VI. QUANTIZATION OF THE ELECTROMAGNETIC FIELD

A prime example of a many-boson system is the electromagnetic field. Since it plays an extremely important role in probing many-particle systems as well as generating new ones using laser techniques, it is meaningful to spend some time developing the photon concept by quantizing the electromagnetic field [54].

A. Maxwell's equations in terms of scalar and vector potentials

Consider first Maxwell's equations (in Gaussian units [55])

$$\nabla \cdot \mathbf{E}(\mathbf{x},t) = 4\pi\rho(\mathbf{x},t) \tag{309}$$

$$\nabla \cdot \mathbf{B}(\mathbf{x},t) = 0 \tag{310}$$

$$\nabla \times \mathbf{E}(\mathbf{x},t) = -\frac{1}{c}\frac{\partial}{\partial t}\mathbf{B}(\mathbf{x},t) \tag{311}$$

$$\nabla \times \mathbf{B}(\mathbf{x},t) = \frac{1}{c}\frac{\partial}{\partial t}\mathbf{E}(\mathbf{x},t) + \frac{4\pi}{c}\mathbf{j}(\mathbf{x},t), \tag{312}$$

where ρ is the total charge density and $\mathbf{j} = \rho\mathbf{v}$ with $\mathbf{v}$ the microscopic velocity field. The hamiltonian for the radiation field can be written as

$$H_{em} = \frac{1}{8\pi}\int_V d^3x\ (\mathbf{E}^2 + \mathbf{B}^2). \tag{313}$$

It is necessary to introduce the scalar and vector potentials since they are the important quantities describing the electromagnetic field in quantum problems. The electric and magnetic field can be obtained from these quantities in the following manner

$$\mathbf{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \tag{314}$$

$$\mathbf{B} = \nabla \times \mathbf{A}. \tag{315}$$

The homogeneous equations (310) and (311) are then automatically solved. The dynamics is therefore obtained by solving the remaining inhomogeneous equations in terms of Φ and $\mathbf{A}$ as follows

$$\nabla^2\Phi + \frac{1}{c}\frac{\partial}{\partial t}(\nabla\cdot\mathbf{A}) = -4\pi\rho \tag{316}$$

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} - \nabla\left(\nabla\cdot\mathbf{A} + \frac{1}{c}\frac{\partial\Phi}{\partial t}\right) = -\frac{4\pi}{c}\mathbf{j}. \tag{317}$$

The coupling between these two equations can be eliminated by employing the freedom to add the gradient of a scalar function to $\mathbf{A}$ since this will not change the magnetic field according to Eq. (315). To leave the electric field unchanged one must then change the scalar potential Φ as prescribed by Eq. (314) accordingly. By choosing

$$\nabla\cdot\mathbf{A} + \frac{1}{c}\frac{\partial\Phi}{\partial t} = 0, \tag{318}$$

one accomplishes this decoupling with the result

$$\nabla^2\Phi - \frac{1}{c^2}\frac{\partial^2\Phi}{\partial t^2} = -4\pi\rho \tag{319}$$

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} = -4\pi\mathbf{j}. \tag{320}$$

The implied freedom of gauge transformations can be used to choose a gauge useful for the case under study. In the following the radiation, Coulomb, or transverse gauge will be considered. It is defined by

$$\nabla\cdot\mathbf{A} = 0. \tag{321}$$

With this choice the scalar potential becomes the instantaneous Coulomb potential given by

$$\Phi(\mathbf{x},t) = \int_V d^3x' \; \frac{\rho(\mathbf{x}',t)}{|\mathbf{x}-\mathbf{x}'|}, \tag{322}$$

which is the solution of the Poisson equation that results from Eq. (316) in this gauge. When no sources are present $\Phi = 0$ and the electic and magnetic fields are obtained from

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \tag{323}$$

$$\mathbf{B} = \nabla \times \mathbf{A}, \tag{324}$$

while the vector potential obeys the homogeneous wave equation according to Eq. (317)

$$\nabla^2 \mathbf{A} - \frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} = 0. \tag{325}$$

