17

Radiation

The theoretical understanding of the emission of light from atoms is inseparably linked with the development of quantum mechanics – the first glimpse of the full answer unraveled by P. A. M. Dirac in February 1927. A minimal model for radiation has to consist of at least one atom and the photons. Thus we fix an infinitely heavy nucleus at the origin, say, and describe the motion of a single electron by the spinless Pauli–Fierz Hamiltonian

$$H = \frac{1}{2m}(p - eA_\varphi(x))^2 + V_{\varphi\mathrm{coul}}(x) + H_\mathrm{f} \tag{17.1}$$

with $V_{\varphi\mathrm{coul}}(x) = -e^2 \int \mathrm{d}^3x_1 \mathrm{d}^3x_2 \varphi(x_1)\varphi(x_2)(4\pi|x + x_1 - x_2|)^{-1}$, the smeared Coulomb potential. Besides radiation, (17.1) describes a multitude of physical processes of interest. If the electron is free, i.e. far away from the nucleus, photons scatter off the electron (Compton effect). As the electron approaches the nucleus it will be scattered under the emission of bremsstrahlung (Rutherford scattering). In contrast, in this chapter we are interested in processes where the electron remains tightly bound to the nucleus. Of course, these two worlds are not strictly separated. The electron might be captured by the nucleus at the expense of radiated energy. Conversely, the atom may become ionized by hitting it with sufficiently energetic radiation (photoelectric effect). Even in the realm of a bound electron, several processes should be distinguished. The most basic one is spontaneous emission, through which the atom in an excited state loses energy and ends up in the radiationless ground state. A photon may be scattered by the atom leaving the atom behind in either its ground state (elastic Rayleigh scattering) or in an excited state (inelastic Rayleigh scattering) which is then followed by spontaneous emission. Both processes will be discussed in separate sections.

Under usual circumstances the wavelength of emitted light is much larger than the size of an atom. In this case one can ignore the variation of the vector potential in (17.1) and replace $A_\varphi(x)$ by $A_\varphi(0)$, the so-called dipole approximation. In

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addition we want to restrict the electron Hilbert space to bound states only. Taking into account the first N of them results in an N-level system coupled to the radiation field. We point out that an enormous effort has been invested precisely to avoid such a mutilation of the Pauli–Fierz Hamiltonian (17.1). Still, in the first round a simplified version will suffice.

Radiation as discussed here has no classical counterpart. Of course, as explained, in the context of the Abraham model a charge loses energy through radiation. Its analog would be an extension of the results given in the previous chapter. There one has to give up $m_{\rm ph} > 0$. Then the spectral gap closes and the strict adiabatic protection is lost. For example, (16.105) would have a dissipative correction at the next order associated with a gradual emission of photons. In contrast, for the radiation processes studied here the emission of photons occurs on the atomic scale.

17.1 N-level system in the dipole approximation

The dipole approximation reads

$$H = \frac{1}{2m}(p - eA_\varphi(0))^2 + V(x) + H_{\rm f}. \tag{17.2}$$

If in addition we were to choose V to be harmonic, $V(x) = \frac{1}{2}m\omega_0^2 x^2$, then (17.2) is a quadratic Hamiltonian, as can be seen, if on top of the Bose fields $a(k,\lambda), a^*(k,\lambda)$ one introduces the annihilation and creation operators b, b^* for the particle; compare with section 13.7(i). The analysis of this model can be reduced to a Hamiltonian on the one-particle space $\mathbb{C}^3 \oplus (L^2(\mathbb{R}^3) \otimes \mathbb{C}^2)$, where $\mathbb{C}^3$ corresponds to the b, b^* degrees of freedom. While such an analysis is very instructive, we stick here to the more realistic Coulomb-type potential. We rewrite (17.2) as

$$H = \frac{1}{2m}p^2 + V(x) + H_{\rm f} - \frac{e}{m}p \cdot A_\varphi(0) + \frac{e^2}{2m}A_\varphi(0)^2, \tag{17.3}$$

drop the $A_\varphi(0)^2$ term, and expand in the eigenbasis of $\frac{1}{2m}p^2 + V(x)$ up to the N-th eigenvalue, including multiplicity. This results in

$$H_\lambda = H_{\rm at} \otimes 1 + 1 \otimes H_{\rm f} + \lambda \tilde{Q} \cdot A_\varphi(0). \tag{17.4}$$

Here $H_{\rm at}$ and $\tilde{Q} = (\tilde{Q}_1, \tilde{Q}_2, \tilde{Q}_3)$ are symmetric $N \times N$ matrices. In our representation $H_{\rm at}$ is diagonal with nondegenerate smallest eigenvalue ε_1 and $\tilde{Q}$ is proportional to the dipole moments

$$\tilde{Q}_{ij} = \langle \psi_i, p\psi_j \rangle = {\rm i}m(\varepsilon_i - \varepsilon_j)\langle \psi_i, x\psi_j \rangle, \tag{17.5}$$

$i, j = 1, \ldots, N$, where we used the facts that ${\rm i}[\frac{1}{2m}p^2 + V(x), x] = \frac{1}{m}p$ and

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$(\frac{1}{2m}p^2 + V(x))\psi_j = \varepsilon_j \psi_j$ counting eigenvalues and eigenfunctions including their multiplicity. We also introduced explicitly the dimensionless small coupling parameter λ. If one follows the conventions of section 13.4, then $\lambda = \alpha^{3/2}$.

Note that in the functional integral representation of e^{-tH_λ}, H_λ of (17.4), the effective action is quadratic with the interaction potential

$$W_{\mathrm{dip}}(t) = \lambda^2 \int \mathrm{d}^3k |\widehat{\varphi}|^2 \frac{1}{2\omega} \mathrm{e}^{-\omega|t|}, \tag{17.6}$$

which decays as t^{-2} for large t. Thus (17.4) is marginally infrared divergent. Generically H_λ will lose its ground state at strong enough coupling, in contrast to the full Pauli–Fierz model, and (17.4) can be trusted only at small coupling.

An alternative route to the N-level approximation is first to transform to the $x \cdot E_\varphi(0)$ coupling through the unitary transformation

$$U = \mathrm{e}^{\mathrm{i}ex \cdot A_\varphi(0)}. \tag{17.7}$$

Then

$$\begin{aligned} &U^* p U = p + eA_\varphi(0)\,, \quad U^* x U = x\,, \\ &U^* a(k,\lambda) U = a(k,\lambda) + \mathrm{i}(e_\lambda(k) \cdot x) e\widehat{\varphi}(k)/\sqrt{2\omega(k)} \end{aligned} \tag{17.8}$$

and therefore

$$U^* H U = \frac{1}{2m}p^2 + V(x) + \Big(\frac{2}{3}e^2 \int \mathrm{d}^3k |\widehat{\varphi}|^2\Big)x^2 + H_{\mathrm{f}} - ex \cdot E_\varphi(0). \tag{17.9}$$

As before, we expand in the eigenbasis of $\frac{1}{2m}p^2 + V(x)$ up to the N-th eigenvalue. This results in the Hamiltonian

$$H_\lambda = H_{\mathrm{at}} + H_{\mathrm{f}} + \lambda Q \cdot E_\varphi \tag{17.10}$$

with the matrix of dipole moments $Q_{ij} = \langle \psi_i, x\psi_j \rangle$, $E_\varphi = E_\varphi(0)$, and $\lambda = -e$. Since now the coupling is to $E_\varphi(0)$, the effective action (17.6) gains an extra factor of ω^2 and therefore has a decay as t^{-4} in accordance with the full model.

For the remainder of the chapter, we take (17.10) as the starting point. The particular origin of H_{at} and Q is of no importance. We only record that they satisfy $H_{\mathrm{at}}^* = H_{\mathrm{at}}$, $Q^* = Q$. H_{at} has the spectrum $\sigma(H_{\mathrm{at}}) \subset \mathbb{R}$. It consists of the eigenvalues labeled without multiplicity as $\varepsilon_1 < \varepsilon_2 < \cdots < \varepsilon_{\bar{N}}$, $\bar{N} \leq N$. The corresponding spectral projections are denoted by $P_1, \ldots, P_{\bar{N}}$. Their degeneracies are $\mathrm{tr}[P_j] = m_j$ with $m_1 = 1$ and $\sum_{j=1}^{\bar{N}} m_j = N$. In particular one has the spectral representation

$$H_{\mathrm{at}} = \sum_{j=1}^{\bar{N}} \varepsilon_j P_j. \tag{17.11}$$

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17.2 The weak coupling theory

We plan to study the emission of light from atoms. The atom is assumed to have already been prepared in an excited state and thus the initial state of the coupled system is of the form $\psi \otimes \Omega$ with the atomic wave function $\psi \in \mathbb{C}^N$. To determine the radiated field one has to understand the long-time asymptotics of the solution $\mathrm{e}^{-\mathrm{i}Ht}\psi \otimes \Omega$ of the time-dependent Schrödinger equation. For small coupling, which is well satisfied physically, the dynamics approximately decouples: the atom is governed by an autonomous reduced dynamics and the field evolves with the decaying atom as a source term. In this section we will first study the reduced dynamics of the atom in the weak coupling regime with our results to be supported through a nonperturbative resonance theory in section 17.3. In a follow-up we discuss the spectral characteristics of the emitted light.

By definition, the reduced dynamics refers to the reduced state of the atom, which allows one to determine atomic observables such as the probability of being in the n-th level at time t. Although by assumption the initial state of the atom is pure, it will not remain so because of the interaction with the radiation field. Thus it will be more natural to work directly in the set of all density matrices. The initial state is then of the form $\rho \otimes P_\Omega$ with ρ the atomic density matrix, and P_Ω the projection onto Fock vacuum. The time evolution is given through

$$\mathrm{e}^{-\mathrm{i}H_\lambda t}\rho \otimes P_\Omega \mathrm{e}^{\mathrm{i}H_\lambda t} = \mathrm{e}^{-\mathrm{i}L_\lambda t}\rho \otimes P_\Omega. \tag{17.12}$$

Here $L_\lambda W = [H_\lambda, W]$ is the Liouvillean as acting on $\mathcal{T}_1(\mathbb{C}^N \otimes \mathcal{F})$, the trace class over $\mathbb{C}^N \otimes \mathcal{F}$. To distinguish typographically, L_λ is written as a slanted symbol, like other operators, sometimes called superoperators, which act either on $\mathcal{T}_1$ or on $B(\mathbb{C}^N \otimes \mathcal{F})$, the space of bounded operators on $\mathbb{C}^N \otimes \mathcal{F}$. Clearly, states evolve into states, i.e. if $W \in \mathcal{T}_1$ is positive and normalized, so is $\mathrm{e}^{-\mathrm{i}L_\lambda t}W$. Sometimes, it is convenient to think of (17.12) as a Schrödinger evolution in a Hilbert space. This can be done by adopting the space $\mathcal{T}_2(\mathbb{C}^N \otimes \mathcal{F})$ of Hilbert–Schmidt operators with inner product $\langle A|B\rangle = \mathrm{tr}[A^*B]$. In this space the Liouvillean L_λ is a self-adjoint operator, which explains our sign convention in front of the commutator. A further choice comes from regarding $B(\mathbb{C}^N \otimes \mathcal{F})$ as the space dual to $\mathcal{T}_1(\mathbb{C}^N \otimes \mathcal{F})$ through the duality relation $W \mapsto \mathrm{tr}[AW]$, $W \in \mathcal{T}_1(\mathbb{C}^N \otimes \mathcal{F})$, $A \in B(\mathbb{C}^N \otimes \mathcal{F})$. Then the dual of L_λ is $-[H_\lambda, \cdot]$, which generates the Heisenberg evolution of operators.

The reduced dynamics is defined through

$$T_t^\lambda \rho = \rho^\lambda(t) = \mathrm{tr}_{\mathcal{F}}[\mathrm{e}^{-\mathrm{i}L_\lambda t}\rho \otimes P_\Omega], \tag{17.13}$$

where $\mathrm{tr}_{\mathcal{F}}[\cdot]$ denotes the partial trace over Fock space. T_t^λ acts on $B(\mathbb{C}^N)$. It is linear, preserves positivity and normalization. In fact, since it originates from a

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Hamiltonian dynamics, the even stronger property of complete positivity is satisfied. In such generality, T_t^λ is intractable. But scales become separated for small λ into atomic oscillations of the uncoupled dynamics $\mathrm{e}^{-\mathrm{i}H_{\mathrm{at}}t}$ and the weak radiative damping of order λ^2 ($= \alpha^3 = 1/137^3$). When viewed on the dissipative scale the atomic oscillations are very rapid and effectively time-averaged. For small λ memory effects are negligible and T_t^λ becomes a dissipative semigroup, which is the autonomous dynamics we are looking for.

