# Notes on quantization of the electromagnetic field

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## 1. Summary of Maxwell's theory

The electromagnetic field is described by the celebrated set of Maxwell's equations, which in absence of electric charges take the form

$$\boldsymbol{\nabla} \cdot \mathbf{E} = 0 \ , \tag{1}$$

$$\boldsymbol{\nabla} \times \mathbf{B} = \frac{\partial \boldsymbol{E}}{\partial t} \ , \tag{2}$$

$$\boldsymbol{\nabla} \times \mathbf{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \ , \tag{3}$$

$$\boldsymbol{\nabla} \cdot \mathbf{B} = 0 \ . \tag{4}$$

Using eq.(4) and the identity stating that, given any vector $\mathbf{v}$, $\boldsymbol{\nabla} \cdot (\boldsymbol{\nabla} \times \mathbf{v}) \equiv 0$, we can rewrite $\mathbf{B}$ as the curl of a new vector $\mathbf{A}$:

$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}. \tag{5}$$

The above equation defines the *vector potential* $\mathbf{A}$. Substitution into eq.(3) yields

$$\boldsymbol{\nabla} \times \left( \mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = 0 \ , \tag{6}$$

implying in turn that the quantity enclosed in round brackets can be written as (minus) the gradient of a *scalar potential* $\phi$ (recall that, for any scalar function $\psi$, $\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \psi) \equiv 0$). As a consequence, the electric field can be rewritten

$$\mathbf{E} = -\boldsymbol{\nabla} \phi - \frac{\partial \mathbf{A}}{\partial t} \ . \tag{7}$$

Obviously, the fields defined by eqs.(5) and (7) satisfy Maxwell's equations (3) and (4) identically. Substitution of eq.(7) into eq.(1) yields

$$\boldsymbol{\nabla} \cdot \left( \boldsymbol{\nabla}\phi + \frac{\partial \mathbf{A}}{\partial t} \right) = 0 \tag{8}$$

i.e.

$$\nabla^2 \phi + \frac{\partial}{\partial t} \boldsymbol{\nabla} \cdot \mathbf{A} = 0 \ , \tag{9}$$

while plugging eqs.(5) and (7) into eq.(2) leads to

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{A}) = -\frac{\partial}{\partial t} \left( \boldsymbol{\nabla}\phi + \frac{\partial \mathbf{A}}{\partial t} \right) \ , \tag{10}$$

implying (use the vector identity $\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{v}) = \boldsymbol{\nabla} \cdot (\boldsymbol{\nabla} \cdot \mathbf{v}) - \nabla^2 \mathbf{v}$)

$$\nabla^2 \mathbf{A} - \frac{\partial^2 \mathbf{A}}{\partial t^2} - \boldsymbol{\nabla} \left( \boldsymbol{\nabla} \cdot \mathbf{A} - \frac{\partial \phi}{\partial t} \right) = 0 \ . \tag{11}$$

Eqs.(5), (7), (9) and (11) provide an alternate formulation of Maxwell's theory, in which the physical fields $\mathbf{B}$ and $\mathbf{E}$ are replaced by the potentials $\phi$ and $\mathbf{A}$. Eqs.(5) and (7) give $\mathbf{B}$ and $\mathbf{E}$ in terms of $\phi$ and $\mathbf{A}$, while eqs.(9) and (11) describe the evolution of the scalar and vector potential. It has to be noted, however, that eqs.(9) and (11) are coupled and that eqs.(5) and (7) *do not* uniquely specify $\mathbf{A}$ and $\phi$. In fact, replacing

$$\mathbf{A} \to \mathbf{A}' = \mathbf{A} - \boldsymbol{\nabla}\Lambda \ , \tag{12}$$

$\Lambda$ being any scalar function, into eq.(5) obvioulsy leaves the magnetic field $\mathbf{B}$ unchanged, since $\boldsymbol{\nabla} \times (\boldsymbol{\nabla}\Lambda) \equiv 0$. Moreover, if we make the substitution

$$\phi \to \phi' = \phi + \frac{\partial \Lambda}{\partial t} \ , \tag{13}$$

and use both eqs.(12) and (13) in eq.(7), the resulting electric field turns out to be also unchanged, as

$$\begin{aligned} \mathbf{E}' &= -\boldsymbol{\nabla} \left( \phi + \frac{\partial \Lambda}{\partial t} \right) - \frac{\partial}{\partial t} \left( \mathbf{A} - \boldsymbol{\nabla}\Lambda \right) \\ &= -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t} = \mathbf{E} \ . \end{aligned}$$

The combination of transformations (12) and (13) goes under the name of *gauge transformation*. The invariance of Maxwell's theory under gauge transformations can be readily

exploited to decouple eqs.(9) and (11), since gauge invariance implies that we can always choose $\mathbf{A}$ and $\phi$ such that

$$\boldsymbol{\nabla}\mathbf{A} + \frac{\partial \phi}{\partial t} = 0 \ . \tag{14}$$

In the gauge specified by the above equation eqs.(9) and (11) reduce to

$$\nabla^2 \phi - \frac{\partial^2 \phi}{\partial t^2} = 0 \tag{15}$$

and

$$\nabla^2 \mathbf{A} - \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0 \ . \tag{16}$$

