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Spontaneous decay and atomic fluorescence near a metal surface or an absorbing dielectric

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Optical properties of an atom in the vicinity of a metal or dielectric are different from those in free space. The spontaneous decay of an atom with two degenerate levels is studied, where the relaxation operator is obtained as a function of the atom-surface separation and the complex bulk dielectric constant $\epsilon(\omega)$. The Einstein coefficient A_{m_e} of an excited state $|j_e m_e\rangle$ appears to depend on the magnetic quantum number m_e. A sum rule for A_{m_e} is derived, and from the rotational symmetry with respect to the surface normal it is found that $A_{m_e}=A_{-m_e}$. A general expression for the fluorescent radiation field in the far zone is then derived, which incorporates the polarization properties of the fluorescence, as they are modified by the presence of the dielectric. It is shown that the angular distribution of the emitted intensity depends strongly on $\epsilon(\omega)$, and it is pointed out how information about the substrate, e.g., $\epsilon(\omega)$, can be extracted from the temporal statistical behavior of the emitted photons. It is emphasized that the major surface effects are purely geometrical, despite the essential quantum nature of the problem.

I. INTRODUCTION

Consider space to be divided by the *xy* plane, which separates a half-space vacuum $z>0$ from an electromagnetically active medium occupying $z<0$. An atom resides on the $+z$ axis at a normal distance $h>0$ to the surface. If the atom is prepared in an excited state at a certain initial time, then it will decay spontaneously to a lower state, together with the emission of a fluorescent photon. As compared to the same process in entirely empty space, the presence of the substrate affects the decay and emission dramatically if the atom-surface separation h is of the order of a wavelength or less. Essentially, there are two distinct features which alter the interaction of an atom with the radiation field when the atom is close to an interface.

First, due to boundary conditions at $z=0$, the allowed modes of the field are different from the common traveling-plane-wave modes in empty space. Since a fluorescent photon can be emitted only in one of the available modes, it is obvious that a modified mode structure will change the lifetime of an excited state. This is a purely geometrical phenomenon, which arises as a consequence of the spatial interference of the different waves, supported by the configuration. In both classical and quantum mechanics the radiation field must obey Maxwell's equations, and therefore the spatial dependence of the field is identical in both theories. In the classical paper by Chance *et al.*[1] the atomic lifetimes near a dielectric were found from semiclassical considerations. Other approaches are the linear-response formalism,[2-4] which relies on the quantum-regression theorem, an expansion in eigenmodes of the geometry,[5-8] and an elimination of the charges and the currents in the medium from the Hamiltonian.[9] In the case of a perfectly conducting solid, the lifetimes can be obtained from a quantum analog of the method of images.[10] There, the surface is replaced by a mirror dipole in $\mathbf{r}=-h\mathbf{e}_z$.

The second effect of the presence of the boundary is again purely geometrical, but it has consequences only in a full quantum treatment of the problem. In free space the system (atom plus radiation) is spherically symmetric, or its Hamiltonian is invariant under any three-dimensional rotation. For an atom near a flat surface only a symmetry for rotation around the *z* axis remains. A convenient choice for the arbitrary quantization axis for the definition of the atomic wave functions (the magnetic degeneracies) is then the normal to the surface. It can in turn be shown[11,12] that a $\Delta m=\pm 1$ dipole transition is always governed by the lifetime of a dipole which is oriented parallel to the surface, whereas a $\Delta m=0$ decay process has a lifetime corresponding to a perpendicular dipole. For an atom in empty space these two lifetimes are equal, due to the spherical symmetry. If the excitation of the atom is brought about by irradiation with a polarized laser beam, then the distribution of population over the various *m* states of an excited level is unambiguous. By a proper choice of the laser polarization we can prepare an atom as a pure parallel or perpendicular dipole with respect to its decay constant. In semiclassical theories of fluorescence the dipole moment is merely a vector in configuration space, which can be given an arbitrary direction. One then averages over a randomization of the direction, which has the quantum analog of a random laser polarization (or, in general, a random excitation of the substates without any coherence between the substates).

We shall assume that the solid can be described by a macroscopic complex-valued and frequency-dependent dielectric constant $\epsilon(\omega)$. Furthermore, we impose the condition that the dielectric is absorptive, which implies that traveling waves inside the medium die out exponentially in amplitude. Sufficient conditions are $\epsilon(\omega)<0$ or

$\mathrm{Im}\epsilon(\omega)>0$. An illustrative example is the lossless free-electron-gas model for a metal, for which we have

$$\epsilon(\omega)=1-\omega_p^2/\omega^2<1 , \tag{1.1}$$

with ω_p the plasma frequency (uv region). Then for $\omega<\omega_p$ we have $\epsilon(\omega)<0$, corresponding to a reflective metal, and for $\omega>\omega_p$ it is assumed that $\epsilon(\omega)$ contains a small positive imaginary part. In this frequency region the metal becomes transparent and behaves as an ordinary dielectric with $0<\epsilon(\omega)<1$. A perfect conductor can be modeled by Eq. (1.1) if we take $\omega_p\rightarrow\infty$, which gives $\epsilon(\omega)\rightarrow-\infty$. Other dielectrics can have $\epsilon(\omega)>1$, or more complicated structures. A metal with dielectric constant $\epsilon(\omega)$ from Eq. (1.1) is perfectly reflecting in the range $0<\omega<\omega_p$, but is only a perfect conductor for $\omega\ll\omega_p$. For low-lying atomic transitions, ω can easily be of the order of ω_p, which changes the lifetimes considerably in comparison with a perfect conductor.

Experiments on atomic fluorescence for transitions in the visible region of the spectrum and near a surface have been reported only recently.[13,14] This is in contrast to molecular spectroscopic measurements on thin films, which have a long history,[15–22] and to microwave transitions between Rydberg atoms in a cavity.[23,24] The main obstruction for accurate experiments in the visible region is that the atoms (from a beam) must fluoresce within a distance shorter than a wavelength from the surface. The inevitable van der Waals attraction between the atoms and the surface then leads to large adsorption probabilities, and thus the surface will be covered with atoms before a measurement can be done.