To write a formal evolution equation for $\rho^\lambda(t)$ one employs the Nakajima–Zwanzig projection operator method. We define the Liouvilleans $L_{\mathrm{at}} = [H_{\mathrm{at}}, \cdot\,]$ as acting on $B(\mathbb{C}^N) = \mathcal{T}_1(\mathbb{C}^N)$, $L_{\mathrm{f}} = [H_{\mathrm{f}}, \cdot\,]$ as acting on $\mathcal{T}_1(\mathcal{F})$, and $L_{\mathrm{int}} = [Q \cdot E_\varphi, \cdot\,]$ as acting on $\mathcal{T}_1(\mathbb{C}^N \otimes \mathcal{F})$. For an arbitrary density matrix W on $\mathbb{C}^N \otimes \mathcal{F}$ the Nakajima–Zwanzig projection is

$$PW = (\mathrm{tr}_{\mathcal{F}} W) \otimes P_\Omega. \tag{17.14}$$

Clearly $P^2 = P$ and

$$P\mathrm{e}^{-\mathrm{i}L_\lambda t}\rho \otimes P_\Omega = \rho^\lambda(t) \otimes P_\Omega\,. \tag{17.15}$$

Let $W(t) = \mathrm{e}^{-\mathrm{i}L_\lambda t}\rho \otimes P_\Omega$. Then

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}PW(t) = PL_\lambda W(t) = PL_\lambda PW(t) + PL_\lambda(1-P)W(t), \tag{17.16}$$

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}(1-P)W(t) = (1-P)L_\lambda W(t) = (1-P)L_\lambda PW(t) + (1-P)L_\lambda(1-P)W(t). \tag{17.17}$$

Substituting (17.17) back in (17.16) and using $PL_{\mathrm{int}}P = 0$, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho^\lambda(t) = -\mathrm{i}L_{\mathrm{at}}\rho^\lambda(t) - \lambda^2\int_0^t \mathrm{d}s\,\mathrm{tr}_{\mathcal{F}}[L_{\mathrm{int}}(1-P)\mathrm{e}^{-\mathrm{i}(1-P)L_\lambda(1-P)(t-s)}(1-P)L_{\mathrm{int}}P_\Omega]\rho^\lambda(s), \tag{17.18}$$

which is an exact memory-type equation.

As argued traditionally, the memory decays rapidly on the time scale of the variation of $\rho^\lambda(t)$. For small λ one may ignore the interaction and replace L_λ by $L_{\mathrm{at}} + L_{\mathrm{f}}$ in the exponential. In this approximation for small λ

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = (-\mathrm{i}L_{\mathrm{at}} + \lambda^2 K_0)\rho(t) \tag{17.19}$$

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is obtained as reduced dynamics with

$$K_0\rho = -\int_0^\infty \mathrm{d}t\ \mathrm{tr}_{\mathcal{F}}[L_{\mathrm{int}}\mathrm{e}^{-\mathrm{i}(L_{\mathrm{at}}+L_{\mathrm{f}})t}L_{\mathrm{int}}P_\Omega]\rho. \tag{17.20}$$

This argument misses the point that both $\rho^\lambda(t)$ and the memory kernel have oscillatory contributions from $\mathrm{e}^{-\mathrm{i}H_{\mathrm{at}}t}$. In general, their products cannot be approximated as in (17.19), (17.20). To subtract the oscillations from the memory kernel we rewrite (17.18) as an integral equation,

$$\begin{aligned}\rho^\lambda(t) = \mathrm{e}^{-\mathrm{i}L_{\mathrm{at}}t}\rho - \lambda^2\int_0^t \mathrm{d}s\mathrm{e}^{-\mathrm{i}L_{\mathrm{at}}(t-s)}\\ \times\int_0^s \mathrm{d}u\ \mathrm{tr}_{\mathcal{F}}[L_{\mathrm{int}}(1-P)\mathrm{e}^{-\mathrm{i}(1-P)L_\lambda(1-P)(s-u)}(1-P)L_{\mathrm{int}}P_\Omega]\rho^\lambda(u).\end{aligned} \tag{17.21}$$

After the change of variables $v = s - u$, one has

$$\begin{aligned}\rho^\lambda(t) = \mathrm{e}^{-\mathrm{i}L_{\mathrm{at}}t}\rho - \lambda^2\int_0^t \mathrm{d}u\ \mathrm{e}^{-\mathrm{i}L_{\mathrm{at}}(t-u)}\\ \times\Big\{\int_0^{t-u}\mathrm{d}v\,\mathrm{e}^{\mathrm{i}L_{\mathrm{at}}v}\mathrm{tr}_{\mathcal{F}}[L_{\mathrm{int}}(1-P])\mathrm{e}^{-\mathrm{i}(1-P)L_\lambda(1-P)v}(1-P)L_{\mathrm{int}}P_\Omega]\Big\}\rho^\lambda(u).\end{aligned} \tag{17.22}$$

Now in the memory kernel the fast oscillations are properly counterbalanced and to a good approximation $\rho^\lambda(t)$ is governed by

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = (-\mathrm{i}L_{\mathrm{at}} + \lambda^2 K)\rho(t), \tag{17.23}$$

where

$$K\rho = -\int_0^\infty \mathrm{d}t\ \mathrm{e}^{\mathrm{i}L_{\mathrm{at}}t}\mathrm{tr}_{\mathcal{F}}[L_{\mathrm{int}}\mathrm{e}^{-\mathrm{i}(L_{\mathrm{at}}+L_{\mathrm{f}})t}L_{\mathrm{int}}P_\Omega]\rho. \tag{17.24}$$

We state our result as

Theorem 17.1 (Weak coupling quantum master equation). *Let*

$$e^2\langle\Omega,\, E_{\varphi\alpha}\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}E_{\varphi\beta}\Omega\rangle_{\mathcal{F}} = h_{\alpha\beta}(t) = \delta_{\alpha\beta}h(t), \tag{17.25}$$

$$h(t) = \frac{e^2}{3}\int \mathrm{d}^3k|\widehat{\varphi}|^2\omega(k)\mathrm{e}^{-\mathrm{i}\omega(k)t}, \tag{17.26}$$

$\alpha, \beta = 1, 2, 3$. *If*

$$\int_0^\infty \mathrm{d}t|h(t)|(1+t)^\delta < \infty \tag{17.27}$$

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for some $\delta > 0$, then

$$\lim_{\lambda\to 0} \sup_{0\le t\le \lambda^{-2}\tau} \| T_t^\lambda \rho - \mathrm{e}^{(-\mathrm{i}L_{\mathrm{at}}+\lambda^2 K)t}\rho\| = 0. \tag{17.28}$$

τ is on the dissipative time scale. Thus in (17.28) a, possibly long, time interval on the dissipative time scale is fixed. Over that time span the true reduced dynamics is well approximated by a Markovian dynamics consisting of fast atomic oscillations, $-\mathrm{i}L_{\mathrm{at}}$, and slow dissipation, K.

The integrability condition (17.27) is seen to hold by transforming back to position space. Then

$$\begin{aligned}\int \mathrm{d}^3k|\widehat{\varphi}|^2\omega\mathrm{e}^{-\mathrm{i}\omega t} &= \int \mathrm{d}^3k|\widehat{\varphi}|^2\omega(\cos\omega t - \mathrm{i}\sin\omega t)\\ &= -\partial_t^3 \int \mathrm{d}^3x\mathrm{d}^3x'\mathrm{d}^3y\varphi(x')|x-x'|^{-2}4\pi\frac{1}{t}\delta(|x-y|-t)\varphi(y)\\ &\quad + \mathrm{i}\partial_t^2 \int \mathrm{d}^3x\mathrm{d}^3y\varphi(x)\frac{1}{4\pi t}\delta(|x-y|-t)\varphi(y),\end{aligned} \tag{17.29}$$

which decays as fast as t^{-4}, since φ is localized.

We still have to carry through properly the time-averaging, accounting for the fast oscillations of $\mathrm{e}^{-\mathrm{i}L_{\mathrm{at}}t}$. We claim that, without further error, K can be replaced by its time average

$$K^\natural\rho = \lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}\mathrm{d}t\,\mathrm{e}^{\mathrm{i}L_{\mathrm{at}}t}K\mathrm{e}^{-\mathrm{i}L_{\mathrm{at}}t}, \tag{17.30}$$

as can be seen from going to the slow time scale and considering the interaction representation

$$\begin{aligned}\mathrm{e}^{\mathrm{i}\lambda^{-2}L_{\mathrm{at}}\tau}\mathrm{e}^{(-\mathrm{i}\lambda^{-2}L_{\mathrm{at}}+K)\tau}\rho = \rho + \int_0^\tau \mathrm{d}u\left\{\mathrm{e}^{\mathrm{i}\lambda^{-2}L_{\mathrm{at}}u}K\mathrm{e}^{-\mathrm{i}\lambda^{-2}L_{\mathrm{at}}u}\right\}\\ \times\,\mathrm{e}^{\mathrm{i}\lambda^{-2}L_{\mathrm{at}}u}\mathrm{e}^{(-\mathrm{i}\lambda^{-2}L_{\mathrm{at}}+K)u}\rho.\end{aligned} \tag{17.31}$$

The term inside { } is rapidly oscillating and we are allowed to replace it by $K^\natural$. Theorem 17.1 remains valid when K is replaced by $K^\natural$.

In conclusion, we have arrived at the approximate reduced dynamics of the atom:

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = -\mathrm{i}[H_{\mathrm{at}},\rho(t)] + \lambda^2 K^\natural\rho(t). \tag{17.32}$$

To understand the properties of this dynamics, the dissipative generator $K^\natural$ must be worked out more concretely. It is time-averaged with respect to the Liouvillean $L_{\mathrm{at}} = [H_{\mathrm{at}},\cdot]$ and thus depends on the spectrum of L_{at}, which is given by

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$\{\varepsilon_i - \varepsilon_j \,|\, i, j = 1, \ldots, \bar{N}\} = \sigma(L_{\rm at})$. Accordingly we define

$$Q(\omega) = \sum_{i,j=1,\, \varepsilon_i - \varepsilon_j = \omega \in \sigma(L_{\rm at})}^{\bar{N}} P_j Q P_i. \tag{17.33}$$

The degeneracy of $H_{\rm at}$ enters through the projections P_j whereas the degeneracy of the Liouvillean is reflected by the sum in (17.33). For instance, a harmonic oscillator has a nondegenerate Hamiltonian but a highly degenerate Liouvillean. The strength of the various transitions is determined by the one-sided Fourier transform of the field correlation (17.25). We decompose it into real and imaginary parts as

$$\int_0^\infty \mathrm{d}t\ \mathrm{e}^{-\mathrm{i}\omega t} h(t) = \frac{1}{2}\Gamma(\omega) - \mathrm{i}\Delta(\omega), \tag{17.34}$$

which gives

$$\frac{1}{2}\Gamma(\omega) = \frac{e^2}{3} \int \mathrm{d}^3k |\widehat{\varphi}(k)|^2 \omega(k) \pi \delta(\omega(k) + \omega), \tag{17.35}$$

$$\Delta(\omega) = \frac{e^2}{3}\, \mathrm{PV} \int \mathrm{d}^3k |\widehat{\varphi}(k)|^2 \omega(k) \frac{1}{\omega(k) + \omega}, \tag{17.36}$$

PV denoting the principal value of the integral. Using this notation, after working out the oscillatory integrals in (17.30), one obtains

$$\begin{aligned} K^\natural \rho = \sum_{\alpha=1}^{3} \sum_{\omega \in \sigma(L_{\rm at})} \Big\{ & -\mathrm{i}\Delta(\omega)[Q_\alpha(\omega) Q_\alpha^*(\omega), \rho] \\ & + \frac{1}{2}\Gamma(\omega)\big([Q_\alpha^*(\omega)\rho, Q_\alpha(\omega)] + [Q_\alpha^*(\omega), \rho Q_\alpha(\omega)]\big)\Big\}, \end{aligned} \tag{17.37}$$

where the ω-sum runs over all eigenvalues of the Liouvillean $L_{\rm at}$.

The first term in (17.37) merely adds an extra term of order λ^2 to the atomic Hamiltonian $H_{\rm at}$. Thereby the eigenvalues ε_j are shifted and their degeneracy is possibly lifted. The second term represents the radiation damping. It is of Lindblad form which ensures that $T_t = \exp[(-\mathrm{i}[H_{\rm at}, \cdot] + \lambda^2 K^\natural)t]$ is completely positive and in particular preserves positivity. For the nonaveraged variant K such a property is in general not valid.

The details of the damping mechanism depend on $H_{\rm at}$, Q, and $\widehat{h}$. Since $\Gamma(\omega) = 0$ for $\omega \geq 0$, only transitions to energetically lower levels are possible. Thus generically we expect that in the long-time limit the atom reaches its ground state,

$$\lim_{t \to \infty} T_t \rho = P_1 \tag{17.38}$$

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independently of the initial state. Basically, there are two obstructions to (17.38). The analog of the classical Wiener condition (5.4) could be violated in the sense that $\Gamma(\varepsilon_i - \varepsilon_j) = 0$ for some $\varepsilon_i < \varepsilon_j$. Even if we assume $\Gamma(\omega) > 0$ for $\omega < 0$, $H_{\rm at}$ and Q could be too commutative. For instance, in the extreme case $[H_{\rm at}, Q] = 0$, the damping vanishes and $K^\natural\rho = -\mathrm{i}\Delta(0)[Q^2, \rho]$. Under the Wiener condition a sufficient criterion for (17.38) to hold is $\{H_{\rm at}, Q_\alpha, \alpha = 1, 2, 3\}' = \mathbb{C}1$, i.e. the commutant of $\{H_{\rm at}, Q_\alpha, \alpha = 1, 2, 3\}$ (all operators which commute with $H_{\rm at}$ and Q) consists only of multiples of the unit matrix.

If the spectrum of $H_{\rm at}$ is nondegenerate, then the set of density matrices commuting with $H_{\rm at}$ is left invariant by T_t. We set $T_t\rho = \sum_{n=1}^N \rho_n(t) P_n$, $\mathrm{tr}[P_n] = 1$. The probabilities $\rho_n(t)$ are governed by the Pauli master equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_n(t) = \sum_{m=1}^N \big(w_{mn}\rho_m(t) - w_{nm}\rho_n(t)\big), \tag{17.39}$$

where

$$w_{mn} = \sum_{\alpha=1}^3 \Gamma(\varepsilon_n - \varepsilon_m)\mathrm{tr}[P_m Q_\alpha P_n Q_\alpha] \tag{17.40}$$

is the transition rate from level m to level n. Thus the coupling to the radiation field induces a Markov jump process on diagonal density matrices with transition rates given through Fermi's golden rule. The ground state is an absorbing state of the Markov chain. If every other state can be linked to the ground state by a sequence of jumps with nonzero rates, then $\lim_{t\to\infty}\rho_1(t) = 1$ and $\lim_{t\to\infty}\rho_n(t) = 0$ for $n \geq 2$ exponentially fast.