Note that eq.(14) still does not define the vector and scalar potential in a unique fashion. In fact, if $\mathbf{A}$ and $\phi$ satisfy eq.(14), so do $\mathbf{A}'$ and $\phi'$ given by

$$\mathbf{A}' = \mathbf{A} - \boldsymbol{\nabla}\Lambda' \tag{17}$$

and

$$\phi' = \phi + \frac{\partial \Lambda'}{\partial t} \ , \tag{18}$$

provided $\Lambda'$ is a solution of

$$\nabla^2 \Lambda' - \frac{\partial^2 \Lambda'}{\partial t^2} = 0 \ . \tag{19}$$

## 2. Fourier decomposition of the classical radiation field

Let us consider the vector potential associated with a radiation field enclosed in a cubic box of volume $V = L^3$. In the Coulomb gauge, implying the transversality condition

$$\boldsymbol{\nabla} \cdot \mathbf{A} = 0 \ , \tag{20}$$

$\mathbf{A}$ can be expanded in Fourier series according to (remember that the vector potential is a real function)

$$\mathbf{A}(\mathbf{x},t) = \sum_{\mathbf{k}} \sum_{r=1}^{2} \left[ c_{\mathbf{k}r}(t) \mathbf{u}_{\mathbf{k}r}(\mathbf{x}) + c^{*}_{\mathbf{k}r}(t) \mathbf{u}^{*}_{\mathbf{k}r}(\mathbf{x}) \right] \tag{21}$$

with

$$\mathbf{u}_{\mathbf{k}r}(\mathbf{x}) = \frac{1}{\sqrt{V}} \boldsymbol{\epsilon}_r \ \mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}} \ , \tag{22}$$

where $\mathbf{k} \equiv (k_x, k_y, k_z)$ satisfy the periodic boundary conditions

$$k_x = n_x \ \frac{\pi}{L} \quad , \quad k_y = n_y \ \frac{\pi}{L} \quad , \quad k_z = n_z \ \frac{\pi}{L} \ , \tag{23}$$

$n_x$, $n_y$ and $n_z$ being positive integers. The real unit vectors $\boldsymbol{\epsilon}_r$ ($r$ = 1,2) are defined in such a way that $\boldsymbol{\epsilon}_1$, $\boldsymbol{\epsilon}_2$ and $\widehat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$ form a set of mutually orthogonal unit vectors, i.e. that

$$\boldsymbol{\epsilon}_r \cdot \boldsymbol{\epsilon}_{r'} = \delta_{rr'} \tag{24}$$

and

$$\boldsymbol{\epsilon}_r \cdot \widehat{\mathbf{k}} = 0 \ . \tag{25}$$

Note that the above equation guarantees that the trasversality requirement (20) be fulfilled.

The Fourier components $\mathbf{u}_{\mathbf{k}r}(\mathbf{x})$ satisfy the orthogonality and normalization condition

$$\int d^3x \ \mathbf{u}^{*}_{\mathbf{k}r}(\mathbf{x}) \mathbf{u}_{\mathbf{k}'r'}(\mathbf{x}) = \frac{\boldsymbol{\epsilon}_r \cdot \boldsymbol{\epsilon}_{r'}}{V} \int d^3x \ \mathrm{e}^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}} = \delta_{rr'}\delta_{\mathbf{k}\mathbf{k}'} \ . \tag{26}$$

The time dependence of the coefficients is given by

$$c_{\mathbf{k}r}(t) = c_{\mathbf{k}r} \ \mathrm{e}^{i\omega t} \quad , \quad c^{*}_{\mathbf{k}r}(t) = c^{*}_{\mathbf{k}r} \ \mathrm{e}^{-i\omega t} \ , \tag{27}$$

where the frequency $\omega$ satisfies the dispersion relation $\omega = \omega_k = |\mathbf{k}|$, following from the requirement that the vector potential $\mathbf{A}(\mathbf{x},t)$ satisfy the wave equation (16).

## 3. Energy of the classical radiation field

The classical energy of the electromagnetic field is

$$H = \frac{1}{2} \int d^3x \ \left( \ |\mathbf{E}|^2 + |\mathbf{B}|^2 \ \right) = \frac{1}{2} \int d^3x \ \left( \ |\boldsymbol{\nabla} \times \mathbf{A}|^2 + \left| \frac{\partial \mathbf{A}}{\partial t} \right|^2 \ \right) \ . \tag{28}$$

Substitution of the expansion (21) into the above definition leads to

$$H = \frac{1}{2} \sum_{\mathbf{k}r} \sum_{\mathbf{k}'r'} \int d^3x \left\{ [c_{\mathbf{k}r}(t) \ \boldsymbol{\nabla} \times \mathbf{u}_{\mathbf{k}r}(\mathbf{x}) + c.c.] \cdot [c^*_{\mathbf{k}'r'}(t) \ \boldsymbol{\nabla} \times \mathbf{u}^*_{\mathbf{k}'r'}(\mathbf{x}) + c.c.] \right.$$
$$\left. + \left[ \frac{\partial c_{\mathbf{k}r}}{\partial t} \ \mathbf{u}_{\mathbf{k}r}(\mathbf{x}) + c.c. \right] \cdot \left[ \frac{\partial c^*_{\mathbf{k}'r'}}{\partial t} \ \mathbf{u}^*_{\mathbf{k}'r'}(\mathbf{x}) + c.c. \right] \right\} \ . \tag{29}$$

