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Atomic collisions in the presence of laser radiation: Time dependence and the asymptotic wave function

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A time-dependent, wave-packet description of atomic collisions in the presence of laser radiation is extracted from the more conventional time-independent, stationary-state description. This approach resolves certain difficulties of interpretation in the time-independent approach which arise in the case of asymptotic near resonance. In the two-state model investigated, the approach predicts the existence of three spherically scattered waves in this asymptotically near-resonant case.

I. INTRODUCTION

The problem of particles colliding in the presence of radiation is one that has received much attention in recent years.[1,2] Generally speaking, the subject has been divided into two regions according to the degree of asymptotic resonance. If, asymptotically, the system is nearly resonant with the incident radiation, the detailed dynamics of the collision are probably not of supreme importance, and a semiclassical trajectory-based approach can be used to treat the problem.[3–7] On the other hand, if the system is far off resonance asymptotically, the collision dynamics play the vital role of bringing the system into a nuclear configuration in which photons can be absorbed or emitted, so that a quantum-mechanical treatment of the collision dynamics[8–10] would be more appropriate, if not essential, for an accurate treatment of the problem. We have previously described such a quantum-mechanical approach, using a time-independent formalism in which molecular and radiative degrees of freedom are treated on an equal footing. In the case of asymptotic far off resonance, or in a situation where the radiative coupling vanishes asymptotically, the approach is relatively straightforward. Certain difficulties of interpretation arise, however, if the system is nearly resonant asymptotically and the radiative coupling does not vanish. In this situation, boundary conditions can only be applied to the "dressed" states (that is, states which diagonalize the total Hamiltonian). If these states are observable, by fluorescence during the collision event, for example, then there would be no difficulty. However, if the fluorescence lifetime is much longer than the duration of the radiation, or if the collision partners themselves are detected, the physical system *will not be in the radiation field when it is observed.* Thus it is the "bare" states which are important. We must then transform between the dressed state time-independent formulation to the bare state time-independent formulation. The "Rabi flopping" of the system is a natural consequence of this transformation.

II. THEORY

In the interest of clarity, we will restrict the investigation to a system of two atoms colliding in the presence of a linearly polarized single mode monochromatic radiation field, and interacting with the field via the electric-dipole interaction, and presume that only two electronically adiabatic states ϕ_1 and ϕ_2 are of interest. (Actually, we will only require that ϕ_1 and ϕ_2 be eigenfunctions in the asymptotic region. However, if ϕ_1 and ϕ_2 are coupled by the electric dipole, they must be of different parity and hence are not electronically coupled at all.) The total Hamiltonian for the system is then

$$H = T + V \,, \qquad V = H_0 + H_{\rm rad} + H' \,, \tag{1}$$

where T is the nuclear kinetic-energy operator, H_0 is the clamped-nuclei Hamiltonian for the system in the absence of radiation (with eigenfunctions ϕ_1, ϕ_2), $H_{\rm rad}$ (with eigenfunctions $|n\rangle$) describes the pure radiation field, and H' is the interaction between the matter and the field, which can be taken to be

$$H' = -e\vec{\mathrm{E}}\cdot\vec{\mathrm{r}} \ . \tag{2}$$

An appropriate basis for V is then $\{\phi_i | n\rangle\}$; depending upon the shapes of the potential curves, it is sometimes possible to truncate the basis to only two states. We will assume such a case, as depicted in Fig. 1(a), and truncate the basis to include only the states $\phi_i | n\rangle$ and $\Phi_2 | n-1\rangle$. [Note that in other cases, as depicted in Fig. 1(b), such a truncation would be clearly erroneous.[11]]

The relevant matrix elements in this basis are then

$$\langle \phi_i n | H_0 | \phi_j n' \rangle = \delta_{ij}\delta_{nn'}E_i(R) \ , \tag{3}$$

$$\langle \phi_i n | H_{\rm rad} | \phi_j n' \rangle = \delta_{ij}\delta_{nn'}n\hbar\omega \ , \tag{4}$$

and the coupling term can be denoted $\epsilon\gamma(R)/2$, where $\gamma(R)$ is the dipole momentum (see the Appendix). The potential matrix can then be written, after redefining the zero of energy, as

$$\underline{V}(R) = \begin{bmatrix} E_1(R)+\hbar\omega & \dfrac{\epsilon\gamma(R)}{2} \\ \dfrac{\epsilon\gamma(R)}{2} & E_2(R) \end{bmatrix} . \tag{5}$$

