Quantum theory of atomic fluorescence near a metal surface

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Quantum electrodynamics of an atom near a surface is a timely problem in current theoretical research. It appears, however, that a full dynamical theory, which includes both the time evolution of the atomic density operator and the details of the fluorescence radiation (temporal photon distribution) has never been formulated. In this paper the quantum theory of an atom near a perfect conductor is presented, and it is indicated how the formalism can be modified to account for more realistic optically active substrates. An expression is derived for the atomic spontaneous-decay Liouville operator from the Hamiltonian, which recovers the familiar results for the lifetimes and energy shifts. Furthermore, the emitted power is calculated as a function of time from the explicit expression for the radiation field. Comparison of the atomic-decay rates with the power of the emitted radiation shows the consistency of the theory, as far as the properties of the fluoresence are concerned. An unusual energy interference in the fluorescence, which is emitted by a multilevel atom, is predicted. Similarities and discrepancies with other theories are pointed out, and it is shown that especially the mirror theory has a very restricted applicability.

I. INTRODUCTION

Emission of fluorescence radiation by an atom in an excited state is inevitably accompanied by spontaneous decay to a lower state, which expresses energy conservation. Comprehension of the apparent quantized nature of the emitted field, and the conversion mechanism of internal atomic energy into radiation, was one of the main goals of the early quantum theory. It was realized that a full understanding of the process could only be achieved if the electromagnetic field were quantized, in the to-date familiar way.[1] Then the coupling of an atomic dipole moment to the vacuum field of the radiation provides a decay channel and the emitted photons are conceived as excitations of the photon field. The first victory of the theory was the prediction of the Einstein *A*-coefficient (inverse lifetime of an atomic state) and its relation to the width of a spectral emission line, which confirmed the Heisenberg uncertainty relation. It is sometimes argued[2] that a quantization of the field can be avoided, and it is possible indeed to construct a semiclassical field theory, which provides the correct expressions for lifetimes and energy flows. This is due to the fact that these features are determined by single-time averages, which merely require the proper geometry for the interference of waves. Recent experiments[3,4] on two-photon correlations of fluorescence radiation, however, have unambiguously established the fundamental quantum character of the radiation field. Especially the observed phenomena antibunching and sub-Poissonian photon statistics[5] are in conflict with semiclassical radiation theories.[6–9]

Spontaneous emission is brought about by the interaction of the atomic dipole with the surrounding radiation field. Hence, it can be anticipated that the presence of optically active media or boundaries will modify the dynamics, since they alter the solution for the free field. Incontestable evidence for the change in lifetimes of molecules which are positioned in the vicinity of a dielectric, was provided by the classic experiments of Drexhage[10] and others.[11–14] Subsequent experiments focused on the absorption profile of atoms near a medium,[15–18] and on the coupling of the atomic dipole to the plasmon field of the substrate.[19–23] Theoretical approaches which were developed to explain the observed phenomena, include semiclassical radiation theory,[24] method of images,[25–30] and the linear-response formalism.[31–36] Disadvantages which are shared by various theories are: (1) a semiclassical component in the formalism can never yield correctly all observable properties of the radiation field, due to its essential quantum nature; (2) the classical concept of images fails in quantum electrodynamics, which is most obvious from the fact that the atomic density operator is merely a matching parameter, as will be explained below, rather than the fundamental operator which reflects the state of the system; (3) linear-response theory is a static formulation of a dynamical problem, although it yields the correct answers. We believe that a more profound comprehension of the basic mechanisms should be achieved from a proper interpretation of the dynamics; (4) a number of computations hinge on the commutator algebra for a two-level model.

We present a full quantum-electrodynamical formalism of fluorescence, emitted by an atom near a metal surface. Atoms are allowed to have many (degenerate) levels, and there are no artificial parametrizations of an initial state (as in the mirror approach). It is pointed out how the various observable properties of the radiation field can be evaluated in a straightforward fashion. In this paper we intend to provide the framework for these calculations, and to show the consistency and applicability of the methods. Extensive results will be the topic of a subsequent paper. We restrict the presentation to the case of a perfectly conducting substrate, which is a limitation since it suppresses interesting features,[37–41] arising from the coupling to plasmon excitations. It should be obvious from the work of Carniglia and Man-

del,[42] however, that a finite optical penetrability of the surface can be included along the very same lines. Besides that, the applicability of the theory pertains to observable properties like decay constants for the atomic density operator, and temporal (and thereby spectral) features of the fluorescence. A nonrelativistic theory will, of course, never yield correct results for the Lamb shift, but can still be regarded as consistent in the sense that it provides the renormalizable expressions, as pointed out by Ackerhalt *et al.*[43] Furthermore, the Casimir–Polder attraction between the atom and the surface will not be addressed here, since it is not directly related to the problem of fluorescent emission. We refer to the paper by Milonni,[44] where this issue is treated with the same approach as in the present paper.

II. BASIC CONCEPT

Divide space into the parts $z > 0$ and $z < 0$ in a Cartesian coordinate system, where the region $z < 0$ is occupied by a medium (perfect conductor) and $z > 0$ is empty space. An atom with dipole-moment operator $\boldsymbol{\mu}$ is located above the surface at $\mathbf{h} = h\mathbf{e}_z$, $h > 0$. The issue is to formulate the appropriate quantum electrodynamics (QED) for this configuration. Since the atom only couples to the electric field through an electric-dipole interaction, we can omit the magnetic field. Vectors and vector operators can be divided into a perpendicular and a parallel part with respect to the xy plane, as for instance

$$\boldsymbol{\mu} = \boldsymbol{\mu}_\perp + \boldsymbol{\mu}_\| \tag{2.1}$$

for the atomic dipole.

In QED the electric field $\mathbf{E}(\mathbf{r},t)$ is a Heisenberg-picture operator field, and its time evolution is governed by the Liouvillian L of the entire system, according to

$$\mathbf{E}(\mathbf{r},t) = e^{iL(t-t_0)}\mathbf{E}(\mathbf{r},t_0), \tag{2.2}$$

where L is related to the Hamiltonian H by

$$L\cdot = \hbar^{-1}[H,\cdot]. \tag{2.3}$$

With Eq. (2.3) we can write $\mathbf{E}(\mathbf{r},t)$ alternatively as

$$\mathbf{E}(\mathbf{r},t) = e^{(i/\hbar)H(t-t_0)}\mathbf{E}(\mathbf{r},t_0)e^{-(i/\hbar)H(t-t_0)}. \tag{2.4}$$

The operator $\exp[iL(t-t_0)]$ is, by definition, the time propagator in the Heisenberg picture, and, therefore, any operator $A(0)$ defines a time-dependent operator $A(t) = \exp(iLt)A(0)$. In radiation theory we have an electromagnetic field $\mathbf{E}(\mathbf{r},t)$, $\mathbf{B}(\mathbf{r},t)$, and moving charges, which are represented by a charge density $\rho(\mathbf{r},t)$ and a symmetrized-current density $\mathbf{j}(\mathbf{r},t)$. The last two operator fields are determined by the position and momentum operators of the electrons and nuclei in a complicated way. Fortunately, it can be proven[45] that these four Heisenberg fields are related in their $\mathbf{r}$ and t dependences by the Maxwell equations. This implies that integrals of the equations are identical in form to the classical integrals, irrespective of the mechanism of generation of the fields. The conditions at a discontinuity especially acquire the same form, and for our system this reads

$$\mathbf{E}(\mathbf{r},t)_\| = 0, \quad \text{in } z = 0. \tag{2.5}$$

Of paramount importance for the development of a consistent theory is the notion that restriction (2.5) is an operator

equation in some Hilbert space, parametrized with $\mathbf{r}$ and t, and Eq. (2.5) expresses that for $z = 0$ the parallel component of every matrix element, which is a vector in three-dimensional configuration space, should vanish identically. We remark that it follows from Eq. (2.2) that it is sufficient if this boundary condition holds for $t = t_0$.

Moving charges in the atom might emit radiation, which produces an incident field on the surface. Charges on the surface experience this field and redistribute accordingly. Due to this rearrangement they also emit radiation, which is usually regarded as the reflected field. Additionally, we have a free field, which is present even if there were no atom. Without a medium, this would be the vacuum field, but this field also interacts with the charges in the substrate, and, hence, it produces a reflected field. Based on this identification we divide the electric field as

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}(\mathbf{r},t)_f + \mathbf{E}(\mathbf{r},t)_d, \tag{2.6}$$

with $f \equiv$ free, $d \equiv$ dipole. It should be noted that $\mathbf{E}(\mathbf{r},t)_f$ is not really a free field, because it is partially generated by the surface charges. Since $\mathbf{E}(\mathbf{r},t)_f$ remains present if we remove the atom, both the f and the d-components in Eq. (2.6) must obey the boundary condition (2.5) separately. It remains to determine $\mathbf{E}_f$ and $\mathbf{E}_d$ and the Hamiltonian which governs their time evolution.