B. Free field solutions and harmonic oscillators

When solving the wave equation (325) one may assume a large volume V (a cube) and expand $\mathbf{A}$ in terms of plane waves satisfying periodic boundary conditions as in section #4

$$\mathbf{A}(\mathbf{x},t) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \mathbf{A}_{\mathbf{k}}(t)\; e^{i\mathbf{k}\cdot\mathbf{x}}, \tag{326}$$

with $\mathbf{k}$ running over the same values as in Eq. (199). The transverse character of $\mathbf{A}$ implied by the choice of gauge in Eq. (321), results in only two components of $\mathbf{A}$ at each point in space. The expansion (326) therefore yields

$$\mathbf{k}\cdot\mathbf{A}_{\mathbf{k}} = 0, \tag{327}$$

showing that each Fourier coefficient is perpendicular to the propagation vector $\mathbf{k}$. Since the coefficients $\mathbf{A}_{\mathbf{k}}$ have only two components one may expand them in unit vectors perpendicular to $\mathbf{k}$

$$\mathbf{A}_{\mathbf{k}} = \sum_{\alpha=1,2} \mathbf{e}_{\mathbf{k}\alpha} A_{\mathbf{k}\alpha}, \tag{328}$$

where $\mathbf{e}_{\mathbf{k}\alpha}$ is a unit vector characterizing the polarization. Substituting Eq. (326) in the wave equation it is clear that

$$\frac{\partial^2 \mathbf{A}_{\mathbf{k}}(t)}{\partial t^2} + c^2 k^2 \mathbf{A}_{\mathbf{k}}(t) = 0. \tag{329}$$

The Fourier coefficients therefore oscillate harmonically with frequency

$$\omega_k = ck, \tag{330}$$

so one can write

$$\mathbf{A}_{\mathbf{k}}(t) = e^{-i\omega_k t}\; \mathbf{A}_{\mathbf{k}}. \tag{331}$$

Since $\mathbf{A}$ may be assumed to be real one can find real solutions by rewriting it in terms of Eq. (326) and its complex conjugate

$$\mathbf{A}(\mathbf{x},t) = \frac{1}{2\sqrt{V}} \sum_{\mathbf{k}} \left[\mathbf{A}_{\mathbf{k}}(t) + \mathbf{A}^*_{-\mathbf{k}}(t)\right] e^{i\mathbf{k}\cdot\mathbf{x}}. \tag{332}$$

Accordingly one finds from Eqs. (323) and (324) the following expressions for the fields

$$\mathbf{E}(\mathbf{x},t) = \frac{i}{2c\sqrt{V}} \sum_{\mathbf{k}} \omega_k \;\left[\mathbf{A}_{\mathbf{k}}(t) - \mathbf{A}^*_{-\mathbf{k}}(t)\right] e^{i\mathbf{k}\cdot\mathbf{x}} \tag{333}$$

$$\mathbf{B}(\mathbf{x},t) = \frac{i}{2\sqrt{V}} \sum_{\mathbf{k}} \;\mathbf{k}\times \left[\mathbf{A}_{\mathbf{k}}(t) + \mathbf{A}^*_{-\mathbf{k}}(t)\right] e^{i\mathbf{k}\cdot\mathbf{x}}. \tag{334}$$

In order to obtain the energy of the electromagnetic field in terms of the Fourier coefficients of the vector potential one can consider the following integrals while noting that both **E** and **B** are real

$$\int_V d^3x\ \mathbf{E}\cdot\mathbf{E}^* = \frac{1}{4c^2}\sum_{\mathbf{k}}\omega_k^2\left|\mathbf{A}_{\mathbf{k}}(t)-\mathbf{A}^*_{-\mathbf{k}}(t)\right|^2 \tag{335}$$

$$\int_V d^3x\ \mathbf{B}\cdot\mathbf{B}^* = \frac{1}{4}\sum_{\mathbf{k}}k^2\left|\mathbf{A}_{\mathbf{k}}(t)+\mathbf{A}^*_{-\mathbf{k}}(t)\right|^2, \tag{336}$$

where the orthogonality of the plane waves in the box has been used according to Eq. (196). Rewriting these results in terms of the Fourier coefficients along the polarization vectors one can show that the hamiltonian for the free radiation field can be written as

$$H_{em} = \frac{1}{8\pi}\sum_{\mathbf{k}\alpha}\ k^2\ \left|A_{\mathbf{k}\alpha}\right|^2. \tag{337}$$