II. RADIATION FIELD

In free space the electric field operator $\mathbf{E}(\mathbf{r},t)$ is usually expanded as a sum of transverse plane waves with wave vector $\mathbf{k}$ and polarization $\boldsymbol{\epsilon}_{\mathbf{k}\sigma}$. In a cubic volume V with periodic boundary conditions, the wave vector assumes only discrete values. In the presence of a half-infinite dielectric in $z<0$, one usually replaces the cube V by a surface area $V^{2/3}$ in the xy plane, and extends the range for z to $-\infty<z<\infty$.[6,25] Since the atom is positioned in the region $z>0$, we only need to consider the field in the vacuum above the surface and hence we can take the quantization volume as a cube V, which is entirely located in $z>0$.

Due to the presence of the substrate in $z<0$, every plane wave will give rise to a reflected wave and a transmitted wave, when incident upon the surface. For the field in the quantization volume we can therefore write[26]

$$\mathbf{E}(\mathbf{r},t)=\sum_{\mathbf{k},\sigma}\left[\frac{\hbar\omega_k}{2\varepsilon_0}\right]^{1/2} a_{\mathbf{k}\sigma}(t)\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r})+\text{h.c.} , \tag{2.1}$$

with $\omega_k=ck$ and where $\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r})$ represents the incident wave and the reflected wave, and is normalized as

$$\int_V d\mathbf{r}\,|\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r})|^2=1 . \tag{2.2}$$

The operator $a_{\mathbf{k}\sigma}(t)$ is the annihilation operator for a photon in the mode $\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r})$.

Any wave vector $\mathbf{k}$, polarization vector $\boldsymbol{\varepsilon}$, and dipole moment $\boldsymbol{\mu}$ can be divided in a perpendicular and parallel part with respect to the xy plane. In terms of these divisions we define primed quantities by

$$\mathbf{k}'=\mathbf{k}_{\parallel}-\mathbf{k}_{\perp} , \tag{2.3}$$

$$\boldsymbol{\varepsilon}'=\boldsymbol{\varepsilon}_{\perp}-\boldsymbol{\varepsilon}_{\parallel} , \tag{2.4}$$

$$\boldsymbol{\mu}'=\boldsymbol{\mu}_{\perp}-\boldsymbol{\mu}_{\parallel} . \tag{2.5}$$

Then an incident wave $\mathbf{k},\boldsymbol{\varepsilon}$ upon a perfectly reflecting surface will produce a reflected wave with wave vector $\mathbf{k}'$ and polarization $\boldsymbol{\varepsilon}'$, and $\boldsymbol{\mu}'$ has the significance of the mirror image of a dipole moment. Because $\boldsymbol{\mu}$ of an atom is an operator in the Hilbert space, which is spanned by the atomic wave functions, Eq. (2.5) is an operator equation. The Fresnel reflection coefficients for s and p waves are[27]

$$R_s(\omega,u)=\frac{[\epsilon(\omega)-1+u^2]^{1/2}-u}{[\epsilon(\omega)-1+u^2]^{1/2}+u} , \tag{2.6}$$

$$R_p(\omega,u)=\frac{u\epsilon(\omega)-[\epsilon(\omega)-1+u^2]^{1/2}}{u\epsilon(\omega)+[\epsilon(\omega)-1+u^2]^{1/2}} , \tag{2.7}$$

with ω the frequency of the wave and u the cosine of the angle of incidence. With these definitions the normalized mode functions attain the form

$$\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r})=\frac{1}{\sqrt{V}}\frac{1}{[1+|R_\sigma(\omega_k,u_{\mathbf{k}})|^2]^{1/2}} \times[\boldsymbol{\varepsilon}_{\mathbf{k}\sigma}e^{i\mathbf{k}\cdot\mathbf{r}}+R_\sigma(\omega_k,u_k)\boldsymbol{\varepsilon}'_{\mathbf{k}\sigma}e^{i\mathbf{k}'\cdot\mathbf{r}}] \tag{2.8}$$

for $k_z<0$. Here, $u_{\mathbf{k}}=-k_z/k>0$. For terms $\mathbf{k}\sigma$ with $k_z>0$ we have

$$\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r})=\mathbf{F}_{\mathbf{k}'\sigma}(\mathbf{r}) . \tag{2.9}$$

III. EQUATIONS OF MOTION

Spontaneous decay is most conveniently described in a density-operator formalism. If we denote by $\rho(t)$ the combined state of the atom and the radiation field, then its time evolution is governed by the equation of motion

$$i\hbar\frac{d}{dt}\rho(t)=[H,\rho(t)] , \tag{3.1}$$

with H the Hamiltonian of the entire system. Since only the state of the atom is of concern, we define the atomic density operator as

$$\rho_a(t)=\mathrm{Tr}_r\,\rho(t) , \tag{3.2}$$

where the trace runs over the states of the radiation field. With standard reservoir theory[28,29] we then easily obtain the equation of motion for $\rho_a(t)$,

$$i\hbar\frac{d}{dt}\rho_a(t)=[H_a,\rho_a(t)]-i\hbar\Gamma\rho_a(t) . \tag{3.3}$$

Here, H_a is the atomic Hamiltonian (internal structure) and the Liouville operator Γ accounts for spontaneous decay.

The general expression for the radiation field $\mathbf{E}(\mathbf{r},t)$ is given by Eq. (2.1), which has only the operators $a_{\mathbf{k}\sigma}(t)$ as unknowns. Their equation of motion reads

$$i\hbar\frac{d}{dt}a_{\mathbf{k}\sigma}(t)=[a_{\mathbf{k}\sigma}(t),H] , \qquad (3.4)$$

and we shall assume that the initial values $a_{\mathbf{k}\sigma}(0)$ coincide with the standard boson annihilation operators $a_{\mathbf{k}\sigma}$.

