Chapter 18
Quantization of the Maxwell Field: Photons

We will now start to quantize the Maxwell field $A_\mu(x) = \{-\Phi(x)/c, \boldsymbol{A}(x)\}$ similar to the quantization of the Schrödinger field. The fact that electromagnetism has a gauge invariance implies that there are more components than actual dynamical degrees of freedom in the Maxwell field. This will make quantization a little more challenging than for the Schrödinger field, but we will overcome those difficulties.

Electromagnetic field theory is implicitly relativistic, and quantized Maxwell theory therefore also provides us with a first example of a relativistic quantum field theory. Appendix B provides an introduction to 4-vector and tensor notation in electromagnetic theory.

18.1 Lagrange density and mode expansion for the Maxwell field

The equations of motion for the Maxwell field are the inhomogeneous Maxwell equations (recall from electrodynamics that the homogeneous equations were solved through the introduction of the potentials A_μ),

$$\partial_\mu F^{\mu\nu} = \partial_\mu \left(\partial^\mu A^\nu - \partial^\nu A^\mu\right) = -\mu_0 j^\nu.$$

These equations can be written as

$$j^\nu + \frac{1}{\mu_0}\partial_\mu \left(\partial^\mu A^\nu - \partial^\nu A^\mu\right) = \frac{\partial\mathcal{L}}{\partial A_\nu} - \partial_\mu \frac{\partial\mathcal{L}}{\partial(\partial_\mu A_\nu)} = 0$$

if we use the Lagrange density

$$\mathcal{L} = j^\nu A_\nu - \frac{1}{4\mu_0}F_{\mu\nu}F^{\mu\nu} = \frac{\epsilon_0}{2}\boldsymbol{E}^2 - \frac{1}{2\mu_0}\boldsymbol{B}^2 + \boldsymbol{j}\cdot\boldsymbol{A} - \varrho\Phi. \tag{18.1}$$

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This Lagrangian provides us with the canonically conjugate momentum for the vector potential $\boldsymbol{A}$:

$$\boldsymbol{\Pi}_A = \frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{A}}} = \epsilon_0(\dot{\boldsymbol{A}} + \nabla\Phi) = -\epsilon_0 \boldsymbol{E},$$

but

$$\Pi_\Phi = \frac{\partial \mathcal{L}}{\partial \dot{\Phi}} = 0$$

vanishes identically! Therefore we cannot simply impose canonical commutation relations between the four components A_μ of the 4-vector potential and four conjugate momenta Π_ν. To circumvent this problem we revisit Maxwell's equations,

$$\Delta\Phi + \nabla\cdot\dot{\boldsymbol{A}} = -\frac{1}{\epsilon_0}\varrho, \tag{18.2}$$

$$\nabla(\nabla\cdot\boldsymbol{A}) - \Delta\boldsymbol{A} + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\boldsymbol{A} + \frac{1}{c^2}\frac{\partial}{\partial t}\nabla\Phi = \mu_0\boldsymbol{j}. \tag{18.3}$$

One way to solve the problem with $\Pi_\Phi = 0$ is to eliminate $\nabla\cdot\boldsymbol{A}$ from the equations of motion through the gauge freedom

$$\Phi(\boldsymbol{x},t) \to \Phi_f(\boldsymbol{x},t) = \Phi(\boldsymbol{x},t) - \dot{f}(\boldsymbol{x},t), \tag{18.4}$$

$$\boldsymbol{A}(\boldsymbol{x},t) \to \boldsymbol{A}_f(\boldsymbol{x},t) = \boldsymbol{A}(\boldsymbol{x},t) + \nabla f(\boldsymbol{x},t), \tag{18.5}$$

i.e. we impose the gauge condition $\nabla\cdot\boldsymbol{A}_f = 0$. The equation

$$\Delta f(\boldsymbol{x},t) = -\nabla\cdot\boldsymbol{A}(\boldsymbol{x},t)$$

can be solved with the Green's function $G(r) = (4\pi r)^{-1}$ for the Laplace operator,

$$\Delta\frac{1}{4\pi|\boldsymbol{x}-\boldsymbol{x}'|} = -\delta(\boldsymbol{x}-\boldsymbol{x}'),$$

see equations (11.11) and (11.17) for $E = 0$,

$$f(\boldsymbol{x},t) = \frac{1}{4\pi}\int d^3x'\,\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\nabla\cdot\boldsymbol{A}(\boldsymbol{x}',t).$$

This gauge is denoted as *Coulomb gauge*.

We denote the gauge transformed fields again with Φ and $\boldsymbol{A}$, i.e. we have

$$\nabla\cdot\boldsymbol{A}(\boldsymbol{x},t) = 0. \tag{18.6}$$

and

$$\Delta\Phi = -\frac{1}{\epsilon_0}\varrho, \tag{18.7}$$

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\boldsymbol{A} - \Delta\boldsymbol{A} + \frac{1}{c^2}\frac{\partial}{\partial t}\nabla\Phi = \mu_0\boldsymbol{j}. \tag{18.8}$$

We can now get rid of Φ by solving (18.7) again with the Green's function for the Laplace operator,

$$\Phi(\boldsymbol{x},t) = \frac{1}{4\pi\epsilon_0}\int d^3\boldsymbol{x}'\,\frac{\varrho(\boldsymbol{x}',t)}{|\boldsymbol{x}-\boldsymbol{x}'|}. \tag{18.9}$$

The resulting equation for $\boldsymbol{A}$ is

$$\begin{aligned}\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta\right)\boldsymbol{A}(\boldsymbol{x},t) &= \mu_0\boldsymbol{j}(\boldsymbol{x},t) + \frac{\mu_0}{4\pi}\int d^3\boldsymbol{x}'\,\frac{\boldsymbol{x}-\boldsymbol{x}'}{|\boldsymbol{x}-\boldsymbol{x}'|^3}\frac{\partial}{\partial t}\varrho(\boldsymbol{x}',t)\\ &= \mu_0\boldsymbol{j}(\boldsymbol{x},t) + \frac{\mu_0}{4\pi}\int d^3\boldsymbol{x}'\,\nabla\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\nabla'\cdot\boldsymbol{j}(\boldsymbol{x}',t)\\ &= \mu_0\boldsymbol{j}(\boldsymbol{x},t) + \frac{\mu_0}{4\pi}\int d^3\boldsymbol{x}'\boldsymbol{j}(\boldsymbol{x}',t)\cdot\nabla\otimes\nabla\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\\ &= \mu_0\boldsymbol{J}(\boldsymbol{x},t).\end{aligned} \tag{18.10}$$

We can also evaluate the derivatives in the integral using

$$\nabla\otimes\nabla\frac{1}{r} = -\nabla\otimes\frac{\boldsymbol{e}_r}{r^2} = -\frac{4\pi}{3}\underline{1}\delta(\boldsymbol{x}) - \frac{\underline{1} - 3\boldsymbol{e}_r\otimes\boldsymbol{e}_r}{r^3}. \tag{18.11}$$

This yields

$$\boldsymbol{J}(\boldsymbol{x},t) = \frac{2}{3}\boldsymbol{j}(\boldsymbol{x},t) + \int d^3\boldsymbol{x}'\,\frac{3(\boldsymbol{x}-\boldsymbol{x}')\otimes(\boldsymbol{x}-\boldsymbol{x}') - |\boldsymbol{x}-\boldsymbol{x}'|^2\underline{1}}{4\pi|\boldsymbol{x}-\boldsymbol{x}'|^5}\cdot\boldsymbol{j}(\boldsymbol{x}',t).$$

The new current density $\boldsymbol{J}$ satisfies

$$\nabla\cdot\boldsymbol{J}(\boldsymbol{x},t) = 0. \tag{18.12}$$

This follows from the definition of $\boldsymbol{J}$ in the first line of (18.10) and charge conservation, or directly from the second or third line of (18.10), which can be considered as projections of the vector $\boldsymbol{j}$ onto its divergence-free part. We also require localization of charges and currents in the sense of

$$\lim_{|\boldsymbol{x}|\to\infty}|\boldsymbol{x}|\boldsymbol{j}(\boldsymbol{x},t) = 0. \tag{18.13}$$

Equation (18.10) can be solved e.g. with the retarded Green's function, cf. equation (J.60),

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2}-\Delta\right)G(\boldsymbol{x},t)=\delta(\boldsymbol{x})\delta(t),\quad G(\boldsymbol{x},t)=\frac{1}{4\pi r}\delta\!\left(t-\frac{r}{c}\right),\tag{18.14}$$

in the form

$$\begin{aligned}\boldsymbol{A}_J(\boldsymbol{x},t)&=\mu_0\int d^3\boldsymbol{x}'\int dt'\,G(\boldsymbol{x}-\boldsymbol{x}',t-t')\boldsymbol{J}(\boldsymbol{x}',t')\\&=\frac{\mu_0}{4\pi}\int d^3\boldsymbol{x}'\,\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\boldsymbol{J}\!\left(\boldsymbol{x}',t-\frac{|\boldsymbol{x}-\boldsymbol{x}'|}{c}\right).\end{aligned}\tag{18.15}$$

This satisfies $\nabla\cdot\boldsymbol{A}_J(\boldsymbol{x},t)=0$ due to (18.12, 18.13).

The vector field is only a special solution of the inhomogeneous equation (18.10), and the general solution will be a superposition

$$\boldsymbol{A}(\boldsymbol{x},t)=\boldsymbol{A}_J(\boldsymbol{x},t)+\boldsymbol{A}_D(\boldsymbol{x},t)$$

of the special inhomogeneous solution with the general solution of the homogeneous equations

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2}-\Delta\right)\boldsymbol{A}_D(\boldsymbol{x},t)=0.\tag{18.16}$$

The homogeneous solution still has to satisfy the gauge condition $\nabla\cdot\boldsymbol{A}_D=0$, because the total vector potential $\boldsymbol{A}$ has to satisfy this condition.

Fourier decomposition

$$\begin{aligned}\boldsymbol{A}_D(\boldsymbol{x},t)&=\frac{1}{4\pi^2}\int d^3\boldsymbol{k}\int d\omega\,\boldsymbol{A}_D(\boldsymbol{k},\omega)\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)]\,,\\\boldsymbol{A}_D(\boldsymbol{k},\omega)&=\frac{1}{4\pi^2}\int d^3\boldsymbol{x}\int dt\,\boldsymbol{A}_D(\boldsymbol{x},t)\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)]\end{aligned}\tag{18.17}$$

transforms the condition $\nabla\cdot\boldsymbol{A}_D(\boldsymbol{x},t)=0$ and the equation (18.16) into

$$\boldsymbol{k}\cdot\boldsymbol{A}_D(\boldsymbol{k},\omega)=0\tag{18.18}$$

and

$$\left(\boldsymbol{k}^2-\frac{\omega^2}{c^2}\right)\boldsymbol{A}_D(\boldsymbol{k},\omega)=0.\tag{18.19}$$

Equation (18.18) is the statement that photons are transverse, whereas equation (18.19) implies that $\boldsymbol{A}_D(\boldsymbol{k},\omega)$ can be written as

$$\boldsymbol{A}_D(\boldsymbol{k},\omega) = \sqrt{\frac{\pi\hbar\mu_0 c}{k}}\sum_{\alpha=1}^{2}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\left(a_\alpha(\boldsymbol{k})\delta(\omega-ck)+a_\alpha^+(-\boldsymbol{k})\delta(\omega+ck)\right), \tag{18.20}$$

where the prefactor so far is a matter of convention and the two vectors $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ are a Cartesian basis in the plane orthogonal to $\boldsymbol{k}$:

$$\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\boldsymbol{\epsilon}_\beta(\boldsymbol{k}) = \delta_{\alpha\beta}, \quad \boldsymbol{k}\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) = 0.$$

Inserting (18.20) into (18.17) yields

$$\begin{aligned}\boldsymbol{A}_D(\boldsymbol{x},t) = {} & \sqrt{\frac{\hbar\mu_0 c}{(2\pi)^3}}\int\frac{d^3\boldsymbol{k}}{\sqrt{2k}}\sum_{\alpha=1}^{2}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\Big(a_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)] \\ & + a_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\Big),\end{aligned} \tag{18.21}$$

and for the fields

$$\begin{aligned}\boldsymbol{E}_D(\boldsymbol{x},t) = {} & -\frac{\partial}{\partial t}\boldsymbol{A}_D(\boldsymbol{x},t) \\ = {} & \mathrm{i}\sqrt{\frac{\hbar\mu_0 c^3}{(2\pi)^3}}\int d^3\boldsymbol{k}\,\sqrt{\frac{k}{2}}\sum_{\alpha=1}^{2}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\Big(a_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)] \\ & - a_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\Big),\end{aligned} \tag{18.22}$$

$$\begin{aligned}\boldsymbol{B}_D(\boldsymbol{x},t) = {} & \nabla\times\boldsymbol{A}_D(\boldsymbol{x},t) \\ = {} & \mathrm{i}\sqrt{\frac{\hbar\mu_0 c}{(2\pi)^3}}\int\frac{d^3\boldsymbol{k}}{\sqrt{2k}}\sum_{\alpha=1}^{2}\boldsymbol{k}\times\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\Big(a_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)] \\ & - a_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\Big).\end{aligned} \tag{18.23}$$

Inversion of equations (18.21, 18.22) yields

$$\begin{aligned}a_\alpha(\boldsymbol{k}) = {} & \int\frac{d^3\boldsymbol{x}}{\sqrt{(2\pi)^3 2\mu_0\hbar c}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\left(\sqrt{k}\boldsymbol{A}_D(\boldsymbol{x},t)+\frac{\mathrm{i}}{c\sqrt{k}}\dot{\boldsymbol{A}}_D(\boldsymbol{x},t)\right) \\ & \times\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)],\end{aligned}$$

$$\begin{aligned}a_\alpha^+(\boldsymbol{k}) = {} & \int\frac{d^3\boldsymbol{x}}{\sqrt{(2\pi)^3 2\mu_0\hbar c}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\left(\sqrt{k}\boldsymbol{A}_D(\boldsymbol{x},t)-\frac{\mathrm{i}}{c\sqrt{k}}\dot{\boldsymbol{A}}_D(\boldsymbol{x},t)\right) \\ & \times\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)].\end{aligned}$$

We can think of the vector potential (18.21) as a state $|A_D(t)\rangle$ with components

$$\langle \boldsymbol{k},\alpha|A_D(t)\rangle = \sqrt{\frac{\hbar\mu_0 c}{2k}}\left(a_\alpha(\boldsymbol{k})\exp(-\mathrm{i}ckt) + a_\alpha^+(-\boldsymbol{k})\exp(\mathrm{i}ckt)\right) \tag{18.24}$$

in wave vector space, and

$$\begin{aligned}\langle \boldsymbol{x},i|A_D(t)\rangle = {} & \sqrt{\frac{\hbar\mu_0 c}{(2\pi)^3}}\int\frac{d^3\boldsymbol{k}}{\sqrt{2k}}\sum_{\alpha=1}^{2}\epsilon_\alpha^i(\boldsymbol{k})\Big(a_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\\ & + a_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\Big)\end{aligned} \tag{18.25}$$

in $\boldsymbol{x}$ space. This corresponds to transformation matrices

$$\langle \boldsymbol{x},i|\boldsymbol{k},\alpha\rangle = \frac{1}{\sqrt{2\pi}^3}\epsilon_\alpha^i(\boldsymbol{k})\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}),$$

and we can easily check the completeness relations

$$\begin{aligned}\langle \boldsymbol{k},\alpha|\boldsymbol{k}',\beta\rangle &= \int d^3\boldsymbol{x}\sum_i\langle \boldsymbol{k},\alpha|\boldsymbol{x},i\rangle\langle \boldsymbol{x},i|\boldsymbol{k}',\beta\rangle = \delta(\boldsymbol{k}-\boldsymbol{k}')\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\boldsymbol{\epsilon}_\beta(\boldsymbol{k})\\ &= \delta(\boldsymbol{k}-\boldsymbol{k}')\delta_{\alpha\beta},\end{aligned} \tag{18.26}$$

$$\begin{aligned}\langle \boldsymbol{x},i|\boldsymbol{x}',j\rangle &= \int d^3\boldsymbol{k}\sum_\alpha\langle \boldsymbol{x},i|\boldsymbol{k},\alpha\rangle\langle \boldsymbol{k},\alpha|\boldsymbol{x}',j\rangle\\ &= \frac{1}{(2\pi)^3}\int d^3\boldsymbol{k}\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]\sum_\alpha\epsilon_\alpha^i(\boldsymbol{k})\epsilon_\alpha^j(\boldsymbol{k})\\ &= \frac{1}{(2\pi)^3}\int d^3\boldsymbol{k}\ \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]P_\perp^{ij}(\boldsymbol{k})\\ &= \frac{1}{(2\pi)^3}\int d^3\boldsymbol{k}\ \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]\left(\delta^{ij}-\frac{k^ik^j}{k^2}\right)\\ &= \delta_\perp^{ij}(\boldsymbol{x}-\boldsymbol{x}').\end{aligned} \tag{18.27}$$

Here the equation

$$\sum_{\alpha=1}^{2}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\otimes\boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) = \underline{\mathbf{1}} - \hat{\boldsymbol{k}}\otimes\hat{\boldsymbol{k}} \tag{18.28}$$

has been used, cf. the decomposition of unity (4.14). Equation (18.27) defines the *transverse δ function.*

Energy-momentum tensor for the free Maxwell field

The Lagrange density for the free Maxwell field,

$$\mathcal{L} = -\frac{1}{4\mu_0}F_{\mu\nu}F^{\mu\nu}, \tag{18.29}$$

yields a canonical energy-momentum tensor

$$\Theta_\mu{}^\nu = \eta_\mu{}^\nu\mathcal{L} - \partial_\mu A_\lambda\frac{\partial\mathcal{L}}{\partial(\partial_\nu A_\lambda)} = \frac{1}{\mu_0}\left(\partial_\mu A_\lambda\cdot F^{\nu\lambda} - \frac{1}{4}\eta_\mu{}^\nu F_{\kappa\lambda}F^{\kappa\lambda}\right) \tag{18.30}$$

which is not gauge invariant. However, the free equation $\partial_\nu F^{\nu\lambda} = 0$ implies a trivial conservation law

$$-\frac{1}{\mu_0}\partial_\nu\left(\partial_\lambda A_\mu\cdot F^{\nu\lambda}\right) = 0 \tag{18.31}$$

which can be added to the conservation law for the free fields, $\partial_\nu\Theta_\mu{}^\nu = 0$. In this way we can improve the energy-momentum tensor $\Theta_\mu{}^\nu$ to a gauge invariant energy-momentum tensor

$$T_\mu{}^\nu = \Theta_\mu{}^\nu - \frac{1}{\mu_0}\partial_\lambda A_\mu\cdot F^{\nu\lambda} = \frac{1}{\mu_0}\left(F_{\mu\lambda}F^{\nu\lambda} - \frac{1}{4}\eta_\mu{}^\nu F_{\kappa\lambda}F^{\kappa\lambda}\right). \tag{18.32}$$

The corresponding energy-momentum density vector $\mathcal{P}_\mu = T_\mu{}^0/c$ yields the well known expressions for the energy and momentum densities of electromagnetic fields,

$$\mathcal{H} = -c\mathcal{P}_0 = -T_0{}^0 = \frac{\epsilon_0}{2}\boldsymbol{E}^2 + \frac{1}{2\mu_0}\boldsymbol{B}^2, \tag{18.33}$$

$$\boldsymbol{\mathcal{P}} = \epsilon_0\boldsymbol{E}\times\boldsymbol{B}. \tag{18.34}$$

The components of the energy current density (the Poynting vector) are given by the components $-cT_0{}^i$ (because $-\partial_t T_0{}^0 = -c\partial_0 T_0{}^0 = c\partial_i T_0{}^i$):

$$\boldsymbol{\mathcal{S}} = \frac{1}{\mu_0}\boldsymbol{E}\times\boldsymbol{B} = c^2\boldsymbol{\mathcal{P}}. \tag{18.35}$$

We are interested in the energy and momentum densities for the free fields $\boldsymbol{A}_D(\boldsymbol{x}, t)$, because those will become the freely evolving field operators in the Dirac picture.

