(t)e^{-i\mathcal{E}_0 t/\hbar} \tag{36}$$

while the amplitudes $c_\nu(t)e^{-i\mathcal{E}_\nu t/\hbar}$ provide the time dependence of the spreading of the initial discrete state over the continuum states.

Inserting the expansion (35) into the Schrödinger equation, using

$$\hat{H}_0\psi_0 = \mathcal{E}_0\psi_0 \quad , \quad \hat{H}_0\psi_\nu = \mathcal{E}_\nu\psi_\nu$$

and projecting on ψ_0 and ψ_μ we obtain coupled equations for the coefficients

$$\begin{aligned} i\hbar\frac{dc_0}{dt} &= \int V_{0\mu}c_\mu e^{-i\omega_{\mu 0}t}\, d\mu \\ i\hbar\frac{dc_\mu}{dt} &= V_{\mu 0}c_0 e^{-i\omega_{0\mu}t} + \int V_{\mu\nu}c_\mu e^{-i\omega_{\nu\mu}t}\, d\nu \end{aligned} \tag{37}$$

with the notation

$$\omega_{\nu\mu} = (\mathcal{E}_\nu - \mathcal{E}_\mu)/\hbar$$

and initial conditions

$$c_0(0) = 1 \quad , \quad c_\nu(0) = 0 \tag{38}$$

The crucial step/approximation in the Weisskopf-Wigner approach is to neglect the coupling between the continuum levels, i.e. to set

$$V_{\mu\nu} = 0 \tag{39}$$

in the equations (37). This approximation allows to integrate the second equation (recall that $c_0(0) = 0$)

$$c_\mu(t) = \frac{1}{i\hbar} \int_0^t V_{\mu 0} e^{-i\omega_{0\mu} t'} \, c_0(t') \, dt' \tag{40}$$

Inserting this into the first equation we obtain a single integro-differential equation for $c_0(t)$

$$\frac{dc_0}{dt} = \int_0^t K(t - t') c_0(t') dt' \tag{41}$$

where we introduced notation for the kernel $K(t - t')$

$$K(t) = -\frac{1}{\hbar^2} \int |V_{0\mu}|^2 e^{i\omega_{0\mu} t} \, d\mu \tag{42}$$

Equations of this type are called equations with memory (for obvious reason). The memory time is finite if the kernel $K(t)$ has finite "range" T, i.e. vanishes for t much larger than some finite time interval T.

Let us make an important observation here - $K(t)$ is proportional to the time correlation of $\hat{V}(t)$ in the initial state ψ_0

$$\int d\mu \langle \psi_0 | \hat{V} | \psi_\mu \rangle \langle \psi_\mu \, | \hat{V} | \psi_0 \rangle e^{i(\mathcal{E}_0 - \mathcal{E}_\mu) t/\hbar} = \langle \psi_0 | \hat{V}(t) \hat{V}(0) | \psi_0 \rangle \tag{43}$$

where

$$\hat{V}(t) = e^{i\hat{H}_0 t/\hbar} \hat{V} e^{-i\hat{H}_0 t/\hbar}$$

is the interaction $\hat{V}$ in the so called interaction representation. In order to understand what this means for the spontaneous photon emission let us recall what are the unperturbed energies and the corresponding wave functions in that problem, cf,. Eq. (32) and the following discussion. Let us also recall the explicit form of the interactions,

$$\hat{H}_{I1} = -\int \hat{\mathbf{j}}(\mathbf{r}) \cdot \hat{\mathbf{A}}_T(\mathbf{r}) \, d^3 r \quad , \quad \hat{H}_{I3} = -\int \hat{\mathbf{m}}(\mathbf{r}) \cdot \hat{\mathbf{B}}(\mathbf{r}) \, d^3 r \tag{44}$$

cf., Eqs. (16,17). Using this in the correlator $\langle\psi_0|\hat{V}(t)\hat{V}(0)|\psi_0\rangle$ we observe that in this case it is a product of the matter part involving correlators of the current $\hat{\mathbf{j}}(\mathbf{r})$ or magnetization $\hat{\mathbf{m}}(\mathbf{r})$ in the initial matter state and the correlations

$$\langle vacuum|\hat{A}_{T,a}(\mathbf{r},t)\hat{A}_{T,b}(\mathbf{r},0)|vacuum\rangle \text{ and } \langle vacuum|\hat{B}_a(\mathbf{r},t)\hat{B}_b(\mathbf{r},0)|vacuum\rangle$$

of the components of the EM field in the vacuum. These correlators measure the vacuum fluctuations of the field which drive the matter (say an atom) in an excited state to spontaneously emit a photon and decay to a lower state.

Returning Eq. (41) we note that it can be formally solved by Laplace transform. To invert the transform however one must use approximations. In Appendix we discuss a different method of solving Eq. (41) using the Markov approximation. To state the results it is useful to rewrite the integral $\int d\mu$ over the continuum states ψ_μ in Eq. (42) by splitting it into the integral over the states with a fixed energy $\mathcal{E}_\mu = \mathcal{E}$ following by the integral over $\mathcal{E}$. This can be done using

$$\int d\mu ... = \int d\mathcal{E} \int d\mu\, \delta(\mathcal{E} - \mathcal{E}_\mu) ... \tag{45}$$

The kernel $K(t)$ is then

$$\begin{aligned} K(t) = &-\frac{1}{\hbar^2}\int d\mathcal{E}\overline{|V_{0\mu}|^2}\Big|_{\mathcal{E}_\mu=\mathcal{E}} e^{i(\mathcal{E}_0-\mathcal{E})t/\hbar} \text{ with} \\ &\overline{|V_{0\mu}|^2}\Big|_{\mathcal{E}_\mu=\mathcal{E}} = \int d\mu\ \delta(\mathcal{E}-\mathcal{E}_\mu)|V_{0\mu}|^2 \end{aligned} \tag{46}$$

Using this we show in the Appendix that using the Markov approximation approach to solve Eq. (41) one finds that the time dependence of the "persistence amplitude" Eq. (36) of the initial state ψ_0 in the long time limit (cf., Eq. (145)) is given by the exponential

$$\langle\psi_0|\Psi(t)\rangle \equiv c_0(t)e^{-i\mathcal{E}_0 t/\hbar} = b_0 e^{-\Gamma t/2} e^{-i(\mathcal{E}_0+\Delta\mathcal{E})t/\hbar} \tag{47}$$

where b_0 is a constant which depends on the short times behavior of $c_0(t)$ and

$$\begin{aligned} \Gamma =& \frac{2\pi}{\hbar}\overline{|V_{0\mu}|^2}\Big|_{\mathcal{E}_\mu=\mathcal{E}_0} = \frac{2\pi}{\hbar}\int d\mu\ \delta(\mathcal{E}_0-\mathcal{E}_\mu)|V_{0\mu}|^2 \\ \Delta\mathcal{E} =& \mathcal{P}\int d\mathcal{E}\ \overline{|V_{0\mu}|^2}\Big|_{\mathcal{E}_\mu=\mathcal{E}}\ \frac{1}{\mathcal{E}_0-\mathcal{E}} \end{aligned} \tag{48}$$

Here $\mathcal{P}$ denotes the "principle value" of the integral, cf.,

$$\mathcal{P}\int_a^b \frac{f(x)}{x}dx \equiv \lim_{\epsilon\to 0}\left[\int_a^{-\epsilon} dx + \int_\epsilon^b dx\right]\frac{f(x)}{x} \ \text{, for } a<0\ , b>0$$

We see that the "survival probability" of the initial state asymptotically decays exponentially with Γ controlling the decay rate

$$w_0(t) \equiv |\langle\psi_0|\Psi(t)\rangle|^2 = |b_0|^2 e^{-\Gamma t} \tag{49}$$

The inverse ratio $1/\Gamma$ is often called the lifetime of the level.

We observe that Γ is a sum

$$\Gamma = \int d\mu \Gamma_{0\to\mu}$$

of partial $\Gamma_{0\,\to\,\mu}$'s given by

$$\Gamma_{0\,\to\,\mu} = \frac{2\pi}{\hbar}|V_{0\mu}|^2\delta(\mathcal{E}-\mathcal{E}_\mu)$$

which are just the golden rule probabilities per unit time of transitions into particular continuous state ψ_μ.

The irreversible dynamics of a discrete state decaying into a continuum may serve as a simple example of how irreversibility appears in a formally reversible theoretical framework. In this respect it is instructive to follow a chain of considerations which starts by replacing the continuum of levels by just one level, then a few, then many but still discrete and finally by the continuum. It should be clear that in the few levels case there will be finite times that the system will "visit" back the initial level. These "return times" are growing with the number of levels and turning to infinite (i.e. to a decay) in the continuum case.

2.1.3 Coupling to the continuum - energy domain. Line shape, shift and width

The quantity $\Delta\mathcal{E}$ in Eq. (47) is the energy shift of the unperturbed energy $\mathcal{E}_0$ caused by the coupling via $V_{0\mu}$ of ψ_0 to the continuum of ψ_μ's. To understand this statement better we would like to present now the "stationary" version of the above discussion, i.e. to determine how the discrete state ψ_0 of the unperturbed Hamiltonian $\hat{H}_0$ gets "smeared", i.e. becomes distributed over the exact states of the problem with the coupling to the continuum states.

We note that the solution (35) which we found to the time dependent Schrödinger equation (33) can be formally expanded in terms of the eigenfunctions Ψ_χ of the "full" Hamiltonian $(\hat{H}_0+\hat{V})\Psi_\chi = E_\chi\Psi_\chi$

$$\Psi(t) = \int d\chi \mathcal{A}_\chi \Psi_\chi e^{-i\Omega_\chi t} \quad , \quad \Omega_\chi = E_\chi/\hbar \tag{50}$$

with the expansion coefficients $\mathcal{A}_\chi$ determined by the initial condition (34)[6]

$$\mathcal{A}_\chi = \langle \Psi_\chi | \psi_0 \rangle \tag{51}$$

The amplitude (47) can then be written as

$$\langle \psi_0 | \Psi(t) \rangle = \int d\chi |\langle \psi_0 | \Psi_\chi \rangle|^2 e^{-i\Omega_\chi t} = \int dE \overline{|\langle \psi_0 | \Psi_\chi \rangle|^2}\Big|_{E_\chi = E} e^{-iEt/\hbar} \tag{52}$$

where for the integral $\int d\chi$ we used the identity Eq. (45) with the notation similar to Eq. (46) for $\overline{|\langle \psi_0 | \Psi_\chi \rangle|^2}\Big|_{E_\chi = E}$. We obtain

$$\overline{|\langle \psi_0 | \Psi_\chi \rangle|^2}\Big|_{E_\chi = E} = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \langle \psi_0 | \Psi(t) \rangle e^{iEt/\hbar} \tag{53}$$

The left hand side is what we are interested in - the distribution of probabilities of the unperturbed discrete state ψ_0 among the exact stationary states of the problem.

To evaluate the integral in the r.h.s. we need to extend the solution (47) to negative times $t < 0$. This is simply done by noting that all the elements of the solution going from $c_\mu(t)$ to $c_0(t)$ keep their formal expressions. The only difference is found in the discussion of the long time limit $t_0 \to \infty$ in Eq. (146) of the Appendix which must be replaced by $t_0 \to -\infty$. To calculate such limit we will again use the shift in the energy integration contour but this time we will need to do this into the positive $Im\,\mathcal{E}$ half plane. It is easy to see that this will lead to the same result as for positive t but with the sign change of Γ. The integral above therefore consists of two parts

$$\frac{1}{2\pi} \left[\int_{-\infty}^{0} dt e^{-i(\mathcal{E}_0 + \Delta\mathcal{E} + i\hbar\Gamma/2 - E)t/\hbar} + \int_{0}^{\infty} dt e^{-i(\mathcal{E}_0 + \Delta\mathcal{E} - i\hbar\Gamma 2 - E)t/\hbar} \right]$$

which are easily evaluated with the result

$$\overline{|\langle \psi_0 | \Psi_\chi \rangle|^2}\Big|_{E_\chi = E} = \frac{1}{\pi} \frac{\hbar\Gamma/2}{(E - \mathcal{E}_0 - \Delta\mathcal{E})^2 + (\hbar\Gamma/2)^2} \tag{54}$$

This shows that the unperturbed discrete state with a fixed energy $\mathcal{E}_0$ gets "smeared" over the exact states in the energy range $\hbar\Gamma$ shifted by $\Delta\mathcal{E}$ relative to $\mathcal{E}_0$. The function in the r.h.s. of the above equality is a Lorentzian (also known as Breit-Wigner distribution). One often says that the discrete state with a sharp position in

[6] We assume that the continuum eigenfunctions Ψ_χ are normalized to the delta function $\langle \Psi_\chi | \Psi_{\chi'} \rangle = \delta(\chi - \chi')$

energy when coupled to a continuum of states "acquires" a line shape with a width and a shift.

One can also describe the result Eq. (54) as a discrete state turning into a resonance. This due to the analogy with what happens to a classical harmonic oscillator with an oscillation frequency ω_0 under an influence of the dissipative force $-\gamma v$. The oscillator motion (for unit mass)

$$q(t) = q_0 e^{-\gamma t/2} \sin(\omega t + \phi_0) \quad , \quad \omega = \sqrt{\omega_0^2 - \gamma^2/4}$$

is damped oscillations with shifted frequency and the amplitude exponentially decaying with time.

2.2 Photon emission rate

Following the discussion in the previous section we will now use the Fermi golden rule

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar} |\langle f|V|i\rangle|^2 \delta(E_n - E_0 - \hbar\omega_k) \tag{55}$$

to calculate the rate (probability per unit time) of spontaneous photon emission in which the state of matter changes from higher to lower energy state. Denoting these matter states as $|n\rangle$ and $|0\rangle$ we have in this case

$$|i\rangle = |n\rangle|\{0_{\mathbf{k}\alpha}\}\rangle \quad |f\rangle = |0\rangle|1_{\mathbf{k}\alpha}, \{0_{\mathbf{k}'\alpha'}\}\rangle \tag{56}$$

where $\mathbf{k}'\alpha'$ denote all photon states except $\mathbf{k}\alpha$. We have already inserted the corresponding initial and final energies E_n and $E_0 + \hbar\omega_k$ in the δ function above.

Using $\hat{H}_{I1}$ of Eq. (21) with these initial and final states we calculate

$$\begin{aligned}
\langle f|\hat{H}_{I1}|i\rangle &= \langle 0| \langle 1_{\mathbf{k}\alpha}, \{0_{\mathbf{k}'\alpha'}\}|\hat{H}_{I1}|\{0_{\mathbf{k}\alpha}\}\rangle |n\rangle = \\
&= -\sum_{\mathbf{k}''\alpha''} \left(\frac{\hbar}{2\epsilon_0\omega_k''\Omega}\right)^{1/2} \langle 0|\hat{\mathbf{j}}_{-\mathbf{k}''} \cdot \boldsymbol{\lambda}_{\mathbf{k}''\alpha''}|n\rangle \langle 1_{\mathbf{k}\alpha}, \{0_{\mathbf{k}'\alpha'}\}|\hat{a}_{\mathbf{k}''\alpha''} + \hat{a}^\dagger_{-\mathbf{k}''\alpha''}|\{0_{\mathbf{k}\alpha}\}\rangle
\end{aligned}$$

We have a sum of products of the matter and the radiation matrix elements. The latter are trivial to calculate

$$\langle 1_{\mathbf{k}\alpha}, \{0_{\mathbf{k}'\alpha'}\}|\hat{a}_{\mathbf{k}''\alpha''} + \hat{a}^\dagger_{-\mathbf{k}''\alpha''}|\{0_{\mathbf{k}\alpha}\}\rangle = \delta_{-\mathbf{k}'',\mathbf{k}}\delta_{\alpha''\alpha} \tag{57}$$

which means that only one term is not zero in the sum over the modes.