For the Hamiltonian we take

$$H=H_a+H_r+H_i , \qquad (3.5)$$

where the Hamiltonian for the radiation field is

$$H_r=\sum_{\mathbf{k}\sigma}\hbar\omega_k a^{\dagger}_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma} . \qquad (3.6)$$

Coupling between the field and atom is established by the dipole interaction

$$H_i=-\boldsymbol{\mu}\cdot\mathbf{E}(\mathbf{h},0) , \qquad (3.7)$$

where $\boldsymbol{\mu}$ is the atomic dipole operator and $\mathbf{E}(\mathbf{h},0)$ equals the radiation field at time zero (when the Schrödinger and Heisenberg picture coincide) and evaluated at the position of the atom. We shall assume that the atom consists of two degenerate levels $|j_e m_e\rangle$ (excited) and $|j_g m_g\rangle$ (ground), which are separated by $\omega_0=\omega_e-\omega_g>0$. Then H_a can be written as

$$H_a=\hbar\omega_e P_e+\hbar\omega_g P_g , \qquad (3.8)$$

where P_e and P_g denote the projectors on the excited level and ground level, respectively.

IV. SPONTANEOUS DECAY

In writing $|j_e m_e\rangle$ for a magnetic substate of the upper level, we implicitly refer to a direction in configuration space, e.g., the quantization axis for the definition of the m_e degeneracy. Evidently, this axis can be chosen arbitrarily, but in our geometry it is most convenient to take this direction to coincide with the normal to the surface (z axis). With this convention the explicit form of the spontaneous-decay operator Γ becomes[11]

$$\begin{aligned}\Gamma\sigma=&\tfrac{1}{2}\sum_{m_e}A_{m_e}(|j_e m_e\rangle\langle j_e m_e|\sigma+\sigma|j_e m_e\rangle\langle j_e m_e|)\\&-A_f\sum_{\tau}b_\tau(h)\sum_{m_e,m_g,m_e',m_g'}(j_g m_g 1\tau|j_e m_e)(j_g m_g' 1\tau|j_e m_e')|j_g m_g\rangle\langle j_e m_e|\sigma|j_e m_e'\rangle\langle j_g m_g'| ,\end{aligned} \qquad (4.1)$$

which gives the action of Γ on an arbitrary density operator σ, and where the zero-temperature limit has been adopted. The relaxation parameters A_{m_e} are defined as

$$A_{m_e}=A_f\sum_{m_g,\tau}b_\tau(h)(j_g m_g 1\tau|j_e m_e)^2 , \qquad (4.2)$$

in terms of the Einstein coefficient A_f for spontaneous decay in free space. The summation index τ assumes the values $-1,0,1$, corresponding to the three possible photon helicities with respect to the z axis. Surface modifications to spontaneous decay are entirely incorporated in the parameter functions $b_\tau(h)$. With $b_{\parallel}=b_{+1}=b_{-1}$ and $b_{\perp}=b_0$ we find

$$\begin{aligned}b_{\parallel}(h)=&1-\tfrac{3}{2}\,\mathrm{Re}\int_0^1 du\, u^2\frac{R_p(\omega_0,u)e^{2i\omega_0 hu/c}}{1+|R_p(\omega_0,u)|^2}\\&-\tfrac{3}{2}\,\mathrm{Re}\int_0^1 du\frac{R_s(\omega_0,u)e^{2i\omega_0 hu/c}}{1+|R_s(\omega_0,u)|^2} ,\end{aligned} \qquad (4.3)$$

$$b_{\perp}(h)=1+3\,\mathrm{Re}\int_0^1 du\,(1-u^2)\frac{R_p(\omega_0,u)e^{2i\omega_0 hu/c}}{1+|R_p(\omega_0,u)|^2} . \qquad (4.4)$$

The integration variable u has the significance of the cosine of the angle of incidence of a plane wave. Therefore, the integrals result from interference of waves [the mode functions $\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r})$], and consequently any modification of relaxation constants due to the presence of the surface is a purely geometrical effect.

Some conclusions are easily drawn from the above formulas. If we take the matrix element $\langle j_e m_e|\ldots|j_e m_e\rangle$ of Eq. (3.3) and use the explicit form (4.1) for Γ, we find immediately

$$\frac{d}{dt}\langle j_e m_e|\rho_a|j_e m_e\rangle=-A_{m_e}\langle j_e m_e|\rho_a|j_e m_e\rangle \qquad (4.5)$$

for the population of state $|j_e m_e\rangle$. Hence A_{m_e} equals the Einstein coefficient, or inverse lifetime, of the state $|j_e m_e\rangle$.

In the limit $h\rightarrow\infty$, where the atom is arbitrarily far away from the surface, we see that Eqs. (4.3) and (4.4) reduce to

$$b_{\parallel}(\infty)=b_{\perp}(\infty)=1 , \qquad (4.6)$$

because the fast-oscillating cosines in the integrands average out to zero. Substitution of Eq. (4.6) into Eq. (4.2) then yields $A_{m_e}=A_f$, and the lifetime of the state $|j_e m_e\rangle$ becomes independent of m_e. Conversely, due to the presence of the surface every excited state has a different relaxation constant A_{m_e}, which is unambiguously defined by Eq. (4.2). The relation $A_{m_e}=A_f$ for an atom in empty space reflects the isotropy of spontaneous emission, or the spherical symmetry of the system. In the vicinity of a boundary this symmetry is destroyed, which gives every state $|j_e m_e\rangle$ a different lifetime. From Eq. (4.2) we deduce

$$A_{m_e} = A_{-m_e} , \tag{4.7}$$

which displays the remaining cylindrical symmetry for rotations about the z axis.

