Photons

We consider a radiation field whose vector potential $\boldsymbol{A}$ satisfies the transversality condition

$$\nabla \cdot \boldsymbol{A} = 0.$$

Because the electric and magnetic fields

$$\begin{aligned} \boldsymbol{E} &= -\frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{A} \\ \boldsymbol{B} &= \nabla \times \boldsymbol{A} \end{aligned}$$

satisfy the free space Maxwell equations

$$\begin{aligned} \nabla \cdot \boldsymbol{E} &= 0 \\ \nabla \times \boldsymbol{E} &= -\frac{\partial \boldsymbol{B}}{\partial t} \\ \nabla \cdot \boldsymbol{B} &= 0 \\ \nabla \times \boldsymbol{B} &= \frac{1}{c}\frac{\partial \boldsymbol{E}}{\partial t}, \end{aligned}$$

the vector potential satisfies the wave equation

$$\nabla^2 \boldsymbol{A} - \frac{1}{c^2}\frac{\partial^2 \boldsymbol{A}}{\partial t^2} = 0.$$

We write the vector potential at the moment $t = 0$ as a superposition of the periodically normalized plane waves (i.e. as a Fourier series) in an L-sided cube,

$$\boldsymbol{u}_{\boldsymbol{k},\alpha}(\boldsymbol{x}) = \hat{\boldsymbol{\epsilon}}^{(\alpha)} e^{i\boldsymbol{k}\cdot\boldsymbol{x}},$$

like:

$$\begin{aligned} \boldsymbol{A}(\boldsymbol{x},t)|_{t=0} &= \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k}}\sum_{\alpha=1,2}(c_{\boldsymbol{k},\alpha}(0)\boldsymbol{u}_{\boldsymbol{k},\alpha}(\boldsymbol{x}) \\ &\quad + c^*_{\boldsymbol{k},\alpha}(0)\boldsymbol{u}^*_{\boldsymbol{k},\alpha}(\boldsymbol{x})). \end{aligned}$$

Here $V = L^3$ and $\hat{\boldsymbol{\epsilon}}(\boldsymbol{k})^{(\alpha)}, \alpha = 1, 2$ are real polarization vectors.
Due to the transversality condition we have

$$\hat{\boldsymbol{\epsilon}}^{(\alpha)} \cdot \boldsymbol{k} = 0,$$

so the polarization can be chosen so that the vectors

$$\hat{\boldsymbol{\epsilon}}^{(1)} \quad , \quad \hat{\boldsymbol{\epsilon}}^{(2)} \quad , \quad \boldsymbol{k}/|\boldsymbol{k}|$$

are orthonormal and form a righthanded rectangular coordinate system.
The Fourier components $\boldsymbol{u}_{\boldsymbol{k},\alpha}$ satisfy the orthogonality conditions

$$\frac{1}{V}\int d^3x\, \boldsymbol{u}_{\boldsymbol{k},\alpha} \cdot \boldsymbol{u}^*_{\boldsymbol{k}',\alpha'} = \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'}.$$

Due to the periodicity conditions the wave vectors can take the values

$$k_x, k_y, k_z = 2n\pi/L, \quad n = \pm 1, \pm 2, \ldots .$$

At the moment $t \neq 0$ the vector potential is obtained simply by setting

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

where

$$\omega = |\boldsymbol{k}|c.$$

Now

$$\begin{aligned} &\boldsymbol{A}(\boldsymbol{x}, t) \\ &\quad = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \sum_{\alpha} (c_{\boldsymbol{k},\alpha}(t)\hat{\boldsymbol{\epsilon}}^{(\alpha)} e^{i\boldsymbol{k}\cdot\boldsymbol{x}} + c^*_{\boldsymbol{k},\alpha}(t)\hat{\boldsymbol{\epsilon}}^{(\alpha)} e^{-i\boldsymbol{k}\cdot\boldsymbol{x}}) \\ &\quad = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \sum_{\alpha} (c_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)} e^{ik^\mu x_\mu} + c^*_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)} e^{-ik^\mu x_\mu}), \end{aligned}$$

where we have employed the four-vector notation

$$k^\mu x_\mu = \boldsymbol{k} \cdot \boldsymbol{x} - \omega t = \boldsymbol{k} \cdot \boldsymbol{x} - |\boldsymbol{k}|ct.$$

The Hamiltonian function of the classical radiation field is

$$\begin{aligned} H &= \frac{1}{2} \int (|\boldsymbol{B}|^2 + |\boldsymbol{E}|^2)\, d^3x \\ &= \frac{1}{2} \int \left[|\nabla \times \boldsymbol{A}|^2 + |(1/c)(\partial \boldsymbol{A}/\partial t)|^2 \right] d^3x. \end{aligned}$$

A straightforward calculation shows that

$$H = \sum_{\boldsymbol{k}} \sum_{\alpha} 2(\omega/c)^2 c^*_{\boldsymbol{k},\alpha} c_{\boldsymbol{k},\alpha}.$$

Because the coefficients

$$c_{\boldsymbol{k},\alpha}(t) = c_{\boldsymbol{k},\alpha}(0)e^{-i\omega t}$$

satisfy the equation of motion

$$\ddot{c}_{\boldsymbol{k},\alpha} = -\omega^2 c_{\boldsymbol{k},\alpha},$$

it would look like the classical radiation field were composed of independent harmonic oscillators.
We define the variables

$$\begin{aligned} Q_{\boldsymbol{k},\alpha} &= \frac{1}{c}(c_{\boldsymbol{k},\alpha} + c^*_{\boldsymbol{k},\alpha}) \\ P_{\boldsymbol{k},\alpha} &= -\frac{i\omega}{c}(c_{\boldsymbol{k},\alpha} - c^*_{\boldsymbol{k},\alpha}). \end{aligned}$$

With the help of these the Hamiltonian function can be written as

$$H = \sum_{\boldsymbol{k}} \sum_{\alpha} \frac{1}{2}(P^2_{\boldsymbol{k},\alpha} + \omega^2 Q^2_{\boldsymbol{k},\alpha}).$$

Since

$$\begin{aligned} \frac{\partial H}{\partial Q_{\boldsymbol{k},\alpha}} &= -\dot{P}_{\boldsymbol{k},\alpha} \\ \frac{\partial H}{\partial P_{\boldsymbol{k},\alpha}} &= +\dot{Q}_{\boldsymbol{k},\alpha}, \end{aligned}$$

the variables $P_{\boldsymbol{k},\alpha}$ and $Q_{\boldsymbol{k},\alpha}$ are canonically conjugated and the Hamiltonian function the sum of the total energies of the corresponding harmonic oscillators.
Thus the classical radiation field can be thought to be a collection of independent harmonic oscillators. There

- every oscillator is characterized by the wave vector $\boldsymbol{k}$ and the polarization $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$,
- the dynamic variables of every oscillator are combinations of Fourier coefficients.