So we obtain

$$\langle f|\hat{H}_{I1}|i\rangle = -\left(\frac{\hbar}{2\epsilon_0\omega_k\Omega}\right)^{1/2}\langle 0|\hat{\mathbf{j}}_{\mathbf{k}}\cdot\boldsymbol{\lambda}_{\mathbf{k}\alpha}|n\rangle \tag{58}$$

The appearance of the inverse quantization volume $1/\Omega$ in the square of this expression is easy to understand. We are calculating the probability rate to find the emitted photon in a given $\mathbf{k}$ momentum state. For a macroscopically large Ω this probability is very small $\sim 1/\Omega$ but the values of $\mathbf{k}$ are very dense. In fact their density is $\sim \Omega$ which will cancel the $1/\Omega$ in the probability rate. We will now consider an example showing this.

2.2.1 What a typical detector measures

Let us consider a practical situation in which the emitted photons are detected by a detector placed sufficiently far from the emitting system and measuring all photons emitted in a small sold angle $d\gamma$ around $\mathbf{k}$.

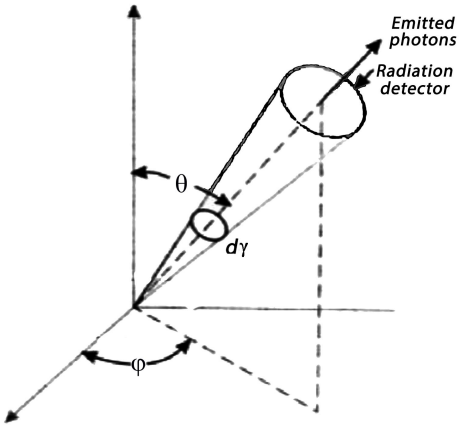

Figure 2: Schematic geometry of the detection of emitted photons. The detector opening spans $d\gamma$ solid angle centered at the direction θ, ϕ along which the emission rate is detected.

To calculate what the detector measures we note that the probability per unit time to measure a photon with a given polarization α and momentum $\hbar\mathbf{k}$ in a small

"volume" $\Delta^3 k$ around a given $\mathbf{k}$ is given by

$$dw_{\mathbf{k}\alpha} = \sum_{\mathbf{k}' \ in \ \Delta^3 k} \Gamma_{i\to\mathbf{k}'\alpha} \approx \Gamma_{i\to\mathbf{k}\alpha} \times \left(\text{number of } \mathbf{k}'\text{s in } \Delta^3\text{k}\right) \to \Gamma_{i\to\mathbf{k}\alpha} \frac{\Omega d^3 k}{(2\pi)^3}$$

where we denoted schematically by $\Gamma_{i\to\mathbf{k}'\alpha}$ the rate of the photon emission into $\mathbf{k}'\alpha$ state and assumed that $\Delta^3 k$ is small enough to have this rate changing little in the above sum. We have also conventionally switched to the differential $d^3 k$ in our notations and used the expression $\Omega d^3 k/(2\pi)^3$ for the number of $\mathbf{k}$'s in $d^3 k$.

To continue with what we assumed this detector measures we should adjust the above expression to account for all the $\mathbf{k}$'s in the solid angle $d\gamma$. For this we express $d^3 k = k^2 dk d\gamma$, keep $d\gamma$ fixed and integrate over dk. Using the explicit expression for $\Gamma_{i\to\mathbf{k}'\alpha}$ with matrix element (58) and changing to $k = \omega/c$ we have that the probability or more practically the relative number of photons per unit time measured by the detector in repeated experiments is given by

$$dN_{\mathbf{k}\alpha} = d\gamma \int \frac{2\pi}{\hbar} \left(\frac{\hbar}{2\epsilon_0 \omega \Omega}\right) |\langle 0|\hat{\mathbf{j}}_{\mathbf{k}} \cdot \boldsymbol{\lambda}_{\mathbf{k}\alpha}|n\rangle|^2 \delta(E_n - E_0 - \hbar\omega) \, \frac{\Omega \omega^2 d\omega}{(2\pi c)^3} \tag{59}$$

We note that Ω cancels out. Using the δ function to do the integral we find

$$\frac{dN_{\mathbf{k}\alpha}}{d\gamma} = \frac{\omega}{8\pi^2 c^3 \epsilon_0 \hbar} |\langle 0|\hat{\mathbf{j}}_{\mathbf{k}} \cdot \boldsymbol{\lambda}_{\mathbf{k}\alpha}|n\rangle|^2 \tag{60}$$

where we must remember that ω and the magnitude of $\mathbf{k}$ are fixed by the energy conservation

$$\hbar\omega = ck = E_n - E_0 \tag{61}$$

The above expression for the emission rate is the main result of this section. It shows all one needs in order to find the deexcitation rate with photon emitted in the small angle in the direction $\mathbf{k}$ with the polarization vector $\boldsymbol{\lambda}_{\mathbf{k}\alpha}$. One should be able to calculate the matrix element

$$\langle 0|\hat{\mathbf{j}}_{\mathbf{k}}|n\rangle$$

of the $\mathbf{k}$-th Fourier component of the matter current, then project it on the polarization $\boldsymbol{\lambda}_{\mathbf{k}\alpha}$, square the result and multiply by the coefficient in front of (60).

Let us indicate that working in spherical coordinates

$$\mathbf{k} = k(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \tag{62}$$

a convenient choice of linear polarization vectors for the photon emission problem is

$$\begin{aligned} \boldsymbol{\lambda}_1 &= (\cos\theta\cos\phi, \cos\theta\sin\phi, -\sin\theta) \quad , \quad \lambda_2 = (-\sin\phi, \cos\phi, 0) \\ \mathbf{k}\cdot\boldsymbol{\lambda}_{1,2} &= \boldsymbol{\lambda}_1\cdot\boldsymbol{\lambda}_2 = 0 \end{aligned} \tag{63}$$

This choice corresponds to $\boldsymbol{\lambda}_1$ lying in the $\mathbf{k}, \mathbf{e}_z$ plane, i.e. parallel to $\mathbf{e}_\theta$ while $\boldsymbol{\lambda}_2$ is perpendicular to it, i.e. parallel to $\mathbf{e}_\phi$.

If the detector does not distinguish between the photon polarizations (as is often the case) one must sum

$$\frac{dN_{\mathbf{k}}}{d\gamma} = \sum_{\alpha=1,2} \frac{dN_{\mathbf{k}\alpha}}{d\gamma} \tag{64}$$

2.2.2 The classical limit

In the following sections we will discuss various properties and simplifications of the current matrix element in (60). Before that let us compare this expression with the corresponding classical result. For this let us multiply it by the photon energy $\hbar\omega$. In this way we will find the power emitted by the system

$$\frac{d\mathcal{P}_{\mathbf{k}\alpha}}{d\gamma} = \frac{\omega^2}{8\pi^2 c^3 \epsilon_0} |\langle 0|\hat{\mathbf{j}}_{\mathbf{k}}|n\rangle| \cdot \boldsymbol{\lambda}_{\mathbf{k}\alpha}|^2 \tag{65}$$

Remarkably there is no explicit $\hbar$ dependence in this expression and the quantum mechanics only manifests itself in the presence of the matrix element of the current.

Comparing this expression with the classical result (cf., Ref.[3], p.279) one finds that the expressions are formally identical[7] provided one identifies the matrix element of the current operator $\hat{\mathbf{j}}(\mathbf{r})$ in quantum mechanical expression with the Fourier component with the frequency (61) of the classical current $\mathbf{j}(\mathbf{r}, t)$.

This correspondence fits the semiclassical rule (cf., Sec.48 in Ref. [4]) that the matrix elements f_{mn} in the classical limit approach the components f_{m-n} of the Fourier expansion of the classical function $f(t)$. This rule was originally guessed by Heisenberg in his matrix quantum mechanics approach.

2.2.3 Momentum conservation and recoil energy

Let us consider the common case that the initial and final states of the photon emitting matter system are momentum eigenstates with total momentum $\mathbf{P}_i$ and $\mathbf{P}_f$

[7] One should remember the extra $1/4\pi\epsilon_0$ factor when passing from CGS to SI of the square of electric charge

respectively. Isolated atoms, molecules, nuclei will be in such states. The initial and the final states in such systems will then be

$$|i\rangle = |n, \mathbf{P}_i\rangle |\{0_{\mathbf{k}\alpha}\}\rangle \quad |f\rangle = |0, \mathbf{P}_f\rangle |1_{\mathbf{k}\alpha}, \{0_{\mathbf{k}'\alpha'}\}\rangle$$

with the transition matrix element (58)

$$|\langle f|V|i\rangle|^2 = \left(\frac{\hbar}{2\epsilon_0 \omega_k \Omega}\right) |\langle 0, \mathbf{P}_f|\hat{\mathbf{j}}_{\mathbf{k}}|n, \mathbf{P}_i\rangle \cdot \boldsymbol{\lambda}_{\mathbf{k}\alpha}|^2 \tag{66}$$

The operator $\hat{\mathbf{j}}_{\mathbf{k}}$ has the property that when acting on a matter state having a given total momentum $\mathbf{P}$ it transforms this state into a state with $\mathbf{P} - \hbar\mathbf{k}$. To show this let us use the momentum operator $\hat{\mathbf{P}} = \sum_{a=1}^{N} \hat{\mathbf{p}}_a$ and calculate the action of its components $\hat{P}_m$ on the state which $\hat{\mathbf{j}}_{\mathbf{k}}$ generates acting on $|n, \mathbf{P}_i\rangle$

$$\hat{P}_m \left(\hat{\mathbf{j}}_{\mathbf{k}}|n, \mathbf{P}_i\rangle\right) = \left[\hat{P}_m\,,\, \hat{\mathbf{j}}_{\mathbf{k}}\right] |n, \mathbf{P}_i\rangle + P_m^{(i)} \hat{\mathbf{j}}_{\mathbf{k}}|n, \mathbf{P}_i\rangle \tag{67}$$

where to avoid confusion we denoted by $P_m^{(i)}$ the m-th component of the $\mathbf{P}_i$ vector and used $\hat{P}_m|n, \mathbf{P}_i\rangle = P_m^{(i)}|n, \mathbf{P}_i\rangle$ in the second term on the r.h.s. Let us now calculate the commutator in the first term using the explicit expression (22) for $\hat{\mathbf{j}}_{\mathbf{k}}$ and the following relation for the components $\hat{\mathbf{p}}_a$ of $\hat{\mathbf{P}}$

$$\left[\hat{\mathbf{p}}_a\,,\, e^{-i\mathbf{k}\cdot\mathbf{r}_b}\right] = -\delta_{ab}\, i\hbar\nabla_a e^{-i\mathbf{k}\cdot\mathbf{r}_b} = -\delta_{ab}\,\hbar\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{r}_b} \quad \rightarrow \quad \left[\hat{P}_m\,,\, \hat{\mathbf{j}}_{\mathbf{k}}\right] = -\hbar k_m\, \hat{\mathbf{j}}_{\mathbf{k}}$$

This gives for Eq. (67)

$$\hat{P}_m \left(\hat{\mathbf{j}}_{\mathbf{k}}|n, \mathbf{P}_i\rangle\right) = (\mathbf{P}_i - \hbar\mathbf{k})_m \left(\hat{\mathbf{j}}_{\mathbf{k}}|n, \mathbf{P}_i\rangle\right) \tag{68}$$

showing that indeed the state $\hat{\mathbf{j}}_{\mathbf{k}}|n, \mathbf{P}_i\rangle$ had a definite value of the momentum $\mathbf{P} = \mathbf{P}_i - \hbar\mathbf{k}$. Since states with different momenta are orthogonal this property means the transitions matrix elements $\langle 0, \mathbf{P}_f|\hat{\mathbf{j}}_{\mathbf{k}}|n, \mathbf{P}_i\rangle$ is non vanishing only for

$$\mathbf{P}_i = \mathbf{P}_f + \hbar\mathbf{k}$$

i.e. the emitted photons conserve the total momentum.

The above discussion concerned the change of the momentum of matter systems emitting photons. But this recoil momentum $\Delta\mathbf{P} \equiv \mathbf{P}_f - \mathbf{P}_1$ implies that there is also a corresponding recoil energy. This energy should in principle be included in the

energy conservation relation Eq.(61). However one can show that for typical photon momenta the recoil energy can to a very good approximation be neglected and the matter system assumed to remain at rest in its c.m. frame.

Indeed for the photon energy $\epsilon_{\rm photon} = \hbar\omega$ the momentum transferred to the recoiling matter is $p_{\rm recoil} = \hbar k = \hbar\omega/c$. Thus the matter recoil kinetic energy $\epsilon_{\rm recoil} = p^2_{\rm recoil}/2M = (\hbar\omega)^2/2Mc^2$ where we assumed that the matter is non relativistic and work in a reference frame in which it was initially at rest.

The ratio of the recoil energy to the photon energy is therefore

$$\frac{\epsilon_{\rm recoil}}{\epsilon_{\rm photon}} \sim \frac{\hbar\omega}{Mc^2}$$

which for typical emitting matter systems (molecules, atoms, nuclei) is

$$\frac{1eV \div 10\, MeV}{(1 \div 100)\, GeV} \ll 1$$

so that the recoil energy is indeed negligible for such system.

Let us note that the dimensionless recoil velocity is given by the same expression

$$\frac{v}{c} = \frac{p}{Mc} = \frac{\hbar\omega}{Mc^2}$$

For e.g. hydrogen atom this gives

$$\frac{v_{\rm recoil}}{c} \sim \frac{10eV}{10^9 eV} \quad \rightarrow \quad v_{\rm recoil} \sim 10^{-8}c = 3m/s$$

2.3 Long wavelength approximation

Consider two typical photon emitting quantum systems - atoms and nuclei and examine the relation between their sizes and the wavelengths of emitted photons. The latter are related to the photon energies as

$$\lambda = \frac{2\pi}{k} = \frac{2\pi c}{ck} = \frac{2\pi\hbar c}{\hbar\omega} \approx \frac{6.28 \times 197\ eV \cdot nm}{\hbar\omega} \approx \frac{1200\ eV \cdot nm}{\hbar\omega}$$

The typical atomic sizes are $\sim 0.1 \div 0.2\ nm$ while typical emission energies of atomic photons are $\sim 1 \div 10^3\ eV$. This means that the emitted photon wavelengths are

$$\lambda \sim (1.2 \div 1200)\ nm \gg 0.1 \div 0.2\ nm \text{ atomic sizes}$$

Similar result holds for nuclei for which the sizes are $5 \div 10 fm$ while typical emission energies are $(1 \div 10)\ MeV$. So

$$\lambda \approx \frac{1200\ MeV \cdot fm}{\hbar\omega} \sim 120 \div 1200\ fm \gg 5 \div 10\ fm \text{ nuclear sizes}$$

Similar estimates hold for solid state emission systems (there the typical size is the crystal unit cell, etc) and small molecules.

