Advanced Quantum Mechanics

Prof. Dr. Stefan Dittmaier

Albert-Ludwigs-Universität Freiburg, Physikalisches Institut
D-79104 Freiburg, Germany

Winter-Semester 2014/15

Draft: February 13, 2015

Contents

Chapter 1

Recapitulation of basic qm. principles

- Mathematical background
- Qm. states, observables, and measurements
- Correspondence principle and time evolution

Chapter 2

Symmetries in quantum mechanics

- Symmetry transformations and Wigner's theorem
- Elements of group theory (representations, irreducibility, Schur's lemma, finite groups, Lie groups, Lie algebras)
- Space translations (continuous and discrete translations, Bloch's theorem)
- Rotations (SO(3) and SU(2), irreducible representations, Wigner's D functions, orbital angular momentum and spin, addition of angular momenta, irreducible tensors, Wigner-Eckart theorem)

Chapter 3

Approximation methods

- WKB method
- Time-independent perturbation theory
- Variational method
- Time-dependent perturbation theory

Chapter 4

Scattering theory

- Potential scattering (Green's functions, wave packets, Lippmann–Schwinger equation, perturbation theory, partial-wave analysis, optical theorem, resonances, complex potentials)
- Basics of general scattering theory (T matrix, S matrix, cross sections, decay widths, general optical theorem)

Chapter 5

Quantization of the electromagnetic field

Experimental observation:

Elmg. fields of frequency ν emits / absorbs	*energy*	in portions $h\nu = \hbar\omega$.
Elmg. fields of frequency ν emits / absorbs	*momentum*	in portions $h/\lambda = \hbar k$.

$\Rightarrow$ Qm. principles should be applied to the elmg. fields !

5.1 Free electromagnetic fields

5.1.1 Classical description

Maxwell's equations:

$$\vec{\nabla}\vec{E} = \rho/\epsilon_0, \qquad \vec{\nabla}\times\vec{E} = -\dot{\vec{B}},$$
$$\vec{\nabla}\vec{B} = 0, \qquad \vec{\nabla}\times\vec{B} = \dot{\vec{E}}/c^2 + \mu_0\vec{j}, \tag{5.1}$$

where the electric charge ρ and the current density $\vec{j}$ vanish for free fields: $\rho = 0, \vec{j} = 0$.

Gauge potentials $\vec{A}$ and Φ:

$\hookrightarrow$ eliminate the homogenous Maxwell eqs. by construction:

$$\vec{B} = \vec{\nabla}\times\vec{A}, \qquad \vec{E} = -\vec{\nabla}\Phi - \dot{\vec{A}}. \tag{5.2}$$

Field eqs. for $\vec{A}$ and Φ:

$$\Box\vec{A} + \vec{\nabla}(\vec{\nabla}\vec{A} + \dot{\Phi}/c^2) = \mu_0\vec{j}, \qquad \triangle\Phi + \vec{\nabla}\dot{\vec{A}} = -\rho/\epsilon_0. \tag{5.3}$$

Recall: $\Box = \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \triangle =$ wave operator

Elmg. gauge invariance:

Field strengths $\vec{E}$ and $\vec{B}$ (which define the physical state of the classial system) are invariant under the "gauge transformation":

$$\vec{A} \to \vec{A}' = \vec{A} + \vec{\nabla}\chi, \qquad \Phi \to \Phi' = \Phi - \dot{\chi}, \tag{5.4}$$

with χ denoting any function $\chi = \chi(\vec{x}, t)$.

$\Rightarrow$ Field eqs. can be simplified by "fixing a gauge", e.g.:

- $\vec{\nabla}\vec{A} = 0$, "Coulomb gauge" (used in the following),
- $\vec{\nabla}\vec{A} + \dot{\Phi}/c^2 = 0$, "Lorenz gauge" (appropriate in relativistic theories).

Free elmg. radiation in Coulomb gauge ("radiation gauge"):

$$\Phi \equiv 0, \tag{5.5}$$

$$\Box \vec{A} = 0, \quad \text{homogenous wave equation}, \tag{5.6}$$

$$\vec{\nabla}\vec{A} = 0. \tag{5.7}$$

Basis solution for finite volume V (cubic box of side length L):

- Ansatz: $\vec{A}(\vec{x},t) = \vec{\varepsilon}\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}-\mathrm{i}\omega t}$, $\vec{\varepsilon} = \text{const.}$
- From Eq.(5.6): $-\frac{\omega^2}{c^2} + \vec{k}^{\,2} = 0$, i.e. $\omega = c|\vec{k}| = ck$.
- From periodicity: $\vec{k} = \frac{2\pi}{L}\vec{n}$, $n_j \in \mathbb{Z}$, i.e. all $\vec{k}$ on discrete lattice.
- From Eq.(5.7): $\vec{k}\cdot\vec{\varepsilon} = 0$ $\to$ 2 independent solutions ("polarizations") for each $\vec{k}$.
  Convenient choice of $\vec{\varepsilon}_\lambda(\vec{k})$: "helicity basis" $\vec{\varepsilon}_\pm(\vec{k})$.

$$\vec{\varepsilon}_\pm = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm\mathrm{i} \\ 0 \end{pmatrix} \quad \text{for} \quad \vec{k} = k\vec{e}_3, \quad \text{other directions via rotations,} \tag{5.8}$$

i.e. $\vec{\varepsilon}_\pm$ describe right/left-circular polarization,

$$\text{normalization:} \quad \vec{\varepsilon}_\lambda \cdot \vec{\varepsilon}^{\,*}_{\lambda'} = \delta_{\lambda\lambda'}, \quad \vec{\varepsilon}^{\,*}_\pm = \vec{\varepsilon}_\mp, \tag{5.9}$$

$$\text{completeness relation:} \quad \sum_{\lambda=\pm} \varepsilon_{\lambda,a}(\vec{k})\varepsilon^*_{\lambda,b}(\vec{k}) = \delta_{ab} - \frac{k_a k_b}{k^2}. \tag{5.10}$$

$\Rightarrow$ General solution for $\vec{A}(\vec{x},t)$:

$$\vec{A}(\vec{x},t) = \sum_{\vec{k}}\sum_{\lambda} \frac{1}{\sqrt{2\omega\epsilon_0 V}} \left(\underbrace{a_\lambda(\vec{k})}_{\text{arbitrary amplitudes}} \vec{\varepsilon}_\lambda(\vec{k})\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}-\mathrm{i}\omega t} + \underbrace{\text{c.c.}}_{\text{complex conjugate}} \right). \tag{5.11}$$

(normalization defined with some foresight)

Field strengths derived from $\vec{A}(\vec{x},t)$:

$$\vec{E}(\vec{x},t) = \mathrm{i}\sum_{\vec{k}}\sum_{\lambda} \sqrt{\frac{\omega}{2\epsilon_0 V}} \left(a_\lambda(\vec{k})\,\vec{\varepsilon}_\lambda(\vec{k})\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}-\mathrm{i}\omega t} - \text{c.c.} \right), \tag{5.12}$$

$$\vec{B}(\vec{x},t) = \mathrm{i}\sum_{\vec{k}}\sum_{\lambda} \frac{1}{\sqrt{2\omega\epsilon_0 V}} \left(a_\lambda(\vec{k})\,\vec{k}\times\vec{\varepsilon}_\lambda(\vec{k})\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}-\mathrm{i}\omega t} - \text{c.c.} \right). \tag{5.13}$$

