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# Spontaneous Decay near a Metal Surface

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Atomic spontaneous decay is influenced by the environment of the atom. The presence of metallic or dielectric media changes the optical vacuum which surrounds the atom, and therefore the dipole coupling to this vacuum, inducing the spontaneous decay, is altered. The decay is accompanied by a time evolution of the atomic state, and therefore also the dynamical behavior of such an atom is modified. Furthermore, during the decay a photon will be emitted, and the properties of this radiation will reflect the time evolution of the atomic state. In this fashion, surface-modified atomic dynamics is amenable to experimental observation. Also, spectral widths of absorption lines are equal to the inverse relaxation times of the process, and this provides an alternative way for observing atomic temporal evolution in an experiment.

We derive an expression for the spontaneous-decay operator for an atom near a dielectric, as it appears in the equation of motion for the reduced atomic density operator. This Liouville operator has the relaxation constants as its matrix elements. The case of a two-state atom is worked out in detail, but the formalism applies equally well for any atom or molecule and also allows for degeneracies of levels.

## I. INTRODUCTION

Atomic spontaneous decay is brought about by the interaction between the atomic electric dipole moment and the electric field of the vacuum surrounding the atom. In the neighborhood of a metallic surface or a dielectric, the electromagnetic vacuum is different from the vacuum of empty space, and therefore also the rate of spontaneous decay can be expected to be different. For a model two-state atom with upper level $|e>$, ground state $|g>$, transition frequency $\omega_0$, and transition dipole moment $\boldsymbol{\mu}_{eg}$, the Einstein $A$ coefficient is given by

$$A=\frac{\omega_o^3}{3\pi\varepsilon_o\hbar c^3}\boldsymbol{\mu}_{eg}\cdot\boldsymbol{\mu}_{eg}^*. \tag{1.1}$$

This constant equals the inverse lifetime of the excited state and also the width at half maximum of the absorption line for the atom in the ground state. In the vicinity of dielectrics or metals, this expression can change considerably. Also, the lifetime can depend on the magnetic quantum numbers of the states because the vacuum near media is not necessarily isotropic anymore. This is due to the loss of spherical symmetry, which introduces a dependence of $A$ on the geometry of the environment.

Effects of the presence of media on the lifetime of an excited state was first observed by Drexhage for molecular transitions near a dielectric flat layer.[1] Later, atomic lifetimes were observed to change for atoms in between mirrors or in a microwave cavity.[2-5] Both an enhancement or an inhibition of spontaneous decay can occur, depending on the distance between the atom and the surface of the medium and on other parameters. In this paper we present the derivation of the equation of motion for the density operator of an atom near a dielectric. Spontaneous decay gives rise to relaxation of the density operator, and the relaxation constants are the Einstein coefficients for the transitions between various atomic states. In this paper, the case of a two-state atom will be worked out in detail, and the modifications of Eq. (1.1) due to the medium will be given explicitly in terms of the dielectric constant.

## II. EQUATION OF MOTION FOR THE DENSITY OPERATOR

The quantum state of an atom or molecule near a medium can be represented by a density operator $\rho(t)$.

Spontaneous decay of an atom is brought about by the interaction between the atom and the radiation field of the vacuum, and therefore the density operator must also include the state of this radiation field. The equation of motion for $\rho(t)$ is

$$i\hbar\frac{d\rho}{dt}=[H,\ \rho],\ H=H_a+H_r+H_{ar}, \tag{2.1}$$

where $H_a$, $H_r$, and $H_{ar}$ are the Hamiltonians of the atom, the radiation, and the interaction, respectively. Equation (2.1) is subject to the constraints

$$\rho^{\dagger}=\rho,\ Tr\rho=1. \tag{2.2}$$

For the description of spontaneous decay, it is convenient to introduce the concept of Liouville space. In this linear vector space, sometimes called superspace, a vector is identified with an operator in Hilbert space. That is, there is by definition a one-to-one correspondence between the operators in Hilbert space and the vectors in this Liouville space. For instance, the three Hamiltonians in Eq. (2.1) are vectors, and so is the density operator. Operators in Liouville space (Liouvillians) act on these vectors, and the result of such an operation is again a vector. Operators can be added, multiplied, exponentiated, etc. in the usual way, and these operations follow the general rules of a linear vector space.

As a first example, we define the Liouvillian $L$ by its action on an arbitrary Liouville vector $\Pi$:

$$L\Pi=\frac{1}{\hbar}[H,\ \Pi] \tag{2.3}$$

where $H$ is the total Hamiltonian of the system. Similarly, the operators $L_a$, $L_r$, and $L_{ar}$ are the commutators with the corresponding Hamiltonians. Then the equation of motion Eq. (2.1) can be written as

$$i\frac{d\rho}{dt}=L\rho, \tag{2.4}$$

or equivalently

$$i\frac{d\rho}{dt}=(L_a+L_r+L_{ar})\rho. \tag{2.5}$$

The solution of Eq. (2.1) is

$$\rho(t)=e^{-\frac{i}{\hbar}Ht}\rho(0)e^{\frac{i}{\hbar}Ht}, \tag{2.6}$$

and the solution of Eq. (2.4) is

$$\rho(t)=e^{-iLt}\rho(0): \tag{2.7}$$

Comparison of Eqs. (2.6) and (2.7) then leads to the important operator identity

$$e^{-iLt}\Pi=e^{-\frac{i}{\hbar}Ht}\Pi e^{\frac{i}{\hbar}Ht}, \tag{2.8}$$

for $\Pi$ arbitrary (as it will be from now on). Relation (2.8) holds, of course, for any Liouvillian which is a commutator with a Hilbert space operator divided by $\hbar$.

