Driven two-level atom

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The two-level atom in an external field of arbitrary time dependence is solved formally using projection techniques. As a particular result of the general solution, an exact expression is presented for the density matrix of a two-level atom in a sinusoidal field.

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I. INTRODUCTION

Traditionally, the two-level atom has been used to model laser dynamics [1], search for quantum chaos [2], and, in general, test new forms of the interaction Hamiltonian [3]. Despite such efforts, the quantum Liouville equation for a two-level system driven by periodic external fields has escaped an exact solution. In this paper, we present a general method that could be used to solve the problem for arbitrary time dependence, including the hitherto unsolved two-level atom in a sinusoidal field.

There is yet another reason for attacking the problem anew. Pulse-shape effects are now in use to investigate molecular dynamics. Pulse-shape technology has achieved 50-fs resolution, to the point that quantum control of molecules is now possible. While the two-level atom is quite simple compared to real molecules, describing the dynamics of two-level atoms under the influence of pulsed fields allows us to develop some physical intuition about molecular processes, as observed by Warren [4]. A review of the possibilities in this new field of chemistry with photons is discussed by Brumer and Shapiro [5] and serves as motivation for this work.

Our goal in this paper is to develop formulas which will allow the exact solution, or systematic approximation, of the density matrix for two-level atoms under the influence of pulses of arbitrary shape. We will provide formulas which can be simplified for specific pulse shapes using symbolic or numeric computation routines, assuming that analytic efforts cannot be continued any further.

In Sec. II we review a proposed general solution using projection techniques. In Sec. III we focus on the two-level atom driven by an external field of arbitrary shape, arriving at the solution for the sinusoidal external field as a particular example. This result could describe a spin-$\frac{1}{2}$ system in an external field, as formulated by Bloch [6], except that we have used the density-matrix formalism just like Kubo and Tomita [7,8]. However, this work does not include Hamiltonian terms responsible for describing magnetic resonance and relaxation phenomena, but has the advantage that the results are exact, in closed form, versus the more realistic, but approximate results.

Once we have arrived at the formal solution, which can be checked by substitution into the quantum Liouville equation, it might not matter anymore what methodology we use to arrive at the solution. So, in Sec. IV, in addition to the stated goal of this paper—which is to provide practical recipes for describing the dynamics of the two-level system—we put the mathematical approach within the context of related research in many-body physics.

II. SUMMARY OF METHOD

Let ρ be the density matrix of a quantum system subjected to a time-dependent Hamiltonian H. Then the quantum Liouville equation is given by

$$i\hbar\frac{\partial\rho}{\partial t}=L\rho=[H,\rho]\ , \tag{1}$$

where $\hbar$ is Planck's constant and [,] is the usual commutator. Let D be a projection operator that picks the diagonal components of the density matrix, $D\rho=\rho_D$. $(1-D)$ picks the off-diagonal part of the same matrix, $(1-D)\rho=\rho_{1-D}$. The formal solution [9] of Eq. (1) is given by

$$\begin{aligned}\rho_D(t)={}&F(t,0)\rho_D(0)\\&+\sum_{n=1}^{\infty,\mathrm{odd}}(-i)^n\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n J(t,t_1,t_2)J(t_2,t_3,t_4)\cdots J(t_{n-3},t_{n-2},t_{n-1})DL(t_n)G(t_n,0)\rho_{1-D}(0)\\&+\sum_{m=2}^{\infty,\mathrm{even}}(-i)^m\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{m-1}}dt_m J(t,t_1,t_2)J(t_2,t_3,t_4)\cdots J(t_{m-2},t_{m-1},t_m)F(t_m,0)\rho_D(0),\end{aligned} \tag{2}$$

where

$$J(t_2,t_3,t_4)=F(t_2,t_3)DL(t_3)G(t_3,t_4)(1-D)L(t_4)\ , \tag{3}$$

$$F(t_2,t_3)=\exp\left[-\frac{i}{\hbar}D\int_{t_2}^{t_3}ds\,L(s)\right]\ , \tag{4}$$

$$G(t_2,t_3)=\exp\left[-\frac{i}{\hbar}(1-D)\int_{t_2}^{t_3}ds\,L(s)\right]\ . \tag{5}$$

All operators have time-ordered product interpretation. Notice that the main mathematical difficulty is the three-point function J of Eq. (3).

