Coherent properties of a system of two identical quantum radiators exhibiting electric or magnetic transitions of arbitrary multipole order

V. L. Lyuboshitz

Joint Institute of Nuclear Research, Dubna
(Submitted October 13, 1976)
Zh. Eksp. Teor. Fiz. 72, 1375–1391 (April 1977)

A study is made of the spectrum and angular distribution of the radiation emitted by a system of two identical two-level centers, one of which is in an excited state B characterized by an integral spin L and the other is in the ground state A with zero spin. The energies and widths of the collective excited states are calculated for an arbitrary distance between the centers of A and B. The energy and angular dependences of the cross section for the resonant scattering of photons by two identical A centers are found. The spin structure of the resonant electromagnetic interaction between excited and unexcited nuclei (atoms) is considered in the case of EL and ML transitions. The influence of a metal mirror on the lifetime and spectrum of multipole radiation of an excited atom is estimated in a similar manner.

PACS numbers: 32.70.Jz, 32.80.−t

§1. INTRODUCTION

Coherent effects in the emission of radiation from a system of excited molecules surrounded by unexcited molecules of the same kind were first considered in the well-known paper of Dicke.[1] He assumed that the photon wavelength is considerably greater than the distance between the molecules ($\lambda \gg R$). The opposite limiting case of $\lambda \ll R$ was then considered by Podgoretskiĭ and Roĭzen[2] within the framework of the classical theory of oscillators coupled by the radiation field. As shown in[3–8], in the case of two identical centers (atoms or nuclei), one of which is in the ground state of zero spin and the other in an excited state of spin 1, the Dicke problem has an exact analytic solution for arbitrary values of the parameter R/λ. The spectrum of the radiation emitted by such a system as well as the energy and angular dependences of the cross section for the resonant scattering of photons by two zero-spin centers[5,7] are described completely by the energies and widths of symmetric and antisymmetric two-particle states corresponding to the excitation of one of the centers. This applies also to the spectrum of the radiation emitted from two identical excited atoms considered in[9]. Explicit expressions for the frequency shifts and spectral line widths follow directly from the resonant interaction theory (see[3,4,6]). The same results are obtained from the purely classical theory of multiple scattering of electromagnetic waves by two identical isotropic oscillators.[5]

In the papers cited above and in other treatments of the various aspects of the Dicke problem (see, for example,[10–13]) it is understood that electromagnetic radiation is of dipole nature. Our aim is to study the spectral and angular characteristics of the emitted radiation and resonant scattering of photons in the case when the interaction between excited and unexcited centers is due to electric or magnetic transitions of arbitrary multipole order. We shall generalize directly the results obtained for $E1$ transitions in[5,6]. The analogy between a system of two identical centers and a radiator located close to a flat surface of a perfect conductor[14] makes it possible to use the relationships obtained for the former case in estimating the influence of a metal mirror on the nature of multipole radiation and on the lifetime of excited atoms. Effects of this kind have been investigated experimentally by the monomolecular film method.[15,16]

§2. COLLECTIVE EXCITED STATES

We shall consider a two-level center (for example, a nucleus) whose excited state has an energy E_B and a spin $L \geqslant 1$ and whose ground state has an energy E_A and zero spin. Depending on the relative parity of the B and A states, the $B \to A + \gamma$ decay results in electric or magnetic radiation of 2^L multipole order and frequency $\omega_0 = (E_B - E_A)/\hbar$. We shall assume that two such centers, one of which is in an excited state and the other in the ground state, are rigidly fixed at points $\mathbf{R}_1$ and $\mathbf{R}_2$. In the absence of electromagnetic interaction between these centers we have $2(2L+1)$ degenerate states $|A(1)\rangle|B_m(2)\rangle$ and $|B_m(1)\rangle|A(2)\rangle$. Here, $m = 0, \pm 1, \pm 2 \ldots \pm L$ are the projections of the spin of the excited state onto the vector $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$. The photon exchange transfers the excitation from one center to the other and the degeneracy is lifted. We can easily see that the axial symmetry and conservation of the spatial parity impart the following structure to the matrix elements of the resonant interaction between the centers A and B:

$$\langle A(1)B_m(2)|\hat{V}|B_{m'}(1)A(2)\rangle = \langle B_{m'}(1)A(2)|\hat{V}|A(1)B_m(2)\rangle = \hbar\gamma_L U^{(L)}_{|m|}(x)\,\delta_{mm'}. \quad (1)$$

In Eq. (1), γ_L denotes the radiative width of an isolated B center, which is independent of the quantum number m ($0 \leqslant |m| \leqslant L$); the quantities $U^{(L)}_{|m|}$ are complex functions of the dimensionless parameter

$$x = k_0 R = (E_B - E_A)\,|\mathbf{R}_1 - \mathbf{R}_2|/\hbar c. \quad (2)$$

We shall show later that the functions $U^{(L)}_{|m|}(x)$ are identical for the EL and ML transitions.

 0038-5646/77/4504-0723$02.40

Allowance for Eq. (1) shows that quasistationary states of the system AB corresponding to the excitation of one of the centers should be symmetric or antisymmetric relative to the transposition $B \rightleftarrows A$[6]:

$$|\psi_m^{(\pm)}\rangle = 2^{-1/2}(|A(1)\rangle|B_m(2)\rangle \pm |B_m(1)\rangle|A(2)\rangle). \quad (3)$$

Their energies are

$$E_m^{(\pm)} = E_A + E_B \pm \hbar\gamma_L \operatorname{Re} U_{|m|}^{(L)}(x), \quad (4)$$

and the radiative widths are

$$\gamma_{L,m}^{(\pm)} = \gamma_L(1 \mp 2 \operatorname{Im} U_{|m|}^{(L)}(x)). \quad (5)$$

In the relationships (4) and (5) the upper sign refers to the symmetric collective states $|\psi_m^{(+)}\rangle$ and the lower—to the antisymmetric states $|\psi_m^{(-)}\rangle$.

Deviations of the radiative widths from the value γ_L are due to the coherent emission of radiation from the two centers. This mechanism clearly has no influence on the partial widths representing the nonradiative decay channels. Therefore, the changes in the total and radiative widths are equal and amount to

$$\Delta\gamma_{L,m} = \gamma_{L,m}^{(+)} - \gamma_L = \gamma_L - \gamma_{L,m}^{(-)} = -2\gamma_L \operatorname{Im} U_{|m|}^{(L)}(x). \quad (6)$$

According to Eq. (6), the average lifetimes of the collective excited states are given by

$$\tau_{L,m}^{(\pm)} = \tau^{(0)}/(1 \pm \tau^{(0)}\Delta\gamma_{L,m}), \quad (7)$$

where $\tau^0 = 1/\gamma_{\rm tot}$ is the average lifetime of an isolated excited center. Clearly, a spectral line of frequency ω_0 and width $\gamma_{\rm tot}$ splits into components of frequencies

$$\omega_{L,m}^{(\pm)} = \omega_0 \pm \Delta\omega_{L,m} = \omega_0 \pm \gamma_L \operatorname{Re} U_{|m|}^{(L)}(x) \quad (8)$$

and widths $\gamma_{L,m(\rm tot)}^{(\pm)} = \gamma_{\rm tot} \pm \Delta\gamma_{L,m}$. Since the degeneracy in respect of the sign of the spin projection still remains, the number of new spectral lines is $2(L+1)$. We shall now assume that the emission of a photon is the only decay channel of the state B, i.e., that $\gamma_{\rm tot} = \gamma_L$.