These estimates have important consequence for the evaluation and magnitude of the current matrix element in the emission rate expression Eq. (60). Writing it out explicitly

$$\langle 0|\hat{\mathbf{j}}_{\mathbf{k}}|n\rangle = \int d^3r\ e^{-i\mathbf{k}\cdot\mathbf{r}} \langle 0|\hat{\mathbf{j}}(\mathbf{r})|n\rangle \tag{69}$$

we see that the range of the integration where the integrand is not vanishing is determined by the matrix element of the current. So this range must be $|\mathbf{r}| \leq a$ where $a \sim$ size of the emitting system. As we have seen above for the majority of the matter systems of interest this range will be $a \ll \lambda$ - the wave lengths of the emitted photons. Written in the form $ka \ll 1$ this shows that one can expand the exponent in the above integral

$$\langle 0|\hat{\mathbf{j}}_{\mathbf{k}}|n\rangle = \int d^3r(1-i\mathbf{k}\cdot\mathbf{r}+...)\langle 0|\hat{\mathbf{j}}(\mathbf{r})|n\rangle = \langle 0|\hat{\mathbf{j}}_0|n\rangle - i\int d^3r\,(\mathbf{k}\cdot\mathbf{r})\langle 0|\hat{\mathbf{j}}(\mathbf{r})|n\rangle + ... \tag{70}$$

and keep only the lowest non-vanishing term.

This is the basis of the important element of the photon emission (and as we will see below photon absorption) treatment – the Long Wavelength Approximation (LWA).

2.4 Electric dipole emission

Let us discuss the photon emission rate which one should expect retaining only the lowest term in the LWA expansion (70). We use

$$\hat{\mathbf{j}}_0 = \int d^3r \sum_{a=1}^{N} \frac{q_a}{2m_a}[\hat{\mathbf{p}}_a\delta(\mathbf{r}-\mathbf{r}_a) + \delta(\mathbf{r}-\mathbf{r}_a)\hat{\mathbf{p}}_a] = \sum_{a=1}^{N} \frac{q_a}{m_a}\hat{\mathbf{p}}_a \tag{71}$$

To evaluate matrix elements of this operator between matter eigenenergy states it is convenient to use the commutation relation

$$[\mathbf{r}_a, \hat{H}_{matter}] = [\mathbf{r}_a, \sum_{b=1}^{N} \frac{\hat{\mathbf{p}}_b^2}{2m_b}] = i\hbar\frac{\hat{\mathbf{p}}_a}{m_b}$$

Therefore

$$\hat{\mathbf{j}}_0 = \sum_{a=1}^{N} \frac{q_a}{m_a} \hat{\mathbf{p}}_a = \frac{1}{i\hbar}[\hat{\mathbf{d}}, \hat{H}_{matter}] \quad \text{with} \quad \hat{\mathbf{d}} = \sum_{a=1}^{N} q_a \mathbf{r}_a \tag{72}$$

where $\hat{\mathbf{d}}$ is the operator of the dipole moment of the matter system.

For the matrix element in the first term of (70) we therefore have

$$\langle 0|\hat{\mathbf{j}}_0|n\rangle = \frac{1}{i\hbar}\langle 0|[\hat{\mathbf{d}}, \hat{H}_{matter}]|n\rangle = \frac{E_n - E_0}{i\hbar}\langle 0|\hat{\mathbf{d}}|n\rangle \tag{73}$$

where we used that $|0\rangle$ and $|n\rangle$ are eigenstates of $\hat{H}_{matter}$. Thus to lowest order in ka

$$\langle 0|\hat{\mathbf{j}}_{\mathbf{k}}|n\rangle \approx -i\omega\langle 0|\hat{\mathbf{d}}|n\rangle$$

Transitions described by these matrix elements are called *electric dipole transitions*. Using this in the expression (60) for the photon emission rate we obtain

$$\frac{dN_{\mathbf{k}\alpha}}{d\gamma} = \frac{\omega^3}{8\pi^2 c^3 \epsilon_0 \hbar} |\langle 0|\hat{\mathbf{d}}|n\rangle \cdot \boldsymbol{\lambda}_{\mathbf{k}\alpha}|^2 \tag{74}$$

Radiation described by this formula is called *electric dipole* radiation.

The above expression depends on three factors - the vector of the matrix elements of the dipole operator between the matter eigenstates,

$$\mathbf{d}_{on} \equiv \langle 0|\hat{\mathbf{d}}|n\rangle \ ,$$

the energy difference $\hbar\omega$ between these states and the polarization $\boldsymbol{\lambda}_{\mathbf{k}\alpha}$ of the emitted photon.

As we will see below the fact that the dipole operator $\hat{\mathbf{d}}$ is a vector allows to determine important general properties of the resulting vector $\mathbf{d}_{on}$ of matrix elements. For the situation in which the initial and final states $|n\rangle$ and $|0\rangle$ are eigenstates of the angular momentum of the matter system it will be possible to determine when $\mathbf{d}_{on}$ is non vanishing and to derive general relations between the components of $\mathbf{d}_{on}$, i.e. to find its direction.

The direction $\mathbf{k}$ of the photon emission enters the dipole emission rate Eq.(74) via its dependence on the polarization vectors $\boldsymbol{\lambda}_{\mathbf{k}\alpha}$ which are perpendicular to $\mathbf{k}$. It is obvious that the angular distribution of the emitted photons is symmetric around the direction of the vector $\mathbf{d}_{on}$. Moreover since $\boldsymbol{\lambda}_{\mathbf{k}\alpha}$ are perpendicular to $\mathbf{k}$, the emission rate is zero along the line of the direction of $\mathbf{d}_{on}$. For an arbitrary direction of $\mathbf{k}$ it is convenient to work with polarization vectors $\boldsymbol{\lambda}_{\mathbf{k}1}$ and $\boldsymbol{\lambda}_{\mathbf{k}2}$ which are respectively

parallel and perpendicular to the plane defined by $\mathbf{d}_{on}$ and $\mathbf{k}$. Choosing the coordinate system with $\mathbf{d}_{on}$ along its z-axis and denoting by θ and ϕ the spherical angles of $\mathbf{k}$ it is easy to see that such a choice corresponds to Eq. (63). Then

$$|\mathbf{d}_{on} \cdot \boldsymbol{\lambda}_{\mathbf{k}1}|^2 = |\mathbf{d}_{on}|^2 \sin^2\theta \tag{75}$$

We plot the resulting pattern in Fig. 3. Clearly the emission rate with the polarization $\boldsymbol{\lambda}_{\mathbf{k}2}$ is identically zero for all the directions of such emission

$$|\mathbf{d}_{on} \cdot \boldsymbol{\lambda}_{\mathbf{k}2}|^2 = 0$$

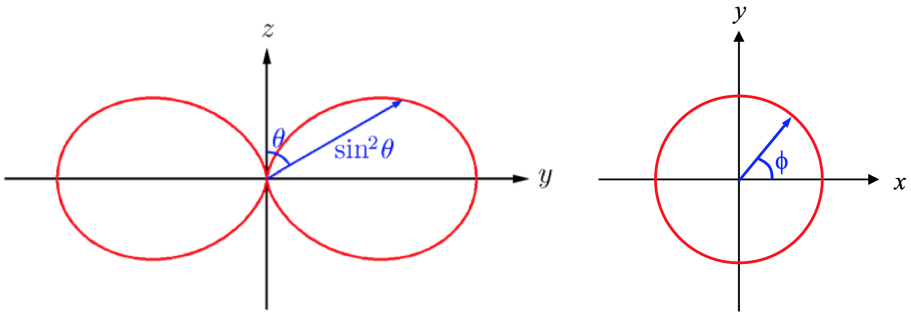

Figure 3: Angular distribution of the electric dipole radiation vs the spherical angles θ and ϕ of the emitted photon wave vector $\mathbf{k}$ with the dipole matrix element vector $\mathbf{d}_{on}$ chosen to lie along the z-axis.

Multiplying Eq. (74) by $\hbar\omega$ gives the power emitted in the dipole radiation

$$\frac{d\mathcal{P}_{\mathbf{k}\alpha}}{d\gamma} = \frac{\omega^4}{8\pi^2 c^3 \epsilon_0} |\langle 0|\hat{\mathbf{d}}|n\rangle \cdot \boldsymbol{\lambda}_{\mathbf{k}\alpha}|^2 \tag{76}$$

As in our discussion following Eq. (65) we note that there is no explicit $\hbar$ dependence in this expression and that the quantum mechanics manifests itself "only" in the matrix element of the dipole operator. Once again comparing with the classical expression, cf.[8] one sees that this matrix element in the classical limit becomes the Fourier component of the classical dipole moment $\mathbf{d}(t)$ with frequency (61).

Here is a pictorial representation of the classical electric dipole radiation.

`https://www.youtube.com/watch?v=UOVwjKi4B6Y`

[8] https://farside.ph.utexas.edu/teaching/em/lectures/node95.html

2.5 Angular momentum and parity selection rules

In discussing photon emission by individual molecules, atoms, nuclei and subnuclear particles one deals with rotationally invariant matter Hamiltonians with eigenstates which are also eigenstates of the total angular momentum (including the spin)

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} = \sum_{a=1}^{N} \mathbf{r}_a \times \hat{\mathbf{p}}_a + \sum_{a=1}^{N} \hat{\mathbf{s}}_a$$

or more precisely of its square $\hat{\mathbf{J}}^2$ and one of its projections, commonly chosen as $\hat{J}_z$. The sum here is over the components of the molecule, atom, etc, which is under consideration. So in these (very common) cases the dipole matrix elements to be considered are

$$\langle 0|\hat{\mathbf{d}}|n\rangle \to \langle \nu_2 J_2 M_2|\hat{\mathbf{d}}|\nu_1 J_1 M_1\rangle \tag{77}$$

where we indicated explicitly the angular momentum quantum numbers and denoted by ν all the remaining ones needed to completely specify the states of the matter system. For example levels of a particle with spin $1/2$ moving in a spherically symmetric potential and with spin-orbit coupling have 4 quantum numbers

$$n_r \ , \ l \ , \ j \ , \ m$$

so ν will stand in this case for n_r, l numbers.

2.5.1 Dipole moment is an $\ell = 1$ object. Spherical components of vectors

When the dipole operator $\hat{\mathbf{d}}$ in the matrix element Eq. (77) acts on the initial state $|\nu_1 J_1 M_1\rangle$ it creates a state which doesn't have the same angular momentum and is in general expected to be a superposition of states with definite J's and M's. The vectorial character of $\hat{\mathbf{d}}$ allows to determine the range of possibles values of these quantum numbers and to a certain extent also the coefficients in the resulting linear combination. To demonstrates this it is useful to transform the vector $\hat{\mathbf{d}}$ from cartesian to the so called spherical components.

The general expressions for such components of any vector $\mathbf{v}$ are by definition

$$v_{\mu=1} = -\frac{v_x + iv_y}{\sqrt{2}} \ \ , \ \ v_{\mu=0} = v_z \ \ , \ \ v_{\mu=-1} = \frac{v_x - iv_y}{\sqrt{2}} = -v^*_{\mu=1} \tag{78}$$

The scalar product of vectors in spherical components is expressed as

$$\mathbf{a}\cdot\mathbf{b} = \sum_{\mu=-1,0,1} (-1)^{\mu} a_\mu b_{-\mu} = \sum_{\mu=-1,0,1} a_\mu b^*_\mu \tag{79}$$

The usefulness of forming the spherical components' combinations can be seen especially clear in terms of the spherical coordinates[9]

$$v_x = v\sin\theta_v\cos\phi_v \quad , \quad v_y = v\sin\theta_v\sin\phi_v \quad , \quad v_z = v\cos\theta_v \tag{80}$$

so that

$$v_0 = v\cos\theta_v \ \ , \ \ v_{\pm 1} = \mp\frac{1}{\sqrt{2}} v\sin\theta_v e^{\pm i\phi_v} \quad \rightarrow \quad v_\mu = \sqrt{\frac{4\pi}{3}}\, v\, Y_{1\mu}(\theta_v,\phi_v) \quad \mu = 1,0,-1 \tag{81}$$

emphasizing that three components of a vector behave under rotations as $Y_{1\mu}$. In the group theoretical terminology one says that vectors transform as $j = 1$ representation of the group $O(3)$ of rotations.

This of course holds true also for the vector $\hat{\mathbf{d}}$ of the electric dipole moment. Let us now explore the consequences of this insight.

2.5.2 Dipole angular momentum selection rules - hydrogen atom first

Let us start with a simplest case of electric dipole transitions in a hydrogen atom. With its single electron the dipole operator and its spherical components in this simple system are just

$$\hat{\mathbf{d}} = e\mathbf{r} \quad \rightarrow \quad \hat{d}_\mu = e\sqrt{\frac{4\pi}{3}}\, r\, Y_{1\mu}(\theta,\phi)$$

We can ignore the spin and consider dipole transitions between the orbital eigenstates of the hydrogen atom

$$|n,l,m\rangle \rightarrow |n',l',m'\rangle$$

with the coordinate representation of these states having the familiar form

$$\langle \mathbf{r}|n,l,m\rangle = R_{nl}(r)Y_{lm}(\theta,\phi)$$

In this representation electric dipole operator acting on the initial state $|n,l,m\rangle$ results in a state $\hat{d}_\mu|n,l,m\rangle$ which in the coordinate representation is

$$\langle \mathbf{r}|\hat{d}_\mu|n,l,m\rangle = \sqrt{\frac{4\pi}{3}} e r R_{nl}(r)Y_{1\mu}(\theta,\phi)Y_{lm}(\theta,\phi) \tag{82}$$

[9]Note that the subscript v in the angles here indicates that they are not necessarily the same as of the real space coordinate vector $\{x,y,z\}$.

Let us use the intuition from the quantum angular momentum algebra and view the product of the two spherical harmonics $Y_{1\mu}Y_{lm}$ as an eigenfunction of the (quantum) sum of two angular momenta $\ell_1 = 1$ and $\ell_2 = l$. As we know the resulting angular momentum ℓ has possible values given by

$$l-1\ ,\ l\ ,\ l+1 \quad \text{with the projection}\ \ \mu+m$$

Continuing with this understanding we expect that the state $\hat{d}_\mu|n,l,m\rangle$ is a linear combination of states with the above values of ℓ and its projection.