III. FREE FIELD

The method of images in classical electrodynamics relies on the fact that the solution of Maxwell's equations is unique. Then we can simply construct a solution from symmetry considerations for $z > 0$, which obeys the boundary condition for $z \downarrow 0$. In the case of an incident plane wave with wave vector $\mathbf{k}$ and polarization $\boldsymbol{\epsilon}$, divided as

$$\mathbf{k} = \mathbf{k}_\| + \mathbf{k}_\perp, \quad \boldsymbol{\epsilon} = \boldsymbol{\epsilon}_\perp + \boldsymbol{\epsilon}_\|, \tag{3.1}$$

with $\mathbf{k}\cdot\boldsymbol{\epsilon} = 0$, $\boldsymbol{\epsilon}\cdot\boldsymbol{\epsilon}^* = 1$, and frequency $\omega_k = ck$, we superpose a plane wave (reflected wave), which has wave number $\mathbf{k}'$ and polarization $\boldsymbol{\epsilon}'$ given by

$$\mathbf{k}' = \mathbf{k}_\| - \mathbf{k}_\perp, \quad \boldsymbol{\epsilon}' = \boldsymbol{\epsilon}_\perp - \boldsymbol{\epsilon}_\|, \tag{3.2}$$

and the same amplitude. It follows from Eqs. (3.1) and (3.2) that $\mathbf{k}'\cdot\boldsymbol{\epsilon}' = 0$, $\boldsymbol{\epsilon}'\cdot\boldsymbol{\epsilon}'^* = 1$, and $\omega_{k'} = \omega_k$. Then the sum field is the desired solution.

Transposition of this approach to the free field of QED requires some care, partially because of the operator nature of that field. In vacuum (no atom, no suface) the expression for the field reads

$$\mathbf{E}(\mathbf{r},t)_v = \sum_{\mathbf{k}s}\sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V}}\boldsymbol{\epsilon}_{\mathbf{k}s}e^{i[\mathbf{k}\cdot\mathbf{r}-\omega_k(t-t_0)]}a_{\mathbf{k}s} + \text{h.c.}, \tag{3.3}$$

where V is the (large) quantization volume, and the summation over $\mathbf{k}$ extends over all modes which are supported by the volume V under periodic boundary conditions. The subscript s denotes two polarization directions, perpendicular to $\mathbf{k}$, and they will be taken to be real. The "amplitudes" of the field modes are the annihilation (creation) operators $a_{\mathbf{k}s} (a_{\mathbf{k}s}^\dagger)$, which are defined by their commutation relations

$$[a_{\mathbf{k}_1 s_1}, a_{\mathbf{k}_2 s_2}] = 0, \quad [a_{\mathbf{k}_1 s_1}, a_{\mathbf{k}_2 s_2}^\dagger] = \delta_{\mathbf{k}_1 \mathbf{k}_2}\delta_{s_1 s_2}. \tag{3.4}$$

Now it is tempting to obtain the free field in the presence of

the surface by adding the reflected wave $\mathbf{k}'s'$ to every mode $\mathbf{k}s$, just as for the classical field. This would indeed give a solution of the homogeneous Maxwell equations and obey the boundary condition. However, every multiple of this field is also a solution. For a single incident plane wave there is no question about this normalization, since the external field is generated by charges and currents, so we merely have to add the reflected wave, which is the response of the medium. The vacuum field $\mathbf{E}(\mathbf{r},t)_v$ is a freely evolving operator field, which has no source, and, hence, its amplitude cannot be determined from classical analogs. In the presence of the conductor, the most general solution of the homogeneous Maxwell equations for the free-field follows after the substitution

$$a_{\mathbf{k}s}\boldsymbol{\epsilon}_{\mathbf{k}s}e^{i\mathbf{k}\cdot\mathbf{r}} \rightarrow \alpha a_{\mathbf{k}s}(\boldsymbol{\epsilon}_{\mathbf{k}s}e^{i\mathbf{k}\cdot\mathbf{r}} + \boldsymbol{\epsilon}'_{\mathbf{k}s}e^{i\mathbf{k}'\cdot\mathbf{r}}) \qquad (3.5)$$

for every mode $\mathbf{k}s$ in the plane-wave expansion (3.3) of the vacuum field. Then $\mathbf{E}(\mathbf{r},t)_f$ is an operator field which obeys the boundary condition by construction. The multiplicative parameter α would equal unity for an external field, but remains yet to be fixed for a free field. Just as for the vacuum field, we require that a single-photon excitation of the mode $\mathbf{k}s$ carries an energy quantum $\hbar\omega_k$. From Eq. (3.5) we see that both the originally present wave and the added wave have the same amplitude, and, therefore, they will contribute equally to the energy. Since the field intensity is proportional to the square of the amplitude, we have the only choice

$$\alpha = 1/\sqrt{2}. \qquad (3.6)$$

Substitution of the replacement (3.5) into Eq. (3.3), then yields for the free field

$$\mathbf{E}(\mathbf{r},t)_f = \sum_{\mathbf{k}s}\sqrt{\frac{\hbar\omega_k}{\epsilon_0 V}}a_{\mathbf{k}s}e^{i[\mathbf{k}_{\|}\cdot\mathbf{r} - \omega_k(t - t_0)]}$$
$$\times [\cos(\mathbf{k}_{\perp}\cdot\mathbf{r})\boldsymbol{\epsilon}^{\perp}_{\mathbf{k}s} + \sin(\mathbf{k}_{\perp}\cdot\mathbf{r})\boldsymbol{\epsilon}^{\|}_{\mathbf{k}s}] + \text{h.c.} \qquad (3.7)$$

An alternative derivation[42] of Eq. (3.7) can be obtained by repeating the quantization procedure, which leads to Eq. (3.3) for the vacuum field, in the presence of a boundary. We have avoided this complication by taking advantage of the fact that the vacuum field is already known, which allows a direct construction of the free-field by symmetry considerations. Of course, this relies on our simple geometry, and is not applicable in general.

IV. DIPOLE FIELD

As in classical electrodynamics, we can find the dipole field from symmetry considerations. In free space the dipole field is explicitly[44]

$$\mathbf{E}(\mathbf{r},t)_1 = -\frac{1}{4\pi\epsilon_0 c^2 r_+}\frac{d^2}{dt^2}[\hat{\mathbf{r}}_+ \times \boldsymbol{\mu}(t - r_+/c)] \times \hat{\mathbf{r}}_+$$
$$-\frac{1}{4\pi\epsilon_0 r_+^2}\left(\frac{1}{c}\frac{d}{dt} + \frac{1}{r_+}\right)$$
$$\times \{\boldsymbol{\mu}(t - r_+/c) - 3[\hat{\mathbf{r}}_+\cdot\boldsymbol{\mu}(t - r_+/c)]\hat{\mathbf{r}}_+\}, \qquad (4.1)$$

with $\mathbf{r}_+ = \mathbf{r} - \mathbf{h}$ and $\hat{\mathbf{r}}_+ = \mathbf{r}_+/r_+$. Then the dipole field in the presence of the conductor becomes

$$\mathbf{E}(\mathbf{r},t)_d = \mathbf{E}(\mathbf{r},t)_1 + \mathbf{E}(\mathbf{r},t)_2, \qquad (4.2)$$

where $\mathbf{E}(\mathbf{r},t)_2$ follows from Eq. (4.1) after the substitution

$\mathbf{r}_+ \rightarrow \mathbf{r}_- = \mathbf{r} + \mathbf{h}$ and the replacement of $\boldsymbol{\mu}$ by its mirror complement

$$\boldsymbol{\mu}' = \boldsymbol{\mu}_\perp - \boldsymbol{\mu}_{\|} \qquad (4.3)$$

in terms of the subdivision of $\boldsymbol{\mu}$ from Eq. (2.1). For $z = 0$ we have $r_+ = r_-$ and it is easy to check with some vector algebra that the operator field $\mathbf{E}(\mathbf{r},t)_d$ is perpendicular to the xy plane.

It is important to note the $\boldsymbol{\mu}$ and $\boldsymbol{\mu}'$ are operators in the same Hilbert space, which allows us to write $(\boldsymbol{\mu})_{\|} + (\boldsymbol{\mu}')_{\|} = 0$. In classical electrodynamics this is obvious, since $\boldsymbol{\mu}$ and $\boldsymbol{\mu}'$ are simply vectors in configuration space, rather than operators. Then the system of a dipole $\boldsymbol{\mu}$ in $\mathbf{r} = \mathbf{h}$ above a conductor is equivalent to a dipole $\boldsymbol{\mu}$ in $\mathbf{r} = \mathbf{h}$ and a dipole $\boldsymbol{\mu}'$ in $\mathbf{r} = -\mathbf{h}$, as long as we only consider the field for $z \geqslant 0$. In QED, the field for $z \geqslant 0$ attains an identical expression in form, but the system is not equivalent to a configuration of two atoms with dipole moments $\boldsymbol{\mu}$ and $\boldsymbol{\mu}'$ anymore. If we would replace the surface by a mirror atom with a dipole moment $\boldsymbol{\mu}'$, positioned at $\mathbf{r} = -\mathbf{h}$, than this $\boldsymbol{\mu}'$ would be an operator in a different atomic Hilbert space (of atom 2), and we could not add $(\boldsymbol{\mu})_{\|}$ and $(\boldsymbol{\mu}')_{\|}$. Consequently, this replacement would violate the boundary condition (2.5). This situation is reminiscent of the superposition of the waves $\mathbf{k}s$ and $\mathbf{k}'s$ from the previous section. There, the annihilation operators $a_{\mathbf{k}s}$ and $a_{\mathbf{k}'s}$ act on a different part of Hilbert space, which prevents a combination of the modes $\mathbf{k}s$ and $\mathbf{k}'s$ in the expansion (3.3) of the vacuum field, in order to construct a field with the correct boundary condition. We conclude that the correspondence with the classical treatment does not go further than Eq. (4.2), which expresses the similarity in geometry.