## III. RESERVOIR THEORY

We will be interested in the behavior of the atom regardless of what happens to the electromagnetic field. This is accounted for by the partial density operator of the atom defined as

$$\rho_a(t)=Tr_r\rho(t). \tag{3.1}$$

Here the trace runs over a complete set of states of the radiation field, and therefore $\rho_a(t)$ is an operator in the Hilbert space of the atom. The purpose of relaxation theory is to derive an equuation of motion for $\rho_a(t)$, which takes into consideration that there is a coupling to the electromagnetic field, leading to spontaneous decay, but such that the photons do not appear explicitly anymore in this equation. In this section we formulate the general theory of relaxation in the Liouville formalism. The electromagnetic field is considered as a large reservoir, or heat bath, and the atom as a small system which interacts with the reservoir. An integral of Eq. (2.5) is

$$\rho(t)=e^{-i(L_a+L_r)t}\rho(t_o)-i\int_0^t dt'\,e^{-i(L_a+L_r)(t-t')}L_{ar}\rho(t'), \tag{3.2}$$

as can be verified by differentiation. Then we substitute this back into (2.5), which yields

$$i\frac{d}{dt}\rho(t)=(L_a+L_r)\rho(t)+L_{ar}e^{-i(L_a+L_r)t}\rho(t_0)$$
$$-iL_{ar}\int_0^t dt'\,e^{-i(L_a+L_r)(t-t')}L_{ar}\rho(t'). \tag{3.3}$$

Then we take the trace over the states of the radiation field and use

$$Tr_rL_r\Pi=0, \tag{3.4}$$

which follows from the fact the $L_r$ is a commutator. This gives

$$i\frac{d}{dt}\rho_a(t)=L_a\rho_a(t)+Tr_rL_{ar}e^{-i(L_a+L_r)t}\rho(t_o)$$
$$-iTr_rL_{ar}\int_0^t dt'\,e^{-i(L_a+L_r)(t-t')}L_{ar}\rho(t'). \tag{3.5}$$

as an exact integral of the equation of motion.

Equation (3.5), however, is not a closed equation for the atomic density operator because the last two terms on the right-hand side still contain the full density operator of the system. The first term on the right-hand side is the free evolution of the atom, without coupling to the radiation field. The radiation field is a large reservoir, and we shall assume it to be in its thermal-equilibrium state $\bar{\rho}_r$. This operator has the properties

$$\bar{\rho}_r^{\dagger}=\bar{\rho}_r,\ Tr_r\bar{\rho}_r=1,\ [H_r,\ \bar{\rho}_r]=0. \tag{3.6}$$

It can be shown that the density operator $\rho(t_o)$ in (3.5) can be factorized according to

$$\rho(t_o)=\rho_a(t_o)\bar{\rho}_r, \tag{3.7}$$

and similarly $\rho(t')$ in the last term can be factorized. This involves a slight approximation (the Markov approximation), but for the present problem this is negligible. Then we assume that the interaction is such that

$$Tr_r L_{ar}(\rho_a(t_o)\bar{\rho}_r)=0, \tag{3.8}$$

which expresses that the average interaction energy is equal to zero at $t_o$. For spontaneous decay, this is exact for all times $t$. From Eqs. (3.6)-(3.8) it then follows that the second term on the right-hand side of Eq. (3.5) vanishes. It can be shown that in the last term the major contribution to the integral comes from the region $t'=t$ in the integrand, and therefore we can safely replace the lower limit by $-\infty$. Then we make the substitution $t-t'=\tau$ which gives

$$i\frac{d}{dt}\rho_a(t)=L_a\rho_a(t)-iTr_r L_{ar}\int_0^\infty d\tau\, e^{-i(L_a+L_r)\tau} \times L_{ar}(\rho_a(t-\tau)\bar{\rho}_r). \tag{3.9}$$

Next, under the integral sign we replace the atomic density operator by its free evolution value during the time $\tau$, e.g.,

$$\rho_a(t-\tau)=e^{iL_a\tau}\rho_a(t), \tag{3.10}$$

and this yields

$$i\frac{d}{dt}\rho_a(t)=L_a\rho_a(t)-iTr_r L_{ar}\int_0^\infty d\tau\, e^{-i(L_a+L_r)\tau} \times L_{ar}e^{iL_a\tau}(\rho_a(t)\bar{\rho}_r). \tag{3.11}$$

Then we define a Liouville operator $\Gamma$ in atomic Liouville space by its action on an arbitrary atomic operator or Liouville vector $\Pi_a$:

$$\Gamma\Pi_a=Tr_r L_{ar}\int_0^\infty d\tau\, e^{-i(L_a+L_r)\tau}L_{ar}e^{iL_a\tau}(\Pi_a\bar{\rho}_r). \tag{3.12}$$

This time-independent operator $\Gamma$ accounts for the relaxation of the atomic density operator, and the equation of motion for $\rho_a(t)$ becomes

$$i\frac{d\rho_a}{dt}=(L_a-i\Gamma)\rho_a. \tag{3.13}$$

The solution has to obey

$$\rho_a^\dagger=\rho_a,\ Tr_a\rho_a=1, \tag{3.14}$$

as follows from Eqs. (2.2) and (3.1).