Energy $H_{\rm rad}$ and momentum $\vec{P}_{\rm rad}$ of the field configuration:

$$
\begin{aligned}
H_{\rm rad} &= \int_V \mathrm{d}^3x\,\frac{1}{2}\left(\epsilon_0\vec{E}^{\,2}+\vec{B}^{\,2}/\mu_0\right)\\
&= -\frac{1}{2V}\int_V \mathrm{d}^3x \sum_{\vec{k},\vec{k}',\lambda,\lambda'}\left\{\frac{\sqrt{\omega\omega'}}{2}\left(a_\lambda(\vec{k})\,\vec{\varepsilon}_\lambda(\vec{k})\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}-\mathrm{i}\omega t}-\text{c.c.}\right)\cdot\left(a_{\lambda'}(\vec{k}')\,\vec{\varepsilon}_{\lambda'}(\vec{k}')\,\mathrm{e}^{\mathrm{i}\vec{k}'\vec{x}-\mathrm{i}\omega' t}-\text{c.c.}\right)\right.\\
&\qquad\left.+\frac{1}{2\underbrace{\epsilon_0\mu_0}_{=1/c^2}\sqrt{\omega\omega'}}\left(a_\lambda(\vec{k})\,\vec{k}\times\vec{\varepsilon}_\lambda(\vec{k})\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}-\mathrm{i}\omega t}-\text{c.c.}\right)\cdot\left(a_{\lambda'}(\vec{k}')\,\vec{k}'\times\vec{\varepsilon}_{\lambda'}(\vec{k}')\,\mathrm{e}^{\mathrm{i}\vec{k}'\vec{x}-\mathrm{i}\omega' t}-\text{c.c.}\right)\right\}\\
&= -\frac{1}{4V}\int_V \mathrm{d}^3x \sum_{\vec{k},\vec{k}',\lambda,\lambda'}\left\{\sqrt{\omega\omega'}\Big(a_\lambda(\vec{k})\,a_{\lambda'}(\vec{k}')\,\vec{\varepsilon}_\lambda(\vec{k})\cdot\vec{\varepsilon}_{\lambda'}(\vec{k}')\,\underbrace{\mathrm{e}^{\mathrm{i}(\vec{k}+\vec{k}')\vec{x}}}_{\int \mathrm{d}^3x\,\to V\delta_{\vec{k},-\vec{k}'}}\mathrm{e}^{-\mathrm{i}(\omega+\omega')t}\right.\\
&\qquad -a_\lambda(\vec{k})\,a^*_{\lambda'}(\vec{k}')\,\vec{\varepsilon}_\lambda(\vec{k})\cdot\vec{\varepsilon}^{\,*}_{\lambda'}(\vec{k}')\,\mathrm{e}^{\mathrm{i}(\vec{k}-\vec{k}')\vec{x}-\mathrm{i}(\omega-\omega')t}+\text{c.c.}\Big)\\
&\qquad +\frac{c^2}{\sqrt{\omega\omega'}}\Big[a_\lambda(\vec{k})\,a_{\lambda'}(\vec{k}')\,\left(\vec{k}\times\vec{\varepsilon}_\lambda(\vec{k})\right)\cdot\left(\vec{k}'\times\vec{\varepsilon}_{\lambda'}(\vec{k}')\right)\,\mathrm{e}^{\mathrm{i}(\vec{k}+\vec{k}')\vec{x}-\mathrm{i}(\omega+\omega')t}\\
&\qquad \left.-a_\lambda(\vec{k})\,a^*_{\lambda'}(\vec{k}')\,\left(\vec{k}\times\vec{\varepsilon}_\lambda(\vec{k})\right)\cdot\left(\vec{k}'\times\vec{\varepsilon}^{\,*}_{\lambda'}(\vec{k}')\right)\,\mathrm{e}^{\mathrm{i}(\vec{k}-\vec{k}')\vec{x}-\mathrm{i}(\omega-\omega')t}+\text{c.c.}\Big]\right\}\\
&= -\frac{1}{4}\sum_{\vec{k},\lambda,\lambda'}\left\{\omega\Big(\cancel{a_\lambda(\vec{k})\,a_{\lambda'}(-\vec{k})\,\vec{\varepsilon}_\lambda(\vec{k})\cdot\vec{\varepsilon}_{\lambda'}(-\vec{k})\,\mathrm{e}^{-2\mathrm{i}\omega t}}-a_\lambda(\vec{k})\,a^*_{\lambda'}(\vec{k})\,\underbrace{\vec{\varepsilon}_\lambda(\vec{k})\cdot\vec{\varepsilon}^{\,*}_{\lambda'}(\vec{k})}_{=\delta_{\lambda\lambda'}}+\text{c.c.}\Big)\right.\\
&\qquad +\frac{c^2}{\omega}\Big[\cancel{a_\lambda(\vec{k})\,a_{\lambda'}(-\vec{k})\,\underbrace{\left(\vec{k}\times\vec{\varepsilon}_\lambda(\vec{k})\right)\cdot\left(-\vec{k}\times\vec{\varepsilon}_{\lambda'}(-\vec{k})\right)}_{=-k^2\vec{\varepsilon}_\lambda(\vec{k})\cdot\vec{\varepsilon}_{\lambda'}(-\vec{k})}\,\mathrm{e}^{-2\mathrm{i}\omega t}}\\
&\qquad \left.-a_\lambda(\vec{k})\,a^*_{\lambda'}(\vec{k})\,\underbrace{\left(\vec{k}\times\vec{\varepsilon}_\lambda(\vec{k})\right)\cdot\left(\vec{k}\times\vec{\varepsilon}^{\,*}_{\lambda'}(\vec{k})\right)}_{=k^2\vec{\varepsilon}_\lambda(\vec{k})\cdot\vec{\varepsilon}^{\,*}_{\lambda'}(\vec{k})=\frac{\omega^2}{c^2}\delta_{\lambda\lambda'}}+\text{c.c.}\Big]\right\}\\
&= \sum_{\vec{k},\lambda}\frac{\omega}{2}\left(a_\lambda(\vec{k})a_\lambda(\vec{k})^*+a_\lambda(\vec{k})^*a_\lambda(\vec{k})\right), \qquad (5.14)
\end{aligned}
$$

$$
\vec{P}_{\rm rad} = \int_V \mathrm{d}^3x\,\epsilon_0\vec{E}\times\vec{B} = \cdots = \sum_{\vec{k},\lambda}\frac{\vec{k}}{2}\left(a_\lambda(\vec{k})a_\lambda(\vec{k})^*+a_\lambda(\vec{k})^*a_\lambda(\vec{k})\right). \qquad (5.15)
$$