We quantize these oscillators by postulating that $P_{\boldsymbol{k},\alpha}$ and $Q_{\boldsymbol{k},\alpha}$ are not any more pure numbers but *operators* which satisfy the canonical commutation rules

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

We define dimensionless combinations $a_{\boldsymbol{k},\alpha}$ and $a^\dagger_{\boldsymbol{k},\alpha}$ of the operators $P_{\boldsymbol{k},\alpha}$ and $Q_{\boldsymbol{k},\alpha}$ as

$$\begin{aligned} a_{\boldsymbol{k},\alpha} &= \frac{1}{\sqrt{2\hbar\omega}}(\omega Q_{\boldsymbol{k},\alpha} + iP_{\boldsymbol{k},\alpha}) \\ a^\dagger_{\boldsymbol{k},\alpha} &= \frac{1}{\sqrt{2\hbar\omega}}(\omega Q_{\boldsymbol{k},\alpha} - iP_{\boldsymbol{k},\alpha}). \end{aligned}$$

Note These are of the same form as the simple harmonic oscillator a,$a^\dagger$ just with x, p replaced with the corresponding (generalized) canonical variables.
Also, these are for radiation field and thus $|\boldsymbol{p}| = h/\lambda \neq |\boldsymbol{p}|_{\text{particle}} = m|\boldsymbol{v}|$
With lidl algebra we see the connection

$$c_{\boldsymbol{k},\alpha} \to c\sqrt{\frac{\hbar}{2\omega}}a_{\boldsymbol{k},\alpha} \qquad c^*_{\boldsymbol{k},\alpha} \to c\sqrt{\frac{\hbar}{2\omega}}a^\dagger_{\boldsymbol{k},\alpha}$$

It is easy to see that they satisfy the commutation relations

$$\begin{aligned}[][a_{\boldsymbol{k},\alpha}, a^\dagger_{\boldsymbol{k}',\alpha'}] &= \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'} \\ [a_{\boldsymbol{k},\alpha}, a_{\boldsymbol{k}',\alpha'}] &= [a^\dagger_{\boldsymbol{k},\alpha}, a^\dagger_{\boldsymbol{k}',\alpha'}] = 0.\end{aligned}$$

Note In these relations the operators must be evaluated at the same moment, i.e. $[a_{\boldsymbol{k},\alpha}, a^\dagger_{\boldsymbol{k}',\alpha'}]$ stands in fact for the commutator $[a_{\boldsymbol{k},\alpha}(t), a^\dagger_{\boldsymbol{k}',\alpha'}(t)]$.
We further define the Hermitean operator

$$N_{\boldsymbol{k},\alpha} = a^\dagger_{\boldsymbol{k},\alpha} a_{\boldsymbol{k},\alpha}.$$

It is easy to see that

$$\begin{aligned}[][a_{\boldsymbol{k},\alpha}, N_{\boldsymbol{k}',\alpha'}] &= \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'} a_{\boldsymbol{k},\alpha} \\ [a^\dagger_{\boldsymbol{k},\alpha}, N_{\boldsymbol{k}',\alpha'}] &= -\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'} a^\dagger_{\boldsymbol{k},\alpha}.\end{aligned}$$

Due to the Hermiticity the eigenvalues $n_{\boldsymbol{k},\alpha}$ of the operator $N_{\boldsymbol{k},\alpha}$ are real and the eigenvectors

$$N_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle = n_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle$$

form an orthonormal complete basis.
With the help of the commutation rule

$$[a^\dagger_{\boldsymbol{k},\alpha}, N_{\boldsymbol{k}',\alpha'}] = -\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\alpha\alpha'} a^\dagger_{\boldsymbol{k},\alpha}$$

we see that

$$\begin{aligned}N_{\boldsymbol{k},\alpha} a^\dagger_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle &= (a^\dagger_{\boldsymbol{k},\alpha} N_{\boldsymbol{k},\alpha} + a^\dagger_{\boldsymbol{k},\alpha})|n_{\boldsymbol{k},\alpha}\rangle \\ &= (n_{\boldsymbol{k},\alpha} + 1) a^\dagger_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle.\end{aligned}$$

Similarly we can show that

$$N_{\boldsymbol{k},\alpha} a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle = (n_{\boldsymbol{k},\alpha} - 1) a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle.$$

Thus we can write

$$\begin{aligned}a^\dagger_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle &= c_+|n_{\boldsymbol{k},\alpha} + 1\rangle \\ a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle &= c_-|n_{\boldsymbol{k},\alpha} - 1\rangle.\end{aligned}$$

Because the states $|n_{\boldsymbol{k},\alpha}\rangle$ are normalized we can calculate the coefficients as

$$\begin{aligned}|c_+|^2 &= |c_+|^2 \langle n_{\boldsymbol{k},\alpha} + 1|n_{\boldsymbol{k},\alpha} + 1\rangle \\ &= \langle n_{\boldsymbol{k},\alpha}|a_{\boldsymbol{k},\alpha} a^\dagger_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle \\ &= \langle n_{\boldsymbol{k},\alpha}|N_{\boldsymbol{k},\alpha} + [a_{\boldsymbol{k},\alpha}, a^\dagger_{\boldsymbol{k},\alpha}]|n_{\boldsymbol{k},\alpha}\rangle \\ &= n_{\boldsymbol{k},\alpha} + 1, \\ |c_-|^2 &= \langle n_{\boldsymbol{k},\alpha}|a^\dagger_{\boldsymbol{k},\alpha} a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle = n_{\boldsymbol{k},\alpha}.\end{aligned}$$

We choose the phase of the coefficients so that at the moment $t = 0$ we have

$$\begin{aligned} a^\dagger_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle &= \sqrt{n_{\boldsymbol{k},\alpha}+1}|n_{\boldsymbol{k},\alpha}+1\rangle \\ a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle &= \sqrt{n_{\boldsymbol{k},\alpha}}|n_{\boldsymbol{k},\alpha}-1\rangle. \end{aligned}$$