In order to be able to quantize the electromagnetic field one needs real canonical variables which can be written in the following form

$$\mathbf{Q}_{\mathbf{k}}(t) = \frac{i}{2c\sqrt{4\pi}}\left[\mathbf{A}_{\mathbf{k}}(t)-\mathbf{A}^*_{\mathbf{k}}(t)\right] \tag{338}$$

$$\mathbf{P}_{\mathbf{k}}(t) = \frac{k}{2\sqrt{4\pi}}\left[\mathbf{A}_{\mathbf{k}}(t)+\mathbf{A}^*_{\mathbf{k}}(t)\right], \tag{339}$$

or

$$\mathbf{A}_{\mathbf{k}}(t) = -i2c\sqrt{\pi}\left[\mathbf{Q}_{\mathbf{k}}(t)+\frac{i}{\omega_k}\mathbf{P}_{\mathbf{k}}(t)\right]. \tag{340}$$

Using these variables and their components along the polarization vectors one can then finally write the hamiltonian as sum of uncoupled oscillators

$$H_{em} = \frac{1}{2}\sum_{\mathbf{k}\alpha}\left(P^2_{\mathbf{k}\alpha}+\omega_k^2 Q^2_{\mathbf{k}\alpha}\right) \tag{341}$$

with no need for time dependence to be specified on account of energy conservation.

C. Photons and many-photon states

A standard procedure for quantization from a classical hamiltonian [27] is to assert that the classical quantities $\mathbf{Q}_{\mathbf{k}}$ and $\mathbf{P}_{\mathbf{k}}$ are to be considered as quantummechanical operators satisfying the canonical commutation relations written here for their components along the two polarization directions (see Eq. (328))

$$[P_{\mathbf{k}\alpha}, P_{\mathbf{k}'\alpha'}] = 0 \tag{342}$$

$$[Q_{\mathbf{k}\alpha}, Q_{\mathbf{k}'\alpha'}] = 0 \tag{343}$$

$$[Q_{\mathbf{k}\alpha}, P_{\mathbf{k}'\alpha'}] = i\hbar\delta_{\mathbf{k},\mathbf{k}'}\delta_{\alpha,\alpha'}. \tag{344}$$

For harmonic oscillators it is of course fruitful to introduce the non-Hermitian operators

$$a_{\mathbf{k}\alpha} = \frac{1}{\sqrt{2\hbar\omega_k}}\left(\omega_k Q_{\mathbf{k}\alpha}+iP_{\mathbf{k}\alpha}\right) \tag{345}$$

$$a^\dagger_{\mathbf{k}\alpha} = \frac{1}{\sqrt{2\hbar\omega_k}}\left(\omega_k Q_{\mathbf{k}\alpha}-iP_{\mathbf{k}\alpha}\right), \tag{346}$$

which obey boson commutation relations (see material of section #2)

$$[a_{\mathbf{k}\alpha}, a_{\mathbf{k}'\alpha'}] = 0 \tag{347}$$

$$\left[a^\dagger_{\mathbf{k}\alpha}, a^\dagger_{\mathbf{k}'\alpha'}\right] = 0 \tag{348}$$

$$\left[a_{\mathbf{k}\alpha}, a^\dagger_{\mathbf{k}'\alpha'}\right] = \delta_{\mathbf{k},\mathbf{k}'}\delta_{\alpha,\alpha'}. \tag{349}$$

All the results obtained for boson states previously are also valid in the present situation and will not all be repeated. Nevertheless it is useful to emphasize that the operators $a_{\mathbf{k}\alpha}$ ($a^\dagger_{\mathbf{k}\alpha}$) must be interpreted as removing (adding) a quantum of the electromagnetic field (photon) with quantumnumbers $\mathbf{k}\alpha$ from (to) all states in Fock space. These states may contain any number of quanta (photons) occupying any possible quantum numbers. Introducing the operator counting the number of photons with $\mathbf{k}\alpha$

$$\hat{N}_{\mathbf{k}\alpha} = a^\dagger_{\mathbf{k}\alpha} a_{\mathbf{k}\alpha}, \tag{350}$$

one can write the hamiltonian now in Fock space as

$$\hat{H}_{em} = \sum_{\mathbf{k}\alpha} \hbar\omega_k \left(\hat{N}_{\mathbf{k}\alpha} + 1/2\right) \Rightarrow \sum_{\mathbf{k}\alpha} \hbar\omega_k \hat{N}_{\mathbf{k}\alpha}. \tag{351}$$