5.1.2 Quantization

Comparison with system of harmonic oscillators:

$$\hat{H} = \sum_k \left(\frac{\hat{p}_k^2}{2m_k} + \frac{m_k \omega_k^2}{2} \hat{q}_k^2 \right), \qquad [\hat{q}_k, \hat{p}_{k'}] = \mathrm{i}\hbar \delta_{kk'} \,, \tag{5.16}$$

$$= \sum_k \frac{\hbar\omega_k}{2} \left(\hat{a}_k \hat{a}_k^\dagger + \hat{a}_k^\dagger \hat{a}_k \right), \qquad [\hat{a}_k, \hat{a}_{k'}^\dagger] = \delta_{kk'}, \quad [\hat{a}_k, \hat{a}_{k'}] = [\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger] = 0, \tag{5.17}$$

$$E_{n_1 n_2 \ldots} = \sum_k \hbar\omega_k \left(n_k + \frac{1}{2} \right), \qquad n_k = 0, 1, 2, \ldots \tag{5.18}$$

⇒ Promote classical amplitudes $a_\lambda(\vec{k})$ and $a_\lambda(\vec{k})^*$
to annihilation and creation operators $\sqrt{\hbar}\, \hat{a}_\lambda(\vec{k})$ and $\sqrt{\hbar}\, \hat{a}_\lambda(\vec{k})^\dagger$:

- Commutators:

$$[\hat{a}_\lambda(\vec{k}), \hat{a}_{\lambda'}(\vec{k}')^\dagger] = \delta_{\lambda\lambda'} \delta_{\vec{k}\vec{k}'}, \quad [\hat{a}_\lambda(\vec{k}), \hat{a}_{\lambda'}(\vec{k}')] = [\hat{a}_\lambda(\vec{k})^\dagger, \hat{a}_{\lambda'}(\vec{k}')^\dagger] = 0. \tag{5.19}$$

- Hamilton operator:

$$\hat{H}_{\mathrm{rad}} = \sum_{\vec{k},\lambda} \frac{\hbar\omega}{2} \left(\hat{a}_\lambda(\vec{k}) \hat{a}_\lambda(\vec{k})^\dagger + \hat{a}_\lambda(\vec{k})^\dagger \hat{a}_\lambda(\vec{k}) \right). \tag{5.20}$$

- Field operator:

$$\hat{\vec{A}}(\vec{x}, t) = \sum_{\vec{k}} \sum_\lambda \sqrt{\frac{\hbar}{2\omega\epsilon_0 V}} \left(\hat{a}_\lambda(\vec{k})\, \vec{\varepsilon}_\lambda(\vec{k})\, \mathrm{e}^{\mathrm{i}\vec{k}\vec{x} - \mathrm{i}\omega t} \; + \; \hat{a}_\lambda(\vec{k})^\dagger\, \vec{\varepsilon}_\lambda^{\,*}(\vec{k})\, \mathrm{e}^{-\mathrm{i}\vec{k}\vec{x} + \mathrm{i}\omega t} \right) \tag{5.21}$$
$$= \hat{\vec{A}}(\vec{x}, t)^\dagger = \text{hermitian}.$$

Perform continuum limit $V \to \infty$:

$$\delta_{\vec{k}\vec{k}'} \;\to\; \frac{(2\pi)^3}{V}\, \delta(\vec{k} - \vec{k}'), \tag{5.22}$$
$$\sum_{\vec{k}} \;\to\; V \int \frac{\mathrm{d}^3 k}{(2\pi)^3},$$
$$\text{rescaling:} \quad a_\lambda(\vec{k})^{(\dagger)} \;\to\; a_\lambda(\vec{k})^{(\dagger)} \,/\, \sqrt{V}.$$

⇒ Results:

- Commutators:

$$[\hat{a}_\lambda(\vec{k}), \hat{a}_{\lambda'}(\vec{k}')^\dagger] = (2\pi)^3\, \delta_{\lambda\lambda'}\, \delta(\vec{k}-\vec{k}'), \quad [\hat{a}_\lambda(\vec{k}), \hat{a}_{\lambda'}(\vec{k}')] = [\hat{a}_\lambda(\vec{k})^\dagger, \hat{a}_{\lambda'}(\vec{k}')^\dagger] = 0. \tag{5.23}$$

- Field operators:

$$\hat{\vec{A}}(\vec{x},t) = \int \frac{\mathrm{d}^3k}{(2\pi)^3} \sum_\lambda \sqrt{\frac{\hbar}{2\omega\epsilon_0}} \left(\hat{a}_\lambda(\vec{k})\, \vec{\varepsilon}_\lambda(\vec{k})\, \mathrm{e}^{\mathrm{i}\vec{k}\vec{x}-\mathrm{i}\omega t} \;+\; \hat{a}_\lambda(\vec{k})^\dagger\, \vec{\varepsilon}^{\,*}_\lambda(\vec{k})\, \mathrm{e}^{-\mathrm{i}\vec{k}\vec{x}+\mathrm{i}\omega t} \right), \tag{5.24}$$

$$\vec{\nabla}\hat{\vec{A}}(\vec{x},t) = 0, \quad \text{Coulomb gauge condition,} \tag{5.25}$$

$$\hat{\vec{E}}(\vec{x},t) = -\frac{\partial \hat{\vec{A}}}{\partial t}(\vec{x},t), \tag{5.26}$$

$$\hat{\vec{B}}(\vec{x},t) = \vec{\nabla} \times \hat{\vec{A}}(\vec{x},t). \tag{5.27}$$

- Hamilton operator:

$$\hat{H}_{\mathrm{rad}} = \int \frac{\mathrm{d}^3k}{(2\pi)^3} \sum_\lambda \frac{\hbar\omega}{2} \left(\hat{a}_\lambda(\vec{k})\hat{a}_\lambda(\vec{k})^\dagger + \hat{a}_\lambda(\vec{k})^\dagger \hat{a}_\lambda(\vec{k}) \right). \tag{5.28}$$

- Operator for field momentum:

$$\hat{\vec{P}}_{\mathrm{rad}} = \int \frac{\mathrm{d}^3k}{(2\pi)^3} \sum_\lambda \frac{\hbar\vec{k}}{2} \left(\hat{a}_\lambda(\vec{k})\hat{a}_\lambda(\vec{k})^\dagger + \hat{a}_\lambda(\vec{k})^\dagger \hat{a}_\lambda(\vec{k}) \right). \tag{5.29}$$

Considerations about the field operators:

- By construction, the field operators obey their "eqs. of motion" (EOM) and thus are defined in the Heisenberg picture of time evolution.
- The quantized elmg. field defines a qm. system with infinitely many degrees of freedom:
  - The field modes characterized by $\vec{k}$ and λ are independent harmonic oscillators.
  - Alternatively, the field can be interpreted to allow for excitations at each point $\vec{x}$, but the fields at different points are NOT independent (derivatives in EOM correspond to interactions of neighbouring points).

- Still to be clarified:
  What is the canonical momentum variable corresponding to $\hat{\vec{A}}(\vec{x},t)$?

