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Spontaneous radiative coupling of atomic energy levels

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Density-matrix equations of motion derived from Heisenberg picture source-field quantum electrodynamics contain damping constants and frequency shifts which are not associated with a single radiative transition but which instead couple two separate transitions together. In the absence of degeneracies in the atomic levels, these coupling terms are normally neglected when the rotating-wave approximation is invoked. These terms cannot be neglected when there are degeneracies or near degeneracies. In this paper, we interpret the generalized frequency shifts, show how they can be renormalized and included in shifts of atomic energy levels and altered damping constants, and discuss their experimental significance.

I. INTRODUCTION

The linewidths and frequency shifts associated with spontaneous radiative transitions can be derived from quantum electrodynamics using two very different physical models. Historically, the derivations were carried out in the Schrödinger picture[1] where one naturally attributes spontaneous emission to the interaction of the atom with the fluctuating vacuum field. Welton[2] showed explicitly that the Lamb shift could indeed be explained in this way. More recently, Heisenberg-picture source-field treatments of these effects have been carried out.[3] These treatments naturally lead one to regard spontaneous emission and the Lamb shift as the effect of radiation reaction. Each atomic transition moment generates a quasimonochromatic field which acts back on the atom and changes its dynamics.

The two alternative descriptions have been shown to be equivalent for two-level atoms.[4] When the Heisenberg-picture calculations were extended to multilevel systems,[5] the equivalence of the two approaches was no longer so obvious. The field given off by a particular transition moment acts back on every transition in the atom, not just on the transition which generates it. If there are no degeneracies or near degeneracies in the atom, then these cross terms are rapidly oscillating and can be dropped in a sort of rotating-wave approximation. This is what has been done in all previous multilevel treatments.

Real atoms do have degeneracies and near degeneracies, so the problem of these cross terms involving two transitions cannot generally be ignored so easily. These cross terms in fact lead to generalized Einstein A coefficients and radiative frequency shifts not associated with one particular transition. The generalized damping constants were originally derived by Landau[6] in his classic paper introducing the density-matrix approach to quantum mechanics, and have been investigated more thoroughly in a recent paper[7] describing interference effects due to their presence. The interpretation of the generalized frequency shifts, however, has been particularly difficult since they could not be renormalized in the usual way, nor could they be eliminated from the dynamics by including them in the transition frequencies. Further, corresponding generalized terms have not appeared in conventional, second-order, nondegenerate perturbative Lamb-shift calculations.

In this paper we will show that analogous terms do occur in perturbation theory if near degeneracies are handled properly, that the generalized frequency shifts can be renormalized, and that these terms may lead to modified line shapes and line strengths as well as to shifted transition frequencies in nearly degenerate systems.

As is well known, the linear divergence which appears in a normal Lamb shift calculation is said to be due to including the electron's divergent self-energy twice.[8] This self-energy appears once in the electron's *observed* mass and once in its vacuum-field interaction energy. The generalized frequency-shift terms cannot be renormalized by merely subtracting this extra self-energy from the calculated energy correction. Instead, the subtraction must occur right at the beginning of the calculation. Therefore in Sec. II we write down a total Hamiltonian which includes the energy of interaction between the electron and its own field only once. Density-matrix equations of motion derived from Heisenberg-picture source-field quantum electrodynamics using this renormalized Hamiltonian then contain generalized frequency-shift terms which are automatically renormalized. Since these

generalized terms are important only in systems with near degeneracies, we specialize the equations to describe just such a system.

The generalized frequency-shift terms in the resulting density-matrix equations of motion do not merely shift the atomic levels, they also mix them. The atom is not simply described then in terms of the usual bare atomic levels, but by a new set of states dressed by the vacuum field. We determine these proper dressed states of the atom-vacuum system to second order in Sec. III and describe how all of the generalized frequency-shift terms may be eliminated from the equations of motion of the dressed-state density matrix. All of the frequency shifts are absorbed into the dressed-state energies and generalized damping constants. Finally, in Sec. IV we discuss the experimental implications of these generalized radiative frequency-shift terms.