By summing Eq. (4.2) over the magnetic quantum numbers m_e, we obtain the sum rule

$$\frac{1}{2j_e+1}\sum_{m_e} A_{m_e} = \tfrac{1}{3}A_\perp + \tfrac{2}{3}A_\parallel , \tag{4.8}$$

with $A_\perp = A_f b_\perp$ and $A_\parallel = A_f b_\parallel$. The right-hand side of Eq. (4.8) is the average value of A_{m_e} over the different substates, because there are $2j_e+1$ excited states $|j_e m_e\rangle$ for a given j_e. If the population of the excited states would be randomly distributed over the various substates, with no coherence between the states, then the atom will decay with the average of A_{m_e}. In this respect the result (4.8) is a quantum-mechanical justification for a randomization of the dipole direction.

Another interesting feature is the dependence of the lifetimes on the distance h between the atom and the surface. Let us consider a real-valued dielectric constant, as in Eq. (1.1), in combination with the limit $h \to 0$. In the case of a perfect conductor ($\epsilon \to -\infty$) or a dielectric with a large polarizability ($\epsilon \to +\infty$) we obtain

$$b_\parallel(0)=0, \quad b_\perp(0)=2 , \tag{4.9}$$

whereas the limit $\epsilon \to 0$ yields

$$b_\parallel(0)=1, \quad b_\perp(0)=0 , \tag{4.10}$$

corresponding to the situation where the atomic transition frequency ω_0 equals the plasma resonance ω_p of the metal. For a perfectly conducting solid the inverse lifetime of a parallel dipole is zero, but if the conductivity becomes smaller, it is the inverse lifetime of a perpendicular dipole which vanishes. This reversal of behavior of parallel and perpendicular dipoles as a function of the conductivity illustrates the drastic effect that the structure of a metal can have on the optical properties of an atom, experiencing its reflected fields. Results (4.9) and (4.10) can qualitatively be understood in view of Eqs. (2.5)–(2.7). For large values of ϵ the solid behaves as a mirror. Since the parallel part of the mirror dipole moment $\boldsymbol{\mu}'$ acquires a minus sign in comparison with $\boldsymbol{\mu}_\parallel$, the emitted fluorescence by $\boldsymbol{\mu}_\parallel$ and $\boldsymbol{\mu}'_\parallel$ is out of phase. Exact cancellation of emitted radiation implies no decay, which explains $b_\parallel(0)=0$ for $|\epsilon| \to \infty$. For $\epsilon \to 0$ we see from Eq. (2.7) that p waves pick up a phase change of 180° upon reflection. Because $\boldsymbol{\mu}_\perp = \boldsymbol{\mu}'_\perp$ it is now the fluorescence emitted by the perpendicular component which vanishes after interference with its reflected field. Figures 1 and 2 give more details about the ϵ dependence of $b_\parallel(0)$ and $b_\perp(0)$.

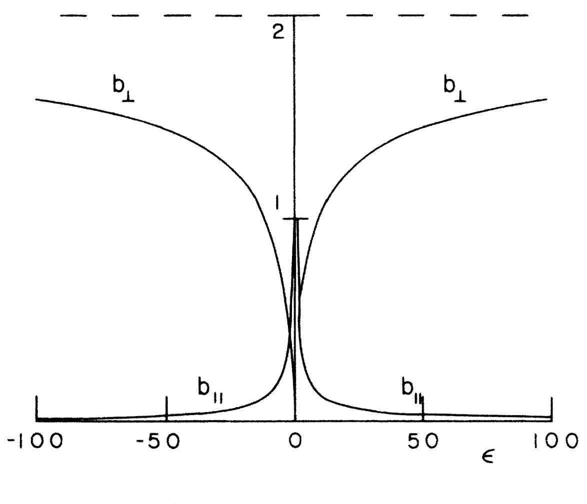

FIG. 1. Normalized inverse lifetime $b_\parallel(0)$ and $b_\perp(0)$ as a function of the dielectric constant ϵ. The dotted line indicates the asymptotic value of $b_\perp(0)$ for $\epsilon \to \pm\infty$, and it is seen that the approach to this limit is extremely slow. On the other hand, $b_\parallel(0)$ is vanishingly small over the entire ϵ range, corresponding to its asymptotic value, except for a small region around $\epsilon=0$. The region $-\infty < \epsilon < 0$ corresponds to a perfectly reflecting metal, the region $0 < \epsilon < 1$ to a transparent metal, and $\epsilon > 1$ represents a dielectric.

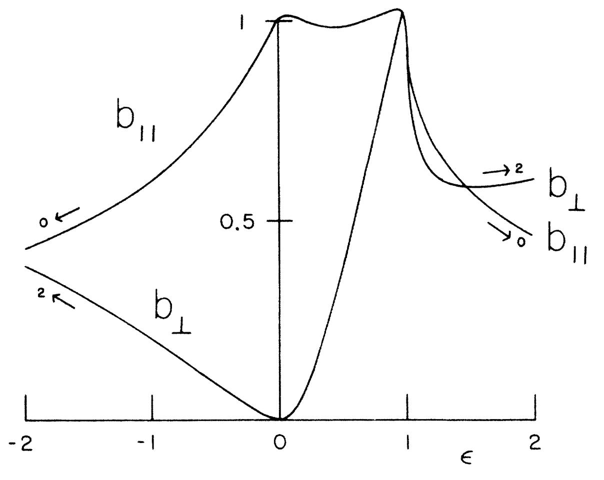

FIG. 2. Enlargement of the region $-2 < \epsilon < 2$ from Fig. 1.

