Slow collisions between identical atoms in a laser field: Application of the Born and Markov approximations to the system of moving atoms

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We have derived reduced-density-matrix equations of motion for a pair of two identical atoms moving in the radiation field as the first step in establishing a theory of collisional redistribution of light from neutral-atom traps. We use the Zwanzig projection-operator technique to average over spontaneous field modes and establish the conditions under which Born and Markov approximations can be applied to the system of moving atoms. It follows from these considerations that when these conditions hold, the reduced-density-matrix equation for moving atoms has the same form as that for the stationary case: time dependence is introduced into the decay rates and interaction potentials by making the substitution $R = R(t)$.

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I. INTRODUCTION

Spontaneous-force light traps provide a way to obtain relatively deep static traps for neutral atoms [1,2]. One of the important characteristics of resonant atom-atom interactions in such traps is that the atoms interact via the long-range dipole-dipole interaction. Our primary goal is to study the collisional modification of the scattered spectrum from the trapped atoms, a theory of which is developed in the following paper [3]. We show there that in the impact region of the spectrum the important impact parameters are in fact of order $\lambda/2\pi$, where λ is the wavelength of the laser. This distance is such that it is clear that retardation effects must also be included. The importance of atom-atom interactions at such large distances is also recognized for collisions resulting in trap losses [4] and for associative ionization [5] in a trap, where the long-range interactions could determine the populations in the entrance channels. The same long-range interactions (which give rise to the so-called "absorption forces") are also important for describing the collective behavior of trapped atoms [6]. The purpose of this paper is to derive atom-atom interactions (including potential and spontaneous-decay terms) which are valid for *moving* atoms that are so far apart that retardation can be important. In particular, we address carefully the validity conditions for the Markov and Born approximations that are used in deriving such interactions. Previous work [7] has usually only considered the interaction between static atoms.

We approach this problem by first writing an equation of motion for the density matrix of the system of atoms interacting with all modes of the spontaneous electromagnetic field, and then use the Zwanzig projection-operator technique to deduce an equation of motion involving only the atomic degrees of freedom. We assume that the atoms are moving at *instantaneous* constant velocities. This is a good approximation for deriving the atom-atom interactions because the correlation time is so short that during that time the effects of any acceleration or diffusion will be negligible. The establishment of this short correlation time, and hence the Markov approximation, is the major theme of this paper. Specifically, in the case of spontaneous emission by a single atom the correlation time is of the order of a/c or $1/\omega_0$ (where a is the size of the atom and ω_0 is the transition frequency). The corresponding correlation time for a pair of atoms will be seen to be of the order R/c or $1/\omega_0$ where R is a distance between atoms.

In our second paper [3] on collisional redistribution (but *not* in this one), we will assume constant velocity (straight-line classical trajectory) for the collision process, the validity of which is discussed in detail in Ref. [3].

In Sec. II we define a Hamiltonian for the system of identical atoms embedded in a continuum of electromagnetic-field modes. One should note that to describe the full geometry of the effects we have to introduce degeneracy in the excited level of the atom. In Sec. III we derive the master equation for the full density matrix and in Sec. IV we present the Zwanzig projection-operator technique and perform the average over all spontaneous field modes. Subsequently, in Secs. V–VII we introduce the Born approximation and discuss second-order quantities averaged over all possible directions of the wave vector $\mathbf{k}$. We then describe (in Secs. VIII and IX) the procedure that allows us to determine the correlation time of the memory kernel, a critical aspect for the Markov approximation. We illustrate how this procedure works in the cases already well established in the literature, rederiving the estimate for the correla-

tion time for single-atom spontaneous emission and a pair of stationary interacting atoms. By the same method, in Sec. X we derive the order of magnitude of the correlation time for the system of atoms that are moving with constant velocities. We then prove that for $v(R/c) \ll \lambda_0 = 2\pi c/\omega_0$ the motion of atoms during the correlation time is insignificant. We can therefore use the equation derived for stationary atoms for the moving case provided we substitute $R = R(t)$ to allow the distance between atoms to change in time. Section XI considers the overall validity for the Born and Markov approximations and a discussion follows in Sec. XII. Finally, in the Appendix we derive the reduced-density-matrix equation for this system of moving atoms and identify interaction potentials and decay rate as the imaginary and real parts of the coefficients in this equation. These results will be used in our second paper to describe the redistribution of radiation by ultracold identical colliding atoms.

II. HAMILTONIAN OF THE SYSTEM

We study a system of N identical neutral atoms, subjected to an external laser field. The atoms are located at positions $\mathbf{r}_a(t)$ and move with velocities $\mathbf{v}_a(t)$ with respect to the laboratory reference frame which is defined by the direction and polarization of the laser beam. All the atoms are identical and their atomic structure is simulated here by two levels only. We use the notation in which $|g\rangle$ is a ground state (nondegenerate for simplicity in our case) and $|m\rangle$ is an excited state that is $(2j+1)$-fold degenerate ($j=1$). The generalization to the case in which both levels are degenerate is obvious.

The Hamiltonian of our system is defined as a sum of four parts,

$$H = H_{\text{atoms}} + H_{\text{field}} + H_{\text{interaction}} + H_{\text{kinetic}} . \tag{1}$$

We have explicitly distinguished between the part of the atomic Hamiltonian that describes its atomic structure from the part that corresponds to the external motion of the atoms.

Nuclear motion of atoms is properly accounted for by the Hamiltonian

$$H_{\text{kinetic}} = -\sum_a \frac{\hbar^2}{2M} \nabla_a^2 ,$$

where $\sum_a$ represents summation over all atoms and M is the mass of the atom. Further, as we will see, the other parts of the Hamiltonian depend on $\mathbf{r}_a(t)$ and will not commute with the kinetic-energy operator. Rather than including this part of the Hamiltonian, we shall for convenience assume that the atoms follow classical line trajectories. Thus the translational degrees of freedom of the atoms will be c-number prescribed functions of time $\mathbf{r}_a(t)$ and $\mathbf{v}_a(t)$. Ultimately, we will have to perform averages over the classical path variables.

The internal atomic structure of the atoms is defined by

$$H_{\text{atoms}} = \frac{\hbar\omega_0}{2} \sum_a S_a^z , \tag{2}$$

where ω_0 is the separation between the ground and excited levels and S_a^z are defined in the standard way, following Courtens and Szöke [8], Cooper and co-workers [9], or Burnett *et al.* [10]. Together with S_a^z

$$S_a^z = \left[\sum_{m=-j}^{j} |m\rangle\langle m| \right] - |g\rangle\langle g| , \tag{3}$$

we define a set of atomic operators for our atoms. For example, the atomic dipole moment operator

$$\begin{aligned} \mathbf{D}_a^+ &= \sum_m |m\rangle\langle m|\mathbf{d}_a|g\rangle\langle g| \\ &= \sum_m |m\rangle\langle g|\mathbf{d}_a^{m+} \equiv \sum_m S_a^{m+}\mathbf{d}_a^{m+} , \end{aligned} \tag{4}$$

where $\mathbf{d}$ is the dipole moment, $\mathbf{d} = e\mathbf{r}$, and its components depend on how we choose the quantization axis for this particular atom.

Similarly, its conjugate,

$$\mathbf{D}_a^- = \sum_m S_a^{m-}\mathbf{d}_a^{m-} , \tag{5}$$

is obtained from Eq. (4) by Hermitian conjugation. Finally, the unit or identity operator

$$I_a = \left[\sum_m |m\rangle\langle m| \right] + |g\rangle\langle g| . \tag{6}$$

Besides the atoms, our system consists of an incoming c-number laser field and all the modes of the spontaneous electromagnetic field. The spontaneous modes have been included in an H_{field} defined by

$$H_{\text{field}} = \sum_{k,\lambda} \hbar\omega_{k\lambda} a_{k\lambda}^+ a_{k\lambda} . \tag{7}$$

Here $a_{k\lambda}^\dagger$ and $a_{k\lambda}$ are the operators that create and destroy a photon of energy $\hbar\omega_{k\lambda}$, and the sum is taken over all photon modes k and polarizations ϵ_λ.

Throughout this paper we use the interaction Hamiltonian, $-\sum_a \mathbf{D}_a \cdot \mathbf{E}[\mathbf{r}_a(t)]$, for the interaction of the atoms with both the external laser field and all the spontaneous radiation modes ($\mathbf{D}_a = \mathbf{D}_a^+ + \mathbf{D}_a^-$). The difference between the interaction Hamiltonian in minimal coupling ($\mathbf{p}\cdot\mathbf{A}$) and multipolar form ($\mathbf{d}\cdot\mathbf{E}$) is not important as long as the systems do not produce strong Doppler [7,11,12] shifts. We have also neglected the contact interaction term $2\pi \int |P|^2 d\tau$, which is required in the ($\mathbf{d}\cdot\mathbf{E}$) gauge [7]. This term, however, is only important for Lamb shifts and self-energies. Moreover, we know that within the nonrelativistic theory, as presented here, they cannot be properly described (remember we use another crude approximation, by simplifying to the two-level atomic structure [7]): We therefore do not intend to discuss these aspects any further. We shall presume instead that the self-energies (ω_0) we use in the averaged (over field modes) density-matrix equation are renormalized with Lamb shifts included. Making explicit the positions of atoms, the interaction Hamiltonian is equal to

$$H_{\text{interaction}}=-\sum_a \mathbf{D}_a\cdot[\mathbf{E}_{\text{spont}}(\mathbf{r}_a(t))+\mathbf{E}_{\text{laser}}(\mathbf{r}_a(t))]$$
$$=\sum_a\left\{\left[-i\sum_{k,\lambda}\left[\frac{2\pi\omega_{k\lambda}\hbar}{V}\right]^{1/2}(\epsilon_{k\lambda}\cdot\mathbf{D}_a)a_{k\lambda}e^{i\mathbf{k}\cdot\mathbf{r}_a(t)}+\text{H.c.}\right]+[-(\mathbf{D}_a^+\cdot\epsilon_L)(E_L/2)e^{i(\mathbf{k}_L\cdot\mathbf{r}_a(t)-\omega_L t)}+\text{H.c.}]\right\}$$
$$=\sum_a\left[\sum_{m_a}\sum_{k,\lambda}[-i\hbar g_{k\lambda}^{a,m_a}S_a^{m_a+}(a_{k\lambda}e^{i\mathbf{k}\cdot\mathbf{r}_a(t)}-a_{k\lambda}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}_a(t)})+\text{H.c.}]\right.$$
$$\left.+[-(\hbar\Omega_a/2)S_a^{0+}e^{-(\mathbf{k}_L\cdot\mathbf{r}_a(t)-\omega_L t)}+\text{H.c.}]\right], \tag{8}$$

where E_L is the amplitude of an external laser field, which is assumed to be linearly polarized along the z direction (this is the reason why only $m=0$ is selected by the interaction with laser field), V is a quantization volume, and the Rabi frequency is

$$\Omega_a=(\mathbf{d}_a^{0+}\cdot\epsilon_L)E_L/\hbar \tag{9}$$

and the coupling constant

$$g_{k\lambda}^{a,m_a}=\left[\frac{2\pi\omega_{k\lambda}}{\hbar V}\right]^{1/2}(\epsilon_{k\lambda}\cdot\mathbf{d}_a^{m_a+}) . \tag{10}$$

It should be noted that in Eq. (8) only the interaction with the laser field is reduced to a form equivalent to making a rotating-wave approximation (RWA). If one makes a full RWA, one also ignores terms such as $a_{k\lambda}^\dagger S_a^{m_a+}$ which, as we discuss below, can have a significant effect on the predicted observables.

