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SYMMETRIES OF SPONTANEOUS DECAY FOR ATOMS NEAR ANY SURFACE

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The structure of spontaneous decay of atoms in the vicinity of a surface is shown to be determined by spatial symmetries. The spontaneous-decay operator for a degenerate two-level atom is derived, and with symmetry considerations the number of free parameters is reduced to two. Only the dimensionless and normalized inverse lifetimes $b_{\parallel}$ and $b_{\perp}$ for a parallel and perpendicular dipole moment with respect to the surface, respectively, enter the expression for the relaxation operator for any atom near any surface. These two parameters incorporate the atom–surface distance dependence of all Einstein coefficients for spontaneous decay, and all optical properties of the substrate material. It is shown that the specific features of spontaneous decay are mainly geometrical, and a consequence of symmetries of the vacuum radiation field, irrespective of the presence of the atom. With an example it is shown how the parameters $b_{\parallel}$ and $b_{\perp}$ can be calculated in a particular case.

1. Introduction

An excited atom will decay to lower states, until it reaches its ground state. This process of spontaneous decay is accompanied by the emission of fluorescent photons and the loss of internal energy of the atom equals the energy gain of the radiation field. Therefore, the processes of spontaneous decay and spontaneous emission of radiation are related through energy conservation. We shall consider a dipole-allowed transition between a degenerate excited level e and a ground level g (also possibly degenerate), and indicate the atomic wave functions of the multiplets by $|j_e m_e\rangle$ and $|j_g m_g\rangle$, respectively. The upper state has $2j_e+1$ magnetic substates, which are coupled by the atomic dipole moment operator $\boldsymbol{\mu}$ to the $2j_g+1$ ground states. If we denote by $\hbar\omega_0$ the energy separation between the levels, then the expression for the Einstein coefficient for spontaneous decay from e to g reads

$$A_{\mathrm{f}} = \frac{\omega_0^3}{3\pi\epsilon_0 \hbar c^3} \frac{|\langle j_{\mathrm{e}} \| \mu \| j_{\mathrm{g}} \rangle|^2}{2 j_{\mathrm{e}} + 1}, \tag{1.1}$$

in terms of the reduced matrix element of the dipole operator. An atom in state $| j_{\mathrm{e}} m_{\mathrm{e}} \rangle$ shall decay exponentially, with a lifetime $1/A_{\mathrm{f}}$, to the various ground states at a rate A_{f} times the population of $| j_{\mathrm{e}} m_{\mathrm{e}} \rangle$, and after completion of the decay the emitted radiation energy equals $\hbar\omega_0$. An important feature of this process is that the relaxation constant for the decay of $| j_{\mathrm{e}} m_{\mathrm{e}} \rangle$ is independent of the magnetic quantum number m_{e}. That this must be so is a consequence of symmetry, as can be understood as follows. If we rotate an atomic wave function $| j_{\mathrm{e}} m_{\mathrm{e}} \rangle$ over the Euler angles α, β, γ, then the transformed wave function can be expressed as [1,2]

$$P_{\mathrm{R}}(\alpha, \beta, \gamma) | j_{\mathrm{e}} m_{\mathrm{e}} \rangle = \sum_{m_{\mathrm{e}}'} | j_{\mathrm{e}} m_{\mathrm{e}}' \rangle D_{m_{\mathrm{e}}' m_{\mathrm{e}}}^{(j_{\mathrm{e}})}(\alpha, \beta, \gamma), \tag{1.2}$$

where $P_{\mathrm{R}}(\alpha, \beta, \gamma)$ indicates the rotation operator, and $D^{(j_{\mathrm{e}})}$ is the rotation matrix. Spontaneous decay of $| j_{\mathrm{e}} m_{\mathrm{e}} \rangle$, or spontaneous emission of photons, is brought about by a coupling of the atomic dipole moment to the electromagnetic field. But since the electromagnetic vacuum (empty space) is isotropic, a rotated state $P_{\mathrm{R}}(\alpha, \beta, \gamma) | j_{\mathrm{e}} m_{\mathrm{e}} \rangle$ must decay in the same way as the original state $| j_{\mathrm{e}} m_{\mathrm{e}} \rangle$, for all rotation angles α, β, γ. From (1.2) it follows that $P_{\mathrm{R}}(\alpha, \beta, \gamma) | j_{\mathrm{e}} m_{\mathrm{e}} \rangle$ is a superposition of all states $| j_{\mathrm{e}} m_{\mathrm{e}}' \rangle$, and therefore this can only hold if the relaxation constant for $| j_{\mathrm{e}} m_{\mathrm{e}} \rangle$ is independent of m_{e}. From a different point of view, we can say that the quantum number m_{e} refers to a particular choice of the quantization z-axis. Rotating an atomic state $| j_{\mathrm{e}} m_{\mathrm{e}} \rangle$ is then equivalent to a change of quantization axis. In isotropic space the choice of the z-axis has no significance, and consequently the decay rate of $| j_{\mathrm{e}} m_{\mathrm{e}} \rangle$ must be independent of this choice, and therefore independent of m_{e}.

Let us now consider an atom which is positioned near a surface. We choose the z-axis (arbitrarily) as the normal to the surface. The region $z < 0$ is filled with an optically-reflecting material, like a metal, dielectric, nonlinear crystal etc., and the atom is situated in the vacuum $z > 0$, with a normal distance h to the surface $z = 0$. Then the presence of the substrate destroys the isotropy of the environment of the atom. For instance, an emitted fluorescent photon in the $-z$ direction can reflect at the surface and travel back into the region $z > 0$, but an emitted photon in the $+z$ direction will never hit the surface. Furthermore, reflection coefficients for media depend in general on the angle of incidence of the radiation, or from the perspective of the atom, these coefficients depend on the emission angle. The reflected radiation will be experienced by the atom as an external field, and a stimulated transition can cause the previously emitted photon to be absorbed again. This mechanism effectively enhances the lifetime of the excited state, and thereby it changes the Einstein coefficient for spontaneous decay. Due to the loss of spherical symmetry, however, the lifetime of a particular state $|j_e m_e\rangle$ of the multiplet is not necessarily independent of m_e anymore.

In this paper we present a general theory for atomic spontaneous decay near a surface, without regard to any of the properties of the medium. We shall only use the remaining symmetries of the system. In this fashion we can disentangle the pure geometrical features of spontaneous decay from the effects which result from particular optical properties of the substrate. We shall only assume that the medium is isotropic, which pertains to most practical situations. The first symmetry which remains is the invariance of the system for rotations around the z-axis. For a rotation over an angle α, eq. (1.2) reduces to

$$P_R(\alpha, 0, 0)\,|j_e m_e\rangle = \exp(-i m_e \alpha)\,|j_e m_e\rangle, \tag{1.3}$$

e.g., the state $|j_e m_e\rangle$ transforms into itself (apart from a phase factor). Therefore, this symmetry does not give any information about the m_e-dependence of a lifetime. A second symmetry is the invariance for reflections in a plane through the z-axis. If we take this plane (arbitrarily) as the xz-plane, then a reflection in this plane is equivalent to the product operation of a rotation over π around the y-axis, followed by a parity operation (point reflection in the origin). Then we have

$$R_{xz}\,|j_e m_e\rangle = P \times P_R(0, \pi, 0)\,|j_e m_e\rangle, \tag{1.4}$$

with R_{xz} the reflection operator and P the parity operator. With

$$D^{(j_e)}_{m'_e m_e}(0, \pi, 0) = (-1)^{j_e - m_e}\delta_{m_e, -m'_e}, \tag{1.5}$$

we find from eq. (1.2)

$$R_{xz}\,|j_e m_e\rangle = \pm\,|j_e - m_e\rangle, \tag{1.6}$$

where the sign depends on the parity of $|j_e - m_e\rangle$. Consequently, the states $|j_e m_e\rangle$ and $|j_e - m_e\rangle$ experience the same electromagnetic environment, and hence their lifetimes are identical. If we denote the Einstein coefficient of the state $|j_e m_e\rangle$ by A_{m_e} then we must have

$$A_{-m_e} = A_{m_e}, \tag{1.7}$$

as a result of the reflection symmetry.