The awkward constant 1/2 in this expression can be left out because only energy differences can be measured (see also Ref. [54]). One can also contruct the momentum operator of the electromagnetic field by using the Poynting vector (in Hermitian form). After some algebra one obtains

$$\begin{aligned}\hat{\mathbf{P}}_{em} &= \frac{1}{8\pi c}\int_V d^3x \, (\mathbf{E}\times\mathbf{B} - \mathbf{B}\times\mathbf{E}) \\ &= \sum_{\mathbf{k}\alpha} \hbar\mathbf{k}\left(\hat{N}_{\mathbf{k}\alpha} + 1/2\right) \Rightarrow \sum_{\mathbf{k}\alpha} \hbar\mathbf{k}\hat{N}_{\mathbf{k}\alpha}.\end{aligned} \tag{352}$$

For a single photon state one has

$$\hat{H}_{em} a^\dagger_{\mathbf{k}\alpha} \left|0\right\rangle = \hbar\omega_k \; a^\dagger_{\mathbf{k}\alpha} \left|0\right\rangle \tag{353}$$

and

$$\hat{\mathbf{P}}_{em} a^\dagger_{\mathbf{k}\alpha} \left|0\right\rangle = \hbar\mathbf{k} \; a^\dagger_{\mathbf{k}\alpha} \left|0\right\rangle, \tag{354}$$

which shows that the mass of this quantum obtained from $m^2 = (E^2 - \mathbf{p}^2c^2)/c^4$ is equal to zero. By redefining the classical quantities $P_{\mathbf{k}\alpha}$ and $Q_{\mathbf{k}\alpha}$ as quantummechanical operators, the vector potential has also become an operator which can be written in terms of photon addition and removal operators as follows

$$\mathbf{A}(\mathbf{x},t) = \left(\frac{hc^2}{\omega_k V}\right)^{1/2} \sum_{\mathbf{k}\alpha} \left\{ a_{\mathbf{k}\alpha}\mathbf{e}_{\mathbf{k}\alpha} e^{i(\mathbf{k}\cdot\mathbf{x} - \omega_k t)} + a^\dagger_{\mathbf{k}\alpha}\mathbf{e}_{\mathbf{k}\alpha} e^{-i(\mathbf{k}\cdot\mathbf{x} - \omega_k t)} \right\}, \tag{355}$$

so that $\mathbf{A}$ can now act on a charged particle at $\mathbf{x}$ and t (still in first quantization) and through the photon operators on many-photon states changing the number of photons by plus or minus one if the state has a definite number of photons. In addition, the electric and magnetic fields have become operators as well.

D. Emission and absorption of photons by atoms

As shown in Eq. (322), the choice of the radiation gauge leads to the result that the scalar potential becomes the instantaneous Coulomb potential. It is therefore plausible that the inclusion of charged particles interacting with each other can be accomplished by adding the standard terms involving the Coulomb interaction. The important missing ingredient is the proper introduction of the interaction between the charged particles and the electromagnetic field in hamiltonian form. This result can be obtained by first considering the hamiltonian of one charged particle in an electromagnetic field starting from the Lorentz force equation

$$\mathbf{F} = e\left\{\mathbf{E} + \frac{1}{c}\mathbf{v}\times\mathbf{B}\right\}. \tag{356}$$

Using Eqs. (314) and (315) the Lorentz force can be rewritten in terms of the scalar and vector potential

$$\mathbf{F} = e\left\{-\nabla\Phi - \frac{1}{c}\frac{\partial\mathbf{A}}{\partial t} + \frac{1}{c}(\mathbf{v}\times\nabla\times\mathbf{A})\right\}. \tag{357}$$