III. MASTER EQUATION

The Liouville (tetradic) operator $\tilde{L}$ that determines the evolution of the complete system, atoms and field, may be expressed as the commutator of the total Hamiltonian defined above,

$$\tilde{L}0=\frac{1}{i\hbar}[H,0] . \tag{11}$$

Correspondingly, the equation of motion for the density matrix for the N-body atomic system plus radiation is given by

$$\partial_t\rho=\tilde{L}\rho . \tag{12}$$

According to our definition of the Hamiltonian, we can decompose the Liouville operator $\tilde{L}$ into four main parts:

$$\tilde{L}=\tilde{L}_A+\tilde{L}_F+\tilde{L}_L(t)+\tilde{L}_{AF}(t) . \tag{13}$$

Here $\tilde{L}_A$ and $\tilde{L}_F$ stand for atomic and free spontaneous field, respectively, $\tilde{L}_L(t)$ corresponds to the interaction with external c-number laser field, and $\tilde{L}_{AF}(t)$ describes the mutual interaction between the atoms and the spontaneous modes of the electromagnetic field. According to Eq. (8), $\tilde{L}_L(t)$ and $\tilde{L}_{AF}(t)$ are time dependent. The total Liouville space, defined above, is a direct product of the atomic and radiation subspaces. We can look on this as if atoms were imbedded in the free-radiation field. Since we are only interested in how this free radiation affects the atomic system, we will contract our master equation [Eq. (11) or (12)] over the free-field degrees of freedom to obtain a reduced-density-matrix equation. We anticipate that this procedure will introduce shifts and damping of the atomic energy levels, and will establish effective forces between the atoms [11,13,14]. We will use a standard procedure based on the Zwanzig projection-operator technique [15].

IV. PROJECTION OPERATORS

Let us now introduce the projection operator P_F (which is time independent) defined by

$$P_F(\cdots)=\rho_0^F\text{Tr}_F(\cdots) , \tag{14}$$

where Tr_F denotes the trace over the spontaneous modes and ρ_0^F is the density matrix of these modes. For Eq. (14) to define a projection operator we need the following to be true:

$$P_F^2=P_F . \tag{15}$$

We therefore require that

$$\text{Tr}_F\rho_0^F=1 . \tag{16}$$

In our case ρ_0^F refers to spontaneous field $\rho_0^F=\rho^F(t_0)$ at some initial time. As discussed in Ref. [9], the initial time t_0 is chosen such that the portions of radiation and matter of the system with which we are concerned may be assumed to be uncorrelated. Any relevant correlations are allowed to build up over time so that errors due to initial correlations become negligible. We choose this initial time to be $t_0=-T$, in the distant past, and assume that all the spontaneous radiation modes were initially empty, i.e.,

$$\rho_0^F=\rho^F(t_0=-T)=\sum_{k,\lambda}|\text{vac}_{k\lambda}\rangle\langle\text{vac}_{k\lambda}| , \tag{17}$$

where $|\text{vac}_{k\lambda}\rangle$ denotes the zero-photon state of the mode with vector K and polarization λ. This means we can ignore any temperature dependence of the Lamb shift which is negligible in most circumstances.

First, we split the density-matrix equation into an equation for P_F and Q_F,

$$Q_F=1-P_F ,$$
$$\partial_t\rho=[\tilde{L}_A+\tilde{L}_F+\tilde{L}_{AF}(t)+\tilde{L}_L(t)]\rho , \tag{18}$$

$$\partial_t P_F\rho = P_F(\tilde{L}_A+\tilde{L}_L(t))P_F\rho + P_F(\tilde{L}_F+\tilde{L}_{AF}(t))P_F\rho + P_F L_{AF}(t)Q_F\rho + P_F(\tilde{L}_A+\tilde{L}_F+\tilde{L}_L(t))Q_F\rho \ , \tag{19a}$$

$$\partial_t Q_F = Q_F(\tilde{L}_A+\tilde{L}_F+\tilde{L}_{AF}(t)+\tilde{L}_L(t))Q_F\rho + Q_F\tilde{L}_{AF}(t)P_F\rho + Q_F(\tilde{L}_A+\tilde{L}_F+\tilde{L}_L(t))P_F\rho \ . \tag{19b}$$

In Eqs. (19a) and (19b) certain terms disappear. Note that all terms that are independent of field variables give no contribution when sandwiched between P_F and Q_F because they commute with P_F and $P_FQ_F=0$. We also have $P_F\tilde{L}_F(\cdots)=0$: This comes from the fact that $\tilde{L}_F$ implies the commutator of the operator in the bracket with H_{field}. Part of P_F consists of taking a trace and therefore $P_F\hat{H}_F\hat{O}=P_F\hat{O}\,\hat{H}_F$. Furthermore, $\tilde{L}_FP_F\{\cdots\}=0$. This is due to the other part of P_F, namely $\rho_0^F(t=-T)$. We assume that initially all the spontaneous modes were empty. Consequently, none of the terms from the commutator $\tilde{L}_F$ contribute as both $a_{k\lambda}|\text{vac}_{k\lambda}\rangle$ and $\langle\text{vac}_{k\lambda}|a_{k\lambda}^\dagger$ are equal to zero. So far, we have proved that the last terms on the right-hand side of Eqs. (19a) and (19b) vanish. Finally, we also observe that $P_F\tilde{L}_{AF}(t)P_F=0$ or, to be more explicit, $\text{Tr}_F[\tilde{L}_{AF}(t)\rho_0^F(t=-T)]=0$. The initial density matrix $\rho_0^F(t=-T)$ has only diagonal terms in its matrix representation. On the other hand, $\tilde{L}_{AF}(t)$ is linear in $a_{k\lambda}$ and $a_{k\lambda}^\dagger$, and as a result the product $\tilde{L}_{AF}(t)\rho_0^F(t=-\infty)$ has all the diagonal elements equal to zero. In conclusion, the second term in Eq. (19a) also vanishes.

Here we make an important remark. One of the standard procedures applied to this kind of problem consists of performing the Laplace transformation (see, for examples, Ref. [11]). This method, however, is not straightforward when we are dealing with collisions. This is due to the motion of atoms. In our problem two parts of the interaction Liouville operators are time dependent. These operators are defined as $\tilde{L}_{AF}(t)$ and $\tilde{L}_L(t)$, and describe the coupling of the atom to spontaneous and laser fields, respectively. The time dependence appears there first through fast oscillations with frequency ω_L (or $\omega_{k\lambda}$), and secondly through the much slower $\mathbf{r}_a(t)$ dependence as a consequence of the relative motion of the atoms. Therefore we have found it more convenient to apply a Green-function approach while remaining in the time domain (see Ref. [9]). To obtain the closed equation for $P_F\rho$ we solve Eq. (19b) formally, i.e., writing in terms of the Green-function propagator

$$Q_F\rho(t) = G_f(t,-T)Q_F\rho(-T) + \int_{-T}^{t} G_F(t,t')Q_F\tilde{L}_{AF}(t')P_F\rho(t')dt' \ . \tag{20a}$$

Here

$$G_F(t,t') = \exp_T\left[Q_F\int_{t'}^{t}[\tilde{L}_0+\tilde{L}_L(t'') + \tilde{L}_{AF}(t'')+\tilde{L}_F]dt''\right] , \tag{20b}$$

where the T subscript in $\exp_T$ indicates time ordering of the exponential. In the present paper, to simplify the derivation, we have introduced "natural initial conditions." By this we mean, as discussed earlier, that at some time in the distant past we may assume that the radiation and matter were uncorrelated, i.e., $\hat{Q}_R\rho(t=-T)=0$. Only after this assumption is made can the "destruction term," $Q_F\rho(-T)$, be eliminated from Eq. (20a). With Eq. (20a) for $Q_F\rho(t)$ we finally reduce our initial density equation [Eq. (19a)] to the equation for $P_F\rho$ only:

$$\partial_t P_F\rho = P_F(\tilde{L}_L(t)+\tilde{L}_A)P_F\rho + P_F\tilde{L}_{AF}(t)\int_{-T}^{t} G_F(t,t')Q_F\tilde{L}_{AF}(t')P_F\rho(t')dt' \ . \tag{21}$$

The most serious complication in the above equation is caused by the last term. It contains the density matrix $\rho(t')$ at all times prior to t, which means it remembers all the "history" of $\rho(t')$. For this reason the kernel $G_F(t,t')$ in this last term is often called the "memory kernel."

In most of this paper, when we discuss the validity criteria for the Born and Markov approximations, we refer to the system in the absence of the laser field. In this case the off-diagonal elements of the density matrix in the Schrödinger picture oscillate with the frequency ω_0 (as defined by the first part of the Liouville equation $\partial_t\rho=-(i\omega_0/2)[S_a^z,\rho]$). However, when the system is driven by the external laser field the off-diagonal elements, in the steady-state limit, will follow the laser and oscillate with the frequency ω_L. One has to be careful in this case in selecting the precise rotating frame for determining the slowly varying part of the density matrix. We will discuss this issue in more detail when we describe the far-field limit of the two-atom interaction.

V. BORN APPROXIMATION FOR SPONTANEOUS MODES

The last term in Eq. (21) contains the full Green-function operator $G_F(t,t')$. Due to the time ordering, this operator is extremely difficult to handle. A substantial simplification is made possible by introducing the Born approximation which we will show to be valid in this case.

There are two time-dependent operators [$\tilde{L}_{AF}(t)$ and $\tilde{L}_L(t)$] that appear in the definition of $G_f(t,t')$. One therefore has to expand the full $G_F(T,t')$ operator in a Dyson series, as a sum of time-dependent terms. According to the Dyson formula

$$G_F(t,t') = G_F^0(t,t') + \int_{t'}^{t} G_F^0(t,t_1)Q_F(\tilde{L}_L(t_1)+\tilde{L}_{AF}(t_1)) \times G_F(t_1,t')dt \ , \tag{22}$$

where $G_F^0(t,t')=\exp[(\tilde{L}_F+\tilde{L}_A)(t-t')]$. Upon iterating Eq. (22), we obtain a power expansion series in the time-dependent operators $[\tilde{L}_L(t)+\tilde{L}_{AF}(t)]$.

Theories of interaction of radiation with matter have been shown to describe spontaneous processes properly when they include the coupling to the second order in

$\tilde{L}_{AF}(t)$. Notice that our memory kernel is explicitly at least second order in interaction Liouvillean $\tilde{L}_{AF}(t)$. Therefore, we expect that the zero-order approximation of $G_F(t,t')$ given by replacing $G_F(t,t')$ with $G_F^0(t,t')$ should be adequate. This is the so-called Born approximation. At this stage of our discussion it is difficult to estimate the error introduced by neglecting the higher-order contributions. We will, however, be able to compare the relative size of consecutive terms after we have also made the Markov approximation. Consequently, we will return to the validity question in Sec. VII.