V. HAMILTONIAN

In the representations (4.1) and (4.2), the time dependence of the radiation field is contained in $\boldsymbol{\mu}(t)$ and $\boldsymbol{\mu}'(t)$, and its $\mathbf{r}$ dependence is the usual dipole distribution. The time evolution of the Heisenberg operator $\boldsymbol{\mu}(t) = \exp[iL(t - t_0)]\boldsymbol{\mu}(t_0)$ is determined after a definition of the Hamiltonian. However, we cannot choose H or L arbitrarily, because they must generate the field $\mathbf{E}(\mathbf{r},t)$ according to Eq. (2.2) or Eq. (2.4). Apart from H, we have to specify the field $\mathbf{E}(\mathbf{r},t)$ and the dipole moment $\boldsymbol{\mu}(t)$ on the time t_0, where the Schrödinger and Heisenberg pictures coincide. Then the Hamiltonian governs their time evolution towards $t > t_0$.

As initial values we choose

$$\boldsymbol{\mu}(t_0) = \boldsymbol{\mu}, \quad \mathbf{E}(\mathbf{r},t_0) = \mathbf{E}(\mathbf{r},t_0)_f, \qquad (5.1)$$

with $\boldsymbol{\mu}$ the dipole moment in the Schrödinger picture. The radiation field is taken to be the free field on $t = t_0$. In analogy with the problem in absence of the surface, we try

$$H = H_a + H_f - \boldsymbol{\mu}\cdot\mathbf{E}(\mathbf{h},t_0)_f, \qquad (5.2)$$

with H_a the atomic Hamiltonian (internal structure), and H_f the free-field Hamiltonian

$$H_f = \sum_{\mathbf{k}s}\hbar\omega_k a^\dagger_{\mathbf{k}s}a_{\mathbf{k}s}. \qquad (5.3)$$

The interaction is established by the dipole coupling

$-\mu(t)\cdot\mathbf{E}(\mathbf{h},t)$, which reduces to $-\mu\cdot\mathbf{E}(\mathbf{h},t_0)_f$ at $t=t_0$, due to Eq. (5.1).

A rigorous check on the consistency of the theory can be made by evaluating the radiation field explicitly. At the initial time the field is given by Eq. (3.7) with $t=t_0$. This expression involves only the operators $a_{\mathbf{k}s}$ and $a_{\mathbf{k}s}^\dagger$, and, hence, for $t>t_0$ the mode expansion of the total field reads

$$\mathbf{E}(\mathbf{r},t)=\sum_{\mathbf{k}s}\sqrt{\frac{\hbar\omega_k}{\epsilon_0 V}}a_{\mathbf{k}s}(t)e^{i\mathbf{k}_\parallel\cdot\mathbf{r}}$$
$$\times[\cos(\mathbf{k}_\perp\cdot\mathbf{r})\epsilon_{\mathbf{k}s}^\perp+i\sin(\mathbf{k}_\perp\cdot\mathbf{r})\epsilon_{\mathbf{k}s}^\parallel]+\text{h.c.},$$
(5.4)

which shows that it is sufficient to consider the time evolution of $a_{\mathbf{k}s}(t)$.

From $a_{\mathbf{k}s}(t)=\exp[iL(t-t_0)]a_{\mathbf{k}s}$ it follows that $a_{\mathbf{k}s}(t)$ obeys the differential equation

$$i\hbar\frac{d}{dt}a_{\mathbf{k}s}(t)=[a_{\mathbf{k}s}(t),H],$$
(5.5)

with initial condition $a_{\mathbf{k}s}(t_0)=a_{\mathbf{k}s}$. After substitution of the Hamiltonian (5.2), and a first integration, we obtain

$$a_{\mathbf{k}s}(t)=e^{-i\omega_k(t-t_0)}a_{\mathbf{k}s}+i\sqrt{\frac{\omega_k}{\hbar\epsilon_0 V}}\int_{t_0}^t dt'\,e^{-i\omega_k(t-t')}$$
$$\times\mu(t')\cdot[\cos(\mathbf{k}\cdot\mathbf{h})\epsilon_{\mathbf{k}s}^\perp-i\sin(\mathbf{k}\cdot\mathbf{h})\epsilon_{\mathbf{k}s}^\parallel],$$
(5.6)

where we used $\mathbf{k}_\perp\cdot\mathbf{h}=\mathbf{k}\cdot\mathbf{h}$ and $\mathbf{k}_\parallel\cdot\mathbf{h}=0$. If we now substitute this expression into Eq. (5.4), then we notice that the term $\exp[-i\omega_k(t-t_0)]a_{\mathbf{k}s}$ gives rise to the free field $\mathbf{E}(\mathbf{r},t)_f$ from Eq. (3.7). The remaining term is by definition $\mathbf{E}(\mathbf{r},t)_d$, which is found to be

$$\mathbf{E}(\mathbf{r},t)_d=\sum_{\mathbf{k}s}\frac{i\omega_k}{\epsilon_0 V}\int_{t_0}^t dt'\exp[-i\omega_k(t-t')+i\mathbf{k}_\parallel\cdot\mathbf{r}]$$
$$\times[\cos(\mathbf{k}_\perp\cdot\mathbf{r})\epsilon_{\mathbf{k}s}^\perp+i\sin(\mathbf{k}_\perp\cdot\mathbf{r})\epsilon_{\mathbf{k}s}^\parallel]$$
$$\times\mu(t')\cdot[\cos(\mathbf{k}\cdot\mathbf{h})\epsilon_{\mathbf{k}s}^\perp-i\sin(\mathbf{k}\cdot\mathbf{h})\epsilon_{\mathbf{k}s}^\parallel]+\text{h.c.}$$
(5.7)

With the relations between $\mathbf{k}$, ϵ and $\mathbf{k}'$, ϵ' we can write

$$e^{i\mathbf{k}_\parallel\cdot\mathbf{r}}[\cos(\mathbf{k}_\perp\cdot\mathbf{r})\epsilon_{\mathbf{k}s}^\perp+i\sin(\mathbf{k}_\perp\cdot\mathbf{r})\epsilon_{\mathbf{k}s}^\parallel]$$
$$=\tfrac{1}{2}(\epsilon_{\mathbf{k}s}e^{i\mathbf{k}\cdot\mathbf{r}}+\epsilon_{\mathbf{k}s}'e^{i\mathbf{k}'\cdot\mathbf{r}})$$
(5.8)

and we notice that the two terms in round brackets contribute equally to the summation in Eq. (5.7). Therefore, we can drop the second term and multiply the remaining expression by a factor of 2. Next we use the relation

$$\mu(t)\cdot\epsilon_{\mathbf{k}s}'=\mu'(t)\cdot\epsilon_{\mathbf{k}s},$$
(5.9)

write $\tau=t-t'$, and take the limit $t_0\to-\infty$, which finally gives

$$\mathbf{E}(\mathbf{r},t)_d=\sum_{\mathbf{k}s}\frac{i\omega_k}{2\epsilon_0 V}\int_0^\infty d\tau\,e^{-i\omega_k\tau}\epsilon_{\mathbf{k}s}$$
$$\times\{\epsilon_{\mathbf{k}s}\cdot[e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{h})}\mu(t-\tau)$$
$$+e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{h})}\mu'(t-\tau)]\}+\text{h.c.}$$
(5.10)

In this form we recognize a source term proportional to $\mu(t-\tau)$, which apparently has its origin at $\mathbf{r}=\mathbf{h}$, and a similar one in $\mathbf{r}=-\mathbf{h}$ with dipole moment $\mu'(t-\tau)$. In the

Appendix we show explicitly that Eq. (5.10) is identical to the dipole field from Sec. IV.

VI. MIRROR IMAGE OF A QUANTUM DIPOLE

Now that we have identified the Hamiltonian, we can raise the question as to what the relation is with the frequently applied method of images, where one takes

$$H=H_a+H_{\text{im}}+H_f-\mu_a$$
$$\cdot\mathbf{E}(\mathbf{h},t_0)_v-\mu_{\text{im}}\cdot\mathbf{E}(-\mathbf{h},t_0)_v.$$
(6.1)

Here the substrate is replaced by an identical mirror atom with Hamiltonian H_{im} and dipole moment μ_{im}. Matrix elements of μ_a and μ_{im} between corresponding states are related as μ and μ' in Eq. (4.3) Although the atoms are regarded as identical, which is evident from the fact that their Hamiltonians are assigned the same matrix elements, their operators act on different portions of Hilbert space. The entire Hilbert space is spanned by direct-product states of radiation, atom, and image states. Furthermore, we note that our free field does not come into the picture anymore, and that the dipoles couple to the vacuum field. As the initial field, one takes the vacuum field at $t=t_0$.