III. THE TWO-LEVEL ATOM

Let us now focus on a system of two-level atoms in the presence of an external field, denoted by the Hamiltonian

$$H=H_0+H_i\ , \tag{6}$$

where

$$H_0=\begin{bmatrix}\hbar\omega_1 & 0\\ 0 & \hbar\omega_2\end{bmatrix}, \tag{7}$$

$$H_i=-pEh(s)\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}. \tag{8}$$

The form of $h(t)$ is determined by the nature of the experiment being performed.

Let us also denote A_D as a diagonal matrix with elements a_{11}, a_{22}, and A_{1-D} as an off-diagonal matrix with elements a_{12}, a_{21}. A is not assumed Hermitian yet.

For 2×2 matrices, we have the following properties:

(A) $L_0A_D=[H_0,A_D]=0$; the commutator of two diagonal matrices is zero .

(B) $L_iA_D=[H_i,A_D]=B_{1-D}$; the commutator of an off-diagonal matrix and a diagonal matrix is off diagonal .

(C) $L_iA_D=[H_i,A_{1-D}]=C_D$; the commutator of two off-diagonal matrices is diagonal .

The above simple statements allow us to simplify Eq. (2) for the two-level atom. We will also define several two-by-two matrices and their commutation relations as we need them. The commutation properties of these matrices are summarized in Eq. (42).

A. The diagonal part

Let us simplify some expressions from Eq. (2). First,

$$F(t,0)\rho_D=\sum_{n=1}^{\infty}(-i/\hbar)^n[D(tL_0+L_i)]\cdots[D(tL_0+L_i]\rho_D\ , \tag{9}$$

where the quantity in the brackets appears n times. Start from the right. Observe that $L_i\rho_D$ is off diagonal, by rule B. Letting D operate on this product, the result is zero. In this way, by successive operations from the left, the contribution of L_i disappears completely. Only L_0 remains, but it commutes with ρ_D so F is a unit operator. The three-point function $J(t_2,t_3,t_4)$ becomes a two-point function $J(t_3,t_4)$. One difficult coupling in Eq. (3) drops out:

$$J(t_2,t_3,t_4)=DL(t_3)G(t_3,t_4)(1-D)L(t_4)=J(t_3,t_4)\ . \tag{10}$$

Second, Eq. (10) simplifies further.

$$\begin{aligned}J(t_3,t_4)D&=D(L_0+L_i)G(t_3,t_4)(1-D)(L_0+L_i)D\\ &=DL_iG(t_3,t_4)(1-D)(L_0+L_i)D\ .\end{aligned} \tag{11}$$

To progress line by line in Eqs. (11), we successively use the following comments: (1) J always acts on a diagonal matrix, hence the reason for appending D from the right. (2) D and L_0 commute.

Next we evaluate

$$G(t_3,t_4)L_i(t_4)A_D=\sum_{j=0}^{\infty}\left[\frac{1}{j!}\right](-i/\hbar)^n\{[(t_3-t_4)L_0]\}^n\times L_i(t_4)A_D\ , \tag{12}$$

where

$$\begin{aligned}&L_0=[H_0,\ ]\ ,\\ &L_i(t)=(-pE/\hbar)h(t)[\sigma_1,\ ]\ ,\\ &\sigma_1=\begin{bmatrix}0&1\\1&0\end{bmatrix}.\end{aligned} \tag{13}$$