II. SOURCE-FIELD QUANTUM ELECTRODYNAMICS

A great deal of effort has gone into accurate calculations of the Lamb shift, including both relativistic and nonrelativistic contributions through fourth order. Erickson and Yennie[9] have developed a particularly powerful technique for these calculations. We will not use this formalism, however, because we are interested in the qualitative effects of radiative corrections on the very closely spaced Rydberg atomic energy levels and not in extremely accurate measurements of hydrogenic energy-level shifts. Also, we have set out to explain the generalized radiative frequency-shift terms which arise quite naturally in second order in the Heisenberg-picture density-matrix formalism, but which do not appear conveniently in second order in conventional nondegenerate perturbation theories. Analogous terms are relegated to fourth order in these theories. We therefore use the Heisenberg-picture density-matrix formalism and quantum electrodynamics to reveal the generalized terms we have described and the procedure for renormalizing them.

As indicated in the Introduction, the renormalization must begin with the initial Hamiltonian. We devise a Hamiltonian which contains the electron's self-energy only once by explicitly subtracting it out of the interaction energy and adding it to the bare-atom energy. Symbolically, this renormalization procedure can be written as

$$\begin{aligned} H &= (H_a + H_{\rm se}) + H_f + (V - H_{\rm se}) \\ &= H_0 + H_f + (V - H_{\rm se}) \, . \end{aligned} \tag{1}$$

The various terms in the Hamiltonian are as follows: H_a, the Hamiltonian for an electron which does not interact with the transverse electromagnetic field; $H_{\rm se}$, the self-energy of the electron interacting with the transverse field; H_f, the Hamiltonian for the free field; and V, the interaction Hamiltonian. The Hamiltonian for the atom in which the electron has the observed mass is $H_0 = H_a + H_{\rm se}$. The self-energy is given to second order by Rayleigh-Schrödinger perturbation theory as[10]

$$H_{\rm se} = \hbar \left(-\frac{2e^2}{3\hbar m^2 c^3} \frac{1}{\pi} \int d\omega \right) \underline{p}^2 \equiv \hbar C \underline{p}^2 \tag{2}$$

in the regions where it can be treated nonrelativistically. The operator $\underline{p}$ is just the electron's momentum.

If we use this renormalized Hamiltonian [Eq. (1)] in the Heisenberg equations of motion and carry through a calculation exactly analogous to Milonni's calculation,[5] we obtain the density-matrix equations of motion

$$\begin{aligned} \dot{\rho}_{ji} = &- \sum_n \left[\sum_{m<n} \gamma_{jmmn} + i \sum_m (S'_{jmmn} - C \underline{p}_{jm} \cdot \underline{p}_{mn}) \right] \rho_{ni} - \sum_n \left[\sum_{m<n} \gamma_{minm} - i \sum_m (S'^{*}_{immn} - C \underline{p}_{nm} \cdot \underline{p}_{mi}) \right] \rho_{jn} \\ &+ \sum_{\substack{m,n \\ m>i}} \gamma_{jnmi} \rho_{nm} + \sum_{\substack{m,n \\ n>j}} \gamma_{mijn} \rho_{nm} - i \sum_{m,n} (S'^{*}_{njim} - S'_{mijn}) \rho_{nm} - i \omega_{ji} \rho_{ji} \, , \end{aligned} \tag{3}$$

where we used the definitions

$$\gamma_{abcd} \equiv \frac{2e^2}{3\hbar m^2 c^3} \underline{p}_{ab} \cdot \underline{p}_{cd} \, | \omega_{cd} | \, , \tag{4a}$$

$$S'_{abcd} \equiv S_{abcd} + C \underline{p}_{ab} \cdot \underline{p}_{cd} \, , \tag{4b}$$

$$S_{abcd} \equiv \frac{2e^2}{3\hbar m^2 c^3} \underline{p}_{ab} \cdot \underline{p}_{cd} \omega_{cd} \frac{1}{\pi} \mathcal{J} \frac{d\omega}{\omega + \omega_{cd}} \, . \tag{4c}$$