Unless $\gamma(R)\to 0$ asymptotically, $V(R=\infty)$ will not be diagonal. But such a diagonal form is necessary in order to apply the appropriate scattering boundary conditions. We must therefore make a change to the basis χ_i such that $V(R=\infty)$ expressed in the χ_i basis is diagonal (with diagonal matrix elements $\mathscr{E}_i$); that is, to diagonalize $V(R=\infty)$. We shall denote the matrix which diagonalizes $V(R)$ by Γ. However, we only require that V be diagonal asymptotically, so only the constant matrix Γ^∞ is of interest to us. The χ_i basis is then given by

$$\begin{bmatrix} \chi_1 \\ \chi_2 \end{bmatrix} = \begin{bmatrix} \Gamma^\infty_{11} & \Gamma^\infty_{21} \\ \Gamma^\infty_{12} & \Gamma^\infty_{22} \end{bmatrix} \begin{bmatrix} \phi_1 & |n\rangle \\ \phi_2 & |n-1\rangle \end{bmatrix} , \tag{6}$$

where the Γ^∞ matrix is explicitly given in the Appendix, Eq. (A6).

In terms of the χ_1 basis, the time-independent scattering problem can be solved, with the asymptotic form of the wave function given by

$$\psi_i(\vec{\mathrm{k}}_i) \overset{R\to\infty}{\to} \frac{1}{(2\pi)^{3/2}} \left[\chi_i e^{i\vec{\mathrm{k}}_i\cdot\vec{\mathrm{R}}} + \sum_j f_{ji}(k_j\hat{R}, \vec{\mathrm{k}}_i)\chi_j \frac{e^{ik_jR}}{R} \right] , \tag{7}$$

which describes particles initially in the χ_i state colliding with wave vector $\vec{\mathrm{k}}_i$ and being scattered with amplitude f_{ji} into the states χ_j with final wave vector $k_j\hat{R}$. (Note that important questions regarding the orientations of $\vec{\mathrm{E}}$ with respect to the collision axis, the angular momentum transferred to the molecular system by the emission or absorption of a photon,[8] etc., are "buried" in the amplitudes f_{ji}, and will not be addressed here.) Transition probabilities and cross sections are then determined from the square of these amplitudes.

If the system is far from asymptotic resonance, or if $\gamma(R)$ vanishes at infinity, that is, if

$$[E_1(\infty)+\hbar\omega-E_2(\infty)] >> \epsilon\gamma(\infty) \ ,$$

then Γ^∞ is really the identity matrix, and

$$\begin{aligned} \chi_1 &\simeq \phi_1 | n\rangle \ , \\ \chi_2 &\simeq \phi_2 | n-1\rangle \ . \end{aligned} \tag{8}$$

We can then say, for example, that $|f_{21}|^2$ is the probability of making a transition from $\phi_1 | n\rangle$ to $\phi_2 | n-1\rangle$, i.e., starting in the electronic state ϕ_1 and absorbing a photon during the course of the collision. This is the regime in which the quantum-mechanical approach has been applied. If we wish to extend the use of this method to the nearly resonant situation, an immediate difficulty arises: Γ^∞ is no longer the identity matrix, so that the χ_i are not given by the simple relations of Eq. (8), but

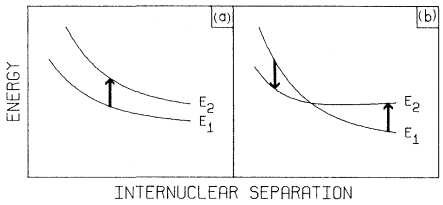

FIG. 1. (a) Electronic state ϕ_1 coupled to state ϕ_2 through absorption of a photon—two states are sufficient to describe the system. (b) State ϕ_1 coupled to ϕ_2 by either absorption *or* emission—three states, $\phi_1 | n\rangle$, $\phi_2 | n-1\rangle$, and $\phi_2 | n+1\rangle$, are required to describe the system.