Apart from these symmetries, we have a causality requirement which imposes restrictions on the values of A_{m_e}. If the atom is far away from the surface, every Einstein coefficient A_{m_e} must reduce to its free-space value A_f. Therefore we have the condition

$$A_{m_e} \to A_f, \quad \text{for} \quad h \to \infty. \tag{1.8}$$

To see this, we recall that spontaneous decay is intimately related to the emission of photons. If the distance between the atom and the surface is larger than the lifetime $1/A_{m_e}$ of the state $|j_e m_e\rangle$, times the speed of light, then there can be no interference between the emission of photons by the atom and reflected photons by the surface (which were emitted earlier), because the travel time of a photon between atom and surface exceeds the emission time. Therefore, for distances h larger than roughly c/A_{m_e}, the atom behaves as an atom in empty space. With $\lambda = 2\pi c/\omega_0$ the wavelength of the radiation, we find that for

$$h > \lambda\omega_0/A_f, \tag{1.9}$$

the surface effects should disappear. For low-lying atomic transitions the ratio ω_0/A_f is of the order of 10^6, and (1.9) overestimates the value of h by many orders of magnitude, for most cases. For dielectrics and metals we know [3–5] that $A_{m_e} \approx A_f$ if $h \gtrsim \lambda$, due to strong interferences of the various incident and reflected waves. Only for very special cases, like four-wave mixing crystals, or phase conjugators [6,7] the causality requirement (1.9) imposes an actual upper limit for h, at which surface effects should disappear.

2. Relaxation

Spontaneous decay is a relaxation phenomenon, which is brought about by the coupling of the atomic dipole $\boldsymbol{\mu}$ to the electromagnetic field. The analysis of spontaneous decay starts with the full equation of motion for the density operator $\rho(t)$ of atom plus radiation

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = (L_\mathrm{a} + L_\mathrm{r} + L_\mathrm{ar})\rho(t), \tag{2.1}$$

where the Liouvillians L_a, L_r and L_ar represent the atom, the radiation and the interaction, respectively. They are related to the corresponding Hamiltonians according to

$$L_i\sigma = \hbar^{-1}[H_i, \sigma], \quad i = \mathrm{a, r, ar}, \tag{2.2}$$

which defines their action on an arbitrary Hilbert space operator σ. The Liouvillian L_r includes the modifications of the radiation field due to the presence of the medium. In other words, H_r is the Hamiltonian for the empty half-space $z > 0$ (the electromagnetic vacuum) and the material in $z < 0$. The quantity of interest for spontaneous decay is the state of the atom, irrespective of the state of the radiation field. This reduced atomic density operator $\rho_\mathrm{a}(t)$ is defined by

$$\rho_\mathrm{a}(t) = \mathrm{Tr}_\mathrm{r}\, \rho(t), \tag{2.3}$$

where the trace runs over all states of the radiation field.

It is a standard procedure in reservoir theory to derive an equation of motion for $\rho_a(t)$. In the compact Liouville notation it reads [8,9]

$$i\frac{d}{dt}\rho_a(t) = (L_a - i\Gamma)\rho_a(t), \tag{2.4}$$

with L_a the free evolution of the atom (no coupling to the radiation), and Γ the spontaneous-decay operator. Explicitly,

$$\Gamma\sigma_a = \mathrm{Tr}_r\, L_{ar}\int_0^\infty d\tau\, \exp[-i(L_a + L_r)\tau]\, L_{ar}\, \exp(iL_a\tau)[\sigma_a\bar{\rho}_r], \tag{2.5}$$

for an arbitrary atomic operator σ_a. Here, $\bar{\rho}_r$ is the thermal-equilibrium density operator of the radiation field, which will be assumed to be the vacuum state $|0\rangle\langle 0|$, defined as the lowest-energy state. Notice that $|0\rangle\langle 0|$ is not necessarily the same as for a radiation field in empty space (zero-photon Fock state), because the medium in $z < 0$ will affect the state of the radiation in $z > 0$.

3. Dipole interaction

Expression (2.5) for the relaxation operator Γ holds quite generally. An explicit evaluation (for instance its matrix elements) requires that we prescribe the interaction Hamiltonian H_{ar}. If we denote by $\boldsymbol{E}(\boldsymbol{r})$ the electric component of the radiation field (although further unspecified), then the coupling Hamiltonian in the dipole approximation assumes the form

$$H_{ar} = -\boldsymbol{\mu}\cdot\boldsymbol{E}(\boldsymbol{h}), \tag{3.1}$$

with $\boldsymbol{h} = h\boldsymbol{e}_z$ the position of the atom.

The eigenstates of the atomic Hamiltonian H_a (internal structure) are the angular momentum states $|j_e m_e\rangle$, $m_e = -j_e, \ldots, j_e$ and $|j_g m_g\rangle$, $m_g = -j_g, \ldots, j_g$. The eigenvalue equations are

$$H_a|j_e m_e\rangle = \hbar\omega_e|j_e m_e\rangle, \tag{3.2}$$

$$H_a|j_g m_g\rangle = \hbar\omega_g|j_g m_g\rangle, \tag{3.3}$$

and the frequency separation between the two doublets is $\omega_e - \omega_g = \omega_0 > 0$. In terms of the projectors onto the e and g levels

$$P_e = \sum_{m_e}|j_e m_e\rangle\langle j_e m_e|, \quad P_g = \sum_{m_g}|j_g m_g\rangle\langle j_g m_g|, \tag{3.4}$$

the Hamiltonian can be represented by

$$H_a = \hbar\omega_e P_e + \hbar\omega_g P_g. \tag{3.5}$$

Then the evaluation of the exponentials $\exp(\pm \mathrm{i} L_{\mathrm{a}}\tau)$ in (2.5) proceeds in two steps. From $L_{\mathrm{a}}\sigma = \hbar^{-1}[H_{\mathrm{a}}, \sigma]$ it follows that

$$\exp(\pm \mathrm{i} L_{\mathrm{a}}\tau)\sigma = \exp(\pm \mathrm{i} H_{\mathrm{a}}\tau/\hbar)\sigma \exp(\mp \mathrm{i} H_{\mathrm{a}}\tau/\hbar), \tag{3.6}$$

and with $P_{\mathrm{e}}^2 = P_{\mathrm{e}}$, $P_{\mathrm{g}}^2 = P_{\mathrm{g}}$ we find

$$\exp(\pm \mathrm{i} H_{\mathrm{a}}\tau/\hbar) = \exp(\pm \mathrm{i}\omega_{\mathrm{e}}\tau) P_{\mathrm{e}} + \exp(\pm \mathrm{i}\omega_{\mathrm{g}}\tau) P_{\mathrm{g}}. \tag{3.7}$$

Combining (3.6) and (3.7) gives

$$\exp(\pm \mathrm{i} L_{\mathrm{a}}\tau)\sigma = \sum_{\substack{\alpha=\mathrm{e,g}\\ \beta=\mathrm{e,g}}} \exp\left[\pm \mathrm{i}(\omega_\alpha - \omega_\beta)\tau\right] P_\alpha \sigma P_\beta. \tag{3.8}$$