Forming the dipole matrix element $\langle n',l',m'|\hat{d}_\mu|n,l,m\rangle$ means that the final state $|n',l',m'\rangle$ is projected on this linear combination. The resulting overlap should be zero unless the final angular momentum $l'm'$ is equal to one of the above values, i.e. satisfy the familiar triangular rule of adding angular momenta

$$|l-1| \le l' \le l+1\ \ ,\ \ m' = m+\mu \tag{83}$$

Formally these considerations are supported and extended by using the known expansion of the product of two spherical harmonics $Y_{l_1m_1}(\theta,\phi)Y_{l_2m_2}(\theta,\phi)$ viewed as a function of the angles θ,ϕ in terms of the complete set $\{Y_{LM}(\theta,\phi)\}$

$$Y_{l_1m_1}(\theta,\phi)Y_{l_2m_2}(\theta,\phi) = \sum_{L=0}^{\infty}\sum_{M=-L}^{L} G^{Mm_1m_2}_{L\,l_1\,l_2}\, Y_{LM}(\theta,\phi) \tag{84}$$

where $G^{Mm_1m_2}_{L\,l_1\,l_2}$ are the so called Gaunt coefficients which are proportional to the respective Clebsh-Gordan (CG) coefficients, cf. Ref.[5], p.57

$$G^{Mm_1m_2}_{L\,l_1\,l_2} = a(l_1,l_2,L)\langle LM|l_1m_1,l_2m_2\rangle \tag{85}$$

Here the proportionality factor $a(l_1,l_2,L)$ doesn't depend on the projections m_1,m_2,M. The CG coefficient is zero unless

$$|l_1-l_2| \le L \le l_1+l_2 \quad \text{and} \quad M = m_1+m_2$$

which constraints the sum over L in the expansion (84) and removes the sum over M. When applied to our case, Eq. (82), with the product $Y_{1\mu}Y_{lm}$ one recovers what we have guessed using qualitative arguments, i.e. the rules (83). These are called electric dipole angular momentum selection rules. In words they state that only transition with at most one unit change in the angular momentum are allowed, i.e $\Delta l = 0,\pm 1$. Below we will complete the discussion of these rules by examining also the consequences of the parity conservation.

Let us further observe that the dependence of the Gaunt coefficients on the angular momentum projection quantum numbers M, m_1, m_2 enter only via the CG coefficient. To see what this means for the electric dipole transitions let us sketch schematically the calculation of the dipole matrix element $\langle n', l', m'|\hat{d}_\mu|n, l, m\rangle$. We will need to calculate

$$\langle n', l', m'|\hat{d}_\mu|n, l, m\rangle = \int(\text{radial part}) \int(\text{angular part}) \tag{86}$$

where

$$\begin{aligned} \int(\text{radial part}) &= e\sqrt{\frac{4\pi}{3}} \int_0^\infty r^2 dr R^*_{n'l'}(r) r R_{nl}(r) \\ \int(\text{angular part}) &= \int Y^*_{l'm'}(\theta, \phi) Y_{1\mu}(\theta, \phi) Y_{lm}(\theta, \phi) \, \sin\theta d\theta d\phi \end{aligned} \tag{87}$$

Expansion (84) shows that the angular integral equals the appropriate Gaunt coefficient $G^{m'\mu m}_{l'\,1\,l}$. Using Eq. (85) we see that

$$\langle n', l', m'|\hat{d}_\mu|n, l, m\rangle = \langle lm, 1\mu|l'm'\rangle \langle n'l'||\hat{d}||nl\rangle \tag{88}$$

where we introduced the common notation $\langle n'l'||\hat{d}||nl\rangle$ called reduced matrix element for the part of the full matrix element which is independent of m, m' and μ. In the present case it is the product of the radial part in (87) and the factor $a(l, 1, l')$ in the relation (85).

Expression (88) is a particular case of a more general relation known as the Wigner-Eckart theorem which will be discussed in the next Section. It shows that the dipole matrix element dependence on $m, , m'$ and μ is entirely determined by known (tabulated) CG coefficients, cf. Ref.[5].

From this it follows that if for given nl and $n'l'$ quantum numbers one needs to find all the matrix elements $\langle n', l', m'|\hat{d}_\mu|n, l, m\rangle$ it is enough to determine just one of them, say, with $m = m', \mu = 0$. Using its value one can calculate the reduced matrix element $\langle n'l'||\hat{d}||nl\rangle$ and then all the $(2l+1) \times 3$ via the relation Eq. (88) with appropriate CG coefficients.

We also note that for given initial and final states the selection rules Eq. (83) show that only one spherical component of the vector[10] $\langle n', l', m'|\hat{d}_\mu|n, l, m\rangle$ is non zero, that with $\mu = m' - m$. Let us recall that in the present context this vector is what was denoted $\langle 0|\hat{\mathbf{d}}|n\rangle$ in the expression (74) for the electric dipole emission

[10]We use the term "vector" for complex valued matrix elements of the dipole operator $\hat{d}$ for the brevity of presentation. It is the relative size of its three components that will be of our interest.

rate. We then conclude that the scalar product $\langle 0|\hat{\mathbf{d}}|n\rangle \cdot \boldsymbol{\lambda}$ in that expression has correspondingly only one term $\langle 0|\hat{d}_\mu|n\rangle\lambda^*_\mu$ with that μ and the angular distribution is given by the angular dependence of $|\lambda_\mu|^2$.

Let us consider as an example the case of transitions between states with equal $m = m'$ for which the only non zero matrix element is $\langle n', l', m|\hat{d}_0|n, l, m\rangle$. This is $\langle 0|d_z|n\rangle$ in the notation of Eq. (74) and correspondingly the angular distribution of the emitted photons is given by λ_z^2 which for the choice (63) of $\boldsymbol{\lambda}_1$ is given by Eq. (75) and zero for $\boldsymbol{\lambda}_2$. More examples and details will be considered in tutorials and homework.

2.5.3 Dipole parity selection rule - hydrogen atom first

Let us now examine limitations which parity conservation imposes on the possible final states of electric dipole transitions from a given initial state. We start by noticing that under the parity transformation $\mathbf{r} \to -\mathbf{r}$, i.e. under mirror reflection

$$x, y, z \quad \to \quad -x, -y, -z \tag{89}$$

of the coordinate system the electric dipole operator changes sign $\hat{\mathbf{d}} \to -\hat{\mathbf{d}}$. Let us make this coordinate change in the integral Eq. (86). In spherical coordinates this change is

$$r, \theta, \phi \quad \to \quad r, \pi - \theta, \phi + \pi$$

so that the radial part doesn't change while the spherical harmonics transform as[11]

$$Y_{lm}(\theta, \phi) \to Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi) \tag{90}$$

The result is that the entire integral on the r.h.s. of Eq. (86) is equal to itself multiplied by $-(-1)^l(-1)^{l'}$. This of course means that it is zero and together with it the matrix element $\langle n', l', m'|\hat{d}_\mu|n, l, m\rangle$ is zero unless

$$(-1)^l(-1)^{l'} = -1 \tag{91}$$

i.e. l' and l are of opposite parity (i.e. odd vs even or even vs odd). This is called parity selection rule. Taken together with the angular momentum we find that electric dipole selection rules can be formulated as

$$l' = l \pm 1 \tag{92}$$

[11] To see this start with the easy $Y_{ll} \sim \sin^l\theta e^{il\phi}$ and then use $Y_{lm} \sim \hat{L}_- Y_{lm+1}$ together with $\hat{L}_-$ being even under $\mathbf{r} \to -\mathbf{r}$ to show that all Y_{lm} transform as Y_{ll}.

In Fig.4 we show examples of electric dipole transitions

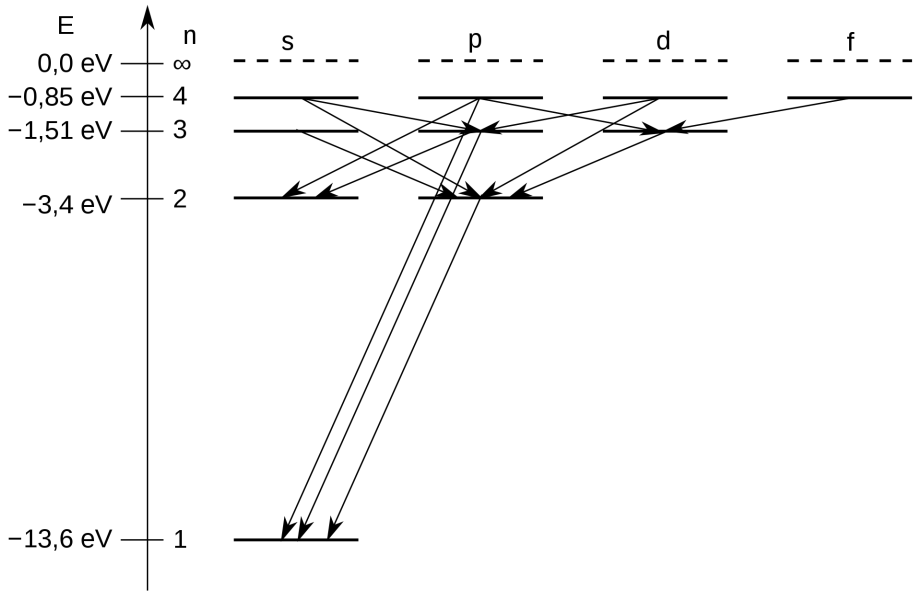

Figure 4: Radiative transitions in hydrogen. Only dipole transitions between adjacent angular momentum columns are allowed, as per combined angular momentum and parity selection rule $\Delta l = \pm 1$

2.5.4 Angular momentum selection rules - general view. The Wigner-Eckart theorem

In this section we will extend and formalize our discussion of the angular momentum selection rules from the simplest case of radiative transitions in a hydrogen atom to a general case of any physical system (e.g. multi-electron atoms, nuclei, molecules) the Hamiltonian of which is invariant under rotations. We will show that the main relation, Eq.(88) holds for such systems with all its consequences.

The general structure of the eigenstates in systems with rotationally invariant Hamiltonian is $|\nu JM\rangle$, cf., Eq. (77), with ν denoting all the quantum numbers needed to specify this state apart of the angular momentum J and its projection M. What this structure means is that under $O(3)$ rotations these states transform as

$$\hat{U}(\alpha\mathbf{n})|\nu JM\rangle \equiv e^{i\alpha\mathbf{n}\cdot\hat{\mathbf{J}}}|\nu JM\rangle = \sum_{M'=-J}^{J} D^J_{MM'}(\alpha\mathbf{n})|\nu JM'\rangle \tag{93}$$

where the matrices

$$D^J_{MM'}(\alpha\mathbf{n}) = \langle \nu JM'|e^{i\alpha\mathbf{n}\cdot\hat{\mathbf{J}}}|\nu JM\rangle$$

are called Wigner matrices. The relations (93) show that the multiplets of states with different J's do not mix. Here we denoted by α the angle of rotation and by the unit vector $\mathbf{n}$ the direction of the rotation axis. In practice one uses the Euler angles θ, ϕ, ψ to parametrize $O(3)$ rotations and the Wigner matrices become Wigner functions $D^J_{MM'}(\theta, \phi, \psi)$ of these angles.

In our discussions of the hydrogen atom case we have seen that the vector character of the dipole operator, i.e. its behavior under rotations played a very important part. We will now generalize this discussion. Let us recall that under any unitary transformation which transforms wavefunctions as $|\psi\rangle \to U|\psi\rangle$ the operators transform as $U\hat{f}U^{-1}$. This is trivially seen by considering how the states obtained by acting with $\hat{f}$ transform

$$\hat{f}|\psi\rangle \to U\hat{f}|\psi\rangle = U\hat{f}U^{-1}U|\psi\rangle$$

which demonstrates that indeed $U\hat{f}U^{-1}$ acting on transformed wavefunctions $U|\psi\rangle$ produces the correctly transformed result.

Following this understanding one defines spherical tensor operators $\hat{T}_{j\mu}$ as a set of $2j+1$ operators which transform among themselves under $O(3)$ rotations

$$\hat{U}^{-1}(\alpha\mathbf{n})\hat{T}_{j\mu}\hat{U}(\alpha\mathbf{n}) = \sum_{\mu'} D^j_{\mu\mu'}(\alpha\mathbf{n})\hat{T}_{j\mu'}$$

Obviously the electric dipole operator $\hat{d}_\mu$ is an example of the spherical tensor $\hat{T}_{j\mu}$ with rank $j = 1$. In the following section we will encounter examples of electric and magnetic multipole operators which will correspond to spherical tensors $\hat{T}_{j\mu}$ with higher rank j. One also encounters similar expansions of physical operators in terms of spherical tensor operators $\hat{T}_{j\mu}$ in other fields of physics, e.g. in the context of atomic and nuclear shell models.

To understand the properties of the spherical tensor operators let us examine how the state which is obtained when $\hat{T}_{j\mu}$ acts on $|\nu JM\rangle$ behaves under rotations

$$U\hat{T}_{j\mu}|\nu JM\rangle = U\hat{T}_{j\mu}U^{-1}U|\nu JM\rangle = \sum_{\mu'}\sum_{M'} D^j_{\mu\mu'}D^J_{MM'}\hat{T}_{j\mu'}|\nu JM'\rangle$$

The product of the two D matrices appearing here is identical to what would be obtained when rotating the direct product of states with angular momentum j, μ and

J, M. This suggests that $\hat{T}_{j\mu}$ acting on $|\nu JM\rangle$ generates a state having total angular momentum equal (quantum mechanically) to the sum of j, μ and J, M. This would mean that in the matrix

$$\langle \nu' J' M' | \hat{T}_{j\mu} | \nu J M \rangle \tag{94}$$

only matrix elements satisfying the quantum mechanical rules of summing the angular momenta

$$|J - j| \leq J' \leq J_1 + j \quad , \quad M' = M + m \tag{95}$$

can be non zero.

These intuitive expectations find rigorous proof in the classic Wigner-Eckart theorem. It generalizes the equality Eq. (88) to matrix elements (94), i.e. to the most general spherical tensor operators and eigenstates of any physical system with spherical symmetry

$$\langle \nu' J' M' | \hat{T}_{j\mu} | \nu J M \rangle = \langle J' M' | j\mu, JM \rangle \langle \nu' J' || \hat{T}_j || \nu J \rangle \tag{96}$$

Here $\langle J'M' | jm, JM \rangle$ are the Clebsh-Gordan coefficients and the notation $\langle \nu' J' || \hat{T}_j || \nu J \rangle$ called *reduced matrix elements* stands for the parts of the full matrix elements which are independent of the projections M, M' and m. This dependence is fully incorporated in the CG coefficients which also carry the information about the angular momentum selection rules, Eq. (95).

As in the hydrogen atom case the reduced matrix elements represent the orientation independent context of the original matrix elements, Eq.(94). To find them it is enough to calculate $\langle \nu' J' M' | \hat{T}_{jm} | \nu J M \rangle$ for one particular set of values of $M, m, M' = M + m$ and divide the result by the corresponding CG coefficient. For fixed νJ and $\nu' J'$ this amounts to just one calculation to determine all the $(2J + 1) \times (2j + 1)$ matrix elements in the left hand side of the relation (96) via the (known, tabulated) CG coefficients.