  $\hookrightarrow$ Use again analogy to harmonic oscillator:

$$\hat{q}_k = \sqrt{\frac{\hbar}{2m_k\omega_k}}\left(\hat{a}_k + \hat{a}_k^\dagger\right) \quad \longrightarrow \quad \hat{\vec{A}}(\vec{x},t),$$

$$\hat{p}_k = \mathrm{i}\sqrt{\frac{\hbar m_k\omega_k}{2}}\left(\hat{a}_k^\dagger - \hat{a}_k\right) \quad \longrightarrow \quad \frac{\partial\hat{\vec{A}}}{\partial t}(\vec{x},t)\ ? \quad \text{(because of factor “i” and sign change)}$$

  Calculation of commutator (at equal times!):

$$\begin{aligned}
\left[\hat{A}_a(\vec{x},t),\frac{\partial\hat{A}_b}{\partial t}(\vec{y},t)\right] &= \int\frac{\mathrm{d}^3k}{(2\pi)^3}\int\frac{\mathrm{d}^3k'}{(2\pi)^3}\,\frac{\mathrm{i}\omega'\hbar}{2\epsilon_0\sqrt{\omega\omega'}}\sum_{\lambda,\lambda'} \\
&\quad\times\left[\left(\hat{a}_\lambda(\vec{k})\,\varepsilon_{\lambda,a}(\vec{k})\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}-\mathrm{i}\omega t} + \hat{a}_\lambda(\vec{k})^\dagger\,\varepsilon^*_{\lambda,a}(\vec{k})\,\mathrm{e}^{-\mathrm{i}\vec{k}\vec{x}+\mathrm{i}\omega t}\right),\right. \\
&\qquad\left.\left(-\hat{a}_{\lambda'}(\vec{k}')\,\varepsilon_{\lambda',b}(\vec{k}')\,\mathrm{e}^{\mathrm{i}\vec{k}'\vec{y}-\mathrm{i}\omega' t} + \hat{a}_{\lambda'}(\vec{k}')^\dagger\,\varepsilon^*_{\lambda',b}(\vec{k}')\,\mathrm{e}^{-\mathrm{i}\vec{k}'\vec{y}+\mathrm{i}\omega' t}\right)\right] \\
&= \int\frac{\mathrm{d}^3k}{(2\pi)^3}\int\frac{\mathrm{d}^3k'}{(2\pi)^3}\,\frac{\mathrm{i}\omega'\hbar}{2\epsilon_0\sqrt{\omega\omega'}}\sum_{\lambda,\lambda'} \\
&\quad\times\Bigg(\underbrace{\left[\hat{a}_\lambda(\vec{k}),\hat{a}_{\lambda'}(\vec{k}')^\dagger\right]}_{=(2\pi)^3\,\delta_{\lambda\lambda'}\,\delta(\vec{k}-\vec{k}')}\varepsilon_{\lambda,a}(\vec{k})\,\varepsilon^*_{\lambda',b}(\vec{k}')\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}-\mathrm{i}\vec{k}'\vec{y}-\mathrm{i}(\omega-\omega')t} \\
&\qquad - \left[\hat{a}_\lambda(\vec{k})^\dagger,\hat{a}_{\lambda'}(\vec{k}')\right]\,\varepsilon^*_{\lambda,a}(\vec{k})\,\varepsilon_{\lambda',b}(\vec{k}')\,\mathrm{e}^{-\mathrm{i}\vec{k}\vec{x}+\mathrm{i}\vec{k}'\vec{y}+\mathrm{i}(\omega-\omega')t}\Bigg) \\
&= \frac{\mathrm{i}\hbar}{2\epsilon_0}\int\frac{\mathrm{d}^3k}{(2\pi)^3}\Bigg(\underbrace{\sum_\lambda\varepsilon_{\lambda,a}(\vec{k})\,\varepsilon^*_{\lambda,b}(\vec{k})}_{=\delta_{ab}-\frac{k_ak_b}{k^2}}\,\mathrm{e}^{\mathrm{i}\vec{k}(\vec{x}-\vec{y})} + \text{c.c.}\Bigg) \\
&= \underbrace{\frac{\mathrm{i}\hbar}{\epsilon_0}\int\frac{\mathrm{d}^3k}{(2\pi)^3}\left(\delta_{ab}-\frac{k_ak_b}{k^2}\right)\mathrm{e}^{\mathrm{i}\vec{k}(\vec{x}-\vec{y})}}_{\equiv\ \delta^\perp_{ab}(\vec{x}-\vec{y}),\ \text{“transverse }\delta\text{-function”}}.
\end{aligned}$$

$\Rightarrow$ Identification of conjugate momentum variable: $\hat{\vec{\Pi}}(\vec{x},t) \equiv \epsilon_0\frac{\partial\hat{\vec{A}}}{\partial t}(\vec{x},t) = -\epsilon_0\hat{\vec{E}}(\vec{x},t)$.

$$\left[\hat{A}_a(\vec{x},t),\hat{\Pi}_b(\vec{y},t)\right] = \mathrm{i}\hbar\,\delta^\perp_{ab}(\vec{x}-\vec{y}). \tag{5.30}$$

Comments:

- Definition of $\vec{\Pi}(\vec{x},t)$ should be verified upon checking the canonical EOMs.
- $\delta^{\perp}_{ab}(\vec{x}) = 3\times 3$ matrix-valued projector on transverse vector fields:

$$\delta^{\perp}_{ab}(\vec{x}) \;=\; \int \frac{\mathrm{d}^3k}{(2\pi)^3}\left(\delta_{ab} - \frac{k_a k_b}{k^2}\right)\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}} \;=\; \delta_{ab}\delta(\vec{x}) + \frac{\partial^2}{\partial x_a \partial x_b}\frac{1}{4\pi|\vec{x}|}, \qquad (5.31)$$

$$V^{\perp}_a(\vec{x}) \;\equiv\; \int \mathrm{d}^3y \sum_b \delta^{\perp}_{ab}(\vec{x}-\vec{y})\, V_b(\vec{y}) \;=\; V_a(\vec{x}) + \int \mathrm{d}^3y\, \frac{\partial}{\partial x_a}\frac{\vec{\nabla}_y \vec{V}(\vec{y})}{4\pi|\vec{x}-\vec{y}|}.$$

$$\hookrightarrow\; \vec{\nabla}\vec{V}^{\perp}(\vec{x}) = 0. \qquad (5.32)$$

$$\sum_a \frac{\partial}{\partial x_a}\delta^{\perp}_{ab}(\vec{x}) \;=\; 0, \qquad \mathrm{Tr}\left\{\delta^{\perp}(\vec{x})\right\} \;=\; 2\delta(\vec{x}). \qquad (5.33)$$

- Relativistic covariance of quantization in Coulomb gauge maintained, but non-trivial to prove.
- Manifestly relativistcally covariant quantization possible ("Gupta–Bleuler method"):
  - ◇ $\left[\hat{A}^{\mu}(\vec{x},t), \hat{\Pi}^{\nu}(\vec{y},t)\right] = \mathrm{i}\hbar g^{\mu\nu}\delta(\vec{x}-\vec{y})$ for field operators.,
  - ◇ $\langle\phi|\partial_\mu \hat{A}^{\mu}|\phi\rangle = 0$ for states $|\phi\rangle$.

