Coherent dynamics of N-level atoms and molecules. IV. Two- and three-level behavior

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(Received 14 June 1979)

The authors demonstrate special cases for which the resonantly excited N-level atom displays particularly simple periodic behavior involving only two levels. The cases, which occur when first and last transitions are weak, have analytic solutions. A striking difference is noted between even-N and odd-N, related to the resonance structure of the dressed $(N-2)$-level atom.

INTRODUCTION

The N-level atom[1,2] provides a valuable mathematical idealization of coherent excitation driven by multiple monochromatic resonantly tuned lasers; both analytical[3-7] and numerical[8,9] solutions provide useful insights into coherent excitation dynamics (which can differ dramatically from incoherent excitation) as well as guiding searches for optimum excitation conditions. The growth of literature[1-9] treating this model attests to both mathematical and physical interest.

By N-level atom we mean the loss-free system of N probability amplitudes $C_n(t)$ whose time evolution is governed by the rotating-wave-approximation (RWA) time-dependent Schrödinger equation[8,9]

$$i\frac{d}{dt}C_n(t)=\sum_m W_{nm}C_m(t)\,, \tag{1}$$

where the RWA Hamiltonian W is a real symmetric tridiagonal matrix expressing adjacent-level linkages along an excitation ladder. In the case of resonant excitation, our sole concern in this paper, the only nonzero elements of W are the $N-1$ values of the Rabi frequencies Ω_n,

$$W_{n,n+1}=W_{n+1,n}=\tfrac{1}{2}\Omega_n\,, \tag{2}$$

that express as frequencies the interaction energy between dipole-transition moments and laser electric fields. For simplicity we take all Ω_n to be positive real numbers, as is always possible by suitable choice of basis-state phases. By permitting $N-1$ separate lasers of adjustable intensity we admit the sequence of Rabi frequencies as arbitrary parameters, adjustable to serve our purposes. Thus previous papers[5-7] have discussed choices for the Ω_n which permitted analytical solution in terms of traditional special functions. In the present paper we describe broad classes of Rabi sequences for which the generally complicated N-level behavior undergoes great simplification, permitting approximate analytic solution. Furthermore, these choices for Rabi frequencies produce the maximum time-averaged population in level N and so, in this sense, they represent a prescription for optimum inversion.

TIME AVERAGES

Although solutions to the Schrödinger equation continue varying with time indefinitely and approach no steady-state quiescent limit, time average probabilities

$$\bar{P}_n(T)=\frac{1}{T}\int_0^T dT\, C_n(t)^2 \tag{3}$$

do approach asymptotic limits fairly rapidly (i.e., within a few population oscillations; see Fig. 1) and thus values of the limiting value $\bar{P}_n\equiv\bar{P}_n(\infty)$ provide useful indicators of average populations. The simplicity of computing $\bar{P}_n$ from eigenvalues and eigenvectors of the RWA Hamiltonian[6] makes this infinite-time average a particularly useful monitor of population dynamics; in the study of laser-induced chemical reactions at low densities (i.e., molecular beams) the values $\bar{P}_n$ measure the availability of excited states to reactions. Thus it is useful to understand the conditions upon the Rabi frequencies which maximize the value of $\bar{P}_n$ for some level (or levels) n.

Figure 2 compares populations for several Rabi-frequency sequences. Previous authors[6,9] have noted that if all Rabi frequencies are equal, then the population averages of an N-level system tend toward the rate-equation equilibrium value of $\bar{P}_n\to 1/N$ (levels 1 and N approach this value from above), and that if Rabi frequencies increase with n then $\bar{P}_n$ decreases with n (although significant level-to-level variations may occur). We further observe that sequences which place the largest Rabi frequencies in middle levels tend to concentrate populations in the end levels—as though population tended to avoid large Rabi frequencies. This observation suggests a strategy for placing maximum population into the most excited state: employ a sequence of Rabi frequencies in which first and last steps have the smallest