We evaluate Eq. (11) term by term by commuting all operators to get the pattern of simplification. Thus

$$G(t_3,t_4)(1-D)L_i(t_4)A_D=(-2pE/\hbar)\left[\frac{a_{11}-a_{22}}{2}\right]\cos[\omega(t_3-t_4)]\sigma_2\ , \tag{14}$$

where we have used

$$[\sigma_1,A_D]=(a_{11}-a_{22})\sigma_2 \tag{15}$$

and

$$\sigma_2=\begin{bmatrix}0&-1\\1&0\end{bmatrix}, \tag{16}$$

$$\omega=\omega_1-\omega_2\ . \tag{17}$$

Next we evaluate

$$D(L_0+L_i(t_3))G(t_3,t_4)L_i(t_4)A_D=\left[\frac{a_{11}-a_{22}}{2}\right]\left[\frac{2pE}{\hbar}\right]^2\times\cos[\omega(t_3-t_4)]h(t_3)h(t_4)\sigma_0\ , \tag{18}$$

where

$$\sigma_0=\begin{bmatrix}1&0\\0&-1\end{bmatrix}. \tag{19}$$

Finally from Eq. (10) we have

$$J(t_1,t_2)J(t_3,t_4)A_D=\left[\frac{a_{11}-a_{22}}{2}\right]\left[\frac{2pE}{\hbar}\right]^4\times\cos[\omega(t_1-t_2)]\times\cos[\omega(t_3-t_4)]\prod_{j=1}^{4}h(t_j)\sigma_0\ , \tag{20}$$

which is exact. It is diagonal.

Let us now consider

$$G(t,0)A_{1-D}=\sum_{j=1}^{\infty}(-i/\hbar)^j\{(1-D)(tL_0)\}^jA_{1-D}\ , \qquad (21)$$

where again the contribution of L_i disappears.

A term-by-term expansion gives

$$G(t,0)A_{1-D}=\cos(\omega t)\zeta_1+i\sin(\omega t)\zeta_2\ , \qquad (22)$$

where

$$\zeta_1=\begin{bmatrix}0 & a_{12}\\ a_{21} & 0\end{bmatrix}\ ,\quad \zeta_2=\begin{bmatrix}0 & a_{12}\\ -a_{21} & 0\end{bmatrix}\ .$$

Evaluating next

$$\begin{aligned}DL(t)G(t,0)A_{1-D}&=D(L_0+L_i(t))G(t,0)A_{1-D}\\ &=DL_i(t)G(t,0)A_{1-D}\\ &=L_i(t)G(t,0)A_{1-D}\ ,\end{aligned} \qquad (23)$$

which gives

$$DL_i(t)G(t,0)A_{1-D}=\left[\frac{-2pE}{\hbar}\right]\sigma_0h(t)\left[\frac{a_{12}e^{-i\omega t}-a_{21}e^{i\omega t}}{2}\right]\ . \qquad (24)$$

The odd integrands are of the form

$$J(t_1,t_2)DL_i(t_3)G(t_3,0)A_{1-D}=\frac{(-2pE/\hbar)^3\sigma_0h(t_1)h(t_2)h(t_3)\cos[\omega(t_1-t_2)][a_{12}e^{-i\omega t_3}-a_{21}e^{i\omega t_3}]}{2} \qquad (25)$$

since

$$[\sigma_1,[\sigma_1,\sigma_0]]=2^2\sigma_0\ . \qquad (26)$$

The even integrands are of the form

$$J(t_1,t_2)J(t_3,t_4)\rho_D(0)=\sigma_0[(a_{11}-a_{22})/2](2pE/\hbar)^4\prod_{j=1}^{4}h(t_j)\ . \qquad (27)$$