The task is now to determine the explicit form of the functions $U_{|m|}^{(L)}(x)$ representing the coherent properties of a system of two identical centers. In the special case of dipole transitions ($L=1$), the relevant expressions are obtained in[6]:[1)]

$$U_1^{(1)}(x) = \frac{3}{4}\left(\frac{1}{x^3} - \frac{1}{x} - \frac{i}{x^2}\right)e^{ix}, \quad U_0^{(1)}(x) = \frac{3}{2}\left(\frac{i}{x^2} - \frac{1}{x^3}\right)e^{ix}. \quad (9)$$

§3. RESONANT INTERACTION IN *EL* AND *ML* TRANSITIONS

We shall calculate the complex functions $U_{|m|}^{(L)}(x)$ using the well-known expression for the effective energy of a retarded electromagnetic interaction between two currents concentrated in the vicinities of points $\mathbf{R}_1$ and $\mathbf{R}_2$ (see[17], § 32.2):

$$\langle B(1)A(2)|\hat V|A(1)B(2)\rangle = \iint j_{AB}^{(1)}(\mathbf{r}_1-\mathbf{R}_1) \times j_{AB}^{(2)*}(\mathbf{r}_2-\mathbf{R}_2)\frac{e^{ik_0|\mathbf{r}_1-\mathbf{r}_2|}}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\mathbf{r}_1\,d^3\mathbf{r}_2. \quad (10)$$

Here, $j_{AB} = \{\rho_{AB}, \mathbf{j}_{AB}\}$ is the four-vector density of the current of transitions between stationary states B and A which are separated by an energy gap $E_B - E_A = \hbar c k_0$. Going over to the Fourier components

$$\left.\begin{aligned} j_{AB}^{(1)}(\varkappa) &= \int j_{AB}^{(1)}(\mathbf{r}_1-\mathbf{R}_1)e^{-i(\varkappa,\mathbf{r}_1-\mathbf{R}_1)}d^3\mathbf{r}_1, \\ j_{AB}^{(2)*}(\varkappa) &= \int j_{AB}^{(2)*}(\mathbf{r}_2-\mathbf{R}_2)e^{i(\varkappa,\mathbf{r}_2-\mathbf{R}_2)}d^3\mathbf{r}_2, \end{aligned}\right\} \quad (11)$$

we can rewrite Eq. (10) in the form of the integral

$$\langle B(1)A(2)|\hat V|A(1)B(2)\rangle = \frac{1}{2\pi^2}\int \frac{[\rho_{AB}^{(1)}(\varkappa)\rho_{AB}^{(2)*}(\varkappa) - j_{AB}^{(1)}(\varkappa)j_{AB}^{(2)*}(\varkappa)]}{\varkappa^2 - k_0^2 - i0}e^{i(\varkappa,\mathbf{R}_1-\mathbf{R}_2)}d^3\varkappa. \quad (12)$$

In the problem of interest to us, we have $j_{AB}^{(1)}(\varkappa) = j_{AB}^{(2)}(\varkappa)$.

It follows from the relativistic invariance and conservation of the current that when the ground-state spin is zero and the spin of the excited state is L, the components of the four-vector transition current for relative parity $\eta_{AB} = (-1)^L$ have the following structure (see[17], § 25.5 and[18], § 143):

$$\left.\begin{aligned} \rho_{AB_m}(\varkappa) &= \left(\frac{4\pi}{2L+1}\right)^{1/2}\frac{\varkappa^L}{(2L-1)!!}Y_{Lm}\left(\frac{\varkappa}{\varkappa}\right)Q_{Lm}^{(e)}f_L^{(e)}(k_0^2-\varkappa^2), \\ \mathbf{j}_{AB_m}(\varkappa) &= \left(\frac{4\pi(L+1)}{L(2L+1)}\right)^{1/2}\frac{k_0\varkappa^{L-1}}{(2L-1)!!}\left\{\mathbf{Y}_{Lm}^{(e)}\left(\frac{\varkappa}{\varkappa}\right) + \left(\frac{L}{L+1}\right)^{1/2}\frac{\varkappa}{\varkappa}Y_{Lm}\left(\frac{\varkappa}{\varkappa}\right)\right\}Q_{Lm}^{(e)}f_L^{(e)}(k_0^2-\varkappa^2). \end{aligned}\right\} \quad (13)$$

If $\eta_{AB} = (-1)^{L+1}$, then

$$\rho_{AB_m}(\varkappa) = 0, \quad \mathbf{j}_{AB_m}(\varkappa) = \left(\frac{4\pi(L+1)}{L(2L+1)}\right)^{1/2} \times \frac{\varkappa^L}{(2L-1)!!}\mathbf{Y}_{Lm}^{(m)}\left(\frac{\varkappa}{\varkappa}\right)Q_{Lm}^{(m)}f_L^{(m)}(k_0^2-\varkappa^2). \quad (14)$$

In Eqs. (13) and (14), $\mathbf{Y}_{Lm}^{(e)}(\varkappa/\varkappa)$ and $\mathbf{Y}_{Lm}^{(m)}(\varkappa/\varkappa)$ are the normalized transverse spherical vectors ($\varkappa = |\boldsymbol{\varkappa}|$); $Y_{Lm}(\varkappa/\varkappa)$ is the spherical function; $Q_{Lm}^{(e)}$ and $Q_{Lm}^{(m)}$ are, respectively, the electric and magnetic multipole moments of the transition governing the probability of emission of a real photon (in the case under discussion, the value of Q_{Lm} is independent of m); $f_L^{(e)}(k_0^2-\varkappa^2)$ and $f_L^{(m)}(k_0^2-\varkappa^2)$ are the form factors which allow for the virtual aspect of the photon and satisfy the condition $f_L(0) = 1$.

We shall use the point center approximation and assume accordingly that $f_L^{(e)}(k_0^2-\varkappa^2) = f_L^{(m)}(k_0^2-\varkappa^2) = 1$ also for values of $z = k_0^2 - \varkappa^2$, not equal to zero.[2)] We shall calculate the integrals (12) employing the expansion of $|\mathbf{Y}_{Lm}^{(e)}(\varkappa/\varkappa)|^2$ and $|\mathbf{Y}_{Lm}^{(m)}(\varkappa/\varkappa)|^2$ in terms of the Legendre polynomials:

$$\left|\mathbf{Y}_{Lm}^{(e)}\left(\frac{\varkappa}{\varkappa}\right)\right|^2 = \left|\mathbf{Y}_{Lm}^{(m)}\left(\frac{\varkappa}{\varkappa}\right)\right|^2 = \frac{2L+1}{4\pi}(-1)^{m+1} \times \sum_{n=0}^{L} C_{L1L-1}^{2n0}C_{LmL-m}^{2n0}P_{2n}(\cos\theta), \quad (15)$$

where C_{LmL-m}^{2n0} are the Clebsch–Gordan coefficients and θ is the angle between $\varkappa$ and the quantization axis of the moment $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$. We know that

$$\int_0^\pi P_l(\cos\theta)e^{i\varkappa R\cos\theta}\sin\theta\,d\theta=2i^l\left(\frac{\pi}{2\varkappa R}\right)^{1/2}J_{l+1/2}(\varkappa R), \qquad (16)$$

where $\varkappa=|\boldsymbol{\varkappa}|$, $R=|\mathbf{R}|$, and

$$J_{l+1/2}(\varkappa R)=\left(\frac{2\varkappa R}{\pi}\right)^{1/2}(-1)^l\left(\frac{R}{\varkappa}\right)^l\left(\frac{d}{RdR}\right)^l\frac{\sin\varkappa R}{\varkappa R}. \qquad (16')$$

Using Eq. (16), we can easily show that if $R\neq 0$ and the indices n and p are integers ($p\geq n$), we have

$$\int\frac{P_{2n}(\cos\theta)e^{i\varkappa R\cos\theta}}{\varkappa^2-k_0^2-i0}\varkappa^{2p}d^3\varkappa$$
$$=(2\pi)^2(-1)^n k_0^{2p+1}\left(\frac{R}{k_0}\right)^{2n}\left(\frac{d}{RdR}\right)^{2n}\frac{e^{ik_0R}}{k_0R}. \qquad (17)$$

It is understood here that after integration we can drop terms which oscillate for infinite values of the argument; in a physical situation terms of this kind vanish in averaging over any (no matter how small) scatter of the distances R.

It readily follows from Eqs. (13) and (14) that the integrands in Eq. (12) corresponding to the EL and ML transitions differ by a term proportional to $\varkappa^{2(L-1)}(\varkappa^2-k_0^2)$. It follows from Eq. (17) that the contribution of this term to the integral is zero.[3)] Thus, the final result is independent of the relative parity of the states A and B. Equations (15) and (17) give

$$U_{|m|}^{(L)}(x)=\frac{1}{2}\sum_{n=0}^{L}(-1)^{n+m}(2L+1)C_{LmL-m}^{2n0}C_{L1L-1}^{2n0}x^{2n}\left(\frac{d}{xdx}\right)^{2n}\frac{e^{ix}}{x}$$
$$=\frac{1}{2}i\sum_{n=0}^{L}(-1)^{n+m}(2L+1)C_{L1L-1}^{2n0}C_{LmL-m}^{2n0}\left(\frac{\pi}{2x}\right)^{1/2}H_{2n+1/2}^{(1)}(x), \quad (18)$$

where $H_{2n+1/2}^{(1)}(x)$ is a Hankel function of the first kind. The radiative width (the probability of radiation of 2^L multipole order), which occurs in the structure formulas of § 2, is

$$\gamma_L=\frac{1}{\hbar}|Q_{Lm}|^2k_0^{2L+1}\frac{2(L+1)}{L(2L+1)!!(2L-1)!!}. \qquad (19)$$

In particular, if $L=1$, then

$$U_1^{(1)}(x)=\left[\frac{1}{2}x^2\left(\frac{d}{xdx}\right)^2\frac{e^{ix}}{x}-\frac{e^{ix}}{x}\right],\quad U_0^{(1)}(x)=-\left[x^2\left(\frac{d}{xdx}\right)^2\frac{e^{ix}}{x}+\frac{e^{ix}}{x}\right].$$

These formulas are completely equivalent to the expressions in Eq. (9).