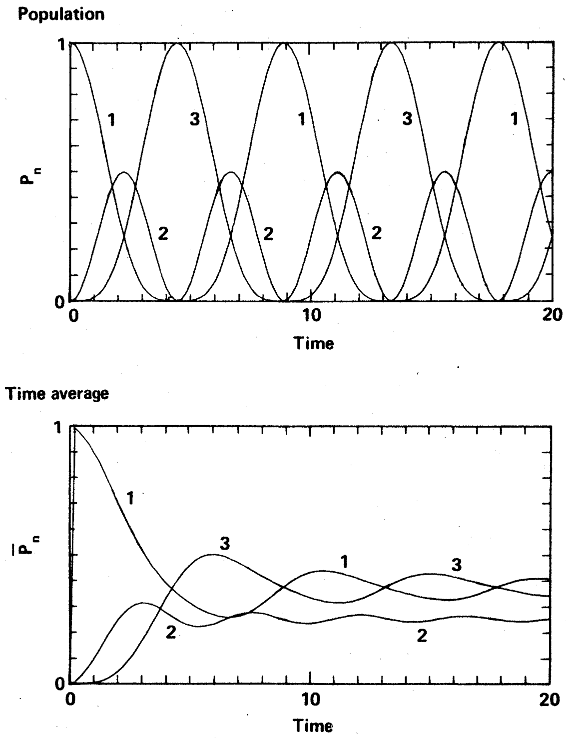

FIG. 1. Populations $P_n(t)$ (upper frames) and time averages $\bar{P}_n$ (lower frames) for resonantly tuned three-level atom, Rabi frequencies $\Omega_1 = \Omega_2 = 1$.

Rabi frequencies.

It is interesting to consider an N-level sequence of Rabi frequencies Ω_n which symmetrically distributes values around a maximum value in the middle level $n = N/2$. The parabolic distribution

$$\Omega_n = 1 - \left(1 - \frac{1}{x}\right)\left(\frac{N-2n}{N-2}\right)^2 \tag{4}$$

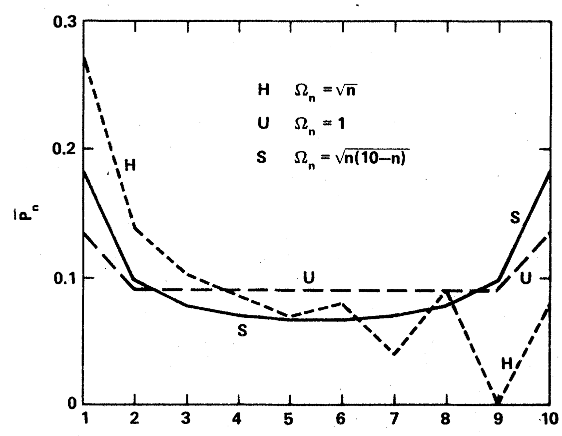

FIG. 2. Time averaged populations $\bar{P}_n$ for $N = 10$-level atom, without detuning, for three choices of Rabi-frequency sequences: case U: $\Omega_n = 1$; case H: $\Omega_n = \sqrt{n}$; case S: $\Omega_n = [n(10-n)]^{1/2}$.

provides one such sequence; here the parameter $x = \Omega_{N/2}/\Omega_1$ gives the ratio of maximum to minimum Rabi frequencies. For example, in a 10-level system we find that as x grows larger population tends to concentrate in levels 1 and 10, with $\bar{P}_1 = \bar{P}_{10} \to 0.5$ as $x \to \infty$. Intermediate-level population averages tend to zero. Thus this limiting case represents a maximum excitation limit.

Examining the details of time-dependent population flows in Fig. 3, we observe a simple pattern both for small $x \to 1.8$, where it becomes nearly