18.2 Photons

In the previous section we got rid of Φ and even of the longitudinal component of $\boldsymbol{A}$. Now we might be tempted to impose canonical commutation relations $[A_i(\boldsymbol{x},t), \Pi_j(\boldsymbol{x}',t)] \sim \mathrm{i}\hbar\delta_{ij}\delta(\boldsymbol{x}-\boldsymbol{x}')$. However, this would be inconsistent, since equation (18.6) implies that application of $\partial/\partial x_i$ and summation over i on the left hand side would yield zero, but on the right hand side would not yield zero! This problem arises irrespective of whether we wish to quantize the full vector potential $\boldsymbol{A}$ or only the free vector potential $\boldsymbol{A}_D$. Therefore we have to invoke the transverse δ-function (18.27) to formulate the canonical commutation relations for the Maxwell field. We will use these relations primarily for the Dirac picture operators, but we omit the index D from now on,

$$\begin{aligned}[A_i(\boldsymbol{x},t), \dot{A}_j(\boldsymbol{x}',t)] &= \frac{\mathrm{i}\hbar}{\epsilon_0(2\pi)^3}\int d^3\boldsymbol{k}\left(\delta_{ij}-\frac{k_ik_j}{\boldsymbol{k}^2}\right)\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')] \\ &= \frac{\mathrm{i}\hbar}{\epsilon_0(2\pi)^3}\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}\epsilon_{\alpha,i}(\boldsymbol{k})\epsilon_{\alpha,j}(\boldsymbol{k})\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')],\end{aligned}$$

or in short form

$$[A_i(\boldsymbol{x},t), \dot{A}_j(\boldsymbol{x}',t)] = \frac{\mathrm{i}\hbar}{\epsilon_0}\delta_{ij}^{\perp}(\boldsymbol{x}-\boldsymbol{x}'). \tag{18.36}$$

This equation can also be written using the zero energy Green's function $G(\boldsymbol{x}-\boldsymbol{x}') = \langle\boldsymbol{x}|G(0)|\boldsymbol{x}'\rangle$ (cf. equations (J.18, J.19) and (J.24)),

$$[A_i(\boldsymbol{x},t), \dot{A}_j(\boldsymbol{x}',t)] = \frac{\mathrm{i}\hbar}{\epsilon_0}\Big(\delta_{ij}\delta(\boldsymbol{x}-\boldsymbol{x}') + \partial_i\partial_j G(\boldsymbol{x}-\boldsymbol{x}')\Big), \tag{18.37}$$

and using (18.11) we find

$$\begin{aligned}[\boldsymbol{A}(\boldsymbol{x},t) \overset{\otimes}{,} \dot{\boldsymbol{A}}(\boldsymbol{x}',t)] = \frac{\mathrm{i}\hbar}{\epsilon_0}\bigg(&\frac{2}{3}\,\underline{1}\,\delta(\boldsymbol{x}-\boldsymbol{x}') \\ &+ \frac{3(\boldsymbol{x}-\boldsymbol{x}')\otimes(\boldsymbol{x}-\boldsymbol{x}') - |\boldsymbol{x}-\boldsymbol{x}'|^2\underline{1}}{4\pi|\boldsymbol{x}-\boldsymbol{x}'|^5}\bigg).\end{aligned} \tag{18.38}$$

The remaining commutation relations are

$$[A_i(\boldsymbol{x},t), A_j(\boldsymbol{x}',t)] = 0, \quad [\dot{A}_i(\boldsymbol{x},t), \dot{A}_j(\boldsymbol{x}',t)] = 0. \tag{18.39}$$

The relations (18.36, 18.39) yield for the operators $a_\alpha(\boldsymbol{k})$, $a_\beta^+(\boldsymbol{k}')$ harmonic oscillator relations,

$$[a_\alpha(\boldsymbol{k}), a_\beta(\boldsymbol{k}')]=0, \quad [a_\alpha^+(\boldsymbol{k}), a_\beta^+(\boldsymbol{k}')]=0, \quad [a_\alpha(\boldsymbol{k}), a_\beta^+(\boldsymbol{k}')] = \delta_{\alpha\beta}\delta(\boldsymbol{k}-\boldsymbol{k}').$$

The prefactor in (18.20) was chosen such that no extra factor appears in the commutation relation of $a_\alpha(\boldsymbol{k})$ and $a^+_\beta(\boldsymbol{k}')$.

The energy and momentum densities (18.33) and (18.34) yield energy and momentum operators

$$H = \int d^3\boldsymbol{x} \left(\frac{\epsilon_0}{2}\boldsymbol{E}^2 + \frac{1}{2\mu_0}\boldsymbol{B}^2 \right) = \sum_\alpha \int d^3\boldsymbol{k}\, \hbar ck\, a^+_\alpha(\boldsymbol{k}) a_\alpha(\boldsymbol{k}), \tag{18.40}$$

$$\boldsymbol{P} = \epsilon_0 \int d^3\boldsymbol{x}\, \boldsymbol{E} \times \boldsymbol{B} = \sum_\alpha \int d^3\boldsymbol{k}\, \hbar\boldsymbol{k}\, a^+_\alpha(\boldsymbol{k}) a_\alpha(\boldsymbol{k}). \tag{18.41}$$

From these expressions we can infer by the meanwhile standard methods that $a^+_\alpha(\boldsymbol{k})$ creates a photon of momentum $\hbar\boldsymbol{k}$, energy $\hbar ck$ and polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$, while $a_\alpha(\boldsymbol{k})$ annihilates such a photon. In particular,

$$|\boldsymbol{k}, \alpha\rangle = a^+_\alpha(\boldsymbol{k})|0\rangle$$

is a single photon state with momentum $\hbar\boldsymbol{k}$, energy $\hbar ck$ and polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$.

In writing the $\boldsymbol{k}$ space integrals for H and $\boldsymbol{P}$ we have used the prescription of *normal ordering*, i.e. writing the creation operators on the left side of the annihilation operators. This ensures that vacuum expectation values of charges and currents vanish. Many authors like to explicitly indicate normal ordering for $\boldsymbol{x}$ space representations of charges or currents through double colons, e.g. for equation (18.40) this would read

$$H =: \int d^3\boldsymbol{x} \left(\frac{\epsilon_0}{2}\boldsymbol{E}^2 + \frac{1}{2\mu_0}\boldsymbol{B}^2 \right) := \sum_\alpha \int d^3\boldsymbol{k}\, \hbar ck\, a^+_\alpha(\boldsymbol{k}) a_\alpha(\boldsymbol{k}).$$

We will not use the double colon notation and instead use the implicit convention that charges and currents have to be normal ordered in terms of creation and annihilation operators.

If we want to construct a creation operator $a^+_\alpha(\boldsymbol{x})$ in $\boldsymbol{x}$ space (corresponding to the operator $\psi^+(\boldsymbol{x})$ in Schrödinger theory) we find

$$\begin{aligned} a^+_\alpha(\boldsymbol{x}) &= \frac{1}{\sqrt{2\pi}^3} \int d^3\boldsymbol{k}\, a^+_\alpha(\boldsymbol{k}) \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \\ &= \frac{1}{(2\pi)^3} \int d^3\boldsymbol{k} \int d^3\boldsymbol{x}'\boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) \cdot \left(\sqrt{\frac{k}{2\mu_0 c\hbar}}\boldsymbol{A}(\boldsymbol{x}', t) \right. \\ &\quad \left. - \frac{\mathrm{i}}{\sqrt{2k\mu_0 c^3\hbar}}\dot{\boldsymbol{A}}(\boldsymbol{x}', t) \right) \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}' - \boldsymbol{x}) - \mathrm{i}ckt]. \end{aligned}$$

The expression on the right hand side is time-independent and can just as well be written in terms of the Schrödinger picture operators $\boldsymbol{A}(\boldsymbol{x}) = \boldsymbol{A}(\boldsymbol{x}, 0)$ and $\dot{\boldsymbol{A}}(\boldsymbol{x}) = \dot{\boldsymbol{A}}(\boldsymbol{x}, 0)$. However, the important observation is that contrary to Schrödinger theory, the original operator in $\boldsymbol{x}$ space, $\boldsymbol{A}(\boldsymbol{x}, t)$, is not a pure annihilation or creation operator any more, but instead is a superposition of annihilation and creation operators. This is a generic feature of relativistic field operators. The property $a^+(\boldsymbol{x}) = \psi^+(\boldsymbol{x})$ is a special feature of the non-relativistic Schrödinger field. It is because of this feature of the Schrödinger field that we did not have to use an explicit double colon notation or an implicit agreement to use normal ordering in Schrödinger field theory. Normal ordered expressions in $\boldsymbol{x}$ space were automatically normal ordered in $\boldsymbol{k}$ space.

The time evolution of the free photon operators in $\boldsymbol{k}$ space is given by the standard Heisenberg evolution equations,

$$a_{D\alpha}(\boldsymbol{k}, t) = a_\alpha(\boldsymbol{k}) \exp(-\mathrm{i}ckt) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right) a_\alpha(\boldsymbol{k}) \exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right), \quad (18.42)$$

$$\frac{\partial}{\partial t} a_{D\alpha}(\boldsymbol{k}, t) = \frac{\mathrm{i}}{\hbar}[H, a_{D\alpha}(\boldsymbol{k}, t)], \quad (18.43)$$

and therefore we also have for the field operators in $\boldsymbol{x}$ space

$$\boldsymbol{A}(\boldsymbol{x}, t) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right) \boldsymbol{A}(\boldsymbol{x}) \exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right), \quad (18.44)$$

but to recover the evolution equation (18.16) in $\boldsymbol{x}$ space we have to use iterated Heisenberg evolution equations,

$$\frac{\partial}{\partial t}\boldsymbol{A}(\boldsymbol{x}, t) = \frac{\mathrm{i}}{\hbar}[H, \boldsymbol{A}(\boldsymbol{x}, t)] = -\boldsymbol{E}(\boldsymbol{x}, t), \quad (18.45)$$

$$\frac{\partial^2}{\partial t^2}\boldsymbol{A}(\boldsymbol{x}, t) = -\frac{\mathrm{i}}{\hbar}[H, \boldsymbol{E}(\boldsymbol{x}, t)] = -\frac{1}{\hbar^2}[H, [H, \boldsymbol{A}(\boldsymbol{x}, t)]]. \quad (18.46)$$

This is a general property of bosonic relativistic fields.

18.3 Coherent states of the electromagnetic field

We can directly apply what we have learned about coherent oscillator states to construct a quantum state with the property that the operator $\boldsymbol{E}(\boldsymbol{x}, t)$ (18.22) yields a classical electromagnetic wave as expectation value,

$$\begin{aligned}\langle\mathcal{E}|\boldsymbol{E}(\boldsymbol{x},t)|\mathcal{E}\rangle &= \mathcal{E}(\boldsymbol{x},t)\\ &= \mathrm{i}\sqrt{\frac{\hbar\mu_0 c^3}{(2\pi)^3}}\int d^3\boldsymbol{k}\,\sqrt{\frac{k}{2}}\sum_{\alpha=1}^{2}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\Big(\zeta_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\\ &\quad -\zeta_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\Big).\end{aligned} \tag{18.47}$$

The results of Section 6.5 imply that the state $|\mathcal{E}\rangle$ can be unitarily generated out of the vacuum[1],

$$|\mathcal{E}\rangle = \exp\left(\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}\big(\zeta_\alpha(\boldsymbol{k})a_\alpha^+(\boldsymbol{k})-\zeta_\alpha^+(\boldsymbol{k})a_\alpha(\boldsymbol{k})\big)\right)|0\rangle.$$

The corresponding equations in the Schrödinger picture are

$$\langle\mathcal{E}(t)|\boldsymbol{E}(\boldsymbol{x})|\mathcal{E}(t)\rangle = \mathcal{E}(\boldsymbol{x},t),$$

$$|\mathcal{E}(t)\rangle = \exp\left(\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}\big(\zeta_\alpha(\boldsymbol{k},t)a_\alpha^+(\boldsymbol{k})-\zeta_\alpha^+(\boldsymbol{k},t)a_\alpha(\boldsymbol{k})\big)\right)|0\rangle, \tag{18.48}$$

with

$$\zeta_\alpha(\boldsymbol{k},t) = \zeta_\alpha(\boldsymbol{k})\exp(-\mathrm{i}ckt).$$

The average photon number in the electromagnetic wave is

$$\langle n\rangle = \langle\mathcal{E}|\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}a_\alpha^+(\boldsymbol{k})a_\alpha(\boldsymbol{k})|\mathcal{E}\rangle = \int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}|\zeta_\alpha(\boldsymbol{k})|^2$$

and we find with

$$\begin{aligned}\left(\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}a_\alpha^+(\boldsymbol{k})a_\alpha(\boldsymbol{k})\right)^2 &= \int d^3\boldsymbol{k}\int d^3\boldsymbol{k}'\sum_{\alpha,\alpha'=1}^{2}a_\alpha^+(\boldsymbol{k})a_{\alpha'}^+(\boldsymbol{k}')a_{\alpha'}(\boldsymbol{k}')a_\alpha(\boldsymbol{k})\\ &\quad+\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}a_\alpha^+(\boldsymbol{k})a_\alpha(\boldsymbol{k})\end{aligned}$$

the relations

$$\langle n^2\rangle = \left(\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}|\zeta_\alpha(\boldsymbol{k})|^2\right)^2 + \int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}|\zeta_\alpha(\boldsymbol{k})|^2,$$

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[1] R.J. Glauber, Phys. Rev. 131, 2766 (1963).

$$\Delta n = \sqrt{\langle n \rangle} = \left(\int d^3\boldsymbol{k} \sum_{\alpha=1}^{2} |\zeta_\alpha(\boldsymbol{k})|^2 \right)^{1/2}, \quad \frac{\Delta n}{\langle n \rangle} = \frac{1}{\sqrt{\langle n \rangle}}.$$

Every free quantum field has an expansion in terms of oscillator operators, and therefore each quantum field has coherent states which yield classical expectation values for the field. They are particularly important for electromagnetic fields because classical electromagnetic waves are so abundant, readily available, and of technical relevance. This is a consequence of boson statistics and of the vanishing mass and charge of photons. Generating and packing together huge numbers of photons is very inexpensive in terms of energy.

18.4 Photon coupling to relative motion

The discussion of photon interactions with atoms or molecules usually does not involve discussions of photon interactions with the individual constituent electrons and nuclei, but assumes either an effective coupling to the quasiparticles which describe the relative motion between nuclei and electrons, or otherwise assumes coupling of the photons to only one kind of particle in a many particle system. A shortcut justification e.g. for assuming that photons should primarily couple to electrons rather than nuclei in atoms is that physical intuition would indicate that an electromagnetic wave should shake a lighter particle more easily than a heavier particle. Indeed, when we calculate the cross section for photon scattering off free charged particles in Section 22.3, we will find that scattering of low energy photons is suppressed with the mass of the scattering particle like m^{-2}, and for high energy photons like m^{-1}. Furthermore, atomic matrix elements for optical dipole transitions scale like m^{-1} which also indicates a preference for coupling to the lighter charged components in a composite system. However, the intuition can be misleading. A simple counterexample is provided e.g. by the absorption or emission of infrared photons by molecules. The dominant degrees of freedom which undergo transitions in these cases are molecular vibrations or rotations, but not electronic transitions, i.e. the dominant photon-matter interaction for infrared photons concerns coupling to clusters of ions or atomic nuclei. What this means is that we have to make judicious calls on which terms in a quantum electronics or quantum electrodynamics Hamiltonian will make the dominant contributions to photon interactions, depending on the photon energy range that we are interested in and the available atomic or molecular transitions. However, if we use standard atomic orbitals to model the states of the unperturbed matter system, then this does imply an approximation of photon coupling to the quasiparticle which describes relative motion, or to the electrons as the lightest charges. It is therefore instructive to revisit the problem of separation of center of mass motion and relative motion in the presence of electromagnetic fields.