According to Eqs. (6), (8), and (18), the changes in the widths of the spectral lines and the shifts of their frequencies are oscillating functions of the parameter $x=k_0R$:

$$\Delta\gamma_{L,m}=\gamma_L\left\{\frac{\sin x}{x}-(2L+1)\sum_{n=1}^{L}(-1)^{n+m}C_{L1L-1}^{2n0}C_{LmL-m}^{2n0}\left(\frac{\pi}{2x}\right)^{1/2}J_{2n+1/2}(x)\right\},$$
$$(20)$$
$$\Delta\omega_{L,m}=\frac{\gamma_L}{2}\left\{-\frac{\cos x}{x}+(2L+1)\sum_{n=1}^{L}(-1)^{n+m}C_{L1L-1}^{2n0}C_{LmL-m}^{2n0}\left(\frac{\pi}{2x}\right)^{1/2}J_{-2n-1/2}(x)\right\}.$$

We shall now consider the limiting cases of short and long distances between the two centers. We can readily see that if $R\ll\lambda$ ($x\ll 1$), the widths of the symmetric excited states are doubled and the widths of the antisymmetric states vanish ($\mathrm{Im}U_{|m|}^{(L)}(0)=-\frac{1}{2}$). Simple calculations give

$$\gamma_{L,m}^{(-)}=\gamma_L x^2\left(\frac{1}{6}+\frac{2L+1}{15}C_{L1L-1}^{20}C_{LmL-m}^{20}(-1)^{m+1}\right)$$
$$=\frac{1}{6}\gamma_L x^2\left\{1+\frac{2[3m^2-L(L+1)][3-L(L+1)]}{(2L-1)L(L+1)(2L+3)}\right\}. \qquad (21)$$

The frequency shifts in the $x\ll 1$ case are proportional to $x^{-(2L+1)}$; if the explicit form of the coefficients C_{LmL-m}^{2L0} is taken into account, we find that

$$\Delta\omega_{L,m}=(-1)^{L+m}\gamma_L\frac{(2L+1)![(2L)!]^2}{(L+m)!(L-m)!(L+1)!(L-1)!}\left(\frac{1}{2x}\right)^{2L+1}. \qquad (22)$$

Then, $|\Delta\omega_{L,m}/\gamma_L|\gg 1$. This result can also be obtained from the explicit form of the operator of the electrostatic (magnetostatic) interaction between two electric (magnetic) 2^L-pole moments:

$$\hat{V}(R)=\sum_{m=-L}^{L}(-1)^{L+m}\frac{(2L)!}{(L+m)!(L-m)!}\hat{Q}_{Lm}^{*(1)}\hat{Q}_{Lm}^{(2)}\frac{1}{R^{2L+1}}. \qquad (23)$$

If $x\gg 1$, it is simpler not to use the relationships (20) but introduce before integration the representation of the spherical vectors in terms of the Wigner d functions (see[19], § 16):

$$\left|\mathbf{Y}_{Lm}^{(M)}\left(\frac{\boldsymbol{\varkappa}}{\varkappa}\right)\right|^2=\left|\mathbf{Y}_{Lm}^{(E)}\left(\frac{\boldsymbol{\varkappa}}{\varkappa}\right)\right|^2=\frac{2L+1}{8\pi}[(d_{|m|,1}^{(L)}(\theta))^2$$
$$+(d_{|m|,-1}^{(L)}(\theta))^2]=\frac{2L+1}{8\pi}\sum_{n=0}^{L}\beta_n^{(L,m)}(\cos\theta)^{2n}. \qquad (24)$$

The functions $U_{|m|}^{(L)}(x)$ can be specified[4)] by means of the coefficients $\beta_n^{(L,m)}$:

$$U_{|m|}^{(L)}(x)=-\frac{2L+1}{4}\sum_{n=0}^{L}(-1)^n\beta_n^{(L,m)}\frac{d^{2n}}{dx^{2n}}\left(\frac{e^{ix}}{x}\right). \qquad (25)$$

If $x\gg 1$, the integral in Eq. (12) is dominated by the small angles, where

$$d_{|m|,\pm1}^{(L)}(\theta)\sim(\sin\theta)^{|(|m|\mp1)|}.$$

Hence, we obtain the following asymptotic expressions:

$$\left.\begin{array}{l} U_1^{(L)}(x)=-\dfrac{2L+1}{4}\dfrac{e^{ix}}{x},\quad U_0^{(L)}(x)=i\dfrac{2L+1}{4}L(L+1)\dfrac{e^{ix}}{x^2},\\ U_{|m|(\geq2)}^{(L)}(x)=-\dfrac{2L+1}{2}\dfrac{(L+|m|)!}{(L-|m|)!L(L+1)}(-i)^{|m|-1}\dfrac{e^{ix}}{(2x)^{|m|}}.\end{array}\right\} \qquad (26)$$

§4. PRINCIPAL EFFECTS

A. Angular distribution of the radiation. The expression (20) for the change in the widths can be obtained by direct calculation of the probability of decay of the collective states (3). In the case under discussion, the helical amplitudes of the decay are

$$A_{1m}^{(\pm)}(\theta,\varphi)=d_{1m}^{(L)}(\theta)e^{im\varphi}b^{(\pm)}(\theta), \qquad (27)$$
$$A_{-1m}^{(\pm)}(\theta,\varphi)=\eta_{AB}(-1)^{L+1}d_{-1m}^{(L)}(\theta)e^{im\varphi}b^{(\pm)}(\theta), \qquad (27')$$

where

$$b^{(\pm)}(\theta)=-\frac{1}{2}\left(\gamma_L\frac{2L+1}{4\pi}\right)^{1/2}\left\{\exp\left(i\frac{k_0R\cos\theta}{2}\right)\pm\exp\left(-i\frac{k_0R\cos\theta}{2}\right)\right\}.$$

Here, θ is the angle between the vector $\mathbf{R}$ and the photon momentum $\mathbf{k}$; the factor $\eta_{AB}(-1)^{L+1}$ is $+1$ for the ML transitions and -1 for the EL transitions. We can easily see that

$$\gamma_{L,m}^{(\pm)}=2\pi\int_{-1}^{1}W_{L,m}^{(\pm)}(\cos\theta)\,d\cos\theta,$$

where

$$W_{L,m}^{(\pm)}(\cos\theta)=|A_{1m}^{(\pm)}(\theta,\varphi)|^2+|A_{-1m}^{(\pm)}(\theta,\varphi)|^2$$
$$=\frac{2L+1}{8\pi}\gamma_L[(d_{1m}^{(L)}(\theta))^2+(d_{-1m}^{(L)}(\theta))^2][1\pm\cos(k_0R\cos\theta)]. \quad (28)$$

It follows that the angular distributions of the electric and magnetic 2^L-pole radiation are the same. The emission of a photon with a linear polarization vector parallel to the $(\mathbf{k},\mathbf{R})$ plane corresponds to the combination

$$2^{-1/2}(A_{1m}^{(\pm)}(\theta,\varphi)+A_{-1m}^{(\pm)}(\theta,\varphi)), \quad (29)$$

and the emission of a photon polarized at right-angles to the $(\mathbf{k},\mathbf{R})$ plane corresponds to the combination

$$2^{-1/2}(A_{1m}^{(\pm)}(\theta,\varphi)-A_{-1m}^{(\pm)}(\theta,\varphi)). \quad (29')$$

Since the amplitudes in Eq. (27) can be factorized, the interference between the radiation emitted from the two centers gives rise to the angular dependence $\cos(k_0R\cos\theta)$ but does not affect the polarization.