VI. SECOND-ORDER QUANTITIES

In Sec. V we introduced the Born approximation, which leaves terms up to second order in the interaction Liouvillean $\tilde{L}_{AF}(t)$ in the memory kernel

$$F(t,\tau)=[P_F\tilde{L}_{AF}(t)G_F^0(t,\tau)Q_F\tilde{L}_{AF}(\tau)P_F]\rho(\tau) . \tag{21}$$

We shall now transform Eq. (21) to the interaction picture both for the spontaneous field and for the atomic variables:

$$\rho^I(t)=e^{-(\tilde{L}_A+\tilde{L}_F)t}\rho(t) \tag{23}$$

where $\rho^I(\tau)$ is so far the full density matrix in the interaction picture. Note that $F^I(t,\tau)$ contains all possible pairwise contributions (each sum is over all atoms in the system), i.e.,

$$F^I(t,\tau)=\sum_a\sum_b P_F M_b(t,\tau)P_F\rho^I(\tau) , \tag{24}$$

where $M_{ab}(t,\tau)$ is a tetradic operator defined by the double commutator

$$M_{ab}(t,\tau)=-\frac{1}{\hbar^2}[A_a(t)+A_a^\dagger(t),[A_b(\tau)+A_b^\dagger(\tau),\cdot]] . \tag{25}$$

$A(t)$ is defined by

$$A(t)=\sum_{m_a}\sum_{k,\lambda}\left[-i\left[\frac{2\pi ck\hbar}{V}\right]^{1/2}\right][(\epsilon_{k\lambda}\cdot d_a^{m_a+})S_a^{m_a+}e^{i\omega_0 t}+(\epsilon_{k\lambda}^*\cdot d_a^{m_a-})S_a^{m_a-}e^{-i\omega_0 t}]a_{k\lambda}e^{-i(\omega_{k\lambda}t-\mathbf{k}\cdot\mathbf{r}_a(t))} . \tag{26}$$

Due to the special form of the initial density matrix in the electromagnetic-field subspace $\rho^F(t=-T)$ defined by the Eq. (17), it is only terms in $a_{k\lambda}a_{k\lambda}^\dagger\rho^F(t=-T)$ (and its permutations) that contribute to the memory kernel, namely,

$$\mathrm{Tr}_{k\lambda}[a_{k\lambda}a_{k'\lambda'}^\dagger\rho^F(t=-T)]=\delta(\mathbf{k}-\mathbf{k}')\delta_{\lambda\lambda'} . \tag{27}$$

All the rest are equal to zero. Therefore, of all the terms in Eq. (25), only four are of interest here, i.e.,

$$\begin{aligned}&A_a(t)A_b^\dagger(\tau)P_F\rho^I(\tau)+P_F\rho^I(\tau)A_b(\tau)A_a^\dagger(t)\\&\quad-A_a^\dagger(t)P_F\rho^I(\tau)A_b(\tau)-A_a^\dagger(\tau)P_F\rho^I(\tau)A_b(t) .\end{aligned} \tag{28}$$

As mentioned above, by using the interaction picture [Eq. (23)] we extract from the off-diagonal matrix elements the part that oscillates near the optical frequency. By doing so we obtain a slowly varying function of time $\rho^I(t)$. (It varies on the time scale γ^{-1}, the lifetime of the excited state.) We note that the interaction with the laser as defined by the second part of Eq. (8) introduces the oscillations with frequency ω_L, so that $\rho^I(t)$ would now contain $e^{i(\omega_L-\omega_0)t}$ terms. To eliminate this frequency we could use the rotating frame picture rather than the interaction picture. In the memory kernel ω_L would then appear instead of ω_0. The remaining oscillations (introduced by $\tilde{L}_A$) are now detuned to $(\omega_0-\omega_L)$ and typically are slow on the time scale $1/\omega_L$. This picture is particularly convenient for discussing the steady-state limit, as in the Born and Markov approximations all the coefficients in the density-matrix equation are time independent. As the difference between ω_0 and ω_L will usually be unimportant, we will, in what follows, continue to use the interaction picture [Eq. (23)].

In the next step we take the trace over spontaneous field modes and make a RWA with respect to the atomic frequency ω_0. Many authors discussing radiative interactions [16] have pointed out that the rotating-wave approximation performed during the evaluation of the "memory kernel" can produce a different result from that made on the Hamiltonian for the system. If we eliminate from Eq. (28) terms which oscillate with frequency $2\omega_0$, which corresponds to making the RWA, we can still include contributions with frequencies $\pm(\omega_0+\omega_{k\lambda})$. The latter would of course not have been present if the RWA had been introduced directly in the Hamiltonian. These non-RWA terms will be necessary to produce a properly retarded interaction. We return to the difference of these two kinds of RWA's in the Appendix.

In making the RWA we are eliminating terms that oscillate with frequency $2\omega_0$. Some of these terms are identically zero, e.g., two S^+'s operating on one side of ρ: (schematically) $S^+S^+\rho$. This is due to the fact that S^+S^+ is zero when operating on any atomic state. There are, however, other terms such as (again schematically) $S^+\rho S^+$. These terms give, for example, couplings between difference coherences. In the present discussion we will neglect them, as they only give the corrections to the interaction energies of the same order as the Bloch-Siegert shifts due to the counter-rotating components.

Next, in the integral of the memory kernel we change the variable τ to $t-\tau$ (we find it more convenient to discuss the Markov approximation this way). In the following equation terms have been grouped together according to their phases:

$$F^I(t,t-\tau)=-\rho_0^F\sum_{k,\lambda}\sum_{a,b}\sum_{m_a,m_b}\left[\frac{2\pi ck}{V\hbar}\right](\epsilon_{k\lambda}\cdot\mathbf{d}_a^{m_a+})(\epsilon_{k\lambda}^*\cdot\mathbf{d}_b^{m_b-})$$
$$\times\{\exp[i(\omega_0-\omega_{k\lambda})\tau+i\mathbf{k}\cdot\mathbf{r}_{ab}(t)+i\mathbf{k}\cdot\mathbf{v}_b\tau][S_a^{m_a+}S_b^{m_b-}\rho_A(t-\tau)-S_b^{m_b-}\rho_A(t-\tau)S_a^{m_a+}]$$
$$+\exp[-i(\omega_0-\omega_{k\lambda})\tau+i\mathbf{k}\cdot\mathbf{r}_{ab}(t)-i\mathbf{k}\cdot\mathbf{v}_a\tau]$$
$$\times[\rho_A(t-\tau)S_a^{m_a+}S_b^{m_b-}-S_b^{m_b-}\rho_A(t-\tau)S_a^{m_a+}]$$
$$+\exp[i(\omega_0+\omega_{k\lambda})\tau-i\mathbf{k}\cdot\mathbf{r}_{ab}(t)-i\mathbf{k}\cdot\mathbf{v}_b\tau]$$
$$\times[\rho_A(t-\tau)S_b^{m_b-}S_a^{m_a+}-S_a^{m_a+}\rho_A(t-\tau)S_b^{m_b-}]$$
$$+\exp[-i(\omega_0+\omega_{k\lambda})\tau-i\mathbf{k}\cdot\mathbf{r}_{ab}(t)+i\mathbf{k}\cdot\mathbf{v}_a\tau]$$
$$\times[S_b^{m_b-}S_a^{m_a+}\rho_A(t-\tau)-S_a^{m_a+}\rho_A(t-\tau)S_b^{m_b-}]\}\ . \tag{29}$$

Here $\rho_A(t-\tau)$ is the reduced interaction picture density matrix, i.e.,

$$\rho_A(t-\tau)=\mathrm{Tr}_F[\rho^I(t-\tau)]\ ,$$

where the trace is taken over all spontaneous modes of the radiation field, and $\mathbf{r}_{ab}=\mathbf{r}_a-\mathbf{r}_b$. As we will take a limit $V\to\infty$, the summation over k should be replaced by the integral over the continuum of modes, i.e.;

$$\sum_{\kappa,\lambda}\frac{2\pi ck}{V}\to\frac{c}{(2\pi)^2}\int kd^3\mathbf{k}\sum_{\lambda}\to\frac{c}{(2\pi)^2}\int k^3dk\int d\Omega\sum_{\lambda}\ . \tag{30}$$

The expressions in Eq. (29) are in the form of sums of four different terms, each distinguished by a different phase. As we will show later, due to these fast oscillating phases multiplying all of the terms, the memory kernel [Eq. (29)] has a "short memory." This will allow us to use

$$\int_0^\infty e^{i(\omega_0-\omega)\tau}d\tau=\pi\delta(\omega_0-\omega)+i\mathrm{P}\int\frac{1}{\omega_0-\omega}d\omega \tag{31}$$

where P is the principal-value integral. This short memory approximation assumes that the relevant matrix elements of $\rho_A(t-\tau)$ will be slowly varying on the correlation time (apart from off-diagonal elements phases such as $e^{\pm i(\omega_0-\omega_L)(t-\tau)}$).

Obviously, then each of the terms in Eq. (29) is complex. The real part, related to the δ-type contribution, introduces damping to the reduced-density equation of motion. As far as the real part is concerned the last two terms in Eq. (29) can be neglected since $\delta(ck+\omega_0)\equiv 0$, which means that this part is independent of how the RWA is made. On the other hand, the imaginary part which describes the mutual two-atom interaction potentials and the Lamb shift of individual atoms is obviously sensitive to this choice. As pointed out by Agarwal [16] whenever questions of frequency shifts involving Lamb shifts, cooperative effects, Casimir-Polder forces, or higher-order forces are considered, the RWA should not be made on the Hamiltonian. To stress this statement we present in the Appendix the comparison of retarded two-atom interaction potentials obtained both ways.

In the expression presented in Eq. (29) two features deserve attention. First, due to relative motion phase factors contain the instantaneous distance between atoms $\mathbf{r}_{ab}(t)$, replacing the constant $\mathbf{r}_{ab}$, which has already been accounted for by the authors discussing the radiation phenomena of the systems of atoms in a fixed configuration (time independent). However, there is an extra phase $\exp[i(\mathbf{k}\cdot\mathbf{v})\tau]$ which may also be attributed to the fact that the atoms are moving. As we will see later, the latter, which represents a Doppler shift, is of particular importance as far as Markov approximation is concerned, because it depends on the local time τ.

So far we have, at least formally, obtained [in Eq. (29)] the full functional dependence of $F^I(t,t-\tau)$ on all important physical parameters. This form, however, is complicated because it contains a threefold integral over d^3k of rapidly oscillating functions. The key to further progress is the observation that due to these fast oscillations $F^I(t,t-\tau)$ as a function of τ is, in fact, practically zero beyond a small interval around $\tau=t$. It is usually stated that $F^I(t,t-\tau)$ has a "short correlation time." This will replace $\rho_a(t-\tau)$ by $\rho_A(t)$. Thus we are assuming $(\omega_0-\omega_L)\tau\ll 1$, i.e., we do not distinguish between ω_0 and ω_L.

The main purpose of this paper is to discuss validity conditions for Born and Markov approximations for the system of moving atoms. The heart of these approximations is this short correlation time of the memory kernel. We shall start with an examination of some simpler cases already well known in quantum optics. We use these simple examples to describe an efficient way of estimating the correlation times, which we shall then apply to the system of moving atoms.