The calculation of the magnetic contribution to $H$ involves integrations of the type

$$\begin{aligned} I_B &= \int d^3x \ (\boldsymbol{\nabla} \times \mathbf{u}_{\mathbf{k}r}(\mathbf{x})) \cdot (\boldsymbol{\nabla} \times \mathbf{u}^*_{\mathbf{k}'r'}(\mathbf{x})) \\ &= \int d^3x \ \boldsymbol{\nabla} \cdot [\mathbf{u}_{\mathbf{k}r}(\mathbf{x}) \times (\boldsymbol{\nabla} \times \mathbf{u}^*_{\mathbf{k}'r'}(\mathbf{x}))] + \int d^3x \ \mathbf{u}_{\mathbf{k}r}(\mathbf{x}) \cdot [\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{u}^*_{\mathbf{k}'r'}(\mathbf{x}))] \\ &= - \int d^3x \ \mathbf{u}_{\mathbf{k}r}(\mathbf{x}) \nabla^2 \mathbf{u}^*_{\mathbf{k}'r'}(\mathbf{x}) \\ &= \frac{|\mathbf{k}|^2}{V} \ \boldsymbol{\epsilon}_r \cdot \boldsymbol{\epsilon}_{r'} \ \int d^3x \ \mathrm{e}^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}} = \omega_k^2 \ \delta_{rr'} \delta_{\mathbf{k}\mathbf{k}'} \ . \end{aligned}$$

The above result can be easily obtained using the periodic boundary conditions and the identities $(\boldsymbol{\nabla} \times \mathbf{u}) \cdot (\boldsymbol{\nabla} \times \mathbf{v}) = \boldsymbol{\nabla} \cdot [\mathbf{u} \times (\boldsymbol{\nabla} \times \mathbf{v})] + \mathbf{u} \cdot [\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{v})]$ and $\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{u}) = \boldsymbol{\nabla} \cdot (\boldsymbol{\nabla} \cdot \mathbf{u}) - \nabla^2 \mathbf{u}$. The electric contribution involves integrals of the type

$$I_E = \int d^3x \ \frac{\partial c_{\mathbf{k}r}}{\partial t} \mathbf{u}_{\mathbf{k}r}(\mathbf{x}) \cdot \frac{\partial c^*_{\mathbf{k}'r'}}{\partial t} \mathbf{u}^*_{\mathbf{k}'r'}(\mathbf{x}) = \omega_k^2 \ \delta_{rr'} \delta_{\mathbf{k}\mathbf{k}'} \ c_{\mathbf{k}r}(t) c^*_{\mathbf{k}'r'}(t) \ . \tag{30}$$

Collecting all terms together we finally find

$$H = \sum_{\mathbf{k}r} \omega_k^2 \ [c_{\mathbf{k}r}(t) c^*_{\mathbf{k}r}(t) + c^*_{\mathbf{k}r}(t) c_{\mathbf{k}r}(t)] \ , \tag{31}$$

where the coefficients $c_{\mathbf{k}r}(t)$ satisfy the differential equation

$$\ddot{c}_{\mathbf{k}r}(t) \ = \ -\omega_k^2 \ c_{\mathbf{k}r}(t) \ , \tag{32}$$

i.e. the equation of motion of a classical harmonic oscillator of angular frequency $\omega_k$ and unit mass. Note that, $c_{\mathbf{k}r}(t)$ being a complex function, $[c_{\mathbf{k}r}(t) c^*_{\mathbf{k}r}(t) + c^*_{\mathbf{k}r}(t) c_{\mathbf{k}r}(t)] = 2 c_{\mathbf{k}r}(t) c^*_{\mathbf{k}r}(t)$. The reason why $H$ has been written as in eq.(31) will become apparent in the next section.

The fact that the energy of the radiation field can be cast in the form (31), with $c_{\mathbf{k}r}(t)$ satisfying eq.(32), suggests that $H$ can be seen as the classical hamiltonian of a collection of independent harmonic oscillators, oscillating in the direction specified by $\boldsymbol{\epsilon}_r$ with angular frequency $\omega_k$. Comparison between eq.(31) and the classical harmonic oscillator hamiltonian

$$H = \sum_{\mathbf{k}r} \frac{1}{2} \left( p_{\mathbf{k}r}^2 + \omega_k^2 x_{\mathbf{k}r}^2 \right) , \tag{33}$$

where $x_{\mathbf{k}r}$ and $p_{\mathbf{k}r}$ are classical canonical variables, shows that the quantities appearing in the left hand side of eqs.(31) and (33)can be identified provided $c_{\mathbf{k}r}$ and $c_{\mathbf{k}r}^*$ are defined as

$$c_{\mathbf{k}r} = \frac{1}{2\omega_k}(\omega_k x_{\mathbf{k}r} + i p_{\mathbf{k}r}) \qquad , \qquad c_{\mathbf{k}r}^* = \frac{1}{2\omega_k}(\omega_k x_{\mathbf{k}r} - i p_{\mathbf{k}r}) , \tag{34}$$

implying in turn the inverse relations

$$x_{\mathbf{k}r} = c_{\mathbf{k}r} + c_{\mathbf{k}r}^* \qquad , \qquad p_{\mathbf{k}r} = -i\omega_k (c_{\mathbf{k}r} - c_{\mathbf{k}r}^*) . \tag{35}$$

## 4. Quantization of the harmonic oscillator

Having pointed out the formal analogy between the energy of the classical radiation field and the energy of a system of classical harmonic oscillators, we now want to generalize to the quantum mechanical case.