The two-particle Hamiltonian (7.1) with the electromagnetic vector potentials included takes the form

$$\begin{aligned} H = {} & \frac{1}{2m_1}\left(\mathbf{p}_1 - q_1\boldsymbol{A}(\mathbf{x}_1,t)\right)^2 + \frac{1}{2m_2}\left(\mathbf{p}_2 - q_2\boldsymbol{A}(\mathbf{x}_2,t)\right)^2 \\ & + V(|\mathbf{x}_1 - \mathbf{x}_2|). \end{aligned} \tag{18.49}$$

Substitution of the single particle momenta with the total momentum and the effective momentum in the relative motion (7.6) yields

$$\begin{aligned} H = {} & \frac{1}{2M}\left(\mathbf{P} - q_1\boldsymbol{A}(\mathbf{x}_1,t) - q_2\boldsymbol{A}(\mathbf{x}_2,t)\right)^2 \\ & + \frac{1}{2\mu}\left(\mathbf{p} - \frac{m_2q_1\boldsymbol{A}(\mathbf{x}_1,t) - m_1q_2\boldsymbol{A}(\mathbf{x}_2,t)}{M}\right)^2 + V(|\mathbf{x}_1 - \mathbf{x}_2|). \end{aligned} \tag{18.50}$$

Now we assume that the electromagnetic potentials vary weakly over the extension of the two-particle system,

$$\boldsymbol{A}(\boldsymbol{x}_1,t) \simeq \boldsymbol{A}(\boldsymbol{x}_2,t) \simeq \boldsymbol{A}(\boldsymbol{R},t). \tag{18.51}$$

This yields an effective Hamiltonian

$$H = \frac{1}{2M}\left(\mathbf{P} - Q\boldsymbol{A}(\mathbf{R},t)\right)^2 + \frac{1}{2\mu}\left(\mathbf{p} - q\boldsymbol{A}(\mathbf{R},t)\right)^2 + V(|\mathbf{r}|), \tag{18.52}$$

with the total charge $Q = q_1 + q_2$ in the kinetic term for center of mass motion, and a reduced charge in the quasiparticle kinetic term,

$$q = \frac{m_2q_1 - m_1q_2}{m_1 + m_2}, \tag{18.53}$$

with inversions

$$q_1 = \frac{m_1}{M}Q + q, \quad q_2 = \frac{m_2}{M}Q - q.$$

The equations of motion of the classical two-particle system are in the approximations $\boldsymbol{B}(\boldsymbol{x}_1,t) \simeq \boldsymbol{B}(\boldsymbol{x}_2,t) \simeq \boldsymbol{B}(\boldsymbol{R},t)$, (same for $\boldsymbol{E}$) given by

$$M\ddot{\boldsymbol{R}} = (Q\dot{\boldsymbol{R}} + q\dot{\boldsymbol{r}}) \times \boldsymbol{B} + Q\boldsymbol{E}, \tag{18.54}$$

$$\mu\ddot{\boldsymbol{r}} = \left(q\dot{\boldsymbol{R}} + \frac{\mu Q + \sqrt{M(M-4\mu)}q}{M}\dot{\boldsymbol{r}}\right) \times \boldsymbol{B} + q\boldsymbol{E} - \frac{\partial V}{\partial \boldsymbol{r}}. \tag{18.55}$$

Even the simplifying assumption (18.51) does not allow for separation of the center of mass motion any more, and the equations do not separate in terms of center of mass and relative coordinates, nor in total and reduced masses or charges. However, equations (18.54, 18.55) show that the coupling of photons to the center of mass motion is suppressed with inverse total mass. Therefore the impact of the photons on the relative motion dominates over the impact on center of mass motion, and in leading order we are left with an effective single-particle Hamiltonian for the relative motion in the center of mass frame,

$$H = \frac{1}{2\mu}\left(\mathbf{p} - q\boldsymbol{A}(t)\right)^2 + V(|\mathbf{r}|). \tag{18.56}$$

The corresponding statement at the classical level (18.54, 18.55) is that in leading order of μ/M, the center of mass frame is preserved and we have an effective single particle problem for relative motion,

$$\mu\ddot{\boldsymbol{r}} = q\dot{\boldsymbol{r}} \times \boldsymbol{B} + q\boldsymbol{E} - \frac{\partial V}{\partial \boldsymbol{r}}.$$

Equation (18.53) for the effective charge q yields $q = q_1$ if $q_2 = -q_1$, and $m_2 \gg m_1$ also implies $q \simeq q_1$. This entails that in atoms or molecules, we can think of photons as effectively coupling to the electrons if the photon wavelengths hc/E_γ are large compared to the size of the atoms or molecules. An alternative justification of using effective single particle Hamiltonians like (18.56) for photon interactions with bound systems is therefore also to discard the contribution for the heavier particle with mass m_2 in the original two-particle Hamiltonian (18.49), but still assume the bound states $|n, \ell, m_\ell\rangle$ which were derived for the relative motion $\boldsymbol{r} = \boldsymbol{x}_1 - \boldsymbol{x}_2$ to hold for the coordinate $\boldsymbol{x}_1$ of the lighter particle. This is an equivalent approximation up to correction terms of the same order $m_1/m_2 \simeq \mu/M$. However, the approximation clearly becomes invalid if transitions for the lighter particles are prohibited either by selection rules or by absence of suitable energy levels.

The derivation of (18.56) required negligible spatial variation of the photon terms over the extension of the unperturbed wave functions for relative motion, to justify minimal photon coupling into the Hamiltonian for relative motion. Dipole approximation and minimal electromagnetic coupling to the Hamiltonian for relative motion in a bound system therefore use the same premise.

18.5 Energy-momentum densities and time evolution in quantum optics

Further discussions of photon-matter interactions and of time evolution of the quantized Maxwell field require the Hamiltonian and momentum operators for coupled electromagnetic and matter fields. The study of electromagnetic interactions with non-relativistic matter fields is the domain of quantum optics or quantum electronics.

A Lagrange density for coupled electromagnetic and non-relativistic matter fields is

$$\begin{aligned}\mathcal{L} = \sum_a \Bigg[& \frac{\mathrm{i}\hbar}{2}\left(\Psi_a^+ \cdot \frac{\partial \Psi_a}{\partial t} - \frac{\partial \Psi_a^+}{\partial t} \cdot \Psi_a\right) - q_a \Psi_a^+ \Phi \Psi_a - \frac{\hbar^2}{2m_a} \boldsymbol{\nabla}\Psi_a^+ \cdot \boldsymbol{\nabla}\Psi_a \\ & - \mathrm{i}\frac{q_a \hbar}{2m_a} \boldsymbol{A} \cdot \left(\Psi_a^+ \overset{\leftrightarrow}{\boldsymbol{\nabla}} \Psi_a\right) - \frac{q_a^2}{2m_a} \Psi_a^+ \boldsymbol{A}^2 \Psi_a \Bigg] - \frac{1}{4\mu_0} F_{\mu\nu} F^{\mu\nu}.\end{aligned} \tag{18.57}$$

Here $\Phi = -cA_0$ is the electric potential, and we use the definition of an alternating derivative operator $\psi^+ \overset{\leftrightarrow}{\nabla} \psi \equiv \psi^+ \cdot \nabla\psi - \nabla\psi^+ \cdot \psi$.

The summation over a refers to different kinds of non-relativistic particles (e.g. electrons, protons etc.), and a summation over spin labels is implicitly understood.

Phase invariance yields the electric charge and current densities

$$\varrho = j^0/c = \sum_a q_a \Psi_a^+ \Psi_a, \tag{18.58}$$

$$\boldsymbol{j} = \sum_a \frac{q_a}{2\mathrm{i}m_a}\left(\hbar\Psi_a^+ \overset{\leftrightarrow}{\nabla} \Psi_a - 2\mathrm{i}q_a\Psi_a^+\boldsymbol{A}\Psi_a\right). \tag{18.59}$$

Like the energy-momentum tensor (18.30), the canonical energy-momentum tensor following from the Lagrange density (18.57) according to the general result (16.16),

$$\Theta_\mu{}^\nu = \eta_\mu{}^\nu\mathcal{L} + \frac{1}{\mu_0}\partial_\mu A_\lambda \cdot F^{\nu\lambda} - \sum_a\left(\partial_\mu\Psi_a\frac{\partial\mathcal{L}}{\partial(\partial_\nu\Psi_a)} + \partial_\mu\Psi_a^+\frac{\partial\mathcal{L}}{\partial(\partial_\nu\Psi_a^+)}\right),$$

is not gauge invariant. Just like in the case of the free Maxwell field, we can cure this by adding the trivially conserved tensor

$$\delta\Theta_\mu{}^\nu = -\frac{1}{\mu_0}\partial_\lambda(A_\mu F^{\nu\lambda}) = -A_\mu j^\nu - \frac{1}{\mu_0}\partial_\lambda A_\mu \cdot F^{\nu\lambda}, \quad \partial_\nu\delta\Theta_\mu{}^\nu \equiv 0.$$

The improved energy-momentum tensor $t_\mu{}^\nu = \Theta_\mu{}^\nu + \delta\Theta_\mu{}^\nu$ yields in particular the gauge invariant energy density for quantum optics,

$$\begin{aligned}\mathcal{H} = -t_0{}^0 = \frac{\epsilon_0}{2}\boldsymbol{E}^2 + \frac{1}{2\mu_0}\boldsymbol{B}^2 + \sum_a\frac{1}{2m_a}\Big[\hbar^2\nabla\Psi_a^+\cdot\nabla\Psi_a \\ + \mathrm{i}q_a\hbar\boldsymbol{A}\cdot\left(\Psi_a^+ \overset{\leftrightarrow}{\nabla} \Psi_a\right) + q_a^2\Psi_a^+\boldsymbol{A}^2\Psi_a\Big],\end{aligned} \tag{18.60}$$

and the gauge invariant momentum density,

$$\mathcal{P} = \frac{1}{c}t_i^0\boldsymbol{e}_i = \epsilon_0\boldsymbol{E}\times\boldsymbol{B} + \frac{1}{2\mathrm{i}}\sum_a\left(\hbar\Psi_a^+ \overset{\leftrightarrow}{\nabla} \Psi_a - 2\mathrm{i}q_a\Psi_a^+\boldsymbol{A}\Psi_a\right). \tag{18.61}$$

In materials science it is convenient to explicitly disentangle the contributions from Coulomb and photon terms in Coulomb gauge $\nabla\cdot\boldsymbol{A} = 0$. We split the electric field components in Coulomb gauge according to

$$\boldsymbol{E}_\parallel = -\nabla\Phi \tag{18.62}$$

and

$$\boldsymbol{E}_\perp = -\frac{\partial\boldsymbol{A}}{\partial t}. \tag{18.63}$$

The equation for the electrostatic potential decouples from the vector potential,

$$\Delta\Phi = -\frac{1}{\epsilon_0}\sum_a q_a \Psi_a^+ \Psi_a,$$

and is solved by

$$\Phi(\boldsymbol{x},t) = \frac{1}{4\pi\epsilon_0}\int d^3\boldsymbol{x}' \sum_a \frac{q_a}{|\boldsymbol{x}-\boldsymbol{x}'|}\Psi_a^+(\boldsymbol{x}',t)\Psi_a(\boldsymbol{x}',t).$$

Furthermore, the two components of the electric field are orthogonal in the Coulomb gauge,

$$\begin{aligned}\int d^3\boldsymbol{x}\,\boldsymbol{E}_\parallel(\boldsymbol{x},t)\cdot\boldsymbol{E}_\perp(\boldsymbol{x},t) &= \int d^3\boldsymbol{k}\,\boldsymbol{E}_\parallel(\boldsymbol{k},t)\cdot\boldsymbol{E}_\perp(-\boldsymbol{k},t)\\ &= -\int d^3\boldsymbol{x}\,\Phi(\boldsymbol{x},t)\frac{\partial}{\partial t}\nabla\cdot\boldsymbol{A}(\boldsymbol{x},t) = 0, \qquad (18.64)\end{aligned}$$

and the contribution from $\boldsymbol{E}_\parallel$ to the Hamiltonian generates the Coulomb potentials

$$\begin{aligned}H_C &= \frac{\epsilon_0}{2}\int d^3\boldsymbol{x}\,\boldsymbol{E}_\parallel^2(\boldsymbol{x},t) = -\frac{\epsilon_0}{2}\int d^3\boldsymbol{x}\,\Phi(\boldsymbol{x},t)\Delta\Phi(\boldsymbol{x},t)\\ &= \frac{1}{2}\int d^3\boldsymbol{x}\,\Phi(\boldsymbol{x},t)\varrho(\boldsymbol{x},t)\\ &= \sum_{aa'}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,q_a q_{a'}\frac{\Psi_a^+(\boldsymbol{x},t)\Psi_{a'}^+(\boldsymbol{x}',t)\Psi_{a'}(\boldsymbol{x}',t)\Psi_a(\boldsymbol{x},t)}{8\pi\epsilon_0|\boldsymbol{x}-\boldsymbol{x}'|}, \qquad (18.65)\end{aligned}$$

where the ordering of the field operators was performed to ensure correct expectation values for the interaction energy of 2-particle states after second quantization. The summation may also implicitly include spinor indices.

The resulting Hamiltonian in Coulomb gauge therefore has the form

$$\begin{aligned}H = \int d^3\boldsymbol{x}\,\Bigg(&\sum_a \frac{1}{2m_a}\Big[\hbar^2\nabla\Psi_a^+(\boldsymbol{x},t)\cdot\nabla\Psi_a(\boldsymbol{x},t)\\ &+ \mathrm{i}q_a\hbar\boldsymbol{A}(\boldsymbol{x},t)\cdot\Big(\Psi_a^+(\boldsymbol{x},t)\overset{\leftrightarrow}{\nabla}\Psi_a(\boldsymbol{x},t)\Big) + q_a^2\Psi_a^+(\boldsymbol{x},t)\boldsymbol{A}^2(\boldsymbol{x},t)\Psi_a(\boldsymbol{x},t)\Big]\\ &+ \frac{\epsilon_0}{2}\boldsymbol{E}_\perp^2(\boldsymbol{x},t) + \frac{1}{2\mu_0}\boldsymbol{B}^2(\boldsymbol{x},t)\Bigg)\\ &+ \sum_{aa'}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,q_a q_{a'}\frac{\Psi_a^+(\boldsymbol{x},t)\Psi_{a'}^+(\boldsymbol{x}',t)\Psi_{a'}(\boldsymbol{x}',t)\Psi_a(\boldsymbol{x},t)}{8\pi\epsilon_0|\boldsymbol{x}-\boldsymbol{x}'|}.\end{aligned}$$

(18.66)

The momentum operator in Coulomb gauge follows from (18.61) and

$$\int d^3\boldsymbol{x}\,\epsilon_0\boldsymbol{E}_\parallel\times\boldsymbol{B}=-\int d^3\boldsymbol{x}\,\epsilon_0\Phi\Delta\boldsymbol{A}=\int d^3\boldsymbol{x}\,\varrho\boldsymbol{A}=\int d^3\boldsymbol{x}\sum_a q_a\Psi_a^+\boldsymbol{A}\Psi_a$$

as

$$\boldsymbol{P}=\int d^3\boldsymbol{x}\left(\frac{\hbar}{\mathrm{i}}\sum_a\Psi_a^+\nabla\Psi_a+\epsilon_0\boldsymbol{E}_\perp\times\boldsymbol{B}\right). \tag{18.67}$$

Recall that Heisenberg or Schrödinger picture field operators satisfy the same canonical commutation relations as the Dirac picture operators because the quantum pictures are related by unitary transformations. For the vector potential $\boldsymbol{A}(\boldsymbol{x},t)$ in Coulomb gauge this implies the same commutation relations (18.36, 18.39) as for the Dirac picture vector potential. The Hamiltonian (18.66) then yields the Schrödinger equations for the matter fields from

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{x},t)=[\Psi(\boldsymbol{x},t),H], \tag{18.68}$$

and the electromagnetic wave equation in Coulomb gauge (18.10) from

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\boldsymbol{A}(\boldsymbol{x},t)=[\boldsymbol{A}(\boldsymbol{x},t),H],\quad\frac{\partial^2}{\partial t^2}\boldsymbol{A}(\boldsymbol{x},t)=\frac{1}{\hbar^2}[H,[\boldsymbol{A}(\boldsymbol{x},t),H]]. \tag{18.69}$$

These relations imply that also after quantization of the Maxwell field, field operators in the Heisenberg and Schrödinger pictures are still related according to

$$\boldsymbol{A}(\boldsymbol{x},t)=\exp(\mathrm{i}Ht/\hbar)\boldsymbol{A}(\boldsymbol{x})\exp(-\mathrm{i}Ht/\hbar), \tag{18.70}$$

and the derivation of scattering matrix elements with the automatic emergence of the interaction picture proceeds exactly as in the previous cases of quantum mechanics and non-relativistic quantum field theory,

$$S_{fi}=\langle f|U_D(\infty,-\infty)|i\rangle, \tag{18.71}$$

$$\begin{aligned}U_D(t,t')&=\exp\left(\frac{\mathrm{i}}{\hbar}H_0t\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0t'\right)\\&=\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau\,H_D(\tau)\right),\end{aligned} \tag{18.72}$$

$$H_D(t)=\exp\left(\frac{\mathrm{i}}{\hbar}H_0t\right)V\exp\left(-\frac{\mathrm{i}}{\hbar}H_0t\right), \tag{18.73}$$

where the identification of $H_0 = H - V$ depends on what part of H we can solve and what part we wish to take into account through perturbation theory. I.e. we find the same basic structure of time-dependent perturbation theory in terms of Hamilton operators also after introduction of the relativistic photon operators. We will see in Chapters 21 and 22 that this property persists in general in quantum field theory also after introduction of other relativistic field operators.

18.6 Photon emission rates

The calculation of transition probabilities between Fock states requires time-dependent perturbation theory in the second quantized formalism.

The relevant part of the Hamiltonian (18.66) for a coupled system of non-relativistic charged particles and photons is

$$\begin{aligned} H &= H_0 + H_I + H_{II} \\ &= \int d^3\boldsymbol{x} \left(\frac{\hbar^2}{2m} \sum_\sigma \nabla\psi_\sigma^+ \cdot \nabla\psi_\sigma + \sum_\sigma \psi_\sigma^+ V \psi_\sigma + \frac{\epsilon_0}{2} \dot{\boldsymbol{A}}^2 + \frac{1}{2\mu_0} (\nabla \times \boldsymbol{A})^2 \right. \\ &\quad \left. + \mathrm{i}\frac{q\hbar}{2m} \boldsymbol{A} \cdot \sum_\sigma \left(\psi_\sigma^+ \overset{\leftrightarrow}{\nabla} \psi_\sigma \right) + \frac{q^2}{2m} \sum_\sigma \psi_\sigma^+ \boldsymbol{A}^2 \psi_\sigma \right), \end{aligned} \tag{18.74}$$

where V is an intra-atomic or intra-molecular potential and the interaction terms between the charged particles and the photons are

$$H_I = \int d^3\boldsymbol{x} \sum_\sigma \mathrm{i}\frac{q\hbar}{2m} \boldsymbol{A} \cdot \left(\psi_\sigma^+ \overset{\leftrightarrow}{\nabla} \psi_\sigma \right), \quad H_{II} = \int d^3\boldsymbol{x}\, \frac{q^2}{2m} \sum_\sigma \psi_\sigma^+ \boldsymbol{A}^2 \psi_\sigma.$$

Here we explicitly included the spin summations and wrote the Hamiltonian in terms of the Schrödinger picture field operators ($\dot{\boldsymbol{A}}(\boldsymbol{x}) \equiv \dot{\boldsymbol{A}}(\boldsymbol{x}, 0)$). In principle there is also the electrostatic repulsion between the particles,

$$H_C = \frac{q^2}{8\pi\epsilon_0} \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \sum_{\sigma,\sigma'} \psi_\sigma^+(\boldsymbol{x}) \psi_{\sigma'}^+(\boldsymbol{x}') \frac{1}{|\boldsymbol{x} - \boldsymbol{x}'|} \psi_{\sigma'}(\boldsymbol{x}') \psi_\sigma(\boldsymbol{x}).$$

However, we will only study transitions with single matter particles in the initial state, where H_C will not contribute.