We can now put Eq. (2) together again using the simplifications we have obtained from Eqs. (9)–(27),

$$\rho_D(t)=\rho_D(0)+(2ipE/\hbar)\sigma_0f_1(t)+\sigma_0\sum_{n=1}^{\infty,\text{odd}}(2ipE/\hbar)^nf_n(t)+[(a_{11}-a_{22})/2]\sigma_0\sum_{m=2}^{\infty,\text{even}}(2ipE/\hbar)^mg_m(t)\ , \qquad (28)$$

where

$$\begin{aligned}f_1(t)&=\int_0^t ds_1\left[\frac{a_{12}e^{-i\omega s_1}-a_{21}e^{i\omega s_1}}{2}\right]\ ,\\ f_n(t)&=\int_0^t ds_1\int_0^{s_1}ds_2\cdots\int_0^{s_{n-1}}ds_n\prod_{j=1}^{n}h(s_j)\cos[\omega(s_1-s_2)]\cos[\omega(s_3-s_4)]\cdots\cos[\omega(s_{n-2}-s_{n-1})]\\ &\qquad\times\left[\frac{a_{12}e^{-i\omega s_n}-a_{21}e^{i\omega s_n}}{2}\right]\ ,\\ g_m(t)&=\int_0^t ds_1\int_0^{s_1}ds_2\cdots\int_0^{s_{m-1}}ds_m\prod_{j=1}^{m}h(s_j)\cos[\omega(s_1-s_2)]\cos[\omega(s_3-s_4)]\cdots\cos[\omega(s_{m-1}-s_m)]\ .\end{aligned} \qquad (29)$$

B. The off-diagonal part

The off-diagonal density matrix can be found by simply exchanging the following operators and matrices:

$$\begin{aligned}&D\Longrightarrow(1-D)\ ,\\ &(1-D)\Longrightarrow D\ ,\\ &F\Longrightarrow G\ ,\\ &G\Longrightarrow F\ ,\\ &J(t_{j-2},t_{j-1},t_j)\Longrightarrow K(t_{j-2},t_{j-1},t_j)\\ &\qquad=G(t_{j-2},t_{j-1})(1-D)L(t_{j-2})F(t_{j-1},t_j)DL(t_j)\ .\end{aligned} \qquad (30)$$

Equation (2) can be rewritten as

$$\rho_{1-D}(t)=G(t,0)\rho_{1-D}(0)$$
$$+\sum_{n=1}^{\infty,\text{odd}}(-i)^n\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n K(t,t_1,t_2)K(t_2,t_3,t_4)\cdots K(t_{n-3},t_{n-2},t_{n-1})(1-D)L(t_n)F(t_n,0)\rho_D(0)$$
$$+\sum_{m=2}^{\infty,\text{even}}(-i)^m\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{m-1}}dt_m K(t,t_1,t_2)K(t_2,t_3,t_4)\cdots K(t_{m-2},t_{m-1},t_m)G(t_m,0)\rho_{1-D}(0)\ , \quad (31)$$

where

$$K(t_{j-2},t_{j-1},t_j)=G(t_{j-2},t_{j-1})(1-D)L(t_{j-1})F(t_{j-1},t_j)DL(t_j)\ . \quad (32)$$

The reduction of Eq. (31) follows all simplifications used in subsection A:

(1) $G(t_m,0)\rho_{1-D}$ is given by Eq. (23) .

(2) F is still a unit operator .

(3) $(1-D)L(t_n)F(t_n,0)\rho_D(0)=(1-D)(L_0+L_i(t_n)\rho_D(0)=L_i(t_n)\rho_D(0)$. (33)

(4) $K(t_{j-2},t_{j-1},t_j)=G(t_{j-2},t_{j-1})(1-D)L(t_{j-1})DL(t_j)$

$$=G(t_{j-2},t_{j-1})L_i(t_{j-1})L_i(t_j) \quad (34)$$

(a) The operator K acts on off-diagonal matrices only.