An important property of an atomic dipole operator $\boldsymbol{\mu}$ is that it cannot have matrix elements between states within a single multiplet. In terms of projectors we can then write

$$P_{\mathrm{e}}\boldsymbol{\mu} P_{\mathrm{e}} = 0, \quad P_{\mathrm{g}}\boldsymbol{\mu} P_{\mathrm{g}} = 0, \tag{3.9}$$

which is essentially Laporte's rule (p. 260 of ref. [1]). On the other hand, the closure relation for the atomic wave functions is

$$P_{\mathrm{e}} + P_{\mathrm{g}} = 1, \tag{3.10}$$

so that $\boldsymbol{\mu} = (P_{\mathrm{e}} + P_{\mathrm{g}})\boldsymbol{\mu}(P_{\mathrm{e}} + P_{\mathrm{g}})$, and with eq. (3.9) this reduces to

$$\boldsymbol{\mu} = \boldsymbol{\mu}^{(+)} + \boldsymbol{\mu}^{(-)}. \tag{3.11}$$

Here we introduced the lowering $(+)$ and raising $(-)$ part of $\boldsymbol{\mu}$ as

$$\boldsymbol{\mu}^{(+)} = P_{\mathrm{g}}\boldsymbol{\mu} P_{\mathrm{e}}, \quad \boldsymbol{\mu}^{(-)} = P_{\mathrm{e}}\boldsymbol{\mu} P_{\mathrm{g}}, \tag{3.12}$$

and from $\boldsymbol{\mu}^\dagger = \boldsymbol{\mu}$ we find

$$\boldsymbol{\mu}^{(-)} = (\boldsymbol{\mu}^{(+)})^\dagger. \tag{3.13}$$

Now we substitute expression (3.8) twice in eq. (2.5), and we expand the dipole moment $\boldsymbol{\mu}$ and the field at the position of the atom, $\boldsymbol{E}(\boldsymbol{h})$, in Cartesian components. After some rearrangements we obtain the representation

$$\Gamma\sigma_{\mathrm{a}} = \sum_{i=x,y,z} \left[\mu_i, Q_i\sigma_{\mathrm{a}} - \sigma_{\mathrm{a}} Q_i^\dagger\right], \tag{3.14}$$

in terms of the Hilbert space operators

$$Q_i = \sum_j \int_0^\infty \mathrm{d}\tau\, f_{ij}(\tau)\left[\exp(-\mathrm{i} L_{\mathrm{a}}\tau)\mu_j\right], \quad i = x, y, z. \tag{3.15}$$

The nine scalar functions $f_{ij}(\tau)$ (not operators) are the field correlation functions

$$f_{ij}(\tau) = \hbar^{-2}\mathrm{Tr}_{\mathrm{r}}\, E_i(\boldsymbol{h}) \exp(-\mathrm{i} L_{\mathrm{r}}\tau)\left(E_j(\boldsymbol{h})\bar{\rho}_{\mathrm{r}}\right), \tag{3.16}$$

which depend on properties of the radiation field only (i.e. $\boldsymbol{E}(\boldsymbol{h})$, L_r and $\bar{\rho}_r$). With

$$\boldsymbol{E}(\boldsymbol{h},\tau)=\exp(\mathrm{i}L_r\tau)\boldsymbol{E}(\boldsymbol{h}),\tag{3.17}$$

the field in the interaction picture, and with $\bar{\rho}_r=|0\rangle\langle 0|$, we can write eq. (3.16) as

$$f_{ij}(\tau)=\hbar^{-2}\langle 0|E_i(\boldsymbol{h},\tau)E_j(\boldsymbol{h},0)|0\rangle,\tag{3.18}$$

which clearly exhibits that $f_{ij}(\tau)$ is the correlation function of the electric field at the space point $\boldsymbol{h}$.

Next, we insert expression (3.8) into the definition (3.15) of Q_i, and we use (3.9). The τ-integral effectively amounts to a Fourier–Laplace transform of $f_{ij}(\tau)$ according to

$$\tilde{f}_{ij}(\omega)=\int_0^\infty \mathrm{d}\tau\, \mathrm{e}^{\mathrm{i}\omega\tau} f_{ij}(\tau).\tag{3.19}$$

Working out expression (3.15) then gives

$$Q_i=\sum_j \tilde{f}_{ij}(\omega_0)P_g\mu_jP_e,\tag{3.20}$$

where we have made the approximation

$$\tilde{f}_{ij}(-\omega_0)\simeq 0.\tag{3.21}$$

That this is a good as exact for the electromagnetic vacuum follows from the representation (3.16) of $f_{ij}(\tau)$. The field $E_j(\boldsymbol{h})$ consists of a creation and an annihilation part, but since it works on $\bar{\rho}_r=|0\rangle\langle 0|$, only the creation part contributes. Therefore, $\exp(-\mathrm{i}L_r\tau)(E_j(\boldsymbol{h})|0\rangle\langle 0|)$ contains mainly positive frequencies. It has terms like $\exp(-\mathrm{i}\omega\tau)$ with $\omega>0$ the frequency of a photon. The integrand of (3.19) then has the factor $\exp[-\mathrm{i}(\omega+\omega_0)\tau]$ for $\tilde{f}_{ij}(-\omega_0)$, and $\exp[-\mathrm{i}(\omega-\omega_0)\tau]$ for $\tilde{f}_{ij}(\omega_0)$. Oscillations with twice the optical frequency, $\omega+\omega_0$, will cause the integral of $\exp[-\mathrm{i}(\omega+\omega_0)\tau]f_{ij}(\tau)$ over τ to vanish almost identically, as compared to the same integral with $\exp[-\mathrm{i}(\omega-\omega_0)\tau]$. This justifies approximation (3.21) for fields in the vacuum state (zero temperature).

We then insert (3.20) into (3.14), work out the commutator, use again (3.9) and (3.10), and drop nonsecular terms [10], which finally yields for Γ

$$\begin{aligned}\Gamma\sigma_a=\sum_{ij}\Big[&\tilde{f}_{ij}(\omega_0)P_e\mu_iP_g\mu_jP_e\sigma_a+\tilde{f}_{ij}^{*}(\omega_0)\sigma_aP_e\mu_jP_g\mu_iP_e\\&-\big(\tilde{f}_{ij}(\omega_0)+\tilde{f}_{ji}^{*}(\omega_0)\big)P_g\mu_jP_e\sigma_aP_e\mu_iP_g\Big].\end{aligned}\tag{3.22}$$

We remark that the only atomic property that comes in the expression for Γ is the dipole operator $\boldsymbol{\mu}$. On the other hand, the functions $\tilde{f}_{ij}(\omega_0)$ embody all necessary details of the radiation field, the wave function $|0\rangle$ of the radiation field, the properties of the substrate (through the modification of $\boldsymbol{E}(\boldsymbol{h})$), and the dependence of the spontaneous-emission operator on the atom–surface distance h (through $\boldsymbol{E}(\boldsymbol{h})$). So far, we have only used the fact that the radiation field is in its lowest energy state, and therefore expression (3.22) is a very general representation for Γ of an atom in an empty part of space, but in the vicinity of active boundaries.

4. Symmetries

Although expression (3.22) for the spontaneous-emission operator of an atom is a great simplification as compared to the general expression (2.5) for a relaxation operator, it still involves nine unknown field correlation functions $\tilde{f}_{ij}(\omega_0)$. In this section we shall show that by imposing the symmetry conditions, as mentioned in the Introduction, the number of unknown parameters reduces from nine to two. For an atom in empty space it follows from the isotropy of space that all levels $| j_e m_e \rangle$ must have the same Einstein coefficient A_f for spontaneous decay, as pointed out in the Introduction. The argument relies on the rotational symmetry only, and is independent of the mechanism of spontaneous emission (e.g., the specific form of H_{ar}). For the remaining symmetry of an atom near a surface, however, we only found relation (1.7) which reduces the number of unknown Einstein coefficients A_{m_e}, $2j_e + 1$, to $j_e + 1$ (j_e integer) or $j_e + \frac{1}{2}$ (j_e half-integer). Since we have already an explicit expression for Γ, eq. (3.22), we can apply the symmetry transformation directly on the result. In this fashion we can take advantage of the knowledge of the details of the interaction ($-\boldsymbol{\mu} \cdot \boldsymbol{E}(\boldsymbol{h})$), rather than working with general symmetry arguments only. Also the fact that (3.22) separates the field properties $\tilde{f}_{ij}(\omega_0)$, from the atomic contribution, μ_i, is particularly convenient. In the Introduction we discussed a rotation of the atom in a fixed environment (the electromagnetic vacuum), which involves complicated rotation matrices (eq. (1.2)). Since we know the explicit occurrence of the radiation field in the expression for Γ, we can now equally well rotate the vacuum and keep the atom fixed. Then symmetry requires that Γ for a rotated vacuum around the z-axis is identical to the original Γ, and the same procedure applies for a reflected vacuum in the xz-plane.