In Sec. VIII we reexamine briefly the spontaneous emission from a single two-level atom using this technique. Then in Sec. IX, we adopt the same method to establish the correlation time for a pair of atoms occupying fixed positions in space. In Sec. X we analyze the importance of the term that arises due to the motion of atoms, and find an extra condition under which we can treat the motion as "adiabatic." In other words, we shall find the condition under which the master equation for moving

atoms may be directly obtained from the corresponding equation for the stationary atoms (as derived by Agarwal [11]) with the simple substitution of $\mathbf{r}_{ab}$ by $\mathbf{r}_{ab}(t)$. Only after we convince ourselves that in all the above cases the correlation time is short (in comparison to the characteristic time of the emission processes) can we proceed with the Markov and Born approximation. We comment on this shortly in Sec. XI.

As mentioned above, $F^I(t,t-\tau)$ contains a threefold integral over d^3k. When atoms are not moving it is easy to do the angular part of this integral, $\int d\Omega$, as we show in Sec. VII, provided we can take $\rho_A(t-\tau)=\rho_A(t)$.

To estimate the correlation time of the memory kernel we use the following procedure. [$F^I(t,t-\tau)$ is a function of both t and τ, but here obviously only the τ dependence is important.] First, we multiply $F^I(t,t-\tau)$ by some function $f(\tau)$ that decays on a known time scale, say $\tau_{\text{corr}}=1/\alpha$. Next, we integrate the above-defined products over $d\tau$ from 0 to ∞. As will be established, for small enough α the result of the integration does not depend on α, which means that the time decay of the product under the integral is entirely due to the decay of $F^I(t,t-\tau)$. For very large values of α, $f(\tau)$ will be responsible for the cutoff of the integral. By estimating the order of magnitude of α for which a transition from one to the other of these regimes occurs, we are able to obtain an estimate of the correlation time of $F^I(t,t-\tau)$. We will check the real and imaginary parts of $F^I(t,t-\tau)$ separately, to make sure that the correlation time for both is of the same order.

VII. ANGULAR AVERAGE OF THE MEMORY KERNEL FOR A SYSTEM OF STATIONARY ATOMS

The memory kernel defined in Eq. (29) contains the sum over all possible values of $\mathbf{k}$. After the transition to the continuous-mode limit [given by Eq. (30)] this sum can be split into two integrals: one over length dk and the other over angles $d\Omega$. In this section we show how to evaluate the angular average when the atoms are motionless [$v_a=v_b=0$ in Eq. (29)]. The final result of this consideration will play a substantial role in the discussion of correlation time in the next two sections. First, we select from Eq. (29) all terms that depend on the geometric factors. As we see here, two angles are important: the angle between $\mathbf{k}$ and $\mathbf{r}_{ab}$ and the angle between $\mathbf{k}$ and the quantization axis (identified with the direction of z axis of our reference frame), i.e., between $\mathbf{k}$ and $\mathbf{d}_a^{m=0}$.

One might think that we could chose the quantization axis along the internuclear distance without losing generality, but usually the geometry of the problem is then more complicated. For example, if the atom is placed in the external laser field it is often more convenient to select the direction of the laser propagation or its polarization as the z axis, and we have to consider all possible positions of $\mathbf{r}_{ab}(t)$ relative to this axis. In the most general stationary case the angle-dependent part of $M_{ab}(t,\tau)$ is equal to (ρ_A does not have any angle dependence)

$$\sum_{\kappa,\lambda}\left[\frac{2\pi ck}{V\hbar}\right](\epsilon_{k\lambda}\cdot\mathbf{d}_a^{m_a})(\epsilon_{k\lambda}\cdot\mathbf{d}^{m_b})^* e^{i\mathbf{k}\cdot\mathbf{r}_{ab}}\ , \tag{32}$$

which in the continuous-mode limit may also be written as

$$\int_0^\infty k^2\,dk\sum_\lambda\frac{ck}{(2\pi)^2\hbar}\int d\Omega(\epsilon_{k\lambda}\cdot\mathbf{d}_a^{m_a})(\epsilon_{k\lambda}\cdot\mathbf{d}_b^{m_b})^* e^{i\mathbf{k}\cdot\mathbf{r}_{ab}}\ . \tag{33}$$

Owing to the close analogy between the degeneracy of the atomic level and angular momentum theory it is beneficial to write the scalar product between the polarization and dipole moment vector $\mathbf{d}_a^{m_a}$ in a spherical basis [17] (we have dropped the plus sign from the $\mathbf{d}^+$ symbol for convenience),

$$\epsilon_{k\lambda}\cdot\mathbf{d}_a^{m_a}=\sum_q(-1)^q\epsilon_{k\lambda,-q}d_{a,q}^{m_a}\ . \tag{34}$$

Here we have introduced the notation in which for any vector $\mathbf{b}$, b_q denotes its q component. We next expand the phase factor $e^{i\mathbf{k}\cdot\mathbf{r}_{ab}}$ in spherical harmonics [18] [again to simplify the notation from here on we will use $\mathbf{R}$ instead of $\mathbf{r}_{ab}(t)$]

$$e^{i\mathbf{k}\cdot\mathbf{R}}=4\pi\sum_{l,m}i^l j_l(kR)Y_{lm}(\theta,\phi)Y_{lm}^*(\theta',\phi')\ . \tag{35}$$

Here $j_l(kR)$ is a spherical Bessel function: θ,ϕ; and θ',ϕ' are the spherical angles characterizing the directions of $\mathbf{R}$ and $\mathbf{k}$, respectively (see Fig. 1). Substituting Eqs. (34) and (35) into (33), we obtain the following result:

$$\begin{aligned}\mathcal{A}(m_a,m_b)&\equiv\frac{ck^3}{(2\pi)^2\hbar}\int d\Omega(\epsilon_{k\lambda}\cdot\mathbf{d}_a^{m_a})(\epsilon_{k\lambda}\cdot\mathbf{d}_b^{m_a})^* e^{i\mathbf{k}\cdot\mathbf{r}_{ab}}\\&=\frac{ck^3}{(2\pi)^2\hbar}\int d\Omega\sum_{q,q'}\sum_\lambda(-1)^{q+q'}\left[\epsilon_{k\lambda,-q}\epsilon_{k\lambda,-q'}^* d_{a,q}^{m_a}\cdot d_{b,q'}^{m_b *}4\pi\sum_{l,m}i^{lj_l}(kR)Y_{l,m}(\theta,\phi)Y_{l,m}^*(\theta',\phi')\right].\end{aligned} \tag{36}$$

Recall that $\mathbf{r}_{ab}$ and $\mathbf{R}$ are the same. To separate out the rest of the angular dependence from Eq. (36) we average over the polarization directions by using

$$\sum_\lambda(\epsilon_{k\lambda,-q}\epsilon_{k\lambda,-q'}^*)=\delta_{qq'}-D_{0-q}^1(\hat{\mathbf{k}})D_{0-q'}^{1*}(\hat{\mathbf{k}})\ . \tag{37}$$

Here $D_{ab}^j(\hat{\mathbf{k}})$ is the rotation matrix of the argument determined by the angles of vector $\hat{\mathbf{k}}$ and may be related to the spherical harmonics by the equation

$$Y_{r,n}(\theta,\phi)=\left[\frac{2r+1}{4\pi}\right]^{1/2} D^{r}_{0n}(\theta,\phi)\ . \tag{38}$$

According to the Wigner-Eckart theorem [17],

$$(d_a^{m_a})_q=(-1)^{1-m_a}(j=1\|d\|j=0)\begin{bmatrix}1 & 1 & 0\\ -m_a & q & 0\end{bmatrix}, \tag{39}$$

where $(j\|d\|j')=d_{jj'}$ is the reduced matrix element of the vector $\mathbf{d}$ and $\begin{pmatrix}j_1 & j_2 & j_3\\ m_1 & m_2 & m_3\end{pmatrix}$ are Wigner 3-j symbols [17]. Thus the evaluation of our angular average reduces to simple angular integrals of spherical harmonics which finally gives

$$\mathcal{A}(m,m')=\frac{2cd_{10}^2k^3}{9\hbar\pi}\left[\delta_{m,m'}j_0(kR)+j_2(kR)Y_{2,m'-m}(\theta,\phi)\sqrt{6}\pi(-1)^{m'}\begin{bmatrix}1 & 1 & 2\\ -m' & m & m'-m\end{bmatrix}\right]. \tag{40}$$

Equation (40) contains the final form of our angular average. Note that it is an even function of kR, which indicates that it does not depend on the sign in the exponent $e^{\pm i\mathbf{k}\cdot\mathbf{r}_{ab}}$. We can therefore substitute this result into all four terms in Eq. (29) (remember we assumed $v_a=v_b=0$), and we have reduced $F^I(t,t-\tau)$ to one integral only.

Finally, $P_FM_{ab}(t,t-\tau)P_F\rho^I(t-\tau)$ takes the form

$$\begin{aligned}P_FM_{ab}(t,t-\tau)\rho_F^I(t-\tau)=-\rho_0^F\int dk\,\mathcal{A}(m_a,m_b)\\ \times\{&\exp[i(\omega_0-ck)\tau][S_a^{m_a+}S_b^{m_b-}\rho^I(t-\tau)-S_b^{m_b-}\rho^I(t-\tau)S_a^{m_a+}]\\ &+\exp[-i(\omega_0-ck)\tau][\rho^I(t-\tau)S_a^{m_a+}S_b^{m_b-}-S_b^{m_b-}\rho^I(t-\tau)S_a^{m_a+}]\\ &+\exp[i(\omega_0+ck)\tau][\rho^I(t-\tau)S_b^{m_b-}S_a^{m_a+}-S_a^{m_a+}\rho^I(t-\tau)S_b^{m_b-}]\\ &+\exp[-i(\omega_0+ck)\tau][S_b^{m_b-}S_a^{m_a+}\rho^I(t-\tau)-S_a^{m_a+}\rho^I(t-\tau)S_b^{m_b-}]\}\end{aligned} \tag{41}$$

with $\mathcal{A}(m_a,m_b)$ defined by Eq. (40).

In the next two sections we will reexamine the correlation time for a single two-level atom and a pair of two-level atoms, using the above result and the procedure described at the end of Sec. VI.

VIII. SPONTANEOUS EMISSION AND LAMB SHIFT FOR A SINGLE STATIONARY TWO-LEVEL ATOM

We will treat the real and imaginary parts separately. The real part is responsible for spontaneous decay of an excited state, while the imaginary part is responsible for an energy shift, i.e., the Lamb shift. In nonrelativistic calculations, the Lamb shift is known to be divergent. When we use the free-electron Hamiltonian the strongest quadratic divergence is removed, and we only have to deal with logarithmic divergence [11].