B. Resonant scattering. Knowing the energies, widths, and amplitudes of the decay of intermediate collective states, we can derive an explicit expression for the amplitude of resonant scattering of a photon by two zero-spin centers. Let θ_0 and θ be the angles between the vector $\mathbf{R}$ and the photon momentum before and after scattering, respectively; let φ be the azimuthal angle between the planes passing through $\mathbf{R}$ and the directions of the momenta of the incident and scattered photons; we shall use r and r' for the helicity of a photon before and after scattering (r and r' have the values ±1). Then,

$$f_{rr'}^{(L)}(\theta_0,\theta,\varphi)=\frac{2L+1}{2k_0}\gamma_L\left\{\cos\left(\frac{k_0R\cos\theta_0}{2}\right)\cos\left(\frac{k_0R\cos\theta}{2}\right)\times\sum_{m=-L}^{L}\frac{d_{rm}^{(L)}(\theta_0)d_{r'm}^{(L)}(\theta)e^{im\varphi}}{\omega_{L,m}^{(+)}-\omega-i\gamma_{L,m}^{(+)}/2}\right.$$
$$\left.+\sin\left(\frac{k_0R\cos\theta_0}{2}\right)\sin\left(\frac{k_0R\cos\theta}{2}\right)\sum_{m=-L}^{L}\frac{d_{rm}^{(L)}(\theta_0)d_{r'm}^{(L)}(\theta)e^{im\varphi}}{\omega_{L,m}^{(-)}-\omega-i\gamma_{L,m}^{(-)}/2}\right\}. \quad (30)$$

The total resonant scattering cross section can easily be found by the optical theorem. In the case of unpolarized photons, we have

$$\sigma^{(L)}=\frac{4\pi}{k_0}\frac{1}{2}\operatorname{Im}(f_{11}^{(L)}(\theta_0,\theta_0,0)+f_{-1-1}^{(L)}(\theta_0,\theta_0,0))$$
$$=\frac{\pi}{k_0^2}(2L+1)\gamma_L\left\{\cos^2\left(\frac{k_0R\cos\theta_0}{2}\right)\sum_{m=-L}^{L}\frac{\gamma_{L,m}^{(+)}(d_{1m}^{(L)}(\theta_0))^2}{(\omega_{L,m}^{(+)}-\omega)^2+(\gamma_{L,m}^{(+)})^2/4}\right.$$
$$\left.+\sin^2\left(\frac{k_0R\cos\theta_0}{2}\right)\sum_{m=-L}^{L}\frac{\gamma_{L,m}^{(-)}(d_{1m}^{(L)}(\theta_0))^2}{(\omega_{L,m}^{(-)}-\omega)^2+(\gamma_{L,m}^{(-)})^2/4}\right\}. \quad (31)$$

We have allowed here for the fact that

$$\sum_m\gamma_{L,m}^{(\pm)}(d_{1m}^{(L)}(\theta_0))^2=\sum_m\gamma_{L,m}^{(\pm)}(d_{-1m}^{(L)}(\theta_0))^2.$$

If $L=1$, Eq. (31) yields directly the results of[5] for the resonant dipole scattering.

According to Eqs. (30) and (31) if the vectors $\mathbf{k}$ and $\mathbf{R}$ are parallel ($\theta_0=0$ or $\theta_0=\pi$), the contribution to the resonant scattering is made only by the collective levels with the spin projections of $+1$ or -1. This is due to the fact that the helicity of a photon assumes the values ±1. In view of the degeneracy of the levels in respect of the sign of m, we then only have two resonances whose frequencies are $\omega_{L,1}^{(+)}$ and $\omega_{L,1}^{(-)}$, and widths are $\gamma_{L,1}^{(+)}$ and $\gamma_{L,1}^{(-)}$. On the other hand, if $\theta_0=\pi/2$, the terms corresponding to the antisymmetric states $|\psi_m^{(-)}\rangle$ disappear from Eqs. (30) and (31); then, the resonance energies of the photons polarized parallel and perpendicular to $\mathbf{R}$ are different. In fact, it follows from the properties of the d functions that if $\theta=\pi/2$, one of the amplitudes (29) or (29′) vanishes. In the case of EL transitions, the resonant scattering of the photons polarized parallel to $\mathbf{R}$ is governed by the levels $|\psi_m^{(+)}\rangle$ with odd values of the sum $L+m$ and the scattering of the photons with the polarization vectors $e\perp\mathbf{R}$ is governed by the levels $|\psi_m^{(+)}\rangle$ with even values of the sum $L+m$. If the resonant scattering is associated with ML transitions, the reverse is true: the odd values of $L+m$ correspond to the polarization vector perpendicular to $\mathbf{R}$ and the even values to the parallel vector.

C. Emission from two excited centers. The results in § 3 can also be used to determine the emission spectrum of two identical excited centers B located at points $\mathbf{R}_1$ and $\mathbf{R}_2$. The levels $|\psi_m^{(\pm)}\rangle$ corresponding to the excitation of one of the centers are then intermediate. The actual relationships for the spectrum can be obtained within the framework of a theory of cascade decay of two excited atoms, which is developed in[9] and which allows for the interference of the two-photon amplitudes associated with the initial equidistant nature of the system. It is assumed in[9] that the excited states are nondegenerate and the radiation is of dipole nature. However, the general structure of the spectrum is not affected by these assumptions. If both centers are in identical states B of spin L, the spectral distribution of the intensity after integration over the angles of emergence of the photons is

$$R_{L,m}(\omega)=R_{L,m}^{(+)}(\omega)+R_{L,m}^{(-)}(\omega),$$

where

$$R_{L,m}^{(\pm)}(\omega)=\frac{1}{4\pi}(\gamma_L\pm\Delta\gamma_{L,m})\left\{\frac{(3\gamma_L\pm\Delta\gamma_{L,m})(1-a_{L,m}^{(\pm)})+b_{L,m}^{(\pm)}(\omega-\omega_0\pm\Delta\omega_{L,m})}{(\omega-\omega_0\pm\Delta\omega_{L,m})^2+(3\gamma_L\pm\Delta\gamma_{L,m})^2/4}\right.$$
$$\left.+\frac{(\gamma_L\pm\Delta\gamma_{L,m})(1+a_{L,m}^{(\pm)})+b_{L,m}^{(\pm)}(\omega_0-\omega\pm\Delta\omega_{L,m})}{(\omega_0-\omega\pm\Delta\omega_{L,m})^2+(\gamma_L\pm\gamma_{L,m})^2/4}\right\},$$
$$a_{L,m}^{(\pm)}=\frac{(\gamma_L\pm\Delta\gamma_{L,m})\gamma_L}{\gamma_L^2+4\Delta\omega_{L,m}^2},\quad b_{L,m}^{(\pm)}=\frac{4(\gamma_L\pm\Delta\gamma_{L,m})\Delta\omega_{L,m}}{\gamma_L^2+4\Delta\omega_{L,m}^2}. \quad (32)$$

The function $R_{L,m}^{(+)}(\omega)$ describes a contribution of the symmetric intermediate state $|\psi_m^{(+)}\rangle$ and the function $R_{L,m}^{(-)}(\omega)$ corresponds to the antisymmetric state $|\psi_m^{(-)}\rangle$.

It follows from Eq. (32) and the asymptotic formulas (26) that if the distance between the centers is large ($x = k_0 R \gg 1$), the emission spectrum reduces—as expected—to a single Lorentz line of frequency ω_0 and width γ_L, i.e., the two centers radiate independently. In the opposite limiting case of $x \ll 1$, the spectrum consists of two nonoverlapping lines of the same intensity, one of which is of frequency $\omega_0 - \Delta\omega_{L,m}$ and width $4\gamma_L$, and the other of frequency $\omega_0 + \Delta\omega_{L,m}$ and width $2\gamma_L$. In this case we can ignore the contribution of the decay of the system via the state $|\psi_m^{(-)}\rangle$ and the interference-caused distortion of the spectrum.[5]

If the spin projections of the excited centers are not equal ($m_1 \neq m_2$), the emission spectrum is governed by four intermediate levels: $|\psi_{m_1}^{(\pm)}\rangle$ and $|\psi_{m_2}^{(\pm)}\rangle$.

§5. SPIN STRUCTURE OF THE RESONANT INTERACTION

For arbitrary spins of the excited and ground states the matrix elements of the operator representing the 2^L-pole interaction of two atoms or nuclei can be expressed in terms of the functions $U_{|m|}^{(L)}(x)$ introduced earlier. In the representation in which the quantization axis of the spin is parallel to the vector $\mathbf{R}$ ($m = m_1 - m_2'$ $= m_1' - m_2$), we have

$$\langle B_{m_1}(1) A_{m_2}(2) | \hat{V}^{(L)} | A_{m_2'}(1) B_{m_1'}(1)\rangle = \hbar\gamma_L C^{s_B m_1}_{s_A m_2' L m} C^{s_B m_1'}_{s_A m_2 L m} U^{(L)}_{|m|}(x), \quad (33)$$

where γ_L is the probability of the 2^L-pole transition $B \to A + \gamma$ per unit time. In particular, if the excited-state spin vanishes and the spin of the ground state is L ($s_B = 0$, $s_A = L$), the frequency shifts and changes in the widths of the collective and excited states [of the type given by Eq. (3) and expressed in units of γ_L] are $2L+1$ times smaller than in the case $s_B = L$, $s_A = 0$ discussed above.