(b) $L_i(t_{j-1})L_i(t_j)$ acting on an off-diagonal matrix results in an off-diagonal matrix, another L_i renders the result diagonal, and $(1-D)$ nullifies the result. Hence

$$K(t_{j-2},t_{j-1},t_j)=\sum_{n=0}^{\infty}(1/n!)[-i(t_{j-2}-t_{j-1})L_0/\hbar]^n L_i(t_{j-1})L_i(t_j)\ . \quad (35)$$

(5) The first odd integrand is

$$L_i(t_1)\rho_D(0)=-[(a_{11}-a_{22})/2](2pE/\hbar)h(t_1)\sigma_2\ . \quad (36)$$

(6) The next odd integrands are

$$K(t,t_1,t_2)L_i(t_3)\rho_D(0)=[(a_{11}-a_{22})/2](-2pE/\hbar)^3h(t_1)h(t_2)h(t_3)\begin{bmatrix}0 & -e^{-i\omega(t-t_1)}\\ e^{i\omega(t-t_3)}- & 0\end{bmatrix}, \quad (37)$$

$$K(t,t_1,t_2)K(t_2,t_3,t_4)L_i(t_5)\rho_D(0)=[(a_{11}-a_{22})/2](-2pE/\hbar)^5\prod_{j=1}^{5}h(t_j)\cos[\omega(t_2-t_3)]\begin{bmatrix}0 & -e^{-i\omega(t-t_1)}\\ e^{i\omega(t-t_3)}- & 0\end{bmatrix}, \quad (38)$$

$$K(t,t_1,t_2)K(t_2,t_3,t_4)K(t_4,t_5,t_6)L_i(t_7)\rho_D(0)$$
$$=[(a_{11}-a_{22})/2](-2pE/\hbar)^7\prod_{j=1}^{7}h(t_j)\cos[\omega(t_2-t_3)]\cos[\omega(t_4-t_5)]\begin{bmatrix}0 & -e^{-i\omega(t-t_1)}\\ e^{i\omega(t-t_1)}- & 0\end{bmatrix}. \quad (39)$$

(7) The first even integrand is

$$K(t,t_1,t_2)G(t_2,0)\rho_{1-D}(0)=(2ipE/\hbar)^2h(t_1)h(t_2)\begin{bmatrix}0 & e^{-i\omega(t-t_1)}\\ -e^{i\omega(t-t_1)} & 0\end{bmatrix} \quad (40)$$

and the second is

$$K(t,t_1,t_2)K(t_2,t_3,t_4)G(t_4,0)\rho_{1-D}(0)$$
$$=(2ipE\hbar)^4\prod_{j=1}^{4}h(t_j)\left[\frac{a_{12}e^{i\omega t_4}-a_{21}e^{-i\omega t_4}}{2}\right]\cos[\omega(t_2-t_3)]\begin{bmatrix}0 & e^{-i\omega(t-t_1)}\\ -e^{i\omega(t-t_1)} & 0\end{bmatrix}. \quad (41)$$

For the sake of completeness, we list below all the commutation relations that we have used to simplify our expressions:

$$\begin{aligned}
&[\sigma_1,\zeta_1]=-(a_{12}-a_{21})\sigma_0, && L_0\sigma_2=(-\hbar\omega)\sigma_1\\
&[\sigma_1,\zeta_2]=+(a_{12}+a_{21})\sigma_0\ , && L_0^2\sigma_2=(-\hbar\omega)^2\sigma_2\\
&[\sigma_1,\sigma_2]=2\sigma_0\ , && L_0\zeta_1=(-\hbar\omega)\zeta_2\\
&[\sigma_1,[\sigma_1,\zeta_1]]=2(a_{12}-a_{21})\sigma_2\ , && L_0^2\zeta_1=(-\hbar\omega)^2\zeta_1\\
&[\sigma_1,[\sigma_1,\zeta_2]]=2(a_{12}+a_{21})\sigma_2\ , && L_0\zeta_2=(-\hbar\omega)\zeta_1\\
&[\sigma_1,[\sigma_1,\sigma_2]]=2^2\sigma_2\ , && L_0^2\zeta_2=(-\hbar\omega)^2\zeta_2\ .
\end{aligned} \tag{42}$$