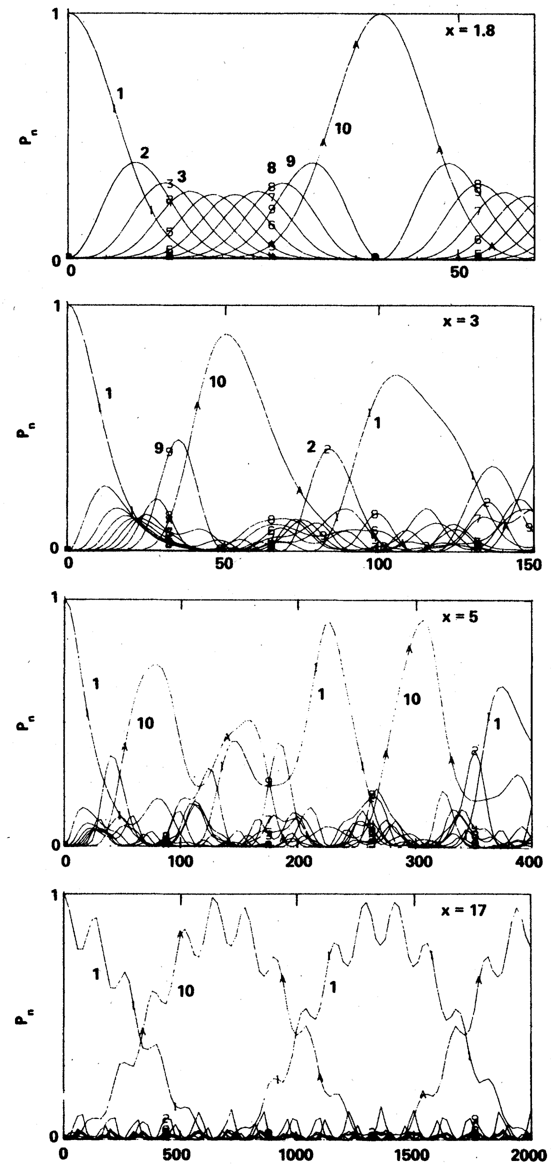

FIG. 3. Populations $P_n(t)$ for $N = 10$-level atom, resonantly excited with parabolic distribution of Rabi frequencies, Eq. (4), for various values of parameter $x = \Omega_5/\Omega_1$.

indistinguishable from the periodic behavior of the spin-$\frac{9}{2}$ model,[10] and for large $x \gtrsim 10$ where the system approaches an effective two-level atom. In both these limits we observe periodic behavior; note that in the two-level limit the time scale becomes quite long.

This two-level limit generalizes the previously described[11] behavior of a virtual level produced by detuning lasers of a two-step excitation. In the present example, however, the lasers remain tuned to the Bohr frequencies.

ANALYTIC DESCRIPTION

It is possible to obtain an analytic description of the two-level limit of the N-level atom. We partition the RWA Hamiltonian into two parts $W=A+B$ such that B contains only the links to levels 1 and N, while A contains the remainder. The only nonzero elements of B are therefore

$$B_{12}=B_{21}=\tfrac{1}{2}\Omega_1\,,\qquad B_{N-1,N}=B_{N,N+1}=\tfrac{1}{2}\Omega_{N-1}\,. \tag{5}$$

We readily verify that the matrix A has a pair of eigenvectors

$$U^{(1)}=\begin{bmatrix}1\\0\\ \cdot\\ \cdot\\ \cdot\\0\\0\end{bmatrix},\quad U^{(N)}=\begin{bmatrix}0\\0\\ \cdot\\ \cdot\\ \cdot\\0\\1\end{bmatrix} \tag{6}$$

whose eigenvalues are zero, $\lambda_1=\lambda_N=0$. The remainder of the eigenvectors of A have the structure

$$U^{(m)}=\begin{bmatrix}0\\u_2^{(m)}\\ \cdot\\ \cdot\\ \cdot\\u_{N-1}^{(m)}\\0\end{bmatrix}\quad (m=2,\ldots,N-1)\,. \tag{7}$$

Let us expand the RWA amplitudes in a basis of these eigenvectors of the A matrix:

$$C_n(t)=C_1(t)U_n^{(1)}+C_N(t)U_n^{(N)}+\sum_m a_m(t)U_n^{(m)}\exp(-i\lambda_m t)\,. \tag{8}$$

Here $a_1(t)\equiv a_N(t)\equiv 0$ so that we can carry the summation as $m=1,N$. Expressed in this basis the RWA Schrödinger equation becomes

$$i\frac{d}{dt}C_1(t)=\tfrac{1}{2}\sum_m \Omega_1 U_2^{(m)}a_m(t)\exp(-i\lambda_m t)\,, \tag{9a}$$

$$i\frac{d}{dt}C_N(t)=\tfrac{1}{2}\sum_m \Omega_{N-1}U_{N-1}^{(m)}a_m(t)\exp(-i\lambda_m t)\,, \tag{9b}$$

$$i\frac{d}{dt}a_m(t)=\tfrac{1}{2}[\Omega_1 U_2^{(m)*}C_1(t)+\Omega_{N-1}U_2^{(m)+}C_N(t)]\times\exp(i\lambda_m t)\,. \tag{9c}$$

So written the equation singles out the first and last levels, those that under suitable limits of Rabi frequencies define a two-level atom.