Finally let us note that the formal proof of Eq. (96) can be found in many references, e.g. p. 252 in Ref. [7].

2.5.5 An aside - review of the parity symmetry

In our discussion of the parity selection rules in hydrogen atom they looked like a special case depending on the behavior of the spherical harmonics $Y_{lm}(\theta, \phi)$ under the transformation of the angles, Eq. (90). We now wish to generalized these considerations to photon radiation in more complicated systems.

Parity transformation is an inversion transformation of a coordinate system in which all of its axes change signs, e.g. Eq. (89). Let us note that in two dimensions

this transformation can be accomplished by a π rotation of the axis. This is not so in three dimensions where the coordinate system changes from right-handed to left-handed. This is the reason the parity transformation probes additional features in three dimensional physical systems.

Let us note that technically the coordinate inversion can be achieved by a reflection in any plane, followed by a π rotation about an axis normal to this plane. We also note that under coordinate inversion vectors are expected to change signs, cf., Fig.5. However as we will see below there exist a category of vectors which do not change signs under parity transformation. Such vectors are called axial vectors or pseudo-vectors to distinguish from the real vectors also called polar vectors.

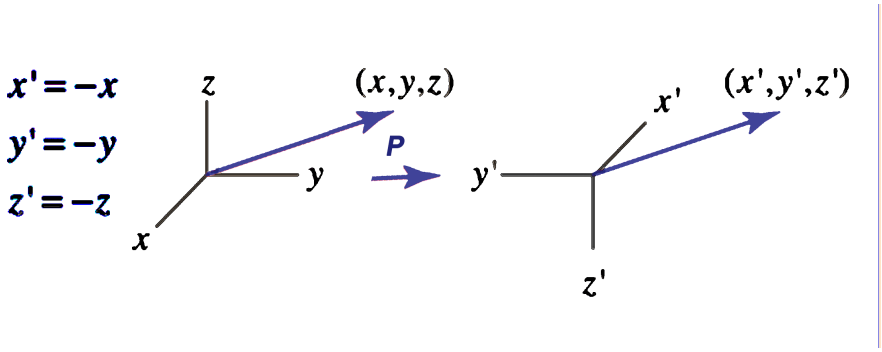

Figure 5: Parity transformation - the same physics (e.g. the same particle position, momentum, etc) is seen in the inverted coordinate axes system with $\mathbf{r} \to -\mathbf{r}$, $\mathbf{p} \to -\mathbf{p}$ etc

Is the nature invariant with respect to the parity transformation? Historically this was a very important question and the brief answer is that physical systems interacting via gravity, electromagnetic and strong interactions are invariant but the weak interactions violate this. It is beyond the scope of these lectures to go into the details of this statement, cf., Ref. [8]. Rather let us remain in the framework of what we study and examine this issue starting with the Hamiltonian given by Eq.(1). We observe that this Hamiltonian remains invariant if we change

$$\mathbf{r}_a \to -\mathbf{r}_a, \quad , \quad \mathbf{p}_a \to -\mathbf{p}_a \quad \mathbf{A}(\mathbf{r}) \to -\mathbf{A}(-\mathbf{r}) \ , \ \mathbf{E}(\mathbf{r}) \to -\mathbf{E}(-\mathbf{r}) \tag{97}$$

which is obviously the parity transformation. The extension to the remaining part $\hat{H}_{I3}$, Eq.(10) of the (non relativistic) matter-EM field Hamiltonian is discussed in the Appendix 3.2 where it is shown that magnetic field $\mathbf{B}(\mathbf{r})$ and particles' angular momenta $\mathbf{l}_a$ and spins $\mathbf{s}_a$ are axial vectors, i.e. they do not change under the coordinate inversion.

Let us now consider what does the invariance of the Hamiltonian under the parity transformation imply. It will be sufficient for our goals to limit the discussion to the matter part of the Hamiltonian $\hat{H}_{matter}$ in Eq. (5). We introduce the parity operator by defining its action on the wavefunctions of the matter particles

$$\hat{P}\psi(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2;...;\mathbf{r}_N,\sigma_N)=\psi(-\mathbf{r}_1,\sigma_1;-\mathbf{r}_2,\sigma_2;...;-\mathbf{r}_N,\sigma_N) \tag{98}$$

or formally

$$\langle \mathbf{r}_1,\sigma_1;...;\mathbf{r}_N,\sigma_N|\hat{P}|\psi\rangle=\langle -\mathbf{r}_1,\sigma_1;...;-\mathbf{r}_N,\sigma_N|\psi\rangle$$

Here σ's denote the particle spin variables (e.g. for spin 1/2 they are $\sigma=\pm 1/2$) and we used the axial vector nature of the spins.

Clearly

$$\hat{P}^2\equiv\hat{P}\hat{P}=1$$

which means that

$$\hat{P}=\hat{P}^{-1} \tag{99}$$

As usual with symmetries the invariance of the matter Hamiltonian under the parity transformation means that to transform the result of $\hat{H}$ acting on any $|\psi\rangle$ will produce the same result as of $\hat{H}$ acting on the transformed $|\psi\rangle$

$$\hat{P}\left(\hat{H}_{matter}|\psi\rangle\right)=\hat{H}_{matter}\hat{P}|\psi\rangle \tag{100}$$

Formally this means

$$\hat{P}\hat{H}_{matter}=\hat{H}_{matter}\hat{P}\quad\rightarrow\quad[\hat{H}_{matter}\ ,\ \hat{P}]=0 \tag{101}$$

or using (99)

$$\hat{P}\hat{H}_{matter}\hat{P}=\hat{H}_{matter}$$

Eigenstates of such Hamiltonian are or can be chosen to be eigenstates of $\hat{P}$. Indeed, acting with $\hat{P}$

$$\hat{H}_{matter}|n\rangle=E_n|n\rangle\ \ \rightarrow\ \ \hat{P}\hat{H}_{matter}|n\rangle=E_n\hat{P}|n\rangle\ \ \rightarrow\ \ \hat{H}_{matter}\hat{P}|n\rangle=E_n\hat{P}|n\rangle$$

we see that if $|n\rangle$ is an eigenstate of $\hat{H}_{matter}$ so is $\hat{P}|n\rangle$ with the same eigenenergy E_n. This implies one of the two possibilities - either $\hat{P}|n\rangle$ is proportional to $|n\rangle$

$$\hat{P}|n\rangle=\text{const}|n\rangle$$

or it is a different state. In the former case we find

$$\hat{P}^2|n\rangle=\text{const}\hat{P}|n\rangle=\text{const}^2|n\rangle$$

and since $\hat{P}^2 = 1$ have $\text{const}^2 = 1 \quad \rightarrow \quad \text{const} = \pm 1$.

When $\hat{P}|n\rangle$ is a different state from $|n\rangle$ we have degeneracy and can form linear combinations of these states

$$|n\rangle_\pm \equiv \frac{1}{2}(1 \pm \hat{P})|n\rangle$$

which are eigenstates of $\hat{P}$

$$\hat{P}|n\rangle_\pm = \hat{P}\frac{1}{2}(1 \pm \hat{P})|n\rangle = \frac{1}{2}(\hat{P} \pm \hat{P}^2)|n\rangle = \pm\frac{1}{2}(1 \pm \hat{P})|n\rangle = \pm|n\rangle_\pm \tag{102}$$

exactly as in the non degenerate case.

2.5.6 Parity selection rule - general view

We now want to learn what limitations the parity symmetry imposes on the dipole matrix elements in the expression (74). Following the discussion in the previous section we can assume that the states $|0|\rangle$ and $|n\rangle$ have well defined parity which we denote respectively by P_f and P_i. Then using

$$\hat{P}^2 = 1 \quad \text{and} \quad \hat{P}\hat{\mathbf{d}}|n\rangle = -\hat{\mathbf{d}}\hat{P}|n\rangle$$

we can write

$$\langle 0|\hat{\mathbf{d}}|n\rangle = \langle 0|\hat{P}^2\hat{\mathbf{d}}|n\rangle = \left(\langle 0|\hat{P}\right)\left(\hat{P}\hat{\mathbf{d}}|n\rangle\right) = -(-1)^{P_f}(-1)^{P_i}\langle 0|\hat{\mathbf{d}}|n\rangle \tag{103}$$

This means that must have

$$(-1)^{P_f}(-1)^{P_i} = -1 \tag{104}$$

in order to have non zero dipole matrix element $\langle 0|\hat{\mathbf{d}}|n\rangle$.

The above relation for the parities of the initial and final states of the transition is called *dipole parity selection rule*. Together with the dipole angular momentum selection rule they impose fairly stringent limitations on the allowed pairs of matter states which can be "connected" by non zero radiative dipole transitions.

To conclude this section we note that formal manipulations in (103) actually take a very simple form if we write explicitly the dipole matrix elements as integrals

$$\langle 0|\hat{\mathbf{d}}|n\rangle = \sum_{\sigma_1,...,\sigma_N} \int \psi_0^*(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_n\sigma_n) \left[\sum_{a=1}^{N} q_a \mathbf{r}_a\right] \psi_n(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_n\sigma_n)\, d^3r_1....d^3r_n$$

where σ's denote the spin variables. Changing the integration variables $\mathbf{r}_a = -\mathbf{r}'_a$ and using

$$\psi_n(-\mathbf{r}'_1\sigma_1, ..., -\mathbf{r}'_n\sigma_n) = (-1)^{P_n}\psi_n(\mathbf{r}'_1\sigma_1, ..., \mathbf{r}'_n\sigma_n)$$

reproduces the formal arguments of Eq. (103).

In the following sections the above discussion will help to derive the parity selection rules for higher terms in the long wavelength expansion Eq. (70).

2.6 "Forbidden" (higher multipole) transitions

When the dipole matrix element between a pair of states $|n_i\rangle$ and $|n_f\rangle$ vanishes because of the selection rules the radiative transitions between such states are traditionally called *forbidden*. But of course there is a possibility that the transitions still occur via higher order terms in the long-wavelength expansion (70) of $\langle 0|\hat{\mathbf{j}}_{\mathbf{k}} \cdot \boldsymbol{\lambda}_{\mathbf{k}\alpha}|n\rangle$.

In this section we examine the next order term after the dipole in this expansion. This term is

$$-i\langle 0| \int d^3r\, (\mathbf{k}\cdot\mathbf{r})(\hat{\mathbf{j}}(\mathbf{r}) \cdot \boldsymbol{\lambda}_{\mathbf{k}\alpha})|n\rangle \tag{105}$$

It is useful to transform the integrand (omitting the subscript of $\boldsymbol{\lambda}$ and using the summation convention)

$$(\mathbf{k}\cdot\mathbf{r})(\hat{\mathbf{j}}\cdot\boldsymbol{\lambda}) = k_l r_l\, \hat{j}_s\lambda_s = \frac{1}{2}k_l\lambda_s[(r_l\hat{j}_s + r_s\hat{j}_l) + (r_l\hat{j}_s - r_s\hat{j}_l)] \tag{106}$$

We shall consider the two parts of this expression separately.

2.6.1 Electric quadrupole transitions

We start by considering the symmetric term in (106). This term contributes

$$-\frac{i}{2}k_l\lambda_s \int d^3r \langle 0|r_l\hat{j}_s(\mathbf{r}) + r_s\hat{j}_l(\mathbf{r})|n\rangle \tag{107}$$

in the transition matrix element (105). We will transform this expression using the continuity equation for the operators $\hat{\rho}$ and $\hat{\mathbf{j}}$

$$\frac{\partial\hat{\rho}(\mathbf{r},t)}{\partial t} = -\nabla\cdot\hat{\mathbf{j}}(\mathbf{r},t) \equiv -\frac{\partial\hat{j}_m}{\partial r_m} \quad \text{(with summation over repeated indices)}$$

Let us consider

$$\int d^3r\, r_s r_l \frac{\partial\hat{\rho}}{\partial t} = -\int d^3r\, r_s r_l \frac{\partial\hat{j}_m}{\partial r_m} = -\int d^3r[\delta_{ms}r_l + r_s\delta_{ml}]j_m = \int d^3r[r_l j_s + r_s j_l]$$

where we used the continuity equation followed by integration by parts. This resulting relation allows to express the matrix element of the symmetric term (107) as

$$-\frac{i}{2}k_l\lambda_s\int d^3r\, r_s r_l\langle 0|\frac{\partial\hat{\rho}}{\partial t}|n\rangle$$

Using the Heisenberg equation for $\hat{\rho}$ we can write

$$\langle 0|\frac{\partial\hat{\rho}}{\partial t}|n\rangle=\frac{1}{i\hbar}\langle 0|[\rho,H_{matter}]|n\rangle=\frac{E_n-E_0}{i\hbar}\langle 0|\rho|n\rangle=-i\omega\langle 0|\rho|n\rangle$$

With this the symmetric term becomes

$$-\frac{\omega}{2}k_l\lambda_s\int d^3r\, r_l r_s\langle 0|\hat{\rho}|n\rangle \tag{108}$$

Using $\mathbf{k}\cdot\boldsymbol{\lambda}\equiv k_l\lambda_l=0$ this can be written

$$-\frac{\omega}{2}k_l\lambda_s\int d^3r\,(r_l r_s-\frac{1}{3}\delta_{ls}r^2)\langle 0|\hat{\rho}|n\rangle=-\frac{\omega}{6}k_l\lambda_s\langle 0|\hat{Q}_{ls}|n\rangle \tag{109}$$

where $\hat{Q}_{ls}$ are components of the operator of the electric quadrupole tensor of the radiation emitting matter

$$\hat{Q}_{ls}=\int d^3r\,(3r_l r_s-\delta_{ls}r^2)\hat{\rho}(\mathbf{r})=\sum_{a=1}^{N}q_a(3r_{a,l}r_{a,s}-\delta_{ls}r_a^2) \tag{110}$$

The emitted photon parameters enter via the factor $(\omega/6)k_l\lambda_s$ in Eq.(109) while the matter is represented by the electric quadrupole moment operator. Radiative transitions arising through this term are called *electric quadrupole transitions*.

2.6.2 Electric quadrupole moment is an $\ell=2$ object. Selection rules

Electric quadrupole moment is a symmetric traceless tensor. This means that it has 5 independent components which transform between themselves under rotations. This is similar to the 5 components of the second order spherical harmonic $Y_{2\mu}$ or in a more formal language to the 5 components of the $\ell=2$ representation (multiplet) of the group of rotations.