All of the radiative frequency shifts S_{abcd} are only logarithmically divergent, as is the usual renormalized result in a nonrelativistic treatment. The terms of the form $\sum_m S_{kmmk}$ are just the usual renormalized Lamb shifts of the atomic levels $| k \rangle$, while all of the other S terms are the so-called "generalized" frequency shifts under scrutiny in this paper. Similarly, the expression $\sum_{m<k} \gamma_{kmmk}$ is the usual phenomenological radiative decay constant for the state $| k \rangle$, while all the other γ terms we refer to as

generalized damping constants.

Equation (3) is quite general. If the usual procedure is followed, a rotating-wave approximation is applied allowing all of the generalized shifts and damping constants to be ignored, unless there are degeneracies or near degeneracies which must be accounted for. In that case, the generalized terms cannot be ignored. In order to examine that case, we will specialize to the simple atomic system illustrated in Fig. 1. The atom is assumed to have a manifold of degenerate or nearly degenerate ground states $|g\rangle$, and another nearly degenerate set of excited states $|e\rangle$. We will assume that there are no other transitions in the atom with frequencies near to the transition frequency ω_{eg} connecting the manifolds $|e\rangle$ and $|g\rangle$. The various states in $|e\rangle$ are assumed to be coupled by electric dipole transitions to the states in $|g\rangle$. Transitions within each manifold will be assumed negligible.

For this system the equations of motion for the density-matrix elements $\rho_{e'e}$ (e' and e may represent the same state) and ρ_{eg} reduce to

$$\dot{\rho}_{e'e} = -[\gamma_{e'e'}+\gamma_{ee}+i(\omega_{e'e}+S_{e'e'}-S_{ee})]\rho_{e'e} - \sum_{e''\neq e'} (\gamma_{e'e''}+iS_{e'e''})\rho_{e''e} - \sum_{e''\neq e} (\gamma_{ee''}-iS_{ee''})\rho_{e'e''} \tag{5a}$$

and

$$\dot{\rho}_{eg} = -[\gamma_{ee}+i(\omega_{eg}+S_{ee}-S_{gg})]\rho_{eg} - \sum_{e'\neq e} (\gamma_{ee'}+iS_{ee'})\rho_{e'g} + \sum_{g'\neq g} iS_{gg'}\rho_{eg'} \, . \tag{5b}$$

To arrive at these simplified equations we have dropped all terms in Eq. (5a) oscillating at frequencies much greater than $\omega_{e'e}$, and all terms in (5b) except those oscillating at approximately ω_{eg}. These terms are dropped in anticipation of making the usual rotating-wave approximation at some later time. We have also introduced the definitions

$$\gamma_{ee'} \equiv \sum_{l<e} \gamma_{elle'} = \gamma^*_{ee'} \tag{6a}$$

and

$$S_{jj'} \equiv \sum_{l} S_{jllj'} = S^*_{jj'} \, . \tag{6b}$$

(The term $S_{jj'}$ with $j=j'$ are just the usual renormalized Lamb shifts.)

In the equations of motion for ρ_{eg} we see not only the usual decay constant and Lamb shift, but additional terms coupling ρ_{eg} to other density-matrix elements $\rho_{eg'}$ and $\rho_{e'g}$. These terms are absent in most phenomenological density-matrix equations, but appear in a complete derivation. They have consequences on the dynamics of a system with near degeneracies and so cannot be ignored. In a previous paper[7] we investigated the generalized damping terms $\gamma_{ee'}$ but left unexamined the generalized frequency shifts $S_{jj'}$.