One can rewrite

$$\mathbf{v} \times \nabla \times \mathbf{A} = \nabla(\mathbf{v} \cdot \mathbf{A}) - (\mathbf{v} \cdot \nabla)\mathbf{A} \tag{358}$$

and realize that

$$\frac{\partial \mathbf{A}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{A} = \frac{d\mathbf{A}}{dt}, \tag{359}$$

representing the total time derivative of the vector potential. The Lorentz force can therefore be rewritten as

$$\mathbf{F} = -\nabla U + \frac{d}{dt}\frac{\partial U}{\partial \mathbf{v}}, \tag{360}$$

where

$$U = e\Phi - \frac{e}{c}\mathbf{A} \cdot \mathbf{v}, \tag{361}$$

representing a generalized potential which is necessary on account of the velocity dependence of the Lorentz force. The Lagrangian of the particle now becomes

$$L = T - U = \frac{1}{2}m\mathbf{v}^2 - e\Phi + \frac{e}{c}\mathbf{A} \cdot \mathbf{v}. \tag{362}$$

One may check that

$$\frac{d}{dt}\frac{\partial L}{\partial \mathbf{v}} - \frac{\partial L}{\partial \mathbf{x}} = 0 \tag{363}$$

indeed gives the appropriate equations of motion. The generalized momentum is then given by

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = m\mathbf{v} + \frac{e}{c}\mathbf{A}. \tag{364}$$

Solving this equation for $\mathbf{v}$ and substituting the result in the hamiltonian yields

$$H = \mathbf{p} \cdot \mathbf{v} - L = \frac{\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2}{2m} + e\Phi, \tag{365}$$

which represents the sought after hamiltonian form.

Considering the case of atoms one can now write the hamiltonian for N (nonrelativistic) electrons in the presence of a heavy nucleus with charge Z together with the quantized energy of the radiation field as follows

$$H = \sum_{i=1}^{N} \frac{\left(\mathbf{p}_i - \frac{e}{c}\mathbf{A}(\mathbf{x}_i, t)\right)^2}{2m} + \sum_{i<j=1}^{N} \frac{e^2}{|\mathbf{x}_i - \mathbf{x}_j|} - \sum_{i=1}^{N} \frac{Ze^2}{|\mathbf{x}_i|} + \hat{H}_{em}. \tag{366}$$

The actual solution of the electron problem in the field of the nucleus will be discussed later in the course when the Hartree-Fock approximation is studied. Suffice it to say that this Hartree-Fock method yields an optimal sp potential that includes in an average way the effect of the other electrons. The sp basis that is generated by this potential may be used to write the second quantized hamiltonian for the electrons only in the following way

$$\hat{H}_{HF} = \sum_{n_{HF}\ell m_\ell m_s} \epsilon_{n_{HF}\ell}\, a^\dagger_{n_{HF}\ell m_\ell m_s} a_{n_{HF}\ell m_\ell m_s}, \tag{367}$$

while neglecting the remaining two-body terms. Using this description one may apply all the results previously discussed for the independent particle model in section #3.

It is important to note that even when no approximation to the many-electron problem is made, the interaction between the photons and the electrons is determined by

$$H_{int} = \sum_{i=1}^{N} \left[-\frac{e}{2mc}\left(\mathbf{p}_i \cdot \mathbf{A}(\mathbf{x}_i, t) + \mathbf{A}(\mathbf{x}_i, t) \cdot \mathbf{p}_i\right) + \frac{e^2}{2mc^2}\mathbf{A}(\mathbf{x}_i, t) \cdot \mathbf{A}(\mathbf{x}_i, t) \right], \tag{368}$$

which can also be used for the interaction with other charged particles (like protons) with minor modifications. To be complete it is necessary to include the interaction of the electron spins with the magnetic field

$$H_{int}^{spin} = -\sum_i^N \frac{e}{mc} \mathbf{s}_i \cdot [\nabla \times \mathbf{A}(\mathbf{x},t)]_{\mathbf{x}=\mathbf{x}_i} . \tag{369}$$