Let us first consider a rotation around the z-axis over an angle α. Then the unit vectors transform according to

$$\boldsymbol{e}_x' = \cos\alpha\, \boldsymbol{e}_x + \sin\alpha\, \boldsymbol{e}_y, \quad \boldsymbol{e}_y' = -\sin\alpha\, \boldsymbol{e}_x + \cos\alpha\, \boldsymbol{e}_y, \quad \boldsymbol{e}_z' = \boldsymbol{e}_z, \tag{4.1}$$

and the field correlations with respect to the rotated basis are

$$f_{ij}'(\tau) = \hbar^{-2}\langle 0 | \big(\boldsymbol{E}(\boldsymbol{h}, \tau) \cdot \boldsymbol{e}_i'\big)\big(\boldsymbol{E}(\boldsymbol{h}, 0) \cdot \boldsymbol{e}_j'\big) | 0 \rangle. \tag{4.2}$$

Then symmetry invariance requires

$$f_{ij}'(\tau) = f_{ij}(\tau), \tag{4.3}$$

for $i = x, y, z$, $j = x, y, z$ and for every angle α, which yields a set of nine equations. For instance, with $i = x$, $j = z$ we find

$$f_{xz}(\tau) = \cos\alpha\, f_{xz}(\tau) + \sin\alpha\, f_{yz}(\tau). \tag{4.4}$$

Since this must hold for every α, we can take $\alpha = \pi$, which gives $f_{xz}(\tau) = 0$. Then eq. (4.4) reduces to $\sin\alpha\, f_{yz}(\tau) = 0$, and if we then take $\alpha = \pi/2$ we obtain $f_{yz}(\tau) = 0$. Working out the nine equations consequently gives the relations

$$f_{xz}(\tau) = f_{zx}(\tau) = f_{yz}(\tau) = f_{zy}(\tau) = 0, \tag{4.5}$$

$$f_{xx}(\tau) = f_{yy}(\tau), \tag{4.6}$$

$$f_{xy}(\tau) = -f_{yx}(\tau), \tag{4.7}$$

and there is no restriction on $f_{zz}(\tau)$.

The second symmetry is the invariance of the vacuum for a reflection in any plane through the z-axis. If we take a reflection in the xz-plane, then the unit-vectors transform as

$$\boldsymbol{e}_x' = \boldsymbol{e}_x, \quad \boldsymbol{e}_y' = -\boldsymbol{e}_y, \quad \boldsymbol{e}_z' = \boldsymbol{e}_z, \tag{4.8}$$

and the symmetry invariance, eq. (4.3), gives immediately

$$f_{xy}(\tau) = f_{yx}(\tau) = 0. \tag{4.9}$$

Therefore, only the three field correlation functions $f_{xx}(\tau)$, $f_{yy}(\tau)$ and $f_{zz}(\tau)$ can be nonzero, and the relation $f_{xx}(\tau) = f_{yy}(\tau)$ reduces the number of independent quantities to two. For an isotropic vacuum we would find additionally that $f_{xx}(\tau)$ equals $f_{zz}(\tau)$, but near a surface there is no universal relation between $f_{xx}(\tau)$ and $f_{zz}(\tau)$. With $f_{ij}(\tau) = 0$ for $i \neq j$ the double summation in eq. (3.22) reduces to a single summation, which is a great simplification.

5. Evaluation of Γ

In eq. (3.22) the μ_i are operators in atomic Hilbert space, and for a further evaluation of Γ we need the matrix elements of μ_i with respect to the angular momentum states. In μ_i, the i refers to a Cartesian component x, y or z, but the matrix elements of $\boldsymbol{\mu}$ are more conveniently expressed in spherical components with respect to the z-axis. In terms of the spherical unit vectors

$$\boldsymbol{e}_{\pm 1} = \mp(\boldsymbol{e}_x \pm \mathrm{i}\boldsymbol{e}_y)/\sqrt{2}, \quad \boldsymbol{e}_0 = \boldsymbol{e}_z, \tag{5.1}$$

we can expand $\boldsymbol{\mu}$ as

$$\boldsymbol{\mu} = \sum_\tau \mu_\tau \boldsymbol{e}_\tau^*, \tag{5.2}$$

with $\tau = -1, 0, 1$. From $\boldsymbol{\mu}^\dagger = \boldsymbol{\mu}$ we find

$$\mu_\tau^\dagger = (-1)^\tau \mu_{-\tau}. \tag{5.3}$$

Then the Wigner–Eckart theorem [11] states that the matrix elements of μ_τ can be written as

$$\langle j_e m_e | \mu_\tau | j_g m_g \rangle = (j_g m_g 1\tau | j_e m_e) \langle j_e \| \mu \| j_g \rangle / \sqrt{2j_e + 1}, \tag{5.4}$$

and $\langle j_g m_g | \mu_\tau | j_e m_e \rangle$ follows after complex conjugation, in combination with (5.3).

Now we insert the expansions (3.4) for the projectors P_e and P_g into (3.22), use the properties of $\tilde{f}_{ij}(\omega_0)$ as found in the previous section, and omit the small imaginary parts of $\tilde{f}_{xx}(\omega_0)$ and $\tilde{f}_{zz}(\omega_0)$ (the Lamb shift), which gives for Γ

$$\Gamma\sigma_a = \tfrac{1}{2} \sum_\tau A_\tau \{ d_\tau d_\tau^\dagger \sigma_a + \sigma_a d_\tau d_\tau^\dagger - 2 d_\tau^\dagger \sigma_a d_\tau \}. \tag{5.5}$$

Here we introduced the "dipole-allowed raising operator"

$$d_\tau = \sum_{m_e m_g} (j_g m_g 1\tau | j_e m_e) | j_e m_e \rangle \langle j_g m_g |, \quad \tau = -1, 0, 1, \tag{5.6}$$

which has the property that it transforms a state $| j_g m_g \rangle$ into $| j_e m_e \rangle$, but only if the Clebsch–Gordan coefficient $(j_g m_g 1\tau | j_e m_e)$ is nonzero, e.g., if the transition is dipole allowed. The coefficients A_τ are defined by

$$A_{\pm 1} = 2\tilde{f}_{xx}(\omega_0) | \langle j_e \| \mu \| j_g \rangle |^2 / \sqrt{2j_e + 1}, \tag{5.7}$$

$$A_0 = 2\tilde{f}_{zz}(\omega_0) | \langle j_e \| \mu \| j_g \rangle |^2 / \sqrt{2j_e + 1}. \tag{5.8}$$

Eqs. (5.5)–(5.8) constitute the central result of this paper. Expression (5.5) is the most general form of the spontaneous-decay operator for an atom near a surface. It is important to realize that the entire operator in curly brackets is parameter free, and therefore its structure is completely determined by the symmetry requirements. Furthermore, the two independent vacuum-field correlation functions and the matrix elements of the dipole operator only enter the expression for Γ through the two parameters $A_{\pm 1}$ and A_0. These parameters are proportional to $\tilde{f}_{xx}(\omega_0)$ and $\tilde{f}_{zz}(\omega_0)$, respectively, and are independent of the level structure (degeneracies) of the multiplets.