  $\hookrightarrow$ Lecture on relativistic QFT !

"Fock space" of photons (follows analogy to harmonic oscillator)

- "vacuum state" $|0\rangle$ (no photons): $\langle 0|0\rangle = 1, \quad a_\lambda(\vec{k})|0\rangle = 0 \quad \forall \lambda, \vec{k}.$

$$\Rightarrow\; E_{\text{vac}} \;=\; \langle 0|\hat{H}_{\text{rad}}|0\rangle \;=\; \sum_{\vec{k},\lambda} \frac{\hbar\omega}{2} \underbrace{\langle 0|\,\hat{a}_\lambda(\vec{k})\hat{a}_\lambda(\vec{k})^\dagger + \cancel{\hat{a}_\lambda(\vec{k})^\dagger\hat{a}_\lambda(\vec{k})}\,|0\rangle}_{=1} \;=\; \sum_{\vec{k},\lambda} \frac{\hbar\omega}{2} \;\to\; \infty,$$

$$\langle 0|\hat{\vec{P}}_{\text{rad}}|0\rangle \;=\; \sum_{\vec{k},\lambda} \frac{\hbar\vec{k}}{2} \;=\; 0. \tag{5.34}$$

Note: Meaning of infinite vacuum energy not really fully understood, but not very problematic in practice, since not directly measureable.

Measured: "Casimir effect" = force between two electrically neutral metal plates = change of vacuum energy with changing volume.

$\hookrightarrow$ Redefine $\hat{H}_{\text{rad}}$ by splitting off unobservable E_{vac}:

$$\hat{H}_{\text{rad}} \;\to\; \hat{H}_{\text{rad}} - E_{\text{vac}}. \qquad \Rightarrow\; \hat{H}_{\text{rad}} = \sum_{\vec{k},\lambda} \hbar\omega\, \hat{a}_\lambda(\vec{k})^\dagger \hat{a}_\lambda(\vec{k}). \tag{5.35}$$

- 1-photon states: $|\vec{k},\lambda\rangle \equiv \hat{a}_\lambda(\vec{k})^\dagger|0\rangle, \quad \langle \vec{k},\lambda|\vec{k}',\lambda'\rangle = (2\pi)^3\,\delta_{\lambda\lambda'}\,\delta(\vec{k}-\vec{k}').$

$$\begin{aligned}
\hat{H}_{\text{rad}}|\vec{k},\lambda\rangle &= \sum_{\vec{k}',\lambda'} \hbar\omega'\,\hat{a}_{\lambda'}(\vec{k}')^\dagger \hat{a}_{\lambda'}(\vec{k}')\;\hat{a}_\lambda(\vec{k})^\dagger|0\rangle \\
&= \sum_{\vec{k}',\lambda'} \hbar\omega' \Big(\hat{a}_{\lambda'}(\vec{k}')^\dagger \underbrace{\Big[\hat{a}_{\lambda'}(\vec{k}'), \hat{a}_\lambda(\vec{k})^\dagger\Big]}_{=\delta_{\lambda\lambda'}\delta_{\vec{k}\vec{k}'}} + \cancel{\hat{a}_{\lambda'}(\vec{k}')^\dagger \hat{a}_\lambda(\vec{k})^\dagger|0\rangle\hat{a}_{\lambda'}(\vec{k}')} \Big)|0\rangle \\
&= \hbar\omega\,\hat{a}_\lambda(\vec{k})^\dagger|0\rangle = \hbar\omega\,|\vec{k},\lambda\rangle, \\
\hat{\vec{P}}_{\text{rad}}|\vec{k},\lambda\rangle &= \hbar\vec{k}\,|\vec{k},\lambda\rangle.
\end{aligned} \tag{5.36}$$

Polarization clarified upon investigating behaviour of $|\vec{k},\lambda\rangle$ under rotations.

$\hookrightarrow$ $|\vec{k},\lambda\rangle$ = state with 1 photon of energy $\hbar\omega$, momentum $\hbar\vec{k}$, and polarization $\vec{\varepsilon}_\lambda(\vec{k})$.

- N-photon state:

$$|\vec{k}_1,\lambda_1;\ldots;\vec{k}_N,\lambda_N\rangle \propto \left(\prod_{n=1}^{N} \hat{a}_{\lambda_n}(\vec{k}_n)^\dagger\right)|0\rangle. \tag{5.37}$$

$|\vec{k}_1,\lambda_1;\ldots;\vec{k}_N,\lambda_N\rangle$ = symmetric under exchange of any pair $(\vec{k}_i,\lambda_i)$ and $(\vec{k}_j,\lambda_j)$.

$\Rightarrow$ Bosonic states !

$$\begin{aligned}
\hat{H}_{\text{rad}}|\vec{k}_1,\lambda_1;\ldots;\vec{k}_N,\lambda_N\rangle &= \sum_{n=1}^{N} \hbar\omega_n\,|\vec{k}_1,\lambda_1;\ldots;\vec{k}_N,\lambda_N\rangle, \\
\hat{\vec{P}}_{\text{rad}}|\vec{k}_1,\lambda_1;\ldots;\vec{k}_N,\lambda_N\rangle &= \sum_{n=1}^{N} \hbar\vec{k}_n\,|\vec{k}_1,\lambda_1;\ldots;\vec{k}_N,\lambda_N\rangle.
\end{aligned} \tag{5.38}$$

"Fock space" $\mathcal{F}$ = Hilbert space spanned by all multi-photon states.

5.2 Interacting electromagnetic fields

5.2.1 Classical fields

Considered system: N particles with masses m_n and electric charges q_n at positions $\vec{x}_n$ $(n = 1, 2, \ldots, N)$.

Charge density: $\rho(\vec{x}) = \sum_n q_n \delta(\vec{x} - \vec{x}_n)$.