V. METALS

From Eq. (1.1) for the lossless electron-gas model we see that for $\omega < \omega_p$ the dielectric constant is negative and real. Therefore, we define an (idealized) metal by $\epsilon(\omega) < 0$, which, of course, only can hold in a certain frequency range. The physical relevance of the assertion $\epsilon(\omega) < 0$ follows immediately from Eqs. (2.6) and (2.7). We notice that, recalling $0 < u < 1$,

$$|R_\sigma(\omega,u)| = 1 \tag{5.1}$$

for every angle of incidence. In other words, the medium is perfectly reflecting. Radiation will still penetrate

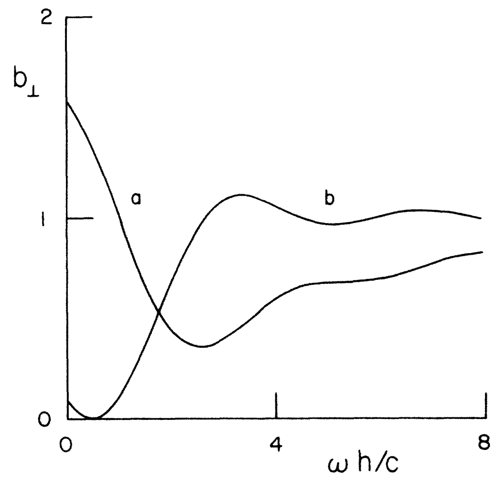

FIG. 3. Normalized inverse lifetime $b_\perp(h)$ as a function of the normalized distance $\omega h/c$ between the atom and surface. Both curves correspond to a perfectly reflecting metal, and the $\epsilon(\omega)$ values are $\epsilon=-100$ and $\epsilon=-0.5$ for curves *a* and *b*, respectively.

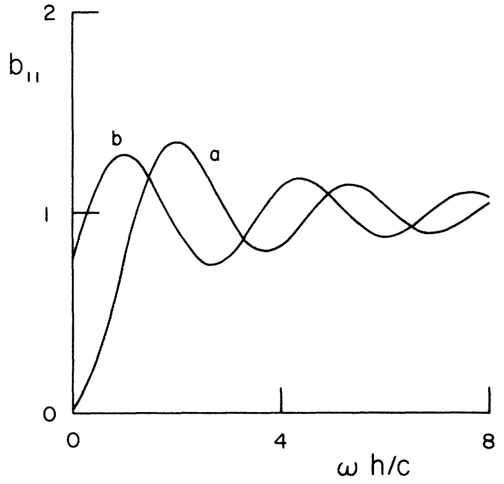

FIG. 4. Normalized inverse parallel lifetimes as a function of the normalized atom-surface distance. The permittivity is $\epsilon=-100$ (curve *a*) and $\epsilon=-0.5$ (curve *b*). From both Figs. 3 and 4 it is seen that the value of the inverse lifetime for $h\rightarrow 0$ depends strongly on ϵ, or the phase shifts ϕ_σ which are picked up by a plane wave upon reflection at the surface.

the substrate, but there is no net energy transport through the surface into the solid. In view of Eq. (5.1) we can write

$$R_\sigma(\omega,u)=e^{2i\phi_\sigma(\omega,u)}\ , \tag{5.2}$$

where the real-valued phases for *s* and *p* waves are given by

$$\tan\phi_s(\omega,u)=\frac{u}{[1-\epsilon(\omega)-u^2]^{1/2}}\ , \tag{5.3}$$

$$\tan\phi_p(\omega,u)=\frac{[1-\epsilon(\omega)-u^2]^{1/2}}{-u\epsilon(\omega)}\ , \tag{5.4}$$

with $0\le\phi_\sigma\le\pi/2$. Substitution of Eq. (5.2) into the definition (2.8) of the mode function $\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r})$ then exhibits that the reflected wave is only shifted in phase (with $2\phi_\sigma$) with respect to the incident wave. For a perfectly conducting metal, $\epsilon(\omega)\rightarrow-\infty$, we find $\phi_\sigma\equiv 0$. This seemingly small effect of only a phase shift upon reflection already has a great impact on the atomic lifetimes, as can be understood from the fact that the alterations of lifetimes are brought about by the interference of incident and reflected waves. In Figs.3 and 4 we have plotted the lifetimes of a perpendicular and parallel dipole as a function of *h*, and for different values of $\epsilon(\omega)$. It is easy to show that our general expressions (4.3) and (4.4) for the lifetimes, in combination with Eqs. (5.3) and (5.4), reduce to the results of Philpott.[6] In Sec. VII we shall study the consequences of the phase shifts ϕ_σ on the angular distribution of the emitted fluoresence.

VI. FLUORESCENCE

Dynamical behavior of an atom can be studied experimentally by observation of its fluorescence. Information on various details, like lifetimes, is reflected in the different statistical properties of the emitted radiation. In Eq. (2.1) we gave the general expression for the electric field $\mathbf{E}(\mathbf{r},t)$. Its time dependence is entirely incorporated in $a_{\mathbf{k}\sigma}(t)$ which is the solution of Eq. (3.4). If we work out the commutator with *H* and differentiate the result with respect to time, then it is easy to show that $a_{\mathbf{k}\sigma}(t)$ obeys

$$\left[\frac{d^2}{dt^2}+\omega_k^2\right]a_{\mathbf{k}\sigma}(t) = \left[\frac{\omega_k}{2\varepsilon_0\hbar}\right]^{1/2}[\omega_k\boldsymbol{\mu}(t)+i\dot{\boldsymbol{\mu}}(t)]\cdot\mathbf{F}^*_{\mathbf{k}\sigma}(\mathbf{h})\ . \tag{6.1}$$

The first term on the right-hand side of Eq. (2.1) is the positive frequency part $\mathbf{E}^+$ of $\mathbf{E}$ (or the annihilation field), and a combination of Eqs. (6.1) and (2.1) yields its equation of motion

$$\left[\nabla^2-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right]\mathbf{E}^+(\mathbf{r},t) = \frac{-1}{2\varepsilon_0 c^2}\sum_{\mathbf{k},\sigma}\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r})\{[\omega_k^2\boldsymbol{\mu}(t)+i\omega_k\dot{\boldsymbol{\mu}}(t)]\cdot\mathbf{F}^*_{\mathbf{k}\sigma}(\mathbf{h})\}\ . \tag{6.2}$$