Let us consider, for simplicity, a single harmonic oscillator of angular frequency $\omega$. Its quantum mechanical hamiltonian reads

$$h = \frac{1}{2}(p^2 + \omega^2 x^2) , \tag{36}$$

where $x$ and $p$ are the position and momentum operators, satisfying the commutation rule

$$[x, p] = i \tag{37}$$

The hamiltonian of eq.(36) can be rewritten in terms of the operators $a$ and $a^\dagger$, defined as

$$a = \frac{1}{\sqrt{2\omega}}(\omega x + ip) \qquad , \qquad a^\dagger = \frac{1}{\sqrt{2\omega}}(\omega x - ip) , \tag{38}$$

and satisfying the commutation rule (following from eq.(37))

$$[a, a^\dagger] = 1 . \tag{39}$$

We find (use eq.(39))

$$h = \frac{\omega}{2}(a^\dagger a + a a^\dagger) = \frac{\omega}{2}(2a^\dagger a + 1) = \omega\left(a^\dagger a + \frac{1}{2}\right) \ . \tag{40}$$

Consider now the hermitean operator $N = a^\dagger a$, whose diagonal matrix elements satisfy the inequality

$$\langle\alpha|N|\alpha\rangle = \langle\alpha|a^\dagger a|\alpha\rangle = \sum_\beta \langle\alpha|a^\dagger|\beta\rangle\langle\beta|a|\alpha\rangle = \sum_\beta |\langle\beta|a|\alpha\rangle|^2 \geq 0 \ , \tag{41}$$

implying in turn that the lowest eigenvalue of $N$, $n_0$, satisfies $n_0 \geq 0$. From the eigenvalue equation

$$N|n\rangle = a^\dagger a|n\rangle = n|n\rangle \tag{42}$$

and the commutation rule (39) it follows that

$$Na|n\rangle = (a^\dagger a)a|n\rangle = (aa^\dagger - 1)a|n\rangle = (n-1)a|n\rangle \ . \tag{43}$$

Hence, $a|n\rangle$ is an eigenstate of $N$ belonging to the eigenvalue $(n-1)$. In the same fashion it is easy to show that

$$Na^\dagger|n\rangle = (n+1)a^\dagger|n\rangle \ , \tag{44}$$

i.e. that $a^\dagger|n\rangle$ is an eigenstate of $N$ belonging to the eigenvalue $(n+1)$.

As $n_0$ is the minimum eigenvalue of $N$, the corresponding eigenstate must satisfy $a|n_0\rangle = 0$. As a consequence, the eigenvalue equation

$$N|n_0\rangle = a^\dagger a|n_0\rangle = n_0|n_0\rangle \tag{45}$$

implies $n_0 = 0$. The normalized eigenstate belonging to the eigenvalue $n$, that can take any positive integer value, can be obtained applying the operator $a^\dagger$ to the state $|0\rangle$ $n$ times. In fact, from

$$a|n\rangle = \sqrt{n}|n-1\rangle \qquad , \qquad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \tag{46}$$

it follows that

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle \ . \tag{47}$$

Finally, substitutions of the operator $N$ defined by eq.(42) into the hamiltonian of eq.(40) shows that the states $|n\rangle$ are eigenstates of $h$ satisfying the eigenvalue equation

$$h|n\rangle = \omega\left(N + \frac{1}{2}\right)|n\rangle = \omega\left(n + \frac{1}{2}\right)|n\rangle \ . \tag{48}$$

In the Heisemberg picture, a generic operator $A$ evolves in time according to

$$A(t) = \mathrm{e}^{iHt}\ A\ \mathrm{e}^{-iHt}\ , \tag{49}$$

$H$ being the hamiltonian operator. The above equation leads to Heisenberg's equation of motion

$$i\dot{A}(t) = [A(t), H] \ . \tag{50}$$

In the case of the harmonic oscillator, using the hamiltonian (40), we find that the time evolution of the operator $a(t)$ is dictated by the equation

$$i\dot{a}(t) = [a(t), H] = \omega[a(t), a^\dagger a]\ , \tag{51}$$

implying

$$\dot{a}(t) = -i\omega a(t)\ , \tag{52}$$

and

$$a(t) = a\ \mathrm{e}^{-i\omega t}\ . \tag{53}$$

## 5. Quantization of the electromagnetic field

Using the results of the previous section, we can write the hamiltonian of a superposition of quantum mechanical harmonic oscillators as

$$H = \sum_{\mathbf{k}r} \omega_k \left(a^\dagger_{\mathbf{k}r} a_{\mathbf{k}r} + a_{\mathbf{k}r} a^\dagger_{\mathbf{k}r}\right)\ . \tag{54}$$