## IV. RELAXATION OPERATOR

In order to evaluate the relaxation operator $\Gamma$ explicitly, we have to specify the three parts of the Hamiltonian and the density operator of the thermal reservoir. We shall assume that the atom is located in empty space, somewhere near a medium. Then $\bar{\rho}_r$ is the density operator of the electromagnetic field. This operator is, therefore, the density operator of black-body radiation, and for the visible region of the optical spectrum, this is simply the vacuum state. Therefore, we can take $\bar{\rho}_r$ as

$$\bar{\rho}_r=|0\rangle\langle 0|\ , \tag{4.1}$$

with $|0\rangle$ the multimode zero-photon Fock state. For visible radiation, the wavelength is much larger than the size of an atom, and therefore the interaction between the atom and the electromagnetic field is governed by the electric dipole coupling. Let the atom have a dipole operator $\mu$ and be located at position $\boldsymbol{r}=\boldsymbol{h}$ in space. The electric field operator is $\boldsymbol{E}(\boldsymbol{r})$ in the Schrödinger picture, and the interaction Hamiltonian is

$$H_{ar}=-\boldsymbol{\mu}\cdot\boldsymbol{E}(\boldsymbol{h})=-\sum_{i=x,y,z}\mu_i E(\boldsymbol{h})_i. \tag{4.2}$$

In the product $\mu_i E(\boldsymbol{h})_i$, the first factor is purely atomic whereas the Cartesian component of the electric field acts only in the Hilbert space of the radiation. Therefore, these two operators commute, and this can be used to simplify the expression for $\Gamma$ considerably. Working out the commutators that define the Liouvillians and applying identity (2.8) a few times then yields

$$\Gamma\Pi_a=\sum_i[\mu_i,\ Q_i\Pi_a-\Pi_a Q_i^\dagger]. \tag{4.3}$$

The Hilbert space operators $Q_i$ are defined by

$$Q_i=\int_0^\infty d\tau\, e^{-iL_a\tau}\sum_j f_{ij}(\tau)\mu_j \tag{4.4}$$

in terms of the functions

$$f_{ij}(\tau)=\frac{1}{\hbar^2}\langle 0|\{e^{iL_r\tau}E(\boldsymbol{h})_i\}E(\boldsymbol{h})_j|0\rangle. \tag{4.5}$$

We have also used the fact that $\mu_i$ and $E(\boldsymbol{h})_i$ are Hermitian operators. In expression (4.3) for $\Gamma$, all operators act in atomic space only, and the same holds for $Q_i$ in Eq. (4.4). The radiation field only appears through the functions $f_{ij}(\tau)$, which can be considered as the vacuum correlation functions for the electric field. Hence, all properties of the surrounding medium, its geometry and the way it modifies the vacuum, are incorporated in these nine (complex-valued) functions. On the other hand, the functions $f_{ij}(\tau)$ are determined completely by the medium and are independent of the presence of the atom. In this way, the problem of spontaneous decay of any atom (or molecule) in the vicinity of media is reduced to the calculation of these vacuum correlation functions.

A great simplification arises when the geometry has a cylindrical symmetry about, say, the z-axis and when the atom is located on this axis. Then it can be shown that[6]

$$f_{ij}(\tau)=0,\ i\neq j, \tag{4.6}$$

and that

$$f_{xx}(\tau)=f_{yy}(\tau). \tag{4.7}$$

Consequently, there are only three nonzero correlation functions, and only two different ones. We shall write

$f_{\parallel}$ for $f_{xx}$ and $f_{\perp}$ for $f_{zz}$. This situation arises, for instance, for any flat substrate. Then the notation $\parallel$ indicates that these functions couple to the parallel component of the dipole moment with respect to the surface, which is the direction perpendicular to the symmetry axis, and vice versa.

## V. TWO-STATE ATOM

In most experimental situations, only two states of an atom will be coupled, for instance, when an upper level is resonantly coupled to a ground state with a driving laser beam.[7] Then the atom can decay from this excited state $|e\rangle$ to the ground state $|g\rangle$ under emission of a photon, and the atomic density operator will evolve according to Eq. (3.13). With $P_e = |e\rangle\langle e|$ and $P_g = |g\rangle\langle g|$, the projectors onto the excited state and ground state, respectively, the atomic Hamiltonian can be represented as

$$H_a = \hbar\omega_e P_e + \hbar\omega_g P_g. \tag{5.1}$$

Then $\hbar\omega_e$ and $\hbar\omega_g$ are the respective energies of the levels. Since only two levels take part in the dynamics, the projectors obey the closure relation:

$$P_e + P_g = 1. \tag{5.2}$$

With the use of Eq. (5.2), the Liouvillian for the free atomic evolution becomes

$$L_a\Pi = \omega_o[P_e,\ \Pi], \tag{5.3}$$

where $\omega_o = \omega_e - \omega_g$ is the level separation. From now on we drop the subscript $a$ on the atomic density operator and on the arbitrary operator $\Pi$, as in Eq. (5.3).

Assuming cylindrical symmetry, the operator $Q_i$ reduces to

$$Q_i = \int_0^\infty d\tau\, f_{ii}(\tau) e^{-iL_a\tau}\mu_i. \tag{5.4}$$

The exponential in Eq. (5.4) can be expanded in projectors as

$$e^{-iL_a\tau}\Pi = \sum_{\alpha\beta} e^{-i(\omega_\alpha - \omega_\beta)\tau} P_\alpha \Pi P_\beta, \tag{5.5}$$

where the summation runs over the four combinations of $e$ and $g$. For an atom, the dipole operator $\mu$ has only transition matrix elements between the excited state and the ground state so that

$$\langle e|\mu_i|e\rangle = \langle g|\mu_i|g\rangle = 0. \tag{5.6}$$

A molecule can have a permanent dipole moment in both states, but it can be shown that this would not contribute to the relaxation operator. We then find

$$e^{-iL_a\tau}\mu_i = e^{-i\omega_o\tau} P_e\mu_i P_g + e^{i\omega_o\tau} P_g\mu_i P_e. \tag{5.7}$$

Substituting Eq. (5.7) into Eq. (5.4) and carrying out the integration then yields

$$Q_i = \tilde{f}_{ii}(-\omega_o) P_e\mu_i P_g + \tilde{f}_{ii}(\omega_o) P_g\mu_i P_e, \tag{5.8}$$

where $\tilde{f}(s)$ is the Fourier-Laplace transform of the vacuum correlation function:

$$\tilde{f}(s) = \int_0^\infty d\tau\, e^{is\tau} f(\tau) \tag{5.9}$$

As we shall see later on, the function $\tilde{f}(s)$ vanishes for $s<0$. This gives for $Q_i$

$$Q_i = \tilde{f}_{ii}(\omega_o) P_g\mu_i P_e, \tag{5.10}$$

and we notice that only the Fourier-Laplace transform of the correlation function, evaluated at the atomic transition frequency, appears in the expression for the relaxation operator.