The solution of this wave equation can be written as

$$\mathbf{E}^+(\mathbf{r},t)=\mathbf{E}_d^+(\mathbf{r},t)+\mathbf{E}_h^+(\mathbf{r},t)\ , \tag{6.3}$$

with $\mathbf{E}_d^+(\mathbf{r},t)$ the particular solution which has the right-hand side of Eq. (6.2) as source. Then $\mathbf{E}_h^+(\mathbf{r},t)$ is an arbitrary solution of the homogeneous equation. Usually[2,4] the particular solution is the radiation field for a dipole in free space, and the homogeneous solution is then chosen in such a way that the boundary conditions at $z=0$ are obeyed. An advantage of the introduction of the mode functions is that every term $\mathbf{k}\sigma$ in Eq. (2.1) satisfies the boundary conditions, and consequently $\mathbf{E}(\mathbf{r},t)$ has the correct behavior at $z=0$, no matter what the time dependence of $a_{\mathbf{k}\sigma}(t)$ is. A disadvantage of the expansion (2.1) concerns the boundary conditions for $r=|\mathbf{r}|\rightarrow\infty$.[11] Traveling waves with periodic boundary conditions on a volume V are a combination of incoming and outgoing spherical waves, which is in conflict with the physical picture of an emitting dipole and surface (moving charges). A way of eliminating the advanced solutions is through the intermediate step of deriving the wave equation (6.2), for which we know how to discard incoming waves.

Solving Eq. (6.2) is most easily accomplished after a Fourier transform. If we define

$$\hat{\mathbf{E}}_d^+(\mathbf{r},\omega)=\int_{-\infty}^{\infty}dt\,e^{i\omega t}\mathbf{E}_d^+(\mathbf{r},t)\;, \tag{6.4}$$

and similar for $\boldsymbol{\mu}(t)$, then the transformed equation reads

$$\left[\nabla^2+\frac{\omega^2}{c^2}\right]\hat{\mathbf{E}}_d^+(\mathbf{r},\omega)=\frac{-1}{2\varepsilon_0c^2}\sum_{\mathbf{k},\sigma}\omega_k(\omega_k+\omega)[\hat{\boldsymbol{\mu}}(\omega)\cdot\mathbf{F}_{\mathbf{k}\sigma}^*(\mathbf{h})]\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r})\;. \tag{6.5}$$

With the retarded Green's function

$$G_k(\mathbf{r}-\mathbf{r}')=|\mathbf{r}-\mathbf{r}'|^{-1}\exp(ik|\mathbf{r}-\mathbf{r}'|),\quad k=\omega/c \tag{6.6}$$

Eq. (6.5) can be integrated to give

$$\hat{\mathbf{E}}_d^+(\mathbf{r},\omega)=\frac{1}{8\pi\varepsilon_0c^2}\sum_{\mathbf{k},\sigma}\int d\mathbf{r}'\omega_k(\omega_k+\omega)[\hat{\boldsymbol{\mu}}(\omega)\cdot\mathbf{F}_{\mathbf{k}\sigma}^*(\mathbf{h})]\times\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r}')G_k(\mathbf{r}-\mathbf{r}')\;. \tag{6.7}$$

Since this solution has the dipole moment $\hat{\boldsymbol{\mu}}(\omega)$ as a source and obeys the boundary conditions by construction, we conclude that Eq. (6.7) represents the fluorescence radiation field in the region $z>0$.

Macroscopic devices which detect the fluorescence are positioned in the far field $r\rightarrow\infty$, and consequently we have to make an asymptotic expansion for $r\rightarrow\infty$ of Eq. (6.7). At first sight this might appear to be a problem, because the quantity

$$\int d\mathbf{r}'\mathbf{F}_{\mathbf{k}\sigma}(\mathbf{r}')G_k(\mathbf{r}-\mathbf{r}') \tag{6.8}$$

does not involve localized source terms with $|\mathbf{r}'|$ small in comparison with r. It is only after summation over the plane-wave modes $\mathbf{k}$ that the expression (6.8) becomes localized, as is most evident from identities such as

$$\int d\mathbf{k}e^{i\mathbf{k}\cdot(\mathbf{r}'\pm\mathbf{h})}=8\pi^3\delta(\mathbf{r}'\pm\mathbf{h})\;. \tag{6.9}$$

Bearing this in mind we can expand the Green's function

$$G_k(\mathbf{r}-\mathbf{r}')\simeq r^{-1}e^{ikr-ik\hat{\mathbf{r}}\cdot\mathbf{r}'}\;, \tag{6.10}$$

with $\hat{\mathbf{r}}=\mathbf{r}/r$. Then it is straightforward to find the asymptotic expansion of $\hat{\mathbf{E}}_d^+(\mathbf{r},\omega)$, and we obtain

$$\hat{\mathbf{E}}_d^+(\mathbf{r},\omega)=\frac{\omega^2}{2\pi\varepsilon_0c^2r}\sum_{\sigma}\frac{R_\sigma(\omega,u)}{1+|R_\sigma(\omega,u)|^2}\boldsymbol{\varepsilon}_{\hat{\mathbf{r}}\sigma}\{\boldsymbol{\varepsilon}_{\hat{\mathbf{r}}\sigma}\cdot[\hat{\boldsymbol{\mu}}(\omega)R_\sigma^*(\omega,u)e^{i\omega(r-hu)/c}+\hat{\boldsymbol{\mu}}'(\omega)e^{i\omega(r+hu)/c}]\} \tag{6.11}$$

for the radiation traveling in the direction $\hat{\mathbf{r}}$ and evaluated at a distance r from the atom. Here, $u=\hat{\mathbf{r}}\cdot\mathbf{e}_z$ is the cosine of the angle between $\hat{\mathbf{r}}$ and the z axis, or the angle of observation. The first term in square brackets corresponds to photons which are emitted by the atom at $\mathbf{r}=\mathbf{h}$ and travel directly to the detector, whereas the second term represents the photons which are emitted by the surface (or reflected by the surface), as can be inferred from the retardation. Notice that the surface photons have as a source the mirror dipole moment $\boldsymbol{\mu}'$.