Comparison with eq.(31) immediately shows that the electromagnetic hamiltonian can be identified with the above hamiltonian, provided the coefficients $c_{\mathbf{k}r}$ and $c^*_{\mathbf{k}r}$ appearing in the Fourier expansion of the vector potential $\mathbf{A}$ are identified with quantum mechanical operators, related to $a_{\mathbf{k}r}$ and $a^\dagger_{\mathbf{k}r}$ through

$$c_{\mathbf{k}r} = \frac{1}{\sqrt{2\omega_k}} a_{\mathbf{k}r} \qquad , \qquad c^*_{\mathbf{k}r} = \frac{1}{\sqrt{2\omega_k}} a^\dagger_{\mathbf{k}r} \ . \tag{55}$$

The vector potential can then be rewritten in terms of the $a_{\mathbf{k}r}$ and $a^\dagger_{\mathbf{k}r}$ according to

$$\begin{aligned} \mathbf{A}(\mathbf{x},t) &= \sum_{\mathbf{k}r} \frac{1}{\sqrt{2V\omega_k}} \boldsymbol{\epsilon}_r \left[ a_{\mathbf{k}r}(t) \mathrm{e}^{i\mathbf{k}\cdot\mathbf{x})} + a^\dagger_{\mathbf{k}r}(t) \mathrm{e}^{i\mathbf{k}\cdot\mathbf{x})} \right] \\ &= \sum_{\mathbf{k}r} \frac{1}{\sqrt{2V\omega_k}} \boldsymbol{\epsilon}_r \left[ a_{\mathbf{k}r} \mathrm{e}^{-i(\omega_k t - \mathbf{k}\cdot\mathbf{x})} + a^\dagger_{\mathbf{k}r} \mathrm{e}^{i(\omega_k t - \mathbf{k}\cdot\mathbf{x})} \right] \qquad (56) \\ &= \mathbf{A}^+(\mathbf{x},t) + \mathbf{A}^-(\mathbf{x},t) \ . \qquad (57) \end{aligned}$$

The coefficients in the above expansion are now to be regarded as quantum mechanical operators acting in the Hilbert space whose state vectors are given by

$$|n_{\mathbf{k}_1 r_1}, n_{\mathbf{k}_2 r_2}, \ldots n_{\mathbf{k}_n r_n} \ldots\rangle \ , \tag{58}$$

where the integer $n_{\mathbf{k}r}$ denotes the number of quanta, which will be called photons, oscillating in the mode specified by the wave vector $\mathbf{k}$ and the polarization vector $\boldsymbol{\epsilon}_r$. From the results of the previous section it follows that the generic state (58) can be obtained from the *vacuum* state, in which no pothons are present, through

$$|n_{\mathbf{k}_1 r_1}, n_{\mathbf{k}_2 r_2}, \ldots\rangle = \prod_{\mathbf{k}_i r_i} \frac{(a^\dagger_{\mathbf{k}_i r_i})^{n_{\mathbf{k}_i r_i}}}{\sqrt{n_{\mathbf{k}_i r_i}!}} |0\rangle \ . \tag{59}$$

For example, the two photon state reads

$$|n_{\mathbf{k}_1 r_1}, n_{\mathbf{k}_2 r_2}\rangle = \frac{a^\dagger_{\mathbf{k}_1 r_1} a^\dagger_{\mathbf{k}_2 r_2}}{\sqrt{2}} |0\rangle \ . \tag{60}$$

Note that we have split the series of eq.(57) in such a way that $\mathbf{A}^+(\mathbf{x},t)$ and $\mathbf{A}^-(\mathbf{x},t)$ contain only annihilation ($a_{\mathbf{k}r}$) or creation ($a^\dagger_{\mathbf{k}r}$) operators, respectivey, implying $\mathbf{A}^+(\mathbf{x},t)|0\rangle \ = \ 0$.

The electromagnetic hamiltonian

$$H = \sum_{\mathbf{k}r} = \omega_k \left( N_{\mathbf{k}r} + \frac{1}{2} \right) \ , \tag{61}$$

with $N_{\mathbf{k}r} = a^\dagger_{\mathbf{k}r} a_{\mathbf{k}r}$, can be rewritten in a slightly different form exploiting the arbitrariness inherent in the choice of the energy scale. Choosing a scale in which the vacuum state has zero energy allows one to replace eq.(61) with

$$H = \sum_{\mathbf{k}r} = \omega_k \ N_{\mathbf{k}r} \ , \tag{62}$$

leading to the eigenvalue equation

$$H|n_{\mathbf{k}_1 r_1}, n_{\mathbf{k}_2 r_2}, \ldots\rangle = \sum_{\mathbf{k}_i r_i} \ n_{\mathbf{k}_i r_i} \omega_{k_i} \ |n_{\mathbf{k}_1 r_1}, n_{\mathbf{k}_2 r_2}, \ldots\rangle \ , \tag{63}$$

and

$$H|0\rangle = \sum_{\mathbf{k}_i r_i} \ \omega_{k_i} N_{\mathbf{k}_i r_i} \ |0\rangle = 0 \ . \tag{64}$$