In order to elucidate the connection with our approach, we first observe that $\mathbf{E}(\mathbf{h},t_0)_f$ equals

$$\mathbf{E}(\mathbf{h},t_0)_f=\sum_{\mathbf{k}s}\sqrt{\frac{\hbar\omega_k}{\epsilon_0 V}}a_{\mathbf{k}s}[\cos(\mathbf{k}\cdot\mathbf{h})\epsilon_{\mathbf{k}s}^\perp$$
$$+i\sin(\mathbf{k}\cdot\mathbf{h})\epsilon_{\mathbf{k}s}^\parallel]+\text{h.c.}$$
(6.2)

Subsequently we write $\epsilon_{\mathbf{k}s}^\perp=\tfrac{1}{2}(\epsilon_{\mathbf{k}s}+\epsilon_{\mathbf{k}s}')$, $\epsilon_{\mathbf{k}s}^\parallel=\tfrac{1}{2}(\epsilon_{\mathbf{k}s}-\epsilon_{\mathbf{k}s}')$ and divide the sine and cosine in sums of exponentials. Comparison with the vacuum field (3.3) then shows that the Hamiltonian (5.2) can alternatively be cast in the form

$$H=H_a+H_f-[\mu\cdot\mathbf{E}(\mathbf{h},t_0)_v+\mu'\cdot\mathbf{E}(-\mathbf{h},t_0)_v]/\sqrt{2}.$$
(6.3)

Obviously, there is no mirror Hamiltonian, but more remarkable is the appearance of the factor $1/\sqrt{2}$, which is not a computational error. This clearly exhibits a difference between the correct quantum-mirror Hamiltonian and the off-the-wall guess (6.1) Furthermore, this clarifies why calculations with Hamiltonian (6.1) always require artificial density operators for the evaluation of expectation values. Depending on the orientation of the dipole, one has to take a symmetric or antisymmetric combination of atom and mirror states in order to match overall factors. It should be emphasized that the choice of density operator has nothing to do with the choice of Hamiltonian. In the next two sections we evaluate the lifetimes of the atomic transitions with the aid of Hamiltonian (6.3), without any reference to a specific density operator. This reveals that the coupling to the free field, which provides the mechanism for spontaneous decay, is a dynamical property of the system, rather than a consequence of the preparation of the atom in a certain state.

VII. SPONTANEOUS DECAY

The time evolution of the density operator $\rho(t)$ for the combined system of atom and radiation is governed by the Liouville equation

$$i\hbar\frac{d}{dt}\rho(t) = [H,\rho(t)], \quad \rho(t)^\dagger = \rho(t), \quad \mathrm{Tr}\,\rho(t) = 1, \tag{7.1}$$

where H is given by Eq. (5.2). Of particular importance is the reduced density operator of the atom, defined by

$$\rho_a(t) = \mathrm{Tr}_r\,\rho(t), \tag{7.2}$$

with the trace taken over all states of the radiation field. With standard reservoir theory[47] we find that $\rho_a(t)$ obeys the equation of motion

$$i\frac{d}{dt}\rho_a(t) = (L_a - i\Gamma)\rho_a(t). \tag{7.3}$$

The free evolution of the atom is represented by the Liouvillian L_a, which acts on an arbitrary density operator σ according to

$$L_a\sigma = \hbar^{-1}[H_a,\sigma]. \tag{7.4}$$

Coupling to the radiation field is incorporated in an effective decay-operator Γ, which is found to be

$$\Gamma\sigma = \sum_i [\mu_i, Q_i\sigma - \sigma Q_i^\dagger], \tag{7.5}$$

where the summation runs over the Cartesian components $i = x, y, z$ of the vector operators $\boldsymbol{\mu}$ and $\mathbf{Q}$. The Hilbert space operator (not a Liouvillian) Q_i is given by

$$Q_i = \frac{1}{2\pi}\int_0^\infty d\tau\, e^{-iL_a\tau}\left[\sum_j G_{ij}(\tau)\mu_j\right], \tag{7.6}$$

in terms of the free-evolution Liouvillian L_a and the reservoir correlation function

$$G_{ij}(\tau) = \frac{2\pi}{\hbar^2}\langle 0|E_i(\mathbf{h},t_0+\tau)_f E_j(\mathbf{h},t_0)_f|0\rangle. \tag{7.7}$$

By taking the vacuum state $|0\rangle\langle 0|$ for the density operator of the radiation field, we have adopted the zero-temperature limit, which is not at all essential but pertains to most practical situations. Note that the radiation field only enters through $G_{ij}(\tau)$ in the relaxation operator. It is precisely this feature that assures the possibility of a generalization to more complicated geometries, and to solids with more realistic optical properties.[48] Sometimes $G_{ij}(\tau)$ is termed the (equal space-point) Green function.

Solving Eq. (7.3) for any particular atom requires an expansion in matrix elements. If we denote the atomic states by $|i,\nu\rangle$, where the quantum number i indicates the energy $\hbar\omega_i$ and ν any degeneracy, then we can write the Hamiltonian H_a as

$$H_a = \sum_i \hbar\omega_i P_i, \tag{7.8}$$

where P_i is the projector onto the subspace with energy $\hbar\omega_i$, e.g.,

$$P_i = \sum_\nu |i,\nu\rangle\langle i,\nu|. \tag{7.9}$$

With this notation, the exponential which occurs in Eq. (7.6) can be expanded as

$$e^{-iL_a\tau}\sigma = \sum_{kl} e^{-i\Delta_{kl}\tau}P_k\sigma P_l, \tag{7.10}$$

in terms of the Bohr frequencies $\Delta_{kl} = \omega_k - \omega_l$. Substitution into Eq. (7.6) then gives

$$Q_i = \frac{1}{2}\sum_{jkl}\widetilde{G}_{ij}(\Delta_{lk})P_k\mu_j P_l, \tag{7.11}$$

where we have introduced the Fourier–Laplace transform of the correlation function as

$$\widetilde{G}_{ij}(\omega) = \frac{1}{\pi}\int_0^\infty d\tau\, e^{i\omega\tau}G_{ij}(\tau). \tag{7.12}$$

Combining expression (7.11) with Eq. (7.5), and using the closure relation $\Sigma P_i = 1$ then amounts to the representation

$$\Gamma\sigma = \frac{1}{2}\sum_{\substack{abc\\ \alpha\beta\gamma}}(g_{\substack{caab\\ \gamma\alpha\alpha\beta}}|c,\gamma\rangle\langle b,\beta|\sigma + g^*_{\substack{caab\\ \gamma\alpha\alpha\beta}}\sigma|b,\beta\rangle\langle c,\gamma|)$$

$$\quad - \frac{1}{2}\sum_{\substack{abcd\\ \alpha\beta\gamma\delta}}(g_{\substack{cdab\\ \gamma\delta\alpha\beta}}|a,\alpha\rangle\langle b,\beta|\sigma|c,\gamma\rangle\langle d,\delta|$$

$$\quad + g^*_{\substack{cdab\\ \gamma\delta\alpha\beta}}|d,\delta\rangle\langle c,\gamma|\sigma|b,\beta\rangle\langle a,\alpha|), \tag{7.13}$$

which contains only the set of parameters

$$g_{\substack{abcd\\ \alpha\beta\gamma\delta}} = \sum_{ij}\widetilde{G}_{ij}(\Delta_{dc})\langle a,\alpha|\mu_i|b,\beta\rangle\langle c,\gamma|\mu_j|d,\delta\rangle. \tag{7.14}$$

This expression clearly disentangles the atomic properties (matrix elements of $\boldsymbol{\mu}$) from the field correlation $\widetilde{G}_{ij}(\Delta_{dc})$, as they appear in the spontaneous-decay operator.

Similarly we can write for L_a,

$$L_a\sigma = \sum_{b\beta}\omega_b(|b,\beta\rangle\langle b,\beta|\sigma - \sigma|b,\beta\rangle\langle b,\beta|), \tag{7.15}$$

which involves only the atomic frequencies ω_b. Taking matrix elements of Eqs. (7.13) and (7.15) then finally leads to the equation of motion (7.3) in matrix elements:

$$\frac{d}{dt}\langle k,\nu|\rho_a|k',\nu'\rangle$$

$$= -i\Delta_{kk'}\langle k,\nu|\rho_a|k',\nu'\rangle - \frac{1}{2}\sum_{\substack{ab\\ \alpha\beta}}(g_{\substack{kaab\\ \nu\alpha\alpha\beta}}\langle b,\beta|\rho_a|k',\nu'\rangle$$

$$\quad + g^*_{\substack{k'aab\\ \nu'\alpha\alpha\beta}}\langle k,\nu|\rho_a|b,\beta\rangle)$$

$$\quad + \frac{1}{2}\sum_{\substack{ab\\ \alpha\beta}}(g_{\substack{bk'ka\\ \beta\nu'\nu\alpha}} + g^*_{\substack{akk'b\\ \alpha\nu\nu'\beta}})\langle a,\alpha|\rho_a|b,\beta\rangle. \tag{7.16}$$

Equation (7.16) constitutes a set of coupled linear first-order differential equations which can easily be solved for any initial state $\rho_a(0)$.