The memory kernel $F^I(t,t-\tau)$ is a threefold integral over the $\mathbf{k}$ vector which is divided into an angular integral $\int d\Omega$ and an integral over the length $\int dk$. The angle average in Eq. (40) can be used universally for both one- and two-atom contributions. Here we discuss the single-atom case only, therefore it is sufficient to consider the limit $r_{ab}\to 0$ in Eq. (40). In this limit the matrix $\mathcal{A}(m,m')$ is diagonal and has three equal elements $(c/2\pi)\gamma(k^3/k_0^3)$ where

$$\gamma=\frac{2}{9\hbar}d_{10}^2k_0^3$$

in which d_{10} is the reduced matrix element, $d_{10}=(j=1\|e\mathbf{r}\|j=0)$, of the dipole moment. Since the angular integral is directly related to the decay rates and energy shifts, one can immediately conclude that due to the interaction with spontaneous modes, all energy sublevels are equally shifted and decay to the ground state with the same rate γ. $F^I(t,t-\tau)$ is now equal to

$$\begin{aligned}-\rho_0^F\frac{c\gamma}{2\pi k_0^3}\int dk\,k^3\sum_m\{&i\sin(\omega_0-ck)\tau[S_a^{m+}S_a^{m-},\rho]-i\sin(\omega_0+ck)\tau[S_a^{m-}s_a^{m+},\rho]\\ &+\cos(\omega_0-ck)\tau[S_a^{m+}S_a^{m-}\rho(t-\tau)+\rho(t-\tau)S_a^{m+}S_a^{m-}-2S_a^{m-}\rho(t-\tau)S_a^{m+}]\\ &+\cos(\omega_0+ck)\tau[S_a^{m-}S_a^{m+}\rho(t-\tau)+\rho(t-\tau)S_a^{m-}S_a^{m+}-2S_a^{m+}\rho(t-\tau)S_a^{m-}]\}\ .\end{aligned} \tag{42}$$

As we see the correlation time of the memory kernel is really determined by the average over the length of the **k** vector. For an isolated two-level atom this average is expressed by integrals of the type

$$\int_0^{k_{\max}} e^{\pm i(ck\pm\omega_0)\tau} k^3\,dk$$

with the upper limit determined by a cut off parameter $k_{\max}$. This cutoff is a consequence of the dipole approximation used in the interaction Hamiltonian in Eq. (1) and can be understood even within a framework of classical electrodynamics. For simplicity, we will think of our atom as a system consisting of an electron (charge $q_1=e$) and nucleus ($q_2=-e$). Both particles interact with spontaneous-radiation modes. This interaction is described by the sum

$$q_1 E(\mathbf{r}_1)e^{i\mathbf{k}\cdot\mathbf{r}_1}+q_2 E(\mathbf{r}_2)e^{i\mathbf{k}\cdot\mathbf{r}_2}\,, \tag{43}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the positions of the particles and $E(\mathbf{r}_1)$ and $E(\mathbf{r}_2)$ are slowly varying amplitudes. The distance between electron and nucleus $|\mathbf{r}_1-\mathbf{r}_2|$ is of the order of the Bohr radius $a_0=\hbar^2/me^2$. For a spontaneous mode with a wave vector **k** it introduces the phase difference between two terms in Eq. (43) of order of ka_0. As long as this relative phase is small, which means $k\ll 1/a_0$, we can introduce the dipole approximation and use $-\mathbf{d}\cdot\mathbf{E}(r)e^{i\mathbf{k}\cdot\mathbf{r}}$ instead of Eq. (43) with **r** defined as the position of the center of mass of our atom. This is exactly the form of the interaction used in the initial Hamiltonian. On the other hand, if the relative phase difference in Eq. (43) becomes substantial it washes out the contribution of Eq. (43) to the total Hamiltonian of the system. The sum over **k** will therefore be restricted to $k_{\max}\lesssim 1/a_0$, i.e., we can cut off the integral over k in the memory kernel [19,20]. This is, however, not the whole story as we shall see in the next section.

We expect that the memory kernel which is now only a function of τ [$F^I(t,t-\tau)\equiv F(\tau)$] has a very short correlation time, or equivalently, decays on a very short time scale. Therefore we would like to replace $\rho(t-\tau)$ with $\rho(t)$. This approximation is valid as long as $\rho(t)$ changes slowly within the correlation time. Remember that ρ is there in the interaction picture. Its characteristic time of variation is γ^{-1} or when the laser field is present it oscillates with frequency $\omega_L-\omega_0$, which is usually small compared with ω_0 and ω_L. To estimate this time scale we multiply it by exponential function $e^{-\alpha\tau}$ and integrate this product over τ from 0 to ∞. As indicated earlier, one would expect that as long as $1/\alpha$ is large in comparison with the correlation time introduction of the latter exponent should not change the result of the integral because over the range of time that exponents differ (appreciably) from 1, $F(\tau)$ is practically equal to zero anyway. We denote the modified function by $f(\alpha)$, and we further investigate the difference $f(0)-f(\alpha)$, looking for the condition on α for which this difference is very small. We treat the real and imaginary parts of $F(\tau)$ separately.

Upon integrating $F(\tau)e^{-\alpha\tau}$, one finds the real part is proportional to

$$\frac{1}{k_0^3}\int_0^{k_{\max}}\frac{\alpha}{\alpha^2+(kc-\omega_0)^2}k^3\,dk\,. \tag{44}$$

Here for convenience only terms with $kc-\omega_0$ have been preserved as they dominate over the $kc+\omega_0$ within the range of integration over K. For small enough α, $f(\alpha)$ represents the Lorentzian peaked at $kc\sim\omega_0$; therefore, we may withdraw the slowly varying function k^3 from under the integral and estimate Eq. (44) as

$$\begin{aligned}&\int_0^{k_{\max}}\frac{\alpha}{\alpha^2+(kc-\omega_0)^2}dk\\ &=\int_{-\omega_0}^{ck_{\max}-\omega_0}\frac{\alpha}{\alpha^2+z^2}dz\\ &=\arctan[(ck_{\max}-\omega_0)/\alpha]-\arctan(-\omega_0/\alpha)\,.\end{aligned} \tag{45}$$

Here we have used the change of variable $z=(ck-\omega_0)$. Using the asymptotic expansion of arctan,

$$\arctan x\cong\frac{\pi}{2}-\frac{1}{x}\quad\text{(for large value of } x)\,,$$

we can rewrite Eq. (45) as

$$\pi-\alpha/(ck_{\max}-\omega_0)+\alpha/\omega_0\,. \tag{46}$$

The second and third terms in Eq. (46) are negligible as long as α is much smaller than both $ck_{\max}$ and ω_0, and under the same condition $f(\alpha)$ is practically equal to $f(0)$. This means that we do not modify the memory kernel $F(\tau)$ with the exponential factor $e^{-\alpha\tau}$ as long as its characteristic time $1/\alpha$ is of order of $1/\omega_0$ or $1/ck_{\max}=a_0/c$. It follows directly from these considerations that the memory kernel correlation time must be of the same order for optical frequencies $\omega_0\sim 10^{-16}$ and $1/ck_{\max}\sim 10^{-18}$. The relative size of these cutoffs will depend on the size of the system. In any case, with average decay rates of $\sim 10^8$ we can see that $\gamma\tau$ will be very small and the Markoff approximation will hold to a very high degree of approximation.

Essentially the same arguments are also valid for the imaginary part. After the time integral we obtain

$$\begin{aligned}&\frac{1}{k_0^3}\int_0^{ck_{\max}}k^3\frac{(ck-\omega_0)}{\alpha^2+(ck-\omega_0)^2}dk\\ &\simeq\int_{-\omega_0/\alpha}^{ck_{\max}-\omega_0}\frac{z}{1+z^2}dz\\ &=\tfrac{1}{2}\ln(1+z^2)\Big|_{-\omega_0/\alpha}^{(ck_{\max}-\omega_0)/\alpha}\\ &\cong\frac{1}{2}\ln\left[\frac{1+[(ck_{\max}-\omega_0)/\alpha]^2}{1+(\omega_0/\alpha)^2}\right].\end{aligned} \tag{47}$$

If the same condition for α that we used for the real part is valid here, we may neglect 1 both in the numerator and denominator and approximate Eq. (47) by

$$\frac{1}{2}\ln\left|\frac{ck_{\max}-\omega_0}{\omega_0}\right|, \tag{48}$$

which is the expected expression for $f(0)$. This as expect-

ed provides the same estimate of the correlation time as we obtained from the discussion of the real part.

IX. EFFECTS ON THE LIFETIME DUE TO THE PRESENCE OF THE SECOND RESONATING ATOM

In this section we will obtain the corresponding correlation time for the memory kernel of the pair of atoms fixed at the positions $\mathbf{r}_1$ and $\mathbf{r}_2$ (this means we are not taking into account their relative motion). We will use the notation in which $\mathbf{r}_a-\mathbf{r}_b=\mathbf{r}_{ab}=\mathbf{R}$. Of course we have to perform the angular average first. The details of the calculations are presented in the Appendix, and for the final result we refer one more time to Eq. (40). Since we are only interested in estimating the correlation time, we will not use the entire formula (40) but simply note that it is proportional to $j_0(kR)$ and $j_2(kR)$. Three terms are used in the definition of these functions: $f_1(kR)=\sin kR/kR$, $f_2(kR)=\cos kR/(kR)^2$, and $f_3(kR)=\sin kR/(kR)^3$. To discuss the correlation time we will focus on integrals of the type

$$\int dt \int d^3k\, e^{ick\tau} e^{\pm i\omega_0\tau} f_i(kR), \quad i=1,2,3\ . \tag{49}$$

Basically, the technique that was introduced in Sec. VIII can also be used here. For completeness we will treat real and imaginary parts separately, as in Sec. VIII. In both cases we will "probe" the memory kernel with the exponentially decaying function ($e^{-\alpha\tau}$ or $e^{-\alpha^2\tau^2}$) and integrate over τ, with the assumption that $\rho(t-\tau)=\rho(t)$.

Let us first consider the imaginary part. When we set together terms in Eq. (29), after integration over τ we have to deal with expressions of the form

$$\int_0^\infty d\omega\omega^3 \left[\frac{(\omega-\omega_0)}{\alpha^2+(\omega-\omega_0)^2}+\frac{(\omega+\omega_0)}{\alpha^2+(\omega+\omega_0)^2}\right] f_i\left[\omega\frac{R}{c}\right]\ . \tag{50}$$

Here we have used a new variable $\omega\equiv ck$ and have replaced the upper limit by ∞. Instead of considering all three functions $f_i(\omega R/c)$ separately we notice that they all may be obtained from $f_3(\omega R/c)$ by differentiating by the parameter R/c under the integral. We have chosen f_3 because in this case the integral (50) is particularly simple:

$$\int_0^\infty \left[\frac{\omega-\omega_0}{\alpha^2+(\omega-\omega_0)^2}+\frac{(\omega-\omega_0)}{\alpha^2+(\omega-\omega_0)^2}\right]\sin\omega\frac{R}{c}d\omega = \pi e^{-\alpha R/c}\cos\left[\frac{R}{c}\omega_0\right]\ . \tag{51}$$

In Eq. (51) α appears only through the argument $\alpha R/c$ of the exponential function, which may be well approximated by 1, as long as $\alpha R/c \ll 1$. This implies that in this case the correlation time is of order of R/c. The same argument holds for f_1 and f_2.