For the following calculations we use hydrogen states as an example to illustrate the method, and we use $\psi_\sigma(\boldsymbol{x})$ and $\psi_\sigma^+(\boldsymbol{x})$ as the Schrödinger picture field operators of the effective quasiparticle which describes relative motion of the proton and electron in the atom,

$$\begin{aligned}|n,\ell,m_\ell,\sigma;t'\rangle &= |\Psi_{n,\ell,m_\ell,\sigma}(t')\rangle = \int d^3\boldsymbol{x}\,\Psi_{n,\ell,m_\ell}(\boldsymbol{x},t')\psi_\sigma^+(\boldsymbol{x})|0\rangle \\ &= \exp(-\mathrm{i}E_{n,\ell}t'/\hbar)\int d^3\boldsymbol{x}\,\Psi_{n,\ell,m_\ell}(\boldsymbol{x})\psi_\sigma^+(\boldsymbol{x})|0\rangle \\ &= \int d^3\boldsymbol{x}\,\Psi_{n,\ell,m_\ell}(\boldsymbol{x})\exp(-\mathrm{i}H_0t'/\hbar)\psi_\sigma^+(\boldsymbol{x})|0\rangle, \qquad (18.75)\end{aligned}$$

i.e. $\psi_\sigma(\boldsymbol{x})$ and $\psi_\sigma^+(\boldsymbol{x})$ are the Schrödinger picture field operators which arise from quantization of the wave function $\langle\boldsymbol{x},\sigma|\Psi(t)\rangle$ in Schrödinger's wave mechanics. See Problem 18.7 for the question why the state (18.75) is an eigenstate of H_0.

According to our results from Section 18.4, the Hamiltonian (18.74) includes an approximation if we use it for coupling the electromagnetic potential to the hydrogen atom, because we introduced the photon operators through minimal coupling into the effective single particle problem that resulted from separation of the center of mass motion. This is a good approximation if the electromagnetic potentials vary only weakly over the size of the atom, $\boldsymbol{A}(\boldsymbol{x}_p,t)\simeq\boldsymbol{A}(\boldsymbol{x}_e,t)$. Indeed, it is an excellent approximation for the study of transitions between bound hydrogen states, because in these cases $\lambda > hc/13.6\,\mathrm{eV} = 91\,\mathrm{nm}$.

We wish to calculate the photon emission rate, i.e. the transition rate from the initial state (18.75) into a final state with the electron in another atomic state and a photon with momentum $\hbar\boldsymbol{k}$ and polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$,

$$\begin{aligned}|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha;t\rangle &= \int d^3\boldsymbol{x}\,\Psi_{n',\ell',m'_\ell}(\boldsymbol{x})\exp(-\mathrm{i}H_0t/\hbar)\psi_{\sigma'}^+(\boldsymbol{x})a_\alpha^+(\boldsymbol{k})|0\rangle \\ &= \exp\!\left[-\mathrm{i}\left(\frac{E_{n',\ell'}}{\hbar}+ck\right)t\right]\int d^3\boldsymbol{x}\,\Psi_{n',\ell',m'_\ell}(\boldsymbol{x})\psi_{\sigma'}^+(\boldsymbol{x})a_\alpha^+(\boldsymbol{k})|0\rangle. \qquad (18.76)\end{aligned}$$

The relevant transition matrix elements for photon emission between t' and t are

$$\begin{aligned}S_{fi}(t,t') &\equiv S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma}(t,t') \\ &= \langle n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha;t|\exp\!\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)|n,\ell,m_\ell,\sigma;t'\rangle \\ &= \langle n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|\mathrm{T}\exp\!\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau H_D(\tau)\right)|n,\ell,m_\ell,\sigma\rangle,\end{aligned}$$

where

$$H_D(\tau) = \exp\!\left(\frac{\mathrm{i}}{\hbar}H_0\tau\right)(H_I+H_{II})\exp\!\left(-\frac{\mathrm{i}}{\hbar}H_0\tau\right)$$

is the time evolution operator on the states in the interaction picture.

The scattering matrix element is in leading order

$$S_{fi} = S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma} = \langle n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|U_D(\infty,-\infty)|n,\ell,m_\ell,\sigma;0\rangle$$

$$\simeq \frac{1}{\mathrm{i}\hbar}\int_{-\infty}^{\infty} dt\, \exp\left[\mathrm{i}(\omega_{n',\ell';n,\ell}+ck)t\right]\langle n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|$$
$$\times\int d^3\boldsymbol{x}\sum_\nu \frac{\mathrm{i}q\hbar}{2m}\boldsymbol{A}(\boldsymbol{x})\cdot\left(\psi_\nu^+(\boldsymbol{x})\overset{\leftrightarrow}{\nabla}\psi_\nu(\boldsymbol{x})\right)|n,\ell,m_\ell,\sigma;0\rangle \qquad (18.77)$$

with the field operators in the Schrödinger picture. We also took into account that the energy levels are ℓ dependent through fine structure. At this stage we are still using $\boldsymbol{A}(\boldsymbol{x})$, although our reasoning in Section 18.4 already indicated that any $\boldsymbol{x}$ dependence in $\boldsymbol{A}(\boldsymbol{x})$ must be negligible to justify minimal photon coupling into the effective Hamiltonian for relative motion in the atom. We will return to this point below.

Substitution of the mode expansion (18.21) for the photon operator and evaluation of the second quantized matrix element transforms the transition matrix element for photon emission into a matrix element of first quantized theory,

$$S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma} \simeq 2\pi\delta(\omega_{n',\ell';n,\ell}+ck)\frac{\mathrm{i}q}{m\hbar}\sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\delta_{\sigma\sigma'}$$
$$\times\langle n',\ell',m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{p}\exp(-\mathrm{i}\boldsymbol{k}\cdot\mathbf{x})|n,\ell,m_\ell\rangle. \qquad (18.78)$$

The operators $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{p}$ and $\boldsymbol{k}\cdot\mathbf{x}$ commute, whence we do not encounter a normal ordering problem in the first quantized matrix element.

Equation (18.78) can be interpreted as a first quantized matrix element of the perturbation operator

$$V(t) = -\frac{q}{2m}\left(\mathbf{p}\cdot\boldsymbol{A}(\mathbf{x},t)+\boldsymbol{A}(\mathbf{x},t)\cdot\mathbf{p}\right), \qquad (18.79)$$

which contains an operator corresponding to a classical transversely polarized plane wave

$$\boldsymbol{A}_\alpha^{(+)}(\boldsymbol{x},t) = \sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]. \qquad (18.80)$$

This classical plane wave apparently represents a single *emitted* photon of sharp energy $\hbar ck$ and momentum $\hbar\boldsymbol{k}$, and second quantization helped us to determine both the proper amplitude for the single photon wave and the $\boldsymbol{k}$-dependent term in the transition matrix element. The corresponding calculation for *absorption* of a photon yields a first quantized matrix element of the perturbation operator (18.79) with a single photon vector potential

$$\boldsymbol{A}_\alpha^{(-)}(\boldsymbol{x},t) = \sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)], \qquad (18.81)$$

see equation (18.93).

We can understand the amplitudes of the single photon wave functions (18.80) and (18.81) in the following way: The mode expansion (18.21) becomes in finite volume V

$$\boldsymbol{A}(\boldsymbol{x},t) = \sqrt{\frac{\hbar\mu_0 c}{V}}\sum_{\boldsymbol{k}}\sum_{\alpha=1}^{2}\frac{\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})}{\sqrt{2k}}\Big(a_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)] + a_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\Big), \tag{18.82}$$

and the corresponding energy and momentum operators[2] are

$$H = \sum_{\boldsymbol{k}}\sum_{\alpha}\hbar ck\, a_\alpha^+(\boldsymbol{k})a_\alpha(\boldsymbol{k}), \quad \boldsymbol{P} = \sum_{\boldsymbol{k}}\sum_{\alpha}\hbar\boldsymbol{k}\, a_\alpha^+(\boldsymbol{k})a_\alpha(\boldsymbol{k}).$$

These equations tell us for a classical amplitude $a_\alpha(\boldsymbol{k})$ that this amplitude would (up to an arbitrary phase φ) have to be a Kronecker δ with respect to momentum and polarization to represent a single photon of momentum $\hbar\boldsymbol{k}$, energy $\hbar ck$ and polarization $\boldsymbol{\epsilon}_\alpha$, and therefore the classical vector potential for the single photon in the continuum limit $V \to 8\pi^3$ is

$$\begin{aligned}\boldsymbol{A}_{\gamma,\boldsymbol{k},\alpha}(\boldsymbol{x},t) &= \sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\Big(\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt+\varphi)] + \exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt+\varphi)]\Big)\\ &= 2\sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cos(\boldsymbol{k}\cdot\boldsymbol{x}-ckt+\varphi).\end{aligned} \tag{18.83}$$

Note however that for emission only the plane wave with $\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x} - ckt + \varphi)]$ contributes to the transition matrix element, whereas for absorption only the other term contributes.

The vector potential in box normalization (18.82) does have the expected units Vs/m, whereas the continuum limit vector potentials (18.21, 18.83) come in units of $\mathrm{m}^{3/2}$Vs/m. This is related to the fact that their transition matrix elements squared yield transition probability densities per volume unit $d^3\boldsymbol{k}$ in the photon state space, see e.g. equation (18.84) below. It is the same effect that we encountered in scattering theory for momentum eigenstates $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})/V^{1/2}$ in box normalization or $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})/(2\pi)^{3/2}$ in the continuum limit.

---

[2] Classically these equations would hold for time averages.

Evaluation of the transition matrix element in the dipole approximation

We have already emphasized that the coupling of the electromagnetic potentials to the effective single particle model for relative motion in atoms assumes a long wavelength approximation in the sense $\boldsymbol{A}(\boldsymbol{x}_p, t) \simeq \boldsymbol{A}(\boldsymbol{x}_e, t)$, see equations (18.51) and (18.56). Therefore the exponential factor $\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})$ must effectively be constant over the extension of the atomic wave functions and can be replaced by $\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \simeq 1$. For an estimate of the product $|\boldsymbol{k}\cdot\boldsymbol{x}|$, we recall that the energy of the emitted photon from an excited bound state cannot exceed the binding energy of hydrogen,

$$\frac{hc}{\lambda} < -E_1 = \frac{e^2}{8\pi\epsilon_0 a_0} = \frac{hc\alpha}{4\pi a_0},$$

and therefore

$$\lambda > \frac{4\pi}{\alpha}a_0 \simeq 1.72 \times 10^3 a_0, \quad ka_0 < \frac{\alpha}{2} \simeq 3.65 \times 10^{-3}.$$

This confirms that the exponential factor will be approximately constant over the extension of the wave functions,

$$\langle n', \ell', m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{p}\exp(-\mathrm{i}\boldsymbol{k}\cdot\mathbf{x})|n, \ell, m_\ell\rangle \approx \langle n', \ell', m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{p}|n, \ell, m_\ell\rangle.$$

The matrix element of the momentum operator between energy eigenstates is usually converted into matrix elements of the position operator $\mathbf{x}$ using the first quantized Hamiltonian $H_0 = (\mathbf{p}^2/2m) + V(\mathbf{x})$ and the relation

$$[H_0, \mathbf{x}] = \frac{\hbar}{\mathrm{i}m}\mathbf{p}.$$

This implies

$$\begin{aligned}\langle n', \ell', m'_\ell|\mathbf{p}|n, \ell, m_\ell\rangle &= \mathrm{i}\frac{m}{\hbar}\langle n', \ell', m'_\ell|[H_0, \mathbf{x}]|n, \ell, m_\ell\rangle \\ &= \mathrm{i}m\omega_{n',\ell';n,\ell}\langle n', \ell', m'_\ell|\mathbf{x}|n, \ell, m_\ell\rangle,\end{aligned}$$

where $\hbar\omega_{n',\ell';n,\ell} = E_{n',\ell'} - E_{n,\ell}$. In the case of emission we have $\omega_{n',\ell';n,\ell} < 0$. The transition matrix element (18.78) therefore becomes

$$\begin{aligned}S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma} \simeq &-2\pi\delta(\omega_{n',\ell';n,\ell} + ck)q\sqrt{\frac{\mu_0 c}{16\pi^3\hbar k}}\delta_{\sigma\sigma'}\omega_{n',\ell';n,\ell} \\ &\times\langle n', \ell', m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n, \ell, m_\ell\rangle\end{aligned}$$

$$
\begin{aligned}
&= \delta(\omega_{n',\ell';n,\ell} + ck)q\sqrt{\frac{\mu_0 c^3 k}{4\pi\hbar}}\delta_{\sigma\sigma'} \\
&\quad\times\langle n',\ell',m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n,\ell,m_\ell\rangle.
\end{aligned}
$$

The differential emission rate into a momentum volume element $d^3\boldsymbol{k}$ around $\boldsymbol{k}$ of a photon of polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ is then with $q = -e$, $\delta(0) \to T/2\pi$,

$$
\begin{aligned}
d\Gamma^{(\alpha)}(\boldsymbol{k})_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} &= d^3\boldsymbol{k}\frac{\left|S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma}\right|^2}{T} \\
&\simeq \frac{\mu_0 c^3 e^2}{8\pi^2\hbar}k\delta_{\sigma\sigma'}\left|\langle n',\ell',m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n,\ell,m_\ell\rangle\right|^2\delta(\omega_{n,\ell;n',\ell'} - ck)d^3\boldsymbol{k},
\end{aligned}
\tag{18.84}
$$

or after integration over the wave number k of the emitted photon,

$$
\begin{aligned}
\frac{d\Gamma^{(\alpha)}(\hat{\boldsymbol{k}})_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'}}{d\Omega} &= \frac{\mu_0 e^2}{8\pi^2\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'} \\
&\quad\times\left|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle\right|^2.
\end{aligned}
\tag{18.85}
$$

Note that if we would have tried to calculate this only within a semi-classical first quantized theory for the monochromatic perturbation (18.79, 18.80), the δ function in energy and the units of the transition matrix element would have tempted us to introduce a density $\varrho(E_{n'})$ of final hydrogen states per energy, similar to the Golden Rule for transitions into a continuum. This factor would then have appeared instead of the factor[3] $\delta(E_n - E_{n'} - \hbar ck)d^3\boldsymbol{k}$ in (18.84). Indeed, we do have a transition into a continuum of final *photon* states, but the semi-classical approximation would have missed that and naive application of the Golden Rule would have tempted us to include a wrong factor with an unjustified interpretation, see also Problem 18.11.

As a consequence of the φ dependence of the spherical harmonics, the vector

$$
\begin{aligned}
\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle &= \langle n',\ell',m'_\ell|r\sin\vartheta\cos\varphi|n,\ell,m_\ell\rangle\boldsymbol{e}_x \\
&\quad+\langle n',\ell',m'_\ell|r\sin\vartheta\sin\varphi|n,\ell,m_\ell\rangle\boldsymbol{e}_y + \langle n',\ell',m'_\ell|r\cos\vartheta|n,\ell,m_\ell\rangle\boldsymbol{e}_z
\end{aligned}
$$

has real x and z components and an imaginary y component. We know already from the dipole selection rules from Section 15.1 that the z component $\langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle$ is only different from 0 if $\Delta m_\ell = m'_\ell - m_\ell = 0$, while the x and y components are only different from 0 if $\Delta m_\ell = \pm 1$.

The different conjugation properties and selection rules imply

---

[3] Recall that densities of states $\varrho(E) \sim k^2 dk/dE$ in the $V \to \infty$ limit have units of $\mathrm{cm}^{-3}\mathrm{eV}^{-1}$, see the remark after equation (12.8).

$$
\begin{aligned}
\left|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle\right|^2 &= \Big(\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\big[\langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x \\
&\quad - \langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y + \langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle\boldsymbol{e}_z\big]\Big) \\
&\quad \times\Big(\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\big[\langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x + \langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y \\
&\quad + \langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle\boldsymbol{e}_z\big]\Big) \\
&= \big[\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x\big]^2 + \big[\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle\boldsymbol{e}_z\big]^2 \\
&\quad + \big[\mathrm{i}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y\big]^2 .
\end{aligned}
$$

This cannot be directly associated with an angle between the polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ and one of the real vectors

$$
\begin{aligned}
\langle n',\ell',m'_\ell|\mathbf{x}_\pm|n,\ell,m_\ell\rangle &= \langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x \pm \mathrm{i}\langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y \\
&\quad + \langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle\boldsymbol{e}_z
\end{aligned}
$$

because of missing cross terms of the form

$$
\pm 2\big[\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x\big]\big[\mathrm{i}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y\big].
$$

However, we can write

$$
\begin{aligned}
\left|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle\right|^2 &= \frac{1}{2}\left|\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle\right|^2 \\
&\quad \times\left(\cos^2\theta_{\alpha,-} + \cos^2\theta_{\alpha,+}\right)
\end{aligned}
$$

where $\theta_{\alpha,-}$ and $\theta_{\alpha,+}$ are the angles between the polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ and the real vectors $\langle n',\ell',m'_\ell|\mathbf{x}_-|n,\ell,m_\ell\rangle$ and $\langle n',\ell',m'_\ell|\mathbf{x}_+|n,\ell,m_\ell\rangle$, respectively.