Obtaining $\mathbf{E}_d^+(\mathbf{r},t)$ from a Fourier inverse of Eq. (6.11) will be cumbersome in general, because the Fresnel coefficients $R_\sigma(\omega,u)$ depend on ω in a complicated way. In deriving Eq. (6.11) we did not use the explicit form of the atomic Hamiltonian H_a, as given by Eq. (3.8). If there were no radiation field present, then the time dependence of $\boldsymbol{\mu}(t)$ would be given by its free evolution

$$\boldsymbol{\mu}(t)=e^{iH_at/\hbar}\boldsymbol{\mu}e^{-iH_at/\hbar}\;, \tag{6.12}$$

and with the explicit form of H_a this becomes

$$\boldsymbol{\mu}(t)=e^{-i\omega_0t}P_g\boldsymbol{\mu}P_e+e^{i\omega_0t}P_e\boldsymbol{\mu}P_g\;. \tag{6.13}$$

The second term on the right-hand side contains only negative frequencies, and therefore its contribution to the positive frequency part $\hat{\mathbf{E}}_d^+(\mathbf{r},\omega)$ of the electric field will be negligible, in view of Eq. (6.11). Consequently, we can omit the raising part of the dipole moment in expression (6.11). Then, $P_g\hat{\boldsymbol{\mu}}(\omega)P_e$ will be strongly peaked around $\omega\simeq\omega_0$, with a frequency spread of the order of the relaxation constant ($\sim A_f$). Over this width A_f of the emission line at ω_0 we can safely replace $R_\sigma(\omega,u)$ and the prefactor ω^2 by their values at ω_0. Furthermore, the retardation time hu/c in the exponential is of the order of a few optical cycles, which implies that we can replace $\exp(\pm i\omega hu/c)$ by $\exp(\pm i\omega_0hu/c)$. Combining everything then finally yields for the fluorescence field in the time domain and the radiation zone

$$\mathbf{E}_d^{+}(\mathbf{r},t)=\frac{\omega_0^2}{2\pi\varepsilon_0 c^2 r}\sum_\sigma \frac{R_\sigma(\omega_0,u)}{1+|R_\sigma(\omega_0,u)|^2}\boldsymbol{\varepsilon}_{\hat{\mathbf{r}}\sigma}\{\boldsymbol{\varepsilon}_{\hat{\mathbf{r}}\sigma}\cdot P_g[\boldsymbol{\mu}(t-r/c)R_\sigma^*(\omega_0,u)e^{-i\omega_0 hu/c}+\boldsymbol{\mu}'(t-r/c)e^{i\omega_0 hu/c}]P_e\}\ . \tag{6.14}$$

Result (6.14) encompasses all statistical properties of the emitted photons, such as the spectral and temporal distribution, including their polarization and angular distribution.

VII. PHOTON DETECTION

A photomultiplier tube above the surface detects the fluorescence and registers the passage of photons through its active medium as a function of time. In order to extract maximum information from the signal, we position a polarizer in front of the detector, which only transmits radiation with polarization $\boldsymbol{\varepsilon}_{\text{pol}}$. Then it can be shown[30] that the photon count distribution is determined by the field

$$\mathcal{E}^{+}(t)=\mathbf{E}_d^{+}(\mathbf{r},t)\cdot\boldsymbol{\varepsilon}_{\text{pol}}^{*}\ , \tag{7.1}$$

evaluated at the position $\mathbf{r}$ of the detector. The detection rate at time t (intensity) is then given by

$$I(t)\propto\langle\mathcal{E}^{-}(t)\mathcal{E}^{+}(t)\rangle\ , \tag{7.2}$$

where the notation $\propto$ indicates the suppression of irrelevant overall factors and $\mathcal{E}^{-}(t)$ is the Hermitian conjugate of $\mathcal{E}^{+}(t)$. Transformation to the Schrödinger picture gives the equivalent expression

$$I(t)\propto \mathrm{Tr}\rho_a(t-r/c)\mathcal{E}^{-}(r/c)\mathcal{E}^{+}(r/c)\ , \tag{7.3}$$

which involves the atomic density operator at time $t-r/c$.

Further evaluation of $I(t)$ depends on the atomic level structure and the preparation of the atom at an initial time. Suppose we wish to design an experiment to observe the enhancement of the perpendicular lifetime with decreasing conductivity, e.g., the dip in the curve for $b_\perp$ of Fig. 1 for $\epsilon\uparrow 0$. First we choose a metal and a dipole-allowed atomic transition, in such a way that $\epsilon(\omega_0)$ is sufficiently close to zero. Assume, for simplicity, that the ground state and the excited state have an angular momentum $j_g=0$ and $j_e=1$, respectively. Since we are looking for the observation of a perpendicular lifetime we have to consider the emission of linearly polarized photons in the decay $|1,0\rangle\rightarrow|0,0\rangle$. At an initial time we prepare the atom in the excited state $|1,0\rangle$, for instance, by laser excitation. Then we place a linear polarization filter in front of the detector, which is inclined by an angle θ with respect to the z axis. It is easy to show from symmetry considerations that the intensity of s-polarized photons equals zero for this configuration. Therefore we take the polarizer direction as $\boldsymbol{\varepsilon}_{\text{pol}}=\boldsymbol{\varepsilon}_{\hat{\mathbf{r}}p}$. With some algebra we then find for the intensity

$$I(t)=I_0 e^{-A_\perp t}\frac{\sin^2\theta\cos^2\theta[\epsilon(\omega_0)^2]}{[1-\epsilon(\omega_0)]\{1-[1+\epsilon(\omega_0)]\cos^2\theta\}}\ , \tag{7.4}$$

where irrelevant constants are absorbed in I_0. First, we notice that this intensity decays exponentially to zero with an inverse lifetime $A_\perp$, which allows a direct determination of $A_\perp$ from a measurement of $I(t)$. Second, the angle of observation θ appears in Eq. (7.4) in a way that $I(t)$ vanishes for $\theta=0$ and $\pi/2$ (detector on z axis or in xy plane), so in order to detect any fluorescence we have to position the detector under a finite angle. From Eq. (7.4) it follows that $I(t)$ is maximum for

$$\theta=\arccos\left[\frac{1-\sqrt{-\epsilon(\omega_0)}}{1+\epsilon(\omega_0)}\right]^{1/2}\ . \tag{7.5}$$