Note that wherever $\mathbf{A}$ appears it can add or remove a photon according to Eq. (355). This means that these two interaction hamiltonians (Eqs. (368) and (369)) can induce transitions between atomic levels in the presence of an electromagnetic field but also when there is no photon around. Note also that the interaction terms represent a one-body operator in the electron coordinates. It is thus possible to use the electron Fock-space formulation using a general sp basis $\{|\alpha\rangle\}$ to rewrite these interaction terms in second quantization. In doing so one may use the transversality of $\mathbf{A}$ to argue that in the first term in Eq. (369) one may rewrite

$$\mathbf{p}_i \cdot \mathbf{A}(\mathbf{x}_i,t) = \mathbf{A}(\mathbf{x}_i,t) \cdot \mathbf{p}_i, \tag{370}$$

since the contribution of acting on the $\mathbf{x}$ dependence in $\mathbf{A}$ vanishes due to the choice of gauge, while $\mathbf{p}$ continues to act as an operator on the electron spatial degrees of freedom. Combining the first two terms in Eq. (368) that are linear in $\mathbf{A}$ then yields

$$\hat{H}_{int}^{I} = -\frac{e}{m}\left(\frac{h}{\omega_k V}\right)^{1/2} \sum_{\beta\gamma}\sum_{\mathbf{k}\alpha} \mathbf{e}_{\mathbf{k}\alpha} \cdot \left\{ \langle\beta| e^{i(\mathbf{k}\cdot\mathbf{x}-\omega_k t)}\, \mathbf{p}\, |\gamma\rangle \;\; a_\beta^\dagger a_\gamma a_{\mathbf{k}\alpha} + \langle\beta| e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega_k t)}\, \mathbf{p}\, |\gamma\rangle \;\; a_\beta^\dagger a_\gamma a_{\mathbf{k}\alpha}^\dagger \right\}, \tag{371}$$

where the first term describes the absorption and the second the emission of a photon. The remaining term in Eq. (368) is quadratic in $\mathbf{A}$ and can be neglected compared to linear terms on account of the smallness of the fine structure constant $\alpha = e^2/\hbar c$ which governs the coupling of electrons to photons. Note that for photon scattering these quadratic terms must be included together with second order contributions coming from Eq. (371) [56]. These quadratic terms will contain two photon operators including terms that remove or add two photons and those that keep the number of photons constant (but change the momentum so appropriate for scattering). The spin contribution can be handled similarly to the linear term in $\mathbf{A}$ which yielded Eq. (371) with the result

$$\hat{H}_{int}^{spin} = -\frac{e}{m}\left(\frac{h}{\omega_k V}\right)^{1/2} \sum_{\beta\gamma}\sum_{\mathbf{k}\alpha} (i\mathbf{k} \times \mathbf{e}_{\mathbf{k}\alpha}) \cdot \left\{ \langle\beta| e^{i(\mathbf{k}\cdot\mathbf{x}-\omega_k t)}\, \mathbf{s}\, |\gamma\rangle \;\; a_\beta^\dagger a_\gamma a_{\mathbf{k}\alpha} + \langle\beta| e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega_k t)}\, \mathbf{s}\, |\gamma\rangle \;\; a_\beta^\dagger a_\gamma a_{\mathbf{k}\alpha}^\dagger \right\}. \tag{372}$$

Eq. (371) can be used to study absorption of light by an atom. In this case only the first term with the photon removal operator will contribute. For example on may start from an initial state $|A; n_{\mathbf{k}\alpha}\rangle$ representing an atomic state A and a photon state with occupation only in the meomentum $\mathbf{k}$ and polarization α state and proceed to a final state with one photon less and a different atomic state $|B; n_{\mathbf{k}\alpha} - 1\rangle$. Using standard time-dependent perturbation theory and the dipole approximation (valid for atomic systems) one may study the absorption cross section. Similarly, one may study the photoelectric effect in which the interaction removes an electron from the atom into the continuum upon absorption of the photon. The term in Eq. (371) containing the photon addition operator may be used to describe the spontaneous emission of an excited atomic state to one lower in energy also using standard time-dependent perturbation theory. It is important to note that the occupation of a mode by n photons has consequences for the matrix element of $\mathbf{A}$ between this state and possible final states. If the final state has one photon more the boson factor $\sqrt{n+1}$ comes in on account of Eq. (93) while the factor $\sqrt{n}$ is obtained for a final state with one photon less as in Eq. (94). This information is critical for the following discussion.