This yields a differential emission rate

$$
\begin{aligned}
d\Gamma^{(\alpha)}(\hat{\boldsymbol{k}})_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} &= \frac{\mu_0 e^2}{8\pi^2\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'}\left|\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle\right|^2 \\
&\quad \times\frac{\cos^2\theta_{\alpha,-} + \cos^2\theta_{\alpha,+}}{2}\,d\Omega. \qquad (18.86)
\end{aligned}
$$

The solid angle element $d\Omega = \sin\vartheta\, d\vartheta d\varphi$ measures the direction of the emission vector $\boldsymbol{k}$ and the calculation of the total polarized emission rate $\Gamma^{(\alpha)}_{n,\ell,m_\ell\to n',\ell',m'_\ell}$ requires integration over $d\Omega$. We can do that e.g. by evaluating the angles $\theta_{\alpha,\pm}$ in terms of the angles $\{\vartheta_\alpha,\varphi_\alpha\}$ of the vector $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ and the angles $\{\vartheta_\pm,\varphi_\pm\}$ of the vectors $\langle n',\ell',m'_\ell|\mathbf{x}_\pm|n,\ell,m_\ell\rangle$. However, a faster way is to choose in each of the two terms the respective angle $\theta_{\alpha,\pm}$ and a corresponding azimuthal angle $\phi_{\alpha,\pm}$ as integration variables. This reduces the calculation of the angular integrals to

$$
\int_0^{2\pi} d\phi_{\alpha,\pm}\int_0^{\pi} d\theta_{\alpha,\pm}\,\sin\theta_{\alpha,\pm}\,\cos^2\theta_{\alpha,\pm} = \frac{4\pi}{3}.
$$

The total emission rate for *polarized* photons is therefore

$$\Gamma^{(\alpha)}_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} = \frac{\mu_0 e^2}{6\pi\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'}\left|\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle\right|^2, \tag{18.87}$$

and the total unpolarized emission rate is

$$\Gamma_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} = \frac{\mu_0 e^2}{3\pi\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'}\left|\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle\right|^2. \tag{18.88}$$

The relation $\Gamma_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} = 2\Gamma^{(\alpha)}_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'}$ follows at a more formal level from the fact that

$$\sum_{\alpha=1}^{2}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\otimes\boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) = \underline{1} - \hat{\boldsymbol{k}}\otimes\hat{\boldsymbol{k}}$$

is the projector onto the plane orthogonal to $\boldsymbol{k}$, and therefore

$$\sum_\alpha\left|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathbf{x}_\pm|n,\ell,m_\ell\rangle\right|^2 = \left|\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle\right|^2\sin^2\theta_\pm,$$

where $\theta_\pm$ are the angles between the wave vector $\boldsymbol{k}$ and the two real vectors $\langle n',\ell',m'_\ell|\mathbf{x}_\pm|n,\ell,m_\ell\rangle$. Therefore we find for the unpolarized differential emission rate

$$\begin{aligned} d\Gamma(\hat{\boldsymbol{k}})_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} = {} & \frac{\mu_0 e^2}{8\pi^2\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'}\left|\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle\right|^2 \\ & \times\frac{\sin^2\theta_- + \sin^2\theta_+}{2}\,d\Omega, \end{aligned} \tag{18.89}$$

and this time the angular integrals yield

$$\int_0^{2\pi}d\phi_\pm\int_0^\pi d\theta_\pm\,\sin^3\theta_\pm = \frac{8\pi}{3},$$

which implies the total emission rate (18.88).

We had to write the polarized and unpolarized differential emission rates (18.86) and (18.89) as averages over two real dipoles $-e\langle n',\ell',m'_\ell|\mathbf{x}_\pm|n,\ell,m_\ell\rangle$, where we used the dipole selection rules for hydrogen states. For general atomic or molecular states, all Cartesian components of $\langle f|\mathbf{x}|i\rangle$ may be complex, and we may have a sum of two dipoles of different magnitude,

$$\begin{aligned} |\boldsymbol{\epsilon}_\alpha\cdot\langle f|\mathbf{x}|i\rangle|^2 &= (\boldsymbol{\epsilon}_\alpha\cdot\Re\langle f|\mathbf{x}|i\rangle)^2 + (\boldsymbol{\epsilon}_\alpha\cdot\Im\langle f|\mathbf{x}|i\rangle)^2 \\ &= (\Re\langle f|\mathbf{x}|i\rangle)^2\cos^2\theta_{\alpha,1} + (\Im\langle f|\mathbf{x}|i\rangle)^2\cos^2\theta_{\alpha,2}, \end{aligned} \tag{18.90}$$

$$\sum_\alpha|\boldsymbol{\epsilon}_\alpha\cdot\langle f|\mathbf{x}|i\rangle|^2 = (\Re\langle f|\mathbf{x}|i\rangle)^2\sin^2\theta_1 + (\Im\langle f|\mathbf{x}|i\rangle)^2\sin^2\theta_2.$$

This yields the same results as (18.86) in a different parametrization. The difference between the construction in (18.86) and (18.90) is that we could construct two dipoles of the same magnitude $-e\left|\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle\right|$ in (18.86) and express the result as an average, whereas the generic construction (18.90) yields a sum of two dipoles of different magnitude.

Since we are observing photons of certain frequency with no regard to the particular transition which generated those photons, it is customary to sum the emission rate over degenerate final states and average over degenerate initial states. The emission rate per excited atom for photons with angular frequency $\omega_{n,\ell;n',\ell'}$ follows from (18.88) as

$$\begin{aligned}\Gamma_{n,\ell\to n',\ell'} &= \frac{1}{2\ell+1}\sum_{m_\ell=-\ell}^{\ell}\sum_{m'_\ell=-\ell'}^{\ell'}\Gamma_{n,\ell,m_\ell\to n',\ell',m'_\ell}\\ &= \frac{\mu_0 e^2}{2\pi mc}\omega^2_{n,\ell;n',\ell'}\left|f_{n',\ell'|n,\ell}\right|.\end{aligned} \qquad (18.91)$$

Here we have set $\sigma = \sigma'$ and omitted the spin indices, and we used the definition (15.29) of the averaged oscillator strength.

The quantity $\Gamma_{n,\ell\to n',\ell'} \equiv A_{n,\ell\to n',\ell'}$ provides a quantum mechanical expression for the Einstein A coefficient for spontaneous emission of photons. Einstein had introduced this coefficient in 1916 in his balance equations for the origin of the Planck spectrum.

We have seen that in leading order the relevant interaction Hamiltonian for photon emission or absorption is

$$H_I = \int d^3\boldsymbol{x}\sum_\sigma \mathrm{i}\frac{q\hbar}{2m}\boldsymbol{A}\cdot\left(\psi^+_\sigma \overset{\leftrightarrow}{\nabla}\psi_\sigma\right),$$

and in the Schrödinger picture this operator contains only time-independent field operators $\boldsymbol{A}(\boldsymbol{x})$, $\psi_\sigma(\boldsymbol{x})$.

Substitution of the mode expansions in terms of the momentum space operators yields (note $q \neq |\boldsymbol{q}|$ in the following equation):

$$\begin{aligned}H_I = &-\frac{q\hbar}{m}\sqrt{\frac{\hbar\mu_0 c}{(2\pi)^3}}\int\frac{d^3\boldsymbol{q}}{\sqrt{2|\boldsymbol{q}|}}\int d^3\boldsymbol{k}\sum_\sigma\sum_\alpha \boldsymbol{k}\cdot\epsilon_\alpha(\boldsymbol{q})\\ &\times\left(c^+_\sigma(\boldsymbol{k}+\boldsymbol{q})a_\alpha(\boldsymbol{q})c_\sigma(\boldsymbol{k}) + c^+_\sigma(\boldsymbol{k}-\boldsymbol{q})a^+_\alpha(\boldsymbol{q})c_\sigma(\boldsymbol{k})\right).\end{aligned} \qquad (18.92)$$

The representation of interaction Hamiltonians in terms of $c_\sigma(\boldsymbol{k})$, $c^+_\sigma(\boldsymbol{k})$ is useful for processes involving (quasi)free electrons, e.g. for the Compton effect ("free-free scattering") or for the discussion of electron-photon interactions in metals (assuming e.g. a jellium model for the electrons). However, for the discussion of emission or absorption from atomic or molecular bound states the $\boldsymbol{x}$-representation is more convenient.

18.7 Photon absorption

We will continue to use energy labels n and n' such that $E_n > E_{n'}$. Therefore the previously discussed transition $n \to n'$ involved photon emission, while the process $n' \to n$ involves photon absorption. Later on we will also compare emission and absorption rates, and it is desirable to make the distinction between emission and absorption rates more visible in the notation. Therefore we will denote absorption rates with the symbol $\tilde{\Gamma}$.

The leading order scattering matrix element for photon absorption due to a transition from a state $|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha\rangle$ to a state $|n,\ell,m_\ell,\sigma;0\rangle$,

$$S_{n,\ell,m_\ell,\sigma|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha} \simeq \frac{1}{\mathrm{i}\hbar}\int_{-\infty}^{\infty} dt\, \exp\left[\mathrm{i}(\omega_{n,\ell;n',\ell'} - ck)t\right]\mathrm{i}\frac{q\hbar}{2m}$$
$$\times\langle n,\ell,m_\ell,\sigma;0|\int d^3\boldsymbol{x}\sum_\nu \boldsymbol{A}(\boldsymbol{x})\cdot\left(\psi_\nu^+(\boldsymbol{x})\overset{\leftrightarrow}{\nabla}\psi_\nu(\boldsymbol{x})\right)|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha\rangle$$

is just the negative complex conjugate of the emission matrix element (18.77). The resulting scattering matrix element after evaluation of the field operators,

$$\begin{aligned} S_{n,\ell,m_\ell,\sigma|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha} &\simeq 2\pi\delta(\omega_{n,\ell;n',\ell'} - ck)\frac{\mathrm{i}q}{m\hbar}\sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\delta_{\sigma\sigma'} \\ &\quad\times\langle n,\ell,m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{p}\exp(\mathrm{i}\boldsymbol{k}\cdot\mathbf{x})|n',\ell',m'_\ell\rangle, \end{aligned} \tag{18.93}$$

therefore has the form of a first quantized scattering matrix element with perturbation (18.79) and vector potential (18.81).

The equality of the scattering matrix elements up to a phase factor also implies that the absorption rate per $\boldsymbol{k}$ space volume of the incoming photons has the same value as the corresponding emission rate (18.84) per $\boldsymbol{k}$ space volume of emitted photons,

$$\begin{aligned} \frac{d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell,\sigma'\to n,\ell,m_\ell,\sigma}}{d^3\boldsymbol{k}} &= \frac{\left|S_{n,\ell,m_\ell,\sigma|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha}\right|^2}{T} \\ &\simeq \frac{\mu_0 c^3 e^2}{8\pi^2\hbar}k\delta_{\sigma\sigma'}\left|\langle n,\ell,m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2\delta(\omega_{n,\ell;n',\ell'} - ck), \end{aligned} \tag{18.94}$$

where $q = -e$ was substituted.

This yields the differential absorption rate for polarized photons in terms of the angles $\theta_{\alpha,\pm}$ between the vectors $\langle n,\ell,m_\ell|\mathbf{x}_\pm|n',\ell',m'_\ell\rangle$ and the polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$,

$$\frac{d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell,\sigma'\to n,\ell,m_\ell,\sigma}}{d^3\boldsymbol{k}} \simeq \frac{\mu_0 c^3 e^2}{8\pi^2\hbar}k\delta_{\sigma\sigma'}\left|\langle n,\ell,m_\ell|\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2 \times\frac{\cos^2\theta_{\alpha,-}+\cos^2\theta_{\alpha,+}}{2}\delta(\omega_{n,\ell;n',\ell'}-ck).$$

The differential absorption rate for unpolarized photons, $d\tilde{\Gamma}(\boldsymbol{k}) = \sum_\alpha d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})$, depends on the angles $\theta_\pm$ between the vectors $\langle n,\ell,m_\ell|\mathbf{x}_\pm|n',\ell',m'_\ell\rangle$ and the incident vector $\boldsymbol{k}$,

$$\frac{d\tilde{\Gamma}(\boldsymbol{k})_{n',\ell',m'_\ell,\sigma'\to n,\ell,m_\ell,\sigma}}{d^3\boldsymbol{k}} \simeq \frac{\mu_0 c^3 e^2}{8\pi^2\hbar}k\delta_{\sigma\sigma'}\left|\langle n,\ell,m_\ell|\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2 \times\frac{\sin^2\theta_-+\sin^2\theta_+}{2}\delta(\omega_{n,\ell;n',\ell'}-ck). \quad (18.95)$$

The total absorption rate between the specified states follows as

$$\tilde{\Gamma}_{n',\ell',m'_\ell,\sigma'\to n,\ell,m_\ell,\sigma} = \frac{\mu_0 e^2}{3\pi\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'}\left|\langle n,\ell,m_\ell|\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2, \quad (18.96)$$

and the total absorption rate per atom for photons of angular frequency $\omega_{n,\ell;n',\ell'}$ is

$$\tilde{\Gamma}_{n',\ell'\to n,\ell} = \frac{1}{2\ell'+1}\sum_{m'_\ell=-\ell'}^{\ell'}\sum_{m_\ell=-\ell}^{\ell}\tilde{\Gamma}_{n',\ell',m'_\ell\to n,\ell,m_\ell} = \frac{\mu_0 e^2}{2\pi mc}\omega^2_{n,\ell;n',\ell'}f_{n,\ell|n',\ell'}. \quad (18.97)$$

This differs from the corresponding spontaneous emission rate (18.91) for photons of angular frequency $\omega_{n,\ell;n',\ell'}$ only through the different averaging factors for the respective initial states,

$$\tilde{\Gamma}_{n',\ell'\to n,\ell} = \frac{2\ell+1}{2\ell'+1}\Gamma_{n,\ell\to n',\ell'}. \quad (18.98)$$

The number of absorption events will be proportional to the flux of incoming photons, and therefore another observable of interest is the absorption rate per flux of incoming photons, i.e. the absorption cross section.

The *photon flux* or current density of monochromatic photons of momentum $\hbar\boldsymbol{k}$ can be calculated by dividing their energy current density $\mathcal{S}(\boldsymbol{k})$ by their energy $\hbar ck$. Equations (18.22, 18.23, 18.35) and (18.83) yield

$$\frac{\mathcal{S}(\boldsymbol{k})}{\hbar ck} = \frac{\boldsymbol{E}\times\boldsymbol{B}}{\mu_0\hbar ck} = \frac{c}{(2\pi)^3}\hat{\boldsymbol{k}}. \quad (18.99)$$

This is actually a photon flux $d\boldsymbol{j}(\boldsymbol{k})/d^3\boldsymbol{k}$ per $\boldsymbol{k}$ space volume due to the use of the photon wave functions in the continuum limit[4].

Equations (18.94) and (18.99) yield the polarized photon absorption cross section

$$\begin{aligned}\sigma^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to n,\ell,m_\ell} &= \frac{d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to n,\ell,m_\ell}}{dj(\boldsymbol{k})}\\ &\simeq \frac{\pi\mu_0 ce^2}{\hbar}\omega_{n,\ell;n',\ell'}\left|\langle n,\ell,m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2\delta(\omega_{n,\ell;n',\ell'}-ck)\\ &= 4\pi^2\alpha\omega_{n,\ell;n',\ell'}\left|\langle n,\ell,m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2\delta(\omega_{n,\ell;n',\ell'}-ck),\end{aligned}\tag{18.100}$$

where we encounter again Sommerfeld's fine structure constant $\alpha=\mu_0 ce^2/4\pi\hbar$ (7.61) (not to be confused with the polarization index, of course).

To average (18.100) over the angles of the incident photons, we can use the same methods that we applied for the calculation of the total polarized emission rate (18.87), except for an extra factor of $(4\pi)^{-1}$ from the averaging over directions. This yields an isotropic cross section for polarized photons

$$\begin{aligned}\sigma^{(\alpha)}(k)_{n',\ell',m'_\ell\to n,\ell,m_\ell} \simeq{}& \frac{4\pi^2}{3}\alpha\omega_{n,\ell;n',\ell'}\left|\langle n,\ell,m_\ell|\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2\\ &\times\delta(\omega_{n,\ell;n',\ell'}-ck),\end{aligned}\tag{18.101}$$

and a total isotropic cross section

$$\begin{aligned}\sigma(k)_{n',\ell',m'_\ell\to n,\ell,m_\ell} \simeq{}& \frac{8\pi^2}{3}\alpha\omega_{n,\ell;n',\ell'}\left|\langle n,\ell,m_\ell|\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2\\ &\times\delta(\omega_{n,\ell;n',\ell'}-ck).\end{aligned}\tag{18.102}$$

The average absorption cross section per atom for photons of angular frequency $\omega_{n,\ell;n',\ell'}$ follows then again through averaging over initial states and summation over final states,

$$\begin{aligned}\sigma(k)_{n',\ell'\to n,\ell} &= \frac{1}{2\ell'+1}\sum_{m'_\ell=-\ell'}^{\ell'}\sum_{m_\ell=-\ell}^{\ell}\sigma(k)_{n',\ell',m'_\ell\to n,\ell,m_\ell}\\ &= \frac{4\pi^2\hbar}{m}\alpha f_{n,\ell|n',\ell'}\delta(\omega_{n,\ell;n',\ell'}-ck).\end{aligned}\tag{18.103}$$

We get a more realistic representation for absorption cross sections if we take into account the representation (2.10) of the δ function,

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[4] The result in box normalization is $\boldsymbol{j}(\boldsymbol{k}) = (c/V)\hat{\boldsymbol{k}}$.

$$\begin{aligned}\delta(\omega_{n,\ell;n',\ell'}-ck) &= \lim_{\gamma\to 0}\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,\exp[\mathrm{i}(\omega_{n,\ell;n',\ell'}-ck)t-\gamma|t|]\\ &= \lim_{\gamma\to 0}\frac{1}{\pi}\frac{\gamma}{(\omega_{n,\ell;n',\ell'}-ck)^2+\gamma^2}.\end{aligned} \tag{18.104}$$

Keeping a finite value of γ yields a Lorentzian absorption line shape of half width 2γ,

$$\sigma(k)_{n',\ell'\to n,\ell} = \frac{4\pi\hbar}{m}\alpha f_{n,\ell|n',\ell'}\frac{\gamma}{(\omega_{n,\ell;n',\ell'}-ck)^2+\gamma^2}. \tag{18.105}$$

A finite width of line shapes arises from many sources. A certainly not exhaustive list of mechanisms includes adiabatic switching of perturbations, lifetime broadening, pressure broadening, Doppler broadening, and broadening through chemical shifts.