From Eqs. (4.3) and (5.10), we then obtain for $\Gamma$

$$\Gamma\Pi = \sum_{i=x,y,z} \{\tilde{f}_{ii}(\omega_o)\mu_i^2 P_e\Pi + \tilde{f}_{ii}(\omega_o)^* \Pi P_e \mu_i^2 - 2\mu_i P_e \Pi P_e \mu_i \mathrm{Re}\tilde{f}_{ii}(\omega_o)\}. \tag{5.11}$$

Here we have dropped the so-called nonsecular terms since they contribute negligibly to the relaxation in the visible domain of the spectrum.[8] It will appear that the function $\tilde{f}_{ii}(\omega_o)$ is real, and therefore we can simplify Eq. (5.11) slightly to

$$\Gamma\Pi = \sum_{i=x,y,z} \tilde{f}_{ii}(\omega_o)\{\mu_i^2 P_e\Pi + \Pi P_e\mu_i^2 - 2\mu_i P_e\Pi P_e\mu_i\}. \tag{5.12}$$

The dipole operator can be written as

$$\mu = \mu_{eg} d + \mu_{eg}^* d^\dagger \tag{5.13}$$

in terms of the atomic raising and lowering operators

$$d = |e\rangle\langle g|\ ,\ d^\dagger = |g\rangle\langle e|\ . \tag{5.14}$$

In Eq. (5.13), $\mu_{eg} = \langle e|\mu|g\rangle$ is the transition dipole matrix element. We shall assume that the two states are chosen such that this matrix element is either parallel or perpendicular in the same sense as for the function $f(\tau)$. With these notations, Eq. (5.12) can be simplified to

$$\Gamma\Pi = \frac{1}{2}A\{P_e\Pi + \Pi P_e - 2d^\dagger \Pi d\}, \tag{5.15}$$

with $A$ as the Einstein coefficient for spontaneous emission (or decay), defined as

$$A = 2\tilde{f}(\omega_o)\mu_{eg}\cdot\mu_{eg}^*. \tag{5.16}$$

There are two possible values for A, depending on the two possibilities for the function $\tilde{f}(\omega_o)$, and we shall indicate them by $A_{\parallel}$ and $A_{\perp}$, in obvious notation. In the more general case that the dipole matrix element has both a parallel and perpendicular component, $A$ in Eq. (5.15) has to be written as $A_{\parallel}$ and a line identical to the right-hand side has to be added, but with $A_{\parallel}$ replaced by $A_{\perp}$. For an atom in empty space, the Einstein coefficient is given by Eq. (1.1), and this should be the limiting value for the case where the atom is far away from any medium.

## VI. TEMPORAL ATOMIC EVOLUTION

For a two-state atom in the vicinity of any medium, but without an external field or collisions with other particles, the equation of motion is Eq. (3.13),

$$i\frac{d\rho}{dt}=(L_a-i\Gamma)\rho, \tag{6.1}$$

with $L_a$ given by Eq. (5.3) and the operartor $\Gamma$ given by Eq. (5.15). Let us indicate the populations of the two levels by $n_e$ and $n_g$. They are equal to the matrix elements

$$n_e=<e|\rho|e>,\ n_g=<g|\rho|g> \tag{6.2}$$

of the atomic density operator, and they are subject to the constraint

$$n_e+n_g=1, \tag{6.3}$$

as follows from $Tr\ \rho=1$. When we take the matrix element $<e|\cdots|e>$ of Eq. (6.1), we find

$$\frac{dn_e}{dt}=-An_e, \tag{6.4}$$

which is an equation for the population of the excited state only. The solution is

$$n_e(t)=n_e(0)e^{-At}, \tag{6.5}$$

which is simple exponential decay from the excited state to the ground state. The time constant for the decay is 1/A, which equals the lifetime of the excited state. The population of the ground state then follws from Eq. (6.3). Taking the matrix element $<e|\cdots|e>$ of Eq. (6.1) gives

$$\frac{d\rho_{eg}}{dt}=(-i\omega_o-\frac{1}{2}A)\rho_{eg}, \tag{6.6}$$

which is an equation for the coherence $\rho_{eg}=<e|\rho|g>$ between the two levels. The solution is

$$\rho_{eg}(t)=\rho_{eg}(0)e^{-i\omega_o t}e^{-\frac{1}{2}At}, \tag{6.7}$$

showing that the coherence decays at a rate $A/2$, which is twice as slow as the decay of the population $n_e$. The coherence also oscillates with the atomic transition frequency.

Observable fluorescence during the decay has a photon emission rate proportional to the population of $|e>$, and the absorption profile for weak external radiation is determined by the regression of the atomic coherence. Consequently, all measurable influence by a medium on the dynamics and the spectroscopic properties of an atom must be contained in the Einstein coefficient $A$, and therefore in the Fourier-Laplace transform of the vacuum correlation function, $\bar{f}(\omega_o)$.

## VII. VACUUM NEAR A DIELECTRIC LAYER

In order to illustrate the dramatic effect that the presence of a medium can have on the Einstein $A$ coefficient, we work out the situation where the medium is a slab of dielectric material with a dielectric constant equal to $\varepsilon$. The boundaries of the medium will be the planes $z=0$ and $z=-\Delta$, and the atom will be located on the positive z-axis at $\boldsymbol{r}=h\boldsymbol{e}_z$, $h>0$. This geometry is illustrated in Fig. 1. We need an expression for the electric field operator in the region $z>0$ and the Hamiltonian of the radiation field in order to evaluate $f_{ii}(\tau)$ from Eq. (4.5).