Because

$$n_{\boldsymbol{k},\alpha} = \langle n_{\boldsymbol{k},\alpha}|N_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle = \langle n_{\boldsymbol{k},\alpha}|a^\dagger_{\boldsymbol{k},\alpha}a_{\boldsymbol{k},\alpha}|n_{\boldsymbol{k},\alpha}\rangle$$

and because the norm of a vectors is always non-negative we must have

$$n_{\boldsymbol{k},\alpha} \geq 0.$$

From this we can deduce that the only possible eigenvalues are

$$n_{\boldsymbol{k},\alpha} = 0, 1, 2, \ldots.$$

We interprete

- the state $|n_{\boldsymbol{k},\alpha}\rangle$ to contain exactly $n_{\boldsymbol{k},\alpha}$ *photons*, each of which is characterized by a wave vector $\boldsymbol{k}$ and a polarization $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$.
- the operator $a^\dagger_{\boldsymbol{k},\alpha}$ to create a photon with the wave vector $\boldsymbol{k}$ and the polarization $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$.
- the operator $a_{\boldsymbol{k},\alpha}$ to destroy a photon with the wave vector $\boldsymbol{k}$ and the polarizartion $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$.
- the operator $N_{\boldsymbol{k},\alpha}$ to count the number of photons with the wave vector $\boldsymbol{k}$ and the polarization $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$ in the state

The state composed of various kind of photons is a direct product of individual vectors $|n_{\boldsymbol{k}_i,\alpha_i}\rangle$:

$$\begin{aligned} &|n_{\boldsymbol{k}_1,\alpha_1}, n_{\boldsymbol{k}_2,\alpha_2}, \ldots, n_{\boldsymbol{k}_i,\alpha_i}, \ldots\rangle \\ &\quad = |n_{\boldsymbol{k}_1,\alpha_1}\rangle \otimes |n_{\boldsymbol{k}_2,\alpha_2}\rangle \otimes \cdots \otimes |n_{\boldsymbol{k}_i,\alpha_i}\rangle \otimes \cdots. \end{aligned}$$

The vector $|0\rangle$ stands for the state that has no kind of photons, i.e.

$$|0\rangle = |0_{\boldsymbol{k}_1,\alpha_1}\rangle \otimes |0_{\boldsymbol{k}_2,\alpha_2}\rangle \otimes \cdots.$$

Application of any operator $a_{\boldsymbol{k},\alpha}$ onto this results always zero. We say that $|0\rangle$ represents the vacuum.
It is easy to see that a general normalized photon state can be constructed applying operations $a^\dagger_{\boldsymbol{k},\alpha}$ consecutively:

$$|n_{\boldsymbol{k}_1,\alpha_1}, n_{\boldsymbol{k}_2,\alpha_2}, \ldots\rangle = \prod_{\boldsymbol{k}_i,\alpha_i} \frac{(a^\dagger_{\boldsymbol{k}_i,\alpha_i})^{n_{\boldsymbol{k}_i,\alpha_i}}}{\sqrt{n_{\boldsymbol{k}_i,\alpha_i}!}}|0\rangle.$$

Note Since the operators $a^\dagger_{\boldsymbol{k},\alpha}$ and $a^\dagger_{\boldsymbol{k}',\alpha'}$ commute the order of operators does not matter. The many photon states are symmetric with respect to the exchange of photons. We say that the photons obey the *Bose-Einstein statistics* or that they are *bosons*.
Since the numbers $n_{\boldsymbol{k},\alpha}$ tell us the number of photons of type $(\boldsymbol{k},\alpha)$ in the volume under consideration we call them the *occupation numbers* of the state. Correspondingly the space spanned by the state vectors is called the *occupation number space*.
In the quantum theory the Fourier coefficients of a classical radiation field must be replaced by the corresponding non-commuting creation and annihilation operators. Substituting

$$\begin{aligned} c_{\boldsymbol{k},\alpha} &\mapsto c\sqrt{\hbar/2\omega}\, a_{\boldsymbol{k},\alpha}(t) \\ c^*_{\boldsymbol{k},\alpha} &\mapsto c\sqrt{\hbar/2\omega}\, a^\dagger_{\boldsymbol{k},\alpha}(t) \end{aligned}$$

we get

$$\boldsymbol{A}(\boldsymbol{x},t) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k},\alpha} c\sqrt{\frac{\hbar}{2\omega}}\Big[a_{\boldsymbol{k},\alpha}(t)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{i\boldsymbol{k}\cdot\boldsymbol{x}} + a^\dagger_{\boldsymbol{k},\alpha}(t)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{-i\boldsymbol{k}\cdot\boldsymbol{x}}\Big].$$

Note Here $\boldsymbol{A}$ is an *operator* defined at every point of the space whereas $\boldsymbol{A}$ of the classical theory is a three component field defined at every point. The variables $\boldsymbol{x}$ and t are both in classical and quantum mechanical cases variables parametrizing the fields. Fields like the operator $\boldsymbol{A}$ are called *field operators* or *quantized fields*.
Also in the quantum theory the Hamiltonian is of the form

$$H = \frac{1}{2}\int (\boldsymbol{B}\cdot\boldsymbol{B} + \boldsymbol{E}\cdot\boldsymbol{E})\, d^3x.$$

Substituting the field operator $\boldsymbol{A}$ into the equations

$$\begin{aligned} \boldsymbol{E} &= -\frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{A} \\ \boldsymbol{B} &= \nabla\times\boldsymbol{A} \end{aligned}$$

and noting that this time the Fourier coefficients do not commute we get

$$\begin{aligned} H &= \frac{1}{2}\sum_{\boldsymbol{k}}\sum_{\alpha}\hbar\omega(a^\dagger_{\boldsymbol{k},\alpha}a_{\boldsymbol{k},\alpha} + a_{\boldsymbol{k},\alpha}a^\dagger_{\boldsymbol{k},\alpha}) \\ &= \sum_{\boldsymbol{k}}\sum_{\alpha}(N_{\boldsymbol{k},\alpha} + \frac{1}{2})\hbar\omega, \end{aligned}$$

where

$$\omega = |\boldsymbol{k}|c.$$

When we choose the energy scale so that

$$H|0\rangle = 0,$$

the Hamiltonian takes the form

$$H = \sum_{\boldsymbol{k}} \sum_{\alpha} \hbar\omega N_{\boldsymbol{k},\alpha}.$$

When it acts on a many photon state the result is

$$\begin{aligned} &H|n_{\boldsymbol{k}_1,\alpha_1}, n_{\boldsymbol{k}_2,\alpha_2}, \ldots\rangle \\ &\quad = \sum_i n_{\boldsymbol{k}_i,\alpha_i} \hbar\omega_i |n_{\boldsymbol{k}_1,\alpha_1}, n_{\boldsymbol{k}_2,\alpha_2}, \ldots\rangle. \end{aligned}$$