by the general relations of Eq. (6). While $|f_{21}|^2$ can still be computed, it can no longer be interpreted as a probability for making a transition from $\phi_1|n\rangle$ to $\phi_2|n-1\rangle$. It is important to stress, however, that the near resonance does not destroy the validity of the time-independent Schrödinger-picture quantum-mechanical approach, although it does invalidate the simple interpretation of $|f_{21}|^2$ given above.

The essence of the problem is that in many instances we are not interested in the stationary-state solutions, such as Eq. (7) and involving the stationary-state eigenvectors χ_i, but rather in the states $\phi_1|n\rangle$ and $\phi_2|n-1\rangle$. This will be the case whenever the measurement process occurs with the system not in the laser field, i.e., if we are detecting the atoms themselves (since the detection apparatus will not be in the laser beam), or if we observe fluorescence at some time when the laser field is off. However, an *arbitrary* state of the system can always be obtained as a linear combination of such stationary states, with the appropriate exponential time dependence. The description of any *particular* state is thus obtained by selecting the appropriate (time-independent) coefficients of the linear combination, i.e., by choosing the appropriate *initial conditions.* (In the Appendix, this approach is used to solve the usual two-state Rabi problem—the approach we develop here is very similar.)

The initial conditions we choose are the following: at some time $t=0$ the system is in the electronic-radiative state $\phi_1|n\rangle$; the atoms are localized in space and separated by a distance R_0, which is sufficiently large as to be in the asymptotic region; and the atoms are moving towards one another with wave vector $\vec{k}$. (That is, the nuclear motion will be described by wave packets.[12]) The general wave function can be written as

$$\Psi(t)=\sum_i c_i \int d\vec{k}\,\Phi(\vec{k})\Psi_i(\vec{k})e^{-i(\mathscr{E}_i/\hbar+\omega_k)t}, \tag{9}$$

where $\omega_k=k^2/2\mu$; the c_i are chosen to make the electronic-radiative states satisfy the initial conditions, and the function $\Phi(\vec{k})$, which is peaked near $\vec{k}_0$, is chosen so as to localize the particles; that is,

$$\frac{1}{(2\pi)^{3/2}}\int d\vec{k}\,\Phi(k)e^{i\vec{k}\cdot\vec{R}}=\Theta(\vec{R}), \tag{10}$$

where $\Theta(\vec{R})$ is localized in the vicinity of $\vec{R}=\vec{R}_0$. Using the results of the Appendix to specify the c_i, we obtain

$$\Psi(t)=\frac{1}{(2\pi)^{3/2}}\sum_i \Gamma_{1i}^{\infty}\left[\chi_i e^{-i\mathscr{E}_i t/\hbar}\int d\vec{k}\,\Phi(\vec{k})e^{i\vec{k}\cdot\vec{R}}e^{-i\omega_k t}+\sum_j \chi_j e^{-i\mathscr{E}_j t/\hbar}\int d\vec{k}\,\Phi(\vec{k})f_{ji}(q_{ji}\hat{R},\vec{k})\frac{e^{iq_{ji}R}}{R}e^{-i\omega q_{ji}t}\right], \tag{11}$$

where we have defined

$$\vec{q}_{ji}=\hat{k}\left[k^2+\frac{2\mu}{\hbar}(\mathscr{E}_i-\mathscr{E}_j)\right]^{1/2}. \tag{12}$$