6. Equation of motion

In this section we consider the equation of motion for an atom near a surface, and the significance of its solution will be discussed in the next section. The solution of eq. (2.4) is

$$\rho_a(t) = \exp[-i(L_a - i\Gamma)t] \rho_a(0), \tag{6.1}$$

for $t > 0$ and a given initial state $\rho_a(0)$. Atomic Liouville space has $(2j_e + 1 + 2j_g + 1)^2$ basis vectors $| j_\alpha m_\alpha\rangle\langle j_\beta m_\beta |$, and therefore a matrix representation of $L_a - \mathrm{i}\Gamma$ on this basis has $16(j_e + j_g + 1)^4$ matrix elements, which is already a large number for very small angular momentum quantum numbers j_e and j_g. The minimum number for a dipole-allowed transition is 256 ($j_e = 1$, $j_g = 0$, or $j_e = 0$, $j_g = 1$, or $j_e = j_g = \frac{1}{2}$), and it might seem that an analytical evaluation of the exponential in eq. (6.1) is intractable. This is not the case, as we shall now show.

If we insert the explicit form of d_τ from (5.6), and its Hermitean conjugate, into (5.5), then $\Gamma\sigma_a$ assumes the form

$$\begin{aligned}\Gamma\sigma_a = \tfrac{1}{2}\sum_{m_e} A_{m_e}\big(| j_e m_e\rangle\langle j_e m_e | \sigma_a + \sigma_a | j_e m_e\rangle\langle j_e m_e |\big) \\ - \sum_{m_e m_g \tau m'_e m'_g} A_\tau (j_g m_g 1\tau | j_e m_e)(j_g m'_g 1\tau | j_e m'_e) \\ \times | j_g m_g\rangle\langle j_g m'_g | \langle j_e m_e | \sigma_a | j_e m'_e\rangle,\end{aligned} \tag{6.2}$$

where we introduced the abbreviation

$$A_{m_e} = \sum_{m_g \tau} A_\tau (j_g m_g 1\tau | j_e m_e)^2. \tag{6.3}$$

Then (6.2) is substituted into (2.4), and we take all possible matrix elements of the equation. We obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle j_e m_e | \rho_a(t) | j_e m'_e\rangle = -\tfrac{1}{2}(A_{m_e} + A_{m'_e})\langle j_e m_e | \rho_a(t) | j_e m'_e\rangle, \tag{6.4}$$

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}t}\langle j_g m_g | \rho_a(t) | j_g m'_g\rangle \\ &\quad = \sum_{m_e m'_e \tau} A_\tau (j_g m_g 1\tau | j_e m_e)(j_g m'_g 1\tau | j_e m'_e)\langle j_e m_e | \rho_a(t) | j_e m'_e\rangle,\end{aligned} \tag{6.5}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle j_e m_e | \rho_a(t) | j_g m_g\rangle = -\big(\tfrac{1}{2}A_{m_e} + \mathrm{i}\omega_0\big)\langle j_e m_e | \rho_a(t) | j_g m_g\rangle, \tag{6.6}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle j_g m_g | \rho_a(t) | j_e m_e\rangle = -\big(\tfrac{1}{2}A_{m_e} - \mathrm{i}\omega_0\big)\langle j_g m_g | \rho_a(t) | j_e m_e\rangle, \tag{6.7}$$

which constitutes a set of $4(j_e + j_g + 1)^2$ equations. The solution is

$$\langle j_e m_e | \rho_a(t) | j_e m'_e\rangle = \exp\big[-\tfrac{1}{2}(A_{m_e} + A_{m'_e})t\big]\langle j_e m_e | \rho_a(0) | j_e m_e\rangle, \tag{6.8}$$

$$\begin{aligned}&\langle j_g m_g | \rho_a(t) | j_g m'_g\rangle \\ &\quad = \langle j_g m_g | \rho_a(0) | j_g m'_g\rangle + \sum_{m_e m'_e \tau} \frac{2A_\tau}{A_{m_e} + A_{m'_e}}\big\{1 - \exp\big[-\tfrac{1}{2}(A_{m_e} + A_{m'_e})t\big]\big\} \\ &\qquad \times (j_g m_g 1\tau | j_e m_e)(j_g m'_g 1\tau | j_e m'_e)\langle j_e m_e | \rho_a(0) | j_e m'_e\rangle,\end{aligned} \tag{6.9}$$

$$\langle j_e m_e | \rho_a(t) | j_g m_g \rangle = \exp\left[-\left(\tfrac{1}{2} A_{m_e} + i\omega_0\right) t \right] \langle j_e m_e | \rho_a(0) | j_g m_g \rangle, \tag{6.10}$$

$$\langle j_g m_g | \rho_a(t) | j_e m_e \rangle = \exp\left[-\left(\tfrac{1}{2} A_{m_e} - i\omega_0\right) t \right] \langle j_g m_g | \rho_a(0) | j_e m_e \rangle, \tag{6.11}$$

for any initial state $\rho_a(0)$. In the limit $t \to \infty$ all matrix elements approach zero, except $\langle j_g m_g | \rho_a(\infty) | j_g m_g' \rangle$, which reflects the fact that all population is in the ground state. Furthermore, we notice that this long-time solution is not unique, due to the term $\langle j_g m_g | \rho_a(0) | j_g m_g' \rangle$ on the right-hand side of (6.9). The solution for $t \to \infty$ depends on the preparation of the system at $t = 0$.

From (3.14) we readily derive

$$\mathrm{Tr}_a(\Gamma \sigma_a) = 0, \quad (\Gamma \sigma_a)^\dagger = \Gamma \sigma_a^\dagger, \tag{6.12}$$

for every σ_a. The first identity guarantees the conservation of trace in the time evolution of $\rho_a(t)$, and the second relation implies that a Hermitean initial density operator $\rho_a(0)$ remains Hermitean in its time evolution. Both properties can easily be verified for the solution (6.8)–(6.11).

7. Einstein coefficients

In the previous section we introduced the parameters A_{m_e}, which are the m_e-dependent Einstein coefficients for spontaneous decay of the level $| j_e m_e \rangle$ to any ground state. This interpretation follows immediately from (6.8), which becomes for $m_e = m_e'$.

$$\langle j_e m_e | \rho_a(t) | j_e m_e \rangle = \exp(-A_{m_e} t) \langle j_e m_e | \rho_a(0) | j_e m_e \rangle. \tag{7.1}$$

The population of m_e decays with a lifetime $1/A_{m_e}$, and from (6.5) we can determine to which ground levels the population decays. We find for $m_g = m_g'$

$$\frac{d}{dt} \langle j_g m_g | \rho_a(t) | j_g m_g \rangle = \sum_{m_e \tau} A_\tau (j_g m_g 1 \tau | j_e m_e)^2 \langle j_e m_e | \rho_a(t) | j_e m_e \rangle, \tag{7.2}$$

showing that $| j_e m_e \rangle$ loses its population to $| j_g m_g \rangle$ at a rate $A_\tau (j_g m_g 1\tau | j_e m_e)^2$. Summed over all possible (three at most) values of m_g, this gives A_{m_e} from eq. (6.3). (The Clebsch–Gordan coefficient $(j_g m_g 1\tau | j_e m_e)$ is only nonzero for $m_g + \tau = m_e$, so that the double sums in (6.3) and (7.2) effectively reduce to single sums.) The splitting of A_{m_e} in contributions from different transitions is called branching, which is illustrated in fig. 1.