The quantum mechanical momentum operator is exactly of the same form as the classical function (the Poynting vector):

$$\begin{aligned} \boldsymbol{P} &= \frac{1}{c}\int (\boldsymbol{E}\times\boldsymbol{B})\, d^3x \\ &= \sum_{\boldsymbol{k}} \sum_{\alpha} \frac{1}{2}\hbar\boldsymbol{k}(a^\dagger_{\boldsymbol{k},\alpha} a_{\boldsymbol{k},\alpha} + a_{\boldsymbol{k},\alpha} a^\dagger_{\boldsymbol{k},\alpha}) \\ &= \sum_{\boldsymbol{k}} \sum_{\alpha} \hbar\boldsymbol{k}(N_{\boldsymbol{k},\alpha} + \frac{1}{2}). \end{aligned}$$

Since here the summation goes over all wave vectors the term associated with the factor $1/2$ will not appear in the final result because the terms $\hbar\boldsymbol{k}$ and $-\hbar\boldsymbol{k}$ cancel each other. For the momentum operator we get thus

$$\boldsymbol{P} = \sum_{\boldsymbol{k}} \sum_{\alpha} \hbar\boldsymbol{k} N_{\boldsymbol{k},\alpha}.$$

For one photon states we have

$$\begin{aligned} H a^\dagger_{\boldsymbol{k},\alpha}|0\rangle &= \hbar\omega a^\dagger_{\boldsymbol{k},\alpha}|0\rangle \\ \boldsymbol{P} a^\dagger_{\boldsymbol{k},\alpha}|0\rangle &= \hbar\boldsymbol{k} a^\dagger_{\boldsymbol{k},\alpha}|0\rangle, \end{aligned}$$

so

$$\begin{aligned} \hbar\omega = \hbar|\boldsymbol{k}|c &= \text{photon energy} \\ \hbar\boldsymbol{k} &= \text{photon momentum.} \end{aligned}$$

The photon mass will be

$$\begin{aligned} (\text{mass})^2 &= \frac{1}{c^4}(E^2 - |\boldsymbol{p}|^2c^2) \\ &= \frac{1}{c^4}[(\hbar\omega)^2 - (\hbar|\boldsymbol{k}|c)^2] \\ &= 0. \end{aligned}$$

The photon state is also characterized by its polarization $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$. Since $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$ transforms under rotations like a vector the photon is associated with one unit of angular momentum, i.e. the spin angular momentum of the photon is one. We define the *circularly polarized* combinations

$$\hat{\boldsymbol{\epsilon}}^{(\pm)} = \mp\frac{1}{\sqrt{2}}(\hat{\boldsymbol{\epsilon}}^{(1)} \pm i\hat{\boldsymbol{\epsilon}}^{(2)}).$$

We rotate these vectors by an infinitesimal angle $\delta\phi$ around the progation direction $\boldsymbol{k}$. Their changes are

$$\begin{aligned} \delta\hat{\boldsymbol{\epsilon}}^{(\pm)} &= \mp\frac{\delta\phi}{\sqrt{2}}(\hat{\boldsymbol{\epsilon}}^{(2)} \mp i\hat{\boldsymbol{\epsilon}}^{(1)}) \\ &= \mp i\delta\phi\,\hat{\boldsymbol{\epsilon}}^{(\pm)}. \end{aligned}$$

We select the propagation direction $\boldsymbol{k}$ as the quantization axis and compare this expression with the transformation properties of angular momentum eigenstates

$$|jm\rangle_R = \left(1 - \frac{i}{\hbar}J_z\delta\phi\right)|jm\rangle = (1 - im\,\delta\phi)|jm\rangle.$$

We see that

- the spin components of the polarizations $\hat{\boldsymbol{\epsilon}}^{(\pm)}$ are $m = \pm 1$.
- the state $m = 0$ is missing due to the transversality condition.
- our original linear polarization states are 50/50 mixtures of $m = 1$ and $m = -1$ states.

Hence the photon spin is always either parallel or antiparallel to the direction of the propagation.
The operators $a_{\boldsymbol{k},\alpha}$ and $a^\dagger_{\boldsymbol{k},\alpha}$ are time dependent and so they satisfy the Heisenberg equations of motion

$$\begin{aligned} \dot{a}_{\boldsymbol{k},\alpha} &= \frac{i}{\hbar}[H, a_{\boldsymbol{k},\alpha}] \\ &= \frac{i}{\hbar}\sum_{\boldsymbol{k}'}\sum_{\alpha'}[\hbar\omega' N_{\boldsymbol{k}',\alpha'}, a_{\boldsymbol{k},\alpha}] \\ &= -i\omega a_{\boldsymbol{k},\alpha} \end{aligned}$$

like also

$$\dot{a}^\dagger_{\boldsymbol{k},\alpha} = i\omega a^\dagger_{\boldsymbol{k},\alpha}.$$

These equations have solutions

$$\begin{aligned} a_{\boldsymbol{k},\alpha} &= a_{\boldsymbol{k},\alpha}(0)e^{-i\omega t} \\ a^\dagger_{\boldsymbol{k},\alpha} &= a^\dagger_{\boldsymbol{k},\alpha}(0)e^{i\omega t}. \end{aligned}$$

The final form of the field operator is then

$$\boldsymbol{A}(\boldsymbol{x},t) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k},\alpha} c\sqrt{\frac{\hbar}{2\omega}}\Big[a_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{i\boldsymbol{k}\cdot\boldsymbol{x}-i\omega t} + a^{\dagger}_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)}e^{-i\boldsymbol{k}\cdot\boldsymbol{x}+i\omega t}\Big].$$

We should note that

- the operator $\boldsymbol{A}$ is Hermitean.
- $\boldsymbol{x}$ and t in the expression for the field operator $\boldsymbol{A}$ are not quantum mechanical variables but simply parameters which the operator $\boldsymbol{A}$ depends on. For example, it is not allowed to interprete the variables $\boldsymbol{x}$ and t as the space-time coordinates of a photon.
- the quantized field $\boldsymbol{A}$ operates at every point $(\boldsymbol{x},t)$ of the space where it with a certain probability creates and annihilates excitation states called photons. Thus photons can be interpreted as the quantum mechanical excitations of the radiation field. They have 2 definitive properties: mass $= 0$ and spin $= 1$.
- (Analogically) quantization of other fields lead to similar definitive properties (mass,spin) for the corresponding force carriers.

RadMatInt revised

We consider photon emission and absorption of non relativistic atomic electrons. The relevant interaction Hamiltonian is of the form

$$H_{\text{int}} = \sum_i \Big[-\frac{e}{m_e c}\boldsymbol{A}(\boldsymbol{x}_i,t)\cdot\boldsymbol{p}_i + \frac{e^2}{2m_e^2c^2}\boldsymbol{A}(\boldsymbol{x}_i,t)\cdot\boldsymbol{A}(\boldsymbol{x}_i,t)\Big],$$

where the transversality condition is taken into account by replacing the operator $\boldsymbol{p}_i\cdot\boldsymbol{A}$ with the operator $\boldsymbol{A}\cdot\boldsymbol{p}_i$. The summation goes over all electrons participating in the process. The symbols $\boldsymbol{x}_i$ stand for their position coordinates.