A much-studied variation is to immerse the atom in a black-body cavity at some temperature T. Based on rather general principles of statistical mechanics, Einstein came up with a phenomenological description of the atomic transitions in terms of his A, B-coefficients. Thereby he completely circumvented the yet nonexistent quantum statistical mechanics. Given such historical importance, we violate for a moment our principle of "zero temperature only", to provide a more fully fledged theory in chapter 18. Since we have already used density matrices, in the definition of the reduced dynamics we only have to replace P_Ω by the thermal state $Z^{-1}\mathrm{e}^{-H_{\rm f}/k_{\rm B}T}$. The physically correct procedure is to first enclose the radiation field in the cavity $[-\ell, \ell]^3$, i.e. the k-integration is to be replaced by a k-sum over the momentum lattice $((\pi/\ell)\mathbb{Z})^3$, followed by the infinite-volume limit $\ell \to \infty$. In the weak coupling approximation, as the only difference to the zero-temperature case, the time-correlation $h_{\alpha\beta}(t)$ for the field is to be computed from the thermal

average. Explicitly, with $\langle\cdot\rangle_{k_BT}$ denoting thermal average,

$$\begin{aligned} h_{\alpha\beta}(t) &= e^2\langle e^{iH_f t}E_{\varphi\alpha}e^{-iH_f t}E_{\varphi\beta}\rangle_{k_BT} \\ &= e^2\sum_{\lambda=1}^{2}\int d^3k\widehat{\varphi}\sqrt{\omega/2}\,e_{\lambda\alpha}(k)\sum_{\lambda'=1}^{2}\int d^3k'\widehat{\varphi}\sqrt{\omega/2}e_{\lambda'\beta}(k') \\ &\quad i^2\langle\big(e^{-i\omega(k)t}a(k,\lambda)-e^{i\omega(k)t}a^*(k,\lambda)\big)\big(a(k',\lambda')-a^*(k',\lambda')\big)\rangle_{k_BT} \\ &= \delta_{\alpha\beta}h(t), \end{aligned} \tag{17.41}$$

$$\begin{aligned} h(t) = \frac{e^2}{3}\int d^3k|\widehat{\varphi}|^2\omega(k)\big(&e^{-i\omega(k)t} \\ &+(e^{\omega(k)/k_BT}-1)^{-1}(e^{-i\omega(k)t}+e^{i\omega(k)t})\big). \end{aligned} \tag{17.42}$$

The friction coefficient, Γ_{k_BT}, and the level shifts are still defined through (17.34). Γ_{k_BT} satisfies the condition of detailed balance as

$$\Gamma_{k_BT}(\omega) = \Gamma_{k_BT}(-\omega)e^{-\omega/k_BT}. \tag{17.43}$$

At nonzero temperatures $\Gamma_{k_BT}(\omega) > 0$ for all ω, except for accidental zeros, and the energy can flow either way between atom and thermal bath. If the atom is well coupled to the black-body radiation, in the sense that $\Gamma_{k_BT}(\omega) > 0$ and $\{H_{at}, Q_\alpha,\ \alpha = 1,2,3\}' = \mathbb{C}1$, then the N-level system relaxes to the thermal state $Z^{-1}e^{-H_{at}/k_BT}$ in the long-time limit. This is most easily seen in case all ε_j are nondegenerate. Then the off-diagonal elements of $T_t\rho$ decay exponentially while the diagonal elements are still governed by the Pauli master equation (17.39), in which the transition rates now satisfy

$$w_{mn} = w_{nm}e^{-(\varepsilon_n-\varepsilon_m)/k_BT} \tag{17.44}$$

as a result of the detailed balance (17.43). Under "good coupling" (17.44) ensures that the thermal state is the only invariant state for (17.39) and therefore

$$\lim_{t\to\infty} T_t\rho = Z^{-1}e^{-H_{at}/k_BT}. \tag{17.45}$$

As will be explained in chapter 18 the relaxation to thermal equilibrium can be established also for small, but fixed coupling strength and in fact should hold at arbitrary λ.

We note that in (17.41) there are two terms inside the big round bracket with the first one being temperature independent. This is the Einstein A-coefficient which regulates the spontaneous emission of a photon. The second term in (17.41) is the B-coefficient of stimulated emission and adsorption of a photon. It dominates for $\hbar|\varepsilon_i - \varepsilon_j| \ll k_BT$. From the point of view of the atom, there is no way to distinguish the two emission processes.

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17.3 Resonances

The virtue of the weak coupling theory consists in yielding a concise dynamical scenario with level shifts and lifetimes computed in terms of the microscopic Hamiltonian. High-precision experiments, e.g. of the Lamb shift in the hydrogen atom, show small deviations from the prediction of the theory, which however should not be regarded as a failure of the weak coupling theory. Rather, it is a failure of the Pauli–Fierz model at relativistic energies. Barring such fine details the weak coupling theory is the standard tool in atomic physics and there seems to be little incentive to go beyond. Still, we have not yet developed a firm link with the Hamiltonian. Are there corrections to the predicted exponential decay? Can one, at least in principle, obtain systematic corrections of higher order in λ? What is the long-time limit for small, but fixed λ? To answer such questions one has to go beyond perturbation theory and simple resummations. At present there is only one sufficiently powerful technique available, which is complex dilation. We explain this method first for the standard example of the Friedrichs–Lee model. The extension to the Pauli–Fierz model requires rather complex technical machinery, certainly beyond the present scope. We will, however, use complex dilations to study the return to equilibrium at nonzero temperatures in chapter 18, which turns out to be much simpler since the spectrum is the full real line and is translated rather than rotated.

We imagine a single energy level $\varepsilon > 0$, coupled to the continuum, which is labeled by $x \geq 0$, and should be thought of as energy. The Hilbert space of wave functions is then $\mathbb{C} \oplus L^2(\mathbb{R}_+, \mathrm{d}x)$ and the Hamiltonian reads

$$H_\lambda = H_0 + \lambda H_{\mathrm{int}} = \begin{pmatrix} \varepsilon & 0 \\ 0 & x \end{pmatrix} + \lambda \begin{pmatrix} 0 & \langle\varphi| \\ |\varphi\rangle & 0 \end{pmatrix} \tag{17.46}$$

in Dirac notation. H_λ is known as the Friedrichs–Lee model. For some time we choose to denote by H_λ the Hamiltonian of (17.46) and will give a warning to the reader when we return to the Hamiltonian (17.10). One needs $\varphi \in L^2$ to have H_λ well defined and $\langle\varphi, x^{-1}\varphi\rangle < \infty$ for λH_{int} to be form-bounded with respect to H_0. With no loss one can choose φ to be real. For $\lambda = 0$ the eigenvalue ε is embedded in the continuum and we want to understand its fate for small λ.

From scattering theory and the stability of the essential spectrum under rank-one perturbations it can be seen that the absolutely continuous spectrum of H_λ is $[0, \infty)$ for all λ. In addition, there exists a critical λ_c such that for $|\lambda| < \lambda_c$ there is no further spectrum, whereas for $|\lambda| > \lambda_c$ the eigenvalue $\varepsilon(\lambda) < 0$ gets expelled from the continuum. We are interested here in small λ only, i.e. $|\lambda| \ll \lambda_c$, but, beyond mere spectral information, we want to know the decay of the survival

amplitude

$$G(t) = \langle \psi_0, \mathrm{e}^{-\mathrm{i}H_\lambda t}\psi_0\rangle \tag{17.47}$$

of the unperturbed eigenstate $\psi_0 = \binom{1}{0}$.

$G(t)$ has the spectral decomposition

$$G(t) = \int \mathrm{d}\omega g(\omega)\mathrm{e}^{-\mathrm{i}\omega t}, \tag{17.48}$$

$g(\omega) \geq 0$ for $\omega \geq 0$, $g(\omega) = 0$ for $\omega < 0$, and $\int \mathrm{d}\omega g(\omega) = 1$. Thus, $|G(t)|^2 \cong 1 - t^2$ for small t and $G(t) \to 0$ as $t \to \infty$ by the Riemann–Lebesgue lemma. On the other hand, $G(t)$ cannot decay exponentially, for this would imply $g(\omega)$ to be analytic in a strip around the real axis and thus $g \equiv 0$, by the reasoning of Paley and Wiener. Since H_{int} is a one-dimensional projection, $g(\omega)$ is in fact easily computed. First, the resolvent is determined as

$$\widehat{G}(z) = \langle \psi_0, (z - H_\lambda)^{-1}\psi_0\rangle = \left[z - \varepsilon - \lambda^2\langle\varphi, \frac{1}{z-x}\varphi\rangle\right]^{-1}, \tag{17.49}$$

$z \in \mathbb{C} \setminus \mathbb{R}_+$. Then

$$g(\omega) = (2\pi\mathrm{i})^{-1} \lim_{\eta\to 0+} [\widehat{G}(\omega + \mathrm{i}\eta) - \widehat{G}(\omega - \mathrm{i}\eta)]. \tag{17.50}$$

Since

$$\lim_{\eta\to 0+} \langle\varphi, (\omega \pm \mathrm{i}\eta - x)^{-1}\varphi\rangle = \Delta(\omega) \mp \mathrm{i}\Gamma(\omega)/2 \tag{17.51}$$

with

$$\Gamma(\omega)/2 = \pi|\varphi(\omega)|^2, \quad \Delta(\omega) = \mathrm{PV}\int_0^\infty \mathrm{d}x|\varphi(x)|^2(x-\omega)^{-1}, \tag{17.52}$$

one has

$$g(\omega) = \frac{1}{2\pi}\frac{\lambda^2\Gamma(\omega)}{(\omega - \varepsilon - \lambda^2\Delta(\omega))^2 + (\lambda^2\Gamma(\omega)/2)^2} \tag{17.53}$$

for $\omega \geq 0$, and $g(\omega) = 0$ for $\omega < 0$. For small λ, $g(\omega)$ has a huge bump located near $\omega = \varepsilon$. In the weak coupling theory, one ignores the variation of Γ and Δ and approximates $g(\omega)$ for all ω by

$$g_{\mathrm{w}}(\omega) = \frac{1}{2\pi}\frac{\lambda^2\Gamma(\varepsilon)}{(\omega - \varepsilon - \lambda^2\Delta(\varepsilon))^2 + (\lambda^2\Gamma(\varepsilon)/2)^2}, \tag{17.54}$$

which corresponds to the survival amplitude

$$G_{\mathrm{w}}(t) = \mathrm{e}^{-(\lambda^2\Gamma(\varepsilon)/2)|t|}\mathrm{e}^{-\mathrm{i}(\varepsilon+\lambda^2\Delta(\varepsilon))t}. \tag{17.55}$$

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For the true survival amplitude one still obtains the bound

$$|G(t) - G_{\mathrm{w}}(t)| \leq c\lambda^2 \tag{17.56}$$

uniformly in t, provided φ has some smoothness. The errors in (17.56) come from very short times, $\lambda^2 t \ll 1$, and very long ones, $\lambda^2 t \gg 1$. In the intermediate regime $G_{\mathrm{w}}(t)$ does very well.

For models like the Pauli–Fierz model one cannot hope for such explicit formulas. Instead, for the purpose of computing $g(\omega)$, the strategy is to continue the resolvent $\widehat{G}(z)$ from the upper half of the complex plane across $\mathbb{R}_+$ into the second Riemann sheet. Ideally, one should discover a simple pole, the resonance, located at $z_{\mathrm{r}}(\lambda) = \varepsilon + \lambda^2\Delta - \mathrm{i}\lambda^2\Gamma/2$ with $\Gamma > 0$. For small λ one expects $\Delta \cong \Delta(\varepsilon)$, $\Gamma \cong \Gamma(\varepsilon)$, but as λ is increased the pole $z_{\mathrm{r}}(\lambda)$ will move further away from the real axis. The resonance pole is responsible for the exponential decay as in (17.55) with $\Delta(\varepsilon)$, $\Gamma(\varepsilon)$ replaced by the true Δ, Γ. The error, as in (17.56), comes from the background spectrum of $\widehat{G}(z)$ on the second Riemann sheet, unavoidable due to the branch cut at $z = 0$.

One would hope that $z_{\mathrm{r}}(\lambda)$ is an intrinsic property of H_λ and not merely of the particular matrix element under study. Of course, we can always pick a bad coupling function φ such that $\langle\varphi, (z - x)^{-1}\varphi\rangle$ cannot be analytically continued across $\mathbb{R}_+$ or for a nice coupling φ, we could pick a bad wave function ψ such that $\langle\psi, (z - H_\lambda)^{-1}\psi\rangle$ cannot be analytically continued across $\mathbb{R}_+$. Thus the best we can expect is that for a given sufficiently smooth φ the location of the resonance pole is independent of the choice of ψ within a reasonably large set. To accomplish the desired analytic continuation we will implement a complex dilation of H_λ.