From (5.2) and (5.4) we see that a factor $(j_g m_g 1\tau | j_e m_e)$ comes from the component $\mu_\tau e_\tau^*$ of the dipole operator. Since the $e_{\pm 1}^*$ lie in the xy-plane and e_0^* is perpendicular to that plane, we can identify

$$A_{\pm 1} = A_\parallel, \quad A_0 = A_\perp, \tag{7.3}$$

where $A_\parallel$ ($A_\perp$) is brought about by the parallel (perpendicular) component of μ. For atoms in empty space we have $\tilde{f}_{xx}(\omega_0) = \tilde{f}_{zz}(\omega_0)$, and therefore $A_\parallel = A_\perp$

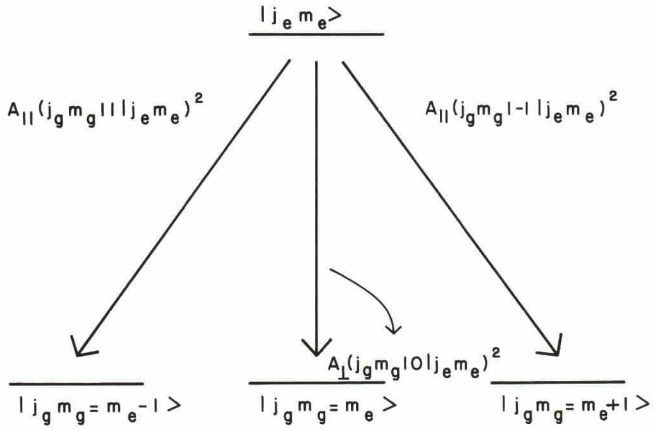

Fig. 1. An excited atomic state $|j_e m_e\rangle$ decays to the ground state, and the lifetime for this process is $1/A_{m_e}$. The dipole selection rule $m_g = m_e - 1$, m_e or $m_e + 1$ allows in general three pathways for the transition to the ground level, as indicated in this figure. The three branches contribute differently to A_{m_e}. Transitions to $|j_g m_e \pm 1\rangle$ have a rate constant $A_\parallel(j_g m_g 1 \mp 1 | j_e m_e)^2$, whereas the vertical transition has an inverse lifetime equal to $A_\perp(j_g m_g 1 0 | j_e m_e)^2$. Their sum equals A_{m_e}. If one or two of the ground levels is not present, then the corresponding Clebsch–Gordan coefficient is zero. For instance, in a $j_e = 1$, $j_g = 0$ system, the only ground level is $|00\rangle$.

(see (5.7), (5.8)), and they both equal A_f from (1.1). With the sum rule for Clebsch–Gordan coefficients

$$\sum_{m_g \tau} (j_g m_g 1 \tau | j_e m_e)^2 = 1, \tag{7.4}$$

we then find from (6.3) that $A_{m_e} = A_f$ for every m_e. Conversely, the m_e-dependence of A_{m_e} for atoms near a surface comes from the possibility that $\tilde{f}_{xx}(\omega_0)$ is not necessarily equal to $\tilde{f}_{zz}(\omega_0)$, e.g., from the lack of spherical symmetry.

With the help of (7.4) we can also perform the summation in (6.3), which gives

$$A_{m_e} = A_\parallel + (j_g m_e 1 0 | j_e m_e)^2 (A_\perp - A_\parallel). \tag{7.5}$$

This shows again that A_{m_e} is independent of m_e whenever $A_\perp$ equals $A_\parallel$. From the properties of Clebsch–Gordan coefficients we can easily prove that $(j_g m_e 1 0 | j_e m_e)^2$ depends only on m_e via m_e^2, which implies

$$A_{-m_e} = A_{m_e}. \tag{7.6}$$

This is the symmetry relation which follows from reflection invariance, as pointed out in the Introduction. Then we recall the relation

$$\sum_{m_e m_g} (j_g m_g 1 \tau | j_e m_e)^2 = \tfrac{1}{3}(2 j_e + 1). \tag{7.7}$$

Summing eq. (6.3) over m_e then gives

$$\frac{1}{2j_e+1}\sum_{m_e} A_{m_e} = \tfrac{1}{3}\sum_{\tau} A_\tau = \tfrac{1}{3}A_\perp + \tfrac{2}{3}A_\parallel. \tag{7.8}$$

Since there are $2j_e+1$ values m_e and three values τ, (7.8) expresses that the average of A_{m_e} equals the average of A_τ. Furthermore, we like to emphasize that the m_e-dependence of A_{m_e} is mainly geometrical and independent of the details of the radiation field in the vacuum. This follows from (6.3), which has only the $A_\parallel$ and $A_\perp$ as parameters. The m_e-dependence comes from a Clebsch–Gordan coefficient and is therefore model independent.

Finally, we recall the causality condition which states that for a large atom–surface separation the A_{m_e} must reduce to their free-space value A_f. If we introduce the parameters

$$b_\tau = A_\tau/A_f, \quad \tau = -1, 0, 1, \tag{7.9}$$

and similarly $b_\parallel$ and $b_\perp$, then (6.3) can be written as

$$A_{m_e} = A_f \sum_{m_g\tau} b_\tau \left(j_g m_g 1\tau \mid j_e m_e\right)^2. \tag{7.10}$$

The two dimensionless parameters $b_\parallel$ and $b_\perp$ determine completely the spontaneous-decay operator. They depend on the details of the radiation field, incorporate the h-dependence of Γ, and contain all necessary information about the substrate, like its dielectric constant or reflectivity. Everything else is determined by symmetry. By definition, the b_τ obey

$$\lim_{h\to\infty} b_\tau = 1. \tag{7.11}$$

8. Determination of $b_\perp$ and $b_\parallel$

So far we have only applied symmetry considerations, and it appeared that the spontaneous-decay process is completely determined by the two dimensionless parameters $b_\parallel$ and $b_\perp$. Evaluation of these quantities requires additional knowledge about the optical properties of the medium, or about the electromagnetic vacuum field. In this section we illustrate with simple examples how $b_\parallel$ and $b_\perp$ can be computed in specific situations.

8.1. Direct method

From (7.9) and the definition of A_τ we find the explicit, defining relations

$$b_\parallel = \frac{6\pi\epsilon_0\hbar c^3}{\omega_0^3}\tilde{f}_{xx}(\omega_0), \tag{8.1}$$

$$b_\perp = \frac{6\pi\epsilon_0\hbar c^3}{\omega_0^3}\tilde{f}_{zz}(\omega_0), \tag{8.2}$$

in terms of the field correlation functions from (3.8). For the calculation of $f_{ij}(\tau)$ or its Fourier–Laplace transform we need to know the quantized radiation field $\boldsymbol{E}(\boldsymbol{r})$ in $\boldsymbol{r}=\boldsymbol{h}$, the Hamiltonian H_{r} of the field, and the wave function $|0\rangle$ of the vacuum. It will be obvious that in most practical cases this information is not available. For the trivial case where the medium is absent, we have

$$\boldsymbol{E}(\boldsymbol{r})=\sum_{\boldsymbol{k}s}\sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V}}\,a_{\boldsymbol{k}s}\boldsymbol{\epsilon}_{\boldsymbol{k}_s}\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})+\mathrm{h.c.},\tag{8.3}$$

with V the quantization volume, $a_{\boldsymbol{k}s}$ the annihilation operator for photons in the mode $\boldsymbol{k}s$, and $\boldsymbol{\epsilon}_{\boldsymbol{k}s}$ a unit polarization vector. The Hamiltonian is

$$H_{\mathrm{r}}=\sum_{\boldsymbol{k}s}\hbar\omega_k a^{\dagger}_{\boldsymbol{k}s}a_{\boldsymbol{k}s},\tag{8.4}$$

with $\omega_k=ck$, and $|0\rangle$ is the zero-photon Fock state. Standard calculations [12] then give

$$f_{ij}(\tau)=\frac{\delta_{ij}}{6\pi^2\epsilon_0\hbar c^3}\int_0^\infty \mathrm{d}\omega\;\omega^3\;\mathrm{e}^{-\mathrm{i}\omega\tau},\tag{8.5}$$

and we find indeed $f_{xx}(\tau)=f_{yy}(\tau)=f_{zz}(\tau)$, and $f_{ij}(\tau)=0$ for $i\neq j$. The Fourier–Laplace transform at ω_0 is

$$\tilde{f}_{ij}(\omega_0)=\delta_{ij}\frac{\omega_0^3}{6\pi\epsilon_0\hbar c^3},\tag{8.6}$$

where we have dropped the imaginary part. Then eqs. (8.1) and (8.2) give

$$b_{\parallel}=b_{\perp}=1,\tag{8.7}$$

as it should for an atom in empty space. For more interesting cases this direct method is probably intractable, because it requires the full quantized electromagnetic field.