Now we turn to the real component of the two "frozen-atoms" memory kernel. In this case we have found it more convenient algebraically to employ the Gaussian function $e^{-\alpha^2\tau^2}$ as a damping factor in our procedure, but it is clear that conclusions about correlation time do not depend on the particular form of this factor. In dealing with the real part we have seen that only two of the four terms in Eq. (29) (with the difference $\omega-\omega_0$ in the phase) are important. If we put these two terms together, include our "correlation-time probe" $e^{-\alpha^2\tau^2}$, as in the previous cases, and select the important components from the angular average (see the corresponding steps in the discussion of imaginary part) $f_3(kR)$ we realize that we only need to analyze the double integral

$$\int_0^{ck_{\max}} d\omega \int_0^\infty d\tau\, e^{-\alpha^2\tau^2}\cos(\omega-\omega_0)\tau\sin\omega\frac{R}{c} = \int_0^{k_{\max}} d\omega\frac{\sqrt{\pi}}{\alpha}\exp\left[\frac{(\omega-\omega_0)^2}{4\alpha^2}\right]\sin kR \tag{52}$$

(here we have omitted all unimportant constants to focus attention on the essentials). If one changes the variable in the integral in Eq. (52) to $z=(\omega-\omega_0)/2\alpha$, we can rewrite it as

$$\sqrt{\pi}\int_{-\omega_0/\alpha}^{(ck_{\max}/\alpha)-\omega_0/\alpha} e^{-z^2}\sin\left[(2\alpha z+\omega_0)\frac{R}{c}\right]dz \sim \pi e^{-[(R/c)\alpha]^2}\sin\left[\omega_0\frac{R}{c}\right]\ . \tag{53}$$

The approximation in Eq. (53) was obtained under the assumption that both $ck_{\max}/\alpha$ and ω_0/α are large, so that we could expand the limits of the integrals to $+\infty$ and $-\infty$, respectively. As we can see, the function on the right-hand side of Eq. (53) is independent of α as long as $\alpha R/c \ll 1$. For two interacting atoms, therefore, we have three conditions: $1/\alpha \gg R/c$, ω_0, a_0/c (since the atoms are well separated, $a_0 \ll R$ and only the first two are important). We identify the correlation time of the real part of the memory kernel for two "frozen" atoms as being of order of the larger of R/c or ω_0^{-1}.

X. DOPPLER EFFECTS IN TWO-ATOM RADIATION INTERACTION

In Sec. VIII we have verified the validity criteria for application of the Markov approximation to cases already well described in the literature. Now we extend the theory to include the relative motion of atoms. As before, we concentrate our attention of the correlation time of the memory kernel $F^I(t,t-\tau)$. When atoms are moving they undergo an extra change in the phase of the electromagnetic field. This refers both to the laser mode (treated classically) as well as to all spontaneous modes. The latter is of special interest here, because it is this phase that enters $F^I(t,t-\tau)$. To include an extra phase difference we have to substitute a $e^{-i\mathbf{k}\cdot\mathbf{r}}$ with a

$$e^{-i\mathbf{k}\cdot\mathbf{r}(t)}=e^{-i\mathbf{k}\cdot[\mathbf{r}(0)+\mathbf{v}t]}\ ,$$

where for the sake of convenience we have chosen the initial time $t_0=0$. Now we have to revise the derivation

presented in Sec. IX. This time we need to use the most general form of the phase functions $F^I(t,t-\tau)$ with the phase factors

$$\exp\{i\mathbf{k}\cdot[\mathbf{r}_{ab}(t)-\mathbf{v}_a\tau]\}=\exp(i\mathbf{k}\cdot\{[\mathbf{r}_a(t)-\mathbf{r}_b(t)]-\mathbf{v}_a\tau\})$$

[see also Eq. (29)].

We apply the same strategy that we used in all previous cases, i.e., we will probe the correlation time by implementing the weak decay factor, $\exp(-\alpha t)$. As we have carefully estimated the correlation time scale for both real and imaginary parts, and are convinced that they are of the same order of magnitude, in the present section only the real part will be analyzed. Let us assume the decay factors, $\exp(-\alpha\tau)$, are included in our phase function in Eq. (29). We have to evaluate the integrals over τ as before. Upon selecting the real part we obtain the "Lorentzian" terms

$$\sum_{a,b}\sum_{m_a,m_b}\int_0^\infty k^3\,dk\int d\Omega\frac{\alpha}{\alpha^2+(\omega_0-ck-\mathbf{v}_a\cdot\mathbf{k})^2}\times e^{i\mathbf{k}\cdot\mathbf{r}_{ab}(t)}C_{ab}(S_a^{m_a\pm},S_b^{m_b\pm}), \tag{54}$$

where $C_{ab}(S_a^{m_a\pm}S_b^{m_b\pm})$ is a function of atomic vectors $S_a^{m_a\pm}$ only, and does not depend on $\mathbf{k}$ or time. The expression, Eq. (50), is weakly dependent on the angular distribution of vector $\mathbf{k}$, and contains information about the atomic dipole direction. The geometry of the system is illustrated schematically in Fig. 1. Notice that the terms with $\omega+ck$ are not important here, as they do not contribute to the real (or δ-type) part of the memory kernel. We only need to consider the two-atom contribution, because the one-atom contribution may be analyzed in basically the same way. The Lorentzian part of Eq. (29) can now be rewritten as

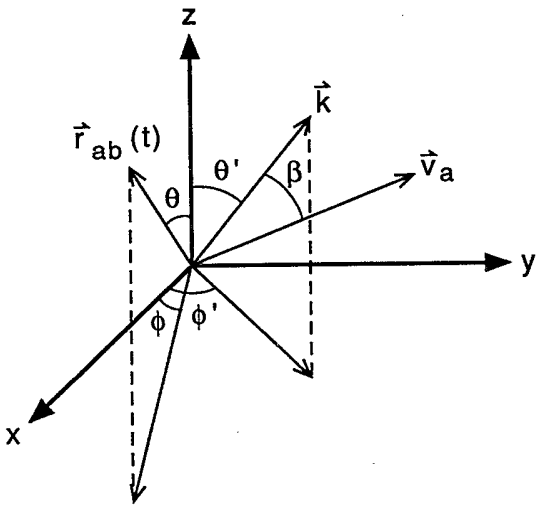

FIG. 1. Illustration of the two-atom configuration.

$$\frac{\alpha}{\alpha^2+(\omega_0-ck-v_ak\cos\beta)^2}=\frac{\alpha}{\alpha^2+\{\omega_0-ck[1+(v_a/c)\cos\beta]\}^2}, \tag{55}$$

where β is an angle between $\mathbf{v}_a$ and $\mathbf{k}$ and cannot be taken out of the angular average because of its dependence on θ' and ϕ'. On the other hand, one can prove that any of the integrals

$$I_{ab}=\int k^3\,dk\int d\Omega M_{ab}(k,\theta',\phi',\beta)$$

are finite. The proof (which contains tedious algebra) is based on the expansion at a fixed time t, i.e.,

$$e^{i\mathbf{k}\cdot\mathbf{r}_{ab}(t)}=4\pi\sum_{l,m}i^l j_l(kr_{ab}(t))Y_{l,m}(\theta,\phi)Y^*_{lm}(\theta',\phi') \tag{56}$$

[where θ,ϕ are the spherical angles of $\mathbf{r}_{ab}(t)$] and the observation that the integral over k gives a finite contribution for any $j_l(kr_{ab}(t))$. Since the two-atom integrals I_{ab} are all finite, we are allowed to change the order of integration

$$\int k^3\,dk\int d\Omega\rightarrow\int d\Omega\int k^3\,dk\ .$$

Next we eliminate $\cos\beta$ From the Lorentzian part of Eq. (54) by a change of variables defined by

$$\omega=ck[1+(v_a/c)\cos\beta]$$

and define a new $r'_{ab}(t)$ as equal to

$$r'_{ab}(t)=\frac{r_{ab}(t)}{1+(v_a/c)\cos\beta}\approx r_{ab}(t)[1-(v/c)\cos\beta]\ . \tag{57}$$

The last approximation is well justified since $(v_a/c)\cos\beta$ is always very small compared to unity. Now the part of the memory kernel defined in Eq. (54) can be written as

$$\int d\Omega\int d\omega\frac{\omega^3}{c^4[1+(v/c)\cos\beta]^4}\frac{\alpha}{\alpha^2+(\omega-\omega_0)^2}\times e^{i\mathbf{k}\cdot\mathbf{r}'_{ab}(t)/c}C_{ab}(S_a^{m_a\pm},S_b^{m_b\pm})\ . \tag{58}$$

In this equation the Lorentzian term in the integrand has exactly the same form as one finds in the "fixed atoms" case. We know from Sec. IV that as long as $\alpha\gg R/c=r_{ab}(t)/c$ the exponential decay $e^{-\alpha\tau}$ does not introduce any changes in the memory kernel (which was a basis for our estimate of the correlation time $\tau_{\rm corr}$). This leads to the conclusion that the important range of k is around k_0 $(=\omega_0/c)$ and the result of the integration over k is to substitute k_0 for k. The angular average then denotes an integral over the surface of the sphere of radius k_0 in k space. In Eq. (58) $\mathbf{v}_a$ appears in the definition of $r'_{ab}(t)$ and in the denominator. The latter can be ignored as long as $v/c\ll1$. On the other hand, $r'_{ab}(t)$ defined above is contained in the phase, and is thus subjected to the angular average integration. Since the angular average is taken over the compact region we still can ignore terms with v_a in $r'_{ab}(t)$ as long as

$$k_0 r_{ab}(t)\frac{v_a}{c} \ll 1 \ . \tag{59}$$

The last condition has a very clear interpretation. As we have noted, $r_{ab}(t)/c$ is a characteristic correlation time of the memory kernel $\tau_{\rm corr}$; our condition can be rewritten as

$$k_0 v_a \tau_{\rm corr} \ll 1 \ . \tag{60}$$

According to Eq. (60) we can ignore the v_a term from Eq. (29) as long as the phase that builds up within a correlation time ($\tau_{\rm corr}$) is small. If we compare condition (60) for two atoms a and b we also notice that

$$k v_{ab} \tau_{\rm corr} = k_0 (r_{ab}(t) - r_{ab}(t+\tau_{\rm corr})) \ll 1 \ ,$$

which means that the relative phase change should be small within the correlation time.

We therefore conclude that, under the above conditions, namely $k_0 v_a \tau_{\rm corr} \ll 1$, the master equation for moving atoms may be obtained directly from the corresponding equations for stationary atoms (as derived, for example, by Agarwal [11]). We simply substitute $r_{ab}(t)$ for r_{ab} in the density-matrix equation for the fixed atoms [in the straight-line trajectory approximation $r_{ab}(t) = |\mathbf{r}_{ab}(0) + \mathbf{v}t|$ with $\mathbf{v}$ relative velocity]. The retarded long-range interactions and two-level decay rates [as a function of $r_{ab}(t)$] are those obtained previously by Power [13] and Kurizki and Ben-Reuven [12] (although the validity conditions were not considered in detail by these authors). Small changes in velocity in the internal τ, due to, e.g., recoil, will not affect these criteria.

XI. VALIDITY CONDITIONS FOR BORN AND MARKOV APPROXIMATIONS

In Sec. IV we derived a reduced-density-matrix equation with a memory kernel that contains the full propagator $G_F(t,t')$ [Eqs. (20a) and (20b) and also (21)]. We also pointed out that to describe spontaneous emission processes it is sufficient to include the $L_{AF}(t)$ coupling (or interaction term) to second order. We then replaced the full propagator $G_F(t,t')$ defined by Eq. (20b) with $G_F^0(t,t')$, defined in Eq. (22). We later inferred that the memory kernel produced by this replacement has a short correlation time.