For real θ a dilation is defined by

$$U(\theta)\psi(x) = \mathrm{e}^{-\theta/2}\psi(\mathrm{e}^{-\theta}x). \tag{17.57}$$

$U(\theta)$ is unitary and H_λ transforms under $U(\theta)$ as

$$\begin{aligned} U(\theta)H_\lambda U(\theta)^{-1} &= H_\lambda(\theta) = H_0(\theta) + \lambda H_{\mathrm{int}}(\theta) \\ &= \begin{pmatrix} \varepsilon & 0 \\ 0 & \mathrm{e}^{-\theta}x \end{pmatrix} + \lambda \begin{pmatrix} 0 & \langle\varphi_\theta| \\ |\varphi_\theta\rangle & 0 \end{pmatrix}, \end{aligned} \tag{17.58}$$

where $\varphi_\theta(x) = \mathrm{e}^{-\theta/2}\varphi(\mathrm{e}^{-\theta}x)$.

We want to extend (17.57), (17.58) to complex θ with θ inside the strip $\mathcal{S}_\beta = \{\theta \,|\, |\mathrm{Im}\theta| < \beta\}$ with some $\beta > 0$. $\mathrm{e}^{-\theta}$ is clearly analytic. For φ we require that φ_θ extends as an analytic function to $\mathcal{S}_\beta$ such that $\int_0^\infty \mathrm{d}x |\mathrm{e}^{-\theta/2}\varphi(\mathrm{e}^{-\theta}x)|^2 < \infty$. Then $H_\lambda(\theta)$ is an analytic family of operators of type A in the sense of Kato, separately for $\theta \in \mathcal{S}_\beta$ and $|\lambda|$ sufficiently small. Note that $H_\lambda(\theta)^* = H_\lambda(\theta^*)$ for real λ, since φ is real. The point of our construction is that for purely imaginary θ, $\theta = \mathrm{i}\vartheta$,

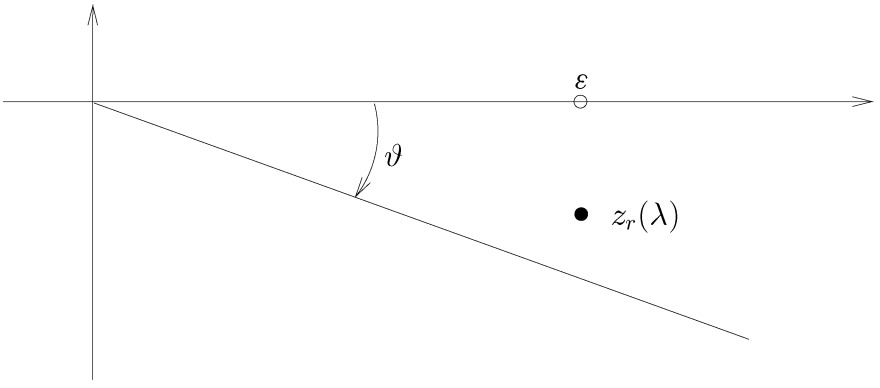

Figure 17.1: Spectrum of the rotated Hamiltonian $H_\lambda(\mathrm{i}\vartheta)$ for small coupling λ.

$0 < \vartheta < \beta$, the continuous spectrum of $H_0(\mathrm{i}\vartheta)$ rotates clockwise by the angle ϑ, see figure 17.1. Thereby the previously embedded eigenvalue ε becomes isolated and we can use ordinary perturbation theory to show that it shifts downwards to become the resonance pole $z_\mathrm{r}(\lambda)$ on the second Riemann sheet. $z_\mathrm{r}(\lambda)$ is analytic in θ as long as it remains isolated. If one sets $\theta = \kappa + \mathrm{i}\vartheta$, $\kappa, \vartheta \in \mathbb{R}$, then $H_\lambda(\kappa + \mathrm{i}\vartheta)$ is unitarily equivalent to $H_\lambda(\kappa' + \mathrm{i}\vartheta)$. Therefore $z_\mathrm{r}(\lambda)$ is constant along lines of fixed $\mathrm{i}\vartheta$ and by analyticity independent of θ. As the continuous spectrum rotates clockwise, the resonance pole is uncovered and stays put. We summarize as

Theorem 17.2 (Analytic continuation of the resolvent). *For λ sufficiently small, there exists a dense set $D \subset \mathcal{H} = \mathbb{C} \oplus L^2(\mathbb{R}_+, \mathrm{d}x)$ such that for $\psi_1, \psi_2 \in D$ the resolvent $\langle \psi_1, (z - H_\lambda)^{-1}\psi_2\rangle$ has an analytic continuation from $\mathbb{C}_+$ across $\mathbb{R}_+$ into the second Riemann sheet. $\langle \psi_1, (z - H_\lambda)^{-1}\psi_2\rangle$ has a simple pole at $z_\mathrm{r}(\lambda)$, $\mathrm{Im} z_\mathrm{r}(\lambda) < 0$, with the property that $\lim_{\lambda\to 0} z_\mathrm{r}(\lambda) = \varepsilon$. $z_\mathrm{r}(\lambda)$ does not depend on the choice of ψ_1, ψ_2.*

Proof: Let $D \subset \mathcal{H}$ be the set of all vectors such that $\theta \mapsto U(\theta)\psi$ is an analytic vector-valued function on $\mathcal{S}_\beta$. D is dense in $\mathcal{H}$. For $\psi_1, \psi_2 \in D$ we have

$$\langle \psi_1, (z - H_\lambda)^{-1}\psi_2\rangle = \langle U(-\theta)^*\psi_1, (z - H_\lambda(\theta))^{-1}U(\theta)\psi_2\rangle. \quad (17.59)$$

For given θ with $\mathrm{Im}\theta > 0$, we can choose δ_0 sufficiently small such that inside the open disc $|z - \varepsilon| \leq \delta_0$ the location $z_\mathrm{r}(\lambda)$ of the pole is an analytic curve starting at $z_\mathrm{r}(0) = \varepsilon$. □

Let us follow the first step of the perturbation expansion. We fix $\theta = \mathrm{i}\vartheta$, $0 < \vartheta < \beta$. For $\lambda = 0$, $H_0(\theta)$ has the eigenvalue ε with corresponding projector $|\psi_0\rangle\langle\psi_0|$. The eigenvalue persists for small λ and we expand in λ. The first-order

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term vanishes and to second order we have

$$\begin{aligned} z_{\mathrm{r}}(\lambda) &= \varepsilon + \lambda^2 \langle \psi_0, H_{\mathrm{int}}(\theta)(\varepsilon - H_0(\theta))^{-1} H_{\mathrm{int}}(\theta)\psi_0 \rangle \\ &= \varepsilon + \lim_{\eta \to 0_+} \lambda^2 \langle \psi_0, H_{\mathrm{int}}(\varepsilon + \mathrm{i}\eta - H_0)^{-1} H_{\mathrm{int}}\psi_0 \rangle \\ &= \varepsilon + \lambda^2 \Delta(\varepsilon) - \mathrm{i}\lambda^2 \Gamma(\varepsilon)/2. \end{aligned} \tag{17.60}$$

No surprise, we recover the result from the weak coupling theory. We will see that this is a rather general fact and argue that the master equation (17.32) can be understood as arising from the resonances of the Liouvillean to lowest order. If the expansion in (17.60) is continued, the next order is λ^4 and the eigenprojection of the resonance will be slightly tilted.

With the Friedrichs–Lee model as a blueprint in hand we plan to implement complex dilation for the Pauli–Fierz model in the N-level approximation (17.10). As in the example above the complex dilation acts only on the photon degrees of freedom. For an n-photon vector we define

$$U_{\mathrm{f}}(\theta)\psi_n(k_1, \lambda_1, \ldots, k_n, \lambda_n) = \mathrm{e}^{-3n\theta/2}\psi_n(\mathrm{e}^{-\theta}k_1, \lambda_1, \ldots, \mathrm{e}^{-\theta}k_n, \lambda_n) \tag{17.61}$$

for $\theta \in \mathbb{R}$. In particular

$$U_{\mathrm{f}}(\theta)a^*(f)U_{\mathrm{f}}(\theta)^{-1} = a^*(f_\theta)\,, \qquad f_\theta(k, \lambda) = \mathrm{e}^{-3\theta/2} f(\mathrm{e}^{-\theta}k, \lambda). \tag{17.62}$$

Then for the field energy

$$U_{\mathrm{f}}(\theta)H_{\mathrm{f}}U_{\mathrm{f}}(\theta)^{-1} = H_{\mathrm{f}}(\theta) = \mathrm{e}^{-\theta}H_{\mathrm{f}} \tag{17.63}$$

and for the electric field

$$\begin{aligned} U_{\mathrm{f}}(\theta)E_\varphi U_{\mathrm{f}}(\theta)^{-1} &= E_\varphi(\theta) \\ &= \sum_{\lambda=1,2} \int \mathrm{d}^3k \mathrm{e}^{-3\theta/2} \widehat{\varphi}(\mathrm{e}^{-\theta}k)\mathrm{e}^{-\theta/2}\sqrt{\omega(k)/2} \\ &\quad \times e_\lambda(k)\mathrm{i}\big(a(k, \lambda) - a^*(k, \lambda)\big). \end{aligned} \tag{17.64}$$

We want to extend (17.63), (17.64) to complex $\theta \in \mathcal{S}_\beta$. Clearly $H_{\mathrm{f}}(\theta)$ is analytic in θ. For the charge distribution we require that $\widehat{\varphi}_\theta(k)$ extends as an analytic function to $\mathcal{S}_\beta$ and

$$\int \mathrm{d}^3k |\widehat{\varphi}_\theta|^2 \big(\omega(k) + \omega(k)^{-1}\big) < \infty. \tag{17.65}$$

Then $E_\varphi(\theta)$ is bounded relative to $H_{\mathrm{f}}(\theta)$ and

$$H_\lambda(\theta) = H_{\mathrm{at}} + H_{\mathrm{f}}(\theta) + \lambda Q \cdot E_\varphi(\theta) \tag{17.66}$$

is an analytic family of operators of type A separately in $\theta \in \mathcal{S}_\beta$ and λ, with $|\lambda| < \lambda_0$ and λ_0 sufficiently small. Thus we have established the abstract framework needed for complex dilation.

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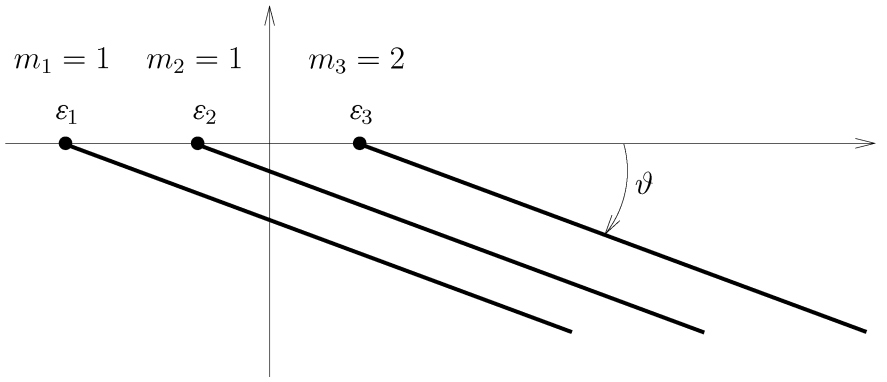

Figure 17.2: Spectrum of the rotated Hamiltonian $H_0(\mathrm{i}\vartheta)$ at zero coupling.

The difficulty already becomes apparent when the case of zero coupling is considered, i.e. $\lambda = 0$ $(= -e)$. H_f has a zero eigenvalue and the continuous spectrum $\mathbb{R}_+$ is of infinite multiplicity. If $\theta = \mathrm{i}\vartheta$, the continuous spectrum rotates by the angle ϑ. Thus for $H_\mathrm{at} + H_\mathrm{f}(\theta)$ we have a spectrum as shown in figure 17.2, where the eigenvalues ε_j, $j = 1, \ldots, \bar{N}$, are at the tip of the continuous spectrum. In contrast to the Friedrichs–Lee model, they are not isolated. We can make them become isolated by giving the photons a small mass m_ph. Then $\omega(k) = (m_\mathrm{ph}^2 + k^2)^{1/2}$ which becomes $\omega_\theta(k) = (\mathrm{e}^{-2\theta}k^2 + m_\mathrm{ph}^2)^{1/2}$ when complex dilated. The eigenvalues are now isolated provided they do not lie in the set of thresholds $\{\varepsilon_j + n m_\mathrm{ph} |\, j = 1, \ldots, \bar{N}, n = 1, 2, \ldots\}$. Our previous arguments apply, but the range of allowed λ is bounded by m_ph.

In a beautiful piece of analysis V. Bach, J. Fröhlich, and I. M. Sigal succeed in controlling the situation depicted in figure 17.3. They prove that for sufficiently small λ and a dense set D of vectors the resolvent $\langle\psi, (z - H_\lambda)^{-1}\varphi\rangle$, $\psi, \varphi \in D$, can be analytically continued into a domain, schematically drawn in figure 17.3. For $\lambda = 0$ the eigenvalues are ε_j with multiplicity m_j. Except for $j = 1$, for small λ they turn into a group of resonances $z_{jm}(\lambda)$, $m = 1, \ldots, m_j$, with the property that $\lim_{\lambda\to 0} z_{jm}(\lambda) = \varepsilon_j$. The ground state energy ε_1 is nondegenerate and $z_1(\lambda)$ stays on the real axis. $z_1(\lambda)$ is the ground state energy of the coupled system. The $z_{jm}(\lambda)$ are eigenvalues of the complex dilated Hamiltonian $H_\lambda(\theta)$. The resonances are located at the apex of a cone, which is tilted by the angle θ and has a square root singularity at its tip.