Let us examine the first integral and expand ω_k about ω_{k_0} using the identity

$$\omega_k=\omega_{k_0}+(\vec{k}-\vec{k}_0)\cdot\vec{v}_{k_0}+\frac{\hbar}{2\mu}(\vec{k}-\vec{k}_0)^2, \tag{13}$$

where

$$\vec{v}_{k_0}=\frac{\hbar}{\mu}\vec{k}_0, \tag{14}$$

is the group velocity of the wave packet. We assume that $\Phi(\vec{k})$ is sufficiently peaked about $\vec{k}_0$ to make the last term of Eq. (13) of negligible importance [e.g., when $(\vec{k}-\vec{k}_0)^2$ is large enough to be significant, $\Phi(\vec{k})$ is vanishingly small]. The first integral then becomes

$$\begin{aligned}\frac{1}{(2\pi)^{3/2}}\int d\vec{k}\,\Phi(k)e^{i\vec{k}\cdot\vec{R}}e^{-i\omega_k t}&=e^{i\omega_{k_0}t}\int d\vec{k}\,\Phi(k)e^{i\vec{k}\cdot(\vec{R}-\vec{v}_{k_0}t)}\\&=e^{i\omega_{k_0}t}\Theta(\vec{R}-\vec{v}_{k_0}t),\end{aligned} \tag{15}$$

a wave packet unchanged in shape but displaced a distance $\vec{v}_{k_0}t$ from its original position. The second integral is more difficult. First, we will assume that the $f_{ji}(q_{ji}\hat{R},\vec{k})$ are slowly varying functions in the vicinity of $\vec{k}_0$, so that they can be taken outside the integral. We are left with the integral

$$\frac{1}{(2\pi)^{3/2}}\int d\vec{k}\,\Phi(k)\frac{e^{iq_{ji}R}}{R}e^{-i\omega_{q_{ji}}t}. \tag{16}$$

We would like to change the variable of integration

from $\vec{k}$ to $\vec{q}_{ji}$, but the relationship between the two variables is nonlinear. We thus define a new function $\bar{\Phi}(\vec{q}_{ji})$ by requiring

$$d\vec{k}\,\Phi(\vec{k})=d\vec{q}_{ji}\bar{\Phi}(\vec{q}_{ji})\ . \tag{17}$$

$\bar{\Phi}$ will be peaked in the vicinity of $\vec{q}^{\,0}_{ji}$, but the shape of the function will be altered from that of Φ. We now replace $q_{ji}R$ by $\vec{q}_{ji}\cdot\hat{q}^0_{ji}R$, and approximate $\omega_{q_{ji}}$ in a manner similar to the treatment of ω_k in Eq. (13), so that the integral becomes

$$\frac{1}{(2\pi)^{3/2}}\frac{e^{i\omega^0_{q_{ji}}t}}{R}\int d\vec{q}_{ji}\bar{\Phi}(\vec{q}_{ji})e^{i\vec{q}_{ji}\cdot(\hat{q}^0_{ji}R-\vec{v}_{q^0_{ji}}t)}\ . \tag{18}$$

The remaining integral is in essentially the same form as Eq. (10). We thus evaluate the integral as $\bar{\Theta}_{ji}(\hat{q}^0_{ji}R-\vec{v}_{q^0_{ji}}t)$, a wave packet similar to Θ, but altered in shape. (Note that if $i=j$, $\bar{\Phi}$ is the same as Φ, and $\bar{\Theta}$ is the same as Θ. Thus for elastic scattering, the wave packet is not distorted.) The wave function of Eq. (11) is thus written as

$$\Psi(t)=\sum_i \Gamma^\infty_{1i}\chi_i\Theta(\vec{R}-\vec{v}_{k_0}t)e^{-i(\mathscr{E}_i/\hbar-\omega_{k_0})t}+\sum_j \chi_j f_{ji}(q^0_{ji}\hat{R},\vec{k}_0)\frac{\Theta_{ji}(\hat{q}^0_{ji}R-\vec{v}_{q^0_{ji}}t)}{R}e^{-i(\mathscr{E}_i/\hbar-\omega_{q^0_{ji}})t}\ . \tag{19}$$