Electric field $\vec{E}$ and potentials in Coulomb gauge ($\vec{\nabla}\vec{A} = 0$):

$$\vec{E} = \underbrace{-\vec{\nabla}\Phi}_{=\vec{E}^{\parallel}} \underbrace{-\dot{\vec{A}}}_{=\vec{E}^{\perp}} = \vec{E}^{\parallel} + \vec{E}^{\perp}. \tag{5.39}$$

$$\vec{\nabla}\vec{E} = \vec{\nabla}\vec{E}^{\parallel} = -\triangle\Phi = \rho/\epsilon_0. \quad \rightarrow \quad \Phi(\vec{x}) = \sum_n \frac{q_n}{4\pi\epsilon_0|\vec{x} - \vec{x}_n|} = \text{no dynamical variable!}$$

$$\vec{E}^{\perp} = -\dot{\vec{A}}, \quad \vec{\nabla}\vec{E}^{\perp} = 0, \quad \vec{\Pi} = \epsilon_0\dot{\vec{A}} = -\epsilon_0\vec{E}^{\perp} = \text{canonical momentum variable to } \vec{A}.$$

Hamilton function:

$$H = H_{\text{matter}} + H_{\text{elmg}}, \tag{5.40}$$

$$H_{\text{matter}}(\{\vec{x}_n, \vec{p}_n\}) = \sum_n \frac{1}{2m_n}\Big(\underbrace{\vec{p}_n - q_n\vec{A}(\vec{x}_n, t)}_{=\, m_n\dot{\vec{x}}_n \,=\, \text{cartesian momentum} \,\neq\, \vec{p}_n.}\Big)^2, \tag{5.41}$$

$$\begin{aligned} H_{\text{elmg}}(\vec{A}, \vec{\Pi}) &= \int_V \mathrm{d}^3x\, \frac{1}{2}\Big(\epsilon_0\vec{E}^{\,2} + \vec{B}^{\,2}/\mu_0\Big) \\ &= \int_V \mathrm{d}^3x\, \frac{1}{2}\Big(\epsilon_0(\vec{E}^{\perp})^2 + 2\epsilon_0\underbrace{\vec{E}^{\perp}\vec{E}^{\parallel}}_{\underset{\text{P.I.}}{=}(\vec{\nabla}\vec{E}^{\perp})\Phi = 0} + \underbrace{\epsilon_0(\vec{E}^{\parallel})^2}_{\underset{\text{P.I.}}{=}-\epsilon_0\Phi\triangle\Phi = \rho\Phi} + \vec{B}^{\,2}/\mu_0\Big) \\ &= \int_V \mathrm{d}^3x\, \frac{1}{2}\Big(\epsilon_0(\vec{E}^{\perp})^2 + \vec{B}^{\,2}/\mu_0\Big) + \frac{1}{2}\sum_n q_n\Phi(\vec{x}_n) \\ &= \underbrace{\int_V \mathrm{d}^3x\, \frac{1}{2}\Big(\vec{\Pi}^{\,2}/\epsilon_0 + (\vec{\nabla}\times\vec{A})^2/\mu_0\Big)}_{\equiv\, H_{\text{rad}}(\vec{A}, \vec{\Pi})} + V_{\text{Coul}}(\{\vec{x}_n\}), \end{aligned} \tag{5.42}$$

$$V_{\text{Coul}}(\{\vec{x}_n\}) = \frac{1}{2}\sum_{m\neq n}\frac{q_m q_n}{4\pi\epsilon_0|\vec{x}_m - \vec{x}_n|} + \underbrace{E_{\text{self}}}_{\substack{= \text{ self-energy of point charges} \\ = \text{ constant, but } \rightarrow \infty}}.$$

$$\Rightarrow H = \underbrace{H_{\text{matter}} + V_{\text{Coul}}}_{\equiv\, H'_{\text{matter}}} + H_{\text{rad}}.$$

5.2.2 Quantization

Consider again system of N point charges as before.

Qm. states of matter particles:

- Operators according to the correspondence principle:

$$H'_{\text{matter}}(\{\vec{x}_n, \vec{p}_n\}) \;\to\; \hat{H}'_{\text{matter}}\left(\{\hat{\vec{x}}_n, \hat{\vec{p}}_n\}\right)$$
$$= \sum_n \frac{1}{2m_n}\left(\hat{\vec{p}}_n - q_n\vec{A}(\hat{\vec{x}}_n, t)\right)^2 \;+\; V_{\text{Coul}}\big(\{\hat{\vec{x}}_n\}\big),$$
$$\text{with} \quad [\hat{x}_{n,a}, \hat{p}_{m,b}] \;=\; \mathrm{i}\hbar\delta_{mn}\delta_{ab}. \tag{5.43}$$

- Many-particle states $|\psi\rangle \equiv |\psi_1\rangle \cdots |\psi_n\rangle$ as direct products (anti-symmetrized/symmetrized if needed).
- Operators and states defined in the Schrödinger or Heisenberg picture as usual.

Quantized radiation field: (Coulomb gauge $\vec{\nabla}\vec{A} = 0$)

New: Φ does not vanish, because $\triangle\Phi = -\vec{\nabla}\vec{E}^{\parallel} = -\rho/\epsilon_0 \neq 0$.
But: Φ completely determined by charge distribution ρ, see Eq. (5.39).
$\hookrightarrow$ Φ and $\vec{E}^{\parallel}$ are not dynamical variables.

Dynamical variables: $\vec{A}(\vec{x}, t)$ and $\vec{\Pi}(\vec{x}, t) = \epsilon_0\dot{\vec{A}}(\vec{x}, t) = -\epsilon_0\vec{E}^{\perp}(\vec{x}, t)$.

- Justification of $\vec{\Pi}$ as canonical mom. variable by verifying EOMs (Maxwell's eqs.).

  Note: Definition formally identical to free-field case, because interactions do not involve $\dot{\vec{A}}$.

- Promotion to field operators: $\vec{A}(\vec{x}, t) \to \hat{\vec{A}}(\vec{x}, t)$, $\vec{\Pi}(\vec{x}, t) \to \hat{\vec{\Pi}}(\vec{x}, t)$.

  Note: $\hat{\vec{A}}$ and $\hat{\vec{\Pi}}$ obey canonical EOMs (in the Heisenberg picture) and thus do not have simple plane-wave expansions as for the free fields given in Eq. (5.24).

- Hamiltonian:

$$\hat{H}_{\text{rad}}\left(\hat{\vec{A}}, \hat{\vec{\Pi}}\right) \;=\; \int_V \mathrm{d}^3x\, \frac{1}{2}\left[\hat{\vec{\Pi}}(\vec{x}, t)^2/\epsilon_0 \;+\; \left(\vec{\nabla} \times \hat{\vec{A}}(\vec{x}, t)\right)^2/\mu_0\right]. \tag{5.44}$$

- Equal-time commutators:

$$\left[\hat{A}_a(\vec{x}, t), \hat{\Pi}_b(\vec{y}, t)\right] = \mathrm{i}\hbar\, \delta^{\perp}_{ab}(\vec{x} - \vec{y}). \tag{5.45}$$

- Photon states $|\phi\rangle \in \mathcal{F}$, but states with fixed number of photons $\neq$ eigenstates of $\hat{H}$.