To ensure that the resonances are strictly below the real axis we use the condition from second-order perturbation and require that

$$\frac{1}{2}\lambda^2 \sum_{\alpha=1}^{3} \sum_{i=1}^{j-1} \Gamma(\varepsilon_i - \varepsilon_j) P_j Q_\alpha P_i Q_\alpha P_j > 0 \tag{17.67}$$

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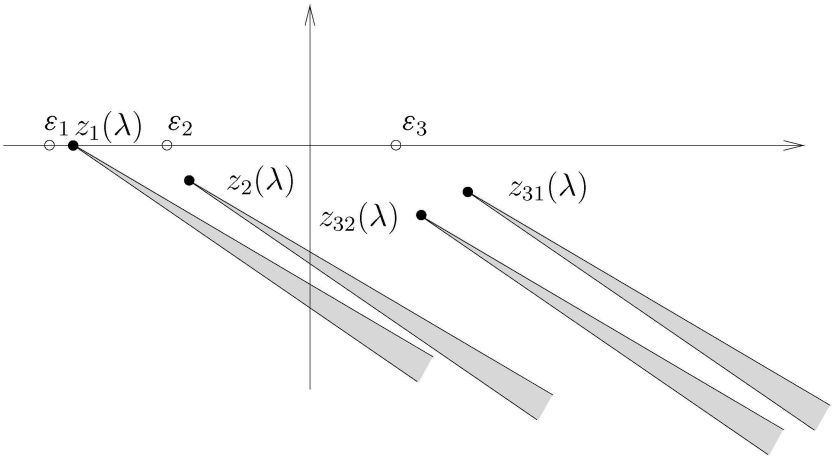

Figure 17.3: Spectrum of the rotated Hamiltonian $H_\lambda(\mathrm{i}\vartheta)$ at small nonzero coupling. The domain of analyticity is $\{z|\mathrm{Im}z > -b_0\}$ with small $b_0 > 0$ and away from the shaded regions.

as an $m_j \times m_j$ matrix for $j = 1, \ldots, \bar{N}$. The eigenvalues of this matrix are: $\mathrm{Im}z_{jm}(\lambda)$, $m = 1, \ldots, m_j$, to order λ^2. To second-order the imaginary part of the resonance poles agrees with the decay rates from the quantum master equation (17.32). Their real part coincides with the eigenvalues of H_{at} corrected by the Hamiltonian part of $K^\natural$ from (17.37). To obtain the full generator $K^\natural$ one has to study the resonances of the Liouvillean as will be discussed in chapter 18.

17.4 Fluorescence

We have described in considerable detail how the atom decays to its ground state, at least for small coupling. So what then are the spectral characteristics of the fluorescent light? How does the theory account for the experimental fact that the line shapes differ for equally and for unequally spaced unperturbed energy levels? We will address such questions only within the weak coupling theory.

The initial state of the atom is chosen to be a pure state $\psi \in \mathbb{C}^N$ and that of the field to be the vacuum. We want to determine $\mathrm{e}^{-\mathrm{i}H_\lambda t}\psi \otimes \Omega$ for small λ and large t, order of λ^{-2}. One method is to use second-order perturbation theory for the resonance poles of the resolvent, as explained for a particular case in the previous section. Another method is to expand the resolvent $\langle \varphi \otimes \prod_{j=1}^n a^*(k_j, \lambda_j)\Omega, (z - H_\lambda)^{-1}\psi \otimes \Omega\rangle$ and to resum all nonoverlapping internal photon lines lying in between either the external photon legs or the atom legs. The results turn out to be identical and have a simple physical interpretation.

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To state the approximation to $\mathrm{e}^{-\mathrm{i}H_\lambda t}\psi\otimes\Omega$, we rewrite the generator of the reduced atom dynamics as, compare with (17.37), (17.32),

$$\begin{aligned}\mathcal{L}_{\mathrm{D}}\rho &= [H_{\mathrm{at}},\rho] + \mathrm{i}\lambda^2 K^\natural\rho \\ &= [H_{\mathrm{at}} + \lambda^2 H_\Delta - \mathrm{i}\lambda^2 H_\Gamma,\rho] + \mathrm{i}\sum_{\alpha=1}^{3}\sum_{\omega\in\sigma(L_{\mathrm{at}})}\Gamma(\omega)Q_\alpha(\omega)^*\rho Q_\alpha(\omega) \\ &= \mathcal{L}_{\mathrm{D}0}\rho + \mathcal{L}_{\mathrm{D}1}\rho. \end{aligned} \tag{17.68}$$

Then

$$H_\Delta = \sum_{\alpha=1}^{3}\sum_{\omega\in\sigma(L_{\mathrm{at}})}\Delta(\omega)Q_\alpha(\omega)Q_\alpha(\omega)^* = \sum_{\alpha=1}^{3}\sum_{i,j=1}^{\bar N}\Delta(\varepsilon_i-\varepsilon_j)P_jQ_\alpha P_iQ_\alpha P_j, \tag{17.69}$$

and

$$H_\Gamma = \sum_{\alpha=1}^{3}\sum_{\omega\in\sigma(L_{\mathrm{at}})}\Gamma(\omega)Q_\alpha(\omega)Q_\alpha(\omega)^* = \sum_{\alpha=1}^{3}\sum_{i<j=1}^{\bar N}\Gamma(\varepsilon_i-\varepsilon_j)P_jQ_\alpha P_iQ_\alpha P_j, \tag{17.70}$$

where we used the relation $\Gamma(\omega)=0$ for $\omega\geq 0$. We introduce the convenient shorthand

$$H_{\mathrm{d}} = H_{\mathrm{at}} + \lambda^2 H_\Delta - \mathrm{i}\lambda^2 H_\Gamma. \tag{17.71}$$

Note that H_{d} is not symmetric. As a photon is emitted, the energy of the atom decreases by at least one level, which is described by the atom lowering part of the interaction Hamiltonian,

$$Q^-\cdot E_\varphi^+ = -\mathrm{i}\sum_{i<j=1}^{\bar N} P_iQP_j\otimes\Big(\sum_{\lambda=1,2}\int \mathrm{d}^3k\,\widehat{\varphi}(k)\sqrt{\omega/2}\cdot e_\lambda(k)a^*(k,\lambda)\Big). \tag{17.72}$$

With this notation the approximate solution is

$$\begin{aligned}\mathrm{e}^{-\mathrm{i}H_\lambda t}\psi\otimes\Omega \cong \mathrm{e}^{-\mathrm{i}H_{\mathrm{d}}t}\psi\otimes\Omega + \sum_{n=1}^{\bar N-1}(-\mathrm{i})^n\int_{0\leq t_1\leq\ldots\leq t_n\leq t}\mathrm{d}t_n\ldots\mathrm{d}t_1 \\ \times\,\mathrm{e}^{-\mathrm{i}(H_{\mathrm{d}}+H_{\mathrm{f}})(t-t_n)}\lambda Q^-\cdot E_\varphi^+\ldots\,\mathrm{e}^{-\mathrm{i}(H_{\mathrm{d}}+H_{\mathrm{f}})(t_2-t_1)} \\ \times\,\lambda Q^-\cdot E_\varphi^+\mathrm{e}^{-\mathrm{i}(H_{\mathrm{d}}+H_{\mathrm{f}})t_1}\psi\otimes\Omega.\end{aligned} \tag{17.73}$$

The sum is finite, since $(Q^-)^{\bar N}\psi = 0$.

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Taking in (17.73) the trace over the atom results in the reduced state of the photon field. Taking the trace over the field yields the reduced state of the atom. But this state was already determined in section 17.2. To be consistent with it we must have

$$\mathrm{tr}_{\mathcal{F}}[|\mathrm{e}^{-\mathrm{i}H_\lambda t}\psi\otimes\Omega\rangle\langle\mathrm{e}^{-\mathrm{i}H_\lambda t}\psi\otimes\Omega|]=\mathrm{e}^{-\mathrm{i}Lt}P_\psi, \tag{17.74}$$

at least for small λ, P_ψ the projection onto ψ. If (17.74) holds, the case of an arbitrary initial density matrix follows by linearity.

To prove (17.74) we insert (17.73) and obtain

$$\begin{aligned}
&\mathrm{tr}_{\mathcal{F}}[|\mathrm{e}^{-\mathrm{i}H_\lambda t}\psi\otimes\Omega\rangle\langle\mathrm{e}^{-\mathrm{i}H_\lambda t}\psi\otimes\Omega|] \qquad (17.75)\\
&=\mathrm{e}^{-\mathrm{i}H_{\mathrm{d}}t}P_\psi\mathrm{e}^{\mathrm{i}H_{\mathrm{d}}^* t}+\sum_{n=1}^{\bar N-1}\lambda^{2n}\int_{0\le t_1\le\ldots\le t_n\le t}\mathrm{d}t_n\ldots\mathrm{d}t_1\\
&\quad\times\int_{0\le s_1\le\ldots\le s_n\le t}\mathrm{d}s_n\ldots\mathrm{d}s_1\sum_{\alpha_1,\beta_1=1}^{3}\ldots\sum_{\alpha_n,\beta_n=1}^{3}\\
&\quad\times\prod_{j=1}^{n}\delta_{\alpha_j\beta_j}h(s_j-t_j)\mathrm{e}^{-\mathrm{i}H_{\mathrm{d}}(t-t_n)}Q^-_{\alpha_n}\mathrm{e}^{-\mathrm{i}H_{\mathrm{d}}(t_n-t_{n-1})}Q^-_{\alpha_{n-1}}\ldots Q^-_{\alpha_1}\mathrm{e}^{-\mathrm{i}H_{\mathrm{d}}t_1}P_\psi\\
&\quad\times\mathrm{e}^{\mathrm{i}H_{\mathrm{d}}^* s_1}Q^{-*}_{\beta_1}\ldots Q^{-*}_{\beta_{n-1}}\mathrm{e}^{\mathrm{i}H_{\mathrm{d}}^*(s_n-s_{n-1})}Q^{-*}_{\beta_n}\mathrm{e}^{\mathrm{i}H_{\mathrm{d}}^*(t-s_n)}.
\end{aligned}$$

Since $[H_{\mathrm{at}},H_\Delta]=0=[H_{\mathrm{at}},H_\Gamma]$, one can use the spectral representation

$$\mathrm{e}^{-\mathrm{i}H_{\mathrm{d}}t}=\sum_{j=1}^{\bar N}\mathrm{e}^{-\mathrm{i}\varepsilon_j t}P_j\mathrm{e}^{-\mathrm{i}\lambda^2H_\Delta t-\lambda^2H_\Gamma t} \tag{17.76}$$

and insert it for each propagator in (17.75). On the time scale $\lambda^{-2}\tau$, $\tau=\mathcal{O}(1)$, $h(t)$ decays quickly and the factors $\mathrm{e}^{-\mathrm{i}\varepsilon t}$ are rapidly oscillating. The generic integral in (17.75) is of the form

$$\int_0^\tau\mathrm{d}t\int_0^{\tau'}\mathrm{d}s\lambda^{-2}h(\lambda^{-2}(s-t))\mathrm{e}^{\mathrm{i}(\varepsilon_i-\varepsilon_j)t/\lambda^2}\mathrm{e}^{-\mathrm{i}(\varepsilon_m-\varepsilon_n)s/\lambda^2}. \tag{17.77}$$

In the limit $\lambda\to0$ it converges to

$$\min(\tau,\tau')\int\mathrm{d}t\;h(t)\mathrm{e}^{-\mathrm{i}(\varepsilon_m-\varepsilon_n)t}\delta_{\varepsilon_i-\varepsilon_j,\varepsilon_m-\varepsilon_n}=\min(\tau,\tau')\Gamma(\varepsilon_m-\varepsilon_n)\delta_{\varepsilon_i-\varepsilon_j,\varepsilon_m-\varepsilon_n}. \tag{17.78}$$

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Using (17.78) and (17.76), the small-λ limit of the expression in (17.75) is given by

$$\begin{aligned} &\mathrm{e}^{-\mathrm{i}L_{\mathrm{D}0}t}P_\psi + \sum_{n=1}^{\bar{N}-1}(-\mathrm{i})^n \int_{0\le t_1\le\ldots\le t_n\le t} \mathrm{d}t_n\ldots\mathrm{d}t_1 \\ &\qquad \times \mathrm{e}^{-\mathrm{i}L_{\mathrm{D}0}(t-t_n)}L_{\mathrm{D}1}\mathrm{e}^{-\mathrm{i}L_{\mathrm{D}0}(t_n-t_{n-1})}\ldots L_{\mathrm{D}1}\mathrm{e}^{-\mathrm{i}L_{\mathrm{D}0}t_1}P_\psi \\ &\qquad = \mathrm{e}^{-\mathrm{i}L_{\mathrm{D}}t}P_\psi \end{aligned} \tag{17.79}$$

as was to be shown.

The approximate solution (17.73) describes the decay of the atom and the build-up of photons. Such details are experimentally inaccessible. However, what can be easily seen are the spectral characteristics of the fluorescent light, which are obtained from (17.73) in the limit $t\to\infty$ (on the time scale λ^{-2}). Then the atom is in its ground state and

$$\mathrm{e}^{-\mathrm{i}H_\lambda t}\psi\otimes\Omega \cong \mathrm{e}^{-\mathrm{i}(\varepsilon_1+\lambda^2\Delta_1)t}\psi_1\otimes\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi, \tag{17.80}$$

where ϕ is a photon state propagating freely to infinity through $\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}$. ϕ can be read off from (17.73) as

$$\begin{aligned} \psi_1\otimes\phi = P_1\psi\otimes\Omega + \sum_{n=1}^{\bar{N}-1}(-\mathrm{i})^n \int_{0\le t_1\le\ldots\le t_n<\infty} \mathrm{d}t_n\ldots\mathrm{d}t_1\; P_1\mathrm{e}^{\mathrm{i}(H_{\mathrm{d}}+H_{\mathrm{f}})t_n} \\ \times\lambda Q^-\cdot E_\varphi^+\ldots\mathrm{e}^{-\mathrm{i}(H_{\mathrm{d}}+H_{\mathrm{f}})(t_2-t_1)}\lambda Q^-\cdot E_\varphi^+\mathrm{e}^{-\mathrm{i}(H_{\mathrm{d}}+H_{\mathrm{f}})t_1}\psi\otimes\Omega. \end{aligned} \tag{17.81}$$

The projection P_1 comes in, since states in (17.73) which are orthogonal to the uncoupled ground state ψ_1 decay exponentially and only the piece parallel to ψ_1 persists in the long-time limit.