To find the amplitude for being in the state $\phi_2\,|\,n-1\rangle$, we simply project $\Psi(t)$ onto this state,

$$a_{2,n-1}(t)=\langle\phi_2 n-1\,|\,\Psi(t)\rangle=\sum_i \Gamma^\infty_{1i}\Gamma^\infty_{2i}\Theta(\vec{R}-\vec{v}_{k_0}t)e^{-i(\mathscr{E}_i/\hbar-\omega_{k_0})t}$$
$$+\sum_i\sum_j \Gamma^\infty_{1i}\Gamma^\infty_{2j}f_{ji}(q^0_{ji}\hat{R},\vec{k}_0)\frac{\Theta_{ji}(\hat{q}^0_{ji}\vec{R}-\vec{v}_{q^0_{ji}}t)}{R}e^{-i(\mathscr{E}_i/\hbar-\omega^0_{q_{ji}})t}\ , \tag{20}$$

where we have used the fact that $\Gamma^\infty_{2j}=\langle\phi_2 n-1\,|\,\chi_j\rangle$. Realizing that $\Theta_{22}=\Theta_{11}=\Theta$, using the explicit forms for Γ^∞, and rearranging terms, we write Eq. (20) as

$$a_{2,n-1}(t)=e^{-i(E_1+\hbar\omega+E_2/\hbar-k_0^2/2\mu)t}$$
$$\times\left[-i\frac{\gamma\epsilon/\hbar}{\Omega}\sin(\Omega t/2)\Theta(\vec{R}-\vec{v}_{k0}t)\right.$$
$$+\frac{\mathrm{sgn}(\delta)}{2}\frac{\gamma\epsilon/\hbar}{\Omega}[e^{-i\,\mathrm{sgn}(\delta)\Omega t/2}f_{11}(k_0\hat{R},\vec{k}_0)-e^{i\,\mathrm{sgn}(\delta)\Omega t/2}f_{22}(k_0\hat{R},\vec{k}_0)]\frac{\Theta(\hat{k}_0R-\vec{v}_{k_0}t)}{R}$$
$$+\frac{\Omega+|\delta|}{2\Omega}e^{3i\,\mathrm{sgn}(\delta)\Omega t/2}f_{21}(q^0_{21}\hat{R},\vec{k}_0)\frac{\Theta_{21}(\hat{q}^0_{21}R-\vec{v}^0_{q_{21}}t)}{R}$$
$$\left.-\frac{(\gamma\epsilon/\hbar)^2}{(\Omega+|\delta|)^2+(\gamma\epsilon/\hbar)^2}e^{-3i\,\mathrm{sgn}(\delta)\Omega t/2}f_{12}(q^0_{12}\hat{R},\vec{k}_0)\frac{\Theta_{12}(\hat{q}^0_{12}R-\vec{v}^0_{q_{12}}t}{R}\right]\ . \tag{21}$$

The projection of $\Psi(t)$ onto $\phi_2\,|\,n-1\rangle$ has 4 terms: the first term corresponds to the nonscattered plane wave; the square of the coefficient is exactly the Rabi probability. That is, this term indicates that two unscattered particles will change their states in exactly the same way as a two-level system in the presence of radiation. This is a totally expected result, of course, but demonstrates the completeness of the present treatment. The second term represents "elastic" scattering. If $f_{11}=f_{22}$, then this term would also give rise to a Rabi flopping. In general, however, $f_{11}\neq f_{22}$, and the time dependence of this term will be more complicated. We note that, in both of these terms, the kinetic energy is unchanged. The next two terms represent "inelastic" scattering, and (when squared) do *not* exhibit any flopping behavior. These terms represent the transfer of energy between radiative and nuclear degrees of freedom, during the course of the collision; one term represents a gain of kinetic energy, the other a loss. After the collision has occurred (which is the only time the f_{ij} have any meaning), the only coupling is between the electronic and radiative states, *not*

the nuclear states. Thus, there is no coupling between these states, and hence no flopping between them.