We have found $\Gamma \propto \delta_{\sigma\sigma'}$ both for photon emission and absorption, i.e. no spin-flips in either process. The same holds in arbitrary order with the Hamiltonian (18.74), since there are no spin flipping terms there. How then can a magnetic field flip spins even for non-relativistic electrons? There is actually a term missing in the Hamiltonian (18.74), the Pauli term:

$$H_B = -\frac{q}{m}\int d^3\boldsymbol{x}\sum_{\sigma,\sigma'}\psi_\sigma^+(\boldsymbol{x})\boldsymbol{S}_{\sigma,\sigma'}\cdot(\nabla\times\boldsymbol{A}(\boldsymbol{x}))\psi_{\sigma'}(\boldsymbol{x}). \tag{18.106}$$

This term induces spin flips through two of the three components of the vector of Pauli matrices $\underline{\boldsymbol{S}} = \hbar\underline{\boldsymbol{\sigma}}/2$, and it follows from the non-relativistic expansion of the relativistic wave equation for electrons, see Section 21.5. We could neglect the Pauli term in the present calculation because a derivative on the vector potential yields a factor k, whereas a derivative on the wave functions amounts approximately to a factor of order $1/a_0$. The Pauli term is therefore suppressed when dipole approximation $\lambda \gg a_0$ applies. E.g. for transition between bound states in hydrogen, $\hbar ck < -E_1$ implies that H_B is suppressed relative to H_I by approximately $ka_0 < \alpha/2$, which translates into a suppression of spin-flipping transitions between bound hydrogen states by about $\alpha^2/4 \simeq 1.3\times 10^{-5}$. An exception to negligibility of spin-flipping transitions with low energy photons concerns situations where spin-preserving electronic transitions do not exist in the same energy range. This is the case e.g. for the 21 cm transition in hydrogen.

Photon absorption into continuous states

The spin labels are omitted in the following discussion because H_I does not induce spin flips.

If we have photon absorption due to transition into continuous states, e.g. from $|n', \ell', m'_\ell\rangle$ to $|E, \ell, m_\ell\rangle$, we have to take into account the proper measure for the continuous states from the completeness relation. E.g. for hydrogen states we have (7.75)

$$\begin{aligned}
&\sum_{\ell=0}^{\infty}\sum_{m_\ell=-\ell}^{\ell}\left(\sum_{n=\ell+1}^{\infty}|n,\ell,m_\ell\rangle\langle n,\ell,m_\ell| + \int_0^\infty dK\,K^2|K,\ell,m_\ell\rangle\langle K,\ell,m_\ell|\right)\\
&=\sum_{\ell=0}^{\infty}\sum_{m_\ell=-\ell}^{\ell}\left(\sum_{n=\ell+1}^{\infty}|n,\ell,m_\ell\rangle\langle n,\ell,m_\ell| + \int dE\,\varrho(E)\,|E,\ell,m_\ell\rangle\langle E,\ell,m_\ell|\right)\\
&=1,
\end{aligned}$$

and if we directly use the Coulomb wave states for the continuous energy eigenstates without rescaling, $|E, \ell, m_\ell\rangle = |K, \ell, m_\ell\rangle$, we have in the continuous part of the spectrum

$$\varrho(E) = \Theta(E)K^2\frac{dK}{dE} = \Theta(E)\frac{1}{\hbar^3}\sqrt{2m^3E}.$$

The first order scattering matrix element with the interaction Hamiltonian H_I then yields a differential absorption rate for polarized photons

$$\begin{aligned}
\frac{d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to E,\ell,m_\ell}}{d^3\boldsymbol{k}dE} &= \varrho(E)\frac{\left|S_{E,\ell,m_\ell|n',\ell',m'_\ell;\boldsymbol{k},\alpha}\right|^2}{T}\\
&\simeq \varrho(E)\frac{e^2ck}{8\pi^2\epsilon_0}\left|\langle E,\ell,m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2\delta(E-E_{n',\ell'}-\hbar ck), \qquad (18.107)
\end{aligned}$$

and integration over the energy E of the ionized state yields

$$\begin{aligned}
\frac{d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to E,\ell,m_\ell}}{d^3\boldsymbol{k}} \simeq \frac{e^2c}{8\pi^2\epsilon_0}k\Big[&\varrho(E)\\
&\times\left|\langle E,\ell,m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2\Big]_{E=E_{n',\ell'}+\hbar ck}.
\end{aligned}$$

The photons appear in the initial state and are therefore taken into account by dividing out their current density from the transition rate, thus yielding an absorption cross section, see the general discussion for initial continuous states in Sections 13.5 and 13.6.

However, for photon absorption due to transition from a discrete into a continuous atomic or electronic state we can also calculate a spectral absorption cross section $d\sigma^{(\alpha)}(\boldsymbol{k})/dE_\gamma$ since $E_\gamma = \hbar ck = E - E_{n',\ell'}$ implies $dE_\gamma = dE$. This allows us to define a spectral absorption cross section for polarized photons according to

$$\frac{d\sigma^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to E,\ell,m_\ell}}{dE_\gamma} = \frac{d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to E,\ell,m_\ell}}{dE dj(\boldsymbol{k})}$$
$$\simeq \varrho(E)\frac{\pi e^2}{\epsilon_0}k\left|\langle E,\ell,m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2\delta(E-E_{n',\ell'}-\hbar ck),\tag{18.108}$$

where (18.99) was used. In practical applications of (18.108) the energy preserving δ function could again be replaced by a Lorentzian line shape as in (18.104).

The absorption cross section for polarized photons with momentum $\hbar\boldsymbol{k}$ follows from $\sigma^{(\alpha)}(\boldsymbol{k}) = d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})/dj(\boldsymbol{k}) = (8\pi^3/c)d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})/d^3\boldsymbol{k}$ or from (18.108) as

$$\sigma^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to E,\ell,m_\ell} \simeq \frac{\pi e^2}{\epsilon_0}k\Big[\varrho(E)$$
$$\times\left|\langle E,\ell,m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2\Big]_{E=E_{n',\ell'}+\hbar ck},$$

and averaging over the directions like in (18.101) yields

$$\sigma^{(\alpha)}(k)_{n',\ell',m'_\ell\to E,\ell,m_\ell} = \frac{1}{2}\sigma(k)_{n',\ell',m'_\ell\to E,\ell,m_\ell}$$
$$\simeq \frac{\pi e^2}{3\epsilon_0}k\Big[\varrho(E)\left|\langle E,\ell,m_\ell|\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2\Big]_{E=E_{n',\ell'}+\hbar ck}.$$

18.8 Stimulated emission of photons

Here we use box normalization in a volume $V = L^3$, i.e. $\boldsymbol{k} = 2\pi\boldsymbol{n}/L$.

If we have already $n_{\boldsymbol{k},\alpha}$ photons of momentum $\hbar\boldsymbol{k}$ and polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ in the initial state,

$$|n,\ell,m_\ell,\sigma;n_{\boldsymbol{k},\alpha}\rangle = \int d^3\boldsymbol{x}\,\psi^+_\sigma(\boldsymbol{x})\frac{(a^+_\alpha(\boldsymbol{k}))^{n_{\boldsymbol{k},\alpha}}}{\sqrt{n_{\boldsymbol{k},\alpha}!}}|0\rangle\langle\boldsymbol{x}|n,\ell,m_\ell\rangle,$$

the basic oscillator relation $\langle n+1|a^+|n\rangle = \sqrt{n+1}$ yields for the leading order scattering matrix elements the relation

$$S_{n',\ell',m'_\ell,\sigma';n_{\boldsymbol{k},\alpha}+1|n,\ell,m_\ell,\sigma;n_{\boldsymbol{k},\alpha}} = \sqrt{n_{\boldsymbol{k},\alpha}+1}S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma},$$

i.e. the emission rate scales with the number of photons of momentum $\hbar\boldsymbol{k}$, energy $\hbar ck = \hbar\omega_{n,\ell;n',\ell'}$ and fixed polarization like

$$\Gamma^{(\alpha)}_{n,\ell;n_{\boldsymbol{k},\alpha}\to n',\ell';n_{\boldsymbol{k},\alpha}+1} = (n_{\boldsymbol{k},\alpha}+1)\Gamma^{(\alpha)}_{n,\ell;0\to n',\ell';1}$$

$$= \frac{n_{\boldsymbol{k},\alpha}+1}{2\ell+1}\sum_{m_\ell=-\ell}^{\ell}\sum_{m'_\ell=-\ell'}^{\ell'}\Gamma^{(\alpha)}_{n,\ell,m_\ell\to n',\ell',m'_\ell}$$

$$= (n_{\boldsymbol{k},\alpha}+1)\frac{\mu_0 e^2}{4\pi mc}\omega^2_{n,\ell;n',\ell'}\left|f_{n',\ell'|n,\ell}\right|.$$

The total polarized emission rate in the presence of the $n_{\boldsymbol{k},\alpha}$ photons therefore differs from the "spontaneous" emission rate $\Gamma^{(\alpha)}_{n,\ell;0\to n',\ell';1}\equiv\Gamma^{(\alpha)}_{n,\ell\to n',\ell'}=\Gamma_{n,\ell\to n',\ell'}/2$ (cf. equation (18.91)) by an additional "stimulated" emission rate

$$\Gamma^{(s,\alpha)}_{n,\ell;n_{\boldsymbol{k},\alpha}\to n',\ell';n_{\boldsymbol{k},\alpha}+1}=n_{\boldsymbol{k},\alpha}\Gamma^{(\alpha)}_{n,\ell;0\to n',\ell';1}=n_{\boldsymbol{k},\alpha}\frac{\mu_0 e^2}{4\pi mc}\omega^2_{n,\ell;n',\ell'}\left|f_{n',\ell'|n,\ell}\right|$$

which is proportional to the number of photons which are already present in the system. This is sometimes metaphorically explained as a consequence of one of the original photons stimulating the emission by shaking the excited state. However, in the end it is nothing but a combinatorial quantum effect of indistinguishable photon operators.

On the other hand, we find for the absorption of a photon in the initial state

$$|n',\ell',m'_\ell,\sigma';n_{\boldsymbol{k},\alpha}\rangle=\int d^3\boldsymbol{x}\,\psi^+_{\sigma'}(\boldsymbol{x})\frac{(a^+_\alpha(\boldsymbol{k}))^{n_{\boldsymbol{k},\alpha}}}{\sqrt{n_{\boldsymbol{k},\alpha}!}}|0\rangle\langle\boldsymbol{x}|n',\ell',m'_\ell\rangle,$$

from $\langle n-1|a|n\rangle=\sqrt{n}$ the relation

$$\begin{aligned}S_{n,\ell,m_\ell,\sigma;n_{\boldsymbol{k},\alpha}-1|n',\ell',m'_\ell,\sigma';n_{\boldsymbol{k},\alpha}} &= \sqrt{n_{\boldsymbol{k},\alpha}}S_{n,\ell,m_\ell,\sigma|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha}\\ &= -\sqrt{n_{\boldsymbol{k},\alpha}}S^*_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma}.\end{aligned}$$

Therefore the polarized absorption rate in the presence of $n_{\boldsymbol{k},\alpha}$ photons of momentum $\hbar\boldsymbol{k}$ and polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ is

$$\tilde{\Gamma}^{(\alpha)}_{n',\ell';n_{\boldsymbol{k},\alpha}\to n,\ell;n_{\boldsymbol{k},\alpha}-1}=n_{\boldsymbol{k},\alpha}\tilde{\Gamma}^{(\alpha)}_{n',\ell';1\to n,\ell;0}$$

$$=\frac{n_{\boldsymbol{k},\alpha}}{2\ell'+1}\sum_{m'_\ell=-\ell'}^{\ell'}\sum_{m_\ell=-\ell}^{\ell}\tilde{\Gamma}^{(\alpha)}_{n',\ell',m'_\ell\to n,\ell,m_\ell}=n_{\boldsymbol{k},\alpha}\frac{\mu_0 e^2}{4\pi mc}\omega^2_{n,\ell;n',\ell'}f_{n,\ell|n',\ell'}.$$

This equals corresponding stimulated and total emission rates up to the different averaging factors for the different initial states which enter into the averaged and summed transition matrix elements,

$$\begin{aligned}\tilde{\Gamma}^{(\alpha)}_{n',\ell';n_{\boldsymbol{k},\alpha}\to n,\ell;n_{\boldsymbol{k},\alpha}-1} &= \frac{2\ell+1}{2\ell'+1}\Gamma^{(\alpha)}_{n,\ell;n_{\boldsymbol{k},\alpha}-1\to n',\ell';n_{\boldsymbol{k},\alpha}}\\ &= \frac{2\ell+1}{2\ell'+1}\Gamma^{(s,\alpha)}_{n,\ell;n_{\boldsymbol{k},\alpha}\to n',\ell';n_{\boldsymbol{k},\alpha}+1}.\end{aligned}$$

Note that it does not matter that we used the single photon absorption rate and current density in the calculation (18.100) of the polarized photon absorption cross section without explicitly taking into account the number $n_{\boldsymbol{k},\alpha}$ of available photons. The common factor $n_{\boldsymbol{k},\alpha}$ cancels in the ratio

$$\begin{aligned}
\sigma^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to n,\ell,m_\ell} &= \frac{d\tilde{\Gamma}^{(\alpha)}_{n',\ell',m'_\ell;n_{\boldsymbol{k},\alpha}\to n,\ell,m_\ell;n_{\boldsymbol{k},\alpha}-1}}{dJ^{(\alpha)}(\boldsymbol{k})} \\
&= \frac{8\pi^3}{n_{\boldsymbol{k},\alpha}c}\frac{d\tilde{\Gamma}^{(\alpha)}_{n',\ell',m'_\ell;n_{\boldsymbol{k},\alpha}\to n,\ell,m_\ell;n_{\boldsymbol{k},\alpha}-1}}{d^3\boldsymbol{k}}.
\end{aligned}$$

18.9 Photon scattering

For the following calculations we switch back to a generic notation $|n,\zeta\rangle$ for atomic or molecular states, where the energy levels E_n depend on the index set n and the index set ζ enumerates the degenerate states.

Scattering concerns transitions which involve a photon both in the initial and in the final state: $|n,\zeta;\boldsymbol{k},\alpha\rangle \to |n',\zeta';\boldsymbol{k}',\alpha'\rangle$. Here we consider scattering of photons by bound non-relativistic systems, i.e. the initial state $|n,\zeta\rangle$ and the final state $|n',\zeta'\rangle$ of the scattering system are discrete, and we use minimal coupling of the photon to effective single particle models for relative motion in the bound system. We have seen in Section 18.4 that photon coupling to the relative motion in materials effectively amounts to photon-electron coupling, and therefore we use photon scattering off bound electrons as the relevant paradigm for the following discussion.

To have a non-vanishing matrix element between different 1-photon states in lowest order requires two copies of the photon operator $\boldsymbol{A}$ – one to annihilate the initial photon and one to create the final photon. The relevant interaction Hamiltonian for photon interactions with non-relativistic electrons is

$$\begin{aligned}
H_{int} &= \int d^3\boldsymbol{x}\left(-\mathrm{i}\frac{e\hbar}{2m}\boldsymbol{A}\cdot\left(\psi^+\overset{\leftrightarrow}{\nabla}\psi\right)+\frac{e^2}{2m}\psi^+\boldsymbol{A}^2\psi+\frac{e\hbar}{2m}\psi^+\boldsymbol{\sigma}\cdot\boldsymbol{B}\psi\right) \\
&= H_I + H_{II} + H_B, \qquad (18.109)
\end{aligned}$$

where H_B is the Pauli term (18.106). Summations over spinor indices are tacitly understood. We have already substituted $q = -e$, because we have seen in Section 18.4 that the coupling of long wavelength photons to bound systems involving electrons can effectively be considered as coupling of the photons to a charge $-e$ if the charge binding the electron is $q_2 = e$ or if the mass m_2 of the binding charge is much larger than the electron mass, $m_2 \gg m_e$. The reduced mass m in the Hamiltonian (18.109) is usually also $m \simeq m_e$ in excellent approximation[5].

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[5] An exception is positronium with $m = m_e/2$.

We can get two copies of $\boldsymbol{A}$ from H_I^2, H_IH_B, H_BH_I and H_B^2 in second order perturbation theory, and from H_{II} in first order perturbation theory. Among these terms, only those involving the Pauli term can induce spin flips. However, we will focus on photon energies in the soft X-ray regime, $E_\gamma \lesssim 1\,\mathrm{keV}$. Due to the suppression of the Pauli term by about a_0/λ the allowed transition matrix elements of H_I in the soft X-ray regime are typically at least an order of magnitude larger than the allowed matrix elements of H_B, see the discussion after (18.106). This implies that spin preserving scattering probabilities $|S_{fi}|^2$ of order H_I^4 will generically be at least two orders of magnitude larger than spin preserving scattering of order $H_I^2H_B^2$ or spin reversing scattering of order $(H_IH_B)^2$.