The limiting regime of interest occurs when $C_1(t)$ and $C_N(t)$ vary much more slowly than any of the factors $a_m(t)\exp(-i\lambda_m t)$. In turn, this condition obtains if all of the eigenvalues λ_m are much larger than the reciprocal of the characteristic time scale for variations in $C_1(t)$ and $C_N(t)$. One can show (see Appendix A) that the eigenvalues occur in pairs $\pm|\lambda_m|$, except for an additional null eigenvalue $\lambda=0$ which occurs when N is an odd integer. Thus we must separately consider even-N and odd-N sequences.

EVEN-N SYSTEMS

When we deal with an even number of energy levels we can require that $C_1(t)$ and $C_N(t)$ vary much more slowly than the function $\exp(-i\lambda_m t)$. We then obtain for $a_m(t)$ the solution, strictly valid in the limit of unchanged C_1 and C_N,

$$a_m(t)=a_m(0)-\left(\frac{1-\exp(i\lambda_m t)}{2\lambda_m}\right)[\Omega_1 U_1^{(m)*}C_1(t)+\Omega_{N-1}U_{N-1}^{(m)}C_N(t)]\,. \tag{10}$$

Upon substituting this expression into Eqs. 9(a) and 9(b) and replacing terms such as $1-\exp(-i\lambda_m t)$ by 1 (a second rotating-wave approximation) we obtain the equations of a two-level atom:

$$i\frac{d}{dt}C_1(t)=d_1C_1(t)+\tfrac{1}{2}\Omega C_N(t)\,, \tag{11a}$$

$$i\frac{d}{dt}C_N(t)=\tfrac{1}{2}\Omega C_1(t)+d_NC_N(t)\,. \tag{11b}$$

Here the effective Rabi frequency is

$$\Omega=\frac{\Omega_1\Omega_{N-1}}{2}\sum_m\frac{U_2^{(m)}U_{N-1}^{(m)*}}{\lambda_m}\,, \tag{12}$$

and the effective detunings are

$$d_1 = \frac{\Omega_1^2}{4} \sum_m \frac{|U_2^{(m)}|^2}{\lambda_m}, \tag{13a}$$

$$d_2 = \frac{\Omega_{N-1}^2}{4} \sum_m \frac{|U_{N-1}^{(m)}|^2}{\lambda_m}. \tag{13b}$$

Interestingly, one can show that these detunings vanish indentically (see Appendix B) for any Rabi sequence

$$d_1 = d_2 \equiv 0, \tag{14}$$

so that the populations undergo complete periodic population inversion as befits the resonant-two-level-atom equations

$$i\frac{d}{dt}C_1(t) = \tfrac{1}{2}\Omega C_N(t), \tag{15a}$$

$$i\frac{d}{dt}C_N(t) = \tfrac{1}{2}\Omega C_1(t). \tag{15b}$$

Furthermore, the excitation average $\bar{P}_N$ approaches the limiting value 0.5 as the two-level approximation becomes better.

For approximation (10) to be valid, and with it the two-level approximation, the frequency Ω must be appreciably smaller in magnitude than the smallest-magnitude eigenvalue $\lambda_<$ of the A matrix:

$$\Omega \ll |\lambda_<|. \tag{16}$$

ODD-*N* SYSTEMS

When N is an odd integer the matrix A has a null eigenvalue and we can no longer satisfy condition (16). Not only do we have slowly varying $C_1(t)$ and $C_N(t)$, but we also have an amplitude $a_0(t)$ associated with the null eigenvalue of A. If we retain only these three terms in Eq. (9), and time average the rapidly varying terms $\exp(i\lambda_m t)$ as is done in deriving the RWA Schrödinger equation, then the equations take the form of a three-level atom:

$$\begin{aligned} i\frac{d}{dt}C_1(t) &= \tfrac{1}{2}\Omega_1 U_2^{(0)} a_0(t) + \tfrac{1}{2}\Omega' C_N(t), \\ i\frac{d}{dt}a_0(t) &= \tfrac{1}{2}\Omega_1 U_2^{(0)} C_1(t) + \tfrac{1}{2}\Omega_{N-1} U_{N-1}^{(0)} C_N(t), \\ i\frac{d}{dt}C_N(t) &= \tfrac{1}{2}\Omega' C_1(t) + \tfrac{1}{2}\Omega_{N-1} U_{N-1}^{(0)} a_0(t). \end{aligned} \tag{17}$$

Here the Rabi frequency Ω' differs from the definition of Eq. (12) by omission of the null eigenvalue term in the sum. As with the two-level equivalence, the sums defining effective detuning vanish identically for all Rabi sequences.

Figures 4 and 5 show examples of even- and odd-N behavior. For this example we chose the Rabi frequencies

$$\begin{aligned} \Omega_1 &= \Omega_0 \times 0.02\sqrt{N} = \Omega_{N-1}, \\ \Omega_m &= \Omega_0 \times 1 \quad m = 2, \ldots, N-2, \end{aligned} \tag{18}$$

with Ω_0 chosen such that we retained the normalization

$$\sum_{n=1}^{N-1} \Omega_n^2 = 1. \tag{19}$$

Thus the inequality $\Omega_{N/2} \gg \Omega_1$ becomes less valid with increasing N; we begin to see failure of the two-level model with $N = 10$.

The difference in time scales for even-N and odd-N atoms becomes increasing evident as we

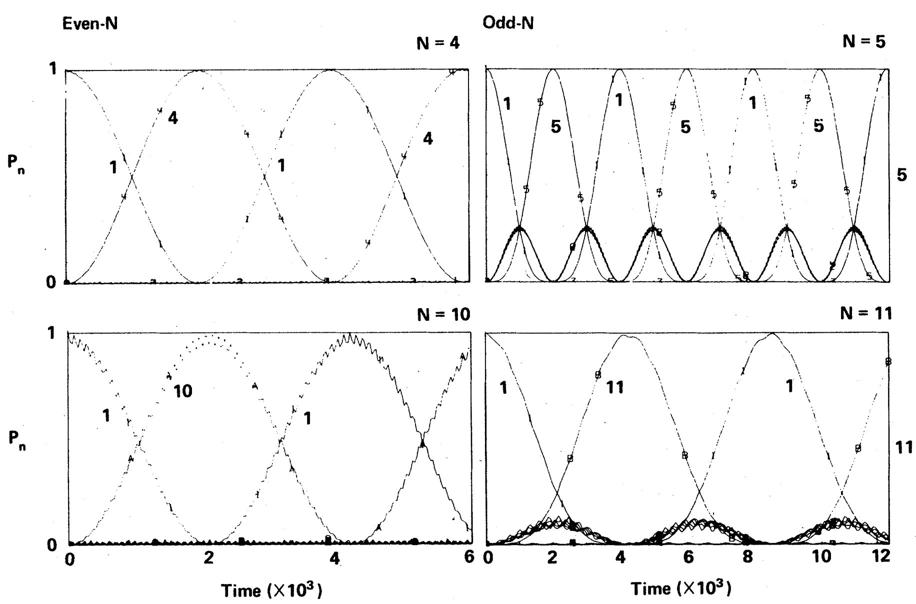

FIG. 4. Populations $P_n(t)$ for N = 4–, 5–, 10–, and 11-level systems, resonantly excited, with Rabi frequencies given by Eqs. (18) and (19).