It is of some interest to examine the coefficients of these terms, to determine their relative importance. We define the coefficients as

$$C_1=C_2=\frac{\gamma\epsilon/\hbar}{\Omega},$$

$$C_3=\frac{\Omega+|\delta|}{2\Omega},$$

$$C_4=\frac{(\gamma\epsilon/\hbar)^2}{(\Omega+|\delta|)^2+(\gamma\epsilon/\hbar)^2},$$

and plot C_i^2 in Fig. 2, as a function of detuning (in units of $\gamma\epsilon/\hbar$). For exact resonance, $C_3^2=C_4^2$, so that the inelastic terms are of equal importance, but as δ increases C_4^2 rapidly goes to zero while C_3^2 goes to unity. The coefficient of the first two terms also goes to zero with increasing detuning. Thus, at exact resonance, all four terms contribute; but as the detuning is increased, only one term will contribute, and that term is associated with inelastic scattering from χ_1 to χ_2. But in this limit, $\chi_1\simeq\phi_1|n\rangle$ and $\chi_2=\phi_2|n1\rangle$, so that we recover the "obvious" result in the far off-resonant case.

III. CONCLUSION

In this paper, we have demonstrated how the time dependence associated with the problem of atoms colliding in the presence of radiation can be extracted from a time-independent treatment of the scattering problem. In general, there are four terms in the asymptotic expression for the wave function: two exhibit a Rabi-like flopping and are associated with the nonscattered plane wave and the elastically scattered spherical wave; and two terms represent nonflopping inelastic spherically scattered waves. For detuning much larger than the radiative coupling between the asymptotic electronic states, all but one term vanishes, and that term is associated with the "usual" inelastic process. Noting that the coupling is usually quite small, typically on the order of 1 cm^{-1} in a radiation field of 1 MW/cm^2 intensity, the detuning need only be on the order of 10 cm^{-1} for this to occur. For detunings larger than this, the usual time-independent approach is satisfactory, but for smaller detunings, a time-dependent analysis, such as presented in this paper, becomes necessary.

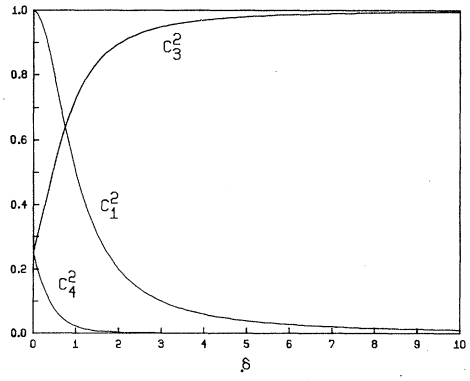

FIG. 2. Square of the coefficients which appear in the asymptotic wave function as a function of detuning δ.

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APPENDIX

The problem of a two-level atom in the presence of radiation is usually treated in either the interaction or Heisenberg representation[13,14]; in either, the mathematical aspect of the problem is the solution of a coupled set of first-order differential equations in time. However, the problem can also be treated in the Schrödinger representation, in which the mathematical aspect reduces to the diagonalization of a Hamiltonian matrix; time dependence is then introduced by an appropriate choice of the initial conditions of the system. These two approaches are of course equivalent; but the Schrödinger picture approach is most appropriate for the generalization of the problem to include collisional processes.

The Hamiltonian for the system can be written as

$$H=H_0+H_{\rm rad}+H', \tag{A1}$$

where H_0 describes the system in the absence of radiation, $H_{\rm rad}$ describes the pure radiation field, and H' describes the interaction between them. H_0 has two eigenfunctions, and eigenvalues, denoted by ϕ_i and E_i, respectively; $H_{\rm rad}$ is assumed to be a monochromatic single-mode field described by the number state ket $|n\rangle$; and H' is assumed to be dominated by the electric-dipole interaction, which we can write as

$$H'=-e\vec{\mathrm{E}}\cdot\vec{\mathrm{r}}\,, \tag{A2}$$

where $\vec{\mathrm{E}}$ is (in Gaussian units)

$$\vec{\mathrm{E}}=\frac{2\pi\hbar\omega}{V}\hat{\epsilon}(a+a^{\dagger})\,, \tag{A3}$$

which is linearly polarized in the $\hat{\epsilon}$ direction, and where $a^{\dagger}$ and a are the usual creation and annihilation operators. The basis for the total system is taken to be $\{\phi_i|n\rangle\}$. This basis is infinite, but is truncated to include only two states for which $E_1+n\hbar\omega\simeq E_2+n'\hbar\omega$; this truncation is the Schrödinger-picture analog of making the rotating-wave approximation to be specific, take $E_2>E_1$. The states of interest are then $\phi_1|n\rangle$ and $\phi_2|n-1\rangle$. Denoting the dipole moment by γ, the coupling terms can then be written as $\epsilon\gamma/2$, where $\epsilon/2=-2\pi\hbar\omega n/v$ and where we have ignored the contribution from spontaneous emission. The matrix representation of the total Hamiltonian is then