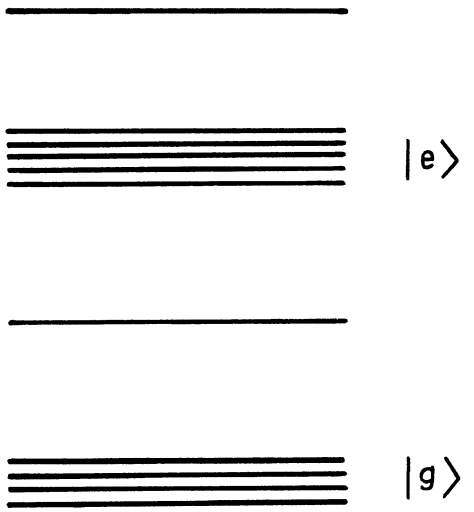

FIG. 1. Multilevel atom with a manifold of closely spaced excited states $|e\rangle$ coupled by electric dipole transitions to the manifold of ground states $|g\rangle$. All the other atomic states are considered to be far from the $|e\rangle$ and $|g\rangle$ manifolds.

III. ATOMIC DRESSING BY THE VACUUM FIELD

The radiative coupling between transitions which we found in Eqs. (5a) and (5b) makes solution difficult, and brings the radiative frequency shifts directly into the atomic dynamics. It is desirable to eliminate these terms from the equations so that only dipole moments and atomic lifetimes appear explicitly. This simplification can be achieved by formulating the theory in terms of atomic states dressed by the vacuum field rather than in terms of bare atomic states.

We can find the proper dressed states by diagonalizing the Hamiltonian, Eq. (1), to second order in the vacuum interaction energy V. The states we wish to study are almost degenerate, i.e., they are not degenerate but are strongly mixed in second order. Such almost degenerate states are treated conveniently using Lennard-Jones—Brillouin—Wigner (LBW) perturbation theory.[11]

We are interested in obtaining the dressed states which will diagonalize the Hamiltonian in Eq. (1) to second order in λ, where the perturbation is

$\lambda V - \lambda^2 H_{se}$ (H_{se} is *second* order in V). With the reordering of the perturbation series in LBW theory, the matrix elements of the perturbation which couple the nondegenerate states to each other are ignored. A partial Hamiltonian matrix $\mathscr{H}$ useful for analyzing the effects of the perturbation on the closely-spaced excited states can be represented schematically as

$$\mathscr{H} = \begin{bmatrix} \mathscr{A} & \mathscr{B} \\ \mathscr{B}^* & \mathscr{D} \end{bmatrix}, \tag{7}$$

where $\mathscr{A}$ is the submatrix of $\mathscr{H}$ in the subspace of the nearly degenerate excited states $|e\rangle$, $\mathscr{B}$ is the submatrix which describes the coupling between the set of nearly degenerate states and all the other atomic states $|l\rangle$, and $\mathscr{D}$ is the submatrix coupling these other atomic states with themselves. The approximation which gives us our second-order LBW theory results is to take $\mathscr{D}$ to be diagonal. A similar matrix can be written for the closely-spaced ground states $|g\rangle$.

Now diagonalizing matrix (7) in the usual fashion (keeping terms to second order in the vacuum interaction energy V) determines the dressed states

$$|E\rangle = \sum_e A_{Ee} |e\rangle \tag{8}$$

and their energies $\hbar\bar{\omega}_E$ through the resulting equations

$$\bar{\omega}_E A_{Ee'} = (\omega_{e'} + S_{e'e'}) A_{Ee'} + \sum_{e \neq e'} S_{e'e} A_{Ee} . \tag{9}$$

We note here that if our manifold of nearly degenerate states $|e\rangle$ were actually degenerate, Eq. (9) would be exactly the equation one would obtain using conventional Rayleigh-Schrödinger degenerate-state perturbation theory.