VIII. RELAXATION CONSTANTS

In view of Eq. (7.14) and the equation of motion (7.16), the effect of the presence of radiation on the atomic density operator $\rho_a(t)$ is completely determined by the reservoir correlation function $G_{ij}(\tau)$. If we insert the expression (3.7) with $\mathbf{r} = \mathbf{h}$ in the definition (7.7) and take the expectation value in the vacuum state, we obtain

$$G_{ij}(\tau) = \frac{2\pi}{\hbar\epsilon_0 V}\sum_{\mathbf{k}s}\omega_k e^{-i\omega_k\tau}$$

$$\times [\cos(\mathbf{k}\cdot\mathbf{h})(\boldsymbol{\epsilon}_{\mathbf{k}s}^\perp\cdot\mathbf{e}_i) + i\sin(\mathbf{k}\cdot\mathbf{h})(\boldsymbol{\epsilon}_{\mathbf{k}s}^\parallel\cdot\mathbf{e}_i)]$$

$$\times [\cos(\mathbf{k}\cdot\mathbf{h})(\boldsymbol{\epsilon}_{\mathbf{k}s}^\perp\cdot\mathbf{e}_j) - i\sin(\mathbf{k}\cdot\mathbf{h})(\boldsymbol{\epsilon}_{\mathbf{k}s}^\parallel\cdot\mathbf{e}_j)]. \tag{8.1}$$

Next we pass to the limit $V \to \infty$, convert the $\mathbf{k}$ summation into an integration, perform the summation over the polarizations s and integrate over the spherical coordinates of $\mathbf{k}$-space in the same fashion as for the radiation field (see the Appendix). Then the correlation function attains the form

$$G_{ij}(\tau) = \frac{1}{3\pi\epsilon_0 \hbar c^3}(\mathbf{e}_z \cdot \mathbf{e}_i)(\mathbf{e}_z \cdot \mathbf{e}_j)$$
$$\times \int_0^\infty d\omega\, e^{-i\omega\tau}\omega^3 b_\perp(\omega h/c)$$
$$+ \frac{1}{3\pi\epsilon_0 \hbar c^3}[(\mathbf{e}_x \cdot \mathbf{e}_i)(\mathbf{e}_x \cdot \mathbf{e}_j) + (\mathbf{e}_y \cdot \mathbf{e}_i)(\mathbf{e}_y \cdot \mathbf{e}_j)]$$
$$\times \int_0^\infty d\omega\, e^{-i\omega\tau}\omega^3 b_\|(\omega h/c), \qquad (8.2)$$

in terms of the auxiliary functions

$$b_\perp(x) = 1 - 3\left[\frac{\cos(2x)}{(2x)^2} - \frac{\sin(2x)}{(2x)^3}\right], \qquad (8.3)$$

$$b_\|(x) = 1 - \frac{3}{2}\left[\frac{\sin(2x)}{(2x)} + \frac{\cos(2x)}{(2x)^2} - \frac{\sin(2x)}{(2x)^3}\right]. \qquad (8.4)$$

Fortunately, we do not have to carry out the integrations over ω in Eq. (8.2), because we only need the Fourier–Laplace transform, Eq. (7.12), of $G_{ij}(\tau)$. With the identity

$$\int_0^\infty d\tau\, e^{i(\omega' - \omega)\tau} = \pi\delta(\omega' - \omega) + P\left(\frac{i}{\omega' - \omega}\right), \qquad (8.5)$$

where P stands for principal value, we readily find

$$\widetilde{G}_{ij}(\omega) = (\mathbf{e}_z \cdot \mathbf{e}_i)(\mathbf{e}_z \cdot \mathbf{e}_j)[\gamma_\perp(\omega) + i\delta_\perp(\omega)]$$
$$+ [(\mathbf{e}_x \cdot \mathbf{e}_i)(\mathbf{e}_x \cdot \mathbf{e}_j) + (\mathbf{e}_y \cdot \mathbf{e}_i)(\mathbf{e}_y \cdot \mathbf{e}_j)]$$
$$\times [\gamma_\|(\omega) + i\delta_\|(\omega)]. \qquad (8.6)$$

Here we have introduced

$$\gamma_k(\omega) = \frac{\omega^3}{3\pi\hbar\epsilon_0 c^3} b_k(\omega h/c) H(\omega), \quad k = \perp, \|, \qquad (8.7)$$

with $H(\omega)$ as the unit-step function. In turn, these functions serve to define the imaginary parts of the damping constants in terms of the real-valued integrals

$$\delta_k(\omega) = \frac{1}{\pi}P\int_0^\infty d\omega' \frac{1}{\omega - \omega'}\gamma_k(\omega'), \quad k = \perp, \|. \qquad (8.8)$$

As usual,[43] these integrals diverge, and the upper limit should be understood as a finite cutoff frequency with $c/\omega_{up} \sim$ dimension of the atom.

The dependence on the distance h to the surface is completely embodied in the functions $b_\perp$ and $b_\|$. For $h \to \infty$, which corresponds to $x \to \infty$ in Eqs. (8.3) and (8.4), we find

$$b_\|(\infty) = b_\perp(\infty) = 1. \qquad (8.9)$$

In the case $h \to \infty$ the spontaneous decay is not affected anymore by the presence of the surface, and so Eq. (8.9) will yield the free-atom result. The quantity $\gamma_f(\omega)$ with $f = $ free follows from Eq. (8.7) after setting $b_k = 1$, which in turn gives $\delta_f(\omega)$ with Eq. (8.8). Then the correlation function reduces to

$$\widetilde{G}_{ij}(\omega) = \delta_{ij}[\gamma_f(\omega) + i\delta_f(\omega)], \quad h \to \infty. \qquad (8.10)$$

Combination of Eqs. (8.6) and (7.14) gives for the relaxation constants

$$g^{abcd}_{\alpha\beta\gamma\delta} = [\gamma_\perp(\Delta_{dc}) + i\delta_\perp(\Delta_{dc})]$$
$$\times \langle a,\alpha|\mu_\perp|b,\beta\rangle \cdot \langle c,\gamma|\mu_\perp|d,\delta\rangle$$
$$+ [\gamma_\|(\Delta_{dc}) + i\delta_\|(\Delta_{dc})]$$
$$\times \langle a,\alpha|\mu_\||b,\beta\rangle \cdot \langle c,\gamma|\mu_\||d,\delta\rangle, \qquad (8.11)$$

which holds for any atom, dipole direction, and distance to the surface. For the case of a two-state atom, this reduces to the familiar results,[32] derived by a different method.

Of particular interest is the limit $h \to 0$. A Taylor expansion of $b_\|(x)$ and $b_\perp(x)$ gives

$$b_\perp(x) = 2 - \tfrac{2}{3}x^2 + \cdots, \qquad (8.12)$$

$$b_\|(x) = 0 + \tfrac{4}{3}x^2 + \cdots, \qquad (8.13)$$

for $x \to 0$. Therefore, the relaxation constants of a dipole, which is oriented parallel to the surface, vanish, as could be anticipated. The atomic dipole is decomposed as $\mu = \mu_\perp + \mu_\|$, and its quantum-mirror image as $\mu' = \mu_\perp - \mu_\|$, and so (matrix elements of) their sum disappears if $\mu_\perp = 0$. More peculiar is the case of a perpendicular dipole, for which one might expect that this system behaves as an atom in free space with dipole moment $2\mu_\perp$. However, we find $b_\perp(x) = 2$ for $h \to 0$, and comparison with Eq. (8.11) shows that the relaxation constants acquire a value which corresponds to an atom in free-space with dipole moment $\mu_\perp\sqrt{2}$. We conclude that the classical mirror picture is not appropriate to explain the QED of an atom near an interface. Our quantum mirror, for which the Hamiltonian can be written as in Eq. (6.3), is consistent, since for $h \to 0$ we find

$$H = H_a + H_f - \sqrt{2}\mu_\perp \cdot \mathbf{E}(0,t_0)_v, \qquad (8.14)$$

corresponding to an atom in free space with dipole moment $\sqrt{2}\mu_\perp$. Furthermore, this shows again that the factor $\sqrt{2}$ in Eq. (6.3) is inevitable.