$$H=\begin{bmatrix} E_1+n\hbar\omega & \frac{\epsilon\gamma}{2} \\ \frac{\epsilon\gamma}{2} & E_2+(n-1)\hbar\omega \end{bmatrix}. \tag{A4}$$

Actually, nothing is changed if we redefine the zero of energy, which we now do, so that H is written as

$$H=\begin{bmatrix} E_1+\hbar\omega & \frac{\epsilon\gamma}{2} \\ \frac{\epsilon\gamma}{2} & E_2 \end{bmatrix}. \tag{A5}$$

We now wish to find the eigenvalues $\mathscr{E}_i$ and eigenvectors χ_i of this matrix. The diagonalizing matrix is easily found to be

$$\Gamma=\left[(\Omega+|\delta|)^2+\left[\frac{\gamma\epsilon}{\hbar}\right]^2\right]^{-1/2}\begin{bmatrix} \Omega+|\delta| & -\mathrm{sgn}(\delta)\frac{\epsilon\gamma}{\hbar} \\ \mathrm{sgn}(\delta)\frac{\gamma\epsilon}{\hbar} & \Omega+|\delta| \end{bmatrix}, \tag{A6}$$

where

$$\delta=(E_1+\hbar\omega-E_2)/\hbar\,, \tag{A7}$$

and

$$\Omega=\left[\delta^2+\left[\frac{\gamma\epsilon}{\hbar}\right]^2\right]^{1/2}. \tag{A8}$$

The eigenvalues are then

$$\mathscr{E}_{(\frac{1}{2})}=1/2[E_1+\hbar\omega+E_2\pm\mathrm{sgn}(\delta)\hbar\Omega]\,. \tag{A9}$$

We have thus found the stationary-state solutions to the problem. However, our interest is not in the stationary states, but rather the evolution of the system in time, subject to the initial condition that at $t=0$ the system is in the state $\phi_1|n\rangle$, for example. That is, an arbitrary state of the system can be written as

$$\Psi(t)=\sum_j c_j\chi_j e^{-i\mathscr{E}_j t/\hbar}\,, \tag{A10}$$

where the c's are constant. We wish to choose the c's such that

$$\Psi(t=0)=\phi_2|n\rangle\,.$$

By reference to the diagonalizing matrix, we have that

$$\phi_1|n\rangle=\sum_j\Gamma_{ij}\chi_j\,, \tag{A11}$$

so $c_j=\Gamma_{1j}$, and

$$\Psi(t)=\sum_j\Gamma_{1_j}\chi_j e^{-i\mathscr{E}_j t/\hbar}\,. \tag{A12}$$

The (time-dependent) amplitude for being in the $\phi_2|n-1\rangle$ state is then simply the projection of $\Psi(t)$ onto this state:

$$\begin{aligned} a_{2,n-1}(t)&\equiv\langle\phi_2 n-1|\Psi(t)\rangle \\ &=\sum_j\Gamma_{1j}\langle\phi_2 n-1|\chi_j\rangle e^{-i\mathscr{E}_j t/\hbar} \\ &=\sum_j\Gamma_{ij}\Gamma_{2j}e^{-i\mathscr{E}_j t/\hbar}\,. \end{aligned} \tag{A13}$$

Using the expressions for Γ_{ij} and $\mathscr{E}_j$, the probability of being in the state $\phi_2|n-1\rangle$ is simply

$$P_{2,n-1} = |a_{2,n-1}|^2 = \left[\frac{\gamma\epsilon}{2\hbar}\right]^2 \frac{\sin^2(\Omega t/2)}{(\Omega/2)^2}, \quad \text{(A14)}$$

which is, of course, identical to the result obtained via the interaction or Heisenberg pictures.

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