Note If we had to consider the interaction of spin and radiation we should also include the term

$$H^{(\text{spin})}_{\text{int}} = -\sum_i \frac{e\hbar}{2m_e c}\boldsymbol{\sigma}_i\cdot\left[\nabla\times\boldsymbol{A}(\boldsymbol{x},t)\right]|_{\boldsymbol{x}=\boldsymbol{x}_i}.$$

This time the Hamiltonian operator H_{int} operates not only on the atomic states but also on the photon states. In the quantum theory of radiation

- the vector describing the initial state $|i\rangle$ is the direct product of an atomic state A and a (many) photon state characterized by the occupation numbers $n_{\boldsymbol{k},\alpha}$:

$$|i\rangle = |A\rangle \otimes |n_{\boldsymbol{k},\alpha}\rangle = |A; n_{\boldsymbol{k},\alpha}\rangle.$$

- the vector describing the final state $|f\rangle$ is the direct product of an atomic state B and a (many) photon state characterized by the occupation numbers $n_{\boldsymbol{k}',\alpha'}$:

$$|f\rangle = |B\rangle \otimes |n_{\boldsymbol{k}',\alpha'}\rangle = |B; n_{\boldsymbol{k}',\alpha'}\rangle.$$

Absorption
Now

$$\begin{aligned} |i\rangle &= |A; n_{\boldsymbol{k},\alpha}\rangle \\ |f\rangle &= |B; n_{\boldsymbol{k},\alpha} - 1\rangle. \end{aligned}$$

In the first order perturbation theory the amplitude of the process

$$|i\rangle \longrightarrow |f\rangle$$

is the matrix element of the interaction operator H_I between the states $|i\rangle$ and $|f\rangle$. Up to this order

- only $a_{\boldsymbol{k},\alpha}$ leads to a nonzero matrix element, even though the field operator $\boldsymbol{A}$ is a linear superposition of creation and annihilation operators $a^\dagger_{\boldsymbol{k},\alpha}$ and $a_{\boldsymbol{k},\alpha}$, respectively.
- the term $\boldsymbol{A}\cdot\boldsymbol{A}$ is out of the question in this process because it either changes the number of photons by two or does not change it at all.

The first order transition matrix element is now

$$\begin{aligned} &\langle B; n_{\boldsymbol{k},\alpha} - 1|H_{\text{int}}|A; n_{\boldsymbol{k},\alpha}\rangle \\ &\quad = -\frac{e}{m_e c}\langle B; n_{\boldsymbol{k},\alpha} - 1| \\ &\qquad \sum_i c\sqrt{\frac{\hbar}{2\omega V}}a_{\boldsymbol{k},\alpha}(0)e^{i\boldsymbol{k}\cdot\boldsymbol{x}_i - i\omega t}\boldsymbol{p}_i\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|A; n_{\boldsymbol{k},\alpha}\rangle \\ &\quad = -\frac{e}{m_e}\sqrt{\frac{n_{\boldsymbol{k},\alpha}\hbar}{2\omega V}}\sum_i\langle B|e^{i\boldsymbol{k}\cdot\boldsymbol{x}_i}\boldsymbol{p}_i\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|A\rangle e^{-i\omega t}. \end{aligned}$$

Comparing this with the matrix element of the semiclassical perturbation potential

$$\mathcal{V}^\dagger_{ni} = -\frac{eA_0}{m_e c}\left(e^{i(\omega/c)\hat{\boldsymbol{n}}\cdot\boldsymbol{x}}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{p}\right)_{ni}$$

we see that they both give exactly the same result provided we use in the semiclassical theory the equivalent radiation field

$$\boldsymbol{A}^{(\mathrm{abs})} = \boldsymbol{A}_0^{(\mathrm{abs})} e^{i\boldsymbol{k}\cdot\boldsymbol{x} - i\omega t},$$

where the amplitude is

$$\boldsymbol{A}_0^{(\mathrm{abs})} = c\sqrt{\frac{n_{\boldsymbol{k},\alpha}\hbar}{2\omega V}}\hat{\boldsymbol{\epsilon}}^{(\alpha)}.$$

Because the transition probability is

- according to the semiclassical theory directly proportional to the intensity of the radiation,

$$|\boldsymbol{A}_0|^2 \propto n_{\boldsymbol{k},\alpha},$$

- according to the quantum theory directly proportional to the occupation number $n_{\boldsymbol{k},\alpha}$,

both the semiclassical and quantum mechanical results give equivalent results also at low intensities, i.e. when $n_{\boldsymbol{k},\alpha}$ is small.
This is not true in the case of emission.

Emission
Now

$$\begin{aligned} |i\rangle &= |A; n_{\boldsymbol{k},\alpha}\rangle \\ |f\rangle &= |B; n_{\boldsymbol{k},\alpha} + 1\rangle \end{aligned}$$

and in the first order the only potential term of the field

$$\begin{aligned} \boldsymbol{A}(\boldsymbol{x}, t) &= \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k},\alpha} c\sqrt{\frac{\hbar}{2\omega}} \Big[a_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)} e^{i\boldsymbol{k}\cdot\boldsymbol{x} - i\omega t} \\ &\quad + a^\dagger_{\boldsymbol{k},\alpha}(0)\hat{\boldsymbol{\epsilon}}^{(\alpha)} e^{-i\boldsymbol{k}\cdot\boldsymbol{x} + i\omega t} \Big] \end{aligned}$$

is $a^\dagger_{\boldsymbol{k},\alpha}$ which adds one photon to the final state. The relevant matrix element is now

$$\begin{aligned} &\langle B; n_{\boldsymbol{k},\alpha} + 1 | H_{\mathrm{int}} | A; n_{\boldsymbol{k},\alpha}\rangle \\ &\quad = -\frac{e}{m_e}\sqrt{\frac{(n_{\boldsymbol{k},\alpha} + 1)\hbar}{2\omega V}} \sum_i \langle B | e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_i} \boldsymbol{p}_i \cdot \hat{\boldsymbol{\epsilon}}^{(\alpha)} | A\rangle e^{i\omega t}. \end{aligned}$$

If $n_{\boldsymbol{k},\alpha}$ is very large then

$$\sqrt{n_{\boldsymbol{k},\alpha} + 1} \approx \sqrt{n_{\boldsymbol{k},\alpha}},$$

and the semiclassical and quantum mechanical treatment coincide.
If $n_{\boldsymbol{k},\alpha}$ is small the semiclassical method fails completely. In particular, the semiclassical treatment of the spontaneous emission, $n_{\boldsymbol{k},\alpha} = 0$, is impossible. The semiclassical method can be applied if we insert the atom into the fictitious radiation field

$$\boldsymbol{A}^{(\mathrm{emis})} = \boldsymbol{A}_0^{(\mathrm{emis})} e^{-i\boldsymbol{k}\cdot\boldsymbol{x}+i\omega t},$$

where

$$\boldsymbol{A}_0^{(\mathrm{emis})} = c\sqrt{\frac{(n_{\boldsymbol{k},\alpha}+1)\hbar}{2\omega V}}\hat{\boldsymbol{\epsilon}}^{(\alpha)}.$$

The field $\boldsymbol{A}^{(\mathrm{emis})}$ is not

- directly proportional to the number of photons $n_{\boldsymbol{k},\alpha}$,
- the complex conjugate of the field $\boldsymbol{A}^{(\mathrm{abs})}$.