The polarization vector $\boldsymbol{\epsilon}_r$ can be associated with the projection of the photon intrinsic angular momentum, i.e. its spin $\mathbf{J}$, along the quantization axis. It can be shown that, in units of $\hbar$, $|\mathbf{J}| = 1$ and the two circularly polarized states resulting from the linear combinations

$$\boldsymbol{\epsilon}^{(\pm)} = \pm \frac{1}{\sqrt{2}} \ (\boldsymbol{\epsilon}_1 \pm i \boldsymbol{\epsilon}_2) \tag{65}$$

correspond to photon spin projections $m_J = \pm 1$ along the direction of $\mathbf{k}$. The fact that the $m_J = 0$ state is missing is a consequence of the fact that photons are massless. We will come back to the issue of photon spin at a later stage.

As a final remark, note that, as $\mathbf{A}(\mathbf{x}, t)$ is linear in the $a_{\mathbf{k}r}$ and $a^\dagger_{\mathbf{k}r}$, from

$$[a_{\mathbf{k}r}, N_{\mathbf{k}'r'}] = \left[ a_{\mathbf{k}r}, a^\dagger_{\mathbf{k}'r'} a_{\mathbf{k}r} \right] = \delta_{rr'} \delta_{\mathbf{k}\mathbf{k}'} a_{\mathbf{k}r} \tag{66}$$

and

$$\left[ a^\dagger_{\mathbf{k}r}, N_{\mathbf{k}'r'} \right] = \left[ a^\dagger_{\mathbf{k}r}, a^\dagger_{\mathbf{k}'r'} a_{\mathbf{k}r} \right] = \delta_{rr'} \delta_{\mathbf{k}\mathbf{k}'} a^\dagger_{\mathbf{k}r} \ , \tag{67}$$

it follows that the operator $N_{\mathbf{k}r}$, whose eigenvalue yields the number of photons in the mode $\mathbf{k}r$, does not commute with the vector potential $\mathbf{A}(\mathbf{x}, t)$. As a consequence, it does not

commute with either the electric field $\mathbf{E}$ or the magnetic field $\mathbf{B}$. This result implies that the number of photons and the strengths of the physical fields cannot be simultaneously determined to arbitrary accuracy. Moreover, since the potential is linear in the photon creation and annihilation operators, the expectation values $\langle \mathbf{E} \rangle$ and $\langle \mathbf{B} \rangle$ in the state defined by eq.(58), containing a definite number of photons, vanish. Hence, these states can never be identified with a classical field, not even in the limit of infinite number of photons.

## 6. Interaction between electrons and the radiation field

As the photon number operatos commutes with the hamiltonian of the radiation field, the occupation numbers $n_{\mathbf{k}r}$, specifying the number of photons in the mode with wave vector $\mathbf{k}$ and polarizzation $r$, are constant of the motion of the free field. However, this is no longer the case as soon as the radiation field interacts with electric charges and currents. In fact, these interactions lead to absorption and emission of photons.

We will discuss emission and absorption of photons by atomic electrons, that will be described using nonrelativistic quantum mechanics. The interaction hamiltonian can be obtained from the standard prescription of replacing the momentum of the i-th electron, $\mathbf{p}_i$, with $\mathbf{p}_i - e\mathbf{A}(\mathbf{x}_i, t)$, $\mathbf{x}_i$ and $e$ being the vector specifying the position of the i-th electron and the absolute value of the electron charge, respectively. The result is

$$H_{int} = \sum_i \left\{ -\frac{e}{2m} \left[ \mathbf{p}_i \cdot \mathbf{A}(\mathbf{x}_i, t) + \mathbf{A}(\mathbf{x}_i, t) \cdot \mathbf{p}_i \right] + \frac{e^2}{2m} \mathbf{A}^2(\mathbf{x}_i, t) \right\} \ , \tag{68}$$

where $m$ is the electron mass and the sum runs all atomic electrons. Note that, due to the tranversality condition implied by the Coulomb Gauge, we can replace $\mathbf{p}_i \cdot \mathbf{A}$ with $\mathbf{A} \cdot \mathbf{p}_i$, as $\mathbf{p}_i \cdot \mathbf{A} = -i[(\boldsymbol{\nabla} \cdot \mathbf{A}) + \mathbf{A} \cdot \mathbf{p}_i]$.

Let us first consider absorption of a photon, characterized by $\mathbf{k}$ and $\boldsymbol{\epsilon}_r$, associated with the transition of an atom from the initial state $|A\rangle$ to the final state $|B\rangle$. The radiation field makes a transition from the state $|n_{\mathbf{k}r}\rangle$ to the state $|n_{\mathbf{k}r} - 1\rangle$ (to simplify the notation, the occupation numbers of the modes not affected by the transition are not listed).

Since the vector potential $\mathbf{A}$ is linear in the photon creation and annihilation operators $a_{\mathbf{k}r}$ and $a^\dagger_{\mathbf{k}r}$, only the terms linear in $\mathbf{A}$ in eq.(68) contribute to the one-photon absorption process. The term quadratic in $\mathbf{A}$ would in fact change the number of photons by 0 or $\pm 2$.