Complete system:

- Hamiltonian:

$$\hat{H} \;=\; \hat{H}'_{\text{matter}}\Big(\{\hat{\vec{x}}_n, \hat{\vec{p}}_n\}\Big) \;+\; \hat{H}_{\text{rad}}\Big(\hat{\vec{A}}, \hat{\vec{\Pi}}\Big)\,. \tag{5.46}$$

- Composite states:

$$|\Psi\rangle \;=\; \underbrace{|\psi\rangle}_{\text{matter part}} \otimes \underbrace{|\phi\rangle}_{\text{photon part}} \;=\; |\psi\rangle\,|\phi\rangle \;\in\; \mathcal{H} \;=\; \mathcal{H}_{\text{matter}} \otimes \mathcal{F}. \tag{5.47}$$

  Note:

  - ◇ $\hat{\vec{x}}_n, \hat{\vec{p}}_n$ act on $|\psi\rangle$,
  - ◇ $\hat{\vec{A}}, \hat{\vec{\Pi}}$ act on $|\phi\rangle$.
  - ◇ $\Big[\hat{\vec{x}}_n, \hat{\vec{A}}(\hat{\vec{x}}_m, t)\Big] \;=\; \Big[\hat{\vec{x}}_n, \hat{\vec{\Pi}}(\hat{\vec{x}}_m, t)\Big] \;=\; 0.$

- Interaction picture:

  - ◇ Free Hamiltonian:

$$\hat{H}_0 \;=\; \sum_n \frac{\hat{\vec{p}}_n{}^2}{2m_n} \;+\; \hat{H}_{\text{rad}} \;=\; \text{Hamiltonian for free particles / photons.} \tag{5.48}$$

    ↪ Mode decomposition (5.24) of $\hat{\vec{A}}(\vec{x}, t)$ and N-photon states (5.37) correspond to exact field operators and states of the unperturbed system.

  - ◇ Interaction Hamiltonian ("perturbation"):

$$\hat{H}_{\text{int}} \;=\; \sum_n \Big(-\frac{q_n}{m_n}\hat{\vec{A}}(\hat{\vec{x}}_n, t)\hat{\vec{p}}_n + \frac{q_n^2}{2m_n}\hat{\vec{A}}(\hat{\vec{x}}_n, t)^2\Big) \;+\; V_{\text{Coul}}\big(\{\hat{\vec{x}}_n\}\big). \tag{5.49}$$

  – Other variants of splitting $\hat{H}$ into $\hat{H}_0$ and $\hat{H}_{\text{int}}$ possible.

  Example: e^- in atoms

  ↪ V_{Coul} considered as part of $\hat{H}_0$.

5.2.3 Application: $1e^-$ atoms in quantized radiation field

Recapitulation of classical elmg. field (see end of Section III.4)

- Classical radiation field: (monochromatic, Coulomb gauge)

$$\vec{A}(\vec{x},t) = A_0\vec{\varepsilon}\cos(\vec{k}\vec{x}-\omega t), \quad \vec{k}\vec{\varepsilon} = 0. \tag{5.50}$$

  Average energy density:

$$\bar{\rho}_{\mathrm{E}} = 2\epsilon_0\omega^2 A_0^2. \tag{5.51}$$

- Unperturbed qm. system: $1e^-$ in Coulomb field of nucleus

$$\hat{H}_0 = \frac{\hat{\vec{p}}^2}{2m_{\mathrm{e}}} + V_{\mathrm{Coul}}(\hat{\vec{x}}). \tag{5.52}$$

- Perturbation: interaction with classical $\vec{A}$ to linear order

$$\begin{aligned}\hat{H}_{\mathrm{int}} &= \frac{e}{m_{\mathrm{e}}}\vec{A}(\hat{\vec{x}},t)\hat{\vec{p}} \\ &= \hat{h}\,\mathrm{e}^{-\mathrm{i}\omega t} + \hat{h}^\dagger\,\mathrm{e}^{\mathrm{i}\omega t}, \quad \hat{h} = \frac{e}{m_{\mathrm{e}}}\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}}\,A_0\,\vec{\varepsilon}\,\hat{\vec{p}}.\end{aligned} \tag{5.53}$$

- Amplitudes for atomic transition $|i\rangle \to |f\rangle$: ($|i\rangle, |f\rangle$ = atomic energy eigenstates)

$$\begin{aligned}h_{fi} &= \langle f|\hat{h}|i\rangle = \frac{e}{m_{\mathrm{e}}}\,A_0\,\underbrace{\langle f|\,\mathrm{e}^{\mathrm{i}\vec{k}\hat{\vec{x}}}\,\vec{\varepsilon}\,\hat{\vec{p}}\,|i\rangle}_{\equiv M_{fi}(\vec{k})}, \\ h_{fi}^\dagger &= \langle f|\hat{h}^\dagger|i\rangle = \frac{e}{m_{\mathrm{e}}}\,A_0\,M_{fi}(-\vec{k}).\end{aligned} \tag{5.54}$$

- Rates of absorption / stimulated emission:

$$\begin{aligned}\frac{W_{fi,\mathrm{abs}}}{T} &= \frac{2\pi}{\hbar}\,|h_{fi}|^2\,\delta(E_f - E_i - \hbar\omega) = \frac{4\pi^2\alpha c\bar{\rho}_{\mathrm{E}}}{m_{\mathrm{e}}^2\omega^2}\,|M_{fi}(\vec{k})|^2\,\delta(E_f - E_i - \hbar\omega), \\ \frac{W_{fi,\mathrm{st.em}}}{T} &= \frac{2\pi}{\hbar}\,|h_{fi}^\dagger|^2\,\delta(E_f - E_i + \hbar\omega) = \frac{4\pi^2\alpha c\bar{\rho}_{\mathrm{E}}}{m_{\mathrm{e}}^2\omega^2}\,|M_{fi}(-\vec{k})|^2\,\delta(E_f - E_i + \hbar\omega).\end{aligned} \tag{5.55}$$

$\hookrightarrow$ Further manipulations with dipole approximation for M_{fi}, average over polarization, and integration over frequency spectrum of radiation.

Interaction with quantized radiation:

- Quantized radiation field: (single mode, Coulomb gauge)

$$\hat{\vec{A}}(\vec{x},t) = \sqrt{\frac{\hbar}{2\omega\epsilon_0 V}} \left(\hat{a}(\vec{k})\,\vec{\varepsilon}(\vec{k})\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}-\mathrm{i}\omega t} + \hat{a}(\vec{k})^\dagger\,\vec{\varepsilon}^*(\vec{k})\,\mathrm{e}^{-\mathrm{i}\vec{k}\vec{x}+\mathrm{i}\omega t} \right), \quad \vec{k}\vec{\varepsilon} = 0. \tag{5.56}$$

Average energy density:

$$\bar{\rho}_\mathrm{E} = \frac{N}{V}\,\hbar\omega, \quad N = \text{number of photons in volume } V. \tag{5.57}$$

- Unperturbed qm. system: $1\mathrm{e}^-$ in Coulomb field of nucleus + free radiation field

$$\hat{H}_0 = \frac{\hat{\vec{p}}^2}{2m_\mathrm{e}} + V_\mathrm{Coul}(\hat{\vec{x}}) + \hat{H}_\mathrm{rad}. \tag{5.58}$$

- Perturbation: interaction with quantized $\hat{\vec{A}}$ to linear order

$$\begin{aligned} \hat{H}_\mathrm{int} &= \frac{e}{m_\mathrm{e}}\hat{\vec{A}}(\hat{\vec{x}},t)\hat{\vec{p}} \\ &= \hat{h}\,\mathrm{e}^{-\mathrm{i}\omega t} + \hat{h}^\dagger\,\mathrm{e}^{\mathrm{i}\omega t}, \quad \hat{h} = \frac{e}{m_\mathrm{e}}\sqrt{\frac{\hbar}{2\omega\epsilon_0 V}}\,\mathrm{e}^{\mathrm{i}\vec{k}\hat{\vec{x}}}\hat{a}(\vec{k})\,\vec{\varepsilon}(\vec{k})\hat{\vec{p}}. \end{aligned} \tag{5.59}$$