To see the relation it is useful to step back to Eq. (108), write the product $r_l r_s$ in spherical components

$$r_m r_{m'}=\frac{4\pi}{3}r^2Y_{1,m}(\Omega)Y_{1,m'}(\Omega)\ \text{ with }\ m,m'=-1,0,1$$

and use the relations Eqs. (84,85) for $l_1 = l_2 = 1$

$$Y_{1,m}(\Omega)Y_{1,m'}(\Omega) = \sum_{l=0,1,2} a(1,1,l)\langle l\mu|1,m;1,m'\rangle Y_{l\mu}(\Omega) \ \ , \ \ \mu = m + m'$$

where in this case

$$a(1,1,l) = \frac{3}{\sqrt{4\pi(2l+1)}}\langle l0|1,0;1,0\rangle$$

Here the allowed values of $l = 0, 1, 2$ in the sum correspond to adding two units of angular momenta and are formally dictated by the CG coefficients. The $l = 1$ term in the sum vanishes since $\langle 10|1,0;1,0\rangle = 0$ reflecting the vanishing of the antisymmetric (vector) product of two identical vectors Y_{1m}, cf, Ref. [5]. In the $l = 0$ term (the scalar product) has $\mu = 0$ and therefore $m = -m'$. Formally this is reflected in the corresponding CG coefficient $\langle 00|1,0;1,0\rangle \sim \delta_{m,-m'}$. Since Eq. (108) written in spherical components is

$$\sum_{m,m'=-1,0,1} k^*_m \lambda^*_{m'}\, r_m r_{m'}$$

the $m = -m'$ term vanishes (as with such terms earlier) due to orthogonality $\mathbf{k}\cdot\boldsymbol{\lambda} = 0$.

We are thus left with only $l = 2$ term which shows that in spherical components the cartesian tensor of the quadrupole moment becomes (a linear combination of) the five components of the spherical representation of this tensor[12]

$$\hat{Q}_{2\mu} = \sqrt{\frac{4\pi}{5}} \int r^2 Y_{2\mu}(\theta,\phi)\hat{\rho}(\mathbf{r})\, d^3r = \sqrt{\frac{4\pi}{5}} \sum_{a=1}^{N} q_a r_a^2 Y_{2\mu}(\theta_a,\phi_a) \tag{111}$$

Summarizing the above and using $\langle 20|1,0;1,0\rangle = \sqrt{2/3}$ we have for Eq. (108)

$$\begin{aligned} -\frac{\omega}{2} k_l \lambda_s \int d^3r\, r_l r_s \langle 0|\hat{\rho}|n\rangle = \\ = -\frac{\omega}{\sqrt{6}} \sum_{\mu} \Phi_\mu(\Omega_k, \boldsymbol{\lambda}) \langle 0|\hat{Q}_{2\mu}|n\rangle \end{aligned} \tag{112}$$

where we denoted

$$\begin{aligned} \Phi_\mu(\Omega_k, \boldsymbol{\lambda}) = \sum_{m,m'=-1,0,1} \langle 2\mu|1,m;1,m'\rangle k^*_m \lambda^*_{m'} = \\ = \sqrt{\frac{4\pi}{3}} \sum_{m,m'=-1,0,1} \langle 2\mu|1,m;1,m'\rangle\, k\, Y^*_{1\mu}(\Omega_k) \lambda^*_{m'} \end{aligned} \tag{113}$$

[12] Explicit expressions relating the spherical components $Q_{2\mu}$ to the cartesian Q_{ls}, Eq. (110) are $Q_{20} = -(1/2)Q_{zz}$, $Q_{2,\pm1} = \pm(1/\sqrt{6})(Q_{xz} \pm iQ_{yz})$, $Q_{2,\pm2} = -(1/2\sqrt{6})(Q_{xx} - Q_{yy} + 2iQ_{xy})$

The above expression is useful for finding the selection rules for electric quadrupole transitions in physical systems with eigenstates having definite angular momentum values

$$\langle 0|\hat{Q}_{2\mu}|n\rangle \to \langle \nu' J' M'|\hat{Q}_{2\mu}|\nu J M\rangle \tag{114}$$

Using the Wigner-Eckart theorem, Eq. (96), for the operator of the electric quadrupole moment one has

$$\langle \nu' J' M'|\hat{Q}_{2\mu}|\nu J M\rangle = \langle J' M'|2\mu, JM\rangle\langle \nu' J'||\hat{Q}_2||\nu J\rangle$$

which shows that the angular momentum selection rules for transitions with this operator, i.e. for electric quadrupole transitions are

$$J' = |J-2|, ..., J+2 \quad , \quad M' = M + \mu \tag{115}$$

Applying the parity transformation $\mathbf{r}_a \to -\mathbf{r}_a$, $a = 1, ..., N$ to $\hat{Q}_{ml}$, Eq. (110) we see that it does not change. Thus the parity selection rule for electric quadrupole transitions is

$$P_f = P_i \tag{116}$$

This rule which is "opposite" to the dipole selection rule, Eq.(104), is the main reason why the electric quadrupole and magnetic dipole transitions explained below are the leading mechanisms for the transition, which are forbidden by the dipole selection rules. Since related to higher order terms in the long wavelength expansion, Eq. (70) such transitions have order of magnitude smaller transition rates in the small ka parameter than the allowed dipole transitions.

This is of course for the levels which satisfy the angular momentum selection rules, Eq. (115). Transitions between levels with larger angular momentum differences are controlled by higher terms in the LWA expansion, which are correspondingly weaker, cf., our discussion below and Ref. [3]. In this respect an interesting situation arises when a matter system has a low lying high angular momentum state. If all the levels below such state have low angular momenta this state will have a long radiative lifetime. Such states are called isomeric and are metastable if probabilities of non radiative transitions (e.g. via collisions in gases or phonon emission in solids) are small too.

2.6.3 Angular distribution of electric quadrupole radiation

Let us now briefly discuss the angular distribution of photons emitted in electric quadrupole transitions in the very common case when the relation (114) is valid.

Since in this case μ is fixed, $\mu = M' - M$ only one term will remain in the sum in Eq. (112). The angular distribution is obviously given by the corresponding function $\Phi_\mu(\Omega_k, \boldsymbol{\lambda})$ with the dependence on the angles of the polarization vectors as given e.g. by the relations Eq. (63). The spherical components of the latter are

$$(\boldsymbol{\lambda}_1)_{\mu=\pm1} = \mp\frac{\cos\theta e^{\pm i\phi}}{\sqrt{2}} \quad , \quad (\boldsymbol{\lambda}_1)_{\mu=0} = -\sin\theta$$
$$(\boldsymbol{\lambda}_2)_{\mu=\pm1} = -\frac{ie^{\pm i\phi}}{\sqrt{2}} \quad , \quad (\boldsymbol{\lambda}_2)_{\mu=0} = 0$$

As an example let us consider transitions with $M = M'$, $\mu = 0$. Using

$$\langle 2, \mu = 0 | 1, m; 1, -m\rangle = (-1)^{1-m}\frac{3m^2 - 1}{\sqrt{6}}$$

one finds that the sum in Eq. (113) is $-3\sin\theta\cos\theta$ for the $\boldsymbol{\lambda}_1$ photon polarization while it vanishes for $\boldsymbol{\lambda}_2$. Accordingly the corresponding angular distributions in electric quadrupole transitions are

$$\frac{dN_{\mathbf{k}1}}{d\gamma} \sim \sin^2\theta\cos^2\theta \quad , \quad \frac{dN_{\mathbf{k}2}}{d\gamma} = 0 \tag{117}$$

cf., Fig. 6.

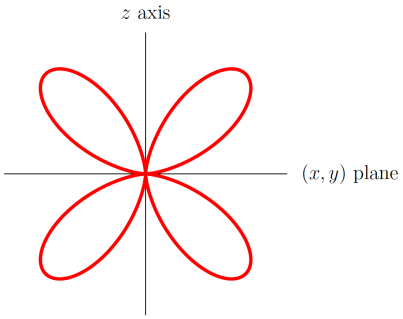

Figure 6: Angular distribution of electric quadrupole radiation with $\boldsymbol{\lambda}_1$ polarization, cf., Eq.(117) plotted in a similar way as in Fig. 3. Note that the independence of the azimuthal angle ϕ means that the 3D version of this figure is obtained by rotating it around the z-axis.

2.6.4 Magnetic dipole transitions

The antisymmetric part of (106) is conveniently expressed via vector products

$$\frac{1}{2}k_l\lambda_m(r_l\hat{j}_m - r_m\hat{j}_l) = \frac{1}{2}k_l\lambda_m\epsilon_{lmn}(\mathbf{r}\times\hat{\mathbf{j}})_n = \frac{1}{2}(\mathbf{k}\times\boldsymbol{\lambda})\cdot(\mathbf{r}\times\hat{\mathbf{j}}) \tag{118}$$

which will contribute in Eq. (105) as

$$-i(\mathbf{k}\times\boldsymbol{\lambda}_{\mathbf{k}\alpha})\cdot\langle 0|\frac{1}{2}\int d^3r(\mathbf{r}\times\hat{\mathbf{j}}(\mathbf{r}))|n\rangle \tag{119}$$

The emitted photon parameters enter via the factor $(\mathbf{k}\times\boldsymbol{\lambda}_{\mathbf{k}\alpha})$ while the matter is represented by the magnetic dipole moment of the current generated by the orbital motion of the matter constituents,

$$\frac{1}{2}\int d^3r(\mathbf{r}\times\hat{\mathbf{j}}(\mathbf{r})) = \frac{1}{2}\sum_{a=1}^{N}\frac{q_a}{2m_a}[-\hat{\mathbf{p}}_a\times\mathbf{r}_a + \mathbf{r}_a\times\hat{\mathbf{p}}_a] = \sum_{a=1}^{N}\frac{q_a}{2m_a}(\mathbf{r}_a\times\hat{\mathbf{p}}_a).$$

At this stage it is important to recall the interaction term H_{I3}, Eq. (23) which we have not treated so far. This term also depends on the magnetic moments of the matter constituents. However not the ones generated by the orbital motion but rather by their intrinsic motion, i.e. their spins.

The contribution of $\hat{H}_{I3}$ to the transition matrix element is straightforward to derive just following the same steps which led us to the expression (58) for $\langle f|\hat{H}_{I1}|i\rangle$ with the result

$$\langle f|\hat{H}_{I3}|i\rangle = -i\left(\frac{\hbar}{2\epsilon_0\omega_k\Omega}\right)^{1/2}(\mathbf{k}\times\boldsymbol{\lambda}_{\mathbf{k}\alpha})\cdot\langle 0|\hat{\mathbf{m}}_{-\mathbf{k}}|n\rangle \tag{120}$$

where

$$\hat{\mathbf{m}}_{\mathbf{k}} = \int\hat{\mathbf{m}}(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}\,d^3r = \sum_{a=1}^{N}\hat{\boldsymbol{\mu}}_a e^{-i\mathbf{k}\cdot\mathbf{r}_a}$$

In the long wavelength limit

$$\langle 0|\hat{\mathbf{m}}_{-\mathbf{k}}|n\rangle \approx \langle 0|\hat{\mathbf{m}}_0|n\rangle = \langle 0|\int d^3\mathbf{r}\,\hat{\mathbf{m}}(\mathbf{r})\,|n\rangle = \langle 0|\sum_{a=1}^{N}\hat{\boldsymbol{\mu}}_a|n\rangle$$

Taking this term into account the expression (119) becomes

$$-i(\mathbf{k}\times\boldsymbol{\lambda}_{\mathbf{k}\alpha})\cdot\langle 0|\hat{\mathbf{M}}|n\rangle \ \ , \tag{121}$$

with

$$\hat{\mathbf{M}}=\int d^3r\left[\frac{1}{2}\left(\mathbf{r}\times\hat{\mathbf{j}}(\mathbf{r})\right)+\hat{\mathbf{m}}(\mathbf{r})\right]=\sum_{a=1}^{N}\left[\frac{q_a}{2m_a}(\mathbf{r}_a\times\hat{\mathbf{p}}_a)+\hat{\boldsymbol{\mu}}_a\right]$$

Radiative transitions arising through this term are called *magnetic dipole transitions*.

Electrons in atoms have equal charge to mass ratio e/m so the orbital part of this expression reduces to

$$\frac{e}{2m}\sum_{a=1}^{N}(\mathbf{r}_a\times\hat{\mathbf{p}}_a)=\frac{e}{2m}\hat{\mathbf{L}} \tag{122}$$

while the spin part

$$\sum_{a=1}^{N}\hat{\boldsymbol{\mu}}_a=g\frac{e}{2m}\sum_{a=1}^{N}\hat{\mathbf{s}}_a=g\frac{e}{2m}\hat{\mathbf{S}} \tag{123}$$

where $\mathbf{L}$ and $\mathbf{S}$ are respectively the total orbital angular momentum and the spin of the emitting matter system. In the spin part expression, Eq. (123) we used the gyromagnetic ratio $g(e/2m)$ to relate intrinsic magnetic moments to the spins. The part $e/2m$ denotes the classical value while g - known as the g-factor - is the dimensionless quantity to account for deviations from the classical $g=1$ value. Dirac relativistic equation for spin 1/2 particles predicts the value $g=2$ while field theoretical corrections change it slightly to $g=2(1+\alpha/2\pi+\cdots)\simeq 2.002319...$ where $\alpha=1/137$.

The expression (121) for electrons is therefore

$$-\frac{ie}{2m}(\mathbf{k}\times\boldsymbol{\lambda}_{\mathbf{k}\alpha})\cdot\langle 0|\hat{\mathbf{L}}+g\hat{\mathbf{S}}|n\rangle \tag{124}$$

i.e. it is proportional to the matrix element of the combination $\hat{\mathbf{L}}+g\hat{\mathbf{S}}\approx\hat{\mathbf{L}}+2\hat{\mathbf{S}}$ of the electronic angular momentum and spin.

2.6.5 Selection rules and angular distribution of magnetic dipole transitions

Let us now focus as in the electric dipole and quadrupole transitions on emitting systems with eigenstates having defined angular momentum values

$$\langle 0|\hat{\mathbf{M}}|n\rangle\to\langle\nu',J',M'|\hat{M}_\mu|\nu,J,M\rangle \ \ , \ \ \mu=-1,0,1 \tag{125}$$

where we also introduced the spherical components of the vector $\hat{\mathbf{M}}$. The angular momentum selection rules are obviously

$$J' = |J-1|, ..., J+1 \quad , \quad M' = M + \mu \tag{126}$$

as in the electric dipole case.

However the parity selection rule is different. Indeed the magnetic dipole is a pseudo vector as it does not change under the parity transformation $\mathbf{r} \to -\mathbf{r}$, $\mathbf{p} \to -\mathbf{p}$. Therefore the parity will not change in the transitions i.e. the *magnetic dipole* parity selection rule is

$$P_f = P_i$$

Let us also note the following. One can rewrite the operator $\hat{\mathbf{L}} + g\hat{\mathbf{S}}$ in Eq. (124) as $\hat{\mathbf{L}} + \hat{\mathbf{S}} + (g-1)\hat{\mathbf{S}} = \hat{\mathbf{J}} + (g-1)\hat{\mathbf{S}}$ where $\hat{\mathbf{J}}$ is the total angular momentum. In emitting systems with eigenstates as in Eq. (125) the operator $\hat{\mathbf{J}}$ can not cause transitions so that the magnetic dipole emission must go via "spin-flips", i.e. (in conventional language) via the change of the spin projection S_z. That in turn means that spin must not be a conserved quantity in the eigenstates of Eq. (125). Which implies that there must be a spin-orbit interaction in the matter Hamiltonian of the emitting system. Thus magnetic dipole emission is the measure of such an interaction.