Putting all the simplifications together we rewrite Eq. (31) as

$$\rho_{1-D}(t)=\begin{bmatrix} 0 & a_{12}e^{i\omega t}\\ a_{21}e^{-i\omega t} & 0\end{bmatrix}+[(a_{11}-a_{22})/2]\sum_{n=1}^{\infty,\text{odd}}(2ipE/\hbar)^n q_n(t)+\left[\frac{a_{11}-a_{22}}{2}\right]\sum_{m=2}^{\infty,\text{even}}(2ipE/\hbar)^m p_m(t)\ , \tag{43}$$

where

$$p_m(t)=\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{m-1}}dt_m\begin{bmatrix}0 & e^{-i\omega(t-t_1)}\\ -e^{i\omega(t-t_1)} & 0\end{bmatrix}\cos[\omega(t_2-t_3)]\cdots\cos[\omega(t_{m-2}-t_{m-1})]$$
$$\times\left[\frac{a_{12}e^{i\omega t_m}-a_{21}e^{-i\omega t_m}}{2}\right]\prod_{j=1}^{n}h(t_j)\ ,$$

$$q_n(t)=\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n\begin{bmatrix}0 & -e^{-i\omega(t-t_1)}\\ e^{i\omega(t-t_1)} & 0\end{bmatrix}\cos[\omega(t_2-t_3)]\cdots\cos[\omega(t_{n-2}-t_{n-1})]\prod_{j=1}^{n}h(t_j)\ , \tag{44}$$

$$q_1(t)=\int_0^t dt_1 h(t_1)\begin{bmatrix}0 & -1\\ 1 & 0\end{bmatrix}\ .$$

Equations (28) and (43) constitute the practical solution of the most general time-dependent external field. Together, the equations represent the most important contribution of this work for the purpose of pulse-shape application. Could they have been arrived at without the use of projection techniques? Probably, but our equations have the virtue of rendering systematic integrations as the main tool. The integrals are far easier to evaluate or approximate than to find the solutions of the corresponding differential equations derived from Eq. (1). In addition, as shown in the last section, we find the opportunity to discuss the significance of some features of our solution in clarifying attempts to solve the quantum Liouville equation (1) for more complex systems.

C. Illustration—the sinusoidal field

As an example of the utility of our solution, we present the exact solution, heretofore unsolved, for a two-level atom subjected to a periodic external field of frequency ν [10]. Here, $h(t)=\cos\nu t$. For simplicity, we assume that the off-diagonal components of the initial density matrix are zero. Then

$$\rho_D(t)=\rho_D(0)+[(a_{11}-a_{22})/2]\sigma_0\sum_{m=2}^{\infty,\text{even}}(2ipE/\hbar)^m$$
$$\times\int_0^t ds_1\int_0^{s_1}ds_2\cdots\int_0^{s_{m-1}}ds_m\cos[\omega(s_1-s_2)]$$
$$\times\cos[\omega(s_3-s_4)]\cdots\cos[\omega(s_{m-1}-s_m)]$$
$$\times\prod_{j=1}^{m}\cos(\nu s_m)\ . \tag{45}$$

We have plotted, in Fig. 1, Eq. (45) containing all terms up to $m=8$ using symbolic computation. The parameters used are $p=1$, $E=1$, $\hbar=1$, $a_{11}=0$, $a_{22}=1$, $a_{12}=a_{21}=0$. Many such physical examples and numerical investigations may be realized beginning with our analytic solutions for possible comparison with experiments, particularly those with intense driving fields. We hope to apply this work to such experimental investigations. In the meantime, we wish to comment on the significance of the suggested solution and the observations that lead to our results. Two possibilities may be mentioned.