In the single-atom spontaneous-emission case we determined that the correlation time is of the order of the larger of a_0/c or $1/\omega_0$ (where a_0 is the size of an atom, and ω_0 is the transition frequency), which is short in comparison with the time scale for spontaneous emission. The corresponding correlation time for two frozen atoms (atoms with velocities equal to 0) is of the order of the larger of R/c or $1/\omega_0$ where R is the distance between the atoms. In Sec. X [Eq. (59)] we show that as long as $v(R/c) \ll \lambda_0$ ($=c/\omega_0 = k_0^{-1}$) the motion of the atoms during the correlation time is insignificantly small and decay rates and interaction potentials for the moving system have the same form as for the stationary case, but with R replaced by the instantaneous value $R(t)$. In this case the correlation time is of order of the larger of R/c or $1/\omega_0$.

As a result of this short correlation time, our integral kernel in the equation for the reduced density matrix [Eq. (21)] makes an important contribution only for times close to $\tau = t$. We can, therefore, introduce the Markov approximation, which means that in the equation for the reduced density matrix we can withdraw from the integral in the memory kernel the density matrix $\rho(t-\tau)$, since it changes on a time scale of order $1/\gamma$ (which is much larger than $\tau_{\rm corr}$) for diagonal elements. In the steady-state off-diagonal elements of $\rho(t-\tau)$ actually vary like $e^{\pm i(\omega_L - \omega_0)\tau}$ in the interaction picture [see Eq. (23)] since we expect a steady-state response varying like $e^{\pm i\omega_L \tau}$. This means that $(R/c)(\omega_L - \omega_0) \ll 1$, which limits our results to distances less than $R \ll c/(\omega_L - \omega_0)$ (which is usually well satisfied for interactions of interest). With $\omega_L - \omega_0 \sim \gamma$ these criteria are equivalent to $\gamma \tau_{\rm corr} \ll 1$. Actually, the condition $(R/c)(\omega_L - \omega_0) \ll 1$ can to some extent be avoided in the steady state if we go to a rotating frame with frequency ω_L in place of Eq. (23). The net result is to replace ω by ω_L in the various formulas [Eqs. (61) and (62), etc., below]. We substitute

$$\rho(t-\tau) \approx \rho(t) \ ,$$

as the time of interest τ is close to zero, and extend the integral of M_{ab} to infinity:

$$\int_{-T}^{t} d\tau \sum_{a,b} P_F M_{ab}(t,\tau) P_F \rho(\tau)$$
$$= \int_0^{t+T} \sum_{a,b} P_F M_{ab}(t, t-\tau) P_F \rho(t-\tau) d\tau$$
$$\cong \int_0^{\infty} \left[\sum_{a,b} P_F M_{ab}(t, t-\tau) P_F d\tau \right] \rho(t) \ .$$

Now our density-matrix equation of motion in the second order of interaction is no longer an integral equation.

Now we have to examine the higher terms in the Dyson expansion given by Eq. (22). It can be shown that upon adding the next term from expansion (22) our reduced memory kernel is modified only by the terms of order $\gamma \tau_{\rm corr}$ or $\Omega_L \tau_{\rm corr}$, where γ is the spontaneous-decay rate of the single atom and Ω_L is the on-resonant Rabi frequency for the external laser field driving the atomic transition $|G\rangle \leftrightarrow |e\rangle$. In other words, the ratio between first- and second-order terms in the Dyson expansion given by Eq. (22) can be expressed as

$$\frac{\text{second-order term}}{\text{first-order term}} \approx \gamma \tau_{\rm corr}, \Omega_L \tau_{\rm corr} \ .$$

Under experimental conditions both $\gamma \tau_{\rm corr}$ and $\Omega_L \tau_{\rm corr}$ are usually much less than 1. This means that the contribution from the other terms in expansion (22) is negligible. This justifies use of the Born approximation.

Thus, it follows from these considerations that the form of the reduced-density-matrix equation remains identical to that obtained from frozen atoms (held at fixed positions as, for example, in Agarwal [11]). To account for the motion of atoms we merely substitute $\mathbf{R}(t)$ for $\mathbf{R}$, as the distance between atoms changes with time.

XII. DISCUSSION

In the appendix we discuss in detail the derivation of the reduced-density-matrix equation averaged over spontaneous modes of radiation. This reduction is made assuming that both Born and Markov approximations are valid. Each term in the reduced-density-matrix equation has a clear physical meaning. The real and imaginary parts stand for excitation decay rates and interaction energy, respectively. Due to the parametric dependence on $R(t)$, these energies and decay rates for slowly moving atoms follow adiabatically the values corresponding to the instantaneous interaction distances.

Full expressions for these quantities as a function of $R(t)=r_{ab}(t)$ are presented in the Appendix. In particular, the critical quantities are $\Omega(R(t))$, which gives the interaction potential between the two atoms, and $\Gamma(R(t))$, which describes the *modification* of the radiative decay rates due to the presence of the other atom. In the degenerate case ($J=0\rightarrow J=1$) those quantities are given by

$$\Gamma_{am}^{bm'}(R(t))=\gamma\left[\delta_{mm'}j_0(k_0R(t))+j_2(k_0R(t))Y_{2,m'-m}(\theta,\phi)\sqrt{6\pi}(-1)^{m'}\begin{bmatrix}1 & 1 & 2\\ -m' & m & m'-m\end{bmatrix}\right]$$

and

$$\Omega_{am}^{bm'}(R(t))=\{j_0\leftrightarrow y_0, j_y\leftrightarrow y_2\}\ .$$

The notation used means $\Omega_{am}^{bm'}$ has the same functional form as $\Gamma_{am}^{bm'}$ with $j_{0,2}$ replaced by $y_{0,2}$, i.e., the spherical Bessel functions of the second kind.

The form of Ω and Γ is rather complicated due to the degeneracy of the excited state. Since we wish to discuss here simple physical effects and limiting cases, we will use the simpler expressions corresponding to the system of atoms with nondegenerate states. We note, however, that this is not physical, since angular momentum is always present.

For the case of nondegenerate states we find

$$\Gamma_{ab}(r_{ab}(t))=\gamma\{j_0(k_0r_{ab}(t))+[\tfrac{3}{2}\cos^2\theta(t)-\tfrac{1}{2}]j_2(k_0r_{ab}(t))\}\ , \qquad (61)$$

where $j_0(x)$ and $j_2(x)$ are spherical Bessel functions of the first kind, and $\theta(t)$ is an angle between quantization axis z, identified with the direction of the atomic dipole of the atoms in the system (since in the two-state atom the dipoles are restricted to being parallel or antiparallel with the quantization axis) and the intermolecular vector $\mathbf{r}_{ab}$. When atoms are in motion, angle θ becomes a slowly varying function of time. Similarly,

$$\Omega_{ab}(r_{ab}(t))=\gamma\{y_0(k_0r_{ab}(t))+[\tfrac{3}{2}\cos^2\theta(t)-\tfrac{1}{2}]y_2(k_0r_{ab}(t))\}\ , \qquad (62)$$

where $y_0(x)$ and $y_2(x)$ are the spherical Bessel functions of the second kind. In the equation of motion for the reduced density matrix these quantities are coefficients multiplied by (time-independent) operators to give the actual damping and interaction potentials between different states.

Both the interatomic potential Ω_{ab} and collective decay Γ_{ab} are functions of interatomic distance r_{ab}. When r_{ab} is very large (in the $r_{ab}\rightarrow\infty$ limit) we expect atoms to radiative independently of one another and therefore $\Gamma_{ab}\rightarrow 0$. Their interatomic potential in this limit is simply the retarded far-field interaction between two oscillating dipoles. Here we define for convenience the complex interaction potential $V_{ab}=i(\Gamma_{ab}+i\Omega_{ab})$. We have used this form with prefactor i to make the comparison with the energy of one of the dipoles in the field generated by the other oscillating dipole more clear [21]. To do this we first note that according to the definitions (61) and (62) we can write

$$V_{ab}=\frac{3}{2}\gamma e^{ikr}\left[(1-\cos^2\theta)\frac{1}{kr}+(3\cos^2\theta-1)\left[\frac{1}{k^3r^3}-\frac{i}{k^2r^2}\right]\right]\ .$$

If we recall that θ is an angle between $\mathbf{d}$ and $\mathbf{r}$ and γ contains the dipole moment in its definition we can rewrite V_{ab} in exactly the same form as the classical interaction, i.e., in the form

$$V_{ab}=e^{ikr}\left[\frac{k^2}{r}(\mathbf{d}\times\mathbf{n})^2+[3(\mathbf{n}\times\mathbf{d})^2-d^2]\left[\frac{1}{r^3}-\frac{ik}{r^2}\right]\right]$$

with $\mathbf{d}$ defined as a dipole moment of the atom. We also note that in the simple two nondegenerate level atom model that we are using for illustration geometrical freedom is restricted; the dipole moments have to be parallel to antiparallel and oriented along the quantization axis.

In the other limit, i.e., for small interatomic distances ($r_{ab}\lesssim\lambda/2\pi$) the mutual potential energy reduces to the well-known dipole-dipole interaction: $\Omega_{ab}\sim(1-3\cos^2\theta)r_{ab}^3$, which can again be written in the familiar form

$$V=\frac{d^2-3(\mathbf{n}\cdot\mathbf{d})^2}{r^3}\ .$$

Retardation effects will start to be important at distances of order $\sim\lambda$. For short distances, Γ_{ab} depends on the atomic states involved. For a pair of identical two-state atoms the states that diagonalize the interatomic coupling due to the interaction potentials are the symmetric and antisymmetric combinations of $|a\rangle$ and $|b\rangle$:

$$\psi_{S,A}=\frac{1}{\sqrt{2}}(|a\rangle\pm|b\rangle)\ .$$

Here $|a\rangle=|1g\rangle|2e\rangle$ and $|b\rangle=|2g\rangle|1e\rangle$.

When our reduced-density-matrix equation is written in this basis we obtain a closed set of differential equations for populations and coherences in which Γ is diagonal. The equation for single-excitation populations (ρ_{SS} and ρ_{AA}) will describe the decay of symmetric and antisymmetric states, respectively,

$$\dot{\rho}_{SS}+\{\gamma+\Gamma_{ab}[r_{ab}(t)]\}\rho_{SS}=\{\gamma+\Gamma_{ab}[r_{ab}(t)]\}\rho_{22}\ , \tag{63}$$

$$\dot{\rho}_{AA}+\{\gamma-\Gamma_{ab}[r_{ab}(t)]\}\rho_{AA}=\{\gamma-\Gamma_{ab}[r_{ab}(t)]\}\rho_{22}\ ,$$

where ρ_{22} represents the population when both atoms are in the excited state. From the above equations we can deduce that for small r_{ab} the decay rate for a symmetric state decay is 2γ while the decay rate of an antisymmetric state tends to 0 in this limit. This property has also been discussed by Power [13] and later by many other authors [11,14].