Finally let us address the angular distribution of photons emitted in magnetic dipole transitions. This is determined by the angular dependence of the components of the vector $(\mathbf{k} \times \boldsymbol{\lambda}_{\mathbf{k}\alpha})$ in Eq. (121) which are weighted by the vector of the matrix elements $\langle 0|\hat{\mathbf{M}}|n\rangle$. Noting that our favorite choice Eq. (63) of polarizations form right handed system of unit vectors with the direction of $\mathbf{k}$ we deduce that the vectors $(\mathbf{k} \times \boldsymbol{\lambda}_{\mathbf{k}\alpha})$ with $\alpha = 1$ and $\alpha = 2$ are respectively proportional to $\boldsymbol{\lambda}_{\mathbf{k}2}$ and $\boldsymbol{\lambda}_{\mathbf{k}1}$. Therefore the angular distribution of the expression (121) is identical to the electric dipole one with $\langle 0|\hat{\mathbf{d}}|n\rangle$ replaced by $\langle 0|\hat{\mathbf{M}}|n\rangle$ and appropriate adjustment of the polarization vectors.

2.6.6 General multipole expansion

What we have seen so far in our discussions of the electric dipole and quadrupole and magnetic dipole emissions is essentially a transformation of the terms in the Taylor expansion (70) to the expansion in terms of "angular" multipoles. The reason the latter is more appropriate is that the small parameter of the long wavelength expansion $ka \ll 1$ concerns the "radial size" a of the system, $|\mathbf{r}| \leq a$ with obviously no limitation on the angles. Perhaps the simplest familiar example of this is a "move"

from the Taylor expansion of the Coulomb potential

$$\phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\int_{r'\le a}\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r'$$

'"outside" of a charge distribution, $r > a$ to the multiple expansion

$$\begin{aligned}\text{Taylor expansion} - \ \phi(\mathbf{r}) &= \frac{1}{4\pi\epsilon_0 r}\int \rho(\mathbf{r}')(1+\mathbf{r}\cdot\mathbf{r}'/r^2+...)d^3r' \ . \\ \text{Multipole expansion} - \ \phi(\mathbf{r}) &= \frac{1}{4\pi\epsilon_0}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{M^E_{lm}}{R^{l+1}}\,Y_{lm}(\Omega_r)\end{aligned} \tag{127}$$

with

$$M^E_{lm} = \frac{4\pi}{2l+1}\int r^l\rho(\mathbf{r})Y^*_{lm}(\Omega_r)d^3r \quad - \quad \text{multipole electric moments}$$

In deriving the latter expression one uses the known expansion of $1/|\mathbf{r}-\mathbf{r}'|$ into a sum of products $Y_{lm}(\Omega_r)Y^*_{lm}(\Omega_{r'})$ which allows to factorize the outside $r > a$ and the inside $r' \le a$ regions. The result is the Coulomb potential represented as a sum of multipole potentials which the electric multipole moments M^E_{lm} generate.

Returning to our problem we want to find a similar multipole expansion for the expressions Eqs. (58) and (120). Let's concentrate on the former and consider

$$\hat{\mathbf{j}}_{\mathbf{k}}\cdot\boldsymbol{\lambda} = \int d^3r\ \hat{\mathbf{j}}(\mathbf{r})\cdot\boldsymbol{\lambda}\ e^{-i\mathbf{k}\cdot\mathbf{r}} \tag{128}$$

Rather than expanding $\exp(-i\mathbf{k}\cdot\mathbf{r})$ in Taylor series as we have done in Eq. (70) we shall use

$$\exp(-i\mathbf{k}\cdot\mathbf{r}) = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-i)^l g_l(kr)Y_{lm}(\Omega_k)Y^*_{lm}(\Omega_r)$$

where the spherical Bessel functions are $g_l(kr) = \sqrt{\pi/2kr}J_{l+1/2}(kr)$. With this expansion of the exponent

$$\hat{\mathbf{j}}_{\mathbf{k}}\cdot\boldsymbol{\lambda} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{q=-1}^{1}(-i)^l Y_{lm}(\Omega_k)\lambda_q\int d^3r\ g_l(kr)\hat{j}^*_q(\mathbf{r})Y^*_{lm}(\Omega_r) \tag{129}$$

where we used the spherical components of the vectors $\boldsymbol{\lambda}$ and $\hat{\mathbf{j}}$.

The resulting expression (129) for $\hat{\mathbf{j}}_{\mathbf{k}}\cdot\boldsymbol{\lambda}$ has similar features with the multiple expansion Eq. (127) of the Coulomb potential. It is a sum of terms each factorized

in the product of components depending on the photon variables $\mathbf{k}$ and $\boldsymbol{\lambda}$ and the matter variables $\mathbf{j}(\mathbf{r})$. One still has the matter component depending on k via $g_l(kr)$ but this will decouple in the long wavelength approximation (LWA) $kr \ll 1$ for which $g_l(kr) \sim k^l r^l$ when the matrix element $\langle 0|\hat{\mathbf{j}}_{\mathbf{k}}|n\rangle \cdot \boldsymbol{\lambda}$ is considered.

The remaining problem in the expansion Eq. (129) is that photon and matter components in each term do not have definite multipolarities. This is most obvious in the photon related parts which transform under rotations as a product of $Y_{lm}(\Omega_k)$ and λ_q, i.e. as a sum of representations $l-1, l$ and $l+1$. The technical reason for this is trivially obvious - the photon related $Y_{lm}(\Omega_k)$ is coupled to the matter related $Y^*_{lm}(\Omega_r)$ and λ_q to $\hat{j}^*_q(\mathbf{r})$. What one needs is to "recouple" the products into the photon and the matter groups. This can be done using the Clebsch-Gordan completeness relation, cf., Ref. [3], p. 338,

$$\sum_{LM} \langle lm, 1q|l1LM\rangle\langle l1LM|lm'1q'\rangle = \delta_{mm'}\delta_{qq'}$$

Inserting it into Eq. (129) one obtains

$$\hat{\mathbf{j}}_{\mathbf{k}} \cdot \boldsymbol{\lambda} = 4\pi \sum_{L,l,M} (-i)^l \Phi_{LM,l}(\Omega_k, \boldsymbol{\lambda}) \hat{\mathcal{M}}_{LM,l} \tag{130}$$

where with $g_l(kr) \approx (kr)^l/(2l+1)!!$ in the long wavelength limit have

$$\Phi_{LM,l}(\Omega_k, \boldsymbol{\lambda}) = \sum_{m,q} \langle lm, 1q|l1LM\rangle k^l Y_{lm}(\Omega_k)\lambda_q \quad , \quad l = L, L \pm 1 \; , \tag{131}$$

and

$$\hat{\mathcal{M}}_{LM,l} = \frac{1}{(2l+1)!!} \sum_{m',q'} \int d^3r \; r^l \langle l1LM|lm'1q'\rangle \hat{j}^*_{q'}(\mathbf{r}) Y^*_{lm'}(\Omega_r) \quad , \quad l = L, L \pm 1 \; , \tag{132}$$

The values of $l = L, L \pm 1$ in both expression correspond of course to the vector addition of a unit angular momentum of the vectors $\boldsymbol{\lambda}$ and $\mathbf{j}$ to the l of $Y_{lm}(\Omega_k)$ and $Y_{lm}(\Omega_r)$ respectively.

The general expansion (130) has the structure we were looking for. Both $\Phi_{LM,l}(\Omega_k, \boldsymbol{\lambda})$ and $\hat{\mathcal{M}}_{LM,l}$ transform as the M components of the L-th representation of rotations. While it is obvious for the photon components a bit more work is needed to show this for the integral representing $\hat{\mathcal{M}}_{LM,l}$. This is left as an exercise.

It is useful to consider a few simple cases.

Monopole emission

Starting with the $L = 0$ term it is easy to show that it vanishes. Indeed for $L = 0$ have $M = 0 \to m = -q$ and only $l = 1$ as a possible value. So $k^l Y_{lm}(\Omega_k) \to kY_{1m}(\Omega_k) \sim k_m$ and

$$\Phi_{00,1} \sim \sum_m (-1)^m k_m \lambda_{-m} = \mathbf{k} \cdot \boldsymbol{\lambda} = 0$$

So - no monopole photon emission. One can intuitively relate this to the fact that photons have spin 1 - one can't emit a photon without changing the emission system angular momentum by at least one unit.

Dipole emission

The terms with $L = 1$ have $l = 0$ and $l = 1$. For $l = 0$ have

$$\Phi_{1M,l=0} \sim \lambda_M \ , \ \hat{\mathcal{M}}_{1M,l=0} \sim \int d^3 r \hat{j}^*_M(\mathbf{r})$$

recovering the electric dipole case, cf. Eq.(73).

For the $l = 1$ value one has

$$\Phi_{1M,l=1} = k \sum_q \langle 1\ M-q, 1q|111M\rangle Y_{1m}(\Omega_k)\lambda_{M-q} \sim (\mathbf{k} \times \boldsymbol{\lambda})_M$$

$$\hat{\mathcal{M}}_{1M,l=1} = \frac{1}{3} \sum_q \int d^3 r\ r \langle 111M|1\ M-q 1q\rangle \hat{j}^*_q(\mathbf{r}) Y^*_{1M-q}(\Omega_r) \sim \int d^3 (\mathbf{r} \times \hat{\mathbf{j}}(\mathbf{r}))_M$$

i.e. the magnetic dipole emission.

Higher multipoles

Discussions of the higher values of L cf., Ref.[3], p.376, confirms this pattern - the $l = L$ terms correspond to magnetic multipoles while the $l = L \pm 1$ terms are electric radiation terms. So the sum over L in Eq.(130) is the sum over different multipoles of the matter "vibrations" (quantum mechanical transition matrix elements) causing the photon emission.

2.6.7 Angular distribution, selection rules of the general multipole terms

The expression (131) for $\Phi_{LM,l}(\Omega_k, \boldsymbol{\lambda})$ can be interpreted as the probability amplitude of the photon emitted by the l, L matter multipole into the solid angle Ω_k with polarization $\boldsymbol{\lambda}$. It reflects the expectation that the total angular momentum of a

photon is a sum of its orbital angular momentum (encoded in $Y_{1m}(\Omega_k)$) and its unit spin (associated with the polarization vector).

Angular momentum selection rules for the terms in the expansion Eq. (130) follow by applying the Wigner-Eckart theorem to matrix elements of the multipole moments operators between matter eigenstates with defined angular momentum values

$$\langle \nu', j', m' | \hat{\mathcal{M}}_{LM,l} | \nu, j, m \rangle = \langle j' m' | LM, jm \rangle \langle \nu', j' || \hat{\mathcal{M}}_{L,l} || \nu, j \rangle \tag{133}$$

From this we have the angular momentum selection rules

$$|L - j| \leq j' \leq L + j \quad , \quad m' = m + M \tag{134}$$

Perhaps not surprisingly they do not involve the l index which distinguishes between electric and magnetic multipoles. This index is important however in the parity selection rules. Perhaps the fastest way to see this is to observe that $\Phi_{LM,l}(\Omega_k, \boldsymbol{\lambda})$ changes under the parity $\mathbf{r} \to -\mathbf{r}$ transformation as $(-1)^{l+1}$ where l comes from the orbital $Y_{lm}(\Omega_k)$ while the extra minus from the polar vector of the polarization. So

$$(-1)^{P_f} = (-1)^{l+1} (-1)^{P_i}$$

As a final remark we note that the above arguments based on the parity properties of the photons amplitudes could be made more formal and rigorous by examining how the matrix elements Eq. (133) behave under the parity transformation, cf., Ref. [3], p. 379.

2.7 Induced photon emission

In our discussion above of the photon emission by an excited state of quantum matter (atom, solid, nucleus, molecule) we have assumed that prior to the emission (i.e. in the initial state) there were no photons present in the radiation mode $\mathbf{k}\alpha$ into which the matter system emits the photon, cf. Eq. (56). Such an emission is called *spontaneous*.

Let us now consider what happens if the initial state already contained N photons before the emission, i.e. have

$$|i\rangle = |n\rangle | N_{\mathbf{k}\alpha}, \{0_{\mathbf{k}'\alpha'}\} \rangle \quad |f\rangle = |0\rangle | (N_{\mathbf{k}\alpha} + 1, \{0_{\mathbf{k}'\alpha'}\} \rangle$$

With this change the calculation of the field matrix element in Eq. (57) becomes

$$\langle N_{\mathbf{k}\alpha} + 1, \{0_{\mathbf{k}'\alpha'}\} | \hat{a}_{\mathbf{k}''\alpha''} + \hat{a}^\dagger_{-\mathbf{k}''\alpha''} | N_{\mathbf{k}\alpha}, \{0_{\mathbf{k}\alpha}\} \rangle = \delta_{-\mathbf{k}'',\mathbf{k}} \delta_{\alpha''\alpha} \sqrt{N_{\mathbf{k}\alpha} + 1}$$

because of the basic matrix element of the harmonic oscillator creation operator

$$\langle N+1|\hat{a}^\dagger|N\rangle = \sqrt{N+1}$$

This produces the following result in the absolute values square of the interaction

$$|\langle f|\hat{H}_{I1}|i\rangle|^2 = \left(\frac{\hbar}{2\epsilon_0\omega_k\Omega}\right)|\langle 0|\hat{\mathbf{j}}_{\mathbf{k}}\cdot\boldsymbol{\lambda}_{\mathbf{k}\alpha}|n\rangle|^2\,(N_{\mathbf{k}\alpha}+1) \tag{135}$$

which means that the emission rate $\Gamma_{n\to 0,\mathbf{k}\alpha}$ is $N_{\mathbf{k}\alpha}+1$ times larger than in the spontaneous emission case. So just the initial presence of $N_{\mathbf{k}\alpha}$ photons in the radiation modes into which the emission occurs leads to this increase of the emission rate. This effect is called *induced or stimulated emission*. It is often interpreted as a quantum mechanical effect of "bosons like to stick together", i.e. to be in the same state and is the key to the idea of lasers.

Very schematically this idea can be outlined as following. Assume a large number of identical "emitters" (e.g. atoms, molecules, etc) which can be "continuously" excited to a certain energy level and then de-excite to low lying levels via photon emission. As we learned earlier the angular distribution and polarization of the emitted photons will depend on the angular momentum projections M and M' of the initial and final states but if only the initial energy is specified the M values will be random and so will be the emitted photons directions and polarizations. This is as long as only the spontaneous emission is considered.

If some particular photon modes $\mathbf{k}\alpha$ contain a (large) number of (pre emitted) photons then high probability ($\sim N_{\mathbf{k}\alpha}$) induced emission, i.e. "lasing" will occur into these particular modes. Schematically the needed accumulation of photons in controlled modes is achieved e.g. by placing the emitters in a resonator. This selects resonating modes in which photons "bounce back and forth" before escaping.

All this is very sketchy of course. More detailed explanations are found in appropriate quantum optics literature.