To see how (17.80) translates to the spectrum of the emitted light, it might be useful to work out two concrete cases.

(i) Two-level atom. We consider two nondegenerate levels $|1\rangle$, $|2\rangle$ with resonance poles $z_j=\varepsilon_j+\Delta_j-\mathrm{i}\Gamma_j/2$, $j=1,2$, $\Gamma_1=0$. Initially the atom is in state $|2\rangle$. Then the scattering state ϕ of (17.80) has only one photon, $\phi=(0,\phi_1,0,\ldots)$, with wave function

$$\phi_1(k_1,\lambda_1) = \big((\Gamma_2/2)+\mathrm{i}(\varepsilon_2+\Delta_2-\varepsilon_1-\Delta_1-\omega(k_1))\big)^{-1} f_{12}(k_1,\lambda_1), \tag{17.82}$$

where

$$f_{12}(k,\lambda) = e\widehat{\varphi}(k)\langle 1|x|2\rangle\cdot e_\lambda(k)\sqrt{\omega(k)/2}. \tag{17.83}$$

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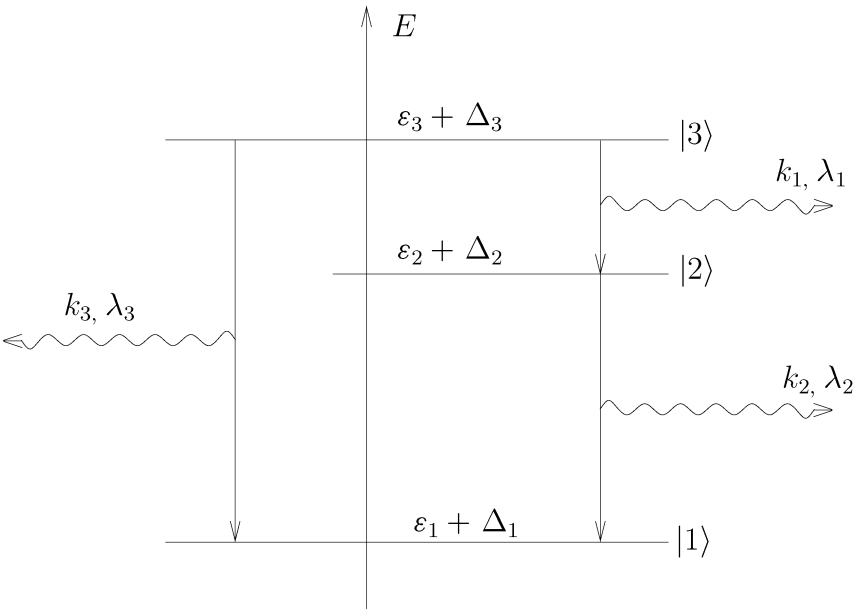

Figure 17.4: Radiation cascade for a three-level atom.

The spectral distribution is $|\phi_1|^2$. Since Γ_2 is small, the variation from f_{12} can be ignored to obtain

$$|\phi_1(k,\lambda)|^2 \cong C\big[(\varepsilon_2 + \Delta_2 - \varepsilon_1 - \Delta_1 - \omega)^2 + (\Gamma_2/2)^2\big]^{-1} = I(\omega, \widehat{k}, \lambda) \tag{17.84}$$

with the constant $C = |f_{12}(k,\lambda)|^2$ evaluated at $\omega(k) = \varepsilon_2 - \varepsilon_1$, $C = e^2|\widehat{\varphi}(\varepsilon_2 - \varepsilon_1)|^2((\varepsilon_2 - \varepsilon_1)/2)|\langle 1|x|2\rangle \cdot e_\lambda(k)|^2$, which depends on the direction of emission, $\widehat{k} = k/|k|$, and on the polarization. As a function of the frequency ω of the emitted light, the line shape is Lorentzian of natural width Γ_2 and centered at $\varepsilon_2 + \Delta_2 - \varepsilon_1 - \Delta_1$, differing from the bare line $\varepsilon_2 - \varepsilon_1$ by the shift $\Delta_2 - \Delta_1$.

If the initial state of the atom is $c_1|1\rangle + c_2|2\rangle$, normalized as $|c_1|^2 + |c_2|^2 = 1$, then $\phi = (c_1\Omega, c_2\phi_1(k_1,\lambda_1), 0, \dots)$. With probability $|c_1|^2$ no photon is emitted and with probability $|c_2|^2$ the line shape is that of (17.84).

(ii) Three-level atom. We consider three nondegenerate levels $|1\rangle, |2\rangle, |3\rangle$ with resonance poles $z_j = \varepsilon_j + \Delta_j - \mathrm{i}\Gamma_j/2$, $j = 1, 2, 3$, $\Gamma_1 = 0$. The initial state of the atom is $|3\rangle$. There is a direct transition $|3\rangle \to |1\rangle$ as in case (i). In addition we have the cascade $|3\rangle \to |2\rangle \to |1\rangle$. Therefore the scattering state is $\phi = (0, \phi_1, \phi_2, 0, \dots)$, see figure 17.4. ϕ_1 is as in (17.82) with label 2 replaced by label 3. For the cascade one obtains

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$$\phi_2(k_1,\lambda_1,k_2,\lambda_2) = \mathsf{S}\big\{\big(\Gamma_3/2 + \mathrm{i}(\varepsilon_3 + \Delta_3 - \varepsilon_1 - \Delta_1 - \omega(k_1) - \omega(k_2))\big)^{-1} \times \big(\Gamma_2/2 + \mathrm{i}(\varepsilon_2 + \Delta_2 - \varepsilon_1 - \Delta_1 - \omega(k_2))\big)^{-1} \times \sqrt{2} f_{12}(k_2,\lambda_2) f_{23}(k_1,\lambda_1)\big\} \tag{17.85}$$

with S denoting symmetrization. If the variation and the direction dependence from f_{12}, f_{23} are ignored, the intensity distribution for the two photons in the cascade is

$$I(\omega_1,\omega_2) = C\big(4(\Gamma_2/2)^2 + (\delta_2 - \omega_1 + \delta_2 - \omega_2)^2\big) \times \big[\big((\Gamma_3/2)^2 + (\delta_2 + \delta_3 - \omega_1 - \omega_2)^2\big)\big((\Gamma_2/2)^2 + (\delta_2 - \omega_1)^2\big)\big((\Gamma_2/2)^2 + (\delta_2 - \omega_2)^2\big)\big]^{-1} \tag{17.86}$$

with the shorthand $\delta_3 = \varepsilon_3 + \Delta_3 - \varepsilon_2 - \Delta_2$, $\quad \delta_2 = \varepsilon_2 + \Delta_2 - \varepsilon_1 - \Delta_1$. If $\varepsilon_3 - \varepsilon_2 \neq \varepsilon_2 - \varepsilon_1$, then in the frequency spectrum one will observe a Lorentzian at δ_2 with natural width Γ_2 and a Lorentzian at δ_3 with natural width $\Gamma_2 + \Gamma_3$. On the other hand if $\varepsilon_3 - \varepsilon_2 = \varepsilon_2 - \varepsilon_1$ and, just as an example, also $\Delta_2 = \Delta_3$, $2\Gamma_2 = \Gamma_3$, then

$$I(\omega_1,\omega_2) = C\big((\Gamma_2/2)^2 + (\delta_2 - \omega_1)^2\big)^{-1}\big((\Gamma_2/2)^2 + (\delta_2 - \omega_2)^2\big)^{-1}, \tag{17.87}$$

which corresponds to a single Lorentzian at $\delta_2 = \delta_3$ of natural width Γ_2 with double intensity. The two photons interfere when emitted. Otherwise, the intensity would be the sum of a Lorentzian of natural width Γ_2 and one of natural width $\Gamma_2 + \Gamma_3 = 3\Gamma_2$. If $\varepsilon_3 - \varepsilon_2 \cong \varepsilon_2 - \varepsilon_1$, the exact intensity distribution (17.86) has to be analyzed anew.

17.5 Scattering theory

From a very general perspective scattering theory is a comparison between an interacting dynamics and a simplified "free" dynamics in the limit of long times. In our context this means a study of

$$\mathrm{e}^{-\mathrm{i}Ht}\psi \quad \text{as } t \to \infty \tag{17.88}$$

for an arbitrary initial state $\psi \in \mathcal{H} = \mathbb{C}^N \otimes \mathcal{F}$. We stay within the dipole approximation and consider

$$H = H_{\mathrm{at}} + H_{\mathrm{f}} - eQ \cdot E_\varphi, \tag{17.89}$$

$E_\varphi = E_\varphi(0)$. Since the coupling is fixed, we omit the index λ and return to $e = -\lambda$, see (17.10). Also, $\langle \cdot, \cdot \rangle$ always denotes the scalar product in $\mathcal{H}$. From the outset we state

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Condition 17.3 (Uniqueness and localization of the ground state). *H has a unique ground state $\psi_{\rm g}$, $H\psi_{\rm g} = E_{\rm g}\psi_{\rm g}$ with the property that $\langle\psi_{\rm g}, {\rm e}^{\delta N_{\rm f}}\psi_{\rm g}\rangle < \infty$ for some $\delta > 0$. H has no other eigenvalues.*

On physical grounds it is easy to conjecture the limit in (17.88). Photons are traveling outwards according to a scattering state ϕ and the atom decays to its ground state $\psi_{\rm g}$. Thus for given $\psi \in \mathbb{C}^N \otimes \mathcal{F}$, there exists a $\phi \in \mathcal{F}$ such that

$$ {\rm e}^{-{\rm i}Ht}\psi \cong {\rm e}^{-{\rm i}E_{\rm g}t}\psi_{\rm g} \otimes_{\rm s} {\rm e}^{-{\rm i}H_{\rm f}t}\phi \quad \text{as } t \to \infty. \tag{17.90} $$

In rough terms, the state ${\rm e}^{-{\rm i}H_{\rm f}t}\phi$ lives far away from the ground state $\psi_{\rm g}$. Still, the bound photons of $\psi_{\rm g}$ must be properly symmetrized with the freely propagating photons of ${\rm e}^{-{\rm i}H_{\rm f}t}\phi$. This is achieved by the symmetrization $\otimes_{\rm s}$ as defined in (17.91), (17.92) below. We note that in the previous sections we have discussed an initial state of the particular form $\chi \otimes \Omega$. The relation (17.90) constitutes a vast generalization thereof. Of course, the limit (17.90) can be considered also for $t \to -\infty$. Combining both limits then yields the S-matrix for Rayleigh scattering of photons from an atom.

To establish the limit (17.90) in this generality is a tough analytical problem, since no exceptions are allowed. The limit is supposed to hold for all states $\psi \in \mathcal{H}$. We will only outline the general framework, in particular the proper definition of the wave operators and their intertwining between the free and interacting dynamics. As an easy step a Cook-type argument is established ensuring (17.90) at least for a large class of states. One important consequence of the limit (17.90) is the relaxation of the atom to its ground state without taking recourse to weak coupling, respectively resonance theory. As will be explained, such a relaxation holds also for local field observables.

Let us first have a look at the right-hand side of (17.90). The symmetrization $\otimes_{\rm s}$ can be defined for two arbitrary states in Fock space. We consider the Fock space $\mathcal{F} = \mathcal{F}(\mathfrak{h})$ over the one-particle space $\mathfrak{h}$. Then $\mathcal{F}(\mathfrak{h} \oplus \mathfrak{h}) = \mathcal{F}(\mathfrak{h}) \otimes \mathcal{F}(\mathfrak{h})$. On the one-particle space we define the map

$$ (u_1, u_2) \mapsto u_1 + u_2 \in \mathfrak{h}. \tag{17.91} $$

The second quantization of this map defines $\psi_1 \otimes \psi_2 \in \mathcal{F}(\mathfrak{h}) \otimes \mathcal{F}(\mathfrak{h}) \mapsto \psi_1 \otimes_{\rm s} \psi_2 \in \mathcal{F}(\mathfrak{h})$. More explicitly, one has

$$ \Big(\prod_{j=1}^{n} a^*(f_j)\Omega\Big) \otimes_{\rm s} \Big(\prod_{i=1}^{m} a^*(g_i)\Omega\Big) = \prod_{j=1}^{n} a^*(f_j) \prod_{i=1}^{m} a^*(g_i)\Omega. \tag{17.92} $$

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In our case one factor is the ground state $\psi_{\rm g}$ which can be thought of as a spinor-valued vector in $\mathcal{F}$. We then define $J : \mathcal{F} \to \mathbb{C}^N \otimes \mathcal{F}$ through

$$J\phi = \psi_{\rm g} \otimes_{\rm s} \phi, \tag{17.93}$$

since $\psi_{\rm g}$ is considered as given. If ϕ is an n-photon vector, $\phi = (0, \dots, \phi_n, 0, \dots)$, then

$$(\psi_{\rm g} \otimes_{\rm s} \phi)_{n+j} = \binom{n+j}{n}^{1/2} \mathsf{S}\psi_{{\rm g}j}\phi_n, \tag{17.94}$$

with S denoting the symmetrizer.