Equation (9) illustrates nicely the significance of the generalized frequency shifts. The normal Lamb-shift terms S_{ee} are merely frequency shifts, while the generalized terms $S_{e'e}$ couple the states $|e'\rangle$ and $|e\rangle$. If we think of a system of classical harmonic oscillators each coupled to the others, we see immediately that not only are the new normal mode frequencies shifted from the old frequencies, but the new normal modes themselves may be quite different from the uncoupled modes, depending on the strengths of the coupling. The atomic system we are considering is affected analogously. The $S_{e'e}$ coupling changes the eigenstates from the bare-atom states $|e\rangle$ to the vacuum-dressed states $|E\rangle$ and at the same time shifts the transition frequencies from $\omega_{e'e}$ to $\bar{\omega}_{E'E}$.

Solving Eq. (9) gives us the dressed-state energies $\hbar\bar{\omega}_E$ and the dressed states themselves. An identical calculation using the manifold of ground states $|g\rangle$ in place of the excited states $|e\rangle$ results in equations analogous to Eqs. (8) and (9), with e,e' replaced by g,g' and E,E' replaced by G,G'.

To connect the Schrödinger-picture calculation of this section with the Heisenberg-picture formalism of Sec. II, we first expand an arbitrary Schrödinger-picture wave function in the basis of bare atom states $|l\rangle$ as

$$|\psi(t)\rangle = \sum_l a_l(t) |l\rangle \tag{10}$$

and then make the identity

$$\rho_{ji} = a_j a_i^* . \tag{11}$$

These are the density-matrix elements which satisfy Eq. (2).

We can remove all explicit reference to the generalized frequency-shift terms from the density-matrix equations of motion (5) if we use the new dressed states found above [Eq. (8)]. This then implies that the effects of those terms are fully absorbed in the new states themselves, as previously discussed. To accomplish this, a procedure similar to the one Fano[12] used to describe the effects of two discrete states embedded in an ionization continuum could be used. (Our discrete state manifolds $|g\rangle$ and $|e\rangle$ are embedded in the spontaneous emission continuum.) This entails reexpanding the wave function $|\psi(t)\rangle$ [Eq. (10)] in the basis of vacuum-dressed states $|L\rangle$ with expansion coefficients $\bar{a}_L(t)$ and then obtaining equations of motion for the density-matrix elements $\bar{\rho}_{JI} = \bar{a}_J \bar{a}_I^*$. Equations (5), (8), (9), (10), and the orthonormality of the dressed states lead finally to the dressed-state density-matrix equations of motion

$$\dot{\bar{\rho}}_{E'E} = -(\bar{\gamma}_{E'E'} + \bar{\gamma}_{EE} + i\bar{\omega}_{E'E})\bar{\rho}_{E'E} - \sum_{E'' \neq E'} \bar{\gamma}_{E'E''} \bar{\rho}_{E''E} - \sum_{E'' \neq E} \bar{\gamma}_{EE''} \bar{\rho}_{E'E''} \tag{12a}$$

and

$$\dot{\bar{\rho}}_{EG} = -(\bar{\gamma}_{EE} + i\bar{\omega}_{EG})\bar{\rho}_{EG} - \sum_{E' \neq E} \bar{\gamma}_{EE'} \bar{\rho}_{E'G} , \tag{12b}$$

where the new generalized damping constants are

$$\bar{\gamma}_{EE'} \equiv \sum_{e,e'} \gamma_{ee'} A_{Ee}^* A_{E'e'} . \tag{13}$$

Note that all the frequency-shift terms have vanished. They appeared originally simply because we used the wrong states to describe the interaction. Using the proper vacuum-dressed states, we see that

not only are the energy levels shifted ($\bar{\omega}_{IJ} \neq \omega_{ij}$) by the generalized frequency-shift terms, but the decay constants are affected as well ($\bar{\gamma}_{EE'} \neq \gamma_{ee'}$), thereby changing the dynamics of the atomic system. In the next section we will examine the importance of these effects.