In case of a perfect conductor this becomes $\theta=\pi/2$, but for a metal with a small conductivity we find $\theta\simeq 0$, and the expression for the intensity reduces to

$$I(t)\simeq I_0 e^{-A_\perp t}[\epsilon(\omega_0)]^2,\quad \epsilon(\omega_0)\uparrow 0\ . \tag{7.6}$$

In conclusion, the detection of p-polarized photons in a $(j_e=1)\rightarrow(j_g=0)$ transition will reveal the dependence of $A_\perp$ on the conductivity, but the photon-detection rate becomes extremely small in the region of interest $\epsilon(\omega_0)\simeq 0$.

VIII. PHOTON CORRELATIONS

Recently[12] we advocated that in designing an experiment for the observation of surface-modified optical properties of atoms, one can greatly benefit from the polarization properties of the fluorescence, which are induced by the presence of the substrate. In particular, the combination with state-selective excitation by an intense polarized cw laser beam, propagating in a well-defined direction, allows the construction of a geometrical configuration for which only a specific combination of $A_\perp$ and $A_\parallel$ determines the statistical properties of the fluorescence. In order to illustrate the idea, we consider again the $(j_e=1)\rightarrow(j_g=0)$ transition. If we irradiate the atom by a linearly polarized laser field which travels in a direction parallel to the surface, then it follows from the dipole-selection rules that only the state $|1,0\rangle$ will be populated. Alternatively, we can assume a circularly polarized beam, which is incident normal to the surface. In this case, only of the substates $|1,\pm 1\rangle$ will be occupied. Since $|1,0\rangle$ and $|1,\pm 1\rangle$ decay with an inverse lifetime equal to $A_\perp$ and $A_\parallel$, respectively, we can simply fix the dipole direction with our choice of external field.

Driving an atomic transition with a cw laser results in a time-independent fluorescent intensity $I=I(t=\infty)$, and consequently the information contained in this quantity is minimal. Therefore we consider the two-photon correlation function $f(t)$, where $f(t)dt$ equals the probability for the detection of a photon in $[t,t+dt]$ after a detection at time zero, and irrespective of possible detections at other times (for instance, in $[0,t]$). Evaluation of $f(t)$ is quite involved, so here we will merely quote the result. Details about the algebra can be found in, for instance, Refs. 31 and 32. For the two different laser polarizations we find

$$f(t)=\bar{I}(1-e^{(-1/2)At})^2 \tag{8.1}$$

for a weak monochromatic laser exactly on resonance with the transition frequency ω_0. Surface-induced effects are entirely incorporated in the Einstein coefficient A, which equals $A_\perp$ for the linearly polarized case ($\Delta m=0$), and $A_\parallel$ for a circularly polarized laser ($\Delta m=\pm 1$). Just as in the situation of measurement of intensities, Sec. VII, the time regression of the observable is governed by the inverse lifetime A, and hence the measurement of photon correlations might provide an alternative technique for the observation of atomic lifetimes near an interface.

IX. CONCLUSIONS

We have presented a quantum-electrodynamical theory for the interaction of radiation with an atom, which is located in the vicinity of an optically active surface. The atom was allowed to have an arbitrary (degenerate) level structure. The optical properties of the substrate were assumed to be represented by its complex dielectric constant $\epsilon(\omega)$, which is the only classical conjecture in the theory. We obtained an explicit expression for the spontaneous-emission operator Γ, and it was pointed out that surface modifications of lifetimes [the parameter functions $b_\tau(h)$], are solely due to geometrical interferences of incident and reflected waves. For the case of a perfectly reflecting metal it was shown that dramatic changes in lifetimes can be found, which are brought about by the phase change of a plane wave upon reflection at the interface. In general, the lifetimes are determined by the classical Fresnel coefficients $R_\sigma(\omega,u)$. Furthermore, we derived the sum rule (4.8) for the Einstein coefficients of an excited level, and the (cylindrical) symmetry relation (4.7) for these coefficients. These quantum-mechanical results are again purely geometrical.

Subsequently, we derived the explicit form of the fluorescence radiation field from the equation of motion for the photon annihilation operator $a_{\mathbf{k}\sigma}(t)$. It appears that $\mathbf{E}_d^+(\mathbf{r},t)$ acquires two contributions [see Eq. (6.14)]. The first term is proportional to

$$\frac{2\,|R_\sigma(\omega,u)|^2}{1+|R_\sigma(\omega,u)|^2}\boldsymbol{\mu}(t-r/c)\;, \tag{9.1}$$

which corresponds to direct emission by the atomic dipole $\boldsymbol{\mu}$ above the surface. A nonunity prefactor of $\boldsymbol{\mu}$ then represents power absorption by the dielectric. For the second term we find that the mirror dipole $\boldsymbol{\mu}'$ emerges automatically as a source of fluorescence, corresponding to emission of radiation by the oscillating charges in the surface.

Polarization-dependent excitation of the atom and detection of fluorescence were considered in some detail. It appears that for a metal with a finite conductivity there are no linearly polarized photons emitted in the direction parallel to the surface. For a poorly conducting metal these photons are emitted under an angle $\theta\simeq 0$ with the z axis, whereas an increase of conductivity directs the angle of emission for linearly polarized photons towards $\theta=\pi/2$. This value is reached arbitrarily close for a perfect conductor. Finally, we mentioned how photon-correlation techniques could be employed in order to study the surface modifications of optical properties of an atom.

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