Therefore we neglect H_B in the following calculations. The relevant scattering matrix elements in order $\mathcal{O}(e^2)$ are then

$$\begin{aligned}
S_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} &= \langle n',\zeta';\boldsymbol{k}',\alpha'|U_D(\infty,-\infty)|n,\zeta;\boldsymbol{k},\alpha\rangle|_{e^2}\\
&= \langle n',\zeta';\boldsymbol{k}',\alpha'|\mathrm{T}\exp\!\left(-\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{\infty}dt\,H_D(t)\right)|n,\zeta;\boldsymbol{k},\alpha\rangle|_{e^2}\\
&= S^{(I)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} + S^{(II)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha},
\end{aligned}$$

with contributions from H_I^2,

$$\begin{aligned}
S^{(I)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} &= -\frac{1}{\hbar^2}\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}dt'\,\exp\!\big[\mathrm{i}(\omega_{n'}+ck')t\big]\exp\!\big[-\mathrm{i}(\omega_n+ck)t'\big]\\
&\quad\times\langle n',\zeta';\boldsymbol{k}',\alpha'|H_I\exp\!\left(-\frac{\mathrm{i}}{\hbar}H_0(t-t')\right)H_I|n,\zeta;\boldsymbol{k},\alpha\rangle,
\end{aligned}$$

and from H_{II},

$$S^{(II)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} = \int_{-\infty}^{\infty}\frac{dt}{\mathrm{i}\hbar}\,\exp\!\big[\mathrm{i}(\omega_{n',n}+\omega_{k',k})t\big]\,\langle n',\zeta';\boldsymbol{k}',\alpha'|H_{II}|n,\zeta;\boldsymbol{k},\alpha\rangle.$$

The first order term $S^{(II)}$ is the easier one to evaluate. Insertion of the mode expansion (18.21) for the photon field yields

$$\begin{aligned}
S^{(II)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} &= \frac{\mu_0ce^2}{8\pi^2\mathrm{i}m\sqrt{kk'}}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\delta(\omega_{n',n}+\omega_{k',k})\\
&\quad\times\int d^3\boldsymbol{x}\,\exp\!\big[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}\big]\,\Psi^+_{n',\zeta'}(\boldsymbol{x})\Psi_{n,\zeta}(\boldsymbol{x})\\
&= \frac{\mu_0ce^2}{8\pi^2\mathrm{i}m\sqrt{kk'}}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\delta(\omega_{n',n}+\omega_{k',k})\\
&\quad\times\int d^3\boldsymbol{q}\,\Psi^+_{n',\zeta'}(\boldsymbol{q}+\boldsymbol{k}-\boldsymbol{k}')\Psi_{n,\zeta}(\boldsymbol{q}).
\end{aligned}$$

This leaves in dipole approximation $\exp\big[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}\big]\simeq 1$ the amplitude

$$S^{(II)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}=\frac{\mu_0 e^2}{8\pi^2\mathrm{i}mk}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\delta(k'-k)\delta_{n'n}\delta_{\zeta'\zeta},\tag{18.110}$$

i.e. only elastic photon scattering, but no Raman scattering from H_{II}.

The term $S^{(I)}$ splits into amplitudes with zero or two photons in virtual intermediate states,

$$S^{(I)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}=S^{(I),0}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}+S^{(I),2}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}.$$

We omit the indices in the amplitudes $S^{(I),0}$ and $S^{(I),2}$ in the following calculations. The amplitude with no photons in the virtual intermediate state is

$$\begin{aligned}S^{(I),0}={}&\frac{e^2}{4m^2}\sum\!\!\!\!\!\!\!\int_{n'',\zeta''}\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}dt'\,\exp\big[\mathrm{i}(\omega_{n',n''}+ck')t\big]\exp\big[\mathrm{i}(\omega_{n'',n}-ck)t'\big]\\&\times\int d^3\boldsymbol{x}'\,\langle n',\zeta';\boldsymbol{k}',\alpha'|\boldsymbol{A}(\boldsymbol{x}')\cdot\Big(\psi^+(\boldsymbol{x}')\overset{\leftrightarrow}{\nabla}\psi(\boldsymbol{x}')\Big)|n'',\zeta'';0\rangle\\&\times\int d^3\boldsymbol{x}\,\langle n'',\zeta'';0|\boldsymbol{A}(\boldsymbol{x})\cdot\Big(\psi^+(\boldsymbol{x})\overset{\leftrightarrow}{\nabla}\psi(\boldsymbol{x})\Big)|n,\zeta;\boldsymbol{k},\alpha\rangle.\end{aligned}$$

The notation $\sum\!\!\!\!\!\!\!\int_{n'',\zeta''}$ takes into account that the intermediate states can also be part of the energy continuum of the scattering system.

We have already evaluated the time integrals in second order perturbation terms in (13.43),

$$\begin{aligned}&\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}dt'\,\exp\big[\mathrm{i}(\omega_{n',n''}+ck')t\big]\exp\big[\mathrm{i}(\omega_{n'',n}-ck)t'+\epsilon t'\big]\\&=-2\pi\mathrm{i}\frac{\delta(\omega_{n',n}+\omega_{k',k})}{\omega_{n'',n}-ck-\mathrm{i}\epsilon}.\end{aligned}$$

Evaluation of the matrix elements of the field operators then yields again in dipole approximation $\exp(-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{x}')\simeq 1$, $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\simeq 1$ the result

$$\begin{aligned}S^{(I),0}={}&\frac{\hbar\mu_0 ce^2}{32\pi^2\mathrm{i}m^2\sqrt{kk'}}\delta(\omega_{n',n}+\omega_{k',k})\sum\!\!\!\!\!\!\!\int_{n'',\zeta''}\frac{1}{\omega_{n'',n}-ck-\mathrm{i}\epsilon}\\&\times\int d^3\boldsymbol{x}'\,\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\Big(\Psi^+_{n',\zeta'}(\boldsymbol{x}')\overset{\leftrightarrow}{\nabla}\Psi_{n'',\zeta''}(\boldsymbol{x}')\Big)\\&\times\int d^3\boldsymbol{x}\,\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\Big(\Psi^+_{n'',\zeta''}(\boldsymbol{x})\overset{\leftrightarrow}{\nabla}\Psi_{n,\zeta}(\boldsymbol{x})\Big).\end{aligned}\tag{18.111}$$

We can transform this from velocity into length form using the by now standard trick $\hbar\mathbf{p}=\mathrm{i}m[H_0,\mathbf{x}]$ to find

$$\begin{aligned}S^{(I),0} = {} & \frac{\mu_0 c e^2}{8\pi^2 \mathrm{i}\hbar\sqrt{kk'}}\delta(\omega_{n',n}+\omega_{k',k})\sum\!\!\!\!\!\!\!\int_{n'',\zeta''}\frac{\omega_{n',n''}\omega_{n'',n}}{\omega_{n'',n}-ck-\mathrm{i}\epsilon}\\ & \times\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n'',\zeta''\rangle\langle n'',\zeta''|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n,\zeta\rangle. \qquad (18.112)\end{aligned}$$

For the amplitude with two photons in the intermediate state we have to take into account that for two-photon states

$$\frac{1}{2}\int d^3\boldsymbol{\kappa}'\int d^3\boldsymbol{\kappa}\sum_{\beta',\beta}|\boldsymbol{\kappa}',\beta';\boldsymbol{\kappa},\beta\rangle\langle\boldsymbol{\kappa}',\beta';\boldsymbol{\kappa},\beta| = 1.$$

This yields

$$\begin{aligned}S^{(I),2} = {} & \frac{e^2}{8m^2}\int d^3\boldsymbol{\kappa}'\int d^3\boldsymbol{\kappa}\sum\int_{n'',\zeta''}\sum_{\beta',\beta}\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}dt'\\ & \times\exp\!\big[\mathrm{i}(\omega_{n',n''}+ck'-c\kappa-c\kappa')t\big]\exp\!\big[\mathrm{i}(\omega_{n'',n}+c\kappa+c\kappa'-ck)t'\big]\\ & \times\int d^3\boldsymbol{x}'\langle n',\zeta';\boldsymbol{k}',\alpha'|\boldsymbol{A}(\boldsymbol{x}')\cdot\Big(\psi^+(\boldsymbol{x}')\overset{\leftrightarrow}{\nabla}\psi(\boldsymbol{x}')\Big)|n'',\zeta'';\boldsymbol{\kappa}',\beta';\boldsymbol{\kappa},\beta\rangle\\ & \times\int d^3\boldsymbol{x}\langle n'',\zeta'';\boldsymbol{\kappa}',\beta';\boldsymbol{\kappa},\beta|\boldsymbol{A}(\boldsymbol{x})\cdot\Big(\psi^+(\boldsymbol{x})\overset{\leftrightarrow}{\nabla}\psi(\boldsymbol{x})\Big)|n,\zeta;\boldsymbol{k},\alpha\rangle.\end{aligned}$$

The matrix elements of the photon operators are given by

$$\begin{aligned}\langle\boldsymbol{\kappa}',\beta';\boldsymbol{\kappa},\beta|\boldsymbol{A}(\boldsymbol{x})|\boldsymbol{k},\alpha\rangle = {} & \sqrt{\frac{\hbar\mu_0 c}{16\pi^3\kappa}}\boldsymbol{\epsilon}_{\beta}(\boldsymbol{\kappa})\exp(-\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{x})\delta(\boldsymbol{\kappa}'-\boldsymbol{k})\delta_{\beta'\alpha}\\ & +\sqrt{\frac{\hbar\mu_0 c}{16\pi^3\kappa'}}\boldsymbol{\epsilon}_{\beta'}(\boldsymbol{\kappa}')\exp(-\mathrm{i}\boldsymbol{\kappa}'\cdot\boldsymbol{x})\delta(\boldsymbol{\kappa}-\boldsymbol{k})\delta_{\beta\alpha}\end{aligned}$$

and a corresponding conjugate expression. This yields in dipole approximation

$$\begin{aligned}&\int d^3\boldsymbol{\kappa}'\int d^3\boldsymbol{\kappa}\sum_{\beta',\beta}\exp\!\big[\mathrm{i}c(\kappa+\kappa')(t'-t)\big]\\ &\times\langle\boldsymbol{k}',\alpha'|\boldsymbol{A}(\boldsymbol{x}')|\boldsymbol{\kappa}',\beta';\boldsymbol{\kappa},\beta\rangle\langle\boldsymbol{\kappa}',\beta';\boldsymbol{\kappa},\beta|\boldsymbol{A}(\boldsymbol{x})|\boldsymbol{k},\alpha\rangle\\ &\simeq\frac{\hbar\mu_0 c}{8\pi^3}\delta_{\alpha\alpha'}\delta(\boldsymbol{k}-\boldsymbol{k}')\int d^3\boldsymbol{\kappa}\sum_{\beta}\frac{\boldsymbol{\epsilon}_{\beta}(\boldsymbol{\kappa})\otimes\boldsymbol{\epsilon}_{\beta}(\boldsymbol{\kappa})}{\kappa}\exp\!\big[\mathrm{i}c(\kappa+k)(t'-t)\big]\\ &+\frac{\hbar\mu_0 c}{8\pi^3}\frac{\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\otimes\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')}{\sqrt{kk'}}\exp\!\big[\mathrm{i}c(k+k')(t'-t)\big]. \qquad (18.113)\end{aligned}$$

The first term in (18.113) corresponds to an electron self-energy contribution where the external photon does not interact with the electron, but there are two

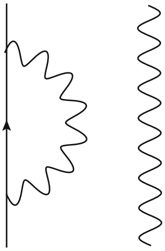

Fig. 18.1 A process with two photons in an intermediate state due to emission and re-absorption of a virtual photon. The straight line represents the electron and the wavy lines represent photons

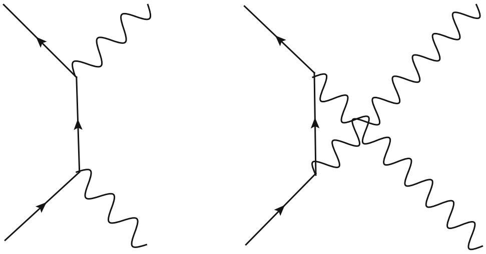

Fig. 18.2 The left diagram corresponds to absorption of the initial photon before emission of the final photon. The diagram on the right hand side corresponds to emission of the final photon before absorption of the initial photon

photons in the intermediate state due to emission and re-absorption of a virtual photon by the electron, see Figure 18.1.

This is an effect which leads to a renormalization of the electron mass in quantum field theory, but does not contribute to photon scattering.

The second term yields an expression for $S^{(I),2}$ which looks almost exactly like $S^{(I),0}$ (18.111), *except* that the polarization vectors are swapped $\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \leftrightarrow \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})$, and $\omega_{n'',n} - ck - \mathrm{i}\epsilon$ is replaced by $\omega_{n'',n} + ck' - \mathrm{i}\epsilon$ in the denominator. After transformation into the length form, $S^{(I),0}$ and $S^{(I),2}$ yield the following expression,

$$\begin{aligned} S^{(I)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} = {} & \frac{\mu_0 ce^2}{8\pi^2\mathrm{i}\hbar\sqrt{kk'}}\delta(\omega_{n',n} + \omega_{k',k}) \sum\!\!\!\!\!\!\!\int_{n'',\zeta''} \omega_{n',n''}\omega_{n'',n} \\ & \times \left(\frac{\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n'',\zeta''\rangle\langle n'',\zeta''|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n,\zeta\rangle}{\omega_{n'',n} - ck - \mathrm{i}\epsilon} \right. \\ & \left. + \frac{\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n'',\zeta''\rangle\langle n'',\zeta''|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n,\zeta\rangle}{\omega_{n'',n} + ck' - \mathrm{i}\epsilon} \right). \end{aligned}$$

The first term corresponds to absorption of the initial photon before emission of the final photon, whereas the second term corresponds to emission of the final photon before absorption of the initial photon, see Figure 18.2.

The total scattering matrix element in order e^2 is

$$\begin{aligned} S_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} = {} & \frac{\mu_0 ce^2}{8\pi^2\mathrm{i}\sqrt{kk'}}\delta(\omega_{n',n} + \omega_{k',k}) \left[\frac{1}{m}\delta_{n'n}\delta_{\zeta'\zeta}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) \right. \\ & + \sum\!\!\!\!\!\!\!\int_{n'',\zeta''} \omega_{n',n''}\omega_{n'',n} \left(\frac{\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n'',\zeta''\rangle\langle n'',\zeta''|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n,\zeta\rangle}{\hbar\omega_{n'',n} - \hbar ck - \mathrm{i}\epsilon} \right. \end{aligned}$$

$$+\left.\left.\frac{\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n'',\zeta''\rangle\langle n'',\zeta''|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n,\zeta\rangle}{\hbar\omega_{n'',n}+\hbar ck'-\mathrm{i}\epsilon}\right)\right].$$

We separate the energy conserving δ function for the calculation of the scattering cross section,

$$S_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}=-\mathrm{i}\mathcal{M}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}\delta(\omega_{n',n}+\omega_{k',k}). \tag{18.114}$$

The differential scattering rate per $\boldsymbol{k}$ space volume of incident photons is then

$$\begin{aligned}\frac{d\Gamma_{n,\zeta;\boldsymbol{k},\alpha\to n',\zeta';\boldsymbol{k}',\alpha'}}{d^3\boldsymbol{k}}&=d^3\boldsymbol{k}'\,\frac{\left|S_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}\right|^2}{T}\\&=\frac{d^3\boldsymbol{k}'}{2\pi}\left|\mathcal{M}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}\right|^2\delta(\omega_{n',n}+\omega_{k',k}),\end{aligned}$$

and the differential scattering cross section for polarized photons is with the incident photon current density per $\boldsymbol{k}$ space volume $d\boldsymbol{j}/d^3\boldsymbol{k}=c\hat{\boldsymbol{k}}/(2\pi)^3$ (18.99),

$$\begin{aligned}d\sigma_{n,\zeta;\boldsymbol{k},\alpha\to n',\zeta';\boldsymbol{k}',\alpha'}&=\frac{d\Gamma_{n,\zeta;\boldsymbol{k},\alpha\to n',\zeta';\boldsymbol{k}',\alpha'}}{dj(\boldsymbol{k})}\\&=\frac{4\pi^2}{c}\left|\mathcal{M}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}\right|^2\delta(\omega_{n',n}+\omega_{k',k})d^3\boldsymbol{k}'.\end{aligned}\tag{18.115}$$

This yields after integration over k'

$$\frac{d\sigma_{n,\zeta;\boldsymbol{k},\alpha\to n',\zeta';\boldsymbol{k}',\alpha'}}{d\Omega}=\frac{4\pi^2}{c^2}k'^2\left|\mathcal{M}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}\right|^2\Big|_{k'=k-(\omega_{n',n}/c)}. \tag{18.116}$$

Substitution of our results for the scattering matrix element yields the result

$$\begin{aligned}\frac{d\sigma}{d\Omega}=\left(\frac{\mu_0e^2}{4\pi}\right)^2\frac{k'}{k}\Bigg|&\frac{1}{m}\delta_{n'n}\delta_{\zeta'\zeta}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})+\sum\!\!\!\!\!\!\!\int_{n'',\zeta''}\omega_{n',n''}\omega_{n'',n}\\&\times\left(\frac{\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n'',\zeta''\rangle\langle n'',\zeta''|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n,\zeta\rangle}{\hbar\omega_{n'',n}-\hbar ck-\mathrm{i}\epsilon}\right.\\&\left.+\frac{\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n'',\zeta''\rangle\langle n'',\zeta''|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n,\zeta\rangle}{\hbar\omega_{n'',n}+\hbar ck'-\mathrm{i}\epsilon}\right)\Bigg|^2_{k'=k-(\omega_{n',n}/c)}\end{aligned}\tag{18.117}$$

If there are non-vanishing transition matrix elements $\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n'',\zeta''\rangle$ and $\langle n'',\zeta''|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n,\zeta\rangle$ with the properties $\omega_{n'',n}\simeq ck$ and $\omega_{n',n''}\simeq -ck'$, or if there are any non-vanishing matrix elements $\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n'',\zeta''\rangle$ and

$\langle n'', \zeta''|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n, \zeta\rangle$ with the properties $\omega_{n'',n} \simeq -ck'$ and $\omega_{n',n''} \simeq ck$, then the differential scattering cross section will be dominated by the resonantly enhanced contributions from those matrix elements, and we will have $\omega_{n',n''}\omega_{n'',n} \simeq -c^2kk'$ for the dominant terms. In these cases we can approximate our result (18.117) by the equation

$$\frac{d\sigma}{d\Omega} \simeq \alpha^2c^2kk'^3\left|\sum\!\!\!\!\!\!\!\int_{n'',\zeta''}\left(\frac{\langle n', \zeta'|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n'', \zeta''\rangle\langle n'', \zeta''|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n, \zeta\rangle}{\omega_{n'',n} - ck - \mathrm{i}\epsilon}\right.\right.$$
$$\left.\left.+\frac{\langle n', \zeta'|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n'', \zeta''\rangle\langle n'', \zeta''|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n, \zeta\rangle}{\omega_{n'',n} + ck' - \mathrm{i}\epsilon}\right)\right|^2_{k'=k-(\omega_{n',n}/c)} \tag{18.118}$$

This is an equation for photon scattering which was proposed already in 1924 by Kramers and Heisenberg based on the correspondence principle[6]. However, note that this is only a suitable approximation to the actual cross section (18.117) if the near resonance conditions $\omega_{n'',n} \simeq ck$ and $\omega_{n',n''} \simeq -ck'$, or $\omega_{n'',n} \simeq -ck'$ and $\omega_{n',n''} \simeq ck$, can be fulfilled, and if there are allowed dipole transitions into the intermediate nearly resonant levels.