Allowance for Eqs. (18) and (33) shows that the electromagnetic interaction between excited and unexcited and unexcited centers has the general structure

$$\hat{V} = \hbar\gamma \hat{f}(x) e^{ix} \hat{P}_{AB}/x, \quad (34)$$

where $\hat{P}_{AB}$ is the exchange operator that transposes the states A and B[6] and γ is the radiative width of an isolated center; for transitions of mixed multipole order, we have

$$\gamma = \sum_L \gamma_L$$

and $\hat{f}(x)$ is the matrix in the spin space of the centers A and B containing polynomials of order $N \leqslant 2(s_A + s_B)$ in the variable $1/x$. Since the eigenvalues of P_{AB} are ± 1, the collective quasistationary states are always symmetric or antisymmetric under the transposition $A \rightleftharpoons B$. They correspond to a definite value of the projection of the total spin of the system $\hat{\mathbf{S}} = \hat{\mathbf{S}}_A + \hat{\mathbf{S}}_B$ onto the vector $\mathbf{R}$, but if $s_A \neq 0$, $s_B \neq 0$, they are generally not the eigenstates of the operator $\hat{\mathbf{S}}^2$. The exception to this rule is the case $s_A = s_B = 1/2$ (see below).

We shall now write the explicit form of $\hat{f}(x)$ for pure dipole transitions ($\gamma \equiv \gamma_1$). If $s_B = 1$ and $s_A = 0$, we have[6]

$$\hat{f}(x) = F(x) + D(x)(\hat{\mathbf{S}}\mathbf{n})^2, \quad (35)$$

where $\mathbf{n} = \mathbf{R}/R$,

$$\left.\begin{aligned} F(x) &= xe^{-ix} U_0^{(1)}(x) = -\frac{3}{2}\left(\frac{1}{x^2} - \frac{i}{x}\right), \\ D(x) &= xe^{-ix}(U_1^{(1)}(x) - U_0^{(1)}(x)) = -\frac{3}{4}\left(1 + \frac{3i}{x} - \frac{3}{x^2}\right). \end{aligned}\right\} \quad (36)$$

If $s_B = 0$ and $s_A = 1$, then

$$\hat{f}(x) = {}^1\!/_3 F(x) + {}^1\!/_3 D(x)(\hat{\mathbf{S}}\mathbf{n})^2. \quad (35')$$

In particular, in the long-wavelength limit the widths of the spectral lines which follow from Eq. (35′) are $\gamma_{1,0}^{(+)} = \gamma_{1,1}^{(+)} = \frac{4}{3}\gamma_1$ and $\gamma_{1,0}^{(-)} = \gamma_{1,1}^{(-)} = \frac{2}{3}\gamma_1$.

We can show that if $s_A = s_B = 1/2$, then

$$\hat{f}(x) = {}^1\!/_3 \{F(x)[1 - 2(\hat{\mathbf{S}}\mathbf{n})^2 + \hat{\mathbf{S}}^2] + 2D(x)[1 - (\hat{\mathbf{S}}\mathbf{n})^2]\}. \quad (37)$$

Table I gives the eigenvalues of the matrix (37) corresponding to certain values of the total spin S and its projection M, and also the frequencies and widths of spectral lines corresponding to $x = k_0 R \ll 1$. It should be noted that when $R \ll 1/k_0 = \lambda$, an antisymmetric level with the quantum numbers $S = 1$ and $M = 0$ is long-lived ($\gamma_{1,10}^{(-)} \ll \gamma_1$).

If the centers are at rest and the frequencies ν characterizing their motion satisfy the conditions $\omega_0 \gg \nu \gg \gamma$, $\nu \ll c/R$, the expression (34) should be regarded as an operator not only in the spin space but also in the coordinate space of the two centers.[6] Clearly, because of the presence of an exponential function with an imaginary argument in Eq. (34), all the collective effects should vanish if the photon wavelength is much less than the linear dimensions of the regions of spatial localization of the radiators. In particular, a considerable change in the lifetime of an excited nucleus in a crystal in the presence of unexcited nuclei of the same type occurs only on condition $\lambda \gtrsim a_{\text{vib}}$, where a_{vib} is the amplitude of the vibrations. The suppression factor is the same as in the Mössbauer effect. An analogous situation occurs also in the case of diatomic molecules with isomeric nuclei whose properties are discussed in[6].

TABLE I.

S	M	$f_{SM}(x)$	$\omega_{1,SM}^{(\pm)}(x \ll 1)$	$\gamma_{1,SM}^{(+)}(x \ll 1)$	$\gamma_{1,SM}^{(-)}(x \ll 1)$
1	± 1	$^1/_3 F(x)$	$\omega_0 \mp \gamma_1/2x^3$	$^4/_3 \gamma_1$	$^2/_3 \gamma_1$
1	0	$F(x) + {}^2/_3 D(x)$	$\omega_0 \mp \gamma_1/2x$	$2\gamma_1$	$^1/_6 \gamma_1 x^2$
0	0	$^1/_3 F(x) + {}^2/_3 D(x)$	$\omega_0 \pm \gamma_1/x^3$	$^4/_3 \gamma_1$	$^2/_3 \gamma_1$

§6. INFLUENCE OF A METAL MIRROR ON THE LIFETIME AND EMISSION SPECTRUM OF EXCITED ATOMS

Morawitz[14] pointed out the analogy between coherent emission of radiation from a system of two identical dipole centers and the emission of radiation from an atom located near the flat surface of a perfect conductor. Using the method of images and basing his treatment directly on the results given in[5,6], Morawitz investigated the interesting effect of a change in the lifetime of an excited atom under the influence of a metal mirror. (The frequency shifts of the radiation emitted by a two-level system obtained by Morawitz[14] are valid only in the limiting case of large distances from the mirror—see below.) This question (again in the dipole approximation framework) has later been considered by many authors.[20–22]

We shall discuss the general case of electric and magnetic transitions of arbitrary multipole order. We shall use the boundary conditions on the surface of an ideal conductor[23]:

$$\mathbf{E}_{\parallel}=\mathbf{E}-\mathbf{n}(\mathbf{En})=0,\quad H_n=\mathbf{Hn}=0. \tag{38}$$

Here, $\mathbf{n}$ is the vector of the normal to the surface. It follows from the Maxwell equations and the expressions in Eq. (38) that an electromagnetic field created by a conductor in vacuum can be regarded as the field of a system of virtual radiators which is obtained from the original system by specular reflection in the boundary plane of the conductor and subsequent reversal of the sign of all components of the four-vector current density Consequently, the Fourier components of the current and charge densities in the original system and of its "image" are related by the following expressions (a tilde above a symbol refers to the image):

$$\tilde{\mathbf{j}}(\mathbf{k})=-\mathbf{j}_{\text{refl}}(\mathbf{k}_{\text{refl}}),\quad \tilde{\rho}(\mathbf{k})=-\rho(\mathbf{k}_{\text{refl}}). \tag{39}$$

Then,

$$\mathbf{j}_{\text{refl}}=\mathbf{j}-2\mathbf{n}(\mathbf{nj}),\quad \mathbf{k}_{\text{refl}}=\mathbf{k}-2\mathbf{n}(\mathbf{kn}). \tag{39'}$$

Subject to Eq. (39), we find that the 2^L-pole moments of a radiator and its image in a coordinate system with the z axis parallel to the normal vector $\mathbf{n}$ are either equal or they differ only in respect of the sign:

$$\tilde{Q}^{(e)}_{Lm}=(-1)^{L+m+1}Q^{(e)}_{Lm},\quad \tilde{Q}^{(m)}_{Lm}=(-1)^{L+m}Q^{(m)}_{Lm}. \tag{40}$$

It follows from the correspondence principle that in the case of quantum radiators the relationships in Eq. (39) link the transition currents and the relationships in Eq. (40) link the multipole moments of the transition. An excited atom at a point $\mathbf{R}_1$ located at a distance D from a metal mirror and its "image" located at the point $\mathbf{R}_2 = -2D\mathbf{n}+\mathbf{R}_1$ emit photons coherently. Hence, the effective density of the current representing the probability of photon emission is

$$J_{AB}(\mathbf{k})=j_{AB}(\mathbf{k})+\tilde{j}_{AB}(\mathbf{k})e^{2iD(\mathbf{kn})} \tag{41}$$