As can be seen from (17.91), the symmetrization $\otimes_{\rm s}$ is unbounded. In particular,

$$\begin{aligned} \|J\phi\|^2 &= \sum_{n=0}^{\infty} \sum_{i=0}^{n} \sum_{j=0}^{n} \binom{n}{i}^{1/2} \binom{n}{j}^{1/2} \langle \mathsf{S}\psi_{{\rm g}i}\phi_{n-i}, \mathsf{S}\psi_{{\rm g}j}\phi_{n-j}\rangle \\ &\le \sum_{n=0}^{\infty} \Big(\sum_{j=0}^{n} \binom{n}{j}^{1/2} \|\psi_{{\rm g}j}\| \|\phi_{n-j}\| \Big)^2 \\ &\le \sum_{n=0}^{\infty} \sum_{j=0}^{n} \binom{n}{j} \|\phi_{n-j}\|^2 {\rm e}^{-\delta j} \sum_{i=0}^{n} \|\psi_{{\rm g}i}\|^2 {\rm e}^{\delta i}. \end{aligned} \tag{17.95}$$

Let us define $D_\delta = \{\phi \,|\, \|\phi_n\| \le c(1 - {\rm e}^{-\delta/2})^n\}$. Then for $\phi \in D_\delta$, we have $\|J\phi\| < \infty$, which is the reason for assuming the exponential bound in condition 17.3. Without it, we would have to go into details in what sense ϕ is far away from the atom.

If the state ϕ shifted to infinity, either by the spatial shift ${\rm e}^{-{\rm i}w\cdot P_{\rm f}}$ or by the time shift ${\rm e}^{-{\rm i}H_{\rm f}t}$, then only the coupled ground state remains in focus. To see this on a more formal level, we introduce the strictly local Weyl algebra $\mathcal{W}_R$ consisting of operators of the form $W(f) = \exp[a^*(f) - a(f)]$ with $f(x, \lambda) = 0$ for $|x| \ge R$. The quasi-local Weyl algebra $\mathcal{W}$ is the norm closure of $\cup_{R>0}\mathcal{W}_R$. The local character is of importance, e.g. $g(H_{\rm f})$ with g bounded is obviously a bounded operator, but $g(H_{\rm f})$ does not lie in $\mathcal{W}$. Let $A \in B(\mathbb{C}^N) \otimes \mathcal{W}$. Shifting to infinity then

$$\lim_{|w|\to\infty} \langle \psi_{\rm g} \otimes_{\rm s} {\rm e}^{-{\rm i}w\cdot P_{\rm f}}\phi, A\psi_{\rm g} \otimes_{\rm s} {\rm e}^{-{\rm i}w\cdot P_{\rm f}}\phi\rangle = \langle \psi_{\rm g}, A\psi_{\rm g}\rangle\langle\phi, \phi\rangle_{\mathcal{F}}, \tag{17.96}$$

$$\lim_{|t|\to\infty} \langle \psi_{\rm g} \otimes_{\rm s} {\rm e}^{-{\rm i}H_{\rm f}t}\phi, A\psi_{\rm g} \otimes_{\rm s} {\rm e}^{-{\rm i}H_{\rm f}t}\phi\rangle = \langle \psi_{\rm g}, A\psi_{\rm g}\rangle\langle\phi, \phi\rangle_{\mathcal{F}} \tag{17.97}$$

for all $\phi \in D_\delta$.

To prove (17.96), (17.97), we choose an n-photon state of the form $\phi = (0, \dots, \phi_n, 0, \dots)$ with $\phi_n(x_1, \lambda_1, \dots, x_n, \lambda_n) = \mathsf{S}\prod_{j=1}^n f_j(x_j, \lambda_j)$, in other

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words $\phi = (n!)^{-1/2} \prod_{j=1}^{n} a^*(f_j)\Omega$. We set $f_{jw}(x_j, \lambda_j) = f_j(x_j - w, \lambda_j)$ and similarly $\widehat{f_{jt}}(k_j, \lambda_j) = \mathrm{e}^{-\mathrm{i}\omega(k_j)t}\widehat{f_j}(k_j, \lambda_j)$. Equations (17.96) and (17.97) go in parallel and we consider only the latter. Then, for $M \in B(\mathbb{C}^N)$, $W(f) \in \mathcal{W}$, and since $W(f)a^*(f_j) = a^*(f_j)W(f) - \langle f, f_j\rangle_{\mathfrak{h}} W(f)$, we get

$$
\begin{aligned}
&\langle J\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi, M \otimes W(f) J\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi\rangle \\
&\quad = \frac{1}{n!}\langle \prod_{j=1}^{n} a^*(f_{jt})\psi_{\mathrm{g}}, M \otimes W(f) \prod_{j=1}^{n} a^*(f_{jt})\psi_{\mathrm{g}}\rangle \\
&\quad = \frac{1}{n!}\langle \prod_{j=1}^{n} a^*(f_{jt})\psi_{\mathrm{g}}, \prod_{j=1}^{n} a^*(f_{jt}) M \otimes W(f)\psi_{\mathrm{g}}\rangle \\
&\qquad + \frac{1}{n!} \sum_{\Lambda \subset \{1,\dots,n\}, \Lambda \neq \emptyset} \prod_{j \in \Lambda} \big(- \langle f, f_{jt}\rangle_{\mathfrak{h}}\big) \langle \prod_{j=1}^{n} a^*(f_{jt})\psi_{\mathrm{g}}, \prod_{j \in \Lambda^c} a^*(f_{jt}) M\psi_{\mathrm{g}}\rangle.
\end{aligned}
\tag{17.98}
$$

Since f is local, by the Riemann–Lebesgue lemma, $\lim_{t\to\infty}\langle f, f_{jt}\rangle_{\mathfrak{h}} = 0$. Similarly, for space translations, $\lim_{|w|\to\infty}\langle f, f_{jw}\rangle_{\mathfrak{h}} = 0$. Therefore each term having at least one contraction vanishes in the limit $t \to \infty$, respectively $|w| \to \infty$. We still have to discuss the first summand corresponding to zero contraction which written out explicitly is

$$
\sum_{j=0}^{\infty} \binom{n+j}{n} \langle \mathsf{S}\psi_{\mathrm{g}j}\phi_{nt}, \mathsf{S}(M \otimes W(f)\psi_{\mathrm{g}})_j \phi_{nt}\rangle, \tag{17.99}
$$

by using (17.94) and setting $\phi_{nt} = (\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi)_n$. There are two types of terms in the scalar product. If a ϕ_{nt} is integrated either against $\psi_{\mathrm{g}j}$ or against $(M \otimes W(f)\psi_{\mathrm{g}})_j$, then all such terms vanish as $t \to \infty$, again by the Riemann–Lebesgue lemma. The only terms which survive in the limit are of the form $\langle \psi_{\mathrm{g}j}, (M \otimes W(f)\psi_{\mathrm{g}})_j\rangle\langle \phi_{nt}, \phi_{nt}\rangle_{\mathcal{F}} = \langle \psi_{\mathrm{g}j}, (M \otimes W(f)\psi_{\mathrm{g}})_j\rangle\langle \phi_n, \phi_n\rangle_{\mathcal{F}}$ by unitarity. We conclude that the limit $t \to \infty$ in (17.99) equals

$$
\sum_{j=0}^{\infty} \langle \psi_{\mathrm{g}j}, (M \otimes W(f)\psi_{\mathrm{g}})_j\rangle\langle \phi_n, \phi_n\rangle_{\mathcal{F}} = \langle \psi_{\mathrm{g}}, M \otimes W(f)\psi_{\mathrm{g}}\rangle\langle \phi, \phi\rangle_{\mathcal{F}}, \tag{17.100}
$$

as claimed. To cover the general case one has to take suitable linear combinations and uniform limits.

With these preparations the limit in (17.90) can be formulated more concisely. We define the wave operators $\Omega^{\mp}$ through the strong limit

$$\Omega^{\mp}\phi = s - \lim_{t\to\pm\infty} \mathrm{e}^{\mathrm{i}(H-E_{\mathrm{g}})t} J \mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi. \tag{17.101}$$

The existence of this limit will be shown for all $\phi \in D_\delta$ by a Cook estimate in Proposition 17.6 below. But we first want to explore some consequences of our definition.

In the usual definition of wave operators one projects onto the scattering states of the comparison dynamics $\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}$. This is not needed here because for $\phi = \Omega$, the limit in (17.101) equals ψ_{g}. The formulation (17.101) assumes that H has no other bound state. If this had been the case, one would have to allow in (17.101) for several atomic channels, corresponding to the possibility that the atom remains in an excited state forever.

The wave operators $\Omega^{\pm}$ are isometries from $\mathcal{F}$ to $\mathbb{C}^N \otimes \mathcal{F}$, as can be seen from

$$\langle \Omega^{\mp}\phi, \Omega^{\mp}\phi\rangle = \lim_{t\to\pm\infty} \langle J\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi, J\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi\rangle = \langle\phi,\phi\rangle_{\mathcal{F}} \tag{17.102}$$

by (17.97) for $\phi \in D_\delta$. By continuity this property extends to all of $\mathcal{F}$. $\Omega^{\pm}$ intertwines between the free and interacting dynamics as

$$\mathrm{e}^{-\mathrm{i}(H-E_{\mathrm{g}})t}\Omega^{\pm} = \Omega^{\pm}\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}, \tag{17.103}$$

which is an immediate consequence of the definition: for $\phi \in D_\delta$ one has $\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi \in D_\delta$ and

$$\begin{aligned}\Omega^{-}\phi &= \lim_{s\to\infty} \mathrm{e}^{\mathrm{i}(H-E_{\mathrm{g}})(t+s)} J \mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}(t+s)}\phi \\ &= \lim_{s\to\infty} \mathrm{e}^{\mathrm{i}(H-E_{\mathrm{g}})t}\mathrm{e}^{\mathrm{i}(H-E_{\mathrm{g}})s} J \mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}s}\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi \\ &= \mathrm{e}^{\mathrm{i}(H-E_{\mathrm{g}})t}\Omega^{-}\mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi.\end{aligned} \tag{17.104}$$

Since D_δ is dense in $\mathcal{F}$, (17.103) holds. As a consequence, Ran $\Omega^{\mp}$ are reducing subspaces for H and $H - E_0$ restricted to Ran $\Omega^{\mp}$ is unitarily equivalent to H_{f} on $\mathcal{F}$.

As emphasized, the limit in (17.90) should not only hold for some states but for *all* $\psi \in \mathbb{C}^N \otimes \mathcal{F}$. It is useful to have a name for such a property.

Definition 17.4 $\Omega^{\pm}$ *are called asymptotically complete if*

$$\text{Ran } \Omega^{\pm} = \mathbb{C}^N \otimes \mathcal{F}. \tag{17.105}$$

If $\Omega^{\pm}$ are asymptotically complete, then they are unitary and diagonalize H as

$$(\Omega^{\pm})^{-1}(H - E_{\mathrm{g}})\Omega^{\pm} = H_{\mathrm{f}}. \tag{17.106}$$

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In particular, H has the absolutely continuous spectrum $[E_{\rm g}, \infty)$ of infinite multiplicity.

Under asymptotic completeness the long-time dynamics is fully characterized through

Proposition 17.5 (Relaxation to the ground state). *Let A be local in the sense that $A \in B(\mathbb{C}^N) \otimes \mathcal{W}$. Then for every $\psi \in \mathrm{Ran}\,\Omega^-$ with $\|\psi\| = 1$ we have*

$$\lim_{t\to\infty} \langle \mathrm{e}^{-\mathrm{i}Ht}\psi,\, A\mathrm{e}^{-\mathrm{i}Ht}\psi\rangle = \langle \psi_{\rm g},\, A\psi_{\rm g}\rangle. \tag{17.107}$$

In particular, if asymptotic completeness holds, then the limit (17.107) is valid for all $\psi \in \mathbb{C}^N \otimes \mathcal{F}$.

Proof: Let $\psi = \Omega^-\phi$ with $\phi \in D_\delta$. By (17.101) one has

$$\lim_{t\to\infty} \langle \mathrm{e}^{-\mathrm{i}Ht}\psi,\; A\mathrm{e}^{-\mathrm{i}Ht}\psi\rangle = \lim_{t\to\infty} \langle J\mathrm{e}^{-\mathrm{i}H_{\rm f}t}\phi,\, AJ\mathrm{e}^{-\mathrm{i}H_{\rm f}t}\phi\rangle, \tag{17.108}$$

which converges to the limit (17.107) as is seen by the argument explained in (17.98). Any $\psi \in \mathrm{Ran}\,\Omega^-$ can be approximated through states of the form $\Omega^-\phi$ with $\phi \in D_\delta$. □

Proposition 17.6 (Cook estimate). *Let the integrability condition (17.27) be satisfied. Then for all $\phi \in D_\delta$ the strong limit*

$$\lim_{t\to\infty} \mathrm{e}^{\mathrm{i}(H-E_{\rm g})t} J\mathrm{e}^{-\mathrm{i}H_{\rm f}t}\phi = \Omega^-\phi \tag{17.109}$$

exists.