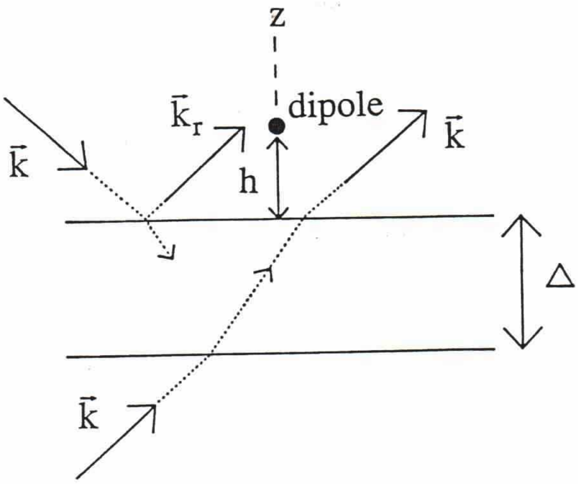

Fig. 1. An atom is located on the z-axis, a distance $h$ above a dielectric layer. Plane electromagnetic vacuum waves are incident upon the layer, and they partially reflect at the two surfaces. Part of such a wave travels through the medium, leaving the layer at the other side. Both the transmitted and reflected waves contribute to the modification of the vacuum, and thereby to the alteration of atomic spontaneous decay.

In empty space, the electric field in a quantization box with volume $V$ is given by

$$\boldsymbol{E}(\boldsymbol{r},\ t)_{empty}=\sum_{k\sigma}E_{k\sigma}\boldsymbol{e}_{k\sigma}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}+H.c., \tag{7.1}$$

where the t-dependence signifies the Heisenberg picture, the operator $E_{k\sigma}$ is defined as

$$E_{k\sigma}=\sqrt{\frac{\hbar\omega}{2\varepsilon_o\ V}}a_{k\sigma} \tag{7.2}$$

with $a_{k\sigma}$ as the annihilation operator for a photon in a mode with wave vector $\boldsymbol{k}$ and polarization $\sigma$, and $\omega=ck$. We shall take the two possible transverse polarization directions as surface ($s$) polarized and plane ($p$) polarized.

The vacuum field for empty space is a superposition of plane-wave modes, and these waves are incident upon the dielectric layer. Since Maxwell's equations also hold in quantum mechanics (in the Heisenberg picture), these plane waves reflect at the dielectric in the same way as in classical optics. The atomic dipole is located in $z>0$, and therefore we only consider the field in that region of space. As illustrated in Fig. 1, an incident vacuum wave from the region $z>0$ reflects partially as a specular wave and is partially refracted into the medium. Waves that enter the medium from the region $z<\Delta$ are partially transmitted through the layer, and they contribute to the field in $z>0$. From the boundary condition at $z=0$, it follows that the specular wave must have a wave vector with the same parallel component with respect to the surface as the incident wave. Therefore, if we write for the wave vector of the incident wave

$$\boldsymbol{k}=\boldsymbol{k}_{\parallel}+\boldsymbol{k}_{\perp}, \tag{7.3}$$

then the specular wave has the wave vector

$$\boldsymbol{k}_r=\boldsymbol{k}_{\parallel}+\boldsymbol{k}_{\perp}. \tag{7.4}$$

The wave vector of the transmitted wave, which originated from $z<\Delta$, is the same as that of the incident wave from $z<\Delta$. If an incident wave is $\sigma$($s$ or $p$) polarized, then the specular wave or the transmitted wave is also $\sigma$-polarized. Given the parallel component of the wave vector of an incident wave, for the $s$-polarized unit polarization vectors, we take

$$\boldsymbol{e}_{ks}=\frac{1}{k_{\parallel}}\boldsymbol{k}_{\parallel}\times\boldsymbol{e}_z. \tag{7.5}$$

For $p$-polarization, we take the unit vectors of the incident and transmitted waves as

$$\boldsymbol{e}_{kp}=\frac{1}{k}\boldsymbol{k}\times\boldsymbol{e}_{ks} \tag{7.6}$$

in terms of the corresponding $s$-polarization unit vectors, and for the specular wave, we take

$$\boldsymbol{e}_{k_rp}=\frac{1}{k}\boldsymbol{k}_r\times\boldsymbol{e}_{ks}\,. \tag{7.7}$$

The amplitude of a specular wave or a transmitted wave is simply a Fresnel coefficient $R_{k\sigma}$ or $T_{k\sigma}$, respectively, times the amplitude of the corresponding incident wave. Combining everything then gives for the electric field operator in $z>0$

$$\begin{aligned}\boldsymbol{E}(\boldsymbol{r},\ t)=&\sum_{k\sigma}E_{k\sigma}\{\boldsymbol{e}_{k\sigma}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}+R_{k\sigma}\boldsymbol{e}_{k_r\sigma}e^{i(\boldsymbol{k}_r\cdot\boldsymbol{r}-\omega t)}\}\\&+\sum_{k\sigma}E_{k\sigma}T_{k\sigma}\boldsymbol{e}_{k\sigma}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}+H.\ c.\end{aligned} \tag{7.8}$$

Here, the first summation runs over wave vectors with $k_z<0$, and the second summation has only wave vectors with $k_z>0$.