We shall now consider a radiative transition between an excited state of an atom whose spin (total angular momentum) is L and the zero-spin ground state. Let m be the projection of the spin onto the normal vector $\mathbf{n}$. Then,

$$J^{(\lambda)}_{AB_m}(\mathbf{k})=j^{(\lambda)}_{AB_m}(\mathbf{k})\left[1+(-1)^{L+m+\lambda}e^{2iD(\mathbf{kn})}\right], \tag{42}$$

where $\lambda=0$ refers to the ML transitions and $\lambda=1$ to the EL transitions, and the currents $j^{(1)}_{AB_m}(\mathbf{k})$ and $j^{(0)}_{AB_m}(\mathbf{k})$ are defined with the aid of Eqs. (13) and (14). We can see that the situation is formally the same as in the case of decay of the collective states of Eq. (3) when the distance between atoms A and B is $2D$. Allowing for Eq. (42), we find that the probability of emission of a photon at an angle θ with respect to the vector $\mathbf{n}$ is given by an expression analogous to Eq. (28):

$$W_{L,m}(\theta)=\frac{2L+1}{4\pi}\gamma_L\left[(d^{(L)}_{1m}(\theta))^2+(d^{(L)}_{-1,m}(\theta))^2\right]\left[1+\eta_{AB}(-1)^{m+1}\cos(2k_0D\cos\theta)\right]. \tag{43}$$

Here, $\eta_{AB}=(-1)^{L+1+\lambda}$ is the relative parity of the ground and excited states of the atom, and the angle has the values in the range $0\leqslant\theta\leqslant\pi/2$ ($\cos\theta\geqslant 0$).

Integrating Eq. (43) up to half the solid angle in question, we find

$$\gamma^{(B)}_{L,m}=2\pi\int_0^{\pi/2}W_{L,m}(\theta)\sin\theta\,d\theta=\gamma_L\left[1+2(-1)^m\eta_{AB}\,\mathrm{Im}\,U^{(L)}_{|m|}(2k_0D)\right], \tag{44}$$

where the function $U^{(L)}_{|m|}(x)$ is described by Eq. (18) [compare with Eq. (5)]. It is important to note that the width $\gamma^{(B)}_{L,m}$ and, consequently, the lifetime of an excited atom is a function of the projection of the spin onto the vector normal to the conductor (mirror) surface. Thus, the conductor (mirror) splits the excited level into components with different lifetimes. The change in the lifetimes is

$$\Delta\tau=-\tau_0\frac{\tau_0(\gamma_{L,m}-\gamma_L)}{1+\tau_0(\gamma_{L,m}-\gamma_L)}.$$

For arbitrary values of s_B and s_A the probability of emission of a photon along a given direction, corresponding to the EL and ML transitions, becomes

$$W_{L,m}(\theta)=\frac{2L+1}{4\pi}\gamma_L\sum_\mu|C^{s_Bm}_{s_Am-\mu L\mu}|^2\times\left[(d^{(L)}_{\mu1}(\theta))^2+(d^{(L)}_{\mu,-1}(\theta))^2\right]\left[1+\eta_{AB}(-1)^{\mu+1}\cos(2k_0D\cos\theta)\right]. \tag{45}$$

Hence,

$$\Delta\gamma^{(B)}_{L,m}=2\eta_{AB}\gamma_L\sum_\mu|C^{s_Bm}_{s_Am-\mu L\mu}|^2(-1)^\mu\,\mathrm{Im}\,U^{(L)}_{|\mu|}(2k_0D). \tag{46}$$

In particular, if the excited-state spin is zero, we have

$$\Delta\gamma^{(B)}=\eta_{AB}\frac{2}{2s_A+1}\sum_{\mu=-s_A}^{s_A}(-1)^\mu\,\mathrm{Im}\,U^{(s_A)}_{|\mu|}(2k_0D). \tag{47}$$

We must stress that Eqs. (43)–(47) retain their meaning also in the case when the lower state A is also excited provided $\gamma_{L,m}$ and γ_L are now understood to be the partial probabilities of decay in the $B_m \to A+\gamma$ channel.

In the limiting case of very short distances from the mirror, we find that

$$\gamma_{L,m}^{(B)} \approx \gamma_L \left(1 + \sum_{\mu} \eta_{AB} (-1)^{\mu+1} |C_{A m-\mu L\mu}^{s_B m}|^2\right). \quad (48)$$

If then $s_B = L$ and $s_A = 0$, we find that $\gamma_{L,m} = \gamma_L [1+\eta_{AB} \times (-1)^{m+1}]$, i.e., the probability of a radiative transition for the same components of the excited level is doubled but for other components it is negligible $[\sim \gamma_L (k_0 D)^2]$. For example, in the case of an $E1$ transition[14]

$$\gamma_{1,+1}^{(B)} = \gamma_{1,-1}^{(B)} = {}^1/_5 \gamma_1 (2k_0 D)^2 \ll \gamma_1, \quad \gamma_{1,0}^{(B)} \approx 2\gamma_1.$$

In the case of magnetic dipole transition, we have the converse situation:

$$\gamma_{1,+1}^{(B)} = \gamma_{1,-1}^{(B)} = 2\gamma_1, \quad \gamma_{1,0}^{(B)} = {}^1/_{10} \gamma_1 (2k_0 D)^2 \ll \gamma_1.$$

It should be noted that, in accordance with Eq. (48), the change in the width of the level for the spins $s_B = 0$ and $s_A = L$ is

$$\Delta\gamma^{(B)} = \eta_{AB} (-1)^{L+1} \frac{\gamma_L}{2L+1}.$$

Thus, near the surface of an ideal conductor the lifetime of a zero-spin level increases if the decay involves a transition of the electric type $[\eta_{AB} = (-1)^L]$ and it decreases if the decay is due to a transition of the magnetic type $[\eta_{AB} = (-1)^{L+1}]$.

It should be stressed that our analysis applies to a mirror which reflects totally the incident electromagnetic radiation and alters its phase by 180°. This corresponds to the limiting case of very high values of the permittivity $\varepsilon(k_0)$. For most conductors the condition $|\varepsilon(k_0)| \gg 1$ is satisfied well up to infrared frequencies and for silver it is satisfied also in the optical range. However, in view of the finite conductivity of a metal, we may expect a nonradiative $B \to A$ transition accompanied by the transfer of the excitation energy to the conducting medium.[24] This process becomes predominant at sufficiently short distances from a mirror and it reduces the excited-state lifetime.[6)] Therefore, even in the case of $|\varepsilon(k_0)| \gg 1$ and $|\mathrm{Im}\,\varepsilon(k_0)| \ll 1$, the above relationships do not apply to widths corresponding to very small values of D.

We shall now estimate the shift of the energies and frequencies of the radiation. For these quantities the corrections to the results obtained for an ideal mirror in the $|\varepsilon(k_0)| \gg 1$ case are small irrespective of the distance D. The level shift is described by a self-energy diagram in which the vertex functions have the structure of Eq. (41). The contribution to this diagram is made by real and virtual intermediate states A. Therefore, the results for a system of two identical centers (see § § 2–4) cannot be applied directly. The radiative shift of a level independent of D is clearly identical with the conventional Lamb shift. Allowance for the influence of the conducting surface is represented by the product of the currents $j_{AB}(\mathbf{q})$ and $\bar{j}_{AB}(\mathbf{q})$ for an atom and its "image." The application of a standard procedure allows us to represent the part of the complex radiative shift $Q^{(B)} = \Delta E^{(B)} - i\Delta\gamma^{(B)}/2$ of interest to us in the form of the integral

$$Q^{(B)} = \frac{1}{2(2\pi)^2} \sum_A \int \frac{\mathrm{Re}\{[\rho_{AB}(\mathbf{q}) \bar{\rho}_{AB}^*(\mathbf{q}) - \mathbf{j}_{AB}(\mathbf{q}) \bar{\mathbf{j}}_{AB}^*(\mathbf{q})] e^{2iD(\mathbf{qn})}\}}{(|\mathbf{q}| - k_0^{(BA)} - i0)|\mathbf{q}|} d^3\mathbf{q}. \quad (49)$$

Here, $k_0^{(BA)} = (E^{(B)} - E^{(A)})/\hbar c$; the summation is carried out over all discrete levels A and integration over the states with a continuous energy spectrum. According to Eq. (49), the change in the width $\Delta\gamma^{(B)}$ is affected only by the levels lying below B characterized by $k_0^{(BA)} > 0$.