Example Spontaneous emission (e.g. isolated atom) from the state A to the state B.
In the first order the transition rate is

$$\begin{aligned} w_{A\to B} & \\ &= \frac{2\pi}{\hbar}|\langle B; 1_{\boldsymbol{k},\alpha}|H_{\mathrm{int}}|A;0\rangle|^2\delta(E_B - E_A + \hbar\omega) \\ &= \frac{2\pi}{\hbar}\frac{e^2\hbar}{2m_e^2\omega V}\left|\sum_i \langle B|e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_i}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\boldsymbol{p}_i|A\rangle\right|^2 \\ &\quad\times\delta(E_B - E_A + \hbar\omega). \end{aligned}$$

Like in the photoelectric effect we can deduce that the number of the allowed photon states $\rho(E, d\Omega)$ in the energy interval $(\hbar\omega, \hbar\omega + d(\hbar\omega))$ and in the solid angle $d\Omega$ is

$$\rho(E, d\Omega) = n^2\, dn\, d\Omega = \frac{V}{(2\pi)^3}\frac{\omega^2}{\hbar c^3}\, d(\hbar\omega)\, d\Omega.$$

The transition rate of photons emitting into a certain solid angle is thus

$$w_{d\Omega} = \frac{2\pi}{\hbar}\frac{e^2\hbar}{2m_e^2\omega V}\left|\sum_i \langle B|e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_i}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\boldsymbol{p}_i|A\rangle\right|^2\frac{V\omega^2\, d\Omega}{(2\pi)^3\hbar c^3},$$

where $\hbar\omega = E_A - E_B$.
We consider only hydrogen like atoms so that only one electron participates in the process and we restrict to the dipole approximation. Then

$$w_{d\Omega} = \frac{e^2\omega}{8\pi^2 m_e^2\hbar c^3}|\langle B|\boldsymbol{p}|A\rangle\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|^2 d\Omega.$$

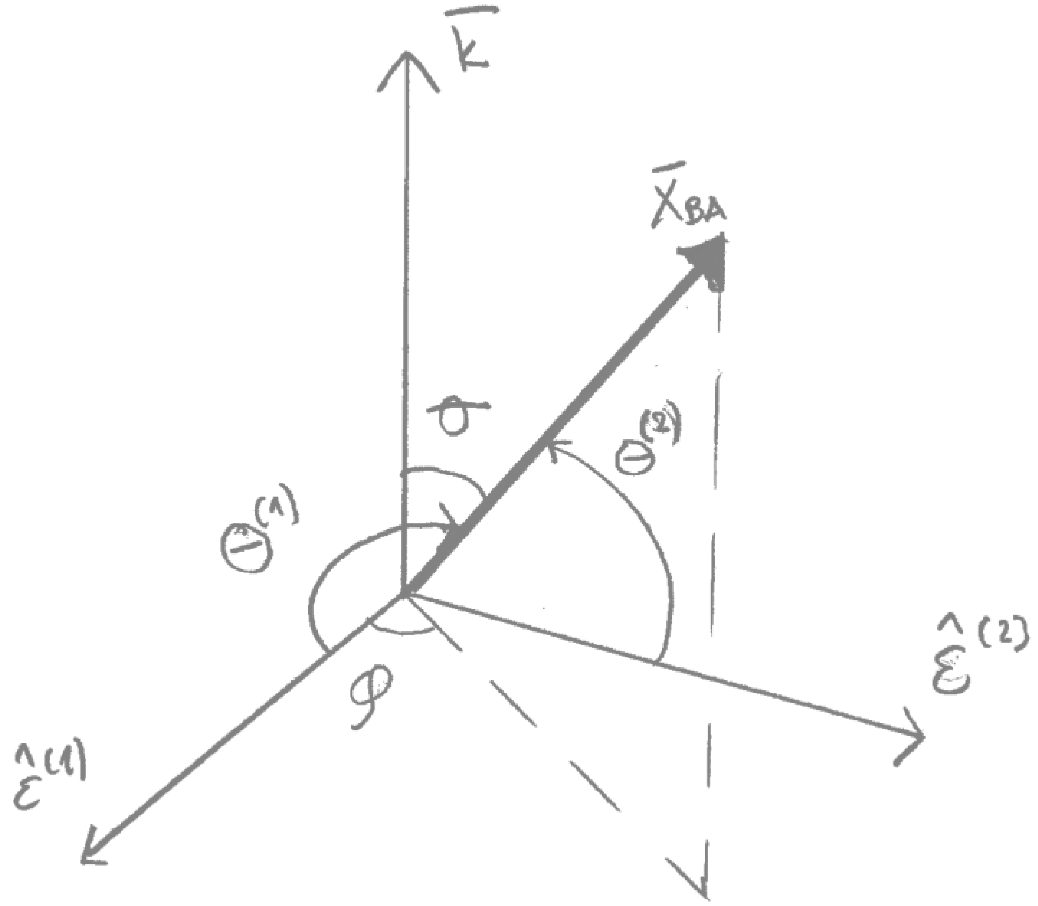
Earlier we saw that

$$\begin{aligned}\langle B|\boldsymbol{p}|A\rangle &= \frac{im_e(E_B - E_A)}{\hbar}\langle B|\boldsymbol{x}|A\rangle \\ &= -im_e\omega\boldsymbol{x}_{BA}.\end{aligned}$$

We let the symbol $\Theta^{(\alpha)}$ stand for the angle between the vector $\boldsymbol{x}_{BA}$ and the polarization direction $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$, i.e.

$$\begin{aligned}\cos\Theta^{(1)} &= \sin\theta\cos\phi \\ \cos\Theta^{(2)} &= \sin\theta\sin\phi,\end{aligned}$$

when θ and ϕ are the direction angles of the vector $\boldsymbol{x}$.