Cooper and Stacey [22] and Power [23] have considered the effects of the motion of atoms on the correlation between the states, i.e., the extent to which the symmetric state decays as 2γ, etc. They found that atoms are coupled coherently (which can be observed as a change from decay rate of the excitation from γ) only under the condition $\mathbf{k}\cdot\mathbf{v}_{ab}\gamma^{-1}\lesssim\pi/2$ (where $\mathbf{v}_{ab}=\mathbf{v}_a-\mathbf{v}_b$). A similar conclusion can be obtained from our Eq. (63). $\Gamma_{ab}(r_{ab}(t))$ is an oscillating function of $k_0r_{ab}(t)$. If we were to integrate any of the equations from Eq. (63) over a time of order of $1/\gamma$ (typical time of deexcitation) the second term Γ_{ab} would make an appreciable contribution, only if during the time of interest the phase factors $k_0r_{ab}(t)$ do not build up too many oscillations of the sine and cosine functions in Γ_{ab} [see Eq. (61)]. This can be expressed by the simple condition $k_0v_{ab}(1/\gamma)\lesssim\pi/2$. This is basically the same condition given by Cooper and Stacey [22]. One should note that this condition has a similar form to that obtained for the validity of the Markov approximation for a system of moving atoms. Both require that the phase factors do not change on the time scale of interest; here that time scale is determined by $1/\gamma$ (deexcitation time) and in the former condition by $\tau_{\rm corr}$ (correlation time). In their development of a theory of cooperative fluorescence from identical neutral atomic fragments, Kurizki and Ben-Reuven [12] derived a proper reduced-density-matrix equation and came to conclusions similar to those discussed here. They did not, however, consider validity conditions for the standard approximation as discussed in this paper.

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APPENDIX: REDUCED-DENSITY-MATRIX EQUATION FOR MOVING ATOMS IN THE BORN AND MARKOV APPROXIMATIONS

Here we derive the general form of the decay rates and interatomic potentials for the system of moving atoms provided that Markov and Born approximations hold. The validity conditions for these approximations are discussed in the text. We first note that some of the terms given in Eq. (29) describe single atom behavior ($a=b$). Both real and imaginary parts of single-atom terms are well known, and they will not be discussed here. We shall instead concentrate on two-atoms tetradic operators ($a\neq b$).

For any particular pair of atoms a, b the corresponding tetradic element consists of a quadratic matrix of rank j (equal to the degeneracy of the excited level; we assume here that the ground state is not degenerate) which has complex elements. Since the ground state is not degenerate j has to be equal at least to 1 in order to enable us to include the geometrical (angular momentum) effects. As already shown, one can write the memory kernel of the reduced-density-matrix equation in the form

$$\int_0^t dt\, P_F M_{a,m_a}^{b,m_b}(t,\tau)P_F\rho(t-\tau)dt=-\tfrac{1}{2}\Gamma_{a,m_a}^{b,m_b}(r_{ab}(t))[S_a^{m_a+}S_b^{m_b-}\rho(t)+\rho(t)S_a^{m_a+}S_b^{m_b-}-2S_b^{m_b-}\rho(t)S_a^{m_a+}]$$
$$-\frac{i}{2}\Omega_{a,m_a}^{b,m_b}(r_{ab}(t))[S_a^{m_a+}S_b^{m_b-},\rho(t)]\ . \tag{A1}$$

We have also used the fact that the τ dependence can be eliminated due to the short correlation time. The real part of $\Gamma_{a,m_a}^{b,m_b}(t)$ characterizes the modification to the spontaneous emission when atoms a and b come close together. Its elements depend on the direction of the vector $\mathbf{r}_{ab}(t)$ with respect to the quantization axis. In the most general case (see the discussion in Sec. VII and Fig. 1) we have to calculate

$$\int_0^\infty\delta(k-k_0)k^3\,dk\sum_\lambda\frac{ck}{(2\pi)^2\hbar}(\epsilon_{k\lambda}\mathbf{d}_c^{m_a})(\epsilon_{k\lambda}\mathbf{d}^{m_b})^*e^{i\mathbf{k}\cdot\mathbf{r}_{ab}(t)}\ . \tag{A2}$$

This shows that the evaluation of $\Gamma_{a,m_a}^{b,m_b}(t)$ is simply the angular average over the memory kernel; in particular, the angular average is over the sphere of the radius k_0 and not arbitrary k. Therefore we are able to use Eq. (40).

Thus $\Gamma_{a,m}^{b,m'}(t)$ reduces to simple angular integrals of spherical harmonics which finally gives

$$\Gamma_{a,m}^{b,m'}(\mathbf{r}_{ab}(t))=\gamma\left[\delta_{m,m'}j_0(k_0r_{ab}(t))+j_2(k_0r_{ab}(t))Y_{2,m'-m}(\theta,\phi)\sqrt{6\pi}(-1)^{m'}\begin{bmatrix}1&1&2\\-m'&m&m'-m\end{bmatrix}\right]\ . \tag{A3}$$

This is the general result for $j=0\rightarrow j=1$ transitions. The imaginary part of matrix M_{ab} may be obtained in a similar way. The only difference is in the integral over dk, which this time is the sum of two principal value integrals around

$k=\pm k_0$

$$\int dk \left[\frac{1}{k-k_0}+\frac{1}{k+k_0}\right](\cdots) .$$

From the theory of frequency-dependent susceptibility we know that these integrals should be closely related to the δ-type contribution. The real and imaginary parts are related by the Kramers-Kronig [24] relations. In our case one can obtain expressions for the interaction potentials (imaginary part) from the corresponding expressions for decay (real part) by simply replacing $\cos k_0 R$ with $\sin k_0 R$ and $\sin k_0 R$ with $-\cos k_0 R$ in the definitions of $j_0(k_0 R)$ and $j_2(k_0 R)$. Thus we have

$$\Omega_{a,m}^{b,m'}(\mathbf{r}_{ab}(t))=\gamma\left\{-\delta_{mm'}\left[\frac{\cos k_0 r_{ab}(t)}{k_0 r_{ab}(t)}\right]\right.$$
$$+(-1)^{m'}\sqrt{6\pi}Y_{2,m'-m}(\theta,\phi)\left[\left[\frac{1}{k_0 r_{ab}(t)}-\frac{3}{[k_0 r_{ab}(t)]^3}\right]\cos[k_0 r_{ab}(t)]\right.$$
$$\left.\left.-\frac{3}{[k_0 r_{ab}(t)]^2}\sin[k_0 r_{ab}(t)]\right]\begin{bmatrix}1 & 1 & 2\\ -m' & m & m'-m\end{bmatrix}\right\} . \tag{A4}$$

Finally, our reduced-density-matrix equation of motion for the atomic system can be written as

$$\partial_t\rho=-\sum_a\left\{\frac{i\tilde{\omega}_0}{2}[S_a^z,\rho(t)]+\sum_{m_a}\frac{\gamma}{2}[S_a^{m_a+}S_a^{m_a-}\rho(t)+\rho(t)S_a^{m_a+}S_a^{m_a-}-2S_a^{m_a-}\rho(t)S_a^{m_a-}]\right.$$
$$\left.-\frac{i}{2}[\Omega_a(S_a^{0+}e^{i(\mathbf{k}_L\mathbf{r}_a(t)-\omega_L t)}+\text{H.c.}),\rho(t)]\right\}$$
$$-\sum_{a\neq b}\{\tfrac{1}{2}\Gamma_{a,m_a}^{b,m_b}(\mathbf{r}_{ab}(t))[S_a^{m_a+}S_b^{m_b-}\rho(t)+\rho(t)S_z^{m_a+}S_b^{m_b-}-2S_b^{m_b-}\rho(t)S_a^{m_a}]+\frac{i}{2}\Omega_{a,m_a}^{b,m_b}(r_{ab}(t))\times[S_a^{m_a+}S_b^{m_b-},\rho(t)]\} , \tag{A5}$$

where $\tilde{\omega}$ and γ are the effective (Lamb-shifted) transition energy and decay rate, respectively (we do not discuss the one-atom terms here since they are well known).

In Sec. VI we mentioned the effect on the interaction potential $\Omega_{a,m_a}^{b,m_b}(\mathbf{R}(t))$, made by the introduction of RWA at different levels. We noted that the real part of Eq. (29), which introduces damping into the reduced-density-matrix equation, is related to the δ-type contribution. Since $\delta(ck+\omega_0)\equiv 0$ (the $ck+\omega_0$ argument is always positive), this part is not sensitive to the difference between different rotating-wave approximations. On the other hand, the imaginary part of Eq. (29), which describes the mutual two-atom interaction potentials $[\Omega_{a,m_a}^{b,m_b}(t)]$ and Lamb shifts of individual atoms obviously includes contributions from terms with $ck+\omega_0$. As was pointed out by Agarwal [11] (see also Sec. IV), the RWA should not be made on the Hamiltonian. Therefore we present here a detailed comparison of $\Omega_{a,m_a}^{b,m_b}(t)$ obtained from two rotating-wave approximations made on the Hamiltonian and on the memory kernel, in the form of a set of simple rules.

We start with a comment concerning $j_0(x)$ and $j_2(x)$, the spherical Bessel functions. Both can be built using three terms

$$\sin x/x,\quad \cos x/x^2,\quad \sin x/x^3 . \tag{A6}$$

When Ω_{a,m_a}^{b,m_b} is derived, it is convenient to integrate each of the terms [in Eq. (A6)] separately and realize that the sum of the principal value integrals acts effectively to exchange $\sin x$ with $-\cos x$ and $\cos x$ with $\sin x$ (similar to ordinary integration). On the other hand, we have noticed that if the RWA is made at the level of the Hamiltonian it leads to the elimination of one of the principal value integrals, namely $\int(1/k+k_0)dk$. As a result, we no longer have that simple rule, but we can still evaluate integrals:

$$\int_0^\infty dk\frac{k^3}{k-k_0}\frac{\sin kR}{(kR)^3}=\frac{1}{R^3}\{\cos(k_0R)[\text{si}(k_0R)+\pi]-\sin(k_0R)\text{ci}(k_0R)\} ,$$
$$\int_0^\infty dk\frac{k^3}{k-k_0}\frac{\cos kR}{(kR)^2}=\frac{k_0}{R^2}\{-\cos(k_0R)\text{ci}(k_0R)-\sin(k_0R)[\text{si}(k_0R)+\pi]\} , \tag{A7}$$
$$\int_0^\infty dk\frac{k^3}{k-k_0}\frac{\sin kR}{kR}=\frac{k_0^2}{R}\{\cos(k_0R)[\text{si}(k_0R)+\pi]-\sin(k_0R)\text{ci}(k_0R)+1\} ,$$

where $\mathrm{ci}(x)$ and $\mathrm{si}(x)$ are integral sine and cosine functions. Now we compare with the $\int(1/k+k_0)dk\{\ \}$ terms, which are

$$\int_0^\infty dk\frac{k^3}{k_0+k}\frac{\sin kR}{(kR)^3}=\frac{1}{R^3}[-\cos(k_0R)\mathrm{si}(k_0R)+\sin(k_0R)\mathrm{ci}(k_0R)]\ ,$$
$$\int_0^\infty dk\frac{k^3}{k_0+k}\frac{\cos kR}{(kR)^2}=\frac{k_0}{R^2}[\cos(k_0R)\mathrm{ci}(k_0R)+\sin(k_0R)\mathrm{si}(k_0R)]\ , \tag{A8}$$
$$\int_0^\infty dk\frac{k^3}{k_0+k}\frac{\sin kR}{kR}=\frac{k_0^2}{R}[-\cos(k_0R)\mathrm{si}(k_0R)+\sin(k_0R)\mathrm{ci}(k_0R)-1]\ .$$

From Eqs. (A7) and (A8) it is clear that for any of the terms, the sum of two corresponding principal value contributions has a much simpler form than any of them individually, and to obtain proper expressions for the interaction potential, one must add the two. Otherwise, we do not get the relativistically correct retarded interaction.

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