## VIII. CORRELATION FUNCTIONS

Equation (7.8) gives the electric field operator of the vacuum near the dielectric in the Heisenberg picture. For $t=0$ and $\boldsymbol{r}=\boldsymbol{h}=h\boldsymbol{e}_z$, this becomes the Schrödinger-picture electric field operator at the position of the atom, as it appears in the interaction Hamiltonian in Eq. (4.2) and the vacuum correlation function in Eq. (4.5). The quantity $\{\exp(iL_r\tau)\}\boldsymbol{E}(\boldsymbol{h})_i$ in Eq. (4.5) is effectively the $i$-th component of the Heisenberg-picture electric field operator at the position of the atom and evaluated at $t=\tau$. When we insert the two expressions for the field in Eq. (4.5) and take the quantum expectation value in the vacuum using

$$\langle 0|a_{k\sigma}a_{k'\sigma}|0\rangle=\langle 0|a_{k\sigma}^{\dagger}a_{k'\sigma}^{\dagger}|0\rangle=\langle 0|a_{k\sigma}^{\dagger}a_{k'\sigma}|0\rangle=0, \tag{8.1}$$

$$\langle 0|a_{k\sigma}a_{k'\sigma}^{\dagger}|0\rangle=\delta_{kk'}\delta_{\sigma\sigma'}, \tag{8.2}$$

we obtain for the correlation function with $j=i$

$$\begin{aligned}f_{ii}(\tau)=&\sum_{k\sigma,\,k_z<0}\frac{\omega}{2\varepsilon_0\hbar V}\ |\{\boldsymbol{e}_{k\sigma}e^{i\boldsymbol{k}\cdot\boldsymbol{h}}+R_{k\sigma}\boldsymbol{e}_{k_r\sigma}e^{i\boldsymbol{k}_r\cdot\boldsymbol{h}}\}_i|^2e^{-i\omega\tau}\\&+\sum_{k\sigma,\,k_z>0}\frac{\omega}{2\varepsilon_0\hbar V}\ |\{T_{k\sigma}\boldsymbol{e}_{k\sigma}e^{i\boldsymbol{k}\cdot\boldsymbol{h}}\}_i|^2e^{-i\omega\tau}.\end{aligned} \tag{8.3}$$

In the limit $V\to\infty$, the first summation over the wave vectors can be replaced by an integration according to

$$\frac{1}{V}\sum_{k\sigma k_z<0}(\cdots)=\frac{1}{8\pi^3}\int_{k_z<0}d^3\boldsymbol{k}(\cdots), \tag{8.4}$$

and in spherical coordinates the integral can be evaluated as

$$\int_{k_z<0}d^3\boldsymbol{k}(\cdots)=\int_0^{\infty}\mathrm{d}k\int_{\pi/2}^{\pi}\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi\ K^2\sin\theta(\cdots). \tag{8.5}$$

The second summation in Eq. (8.3) can be transformed in a similar way. In spherical coordinates, we have $\boldsymbol{k}=k\boldsymbol{e}_r$, and with Eq. (7.4) and the fact that $\boldsymbol{h}$ has only a perpendicular component, we conclude thhat $\boldsymbol{k}_r\cdot\boldsymbol{h}=-\boldsymbol{k}\cdot\boldsymbol{h}$. With our phase conventions, Eqs. (7.5)-(7.7), the polarization vectors become

$$\boldsymbol{e}_{ks}=\boldsymbol{e}_{k_rs}=-\boldsymbol{e}_{\phi}, \tag{8.6}$$

$$\boldsymbol{e}_{kp}=\boldsymbol{e}_{\theta},\ \boldsymbol{e}_{k_rp}=-\boldsymbol{e}_{\theta}-2\boldsymbol{e}_z\ \sin\theta. \tag{8.7}$$

The Fresnel reflection and transmission coefficients depend on the polar angle $\theta$, but not on the angle $\phi$. For $k_z>0$ the polar angle is equal to the angle of incidence $\theta_i$, but for $k_z<0$ the two angles are related as $\theta_i=\pi-\theta$. Furthermore, the Fresnel coefficients depend on $\theta_i$ through $\cos\theta_i$, and we shall write

$$P_{k\sigma}=P_{\sigma}(\omega,\ \cos\theta_i),\ T_{k\sigma}=T_{\sigma}(\omega,\ \cos\theta_i). \tag{8.8}$$

For the integrations over $\theta$ and $k$, we make the substitutions $u=\cos\theta_i$ and $\omega=ck$, respectively. We then obtain for the two correlation functions

$$\begin{aligned}f_{\perp}(\tau)=&\frac{1}{8\pi^2\varepsilon_0\hbar c^3}\int_0^{\infty}\mathrm{d}\omega\,\omega^3e^{-i\omega\tau}\int_0^1\mathrm{du}(1-\mathrm{u}^2)\\&\times\{|1+R_p(\omega,\ u)e^{2ih\omega u/c}|^2+\ |T_p(\omega,\ \mathrm{u})|^2\},\end{aligned} \tag{8.9}$$

$$\begin{aligned}f_{\parallel}(\tau)=&\frac{1}{16\pi^2\varepsilon_0\hbar c^3}\int_0^{\infty}\mathrm{d}\omega\,\omega^3e^{-i\omega\tau}\int_0^1\mathrm{du}\\&\times\{|1+R_s(\omega,\ u)e^{2ih\omega u/c}|^2+\ |T_s(\omega,\ \mathrm{u})|^2\}\\&+\frac{1}{16\pi^2\varepsilon_0\hbar c^3}\int_0^{\infty}\mathrm{d}\omega\,\omega^3e^{-i\omega\tau}\int_0^1\mathrm{du}\ \mathrm{u}^2\\&\times\{|1-R_p(\omega,\ u)e^{2ih\omega u/c}|^2+\ |T_p(\omega,\ \mathrm{u})|^2\}.\end{aligned} \tag{8.10}$$

The perpendicular correlation function is determined by the Fresnel coefficients for p-waves only, but the parallel function depends on both s-waves and p-waves. Also notice that the geometrical factor in the u-integrands is different in all three integrals. Furthermore, if we would have taken $i \neq j$ in Eq. (8.3), then the integral over $\phi$ would give zero, and thus this correlation function equals zero.