$\bar{X}_{BA}$ ORIENTATION

Then

$$w_{d\Omega} = \frac{e^2\omega^3}{8\pi^2\hbar c^3}|\boldsymbol{x}_{BA}|^2 \cos^2\Theta^{(\alpha)} d\Omega.$$

The total transition rate is obtained by integrating over all propagation directions $\boldsymbol{k}/|\boldsymbol{k}|$ and summing over both polarizations:

$$w = \frac{e^2\omega^3}{3\pi\hbar c^3}|\boldsymbol{x}_{BA}|^2.$$

The life time of a state was obtained from the formula

$$\frac{1}{\tau_A} = \sum_i w_{A \to B_i},$$

where we have to sum also over the magnetic quantum numbers m. For example the life time of the hydrogen $2p$ state is

$$\tau(2p \longrightarrow 1s) = 1.6 \times 10^{-9}\mathrm{s}.$$

Note There are constraints for the allowed matrix elements ($\Delta l = 1, \Delta m = 0$ and parity constraint)

Electron photon scattering
We consider the process

$$|1_{\boldsymbol{k},\alpha}\rangle \longrightarrow |1_{\boldsymbol{k}',\alpha'}\rangle,$$

i.e.

- before the scattering the atom is in the state A, and $\boldsymbol{k}$ and $\hat{\boldsymbol{\epsilon}}^{(\alpha)}$ are the wave vector and polarization of the incoming photon.
- after the scattering the atom is in the state B, $\boldsymbol{k}'$ is the wave vector and $\hat{\boldsymbol{\epsilon}}^{(\alpha')}$ the polarization vector of the outgoing photon.

The Hamiltonian of the interaction is

$$H_{\mathrm{int}} = -\frac{e}{m_e c}\boldsymbol{A}(\boldsymbol{x},t)\cdot\boldsymbol{p} + \frac{e^2}{2m_e^2c^2}\boldsymbol{A}(\boldsymbol{x},t)\cdot\boldsymbol{A}(\boldsymbol{x},t).$$

Because

- the number of photons does not change in the scattering,
- in order to be non zero the matrix element of the interaction must contain products of photon creation and annihilation operators,
- in the term $\boldsymbol{A}\cdot\boldsymbol{p}$ creation and annihilation operators appear as linear,
- in the term $\boldsymbol{A}\cdot\boldsymbol{A}$ creation and annihilation operators appear as quadratic,

only the quadratic term $\boldsymbol{A}\cdot\boldsymbol{A}$ contributes in the first order perturbation theory.
Only two of the terms of the form

$$aa^\dagger, a^\dagger a, aa, a^\dagger a^\dagger$$

in the operator $\boldsymbol{A}\cdot\boldsymbol{A}$ have non zero matrix elements provided that

- $a^\dagger$ creates a photon of the type $(\boldsymbol{k}', \hat{\boldsymbol{\epsilon}}^{(\alpha')})$,

- a annihilates a photon of the type $(\boldsymbol{k}, \hat{\boldsymbol{\epsilon}}^{(\alpha)})$,

and then
$$\langle 1_{\boldsymbol{k}',\alpha'}|a_{\boldsymbol{k},\alpha}a^\dagger_{\boldsymbol{k}',\alpha'}|1_{\boldsymbol{k},\alpha}\rangle = 1.$$
Now
$$\begin{aligned}
&\langle B; 1_{\boldsymbol{k}',\alpha'}|H_{\rm int}|A; 1_{\boldsymbol{k},\alpha}\rangle \\
&\quad= \langle B; 1_{\boldsymbol{k}',\alpha'}\left|\frac{e^2}{2m_e c^2}\boldsymbol{A}(\boldsymbol{x},t)\cdot\boldsymbol{A}(\boldsymbol{x},t)\right|A; 1_{\boldsymbol{k},\alpha}\rangle \\
&\quad= \langle B; 1_{\boldsymbol{k}',\alpha'}\left|\frac{e^2}{2m_e c^2}(a_{\boldsymbol{k},\alpha}a^\dagger_{\boldsymbol{k}',\alpha'} + a^\dagger_{\boldsymbol{k}',\alpha'}a_{\boldsymbol{k},\alpha})\right. \\
&\qquad\times\left.\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}-i(\omega-\omega')t}\right|A; 1_{\boldsymbol{k},\alpha}\rangle \\
&\quad= \frac{e^2}{2m_e c^2}\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}2\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}e^{-i(\omega-\omega')t}\langle B|A\rangle,
\end{aligned}$$
where again the exponential functions $e^{\pm\boldsymbol{k}\cdot\boldsymbol{x}}$ are replaced by the constant 1 (the long wave length approximation).
In the first order we have thus
$$\begin{aligned}
c^{(1)}(t) &= -\frac{i}{\hbar}\int_{t_0}^t e^{i\omega_{fi}t'}V_{fi}(t')\,dt' \\
&= \frac{1}{i\hbar}\frac{e^2}{2m_e c^2}\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}2\delta_{AB}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')} \\
&\quad\times\int_0^t e^{i(\hbar\omega'+E_B-\hbar\omega-E_A)t'/\hbar}\,dt',
\end{aligned}$$
where $\omega = |\boldsymbol{k}|c$ and $\omega' = |\boldsymbol{k}'|c$. Now

- in the transition amplitude $c^{(1)}(t)$ the interaction is in fact of second order: $\boldsymbol{A}\cdot\boldsymbol{A}$.
- in the second order correction $c^{(2)}(t)$ the term $\boldsymbol{A}\cdot\boldsymbol{p}$ is also of second order.

To collect all contributions up to the second order in the interaction we have to consider also the correction $c^{(2)}(t)$, into which we take all double actions of the operator $\boldsymbol{A}\cdot\boldsymbol{p}$. Now
$$\begin{aligned}
c^{(2)}(t) &= \left(-\frac{i}{\hbar}\right)^2\sum_m\int_{t_0}^t dt'\int_{t_0}^{t'}dt''\,e^{i\omega_{fm}t'}V_{fm}(t') \\
&\quad\times e^{i\omega_{mi}t''}V_{mi}(t'').
\end{aligned}$$
Thus there are two possibilities: the interaction $\boldsymbol{A}\cdot\boldsymbol{p}$ can

- at the moment t_1 annihilate the incoming photon $(\boldsymbol{k}, \hat{\boldsymbol{\epsilon}}^{(\alpha)})$ and at some later time t_2 create the outgoing photon $(\boldsymbol{k}', \hat{\boldsymbol{\epsilon}}^{(\alpha')})$ or

- at the moment t_1 create the outgoing photon $(\boldsymbol{k}', \hat{\boldsymbol{\epsilon}}^{(\alpha')})$ and at some later time t_2 annihilate the incoming photon $(\boldsymbol{k}, \hat{\boldsymbol{\epsilon}}^{(\alpha)})$.