First, for nonlinear optics. Unlike Eq. (45), the expression for the off-diagonal components of the density ma-

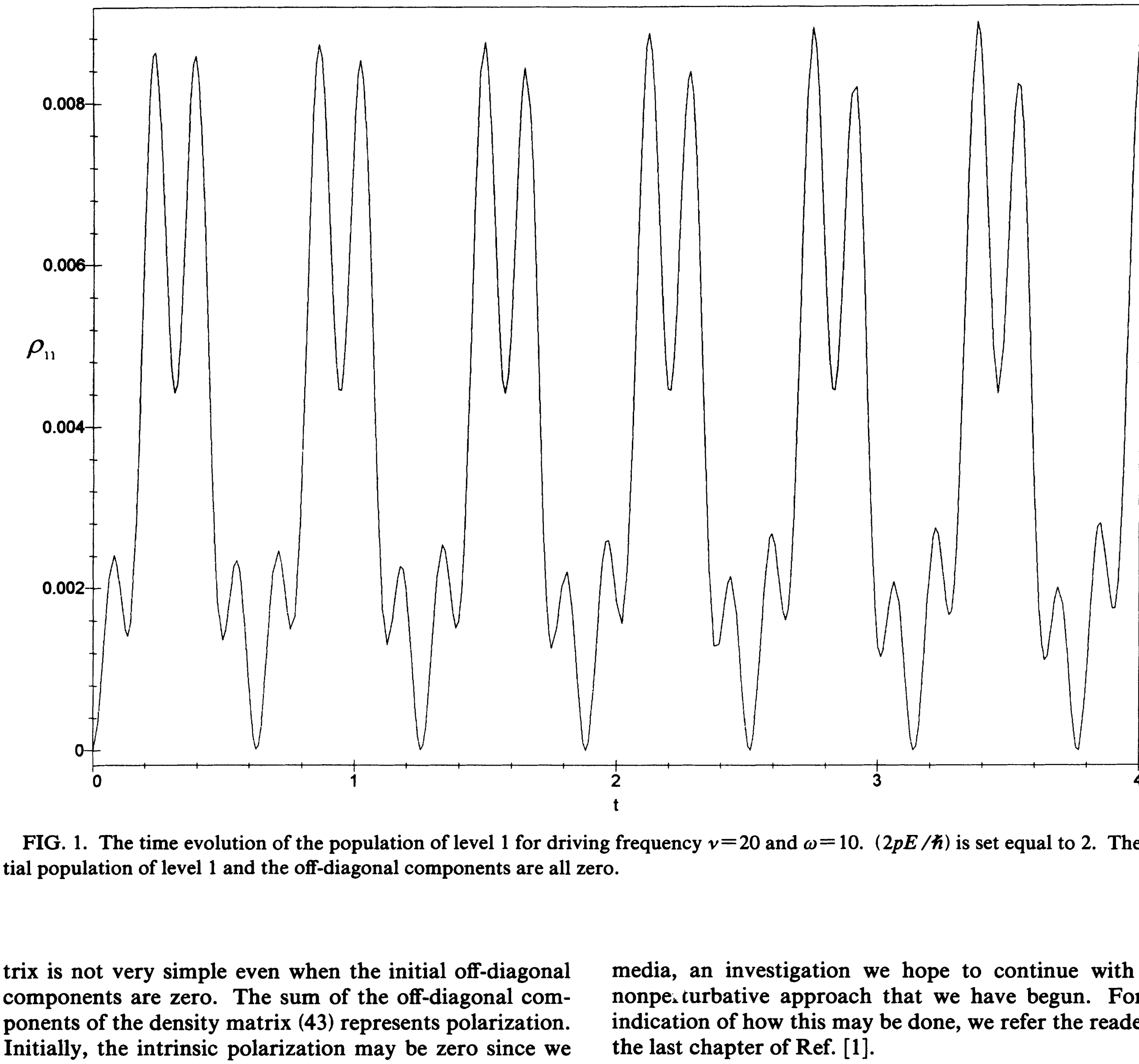

FIG. 1. The time evolution of the population of level 1 for driving frequency $\nu=20$ and $\omega=10$. $(2pE/\hbar)$ is set equal to 2. The initial population of level 1 and the off-diagonal components are all zero.