- Amplitudes for transition $|\Psi_i\rangle \to |\Psi_f\rangle$: $|\Psi_i\rangle = |i\rangle|\phi_i\rangle$, $|\Psi_f\rangle = |f\rangle|\phi_f\rangle$,

$$\begin{aligned} h_{fi} &= \langle\Psi_f|\hat{h}|\Psi_i\rangle = \frac{e}{m_\mathrm{e}}\sqrt{\frac{\hbar}{2\omega\epsilon_0 V}}\,\langle\phi_f|\hat{a}(\vec{k})|\phi_i\rangle\,\underbrace{\langle f|\,\mathrm{e}^{\mathrm{i}\vec{k}\vec{x}}\,\vec{\varepsilon}\hat{\vec{p}}\,|i\rangle}_{\equiv M_{fi}(\vec{k})}, \\ h^\dagger_{fi} &= \langle\Psi_f|\hat{h}^\dagger|\Psi_i\rangle = \frac{e}{m_\mathrm{e}}\sqrt{\frac{\hbar}{2\omega\epsilon_0 V}}\,\langle\phi_f|\hat{a}^\dagger(\vec{k})|\phi_i\rangle\,M_{fi}(-\vec{k}). \end{aligned} \tag{5.60}$$

Photon states:

$$\begin{aligned} |\phi_i\rangle &= \frac{\left(\hat{a}^\dagger(\vec{k})\right)^N}{\sqrt{N!}}\,|0\rangle, \quad \text{normalized } N\text{-photon state}, \\ |\phi_f\rangle &= \frac{\left(\hat{a}^\dagger(\vec{k})\right)^{N'}}{\sqrt{N'!}}\,|0\rangle. \end{aligned} \tag{5.61}$$

$$\Rightarrow \quad \langle\phi_f|\hat{a}(\vec{k})|\phi_i\rangle = \underbrace{\sqrt{N}\,\delta_{N',N-1}}_{\text{1-photon absorption}}, \qquad \langle\phi_f|\hat{a}^\dagger(\vec{k})|\phi_i\rangle = \underbrace{\sqrt{N+1}\,\delta_{N',N+1}}_{\text{1-photon emission}}. \tag{5.62}$$

Squared amplitudes:

$$
\begin{aligned}
|h_{fi}|^2 &= \frac{\hbar e^2}{2\omega\epsilon_0 m_{\rm e}^2}\,\frac{N}{V}\,|M_{fi}(\vec{k})|^2 = \frac{e^2\bar{\rho}_{\rm E}}{2\omega^2\epsilon_0 m_{\rm e}^2}\,|M_{fi}(\vec{k})|^2, \\
|h^\dagger_{fi}|^2 &= \frac{\hbar e^2}{2\omega\epsilon_0 m_{\rm e}^2}\,\frac{N+1}{V}\,|M_{fi}(-\vec{k})|^2 \\
&= \frac{e^2\bar{\rho}_{\rm E}}{2\omega^2\epsilon_0 m_{\rm e}^2}\,|M_{fi}(-\vec{k})|^2 \;+\; \frac{\hbar e^2}{2\omega\epsilon_0 m_{\rm e}^2}\,\frac{1}{V}\,|M_{fi}(-\vec{k})|^2. \qquad (5.63)
\end{aligned}
$$

- Rates of absorption / stimulated emission as for classical radiation:

$$
\begin{aligned}
\frac{W_{fi,\rm abs}}{T} &= \frac{4\pi^2\alpha c\bar{\rho}_{\rm E}}{m_{\rm e}^2\omega^2}\,|M_{fi}(\vec{k})|^2\,\delta(E_f - E_i - \hbar\omega), \\
\frac{W_{fi,\rm st.em}}{T} &= \frac{4\pi^2\alpha c\bar{\rho}_{\rm E}}{m_{\rm e}^2\omega^2}\,|M_{fi}(-\vec{k})|^2\,\delta(E_f - E_i + \hbar\omega). \qquad (5.64)
\end{aligned}
$$

NEW: contribution for "spontaneous emission" (independent of $\bar{\rho}_{\rm E}$!):

$$
\frac{W_{fi,\rm sp.em}}{T} = \frac{\pi e^2}{\epsilon_0\omega m_{\rm e}^2}\,\frac{1}{V}\,|M_{fi}(-\vec{k})|^2\,\delta(E_f - E_i + \hbar\omega) \qquad (5.65)
$$

$= $ transition rate for emitting a photon with specific momentum $\hbar k$ and polarization $\vec{\varepsilon}$ (5.66)

- Decay width $\Gamma_{fi} = \hbar\times$rate for the atomic transition $|i\rangle \to |f\rangle$ via spontaneous emission of any photon in dipole approximation:

$$
\begin{aligned}
\Gamma_{fi} &= \sum_{\vec{k}}\sum_{\gamma\,\rm pol} \frac{\pi\hbar e^2}{\epsilon_0\omega m_{\rm e}^2}\,\frac{1}{V}\,|M_{fi}(-\vec{k})|^2\,\delta(E_f - E_i + \hbar\omega) \\
&= \underbrace{\frac{1}{V}\sum_{\vec{k}}}_{=\int\frac{{\rm d}^3k}{(2\pi)^3}} \frac{\pi\hbar e^2}{\epsilon_0\omega m_{\rm e}^2} \underbrace{\sum_{\gamma\,\rm pol}|M_{fi}(-\vec{k})|^2}_{\substack{=\,2m_{\rm e}^2\omega_{if}^2\vec{x}_{fi}^{\,2}/3 \text{ in dipole approximation,} \\ \hbar\omega_{if} = E_i - E_f, \quad \vec{x}_{fi} = \langle f|\hat{\vec{x}}|i\rangle.}}\;\delta(E_f - E_i + \hbar\omega) \\
&= \int\frac{{\rm d}^3k}{(2\pi)^3}\,\frac{2\pi e^2\omega_{if}^2\vec{x}_{fi}^{\,2}}{3\epsilon_0\omega}\;\delta(\omega - \omega_{if}), \qquad \omega = ck \\
&= \frac{e^2\omega_{if}^3\vec{x}_{fi}^{\,2}}{3\pi\epsilon_0 c^3} \;=\; \frac{4\alpha\hbar\omega_{if}^3\vec{x}_{fi}^{\,2}}{3c^2}. \qquad (5.67)
\end{aligned}
$$

Total decay width ("natural width") Γ_i of atomic state $|i\rangle$:

$$
\Gamma_i = \frac{\hbar}{\tau_i} = \sum_{\substack{f \\ E_f<E_i}} \Gamma_{fi}, \quad \tau_i = \text{lifetime of } |i\rangle. \qquad (5.68)
$$