IV. EXPERIMENTAL IMPLICATIONS

We now have a complete physical interpretation for the generalized radiative frequency shifts. The vacuum field not only shifts atomic levels, but in the case of nearly degenerate transition frequencies, it also mixes the atomic states. The frequency shifts can be attributed to given transitions and thus to given levels only when the system is described in terms of the proper dressed levels. In Eqs. (12) we have written out the density-matrix equations of motion in terms of these dressed states. The frequency-shift terms do not appear in these equations because they have been included in the dressed-state transition frequencies and altered generalized decay constants. The vacuum field is real and always present so these transition frequencies and damping constants are the experimentally relevant quantities entering fluorescent line strengths, linewidths, branching ratios, etc.

When Eq. (9) is solved for the dressed-state mixing amplitudes $A_{Ee'}$ to first order in the ratio $S_{e'e}/\omega_{e'e'}$, we find

$$A_{Ee'} \approx \frac{S_{e'e}}{\omega_{ee'}} , \tag{14a}$$

$$A_{Ee} \approx 1 , \tag{14b}$$

if we order the dressed states $|E\rangle$ and the bare states $|e\rangle$ so that $|E\rangle \rightarrow |e\rangle$ in the absence of the vacuum field. By way of illustration, let us consider an excited-state manifold having two states, $|1\rangle$ and $|2\rangle$. Then the new diagonal damping rates (good to first order in $S_{e'e}/\omega_{e'e}$) are given by Eq. (13) as

$$\bar{\gamma}_{11} \approx \gamma_{11} - (\gamma_{12}+\gamma_{21})\frac{S_{21}}{\omega_{21}} , \tag{15a}$$

$$\bar{\gamma}_{22} \approx \gamma_{22} + (\gamma_{12}+\gamma_{21})\frac{S_{12}}{\omega_{21}} . \tag{15b}$$

Since γ_{11},γ_{22} are measures of the unperturbed transition strengths and $\bar{\gamma}_{11},\bar{\gamma}_{22}$ are the corresponding transition-strength indicators for the atom dressed by the vacuum, Eqs. (15) show that one set of fluorescent lines will be stronger than expected and one will be weaker.

The quantity of interest which will determine the observability of these changes in fluorescent-line intensities is the ratio $S_{e'e}/\omega_{e'e}$. The occurrence of a near degeneracy is not sufficient to guarantee that this ratio is large. Angular momentum selection rules enter the evaluation of $S_{e'e}$. Consider the case of fine-structure levels of a given principal quantum number. The definition of the generalized frequency-shift terms connecting two levels $|e\rangle$ and $|e'\rangle$ [Eq. (6b) coupled with (4c)] indicates that both states must have the same magnetic quantum number so that $\underline{p}_{e'l}\cdot\underline{p}_{le}$ is nonzero. It can also be shown that $S_{e'e}$ can be expressed in the form

$$\sum_r c_r \sum_l \underline{p}_{e'l}\cdot\underline{p}_{le}\omega_{le}^r$$

(the c_r are expansion constants) and that $\sum_l \underline{p}_{e'l}\cdot\underline{p}_{le}\omega_{le}^r$ is the $e'-e$ matrix element of a spherically symmetric operator. It then follows that the generalized shift terms are zero unless *all* of the angular momentum quantum numbers for the two states $|e\rangle$ and $|e'\rangle$ are equal. This can occur only when the two states have different principal quantum numbers.

For these generalized frequency-shift terms to have an experimentally significant effect we must have nearly degenerate states with identical angular momentum quantum numbers. This can occur in the higher excited states of hydrogenic ions with large Z, or in multielectron atoms and molecules where different electronic configurations can overlap. In such systems these vacuum dressing terms can lead to anomalous branching ratios and line strengths. These terms would then have to be included to obtain a proper interpretation of the spectra in these systems.

Even when there is no degeneracy or near degeneracy the generalized radiative frequency shifts occur, but in those cases the shifts are quite small, and are in fact included in normal fourth-order perturbation theory. It is only the occurrence of near degeneracies which causes these terms to enter in second order as does the normal Lamb shift.

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