Proof: If $\phi = \Omega$, the limit exists and is $\psi_{\rm g}$. Let then $\langle\Omega, \phi\rangle = 0$ and $\phi \in D_\delta \cap D(H_{\rm f})$. Then $J\mathrm{e}^{-\mathrm{i}H_{\rm f}t}\phi \in D(H)$ and we have

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{e}^{\mathrm{i}(H-E_{\rm g})t} J\mathrm{e}^{-\mathrm{i}H_{\rm f}t}\phi &= \mathrm{i}\mathrm{e}^{\mathrm{i}(H-E_{\rm g})t}(HJ - E_{\rm g}J - JH_{\rm f})\mathrm{e}^{-\mathrm{i}H_{\rm f}t}\phi \\ &= -\mathrm{e}^{\mathrm{i}(H-E_{\rm g})t} eQ\psi_{\rm g} \otimes_{\rm s} \cdot E_\varphi^- \mathrm{e}^{-\mathrm{i}H_{\rm f}t}\phi. \end{aligned}\tag{17.110}$$

Here

$$E_\varphi^- = \mathrm{i}\sum_{\lambda=1,2}\int \mathrm{d}^3k\widehat{\varphi}(k)\sqrt{\omega(k)/2}e_\lambda(k)a(k,\lambda) \tag{17.111}$$

and we used

$$a(f)(\psi_{\rm g}\otimes_{\rm s}\phi) = a(f)\psi_{\rm g}\otimes_{\rm s}\phi + \psi_{\rm g}\otimes_{\rm s} a(f)\phi, \tag{17.112}$$

$$a^*(f)(\psi_{\rm g}\otimes_{\rm s}\phi) = a^*(f)\psi_{\rm g}\otimes_{\rm s}\phi, \tag{17.113}$$

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which follow from the definition (17.92). Thus

$$\mathrm{e}^{\mathrm{i}(H-E_{\mathrm{g}})t} J \mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi = J\phi - e\int_0^t \mathrm{d}s\ \mathrm{e}^{\mathrm{i}(H-E_{\mathrm{g}})s} Q\psi_{\mathrm{g}} \otimes_{\mathrm{s}} \cdot E_\varphi^- \mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}s}\phi \qquad (17.114)$$

and it is to be shown that $t \to \|Q\psi_{\mathrm{g}} \otimes_{\mathrm{s}} \cdot E_\varphi^- \mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi\|$ is integrable for a dense set of ϕ's. For this purpose we define $L_\varphi \subset L^2_\perp(\mathbb{R}^3, \mathbb{R}^3)$ to be the linear subspace spanned by the set $\{\mathrm{e}^{-\mathrm{i}\omega t}\widehat{\varphi}\sqrt{\omega/2}e_\lambda \,|\, t \in \mathbb{R}\}$. We choose an n-photon vector in product form, $\phi = (0, \dots, \phi_n, 0, \dots)$, $\phi_n = \mathsf{S}\prod_{j=1}^n \widehat{f_j}$ with each factor being a sum

$$\widehat{f_j}(k,\lambda) = \sum_{\ell=1}^{\ell_j} \alpha_{j\ell}\mathrm{e}^{-\mathrm{i}\omega(k)t_{j\ell}}\widehat{\varphi}(k)\sqrt{\omega(k)/2}e_\lambda(k) + \widehat{f_j^\perp}(k,\lambda) \qquad (17.115)$$

with $\widehat{f_j^\perp}$ orthogonal to L_φ. Then

$$\|Q\psi_{\mathrm{g}} \otimes_{\mathrm{s}} \cdot E_\varphi^- \mathrm{e}^{-\mathrm{i}H_{\mathrm{f}}t}\phi\| \le \sum_{j=1}^n \Big| \sum_{\lambda=1,2} \int \mathrm{d}^3k \widehat{\varphi}(k)\sqrt{\omega(k)/2}e_\lambda(k) \cdot \widehat{f_j}(k,\lambda)\mathrm{e}^{-\mathrm{i}\omega(k)t}\Big|. \qquad (17.116)$$

Inserting from (17.115) yields a finite sum of terms of the form

$$\int \mathrm{d}^3k |\widehat{\varphi}(k)|^2 \omega(k) Q_\perp(k) \mathrm{e}^{-\mathrm{i}\omega(k)(t+s)} \qquad (17.117)$$

which are integrable, either by assumption or as a matter of fact for the Pauli–Fierz model, cf. the remark below Theorem 17.1.

Our argument establishes the limit (17.109) for a dense set of vectors in the n-photon subspace. By linearity and by taking uniform limits, this extends to all of D_δ. □

For $\psi \in \mathrm{Ran}\ \Omega^\pm$ one has all the desired properties, relaxation to the ground state as in Proposition 17.5, long-time asymptotics as in (17.90), and spectral measures which are absolutely continuous except for a possible mass at E_{g} with weight $\langle\psi, \psi_{\mathrm{g}}\rangle$. Asymptotic completeness, i.e. the property $\mathrm{Ran}\ \Omega^\pm = \mathbb{C}^N \otimes \mathcal{F}$, ensures that there are no states with unphysical dynamics.

Notes and references

Section 17.1

The dipole approximation in conjunction with the N-level approximation is common practice in atomic physics, for example Agarwal (1974), Cohen-Tannoudji

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et al. (1992). The unitary transformation (17.7) is linked with Power and Zienau (1959). It is also used by Bloch and Nordsieck (1937). For the special case of $N = 2$ the transition from Fock to non-Fock ground state is studied in considerable detail by Leggett *et al.* (1987), Spohn (1989), Amann (1991), and Weiss (1999). The corresponding Hamiltonian, H_{sb}, is known as the spin-boson model. The vector character of the Bose field is ignored and one sets $H_{\mathrm{at}} = \varepsilon\sigma_z$, $Q \cdot A_\varphi = \sigma_x \int \mathrm{d}^3k(\widehat{g}(k)a^*(k) + \widehat{g}(k)^*a(k))$. The t^{-2}-decay of (17.6) is the so-called Ohmic case, which is marginal for the transition to non-Fock. For small coupling H_{sb} has a unique ground state in $\mathbb{C}^2 \otimes \mathcal{F}$, whereas for large coupling H_{sb} acquires an infinite number of bosons, which leads to a two-fold degenerate ground state, both lying outside Fock space. Form factors with a decay different from t^{-2} have been also investigated.

Section 17.2

Landau (1927) uses density matrices in the description of the reduced state of the atom. He arrives at a variant of the master equation (17.32). Its diagonal part is often referred to as the Pauli master equation (Pauli 1928). A further influential work is Bloch (1928). The systematic weak coupling theory goes back to van Hove (1955, 1957) and has been further developed in response to the theoretical challenges in quantum optics. Just to remind the reader: In theoretical models of the laser one has to include dissipation for the field modes of the cavity to account for lossy reflection at the walls. For photon counting statistics one has to devise a simple model of a detector. An interesting exchange is Srinivas and Davies (1981) and Mandel (1981). For laser cooling and trapping the spontaneous emission and its associated recoil must be described in a concise way (Metcalf and van der Straten 1999). Thus the general problem of how to model open quantum systems necessarily comes into focus. On the classical level the addition of friction forces and possibly of noise serves well. But quantum mechanics poses constraints which are still of current research interest. As a short sample out of a large body of literature we refer to Lax (1968), Glauber (1969), Kossakowski (1972), Haake (1973), Spohn (1980), Carmichael (1999), Weiss (1999), and Breuer and Petruccione (2002). Our presentation here is based on Davies (1974, 1975, 1976a). He emphasizes time-averaging which has been overlooked mostly, but is done correctly in Cohen-Tannoudji *et al.* (1992) and Breuer and Petruccione (2002). The various generators of the dissipative evolution in the weak coupling limit are compared in Dümcke and Spohn (1979). In the text we discussed only single-time statistics. Stationary two-time statistics appear frequently in applications. Multitime statistics are studied by Dümcke (1983) within the presented framework.

Although even the most simplistic theory yields a shift of the spectral line, such predictions were not taken seriously. The rough estimate of Bethe (1947) and the more sophisticated computation of Grotch (1981) resulting in a cutoff-independent shift could have been done as early as 1930. It is only through the war-related research on radar that experimental techniques became available to measure such fine effects. The theory followed soon; see Schweber (1994) for an excellent account.

The weak coupling theory is also a useful tool in studying decoherence. In essence one starts the dynamics with a coherent superposition of two spatially well-separated wave packets. According to the appropriate quantum master equation such a coherence is destroyed on a time scale which is much, much shorter than the friction time scale. Properly speaking the master equation should not be used on such short time scales. When decoherence is due to the coupling to the quantized rediation field, Dürr and Spohn (2002) provide an analysis based on the dipole approximation. A complete discussion, avoiding the dipole approximation, is given by Breuer and Petruccione (2001), who also list references to earlier work.

The weak coupling theory had a mathematical spin-off, going way beyond the specific application at hand. The basic observation is that the dissipative semigroup T_t is the classical analog of the transition probability of a classical Markov process, the Markov character being embodied in the semigroup property $T_t T_s = T_{t+s}$, $t, s \geq 0$. T_t is positivity and normalization preserving, in the sense that if ρ is a density matrix so is $T_t \rho$. As recognized by Lindblad (1976) the stronger notion of complete positivity is very natural. It means that if $\mathcal{H}$ is extended to $\mathcal{H} \otimes \mathbb{C}^n$ and T_t in the trivial way to $T_t \otimes 1$, then $T_t \otimes 1$ is positivity preserving for every n. In this framework the possible types of generators are classified by Lindblad (1976). He also characterizes dissipation through the decrease of relative entropy (Lindblad 1975). Mixing and the long-time limit $t \to \infty$ are studied by Spohn (1976), Frigerio (1978), and Frigerio and Verri (1982). The generalization of the notion of detailed balance to the quantum context is discussed by Gorini *et al.* (1984). Most recommended introductions are Davies (1976b) and Alicki and Lendi (1987). Clearly the next level is to inquire about multitime statistics and their build-up from the semigroup T_t. This is a fairly straightforward step for classical Markov processes through the concept of conditional independence of past and future. No such thing seems to exist on the quantum level and the theory of quantum stochastic processes tries to provide a consistent framework, possibly guided by specific model systems, that can be analyzed in detail. We refer to Accardi, Frigerio and Lewis (1982), Lindblad (1983), Hudson and Parthasarathy (1984), Accardi *et al.* (1991), and Parthasarathy (1992), and the recent monographs by Alicki and Fannes (2001) and by Accardi *et al.* (2001).

Section 17.3

Already in his first work on radiation theory Dirac (1927) simplifies the problem to a single level coupled to a continuum of modes. A two-level atom coupled to the radiation field in the rotating wave approximation also reduces to a Friedrich–Lee-type Hamiltonian.

Complex dilations were investigated in connection with the study of Regge poles, cf. Reed and Simon (1978) for references. The mathematical framework is developed by Aguilar and Combes (1971) and Balslev and Combes (1971). A beautiful survey is Simon (1978). For an introduction we refer to Cycon *et al.* (1987). Hunziker (1990) focuses on the question of how to translate the results on the resolvent back to the real time-domain. Okamoto and Yajima (1985) observe that the dilation of the massive photon field can be used to unfold resonances. Resonances of the Pauli–Fierz model are studied in Bach, Fröhlich and Sigal (1995, 1998a, 1998b, 1999). They develop a renormalization-type iterative procedure to pin down the domain of analyticity of the complex dilated resolvent. This method is refined by Bach *et al.* (2002). An infinitesimal version based on Mourre-type estimates and the Feshbach method is Dereziński and Jakšić (2001).

Section 17.4

Our discussion is based on Davies (1976a). L_{D} is the Davies generator in the weak coupling theory. Line shapes are discussed by Weisskopf and Wigner (1930). Our examples for the spectral characteristics of the emitted light are taken from Cohen-Tannoudji *et al.* (1992), Chapter IIIC and Exercise 15.

Section 17.5

Potential scattering is discussed in Reed and Simon (1979) and N-body scattering in Cycon *et al.* (1987). We follow the presentation in Hübner and Spohn (1995a). The Cook argument is based on Høegh-Krohn (1970) who also studies the asymptotic electromagnetic fields; for a complete discussion see (Fröhlich, Griesemer and Schlein 2001). In the meantime the mathematical investigation of scattering of photons from an atom has flourished. For simplicity often the scalar field model of section 19.2 is studied. An important step is Dereziński and Gérard (1999) who establish asymptotic completeness in the case of massive photons, $\omega(k) = (k^2 + m_{\mathrm{ph}}^2)^{1/2}$, $m_{\mathrm{ph}} > 0$, and a strictly confining potential. Earlier work restricted to an N-level atom is Gérard (1996) and Skibsted (1998). An extension to massless photons under the condition $\widehat{\varphi}(0) = 0$ is Gérard (2002). For $m_{\mathrm{ph}} > 0$ Fröhlich, Griesemer and Schlein (2001, 2002) allow for potentials which are not

strictly confining, like the Coulomb potential. Thereby the channel for a freely propagating electron is opened up as it occurs in the description of the photoelectric effect (Bach, Klopp and Zenk 2002). Ammari (2000) establishes asymptotic completeness for the Nelson model of section 19.2 with ultraviolet cutoff removed. In these works asymptotic completeness is defined in such a way that H could have other eigenvalues besides its ground state. To exclude them one has to resort to Bach, Fröhlich and Sigal (1998a) and Fröhlich, Griesemer and Schlein (2002).

A different approach is to take the dipole approximation with harmonic confining potential. Since the Hamiltonian is quadratic, the scattering theory can be reduced to one-particle scattering with a finite rank perturbation. Maassen (1984) notices that for a weakly anharmonic confining potential the time-dependent perturbation series can be controlled uniformly in time. His estimates are improved and optimized in Maassen, Gută and Botvich (1999) and Fidaleo and Liverani (1999). With this input one can prove asymptotic completeness in the strong sense of Definition 17.4. The perturbing potential must be bounded and so small that the confining potential remains convex (Spohn 1997). The harmonic case is investigated by Arai (1983b).