IX. FLUORESCENT EMISSION

Dynamical features of the adsorbed atoms are amenable to observation in an experiment, since the details of the time evolution of the density operator are reflected in the properties of the emitted fluorescence. We consider the most simple situation of a photomultiplier tube which detects the intensity of the radiation in the far field, without spectral, temporal, or polarization resolution. This intensity $I(t)$ is proportional to the photon counting rate and is given by[49]

$$I(t) = 2\epsilon_0 c \langle \mathbf{E}^{(-)}(\mathbf{r},t)_d \cdot \mathbf{E}^{(+)}(\mathbf{r},t)_d\rangle r^2 \Delta\Omega \qquad (9.1)$$

for detection at position $\mathbf{r}$ at time t and in the far field. Here $\Delta\Omega$ is the small solid angle (aperture), the $(+)$ and $(-)$ indicate the annihilation and creation part of the field, respectively, and the angle brackets denote a quantum average.

Far away from the radiator, the contributions which go as r^{-1} will dominate the dipole field, Eqs. (4.1) and (4.2). Retaining only these terms and using

$$|\mathbf{r} \pm \mathbf{h}| = r \pm \hat{\mathbf{r}} \cdot \mathbf{h} + \mathcal{O}(h^2/r), \qquad (9.2)$$

gives for the field in the far zone

$$E(r,t)_d = \frac{-1}{4\pi\epsilon_0 c^2 r}\frac{d^2}{dt^2}$$

$$\times \{\hat{r}\times[\mu(t-r/c+\tau)$$

$$+\mu'(t-r/c-\tau)]\}\times\hat{r}. \qquad (9.3)$$

We have introduced the abbreviation

$$\tau = c^{-1}\hat{r}\cdot h, \qquad (9.4)$$

which equals half the difference between the retardation times of the directly emitted and reflected fields. Next we recall that the time-evolution operator for a Heisenberg operator equals exp (iLt), which allows us to write

$$E(r,t)_d = \frac{1}{4\pi\epsilon_0 c^2 r}e^{iL(t-r/c)}L^2(\mu(\tau)+\mu'(-\tau)$$

$$-\{[\mu(\tau)+\mu'(-\tau)]\cdot\hat{r}\}\hat{r}), \qquad (9.5)$$

where we have used a vector identity to rewrite the double cross product. In order to reduce the length of formulas a little, we define

$$m(\tau) = L^2\mu(\tau) = e^{iL\tau}L^2\mu, \qquad (9.6)$$

and similarly m', which follows after replacing μ by μ'. Any dipole operator μ can be subdivided as $\mu = \mu^{(+)} + \mu^{(-)}$, with $\mu^{(+)}$ the lowering (emissive) part and $\mu^{(-)}$ the raising (absorptive) part. With Eq. (9.5), this divides $m(\tau)$ into a (+) and a (−) part, and similarly the radiation field $E(r,t)_d$ splits up. Obviously, this separation gives the (+) and the (−) parts of the field, which appeared in the definition of the intensity, Eq. (9.1). With $\langle\cdots\rangle = \mathrm{Tr}\,\rho(0)(\cdots)$ and the cyclic invariance of the trace, we then find

$$I(t) = \frac{\Delta\Omega}{8\pi^2\epsilon_0 c^3}\,\mathrm{Tr}\,\rho(t-r/c)$$

$$\times([m^{(-)}(\tau)+m^{(-)}(-\tau)']$$

$$\cdot[m^{(+)}(\tau)+m^{(+)}(-\tau)']$$

$$-\{[m^{(-)}(\tau)+m^{(-)}(-\tau)']\cdot\hat{r}\}$$

$$\times\{[m^{(+)}(\tau)+m^{(+)}(-\tau)']\cdot\hat{r}\}), \qquad (9.7)$$

which is an exact, although not very transparent, expression for the intensity in r at time t.

A great simplification arises if we neglect the dipole coupling $-\mu\cdot E(h,t_0)_f$ in the Liouvillians L from Eq. (9.5). Physically this means that the atom does not decay on a time scale τ which is a few optical cycles. In the optical region the decay constants are six orders of magnitude smaller than the level separations (photon frequencies), so this approximation is rigorously justified. Then we notice that L acts on a pure atomic operator μ or μ', and, therefore, the commutator with H_f vanishes. In conclusion, we can safely replace L by L_a in Eq. (9.5).

In a similar way as we evaluated the operator Q_i from Eq. (7.6) by an expansion in projectors onto atomic states, we can now write

$$m(\tau) = L_a^2\sum_{kl}e^{i\Delta_{kl}\tau}P_k\mu P_l, \qquad (9.8)$$

and with some operator algebra this becomes

$$m(\tau) = \sum_{kl}e^{i\Delta_{kl}\tau}\Delta_{kl}^2 P_k\mu P_l. \qquad (9.9)$$

For $m'(-\tau)$ we replace τ by $-\tau$ and μ by μ', and for the (+) and (−) parts we replace μ by $\mu^{(+)}$ and $\mu^{(-)}$, respectively. Furthermore, we note that the factor in parentheses in Eq. (9.6) is pure atomic, so that the trace over the states of the radiation field merely turns ρ into ρ_a. Next we substitute expansion (9.8) in the various places in Eq. (9.6) and subdivide the dipole operators in perpendicular and parallel, which yields

$$I(t) = \frac{\Delta\Omega}{2\pi^2\epsilon_0 c^3}\sum_{klm}\mathrm{Tr}_a\,P_m\rho_a(t-r/c)P_k\Delta_{kl}^2\Delta_{ml}^2$$

$$\times\{[\mu_\perp^{(-)}\cos(\Delta_{kl}\tau)+i\mu_\parallel^{(-)}\sin(\Delta_{kl}\tau)]$$

$$\cdot P_l[\mu_\perp^{(+)}\cos(\Delta_{lm}\tau)+i\mu_\parallel^{(+)}\sin(\Delta_{lm}\tau)]$$

$$-[\mu_\perp^{(-)}\cdot\hat{r}\cos(\Delta_{kl}\tau)+i\mu_\parallel^{(-)}\cdot\hat{r}\sin(\Delta_{kl}\tau)]$$

$$\times P_l[\mu_\perp^{(+)}\cdot\hat{r}\cos(\Delta_{lm}\tau)+i\mu_\parallel^{(+)}\cdot\hat{r}\sin(\Delta_{lm}\tau)]\}. \qquad (9.10)$$

Of course, the distance r between the atom and the detector only enters as a trivial retardation $t-r/c$ in the argument of the density operator. The state of the atom is determined by ρ_a, and a spontaneous decay, together with a photon emission, can only give rise to the observation of a photon at a time r/c later. Equation (9.10) displays the full angular distribution of emitted power. Recall that, besides the $\hat{r}$ in the various terms, τ also depends on $\hat{r}$ as $\tau=\hat{r}\cdot h/c$, which gives rise to many interferences between the different transitions. We recognize this structure to result from the interference between the directly emitted and reflected waves or photons. Equation (9.10) should reduce to the result for a free atom in the limit $h\to\infty$, but from the discussion in the previous section we know that $h\to 0$ also yields the free-atom result (apart from a possible factor). Then $h\to 0$ is equivalent to $\tau\to 0$, and the structure disappears. We shall see in the next section that the situation $\tau\neq 0$ amounts to strange properties of this system which are not present for free atoms.

X. EMITTED POWER

Usually the detailed structure of the angular distribution is not resolved in an experiment. Then the quantity of interest is the totally emitted power, which equals

$$I(t)_{\mathrm{tot}} = \int\frac{d\Omega\,I(t)}{\Delta\Omega}, \qquad (10.1)$$

where the integration extends over the solid angle in which the atom radiates, which is the half-sphere $z\geqslant 0$ in our geometry. With the explicit expression (9.10) the integration is readily performed, and we find after an expansion in matrix elements

$$I(t)_{\mathrm{tot}} = \frac{1}{3\pi\epsilon_0 c^3}\sum_{\substack{abc\\ \alpha\beta\gamma}}\Delta_{ab}^2\Delta_{cb}^2\langle c,\gamma|\rho_a(t-r/c)|a,\alpha\rangle$$

$$\times(b_{abc}^\perp\langle a,\alpha|\mu_\perp^{(-)}|b,\beta\rangle\cdot\langle b,\beta|\mu_\perp^{(+)}|c,\gamma\rangle$$

$$+b_{abc}^\parallel\langle a,\alpha|\mu_\parallel^{(-)}|b,\beta\rangle\cdot\langle b,\beta|\mu_\parallel^{(+)}|c,\gamma\rangle), \qquad (10.2)$$

which involves the constants

$$b_{abc}^{\perp} = 3\left[\frac{\sin \tau_{ac}}{\tau_{ac}^3} - \frac{\cos \tau_{ac}}{\tau_{ac}^2}\right.$$

$$\left. + \frac{\sin(\tau_{ab} + \tau_{cb})}{(\tau_{ab} + \tau_{cb})^3} - \frac{\cos(\tau_{ab} + \tau_{cb})}{(\tau_{ab} + \tau_{cb})^2}\right], \quad (10.3)$$

$$b_{abc}^{\parallel} = \frac{3}{2}\left[-\frac{\sin \tau_{ac}}{\tau_{ac}^3} + \frac{\cos \tau_{ac}}{\tau_{ac}^2} + \frac{\sin \tau_{ac}}{\tau_{ac}}\right.$$

$$+ \frac{\sin(\tau_{ab} + \tau_{cb})}{(\tau_{ab} + \tau_{cb})^3} - \frac{\cos(\tau_{ab} + \tau_{cb})}{(\tau_{ab} + \tau_{cb})^2}$$

$$\left. - \frac{\sin(\tau_{ab} + \tau_{cb})}{\tau_{ab} + \tau_{cb}}\right], \quad (10.4)$$

in terms of the parameters

$$\tau_{ab} = \Delta_{ab} h / c. \quad (10.5)$$

The remarkable situation appears that the constants $b_{abc}^{\perp}$ and $b_{abc}^{\parallel}$ depend on three atomic frequencies rather than two, which reflects an energy interference in a decay from $|a,\alpha\rangle$ to $|b,\beta\rangle$ due to the presence of the level $|c,\gamma\rangle$, irrespective of whether this level is populated or not. It is essentially a multilevel phenomenon. A second noteworthy feature is that the emitted power in the transition $|a,\alpha\rangle \to |b,\beta\rangle$ cannot be expressed in the relaxation constants, Eq. (8.11), for the same transition but that it requires additional information. This is in contrast to the generic point of view that knowledge of the Green function $G_{ij}(\tau)$ is tantamount to a full dynamical description (with a Hamiltonian).