We shall now obtain the explicit expressions for the level and frequency shifts of the radiation emitted by a quantum system located at a fixed distance D from an ideal mirror and we shall use the two-level model with a degenerate upper level. If the spin of the excited state B is L and the spin of the ground state A is zero, it follows from Eqs. (49) and (42) that

$$\Delta E_m^{(B)} = \hbar \eta_{AB} (-1)^{m+1} \frac{\gamma_L}{\pi} \lim_{\varepsilon \to +0} \int_0^\infty \frac{(y/x)^{2L+1}\, \mathrm{Im}\, U_{|m|}^{(L)}(y) e^{-\varepsilon y}}{y-x} dy, \quad (50)$$

where $x = 2(E^{(B)} - E^{(A)})D/\hbar c > 0$. The power factor in the integral of Eq. (50) is related to the energy dependence $\gamma_L(q) = (q/k_0)^{2L+1} \gamma_L$ [see Eq. (19)] and the factor $e^{-\varepsilon y}$ automatically removes the nonphysical terms which oscillate at infinite values of the argument. The energy shift of the ground state can be found by replacing x with $-x$ in Eq. (50) and summing over the projections of the spin μ of the level B, which is now intermediate. Applying the representation (18) to the functions $U_{|m|}^{(L)}(x)$, we find that integration gives

$$\left.\begin{aligned} \Delta E_m^{(B)} &= {}^1/_2 \hbar \eta_{AB} (-1)^{m+1} \gamma_L [\mathrm{Re}\, U_{|m|}^{(L)}(x) + f_{|m|}^{(L)}(x)], \\ \Delta E^{(A)} &= -{}^1/_2 \hbar \eta_{AB} \gamma_L \sum_{\mu=-L}^{L} (-1)^\mu [\mathrm{Re}\, U_{|\mu|}^{(L)}(x) - f_{|\mu|}^{(L)}(x)], \end{aligned}\right\} \quad (51)$$

where

$$\left.\begin{aligned} f_{|m|}^{(L)}(x) &= (-1)^{L+m} \frac{2L+1}{4\pi} \sum_{n=0}^{L} C_{L1L-1}^{2n0} C_{LmL-m}^{2n0} x^{2n} \left(\frac{d}{x\,dx}\right)^{2n} \\ &\times \left\{\frac{1}{x} \frac{d^{2(L-n)}}{dx^{2(L-n)}} [\cos x\, \mathrm{Si}\, x - \sin x\, \mathrm{Ci}\, x]\right\}, \\ \mathrm{Si}\, x &= \int_0^x \frac{\sin y}{y} dy, \quad \mathrm{Ci}\, x = -\int_x^\infty \frac{\cos y}{y} dy. \end{aligned}\right\} \quad (52)$$

Hence, it follows that the frequency shifts are given by

$$\Delta\Omega_{L,m} = \frac{1}{\hbar}(\Delta E_m^{(B)} - \Delta E^{(A)}) = \eta_{AB} \gamma_L (-1)^{m+1} f_{|m|}^{(L)}(x) + \frac{\gamma_L}{2} \eta_{AB} \sum_{m' \neq m} (-1)^{m'} [\mathrm{Re}\, U_{|m|}^{(L)}(x) - f_{|m|}^{(L)}(x)]. \quad (53)$$

In this model the widths of the spectral lines are given by Eq. (44).

It follows from the asymptotic properties of the functions of Six and Cix that in the limiting case of $x = 2k_0 D \gg 1$, the difference is given by

$$\mathrm{Re}\, U_{|m|}^{(L)}(x) - f_{|m|}^{(L)}(x) \sim x^{-(2L+2)}$$

and, therefore,

$$\Delta\Omega_{L,m} \approx \Delta E_m^{(B)}/\hbar \approx \hbar\eta_{AB}(-1)^{m+1}\gamma_L\, \mathrm{Re}\, U_{|m|}^{(L)}(x). \tag{54}$$

An analysis shows that if $x \ll 1$, we can ignore the contribution of the functions $f_{|m|}^{(L)}(x)$. Allowing for this fact we find that at short distances from the mirror

$$\left.\begin{aligned} &\Delta E_m^{(B)} = \frac{1}{2}\hbar(-1)^{L+1}\eta_{AB}|\Delta\omega_{L,m}|, \quad \Delta E^{(A)} = \sum_{m'=-L}^{L}\Delta E_{m'}^{(B)} \\ &\Delta\Omega_{L,m} \approx \frac{1}{2}\eta_{AB}(-1)^L \sum_{m'\neq m}|\Delta\omega_{L,m'}|, \end{aligned}\right\} \tag{55}$$

where the quantity $\Delta\omega_{L,m}$ is found from Eq. (22). In the case of EL transitions, we have $\eta_{AB} = (-1)^L$ and the frequency shifts are positive; conversely, for ML transitions, we have $\Delta\Omega_{L,m} < 0$.

If $L = 1$ and $\eta_{AB} = -1$ (electric dipole radiation), the relationships (51)–(53) give

$$\Delta\Omega_{1,m} = \frac{1}{\hbar}(\Delta E_m^{(B)} - \Delta E^{(A)}),$$

where

$$\left.\begin{aligned} &\Delta E_{+1}^{(B)} = \Delta E_{-1}^{(B)} = -\frac{3\hbar\gamma_1}{8}\left(\frac{\sin x}{x^2} + \frac{\cos x}{x^3} - \frac{\cos x}{x}\right) + \frac{3\hbar}{4\pi}\gamma_1 \\ &\times\left\{[\sin x\,\mathrm{Ci}\,x - \cos x\,\mathrm{Si}\,x]\left(\frac{1}{x^3} - \frac{1}{x}\right) - \frac{1}{x^2}[\cos x\,\mathrm{Ci}\,x + \sin x\,\mathrm{Si}\,x] + \frac{1}{x^2}\right\}, \\ &\Delta E_0^{(B)} = -\frac{3\hbar\gamma_1}{4}\left(\frac{\cos x}{x^3} - \frac{\sin x}{x^2}\right) + \frac{3\hbar\gamma_1}{2\pi} \\ &\left\{\frac{1}{x^3}(\sin x\,\mathrm{Ci}\,x - \cos x\,\mathrm{Si}\,x) - \frac{1}{x^2}(\cos x\,\mathrm{Ci}\,x + \sin x\,\mathrm{Si}\,x)\right\}, \\ &\Delta E^{(A)} = -\frac{3\hbar\gamma_1}{4}\left[\frac{2\sin x}{x^2} + \cos x\left(\frac{2}{x^3} - \frac{1}{x}\right)\right]\frac{3\hbar\gamma_1}{4\pi} \\ &-\left\{[\sin x\,\mathrm{Ci}\,x - \cos x\,\mathrm{Ci}\,x]\left(\frac{2}{x^3} - \frac{1}{x}\right) - \frac{2}{x^2}(\cos x\,\mathrm{Ci}\,x + \sin x\,\mathrm{Si}\,x) + \frac{1}{x^2}\right\} \end{aligned}\right\} \tag{56}$$

For values obeying $D \ll 1/k_0$ we have

$$\Delta\Omega_{1,+1} = \Delta\Omega_{1,-1} \approx {}^3/_2\Delta\Omega_{1,0} \approx {}^9/_4\gamma_1(2k_0D)^{-3}, \tag{57}$$

i.e., the frequency shifts are proportional to $1/D^3$. This is in agreement with the general conclusions reached by Barton.[22] On the other hand, for $x \lesssim 1$, the expressions (56) and (57) differ considerably from the corresponding formulas of Agarwal[21] which have the following form in our notation:

$$\Delta\Omega_{L,m} = (-1)^m f_{|m|}^{(1)}(x)\gamma_1.$$

This is due to the fact that Agarwal uses an unrealistic model with a nondegenerate upper level. In his model the energy shift of the ground state depends on the direction of the dipole moment of the transition, which is assumed to be always strictly defined. A critique of these results can be found in Barton's paper.[22]

It should be noted that Morawitz[14] gives the shifts of the frequencies of the dipole radiation in the form $(-1)^m \mathrm{Re}U_{|m|}^{(1)}(x)\gamma_1$, which corresponds to our asymptotic expression (54). This result follows from the classical theory of an oscillator interacting with its mirror image and it remains valid also in the case of a quantum oscillator whose levels are equidistant. However, on going over to a two-level system, the approach developed by Morawitz[14] becomes incorrect. The limited validity of the analogy between an oscillator and a two-level system is considered in a different connection by Gribkovskiĭ and Stepanov.[25]

The author is grateful to V. G. Baryshevskiĭ and M. I. Podgoretskiĭ for their interest and valuable comments.