As shown in Section V, we need the Fourier-Laplace transform of the correlation functions, evaluated at $s=\omega_0$. The $\tau$ dependence in Eqs. (8.9) and (8.10) is only through the exponentials in the integrands, and therefore the Fourier-Laplace transformation leads to the following integral:

$$\int_0^\infty d\tau\, e^{i(\omega_0-\omega)\tau} = \pi\delta(\omega_0-\omega) + P\frac{i}{\omega_0-\omega}, \tag{8.11}$$

where $P$ stands for the principal value. This principal value part gives an imaginary contribution to the relaxation constants, which leads to an effective level shift (the Lamb shift). In the present nonrelativistic theory, this imaginary part diverges in the upper integration limit over $\omega$. For these high frequencies, the dipole approximation (which is the long-wavelength limit) breaks down, and also relativistic effects have to be taken into account. The final result is a very small value for this imaginary part, and we shall therefore omit it. With Eq. (8.11), the Fourier-Laplace transforms of Eqs. (8.9) and (8.10) become

$$\tilde{f}_\perp(\omega_0) = \frac{\omega_0^3}{8\pi\varepsilon_0\hbar c^3}\int_0^1 du(1-u^2) \times\{|1+R_p(\omega_0, u)e^{2ih\omega_0 u/c}|^2 + |T_p(\omega_0, u)|^2\}, \tag{8.12}$$

$$\tilde{f}_\parallel(\omega_0) = \frac{\omega_0^3}{16\pi\varepsilon_0\hbar c^3}\int_0^1 du \times\{|1+R_s(\omega_0, u)e^{2ih\omega_0 u/c}|^2 + |T_s(\omega_0, u)|^2\} + \frac{\omega_0^3}{16\pi\varepsilon_0\hbar c^3}\int_0^1 du\, u^2 \times\{|1-R_p(\omega_0, u)e^{2ih\omega_0 u/c}|^2 + |T_p(\omega_0, u)|^2\}. \tag{8.13}$$

The Fresnel coefficients now only appear with their values at the atomic resonance frequency $\omega_0$, and the integration is over the cosine of the angle of incidence.

The Fresnel coefficients appearing in Eqs. (8.12) and (8.13) can be calculated from Maxwell's equations in the usual way. They are found to be

$$R_s = (e^{2i\delta v}-1)\frac{v^2-u^2}{D_s}, \quad R_p = (e^{2i\delta v}-1)\frac{v^2-(u\varepsilon)^2}{D_p}, \tag{8.14}$$

$$T_s = \frac{4uv}{D_s}e^{i(v-u)\delta}, \quad T_p = \frac{4uv\varepsilon}{D_p}e^{i(v-u)\delta}, \tag{8.15}$$

with

$$u = \cos\theta_i, \quad v = \sqrt{\varepsilon - 1 + u^2}, \tag{8.16}$$

and

$$D_s = (v+u)^2 - (v-u)^2 e^{2i\delta v}, \tag{8.17}$$

$$D_p = (v+u\varepsilon)^2 - (v-u\varepsilon)^2 e^{2i\delta v}, \tag{8.18}$$

and the dimensionless layer thickness

$$\delta = k\Delta = \frac{\omega_0\Delta}{c}. \tag{8.19}$$

The u-dependence appears to be too complicated to perform the integrations in Eqs. (8.12) and (8.13) explicitly. For the dielectric constant $\varepsilon$, we have to take its value at frequency $\omega_0$. It can be verified easily from Eqs. (8.14) and (8.15) that for $\varepsilon \geq 1$ the reflection and transmission coefficients are related as

$$|R_\sigma|^2 + |T_\sigma|^2 = 1, \quad \sigma = s, p, \tag{8.20}$$

where both Fresnel coefficients are evaluated at the same angle of incidence.

## IX. EINSTEIN COEFFICIENTS FOR SPONTANEOUS DECAY

The perpendicular and parallel Einstein coefficients for spontaneous decay can now be found from Eq. (5.16). We shall write

$$A_i = Ab_i, \quad i = \perp, \parallel \tag{9.1}$$

where $A$ is the value from Eq. (1.1) for decay in empty space. The correction factors due to the presence of the surface are then

$$b_\perp = \frac{3}{4}\int_0^1 du(1-u^2)\{|1+R_p e^{i\beta u}|^2 + |T_p|^2\}, \tag{9.2}$$

$$b_\parallel = \frac{3}{8}\int_0^1 du\{|1+R_s e^{i\beta u}|^2 + |T_s|^2 + u^2 \times[|1-R_p e^{i\beta u}|^2 + |T_p|^2]\}, \tag{9.3}$$

with

$$\beta = \frac{2\omega_0 h}{c}. \tag{9.4}$$

In the absense of the medium, we have effectively $R_s = R_p = 0$ and $T_s = T_p = 1$ as follows from Eqs. (8.14) and (8.15) with $\varepsilon = 1$ or $\delta = 0$. Then Eqs. (9.2) and (9.3) give $b_\perp = b_\parallel = 1$, as it should.

For a dielectric, we have $\varepsilon \geq 1$, and we can use Eq. (8.20) to simplify the expressions for $b_\perp$ and $b_\parallel$. Eliminating the transmission coefficients gives

$$b_\perp = \frac{3}{2}\int_0^1 du\,(1-u^2)Re(1+R_p e^{i\beta u}), \tag{9.5}$$

$$b_\parallel = \frac{3}{4}\int_0^1 du\, Re(1+R_s e^{i\beta u} + u^2[1-R_p e^{i\beta u}]), \tag{9.6}$$

which can be simplified to

$$b_\perp = 1 + \frac{3}{2}\int_0^1 du\,(1-u^2)Re R_p e^{i\beta u}, \tag{9.7}$$

$$b_\parallel = 1 + \frac{3}{4}\int_0^1 du\, Re(R_s - u^2 R_p)e^{i\beta u}. \tag{9.8}$$

The dependence on the atom-surface normal distance $h$ is incorporated in the parameter $\beta$. When the atom is far away from the surface ($\beta \to \infty$), then the exponentials oscillate very fast as a function of $u$, and they integrate out to zero. This gives $b_\perp = b_\parallel = 1$, as expected.