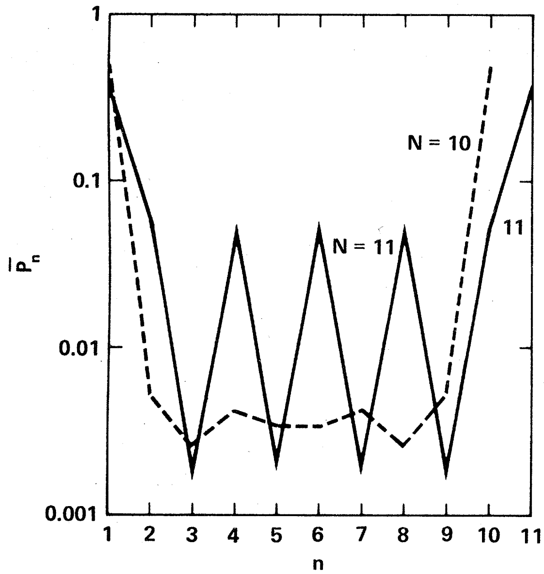

FIG. 5. Time averaged populations $\bar{P}_n$ for $N=10$– and 11-level atoms, resonantly tuned, with Rabi frequencies given by Eq. (18).

increase the ratio $x=\Omega_{N/2}/\Omega_1$, thereby dramatically slowing the even-N two-level oscillations. (In Fig. 4 the time scales differ only by a factor of 2.)

ac STARK EFFECT

The dramatic differences between even-N and odd-N systems, which appear puzzling at first, seem more natural when we consider the effect of detuning one of the weak lasers. Recall that our analysis treats an N-level system whose $N-1$ lasers are each tuned to the appropriate atomic-transition frequency; the RWA Hamiltonian W of Eq. (1) has no diagonal (detuning) elements. We have seen that when the first and last Rabi frequencies are much weaker than the others then we have a strongly coupled $(N-2)$-level subsystem weakly coupled into level 1 and level N. Under these conditions we expect manifestation of the dynamic (ac) Stark effect: the weak transitions lead into maximum excitation only when they are detuned to match one of the "dressed-atom" frequencies of the $(N-2)$-level subsystem. To exhibit the effect of Stark splitting, consider an $M=(N-2)$-level ladder, whose transitions all have unit Rabi frequency $\Omega_m=1$ and zero detuning (from the field-free Bohr frequencies). Let two weak-probe transitions $\Omega_1=\Omega_M=0.01$ be linked, respectively, to the first and last of these levels (see Fig. 6). As we sweep the frequencies of these probe lasers, with one red shifted and the other blue shifted to preserve overall null detuning, the average population $\bar{P}_{M+1}$ traces a succession of M resonances, the ac Stark shifts, symmetrically distributed around zero detuning. We observe that when M is odd a resonance occurs at zero detuning, whereas when M is even the population $\bar{P}_{M+1}$ is three orders of magnitude

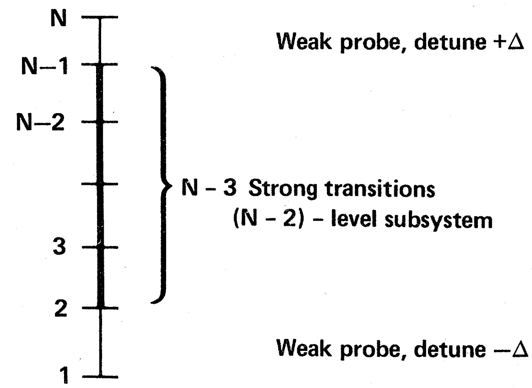

FIG. 6. Excitation linkage for N-level atom ac Stark effect.