If the intermediate-level energy $\hbar\omega_c$ approaches the initial-level energy $\hbar\omega_a$, then the interference effect vanishes, as can be found from taking the limit $\tau_{ac} \to 0$ in Eqs. (10.3) and (10.4). Comparison with the decay functions (8.3) and (8.4) then shows that

$$b_{aba}^{\perp} = b_{\perp}(\tau_{ab}), \quad b_{aba}^{\parallel} = b_{\parallel}(\tau_{ab}), \quad (10.6)$$

which shows that the energy-emission constants equal the spontaneous-decay constants if only two (possible degenerate) atomic levels are involved.

To see the modifications due to the presence of the surface more clearly, we compare Eq. (10.2) with its free-atom analog. Since we already have Eq. (10.2), we can obtain this expression by taking the limit $h \to \infty$. From Eqs. (10.3) and (10.6) we derive the limits

$$\lim_{h \to \infty} b_{abc}^{\perp} = \lim_{h \to \infty} b_{abc}^{\parallel} = \delta_{ac} \quad \text{for} \quad a \neq b, \quad (10.7)$$

which gives for the emitted power

$$I(t)_{\text{tot}} = \sum_{\substack{ab \\ \alpha\beta\gamma}} \frac{\Delta_{ab}^4}{3\pi\epsilon_0 c^3}\langle a,\gamma|\rho_a(t - r/c)|a,\alpha\rangle$$

$$\times \langle a,\alpha|\boldsymbol{\mu}^{(-)}|b,\beta\rangle\cdot\langle b,\beta|\boldsymbol{\mu}^{(+)}|a,\gamma\rangle. \quad (10.8)$$

Transitions from ω_a to ω_b occur at a rate proportional to the population of $|a\rangle$ (if we neglect degeneracy) and the matrix elements of $\boldsymbol{\mu}$ between $|a\rangle$ and $|b\rangle$. There are no couplings with intermediate states $|c,\gamma\rangle$ in the free-atom case, so this energy-interference effect is a result of the presence of the surface indeed. Recall that $\boldsymbol{\mu}^{(+)}$ is the lowering operator, so that for the nonzero terms in Eq. (10.2) we must have

$\omega_a > \omega_c > \omega_b$. Interference in $\omega_a \to \omega_b$ transitions is only induced by intermediate states.

As far a spontaneous decay is concerned, it has appeared in the previous sections that the limit $h \to 0$ corresponds to a decaying atom with dipole moment $\mu_{\perp}\sqrt{2}$ in free space, which supported the mirror picture provided that the factor $\sqrt{2}$ is included in the appropriate places. Even this analogy has only a very limited significance, as we can now easily demonstrate. From Eqs. (10.3) and (10.4) we find

$$\lim_{h \to 0} b_{abc}^{\perp} = 2, \quad \lim_{h \to 0} b_{abc}^{\parallel} = 0, \quad (10.9)$$

which gives for the emission rate

$$I(t)_{\text{tot}} = \frac{2}{3\pi\epsilon_0 c^3}\sum_{\substack{abc \\ \alpha\beta\gamma}} \Delta_{ab}^2 \Delta_{cb}^2 \langle c,\gamma|\rho_a(t - r/c)|a,\alpha\rangle$$

$$\times \langle a,\alpha|\boldsymbol{\mu}_{\perp}^{(-)}|b,\beta\rangle\cdot\langle b,\beta|\boldsymbol{\mu}_{\perp}^{(+)}|c,\gamma\rangle. \quad (10.10)$$

Comparison with Eq. (10.8) shows that the limit $h \to 0$ is not identical to the free-atom result with $\boldsymbol{\mu}$ replaced by $\boldsymbol{\mu}_{\perp}\sqrt{2}$. The interference between ω_a and ω_c in a $\omega_a \to \omega_b$ transition persists in the limit $h \to 0$, whereas this vanishes for free atoms. We conclude that the dynamics of an atom near a metal surface is essentially different from an atom in free space, and its properties can only be partially understood from classical analogs, like the mirror picture.

XI. TWO-STATE ATOM

In order to illuminate the various interpretations of formulas, to show the applicability of the dynamical approach, and to make sure that all the factors of $\sqrt{2}$ are consistent we consider the situation of a two-state atom. Two nondegenerate levels $|1\rangle$ and $|2\rangle$ are separated by $\omega_0 = \omega_2 - \omega_1 > 0$, and their transition dipole moment is $\boldsymbol{\mu}_{12} = \langle 1|\boldsymbol{\mu}|2\rangle$, assumed to be nonzero and real. From parity considerations it follows that $\langle 1|\boldsymbol{\mu}|1\rangle = \langle 2|\boldsymbol{\mu}|2\rangle = 0$, which implies that only the decay constants g_{2121}, g_{1212}, g_{2112}, and g_{1221} are nonzero. Then the equation of motion (7.16) for the atomic density operator involves only the combination of parameters

$$A_2 = \text{Re}\, g_{2112}, \quad (11.1)$$

$$A_1 = \text{Re}\, g_{1221} = 0, \quad (11.2)$$

$$\beta = \tfrac{1}{2}\,\text{Im}(g_{2121} + g_{1212}^*), \quad (11.3)$$

where $A_1 = 0$ implies that the lowest state does not decay. This is a consequence of the step function in Eq. (8.7), which in turn follows from the assumption of zero temperature. The equation of motion assumes the simple form

$$\frac{d}{dt}\langle 2|\rho_a|2\rangle = -A_2\langle 2|\rho_a|2\rangle, \quad (11.4)$$

$$\frac{d}{dt}\langle 2|\rho_a|1\rangle = -i(\omega_0 - \beta)\langle 2|\rho_a|1\rangle - \tfrac{1}{2}A_2\langle 2|\rho_a|1\rangle$$

$$+ (\tfrac{1}{2}A_2 + i\beta)\langle 1|\rho_a|2\rangle, \quad (11.5)$$

and the other two matrix elements follow from $\rho_a^{\dagger} = \rho_a$ and $\text{Tr}_a\,\rho_a = 1$. Equation (11.4) for the population of the highest state does not couple to Eq. (11.5) for the coherence between the two states. We recognize A_2 as the surface-modified Einstein coefficient for spontaneous decay of level $|2\rangle$ and β as the Lamb shift. The last term on the right-hand side

of Eq. (11.5) is a nonsecular coupling between $\langle 1|\rho_a|2\rangle$ and $\langle 2|\rho_a|1\rangle$, which gives a vanishingly small contribution to the time evolution of $\rho_a(t)$ for low-lying atomic transition[50] and can, therefore, be discarded. Explicitly we find

$$A_2 = \frac{\omega_0^3 \langle 1|\boldsymbol{\mu}|2\rangle^2}{3\pi\hbar\epsilon_0 c^3}[b_\perp(\omega_0 h/c)\cos^2\theta + b_\parallel(\omega_0 h/c)\sin^2\theta],$$

(11.6)

where θ is the angle between the dipole direction and the z axis. The possible values of A_2/A_0 are represented by the shaded area in Fig. 1, where A_0 is the factor in front of the brackets, which equals the Einstein coefficient in free space.

The emitted power follows immediately from Eq. (10.2), and we obtain

$$I(t)_{\mathrm{tot}} = \hbar\omega_0\langle 2|\rho_a(t-r/c)|2\rangle A_2.$$

(11.7)

From Eq. (11.4) we then find

$$I(t)_{\mathrm{tot}} = \hbar\omega_0 A_2 e^{-A_2(t-r/c)}H(t-r/c)$$

(11.8)

if we choose the atom to be in its excited state $|2\rangle$ at time $t = 0$. The detected power as a function of time decays exponentially, and the detected energy equals

$$\int_0^\infty dt\, I(t)_{\mathrm{tot}} = \hbar\omega_0.$$

(11.9)

This result might not seem very surprising, but it certainly demonstrates the consistency between the equation of motion of $\rho_a(t)$ (derived from the Hamiltonian) and the expression for the emitted power (derived from the explicit form of the dipole field). Furthermore, it illustrates that only the energy $\hbar\omega_0$ which is stored in the atom at $t = 0$ ends up in the detector. This implies that the surface merely reflects radiation, although with a delay, which is incorporated

within the h dependence of A_2. The surface can only temporarily accumulate energy, which effectively alters the lifetimes of transitions.