## X. MIRROR

A special case of practical importance is when the layer is a metal. This is characterized by $\varepsilon < 0$, and this makes the parameter $v$ from Eq. (8.16) positive imaginary. In addition we shall assume that the layer thickness is much larger than an optical wavelength ($\delta \gg 1$). Then the Fresnel coefficients simplify to

$$T_s = T_p = 0, \quad R_s = \frac{u-v}{u+v}, \quad R_p = \frac{u\varepsilon - v}{u\varepsilon + v}, \tag{10.1}$$

and since $v$ is imaginary and $u$ is real, this gives

$$|R_\sigma| = 1, \quad \sigma = s, p. \tag{10.2}$$

Therefore, the reflectivity at a metal surface (mirror) equals unity, and there can only be a phase shift upon reflection. If we define the angles

$$\phi_s = \arctan\left(\frac{\sqrt{1-\varepsilon-u^2}}{u}\right), \tag{10.3}$$

$$\phi_p = \arctan\left(\frac{\sqrt{1-\varepsilon-u^2}}{u\varepsilon}\right), \tag{10.4}$$

then the Fresnel coefficients can be represented as

$$R_\sigma = e^{-2i\phi_\sigma}. \tag{10.5}$$

For a metal, relation (8.20) also holds, and therefore the Einstein coefficients relative to empty space become, with Eqs. (9.7) and (9.8), become

$$b_\perp = 1 + \frac{3}{2}\int_0^1 du\ (1-u^2) Re\, e^{i(\beta u - 2\phi_p)}, \tag{10.6}$$

$$b_\parallel = 1 + \frac{3}{4}\int_0^1 du\ Re(e^{-2i\phi_s} - u^2 e^{-2i\phi_p}) e^{i\beta u}. \tag{10.7}$$

Metals like silver are nearly perfect conductors, and they can be modelled effectively by $\varepsilon \to -\infty$. Then the phase angles from Eqs. (10.3) and (10.4) become

$$\phi_s = \pi/2, \quad \phi_p = 0, \tag{10.8}$$

and the Fresnel reflection coefficients are

$$R_s = -1, \quad R_p = 1. \tag{10.9}$$

With these values, the integrals in Eqs. (10.6) and (10.7) can be performed analytically, and the result is

$$b_\perp = 1 - 3\left[\frac{\cos\beta}{\beta^2} - \frac{\sin\beta}{\beta^3}\right], \tag{10.10}$$

$$b_\parallel = 1 - \frac{3}{2}\left[\frac{\sin\beta}{\beta} + \frac{\cos\beta}{\beta^2} - \frac{\sin\beta}{\beta^3}\right]. \tag{10.11}$$

For $\beta \to \infty$, we find again that $b_\perp = b_\parallel = 1$, as it should. When the atom is very close to the surface (within a fraction of a wavelength), we find

$$b_\perp = 2, \quad b_\parallel = 0. \tag{10.12}$$

In this limit, an atom with its transition dipole moment perpendicular to the surface has twice the Einstein coefficient for decay compared to an atom in empty space, and therefore the excited state has half the lifetime. On the other hand, when the dipole is parallel to the surface, the Einstein coefficient approaches zero, and this indicates that the atom in its excited state will not decay spontaneously at all. In Fig. 2, the behavior of the Einstein coefficients as a function of the distance between the atom and the surface is shown. The oscillatory behavior of these functions is due to interference between radiation which is emitted directly during the decay and radiation which is reflected by the metal. In Eqs. (10.6) and (10.7), the factor exp($i\beta$u) accounts for the retardation in this process.

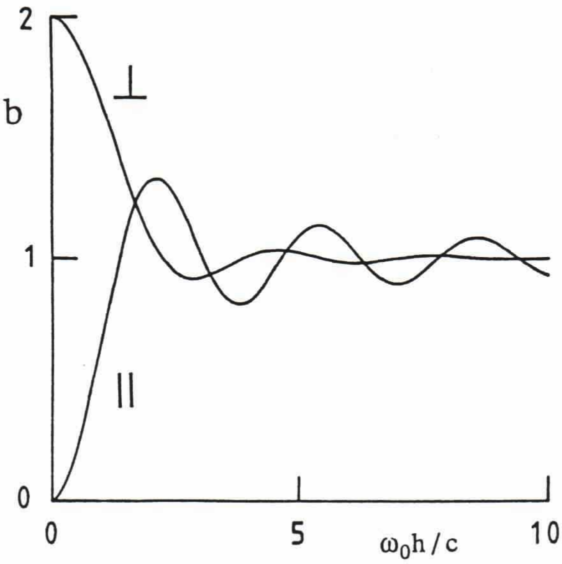

Fig. 2. The two curves show the Einstein coefficients, normalized by their free-space values, for a perpendicular and parallel dipole moment, as a function of the normalized atom-surface separation $h$. For large $h$, compared to a wavelength of the emitted radiation during the decay, both curves approach the free-space value of b=1.

## XI. CONCLUSIONS

The equation of motion for the reduced density operator of a two-state atom near a dielectric layer has been derived using the Liouville formulation of reservoir theory. The presence of the medium was accounted for by a modification of the matrix elements of the effective damping operator $\Gamma$. These matrix elements, which are the relaxation constants, depend on the properties of the medium, like the dielectric constant, the layer thickness, etc. Due to the loss of spherical symmetry, as compared to spontaneous decay in empty space, the relaxation times depend on the orientation, with respect to the surface, of the transition dipole matrix element. When the atomic levels are degenerate, then the operator $\Gamma$ can be derived in the same way without any complications,[9] and the same holds for multilevel systems. However, when the medium has a different geometry, the present approach might become too cumbersome because the mode structure of the electric field operator becomes more complicated, and this might prohibit the evaluation of the field correlation functions. In this case, one has to resort to different methods for calculating atomic lifetimes.[10-14]

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