E. Blackbody radiation and the laser principle

One can use Fermi's golden rule obtained from time-dependent perturbation theory to study general features of a photon gas. Starting from

$$w_{ji} = \frac{2\pi}{\hbar} \left| \langle j| \hat{H}_{int}^{I} |i\rangle \right|^2 \rho_j , \tag{373}$$

which describes the transition probability from an initial state for a system of charges and photons denoted by state $|i\rangle$ to a final state denoted by $|j\rangle$ with corresponding density of states ρ_j at the energy of state j. In using $\hat{H}_{int}^{I}$ one may drop its time-dependence since it has been used to generate the energy conservation implied by the use of ρ [26]. One can immediately state that this transition probability from an initial state containing zero photons to one photon and from the otherwise identical state but with n photons to the same final state with $n+1$ photons are related by

$$w_{ji}(n_{\mathbf{k}\alpha}+1 \leftarrow n_{\mathbf{k}\alpha}) = (n_{\mathbf{k}\alpha}+1)\; w_{ji}(1_{\mathbf{k}\alpha} \leftarrow 0). \tag{374}$$

For the absorption one has accordingly

$$w_{ij}(n_{\mathbf{k}\alpha}-1 \leftarrow n_{\mathbf{k}\alpha}) = n_{\mathbf{k}\alpha}\; w_{ij}(0 \leftarrow 1_{\mathbf{k}\alpha}), \tag{375}$$

while finally

$$w_{ij}(0 \leftarrow 1_{\mathbf{k}\alpha}) = w_{ji}(1_{\mathbf{k}\alpha} \leftarrow 0) \tag{376}$$

since the matrix elements entering here differ only by phase factors while the density of states factor reverses its role between emission and absorption: for emission ρ describes the final states of the photon continuum while for absorption one sums over a distribution of initial states yielding the same density of states. As a result of this detailed balancing the ratio of emission to absortion is given by the ratio of photon occupancy factors only

$$\frac{w_{ji}(n_{\mathbf{k}\alpha}+1 \leftarrow n_{\mathbf{k}\alpha})}{w_{ij}(n_{\mathbf{k}\alpha}-1 \leftarrow n_{\mathbf{k}\alpha})} = \frac{n_{\mathbf{k}\alpha}+1}{n_{\mathbf{k}\alpha}}. \tag{377}$$

Consider two levels belonging to atoms that form a gas. Assume that the energies of these levels are E_a and E_b with $E_a < E_b$. Energy conservation requires the photon energy that links these two levels to be

$$\hbar\omega_k = E_b - E_a. \tag{378}$$

The relative population of these levels when they are in equilibrium at temperature T is given by the Boltzmann factors e^{-E_b/k_BT} and e^{-E_a/k_BT}, respectively. When emission and absorption are possible equilibrium requires that there is a balance between these processes. In the present example this condition is given by

$$w_{ji}(\bar{n}_{\mathbf{k}\alpha}+1 \leftarrow \bar{n}_{\mathbf{k}\alpha})e^{-E_b/k_BT} = w_{ij}(\bar{n}_{\mathbf{k}\alpha}-1 \leftarrow \bar{n}_{\mathbf{k}\alpha})e^{-E_a/k_BT}, \tag{379}$$

where $\bar{n}_{\mathbf{k}\alpha}$ refers to the average occupation at this temperature of the mode $\mathbf{k}\alpha$. Using Eq. (377) one obtains

$$\frac{\bar{n}_{\mathbf{k}\alpha}+1}{\bar{n}_{\mathbf{k}\alpha}} = e^{(E_b-E_a)/k_BT} = e^{\hbar\omega_k/k_BT}, \tag{380}$$

which can be solved for the average occupation number

$$\bar{n}_{\mathbf{k}\alpha} = \frac{1}{e^{\hbar\omega_k/k_BT}-1}. \tag{381}$$

This result is of course Planck's law for blackbody radiation.

One can achieve a significant deviation from the Boltzmann factors by the process of optical pumping for example by shining "blue" light into a system of atoms which make a transition from the ground state to reach an excited state. This excited state spontaneously decays to a lower-energy state which must be metastable so that the population of that state increases with time. A photon matched to the energy difference of this state and the ground state will then be able to stimulate the emission of another photon in this mode so that an exponential avalanche of photons all in this mode builds up. Enclosing the active atoms between parallel mirrors helps this process since it avoids wasting photons that would otherwise escape. This process is therefore able to transfer atomic energy into the energy of a single mode of the electromagnetic field which is the basic idea of the laser.