XII. CONCLUSIONS

Many papers have been devoted to QED of atoms near a surface, and they all share expression (11.6) for the inverse lifetime of a two-state atom, as a function of the distance to the conductor. Nevertheless, we have observed that a consistent QED treatment from first principles is not available. It was pointed out in several places that the mirror approach is very limited and leads to inconsistencies, whereas the Green function theory suffers from a lack of dynamics. We started from the solution of Maxwell's equations for an atom above a perfect conductor, which can be found from symmetry. Then we constructed the Hamiltonian that generates the correct time dependence of the field, and in Sec. VI, Eq. (6.3), we wrote it in a mirrorlike form. It appeared that a factor of $\sqrt{2}$ emerged in this mirror image of a quantum dipole, which was traced back to the fact that the dipole does not couple with the surface-free vacuum field but with the free-field, quantized in the presence of a surface. We emphasize that this term has no classical analog because there is no vacuum field in classical electrodynamics. Hence, it is not possible to decide a priori what the coupling Hamiltonian should be. In the usual mirror approach, there is no $\sqrt{2}$, and one has to remedy this in some artificial way.

We applied the general theory to derive the spontaneous-emission operator for an arbitrary multilevel atom, and we obtained an exact expression for the emitted power. It appeared that the field intensity of the dipole radiation, modified by the surface, cannot be expressed in the relaxation constants for spontaneous decay, as is the case for a free atom. To our knowledge, this has not been noticed before which is probably due to the fact that this is a genuine multilevel feature.

APPENDIX

For completeness we show that the dipole field $\mathbf{E}(\mathbf{r},t)_d$ from Eq. (5.10) is indeed identical to the expression in Eqs. (4.1) and (4.2). To this end, we first notice that the summation over the polarization directions filters out the transverse component of the dipole operator and, therefore, we can write

$$\sum_s \boldsymbol{\epsilon}_{\mathbf{k}s}(\boldsymbol{\epsilon}_{\mathbf{k}s}\cdot\mathbf{v}) = \mathbf{v} - (\mathbf{v}\cdot\hat{\mathbf{k}})\hat{\mathbf{k}}$$

(A1)

for any vector $\mathbf{v}$. Next we use the identity

$$(\mathbf{v}\cdot\hat{\mathbf{k}})\hat{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}} = -k^{-2}(\mathbf{v}\cdot\nabla)\nabla e^{i\mathbf{k}\cdot\mathbf{r}},$$
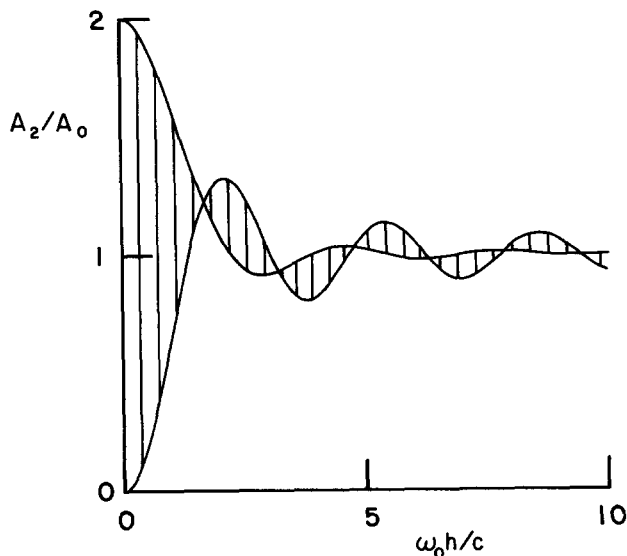
(A2)

FIG. 1. Plot of the possible values of the inverse lifetime A_2/A_0 of a two-state atom as a function of $\omega_0 h/c$. The curve which starts at $A_2/A_0 = 2$ for $h = 0$ corresponds to a dipole direction perpendicular to the surface, whereas the other curve represents a parallel orientation. In general, A_2/A_0 assumes a value in between these two boundary lines, as follows from Eq. (11.6) by varying the angle of orientation θ. Notice that for certain distances h from the surface, the lifetime is independent of the dipole direction, which corresponds to the intersection of both curves.

after which the dipole field becomes

$$
\begin{aligned}
\mathbf{E}(\mathbf{r},t)_d = \sum_{\mathbf{k}} \frac{i\omega_k}{2\epsilon_0 V} \int_0^\infty d\tau\, e^{-i\omega_k \tau} (\{\boldsymbol{\mu}(t-\tau) \\
+ k^{-2}[\boldsymbol{\mu}(t-\tau)\cdot\nabla]\nabla\} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{h})} + \{\boldsymbol{\mu}'(t-\tau) \\
+ k^{-2}[\boldsymbol{\mu}'(t-\tau)\cdot\nabla]\nabla\} e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{h})}) + \text{h.c.} \quad (A3)
\end{aligned}
$$

Then we pass to the limit $V \to \infty$, which allows us to make the replacement

$$
\frac{1}{V} \sum_{\mathbf{k}} \to \frac{1}{8\pi^3} \int_0^\infty dk\, k^2 \int_{\substack{\text{unit} \\ \text{sphere}}} d\Omega_{\mathbf{k}}. \quad (A4)
$$

If we insert this into Eq. (A3), then the angular integration is easily performed according to

$$
\int_{\substack{\text{unit} \\ \text{sphere}}} d\Omega_{\mathbf{k}}\, e^{i\mathbf{k}\cdot(\mathbf{r}\pm\mathbf{h})} = 4\pi \sin(k r_{\mp})/k r_{\mp}, \quad (A5)
$$

where $r_{\pm} = |\mathbf{r} \mp \mathbf{h}|$. Combining the first term on the right-hand side in Eq. (A3) with its Hermitian conjugate and writing $\omega_k = ck$ then yields for the field

$$
\begin{aligned}
\mathbf{E}(\mathbf{r},t)_d = \frac{i}{4\pi^2\epsilon_0} \int_0^\infty d\omega \int_0^\infty d\tau (e^{-i\omega\tau} - e^{i\omega\tau}) \\
\times \left(\left\{ \frac{\omega^2}{c^2}\boldsymbol{\mu}(t-\tau) + [\boldsymbol{\mu}(t-\tau)\cdot\nabla]\nabla \right\} \right. \\
\times \sin(\omega r_+/c)/r_+ \\
+ \left\{ \frac{\omega^2}{c^2}\boldsymbol{\mu}'(t-\tau) + [\boldsymbol{\mu}'(t-\tau)\cdot\nabla]\nabla \right\} \\
\left. \times \sin(\omega r_-/c)/r_- \right). \quad (A6)
\end{aligned}
$$

The double integral is most easily found after a Fourier transform

$$
\widehat{\mathbf{E}}(\mathbf{r},\omega)_d = \int_{-\infty}^\infty dt\, e^{i\omega t}\mathbf{E}(\mathbf{r},t), \quad (A7)
$$

and similarly for the dipole moments. Then the integration over τ can be carried out with Eq. (8.5) and we obtain

$$
\begin{aligned}
\widehat{\mathbf{E}}(\mathbf{r},\omega)_d = \frac{i}{4\pi\epsilon_0} \left(\left\{ \frac{\omega^2}{c^2}\hat{\boldsymbol{\mu}}(\omega) + [\hat{\boldsymbol{\mu}}(\omega)\cdot\nabla]\nabla \right\} \right. \\
\times \sin(\omega r_+/c)/r_+ \\
+ \left\{ \frac{\omega^2}{c^2}\hat{\boldsymbol{\mu}}'(\omega) + [\hat{\boldsymbol{\mu}}'(\omega)\cdot\nabla]\nabla \right\} \\
\left. \times \sin(\omega r_-/c)/r_- \right) + P\text{-value integral}, \quad (A8)
\end{aligned}
$$

for $\omega > 0$, whereas $\widehat{\mathbf{E}}(\mathbf{r},-\omega) = \widehat{\mathbf{E}}(\mathbf{r},\omega)^\dagger$ determines the field for $\omega < 0$. Then we discard the advanced solution in Eq. (A8), which amounts to the replacement $i\sin(\omega r_{\pm}/c) \to \exp(i\omega r_{\pm}/c)$, calculate the derivatives, omit the small principle-value integral, and transform back to the time domain. This leaves us with the desired solution, Eqs. (4.1) and (4.2). It is an artifact of the quantization procedure on the volume V that the advanced solution appears. Actually, a plane-wave expansion for the free field at $t = t_0$ is in conflict with the boundary condition (outgoing waves) for the Green function for the emission of radiation. Therefore, we

have to remove the advanced solution at the end.

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