[1)]Here and later, it is assumed that the lifetime of the system is long compared with the transit time of a signal between the two centers: $\gamma_{tot}R/c \ll 1$.

[2)]The energy dependence of the form factors on the variable $z = k_0^2 - x^2$ corresponds to the contact interaction which disappears if the spatial distributions of the currents do not overlap. Real atoms and nuclei do not have sharp boundaries and, consequently, our analysis is valid for values of R which are considerably greater than the effective size of the centers.

[3)]In particular, in the case of zero-spin B centers [$L = 0$, $E(0)$ transition], the resonant interaction does not appear for any finite value of R.

[4)]It is convenient to use Eq. (25) in the case of small values of L, when the angular dependence of the d functions is simple. In particular, if $L = 2$, we have

$$U_1^{(2)}(x) = -\frac{5}{8}\left(1 + 3\frac{d^2}{dx^2} + 4\frac{d^4}{dx^4}\right)\frac{e^{ix}}{x},$$

$$U_0^{(2)}(x) = \frac{15}{4}\left(\frac{d^2}{dx^2} + \frac{d^4}{dx^4}\right)\frac{e^{ix}}{x}, \quad U_2^{(2)}(x) = -\frac{5}{8}\left(1 - \frac{d^4}{dx^4}\right)\frac{e^{ix}}{x}.$$

[5)]Strictly speaking, if $R \ll \lambda$, a narrow peak is superimposed on a line of frequency $\omega_0 - \Delta\omega_{L,m}$ and width $4\gamma_L$, in accordance with Eq. (32), and the amplitude of this peak is twice the amplitude of the main peak. However, the narrow peak representing the decay of the antisymmetric state makes a negligible contribution to the integrated intensity (the order of magnitude of this contribution is $\gamma_{Lm}^{(-)}/\gamma_L \sim x^2 \ll 1$).

[6)]We can show that in the $k_0 D \to 0$ case the width of a level associated with a nonradiative EL transition is proportional to

$$\frac{\mathrm{Im}\,\varepsilon(k_0)}{|\varepsilon(k_0)+1|^2}(2k_0D)^{-(2L+1)}.$$

[1]R. H. Dicke, Phys. Rev. 93, 99 (1954).
[2]M. I. Podgoretskiĭ and I. I. Roĭzen, Zh. Eksp. Teor. Fiz. 39, 1473 (1960) [Sov. Phys. JETP 12, 1023 (1961)].
[3]M. J. Stephen, J. Chem. Phys. 40, 669 (1964).
[4]D. A. Hutchinson and H. F. Hameka, J. Chem. Phys. 41, 2006 (1964).
[5]V. L. Lyuboshits, Zh. Eksp. Teor. Fiz. 52, 926 (1967) [Sov. Phys. JETP 25, 612 (1967)].
[6]V. L. Lyuboshits, Zh. Eksp. Teor. Fiz. 53, 1630 (1967) [Sov. Phys. JETP 26, 937 (1968)].
[7]J. W. Czarnik and P. R. Fontana, J. Chem. Phys. 50, 4071 (1969).
[8]Yu. A. Vdovin and A. M. Ermachenko, Sb. Voprosy teorii atomnykh stolknoveniĭ (Problems in the Theory of Atomic Collisions), Atomizdat, M., 1970, p. 111.
[9]D. F. Smirnov, I. V. Sokolov, and E. D. Trifonov, Zh. Eksp. Teor. Fiz. 63, 2105 (1972) [Sov. Phys. JETP 36, 1111 (1973)].

[10]R. H. Lehmberg, Phys. Rev. A 2, 883, 889 (1970).
[11]F. T. Arecchi and E. Courtens, Phys. Rev. A 2, 1730 (1970).
[12]N. E. Rehler and J. H. Eberly, Phys. Rev. A 3, 1735 (1971).
[13]H. Morawitz, Phys. Rev. A 7, 1148 (1973).
[14]H. Morawitz, Phys. Rev. 187, 1792 (1969).
[15]K. H. Drexhage, Sci. Am. 222, No. 3, 108 (1970).
[16]K. H. Tews, O. Inacker, and H. Kühn, Nature (London) 228, 276 (1970).
[17]A. I. Akhiezer and V. B. Berestetskiĭ, Kvantovaya élektrodinamika, Nauka, M., 1969 (Quantum Electrodynamics, Interscience, New York, 1965).
[18]E. M. Lifshits and L. P. Pitaevskiĭ, Relyativistskaya kvantovaya teoriya, chast' 2, Nauka, M., 1971 (Relativistic Quantum Theory, Part II, Pergamon Press, Oxford, 1974).
[19]V. B. Berestetskiĭ, E. M. Lifshits, and L. P. Pitaevskiĭ, Relyativistskaya kvantovaya teoriya, chast' 1, Nauka, M., 1968 (Relativistic Quantum Theory, Part I, Pergamon Press, Oxford, 1971).
[20]R. R. Chance, A. Prock, and R. Silbey, J. Chem. Phys. 60, 2184 (1974); A. Prock, R. Silbey, and R. R. Chance, J. Chem. Phys. 60, 2744 (1974); R. R. Chance, A. Prock, and R. Silbey, Phys. Rev. A 12, 1448 (1975).
[21]G. S. Agarwal, Phys. Rev. Lett. 32, 703 (1974); Phys. Rev. A 12, 1475 (1975).
[22]G. Barton, J. Phys. B. 7, 2134 (1974).
[23]L. D. Landau and E. M. Lifshits, Élektrodinamika sploshnykh sred, Fizmatgiz, M., 1959 (Electrodynamics of Continuous Media, Pergamon Press, Oxford, 1960).
[24]R. R. Chance, A. Prock, and R. Silbey, J. Chem. Phys. 62, 2245 (1975).
[25]V. P. Gribkovskiĭ and B. I. Stepanov, Izv. Akad. Nauk SSSR Ser. Fiz. 24, 529 (1960); Opt. Spektrosk. 8, 176 (1960) [Opt. Spectrosc. (USSR) 8, 92 (1960)]; B. I. Stepanov and V. P. Gribkovskiĭ, Opt. Spektrosk. 8, 224 (1960) [Opt. Spectrosc. (USSR) 8, 114 (1960)].

Translated by A. Tybulewicz

Recombination of an electron and a complex ion

B. M. Smirnov

I. V. Kurchatov Institute of Atomic Energy
(Submitted October 26, 1976)
Zh. Eksp. Teor. Fiz. 72, 1392–1396 (April 1977)

The recombination of an electron and a complex ion is investigated on the basis of two models. In the first it is assumed that the complex ion interacts strongly with the electron in a certain region near the ion, so that the landing of the electron in this region leads to recombination. In the second model, account is taken of a large number of autoionization states that lead to recombination. The two models lead to the same result at low electron energies. The cross section for the recombination of the electron and the complex ion is inversely proportional to the electron energy, and the dissociative-recombination coefficient is inversely proportional to the square root of the electron temperature. The experimental data are analyzed.

PACS numbers: 34.80.–i

The purpose of this paper is to establish the dependence of the coefficient of dissociative recombination of an electron and a complex ion on the electron temperature. In the general case, the coefficient of dissociative recombination of an electron and a molecular ion is determined by the character of the interaction between the transition channels. An analysis of these relations, with account taken of the experimental data, is the subject of a number of reviews and monographs.[1–4] A distinguishing feature of recombination of an electron and a complex ion is the strong interaction between them. There are many channels for the transfer of the electron energy to the internal degrees of freedom of the produced complex, and it is this fact which determines the sought dependence.

The mechanism of dissociative recombination of an electron and an ion is connected with the change of the electronic state of the ion when it collides with the electron, which leads to formation of a bound autoionization state of the electron and the molecular ion. This autoionization state corresponds to repulsion between fragments of the produced molecule, and the spreading of these fragments leads to the formation of stable states of the neutral particles. The singularity of the complex ion is thus connected with the large autoionization levels of the ion and the electron. Motion of the nuclei leads to a smearing and overlap of the autoionization levels, so that the resonant character of the process is lost in dissociative recombination of the electron and complex ion.

We consider the dissociative recombination of an electron and a complex ion on the basis of two models. In the first was regard the incident electron as a classical particle that collides with the electrons of the complex ion and excites them. As a result, the incident electron loses energy and goes over into an autoionization bound state, which leads subsequently to recombination. In accord with the mechanism of the process, we introduce model assumptions, according to which the recombination has a probability ζ if the electron lands in a region of

 0038-5646/78/4504-0731$02.40