In first order perturbation theory, we can write the transition matrix element as

$$\begin{aligned} M_{if} &= \langle f|\ H_{int}\ |i\rangle = \langle B,\ n_{\mathbf{k}r}-1|\ H_{int}\ |A,\ n_{\mathbf{k}r}\rangle \\ &= -\frac{e}{m}\ \langle B,\ n_{\mathbf{k}r}-1|\ \sqrt{\frac{1}{2V\omega_k}}\sum_i a_{\mathbf{k}r}\mathrm{e}^{-i(\omega_k t-\mathbf{k}\cdot\mathbf{x}_i)}(\mathbf{p}_i\cdot\boldsymbol{\epsilon}_r)\ |A,\ n_{\mathbf{k}r}\rangle \\ &= -\frac{e}{m}\ \sqrt{\frac{n_{\mathbf{k}r}}{2V\omega_k}}\sum_i\langle B|\ \mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}_i}(\mathbf{p}_i\cdot\boldsymbol{\epsilon}_r)\ |A\rangle\ \mathrm{e}^{-i\omega_k t}\ . \end{aligned} \tag{69}$$

The corresponding matrix element for the case of photon emission reads

$$\begin{aligned} M_{if} &= \langle f|\ H_{int}\ |i\rangle = \langle B,\ n_{\mathbf{k}r}+1|\ H_{int}\ |A,\ n_{\mathbf{k}r}\rangle \\ &= -\frac{e}{m}\ \sqrt{\frac{n_{\mathbf{k}r}+1}{2V\omega_k}}\sum_i\langle B|\ \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{x}_i}(\mathbf{p}_i\cdot\boldsymbol{\epsilon}_r)\ |A\rangle\ \mathrm{e}^{i\omega_k t}\ . \end{aligned} \tag{70}$$

A remarkable feature of the above result is that $M_{if}\neq 0$ for $n_{\mathbf{k}r}=0$, implying the possibile occurrence of *spontaneous photon emission*. This prediction is a consequence of the quantum mechanical treatment of the radiation field, having no classical analogue.

We will now evaluate the matrix element of eq.(70) in the so called *dipole approximation*. This approximation can be applied when the spacial variation of the radiation field over the atomic size is negligible, so that we can replace its values at the points $\mathbf{x}_i$ with the value at $\mathbf{x}=0$. This amounts to replacing

$$\mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}_i}\to 1 \tag{71}$$

when the wavelength of the radiation field $\lambda$ is such that $\lambda=|\mathbf{k}|^{-1}\gg R$, $R$ being the typical atomic size. Substitution into eq.(70) yields

$$M_{if} = -\frac{e}{m}\ \langle B|\ \sum_i(\mathbf{p}_i\cdot\boldsymbol{\epsilon}_r)\ |A\rangle\ \mathrm{e}^{i\omega_k t}\ . \tag{72}$$

The transition probability per unit time can be readily obtained from Fermi's golden rule of time dependent perturbation theory

$$w_{if} = 2\pi |M_{if}|^2 \delta(E_A - E_B - \omega_k) \ , \tag{73}$$

where $E_A$ and $E_B$ denote the energies of the initial and final atomic state, respectively. The $\delta$-function can be eliminated integrating over the final states available to the emitted photon. From

$$\sum_{\mathbf{k}} = \frac{V}{(2\pi)^3} \int d^3k \tag{74}$$

it follows that the phase-space available to a photon emitted in the solid angle $d\Omega_k$ with magnitude of the wave vector between $|\mathbf{k}|$ and $|\mathbf{k}| + d|\mathbf{k}|$ is $(V/(2\pi)^3) d\Omega_k |\mathbf{k}|^2 d|\mathbf{k}|$. Hence

$$\begin{aligned} \frac{dw_{if}}{d\Omega_k} &= \frac{e^2}{m^2} \frac{V}{(2\pi)^2} \int |\mathbf{k}|^2 d|\mathbf{k}| \ \frac{n_{\mathbf{k}r} + 1}{2V\omega_k} |\langle B| \sum_i (\mathbf{p}_i \cdot \boldsymbol{\epsilon}_r) \ |A\rangle|^2 \ \delta(E_A - E_B - \omega_k) \\ &= \frac{1}{8\pi^2} \frac{e^2 \omega_k}{m^2} \ (n_{\mathbf{k}r} + 1) |\mathbf{P}_{AB} \cdot \boldsymbol{\epsilon}_r|^2 \ , \end{aligned} \tag{75}$$

with

$$\omega_k = |\mathbf{k}| = E_A - E_B \tag{76}$$

and

$$\mathbf{P}_{AB} = \langle B| \sum_i \mathbf{p}_i \ |A\rangle \ . \tag{77}$$

Eqs.(75)-(77) yield the probability of emitting a photon with energy given by (76) and polarization vector $\boldsymbol{\epsilon}_r$ in the solid angle $d\Omega_k$. The matrix element of eq.(77) can be rewritten in a more familiar form, making it clear why the approximation of eq.(71) goes under the name of dipole approximation. Using Heisenberg's picture we can rewrite $\mathbf{P}_{AB}$ as

$$\begin{aligned} \mathbf{P}_{AB} &= \langle B| \sum_i \mathbf{p}_i \ |A\rangle = m\langle B| \sum_i \dot{\mathbf{x}}_i \ |A\rangle = -im\langle B| \ [ \sum_i \mathbf{x}_i, H \ ] \ |A\rangle \\ &= -im(E_A - E_B)\langle B| \sum_i \mathbf{x}_i \ |A\rangle = -im\omega_k \mathbf{X}_{AB} \ , \end{aligned} \tag{78}$$

where

$$\mathbf{X}_{AB} = \langle B| \sum_i \mathbf{x}_i \ |A\rangle = \frac{1}{e} \langle B| \ \mathbf{D} \ |A\rangle = \frac{1}{e} \mathbf{D}_{AB} \ , \tag{79}$$