Thomson cross section

The contribution from the first term in (18.117) coincides with the classical Thomson cross section for elastic scattering of light which we will encounter again in Section 22.3 when we discuss photon scattering off free electrons. The first term yields for scattering of polarized photons

$$\left.\frac{d\sigma_T}{d\Omega}\right|_{\alpha\to\alpha'} = \left(\frac{\mu_0e^2}{4\pi m}\right)^2\left(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\right)^2 = \left(\frac{\mu_0e^2}{4\pi m}\right)^2\cos^2\theta_{\alpha\alpha'},$$

The resulting cross section for unpolarized light involves a sum over final polarizations and an average over initial polarizations,

$$\begin{aligned}&\frac{1}{2}\sum_{\alpha,\alpha'}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\otimes\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\\&=\frac{1}{2}\sum_{\alpha'}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\left(\underline{1}-\hat{\boldsymbol{k}}\otimes\hat{\boldsymbol{k}}\right)\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\\&=\frac{1}{2}\mathrm{tr}\left[\left(\underline{1}-\hat{\boldsymbol{k}}\otimes\hat{\boldsymbol{k}}\right)\cdot\left(\underline{1}-\hat{\boldsymbol{k}}'\otimes\hat{\boldsymbol{k}}'\right)\right]=\frac{1+\cos^2\theta}{2},\end{aligned} \tag{18.119}$$

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[6] H.A. Kramers, W. Heisenberg, Z. Phys. 31, 681 (1925).

where $\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{k}}' = \cos\theta$, i.e. θ is the scattering angle. This yields[7]

$$\frac{d\sigma_T}{d\Omega} = \left(\frac{\mu_0 e^2}{4\pi m}\right)^2 \frac{1+\cos^2\theta}{2}, \tag{18.120}$$

and

$$\sigma_T = \frac{8\pi}{3}\left(\frac{\mu_0 e^2}{4\pi m}\right)^2. \tag{18.121}$$

The first term in equation (18.117) would hypothetically dominate the cross section $d\sigma/d\Omega$ if the photon energy is much larger than all the excitation energies of dipole allowed transitions, i.e. if $ck \gg |\omega_{n'',n}|$ for all $\langle n'',\zeta''|\mathbf{x}|n,\zeta\rangle \neq 0$. However, there will always be allowed transitions into intermediate continuum states. Therefore the condition $ck \gg |\omega_{n'',n}|$ for all dipole allowed transitions will not be fulfilled and the first term in (18.117) will never dominate light scattering by atoms or molecules[8]. However, the Thomson cross section plays an important role in the scattering of light by free electrons, which will be discussed in Section 22.3.

Rayleigh scattering

Molecules in a gas or a liquid have many dense lying rotational and vibrational levels, and the condition of dipole allowed resonant excitation of intermediate levels will practically always be fulfilled. The Kramers-Heisenberg formula (18.118) will therefore always be an excellent approximation to (18.117) for molecules in a fluid phase. In particular, the cross section for elastic photon scattering $|g;\boldsymbol{k},\alpha\rangle \to |g;\boldsymbol{k}',\alpha'\rangle$ from a ground state $|g\rangle$ or a state $|g\rangle$ near the ground state will be

$$\frac{d\sigma_R}{d\Omega} \simeq (\alpha ck^2)^2 \left| \sum_{n,\zeta,\omega_{n,g}\simeq ck} \frac{\langle g|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n,\zeta\rangle\langle n,\zeta|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|g\rangle}{\omega_{n,g} - ck - \mathrm{i}\epsilon} \right|^2. \tag{18.122}$$

A formula for resonance fluorescence which is equivalent to (18.122) was given for the first time by Viktor Weisskopf in his Ph.D. thesis[9].

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[7] The combination $r_e \equiv \mu_0 e^2/4\pi m = 2.82\,\mathrm{fm}$ is also denoted as the *classical radius of the electron*.

[8] A loophole in this argument concerns the remote possibility that all the matrix elements $\langle n'',\zeta''|\mathbf{x}|n,\zeta\rangle$ with $\omega_{n'',n} \gtrsim ck$ are extremely small.

[9] V. Weisskopf, Annalen Phys. 401, 23 (1931). He used a dipole operator $H = -e\boldsymbol{x}\cdot\dot{\boldsymbol{A}}(\boldsymbol{x},t)$ for atom-photon interactions throughout his calculations.

The reasoning with only one kind of resonantly enhanced terms is correct as long as the alternative resonance condition $\omega_{n,g} \simeq -ck$ cannot be fulfilled, i.e. as long as the energy E_g of the initial state $|g\rangle$ is less than $\hbar ck$ above the ground state energy. This applies e.g. to molecules at room temperature. These molecules will generically occupy states with energies less than 0.1 eV above their ground state energy. Scattering of optical photons by these molecules can be described by equation (18.122).

We can connect (18.122) to the polarizability properties of the scattering centers by noting that the dynamical polarizability tensor (15.26) for $\omega_{mn} \simeq \omega = ck$ has exactly the same form as the tensor multiplying the polarization vectors in (18.122). Therefore we can rewrite this equation also in the form

$$\left.\frac{d\sigma_R}{d\Omega}\right|_{\alpha\to\alpha'} = \left(\frac{\mu_0}{4\pi}\right)^2 \omega^4 \left(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \underline{\alpha}_{(g)} \cdot \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\right)^2, \tag{18.123}$$

where it is understood that the sum over intermediate levels in (15.26) is dominated by terms which are almost resonant with the frequency ω of the elastically scattered photons.

Directional averaging over the orientation of the molecules will lead to an isotropic effective polarization tensor,

$$\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \underline{\alpha}_{(g)} \cdot \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) = \alpha_{(g)}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}),$$

$$\left.\frac{d\sigma_R}{d\Omega}\right|_{\alpha\to\alpha'} = \left(\frac{\mu_0}{4\pi}\alpha_{(g)}\right)^2 \omega^4 \cos^2\theta_{\alpha\alpha'},$$

and averaging and summation over the polarizations of the incoming and scattered photons (18.119) yields the same angular dependence on the scattering angle as for Thomson scattering (18.120),

$$\frac{d\sigma_R}{d\Omega} = \left(\frac{\mu_0}{4\pi}\alpha_{(g)}\right)^2 \omega^4 \frac{1+\cos^2\theta}{2} \tag{18.124}$$

and

$$\sigma_R = \frac{8\pi}{3}\left(\frac{\mu_0}{4\pi}\alpha_{(g)}\right)^2 \omega^4. \tag{18.125}$$

Equations (18.124, 18.125) are quantum mechanical versions of Lord Rayleigh's ω^4 law (Rayleigh 1871, 1899; see also Jackson [19] for a derivation of Rayleigh scattering in classical electrodynamics). It is sometimes stated (but neither in [19] nor in Weisskopf's thesis) that Rayleigh scattering is a small frequency approximation in the sense that $\hbar\omega = \hbar ck$ should be small compared to the internal excitations of the scattering system. This is not true. The quantum mechanical derivation (as well as Jackson's classical derivation) does not require this assumption. The only assumption that went into our derivation above was resonantly enhanced dipole scattering. Besides, energies of optical photons are not small compared to excitation energies for nitrogen or oxygen molecules. Indeed, the assumption of resonantly enhanced dipole scattering *implies* that the photon frequency $\omega = ck$ should be comparable to the transition frequencies of some dipole allowed transitions.

18.10 Problems

18.1. We consider a gauge invariant Lagrange density which contains matter fields $\Phi(x)$ besides the electromagnetic fields $A_\mu(x)$,

$$\mathcal{L} = \mathcal{L}_m(\Phi, \Phi^+, \partial\Phi - \mathrm{i}(q/\hbar)A\Phi, \partial\Phi^+ + \mathrm{i}(q/\hbar)\Phi^+A) - \frac{1}{4\mu_0}F_{\mu\nu}F^{\mu\nu}.$$

Equation (16.13) yields for the conserved charged current density from phase invariance

$$\delta\Phi(x) = \frac{\mathrm{i}}{\hbar}q\varphi\Phi(x), \quad \delta\Phi^+(x) = -\frac{\mathrm{i}}{\hbar}q\varphi\Phi^+(x)$$

after division by the irrelevant constant factor φ the expression

$$\begin{aligned} j_q^\mu &= -\frac{1}{\varphi}\delta\Phi\cdot\frac{\partial\mathcal{L}}{\partial(\partial_\mu\Phi)} - \frac{1}{\varphi}\delta\Phi^+\cdot\frac{\partial\mathcal{L}}{\partial(\partial_\mu\Phi^+)} \\ &= -\frac{\mathrm{i}}{\hbar}q\Phi\cdot\frac{\partial\mathcal{L}}{\partial(\partial_\mu\Phi)} + \frac{\mathrm{i}}{\hbar}q\Phi^+\cdot\frac{\partial\mathcal{L}}{\partial(\partial_\mu\Phi^+)}. \end{aligned}$$

On the other hand, the current density that appears in Maxwell's equations

$$\partial_\mu F^{\mu\nu} = -\mu_0 j^\nu$$

is $j^\mu = \partial\mathcal{L}/\partial A_\mu$. Why are those two current densities the same, $j_q^\mu = j^\mu$?

18.2. Prove that the vector field (18.15) satisfies $\nabla\cdot\boldsymbol{A}_J(\boldsymbol{x},t) = 0$.

18.3. Show that in the gauge $\Phi = 0$ the conjugate momentum $\boldsymbol{\Pi}_A = \partial\mathcal{L}/\partial\dot{\boldsymbol{A}} = \epsilon_0\dot{\boldsymbol{A}}$ also yields the Hamiltonian density $\mathcal{H}$ through the standard Lagrangian expression

$$\mathcal{H} = \boldsymbol{\Pi}_A\cdot\dot{\boldsymbol{A}} - \mathcal{L} = \epsilon_0\dot{\boldsymbol{A}}^2 - \mathcal{L}.$$

18.4. We can solve the Coulomb equation (18.2) for the scalar potential Φ also without invoking any particular gauge. How does this generalize equations (18.9) and (18.10)?

Show that taking the divergence of the generalization of equation (18.10) yields a trivially fulfilled equation.

18.5a. The action (18.29) of electromagnetic fields is invariant under Lorentz transformations

$$\epsilon^{\mu} = -\delta x^{\mu} = -\varphi^{\mu\nu}x_{\nu}, \quad \varphi^{\mu\nu} = -\varphi^{\nu\mu},$$

$$\delta A_{\mu}(x) = A'_{\mu}(x') - A_{\mu}(x) = \varphi_{\mu\nu}A^{\nu}(x).$$

Use a procedure similar to the derivation of the energy-momentum tensor (18.32) to derive the densities and currents

$$\mathcal{M}_{\alpha\beta}{}^{\mu} = \frac{1}{c}\left(x_{\alpha}T_{\beta}{}^{\mu} - x_{\beta}T_{\alpha}{}^{\mu}\right) \tag{18.126}$$

of the corresponding conserved charges

$$M_{\alpha\beta} = \int d^3\boldsymbol{x}\,\mathcal{M}_{\alpha\beta}{}^{0}.$$

Hint: You have to add the improvement term $\partial_{\nu}(x_{\beta}A_{\alpha}F^{\mu\nu} - x_{\alpha}A_{\beta}F^{\mu\nu})/\mu_0$ to j^{μ} from equation (16.13) to get the gauge invariant expression (18.126) for the angular momentum densities and currents.

18.5b. The angular momentum of the electromagnetic fields is

$$\boldsymbol{M} = \frac{1}{2}\boldsymbol{e}_i\epsilon_{ijk}M_{jk} = \int d^3\boldsymbol{x}\,\epsilon_0\boldsymbol{x}\times(\boldsymbol{E}\times\boldsymbol{B}), \tag{18.127}$$

but what is the meaning of the conserved quantities M^{0i}?

We define an energy weighted location of the electromagnetic fields,

$$\langle\boldsymbol{x}\rangle = \frac{1}{E}\int d^3\boldsymbol{x}\,\boldsymbol{x}\mathcal{H}, \tag{18.128}$$

where $\mathcal{H}$ is the energy density (18.33) of the electromagnetic fields. Show that the conservation of M^{0i} implies a conservation law for "center of energy" motion for the freely evolving electromagnetic fields,

$$\langle\boldsymbol{x}\rangle(t) = \langle\boldsymbol{x}\rangle(0) + \frac{c^2\boldsymbol{P}}{E}t. \tag{18.129}$$

18.6. A helium-neon laser produces a light wave with a central wavelength of 632.8 nm and a power of 5 mW. Suppose the electric component is a sine oscillation $|\boldsymbol{E}(\boldsymbol{x},t)| \propto \sin(\boldsymbol{k}\cdot\boldsymbol{x} - ckt)$ and is polarized in x direction. We also assume that the frequency profile is Gaussian with a relative width $\Delta f/f = 3.16 \times 10^{-6}$. Which photon state describes this light wave? How many photons does the electromagnetic wave contain?

18.7. Show that the state

$$|n,\ell,m_\ell,\sigma;\boldsymbol{k},\alpha\rangle = \int d^3\boldsymbol{x}\,\Psi_{n,\ell,m_\ell}(\boldsymbol{x})\psi_\sigma^+(\boldsymbol{x})a_\alpha^+(\boldsymbol{k})|0\rangle$$

satisfies

$$H_0|n,\ell,m_\ell,\sigma;\boldsymbol{k},\alpha\rangle = (E_{n,\ell} + \hbar ck)|n,\ell,m_\ell,\sigma;\boldsymbol{k},\alpha\rangle,$$

where

$$H_0 = \int d^3\boldsymbol{x}\left(\frac{\hbar^2}{2m}\sum_\sigma \nabla\psi_\sigma^+\cdot\nabla\psi_\sigma + \sum_\sigma \psi_\sigma^+ V\psi_\sigma + \frac{\epsilon_0}{2}\dot{\boldsymbol{A}}^2 + \frac{(\nabla\times\boldsymbol{A})^2}{2\mu_0}\right).$$

You have to use that the atomic orbital satisfies

$$-\frac{\hbar^2}{2m}\Delta\Psi_{n,\ell,m_\ell}(\boldsymbol{x}) + V(\boldsymbol{x})\Psi_{n,\ell,m_\ell}(\boldsymbol{x}) = E_{n,\ell}\Psi_{n,\ell,m_\ell}(\boldsymbol{x}).$$

It is also useful to keep the $\boldsymbol{x}$ representation for the electronic part of H_0, but to use the $\boldsymbol{k}$ representation for the photon contributions in H_0.

18.8. Calculate the emission rate for unpolarized photons from the 2p state to the ground state of hydrogen in first order and dipole approximation.

Which estimate do you get from this for the lifetime of 2p states?

Which estimate do you get from this for the radiated power from decay of 2p states?

18.9. Calculate the integrated photon absorption cross section,

$$G_{1s\to 2p} = \int_0^\infty \frac{dk}{k}\,\sigma_{1,0\to 2,1}(k)$$

due to the transition from 1s to 2p states in hydrogen.

18.10a. Show that the first order scattering matrix elements (18.78) and (18.93) for emission and absorption can also be gotten in a semi-classical approximation from a perturbation operator

$$V(t) = -q\mathbf{x}\cdot\boldsymbol{E}(\mathbf{x},t) \tag{18.130}$$

with $\boldsymbol{E}(\mathbf{x},t)$ corresponding to a single photon electric field

$$\boldsymbol{E}_\alpha^{(+)}(\boldsymbol{x},t) = -\dot{\boldsymbol{A}}_\alpha^{(+)}(\boldsymbol{x},t) = -\mathrm{i}\sqrt{\frac{\hbar\mu_0 c^3 k}{16\pi^3}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]$$

for emission, and to

$$\boldsymbol{E}_\alpha^{(-)}(\boldsymbol{x},t) = -\dot{\boldsymbol{A}}_\alpha^{(-)}(\boldsymbol{x},t) = \mathrm{i}\sqrt{\frac{\hbar\mu_0 c^3 k}{16\pi^3}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]$$

for absorption.

18.10b. If we would use the same substitution of semi-classical perturbation operators $V(t)$ from (18.79) to (18.130) for the calculation of scattering in dipole approximation $\exp(\pm\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \simeq 1$, we would find the Kramers-Heisenberg formula (18.118) from (18.130), while (18.79) yields the correct result (18.117). Why does the substitution (18.79) → (18.130) not work beyond first order perturbation theory, except in the case of resonances?

Hint: The justification for the transition from the velocity form to the length form of matrix elements is based on

$$\frac{\mathbf{p}}{m} = \frac{\mathrm{i}}{\hbar}[H,\mathbf{x}] \Rightarrow \langle f|\frac{\mathbf{p}}{m}|i\rangle = \mathrm{i}\omega_{fi}\langle f|\mathbf{x}|i\rangle.$$

18.11. Show that the transition rate (18.85) can formally be derived by incorrectly assuming a Golden Rule for transition between the discrete states $|n,\ell,m_\ell\rangle \to |n',\ell',m'_\ell\rangle$ in a semi-classical approximation (18.130) for the monochromatic perturbation $V(t)$, if we use the density of final states

$$\varrho(E)dE = d^3\boldsymbol{k} = d\Omega k^2 dk = d\Omega E^2 dE/(\hbar c)^3. \tag{18.131}$$

This works because (18.131) is the *density of continuous final states of the emitted photon* in the infinite volume limit, but we would have missed that important piece of information if we would just have naively insisted on using the Golden Rule for calculating the transition rate between states $|n,\ell,m_\ell\rangle \to |n',\ell',m'_\ell\rangle$ due to the monochromatic perturbation $V(t)$. Instead, we would have tried to make sense of the energy preserving δ function by invoking a final electron density of states $\varrho(E_{n'})$, e.g. by using some finite energy width of the final electron state. Any such guess would certainly not have produced the correct factor E^2, and we would also have missed the factor $d\Omega$ because the final electron state $|n',\ell',m'_\ell\rangle$ uses angular momentum quantum numbers instead of angles.

18.12. Ultraviolet photons with an energy $E_\gamma = 10.15\,\mathrm{eV}$ are nearly resonant with the $n = 1 \to n'' = 2$ transition in hydrogen. Use both the result (18.117) and the Kramers-Heisenberg formula (18.118) to estimate the differential scattering cross section for a photon scattering angle of $\pi/2$ if the incident photons are polarized in z direction and move in x direction. Assume that the scattered photons move in y direction with polarization $\boldsymbol{e}_z \cos\alpha + \boldsymbol{e}_x \sin\alpha$.

18.13. Express the photon absorption cross sections from Section 18.7 using the velocity form (instead of the length form) for the matrix elements.