8.2. Indirect methods

If we would be able to calculate a quantity which depends on $b_{\parallel}$ or $b_{\perp}$ in an independent way (thus without reference to field correlation functions), then we could possibly extract the value of $b_{\parallel}$ or $b_{\perp}$ from this additional information. Let us consider the expression for the Einstein coefficient $A_{m_{\mathrm{e}}}$ from (7.10), which holds for every level configuration. For the situation of a $j_{\mathrm{g}}=0$, $j_{\mathrm{e}}=1$ transition, the relevant Clebsch–Gordan coefficients are

$$(0\,0\,1\,\tau\,|\,1\,m_{\mathrm{e}})=\delta_{\tau m_{\mathrm{e}}},\tag{8.8}$$

and we see that $A_{m_{\mathrm{e}}=\pm1}=A_{\mathrm{f}}b_{\parallel}$ and $A_{m_{\mathrm{e}}=0}=A_{\mathrm{f}}b_{\perp}$. If we could evaluate the

Einstein coefficients for the levels $|1\,1\rangle$ and $|1\,0\rangle$ by a different method, then this would give directly $b_{\|}$ and $b_{\perp}$. In turn this would determine A_{m_e} for every other level configuration via eq. (7.10).

As mentioned in the Introduction, spontaneous decay is accompanied by the emission of fluorescent photons, and in such way that energy is conserved. From eq. (6.4) with $m_e' = m_e$ we know that the state $|\,j_e m_e\rangle$ loses population at a rate equal to A_{m_e} times the population. A transition from $|\,j_e m_e\rangle$ to any of the ground states corresponds to the emission of a photon with energy $\hbar\omega_0$, and therefore the energy gain of the radiation field per unit of time and at time t equals

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \hbar\omega_0 A_{m_e}\langle\, j_e m_e\,|\,\rho_a(t)\,|\,j_e m_e\rangle, \tag{8.9}$$

provided that only the state $|\,j_e m_e\rangle$ is populated. If we prepare the atom at time zero in the excited state $|\,j_e m_e\rangle$, then we obtain from (7.1)

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \hbar\omega_0 A_{m_e}\exp(-A_{m_e}t), \tag{8.10}$$

and the emitted energy after completion of the decay is

$$W = \int_0^\infty \mathrm{d}t\,\frac{\mathrm{d}W}{\mathrm{d}t} = \hbar\omega_0, \tag{8.11}$$

as it should be. From (8.10) we also find

$$\left.\frac{\mathrm{d}W}{\mathrm{d}t}\right|_{t=0} = \hbar\omega_0 A_{m_e}. \tag{8.12}$$

This implies that we know A_{m_e} (and thereby $b_{\|}$ and $b_{\perp}$), as soon as we obtain an expression for the emission rate at $t=0$, or, for an atom with density operator $|\,j_e m_e\rangle\langle\, j_e m_e\,|$. In the next section we illustrate this method for a particular example.

9. Perfect conductor

The emitted atomic fluorescence is dipole radiation, and for an atom in empty space the electric and magnetic fields are well known [13]. Now let us suppose that the plane $z=0$ is a mirror, e.g., the substrate is a perfect conductor like silver. Then the reflected field can be found from symmetry considerations (method of images), and the total field in the region $z>0$ is the sum of the free-dipole field and the reflected field. Inside the perfect conductor the field vanishes identically. In order to find the radiated power we look at the field far away from the dipole. If we adopt a spherical coordinate system (r, θ, ϕ) with respect to the z-axis, then the positive frequency parts of the electric and magnetic fields for large r are [14]

$$\boldsymbol{E}^{(+)}(\boldsymbol{r}, t)=\frac{\omega_0^2}{4\pi\epsilon_0 rc^2}\left(\boldsymbol{m}^{(+)}(t-r/c, \cos\theta)-\left(\hat{\boldsymbol{r}}\cdot\boldsymbol{m}^{(+)}(t-r/c, \cos\theta)\right)\hat{\boldsymbol{r}}\right), \tag{9.1}$$

$$\boldsymbol{B}^{(+)}(\boldsymbol{r}, t)=\frac{\mu_0\omega_0^2}{4\pi cr}\hat{\boldsymbol{r}}\times\boldsymbol{m}^{(+)}(t-r/c, \cos\theta), \tag{9.2}$$

with $\hat{\boldsymbol{r}}=\boldsymbol{r}/r$ as the direction of propagation. The vector operator $\boldsymbol{m}^{(+)}(t, \cos\theta)$ is given by

$$\boldsymbol{m}^{(+)}(t, \cos\theta)=2\boldsymbol{\mu}_{\perp}^{(+)}(t)\cos\left(\omega_0 hc^{-1}\cos\theta\right)-2\mathrm{i}\boldsymbol{\mu}_{\|}^{(+)}(t)\sin\left(\omega_0 hc^{-1}\cos\theta\right), \tag{9.3}$$

where the t-dependence signifies the Heisenberg picture of an operator, and $\boldsymbol{\mu}_{\perp}^{(+)}$ and $\boldsymbol{\mu}_{\|}^{(+)}$ are the perpendicular and parallel components of the lowering part of the dipole operator (eq. (3.12)) with respect to the xy-plane. The operator $\boldsymbol{m}^{(+)}(t, \cos\theta)$ represents the combination of an atomic dipole $\boldsymbol{\mu}$ in $\boldsymbol{r}=\boldsymbol{h}$ and its mirror image in $\boldsymbol{r}=-\boldsymbol{h}$, including retardation. The argument $\omega_0 hc^{-1}\cos\theta$ equals half the phase shift between the radiation emitted directly in the direction $\hat{\boldsymbol{r}}$ by $\boldsymbol{\mu}$ and the radiation that is first reflected by the surface and subsequently emitted in the $\hat{\boldsymbol{r}}$-direction.

Now it is an easy matter to compute the radiated power. The emitted energy per unit of time per unit solid angle Ω in the direction $\hat{\boldsymbol{r}}$ should be defined as [15]

$$\frac{\partial^2 W}{\partial t\,\partial\Omega}=\frac{r^2}{\mu_0}\langle\boldsymbol{E}^{(-)}(\boldsymbol{r}, t)\times\boldsymbol{B}^{(+)}(\boldsymbol{r}, t)-\boldsymbol{B}^{(-)}(\boldsymbol{r}, t)\times\boldsymbol{E}^{(+)}(\boldsymbol{r}, t)\rangle\cdot\hat{\boldsymbol{r}}, \tag{9.4}$$

where a minus $(-)$ field is the Hermitean conjugate of the corresponding plus $(+)$ field. With (9.1) and (9.2) we can write (9.4) as

$$\frac{\partial^2 W}{\partial t\,\partial\Omega}=\frac{2r^2}{c\mu_0}\langle\boldsymbol{E}^{(-)}(\boldsymbol{r}, t)\cdot\boldsymbol{E}^{(+)}(\boldsymbol{r}, t)\rangle. \tag{9.5}$$