trix is not very simple even when the initial off-diagonal components are zero. The sum of the off-diagonal components of the density matrix (43) represents polarization. Initially, the intrinsic polarization may be zero since we can put $a_{12}=a_{21}=0$. But as the external field is applied, the polarization term evolves to include not just the driving frequency ν, but other frequencies as well. Since the polarization term acts as a source for Maxwell's equation, other radiation frequencies will appear. The medium which may start out without an intrinsic polarization, becomes polarizable, inviting the possibility of studying nonlinear optics when the external field becomes intense. An even richer possibility is to start with an intrinsically nonlinear medium, where $a_{12}=a_{21}\neq 0$, so that Eq. (43) becomes more complex even when one limits the calculation to q_1 or q_3 in Eqs. (43) and (44). Such low-order calculations in the amplitude of the external field yields polarization terms with frequencies ν, 2ν, ω, 2ω, $\nu+\omega$, $\nu-\omega$, allowing one to study second-harmonic light generation, as well as other higher harmonics and other frequency combinations. The intensities of the resulting frequencies may be calculated and compared with actual experiments. Such extension of this work is best continued with real experimental possibilities using nonlinear media, an investigation we hope to continue with the nonperturbative approach that we have begun. For an indication of how this may be done, we refer the reader to the last chapter of Ref. [1].

Second, note that the infinite series solutions (43) and (45) are expressed in powers of $(2pE/\hbar)$ which is proportional to the Bloch-Siegert shift [11,12] for a spin system in an rf field. Since our solution includes all higher powers of this shift, we raise the possibility of improving NMR calculations when the rf fields are intense, again a situation where experiments could dictate the need for more accurate, nonperturbative solution.

IV. SOME REMARKS ON THE SIGNIFICANCE OF THE REDUCTION PROCEDURE

Although our main result has not been previously reported, neither the problem, nor the method employed is new. What is different is the identification of the "units of difficulty," J and K. In fact, some very interesting recursion relations between the J and K operators can be written. In the most general case where J and K are three-point functions, the series proposed in Eqs. (2) and (31) are extremely complex. But for the Quantum Kac Ring Model [13] and the linear Ising chain, these operators simplify by losing their time dependence. F and G as given by Eqs. (4) and (5) reduce to the identity operator. The telescoping time integrals of Eqs. (2) and (31) become trivial.

In this work, both J and K become two-point functions. F is still the identity operator, but G is not, although it could still be evaluated exactly. The common time variable of adjacent operators in J and K drops out, uncoupling the operators. They then connect only via integrations over time.

In attempting to solve problems more difficult than what we have addressed here, such as the time evolution of other classical and quantum systems, where J and K cannot be so easily simplified, we have found it convenient to make a generalized weak-coupling approximation. Historically, the weak-coupling approximation is taken only to second order in a coupling parameter, a dimensionless number that multiplies L_i, for example. By contrast, our generalized weak-coupling approximation drops terms in an infinite number of places, but at the exponents, as in Eqs. (4) and (5), leaving the effects of high powers (up to infinity) of the operators L_i outside the exponential operators of Eqs. (2) and (31). We thus think that our method—when approximated—yields results intermediate between the traditional weak-coupling approach and the exact solution, whatever the exact solution may be. This approximation arbitrarily puts F and G as unity, a procedure that we have justified only on the strength of physical reasoning.

In the present work, because of the fortunate use of 2×2 matrices whose commutation rules, as shown by Eqs. (42), are very simple, we found that the rigorous reduction of F to unity, and the exact evaluation of G, simplify our work tremendously. It is our hope that in addition to possible practical applications to pulse-shape control in photon chemistry, nonlinear optics, and intense field NMR, the observations and simplifications used here can be employed also as a guide for attacking more difficult problems.

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[1] See, for example, P. W. Milonni and J. H. Eberly, *Lasers* (Wiley, New York, 1988), and references cited therein.

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