**D** being the electric dipole moment associated with the atomic electrons.

Substitution of eqs.(78) and (79) into eq.(75) leads to

$$\frac{dw_{if}}{d\Omega_k} = \frac{1}{8\pi^2}\,\omega_k^3(n_{\mathbf{k}r}+1)|\mathbf{D}_{AB}\cdot\boldsymbol{\epsilon}_r|^2\ . \tag{80}$$

We now have to carry out the sum over possible photon polarizations. From $\boldsymbol{\epsilon}_r\cdot\boldsymbol{\epsilon}_{r'}=\delta_{rr'}$ and $\boldsymbol{\epsilon}_r\cdot\mathbf{k}=0$ it follows that ($\widehat{\mathbf{k}}=\mathbf{k}/|\mathbf{k}|$)

$$\sum_r|\mathbf{D}_{AB}\cdot\boldsymbol{\epsilon}_r|^2=|\mathbf{D}_{AB}|^2-(\mathbf{D}_{AB}\cdot\widehat{\mathbf{k}})(\mathbf{D}^*_{AB}\cdot\widehat{\mathbf{k}})=|\mathbf{D}_{AB}|^2(1-\cos^2\theta)=|\mathbf{D}_{AB}|^2\sin^2\theta\ , \tag{81}$$

$\theta$ being the angle between $\mathbf{D}_{AB}$ and $\widehat{\mathbf{k}}$.

In conclusion, the probability per unit time of spontaneous (i.e. $n_{\mathbf{k}r}=0$) photon emission in the atomic transition $A\to B$ is

$$\begin{aligned} w_{A\to B}=\int d\Omega_k\left(\frac{dw_{if}}{d\Omega_k}\right) &= \frac{1}{8\pi^2}\,\omega_k^3|\mathbf{D}_{AB}|^2 2\pi\int_{-1}^{+1}(1-\cos^2\theta)d\cos\theta \\ &= \frac{\omega_k^3}{3\pi}\,|\mathbf{D}_{AB}|^2 \end{aligned} \tag{82}$$

Note that the same result might have been obtained using the dipole approximation from the very beginnig, i.e. writing the interaction hamiltonian in the form

$$H_{int}=-\mathbf{D}\cdot\mathbf{E}(\mathbf{x}=0,t)\ , \tag{83}$$

where **D** is the dipole moment and $\mathbf{E}(\mathbf{x}=0,t)=-(\partial\mathbf{A}/\partial t)_{\mathbf{x}=0}$.

The lifetime of the quantum state $A$, denoted by $\tau$, is defined through

$$\frac{1}{\tau}=\sum_n w_{A\to B_n} \tag{84}$$

where the sum includes all possible atomic final states $B_n$, i.e. all states compatible with the appropriate selection rules.

First of all, the states $|A\rangle$ and $|B_n\rangle$ are required to have opposite parity. The parity of the states $|A\rangle$ and $|B_n\rangle$ is specified by the eigenvalues of the equations

$$\Pi|A\rangle=\Pi_A|A\rangle \qquad , \qquad \Pi|B_n\rangle=\Pi_{B_n}|B_n\rangle\ , \tag{85}$$

where $\Pi_A$, $\Pi_{B_n} = \pm\ 1$ and the parity operator $\Pi$ satisfies the relations $\Pi^{-1} = \Pi^\dagger = \Pi$. As under parity transformation $\mathbf{x}$ goes into $\Pi^\dagger\ \mathbf{x}\ \Pi = -\mathbf{x}$, we can write

$$\langle B_n|\mathbf{x}|A\rangle = \langle B_n|\mathbf{x}|A\rangle = -\langle B_n|\Pi^\dagger\mathbf{x}\Pi|A\rangle = -\Pi_{B_n}\Pi_A\langle B_n|\mathbf{x}|A\rangle\ , \tag{86}$$

implying $\Pi_{B_n}\Pi_A = -1$.

The total angular momenta of the states $|A\rangle$ and $|B_n\rangle$, $J_A$ and $J_{B_n}$, and their projections, $M_{J_A}$ and $M_{J_{B_n}}$, must be such that $\Delta J = J_A - J_{B_n} = 0, \pm 1$ and $\Delta M_J = M_{J_A} - M_{J_{B_n}} = 0, \pm 1$. In addition, as the projection of the photon angular momentum cannot take the value $m_J = 0$, transitions between states with $J_A = J_{B_n} = 0$ are forbidden.