Between the moments t_1 and t_2 the atom is in the state I, which normally is neither of the states A and B.
In the intermediate state I there are thus two possibilities: either there are no photons present or both incoming and outgoing photons are present. We get thus (in the dipole approximation)

$$
\begin{aligned}
c^{(2)}(t) &= \frac{1}{(i\hbar)^2}\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}\left(-\frac{e}{m_e c}\right)^2\int_0^t dt_2\int_0^{t_2} dt_1 \\
&\quad\times\Bigg[\sum_I \langle B|\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}|I\rangle e^{i(E_B-E_I+\hbar\omega')t_2/\hbar} \\
&\qquad\qquad\times\langle I|\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|A\rangle e^{i(E_I-E_A-\hbar\omega)t_1/\hbar} \\
&\quad+\sum_I \langle B|\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}|I\rangle e^{i(E_B-E_I+\hbar\omega)t_2/\hbar} \\
&\qquad\qquad\times\langle I|\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}|A\rangle e^{i(E_I-E_A-\hbar\omega')t_1/\hbar}\Bigg] \\
&= -\frac{c^2\hbar}{i\hbar 2V\sqrt{\omega\omega'}}\left(\frac{e}{m_e c}\right)^2 \\
&\qquad\times\sum_i\left(\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}}{E_I-E_A-\hbar\omega}\right. \\
&\qquad\quad\left.+\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}}{E_I-E_A+\hbar\omega'}\right) \\
&\qquad\times\int_0^t dt_2\, e^{i(E_B-E_A+\hbar\omega'-\hbar\omega)t_2/\hbar}.
\end{aligned}
$$

For the transition rate we get combining the terms $c^{(1)}(t)$ and $c^{(2)}(t)$ and taking into account the relation

$$
\lim_{t\to\infty}\left|\int_0^t e^{ixt'}\,dt'\right|^2 = 2\pi t\delta(x)
$$

the expression

$$
\begin{aligned}
w_{d\Omega} &= \int(|c^{(1)}+c^{(2)}|^2/t)\rho(E,d\Omega)\,dE \\
&= \frac{2\pi}{\hbar}\left(\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}\right)^2\left(\frac{e^2}{m_e c^2}\right)^2\frac{V}{(2\pi)^3}\frac{\omega'^2}{\hbar c^3}\,d\Omega
\end{aligned}
$$

$$\times\Bigg|\delta_{AB}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}$$
$$-\frac{1}{m_e}\sum_I\left(\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}}{E_I-E_A-\hbar\omega}\right.$$
$$\left.+\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}}{E_I-E_A+\hbar\omega'}\right)\Bigg|^2.$$

Because in the initial state there was exactly one photon in the volume V and the flux density of the incoming photons c/V, so the differential cross section is

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= r_0^2\left(\frac{\omega'}{\omega}\right)\Bigg|\delta_{AB}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}\\ &\quad -\frac{1}{m_e}\sum_I\left(\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}}{E_I-E_A-\hbar\omega}\right.\\ &\quad \left.+\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{BI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}}{E_I-E_A+\hbar\omega'}\right)\Bigg|^2,\end{aligned}$$

where $r_0 = e^2/4\pi mc^2 \approx 2.82\times 10^{-13}$cm is the classical radius of electron. This expression is known as the *Kramers-Heisenberg formula.*

Example Elastic scattering.

Now $A = B$ ja $\hbar\omega = \hbar\omega'$. Using the commutation relations of the operators $\boldsymbol{x}$ and $\boldsymbol{p}$, the completeness of the intermediate states and the relation

$$\boldsymbol{p}_{AB} = im_e\omega_{AB}\boldsymbol{x}_{AB}$$

we can write

$$\begin{aligned}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')} &= \frac{1}{i\hbar}\sum_I\Big[(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}\\ &\quad -(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}\Big]\\ &= \frac{1}{m_e\hbar}\sum_I\frac{2}{\omega_{IA}}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA},\end{aligned}$$

where $\omega_{IA} = (E_I - E_A)/\hbar$.

We see that

$$\begin{aligned}&\delta_{AA}\hat{\boldsymbol{\epsilon}}^{(\alpha)}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')}\\ &\quad -\frac{1}{m_e\hbar}\sum_I\left[\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}}{\omega_{IA}-\omega}\right.\\ &\quad \left.+\frac{(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}}{\omega_{IA}+\omega}\right]\\ &= -\frac{1}{m_e\hbar}\sum_I\left[\frac{\omega(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}}{\omega_{IA}(\omega_{IA}-\omega)}\right.\end{aligned}$$

$$-\frac{\omega(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}}{\omega_{IA}(\omega_{IA}+\omega)}\Bigg].$$

If ω is small then

$$\frac{1}{\omega_{IA}\mp\omega}\approx\frac{1\pm(\omega/\omega_{IA})}{\omega_{IA}}.$$

$(\omega_{IA}^2\to\omega_{IA}^2\pm\omega^2)$
Then

$$\begin{aligned}
&\sum_I\frac{1}{\omega_{IA}^2}\Big[(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}\\
&\qquad-(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}\Big]\\
&\quad=m_e^2\sum_I\Big[(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}\\
&\qquad-(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}\Big]\\
&\quad=m_e^2([\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')},\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)}])_{AA}\\
&\quad=0.
\end{aligned}$$

The differential cross section is now

$$\begin{aligned}
\frac{d\sigma}{d\Omega}&=\left(\frac{r_0}{m_e\hbar}\right)^2\omega^4\Bigg|\sum_I\left(\frac{1}{\omega_{IA}}\right)^3\\
&\qquad\times[(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}\\
&\qquad\quad+(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{p}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}]\Bigg|^2\\
&=\left(\frac{r_0m_e}{\hbar}\right)^2\omega^4\Bigg|\sum_I\frac{1}{\omega_{IA}}\\
&\qquad\times[(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{AI}(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{IA}\\
&\qquad\quad+(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha)})_{AI}(\boldsymbol{x}\cdot\hat{\boldsymbol{\epsilon}}^{(\alpha')})_{IA}]\Bigg|^2.
\end{aligned}$$

At long wave lengths the differential cross section obeys the *Rayleigh law* or

$$\frac{d\sigma}{d\Omega}\propto\frac{1}{\lambda^4}.$$

Now

- for ordinary colourless gases ω_{IA} corresponds to wave lengths in the ultraviolet,
- for the visible light we have then $\omega\ll\omega_{IA}$,

so our approximations are valid in the atmosphere. The theory explains why the sky is blue and the sunset red.