Let us note that historically it is common to write the expression for the emission rate as a sum of the term containing the $N_{\mathbf{k}\alpha}$ and the term containing 1 from the sum $N_{\mathbf{k}\alpha}+1$

$$\Gamma = \Gamma^{\text{induced}} + \Gamma^{\text{spontaneous}}$$

This the expression for the spontaneous photon emission rate (60) is changed to

$$\frac{dN_{\mathbf{k}\alpha}}{d\gamma} = \left(\frac{dN_{\mathbf{k}\alpha}}{d\gamma}\right)^{\text{induced}} + \left(\frac{dN_{\mathbf{k}\alpha}}{d\gamma}\right)^{\text{sponteneous}} \tag{136}$$

with

$$\left(\frac{dN_{\mathbf{k}\alpha}}{d\gamma}\right)^{\text{induced}} = N_{\mathbf{k}\alpha}\left(\frac{dN_{\mathbf{k}\alpha}}{d\gamma}\right)^{\text{sponteneous}} \tag{137}$$

2.8 Photon absorption

Consider now the process of the photon absorption. We have

$$|i\rangle = |0\rangle|N_{\mathbf{k}\alpha}, ...\rangle \quad , \quad |f\rangle = |n\rangle|N_{\mathbf{k}\alpha} - 1, ...\rangle \tag{138}$$

The matrix element of $\hat{H}_{I1}$ between these states gives

$$|\langle f|\hat{H}_{I1}|i\rangle|^2 = \left(\frac{\hbar}{2\epsilon_0\omega_k\Omega}\right)|\langle n|\hat{\mathbf{j}}_{-\mathbf{k}}\cdot\boldsymbol{\lambda}_{\mathbf{k}\alpha}|0\rangle|^2 N_{\mathbf{k}\alpha} \tag{139}$$

Since

$$\langle n|\hat{\mathbf{j}}_{-\mathbf{k}}\cdot\boldsymbol{\lambda}_{\mathbf{k}\alpha}|0\rangle = \langle 0|\hat{\mathbf{j}}_{\mathbf{k}}\cdot\boldsymbol{\lambda}_{\mathbf{k}\alpha}|n\rangle^*$$

we find equality relation

$$\Gamma_{0\to n}^{\text{absorption}} = \Gamma_{n\to 0}^{\text{induced emission}} \tag{140}$$

for absorption and induced emission rates of photons with the same $\mathbf{k}$ and $\boldsymbol{\lambda}$. This relation is crucial for laser physics. Indeed it shows that having $N_{\mathbf{k}\alpha}$ incident photons (per unit time) of energy $\hbar\omega_k$ a photon has an equal probability of being absorbed by a ground-state atom or being duplicated (amplified!) via an induced emission by an excited-state atom. To favor emission over absorption, there need to be more excited-state atoms than ground-state atoms. This of course doesn't happen in thermally equilibrated systems. A non equilibrium situation must be created by adding energy via a process known as "pumping" in order to raise enough atoms to the upper level. The result called "population inversion" leads to light amplification. Pumping may be electrical, optical or chemical.

3 Appendix

3.1 Discrete level coupled to continuum

Here we present details of a simple non perturbative approach to deal with the Weisskopf-Wigner model as defined in Section (2.1.2). A more general treatment of this problem is reviewed in e.g. Ref.[2].

3.1.1 Neglecting coupling between continuum levels

As was described following Eq. (37) the crucial step/approximation in the Weisskopf-Wigner approach is to neglect the coupling between the continuum levels, i.e. to set $V_{\mu\nu} = 0$. This means that the Hamiltonian matrix in the basis $\{\psi_0, \psi_\nu\}$ has the "bordered" form

$$H = \begin{pmatrix} E_0 & V_{01} & ... & V_{0\nu} & ... \\ V_{10} & E_1 & ... & 0 & .... \\ ... & ... & ... & ... & ... \\ V_{\nu 0} & 0 & ... & E_\nu & ... \\ ... & ... & ... & ... & ... \end{pmatrix}$$

Here we tacitly assumed discrete values of the ν index. Such matrices are easy to diagonalize especially when simplifying assumptions about E_ν's and $V_{0\nu}$ are made. This is described in e.g. Ref. [1].

3.1.2 Markov approximation

Examining the integral expression Eq. (46) for the kernel $K(t)$ which for convenience we rewrite here

$$K(t) = -\frac{1}{\hbar^2}\int d\mathcal{E}\overline{|V_{0\mu}|^2}\big|_{\mathcal{E}_\mu=\mathcal{E}} e^{i(\mathcal{E}_0-\mathcal{E})t/\hbar}$$

we observe that the integrand is a product of in general a smooth function of $\mathcal{E}$ and an exponential which oscillates in $\mathcal{E}$ with the period $\sim \hbar/t$. Denoting by Δ the scale over which $\overline{|V_{0\mu}|^2}\big|_{\mathcal{E}_\mu=\mathcal{E}}$ changes it is clear that the integral will tend to zero for long times $t \gg \hbar/\Delta$. Under this condition the kernel $K(t)$ has the "range"

$$T \sim \frac{\hbar}{\Delta}$$

Let us change the variable t' in the integral in (41) to $\tau = t - t'$

$$\frac{dc_0}{dt} = \int_0^t K(t-t')c_0(t')dt' = \int_0^t K(\tau)c_0(t-\tau)d\tau \tag{141}$$

For a given t only the values of $c_0(t-\tau)$ within "memory times" $\tau \leq T$ of $K(\tau)$ contribute in the integral. To simplify further we next assume that $c_0(t)$ changes little over the time T. We will address below the meaning of this assumption. When it is valid we can approximate under the integral

$$c_0(t-\tau) \approx c_0(t)$$

and write

$$\frac{dc_0}{dt} = c_0(t) \int_0^t K(\tau) d\tau \tag{142}$$

This approximation is called the Markov approximation - dynamics of $c(t)$, i.e. how it changes at the time t depends only on its value at the time t and not on earlier times $t' < t$, i.e., it has no memory of the past.

The integral on the right hand side of the above equation is a known function of t so the equation can be integrated but let us first make one more simplification. We will be interested in the long time behaviour of $c_0(t)$ for $t \gg T$. Since by assumption $K(\tau)$ is small for $\tau \gg T$ we can approximate

$$\int_0^t K(\tau) d\tau \approx \int_0^\infty K(\tau) d\tau$$

Let us introduce the following notation for the real and imaginary part of this integral

$$\mathrm{Im} \int_0^\infty K(\tau) d\tau = -\frac{\Delta\mathcal{E}}{\hbar} \quad , \quad Re \int_0^\infty K(\tau) d\tau = \frac{\Gamma}{2} \tag{143}$$

With this we have for the time dependence of the "persistence amplitude" of the initial state ψ_0

$$\langle \psi_0 | \Psi(t) \rangle = c_0(t) e^{-i\mathcal{E}_0 t/\hbar}|_{t \gg T} = c(0) e^{-i(\mathcal{E}_0 + \Delta\mathcal{E})t/\hbar} e^{-\Gamma t/2} \tag{144}$$

We will see below that Γ is positive so this amplitude decays exponentially with the decay rate Γ. Its phase acquires energy shift $\Delta\mathcal{E}$.

We will discuss the explicit form of $\Delta\mathcal{E}$ and Γ in the next subsection. Here we note that the time scale over which $c_0(t)$ changes is $\sim 1/\Gamma$ or $\sim \hbar/\Delta\mathcal{E}$. This our assumption of $c_0(t)$ changing slowly in the interval $T = \hbar/\Delta$ means that must have

$$\hbar\Gamma \ll \Delta \quad , \quad \Delta\mathcal{E} \ll \Delta \tag{145}$$

3.1.3 Decay rate (width) and the energy shift of a decaying state

We now provide explicit expressions for Γ and $\Delta\mathcal{E}$. Consider the integral

$$\hbar \lim_{t_0 \to \infty} \int_0^{t_0} K(\tau) d\tau = i \lim_{t_0 \to \infty} \int d\mathcal{E}\, \overline{|V_{0\mu}|^2}\big|_{\mathcal{E}_\mu = \mathcal{E}} \; \frac{e^{i(\mathcal{E}_0 - \mathcal{E})t_0/\hbar} - 1}{\mathcal{E}_0 - \mathcal{E}} \tag{146}$$

where we used Eq. (46) for $K(t)$. To calculate the $t_0 \to \infty$ limit we will use the following device (cf., Ref. [4], Sec. 43). Let us shift the integration contour over $\mathcal{E}$ slightly into the lower imaginary half plane (with $\mathrm{Im}\,\mathcal{E} < 0$), cf. dashed line in Fig.7

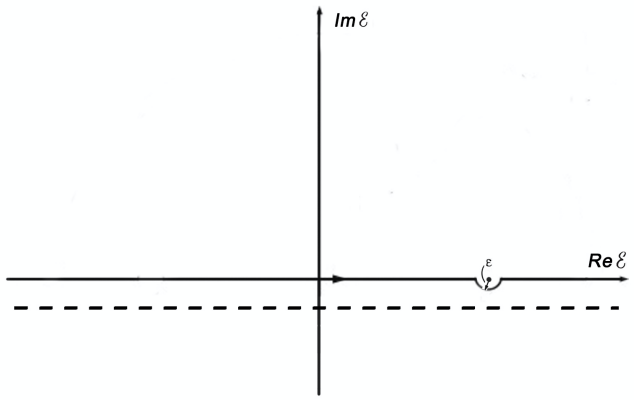

Figure 7: The resulting integration contour in the $i\epsilon$ prescription. It was obtained first shifting the integration contour along the real axis in Eq.(146) to the lower $Im\mathcal{E} < 0$ half-plane, then letting $t_0 \to \infty$ for which the 1st term in the integrand vanishes and then bringing the contour back to the real axis with a small semicircle around the singularity point at $\mathcal{E} = \mathcal{E}_0$. Note that choosing the semicircular shape is a matter of convenience allowing to obtain easily the conventional result (149) as explained in the text.

This can be done without changing the value of the integral since the integrand has no singularities on the real axis[13]. The integral above can then be separated into a sum of two

$$\int d\mathcal{E}\, \overline{|V_{0\mu}|^2}\big|_{\varepsilon_\mu=\varepsilon}\ \frac{e^{i(\mathcal{E}_0-\mathcal{E})t_0/\hbar}}{\mathcal{E}_0-\mathcal{E}} \quad \text{and} \quad -\int d\mathcal{E}\, \overline{|V_{0\mu}|^2}\big|_{\varepsilon_\mu=\varepsilon}\ \frac{1}{\mathcal{E}_0-\mathcal{E}}$$

This was not possible when the integration was over the real $\mathcal{E}$ axis because each term separately is singular at $\mathcal{E} = \mathcal{E}_0$.

In the limit $t_0 \to \infty$ the first integral tends to zero (due to the presence of the $e^{Im\mathcal{E}\, t_0}$ factor in its integrand) and we are left with the second integral. There we can bring the integration over $\mathcal{E}$ back to the real axis taking care that it doesn't cross the

[13]To be precise one should write the definite energy integral with its limits $\int_{\mathcal{E}_{min}}^{\mathcal{E}_{max}} d\mathcal{E}...$ and assume that the contour end points (which are fixed and can't be moved to the complex plane) give negligible contribution.

pole at $\mathcal{E} = \mathcal{E}_0$, cf., Fig.7

$$\hbar \int_0^\infty K(\tau) d\tau = i \int_{\text{contour in Fig.7}} d\mathcal{E}\, \overline{|V_{0\mu}|^2}\Big|_{\varepsilon_\mu = \varepsilon} \;\; \frac{1}{\mathcal{E} - \mathcal{E}_0} \tag{147}$$

It is convenient and conventional to view the resulting integration contour in the above integral in a following way. Let us first add a small positive imaginary quantity $i\epsilon$ to $\mathcal{E}_0$, then shift the contour to the real axis (it goes under the pole so there is no problem) and at the end consider the limit of $\epsilon \to 0$ deforming the contour to prevent the pole crossing it.

This procedure is often called the $i\epsilon$ prescription and using it we write the expression (147) as

$$\hbar \int_0^\infty K(\tau) d\tau = i \lim_{\epsilon \to 0} \int d\mathcal{E}\, \overline{|V_{0\mu}|^2} \;\; \frac{1}{\mathcal{E} - \mathcal{E}_0 - i\epsilon} \tag{148}$$

The integral here can be transformed using the formula

$$\lim_{\epsilon \to 0} \int_a^b \frac{f(x)}{x \pm i\epsilon} dx = \mathcal{P} \int_a^b \frac{f(x)}{x} dx \mp i\pi f(0) \tag{149}$$

valid for $a < 0$ and $b > 0$. Here $\mathcal{P}$ denotes the principle value of the integral

$$\mathcal{P} \int_a^b \frac{f(x)}{x} dx = \lim_{\epsilon \to 0} \left[\int_a^{-\epsilon} dx + \int_\epsilon^b dx \right] \frac{f(x)}{x} \tag{150}$$

The two terms in (149) correspond to the integral along the real axis with the excluded interval $-\epsilon < x < \epsilon$ and the integral along the semicircle of radius ϵ around the singularity at $x = 0$, cf., Fig.7. The value of the second term is just half of the $\mp 2\pi i f(0)$ from the application of the Cauchy's residue theorem to the full circle (or just calculating the integral using polar coordinates $Re\, x = r\cos\phi, Im\, x = r\sin\phi$ in the complex plane).

Using this for the integral in (148) we arrive at the expressions (48) for the energy shift $\Delta\mathcal{E}$ and the width Γ.

3.2 The $\hat{H}_{I3}$ part of the Hamiltonian and the parity transformation

The invariance under parity transformation of the part $\hat{H}_{I3}$, Eq.(10) of the (non relativistic) matter-EM field Hamiltonian follows since both $\mathbf{B}$ and the particle spins

$\hat{\mathbf{s}}_a$ do not change their signs under the parity transformation. They are axial (or pseudo) vectors. For the magnetic field this is already seen in the Lorenz force

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

Since the force $\mathbf{F} = md\mathbf{v}/dt$ it must be a polar vector so must be $\mathbf{E}$. In the second term since $\mathbf{v}$ is polar $\mathbf{B}$ must be axial. This is also seen in the Maxwell equations

$$\nabla \times \mathbf{E} = -\partial \mathbf{B}/\partial t \quad , \quad c^2 \nabla \times \mathbf{B} = \partial \mathbf{E}/\partial t + \mathbf{j}/\epsilon_0$$

as well as in the relation $\mathbf{B} = \nabla \times \mathbf{A}$.

Spin vectors $\mathbf{s}$ are axial as they are part of the total angular momentum $\mathbf{j} = \mathbf{l} + \mathbf{s}$ with the orbital part $\mathbf{l} = \mathbf{r} \times \mathbf{p}$ which obviously doesn't change under the parity transformation. It is not difficult to gain intuition about this peculiar property of $\mathbf{l}$. Indeed the orbital angular momentum reflects/measures the magnitude and the direction of the "rotational" component with respect to the origin $\mathbf{r} = 0$ in a (chosen) coordinate system of a particle motion at a position $\mathbf{r}$ moving with the momentum $\mathbf{p}$. Changing the particle position $\mathbf{r} \to -\mathbf{r}$ and the momentum $\mathbf{p} \to -\mathbf{p}$ leave the direction and the magnitude of the rotational component of the motion the same.

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