Then we recall that $\langle\cdots\rangle$ in the Heisenberg picture stands for $\mathrm{Tr}_a\,\rho_a(0)(\cdots)$, and subsequently we tranform the expression (9.5) to the Schrödinger picture, which yields

$$\frac{\partial^2 W}{\partial t\,\partial\Omega}=\frac{\omega_0^4}{8\pi^2\epsilon_0 c^3}\mathrm{Tr}_a\,\rho_a(t-r/c)\left[\boldsymbol{m}^{(-)}(\cos\theta)\cdot\boldsymbol{m}^{(+)}(\cos\theta)\right.$$
$$\left.-\left(\hat{\boldsymbol{r}}\cdot\boldsymbol{m}^{(-)}(\cos\theta)\right)\left(\hat{\boldsymbol{r}}\cdot\boldsymbol{m}^{(+)}(\cos\theta)\right)\right]. \tag{9.6}$$

Here, $\boldsymbol{m}^{(+)}(\cos\theta)$ is the Schrödinger representation of $\boldsymbol{m}^{(+)}(t, \cos\theta)$, which follows from (9.3) with the substitution $\boldsymbol{\mu}(t)\to\boldsymbol{\mu}$, and $\boldsymbol{m}^{(-)}=\boldsymbol{m}^{(+)\dagger}$.

Result (9.6) gives the full angular distribution of the fluorescence in the half-space $z > 0$ for any state $\rho_a(t - r/c)$ of the atom. The radiated power then follows from

$$\frac{dW}{dt} = \int d\Omega \frac{\partial^2 W}{\partial t\, \partial\Omega}, \tag{9.7}$$

where the integration extends over half a unit sphere in $z > 0$, and around $\boldsymbol{r} = \boldsymbol{0}$. Elementary integration gives

$$\frac{dW}{dt} = \frac{\omega_0^4}{3\pi\epsilon_0 c^3} \mathrm{Tr_a}\, \rho_a(t - r/c)\left[b_\perp \boldsymbol{\mu}_\perp^{(-)} \cdot \boldsymbol{\mu}_\perp^{(+)} + b_\| \boldsymbol{\mu}_\|^{(-)} \cdot \boldsymbol{\mu}_\|^{(+)} \right], \tag{9.8}$$

where we introduced the parameters

$$b_\perp = 1 - 3\left[\frac{\cos(2\beta)}{(2\beta)^2} - \frac{\sin(2\beta)}{(2\beta)^3} \right], \tag{9.9}$$

$$b_\| = 1 - \frac{3}{2}\left[\frac{\sin(2\beta)}{2\beta} + \frac{\cos(2\beta)}{(2\beta)^2} - \frac{\sin(2\beta)}{(2\beta)^3} \right], \tag{9.10}$$

with

$$\beta = \omega_0 h/c. \tag{9.11}$$

We shall see in due course that $b_\perp$ and $b_\|$ are indeed the two parameters which determine the spontaneous-decay operator Γ, and thereby the Einstein coefficients A_{m_e} of the atomic states $| j_e m_e\rangle$.

The raising part $\boldsymbol{\mu}^{(-)}$ of the dipole operator $\boldsymbol{\mu}$ an be expressed in the dipole-allowed raising operator d_τ from (5.6) according to

$$\boldsymbol{\mu}^{(-)} = \frac{\langle j_e \| \mu \| j_g \rangle}{\sqrt{2 j_e + 1}} \sum_\tau d_\tau \boldsymbol{e}_\tau^*, \tag{9.12}$$

and $\boldsymbol{\mu}^{(+)}$ follows after a Hermitean conjugation. The two terms $\tau = \pm 1$ then give the parallel part of $\boldsymbol{\mu}^{(-)}$, and the $\tau = 0$ term is the perpendicular component. Combining everything gives

$$\frac{dW}{dt} = \hbar\omega_0 A_f\, \mathrm{Tr_a}\, \rho_a(t - r/c) \sum_\tau b_\tau d_\tau d_\tau^\dagger, \tag{9.13}$$

where we used (1.1) for the Einstein coefficient A_f in empty space. Next, we substitute the expressions for d_τ and $d_\tau^\dagger$ and perform the summations over the magnetic quantum numbers. We then obtain

$$\frac{dW}{dt} = \hbar\omega_0 A_f \sum_{m_e m_g \tau} b_\tau \left(j_g m_g 1\tau \,|\, j_e m_e \right)^2 \langle j_e m_e | \rho_a(t - r/c) | j_e m_e \rangle, \tag{9.14}$$

which involves only the populations $\langle j_e m_e | \rho_a(t - r/c) | j_e m_e \rangle$ of the states

$| j_e m_e \rangle$ at the retarded time $t - r/c$. If the parameters b_τ, found in this section, would indeed be the correct b_τ for the Einstein coefficients, then we could use (7.10), and (9.14) would reduce to

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \hbar\omega_0 \sum_{m_e} A_{m_e} \langle j_e m_e | \rho_a(t - r/c) | j_e m_e \rangle. \tag{9.15}$$

This is exactly eq. (8.9), summed over m_e, and as pointed out in section 8.2, an expression of the form (9.15) unambiguously identifies the parameters $b_\perp$ and $b_\parallel$. Therefore, we conclude that (9.9) and (9.10) are the correct results for $b_\perp$ and $b_\parallel$ for the situation of a perfectly-conducting substrate. But then we also know the field-correlation functions $\tilde{f}_{xx}(\omega_0)$ and $\tilde{f}_{zz}(\omega_0)$, according to (8.1) and (8.2), which are now found without any knowledge of the quantized field $\boldsymbol{E}(\boldsymbol{r})$, the Hamiltonian H_r, or the wave function of the vacuum, $|0\rangle$. Of course, results (9.9) and (9.10) can also be obtained from the field-correlation functions in an explicitly-quantized radiation field theory for an empty half-space near a mirror [16,17], or from linear response theory [18,19].

10. Conclusions

We have studied the spontaneous decay of an atom which is positioned in the vicinity of an optically-reflective surface, but without reference to any specific characteristics of the medium. An expression for the spontaneous-decay operator Γ of a degenerate two-level atom was derived from symmetry considerations. It appears that Γ only involves the two dimensionless parameters $b_\parallel$ and $b_\perp$, which are independent of any of the atomic properties, and are determined by the vacuum-field correlation functions $\tilde{f}_{xx}(\omega_0)$ and $\tilde{f}_{zz}(\omega_0)$ at the position $\boldsymbol{h}$ of the atom. The parameters $b_\parallel$ and $b_\perp$ incorporate the h-dependence of atomic lifetimes and the details of the characteristics of the medium (like a dielectric constant or a nonlinear susceptibility). We have found that the Einstein coefficients for spontaneous decay of the levels $| j_e m_e \rangle$ depend on the magnetic quantum number m_e, due to the absence of spherical symmetry. Nevertheless, the m_e-dependence of A_{m_e} is almost entirely geometrical, as is reflected in the existence of the sum rule (7.8) and the symmetry relation (7.6).

Although we only worked out the case of a two-level atom near a surface, it should be obvious that the same procedure applies to any configuration which has a symmetry for rotation around an axis, and a reflection symmetry for a plane through that axis. For instance, the configuration of an atom in between two parallel mirrors, as in a recent experiment [20], and a geometry with an atom near a spherical or ellipsoidal macroscopic body have these symmetries. For these cases the expression for Γ is exactly the same, as are the properties of the Einstein coefficients and the solution of the equation of motion.

Furthermore, the spontaneous-decay operator for an arbitrary multilevel atom in a configuration with these symmetries can also depend only on the two parameters $b_{\|}$ and $b_{\perp}$. This follows from the fact that the vacuum-field correlation functions are independent of the presence of atom. It is the symmetry of the vacuum which determines the structure of the spontaneous-decay process.

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