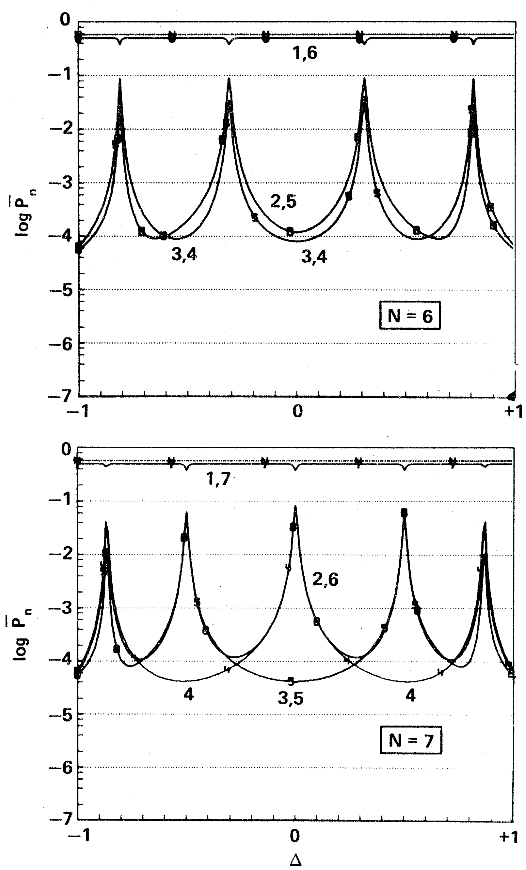

FIG. 7. ac Stark effect for $N=6$– and $N=7$– level atoms: time-averaged populations $\bar{P}_n$ as a function of probe laser detuning Δ. Top frame: $N=6$. Bottom frame: $N=7$.

smaller for zero detuning (see Fig. 7). Our preceding discussion treated an $N=(M+2)$-level system having zero detuning; we see that the dramatic difference between even and odd N originates in the dressed-atom resonance structure of the $(N-2)$-level strongly coupled subsystem.

CONCLUSION

We see that it is possible to obtain classes of periodic solutions to the resonantly tuned N-level atom in which long-time average population in level N approaches the limit in value of $\frac{1}{2}$. These occur when first and last Rabi frequencies are significantly smaller than the remaining values. For even N we obtained a two-level description, with analytic expressions for the effective Rabi frequency and detuning. For odd N we found a three-level description. The dramatic difference between even N and odd N originates in the spectra of the $(N-2)$-level dressed atom.

APPENDIX A: SYMMETRIC DISTRIBUTION OF EIGENVALUES

Consider the eigenvalues λ_m of the real symmetric null-diagonal N-dimensional matrix X:

$$X=\begin{bmatrix} 0 & x_1 & & \\ x_1 & 0 & x_2 & \cdot \\ 0 & x_2 & 0 & \ddots \end{bmatrix}.$$

These satisfy the determinantal equation

$$D_N(\lambda)\equiv\begin{vmatrix} -\lambda & x_1 & 0 & & & \\ x_1 & -\lambda & x_2 & & & \\ 0 & x_2 & -\lambda & & & \\ & & & \ddots & & \\ & & & & -\lambda & x_{N-1} \\ & & & & x_{N-1} & -\lambda \end{vmatrix}=0.$$

We readily see that the determinants of various orders N satisfy the recursion relation

$$D_N(\lambda)=-\lambda D_{N-1}(\lambda)-x_{N-1}^2 D_{N-2}(\lambda).$$

Thus for even-integer N the determinant $D_N(\lambda)$ is a function of λ^2, whereas for odd-integer N the determinant is λ times a function of λ^2:

$$\begin{aligned} D_N(\lambda)&=F_N(\lambda^2), \quad N=\text{even} \\ &=\lambda G_N(\lambda^2), \quad N=\text{odd}. \end{aligned}$$

In turn we find that if $+\lambda$ is a solution to $D_N(\lambda)=0$, then $D_N(-\lambda)=0$ and so $-\lambda$ is also an eigenvalue; the eigenvalues are symmetrically distributed about zero. Moreover, when N is an odd integer there always exists a null eigenvalue $\lambda=0$.

APPENDIX B: SYMMETRY OF EIGENVECTORS

Consider the tridiagonal matrix X of Appendix A and let U and $\bar{U}$ be the eigenvectors corresponding, respectively, to eigenvalues $+\lambda$ and $-\lambda$:

$$XU=\lambda U, \quad X\bar{U}=-\lambda\bar{U}.$$

Written out these matrix equations yield, in part, the recurrence relations

$$\begin{aligned} x_1u_2&=\lambda u_1, & x_1\bar{u}_2&=-\lambda\bar{u}_2, \\ x_2u_3&=\lambda u_2-x_1u_1, & x_2\bar{u}_3&=-\lambda\bar{u}_2-x_1\bar{u}_1, \\ &\vdots & &\vdots \\ x_mu_{m+1}&=\lambda u_m-x_{m-1}u_{m-1}, & x_m\bar{u}_{m+1}&=-\lambda\bar{u}_m-x_{m-1}\bar{u}_{m-1}, \end{aligned}$$

which permit construction of all the components of U and $\bar{U}$ given the first elements u_1 and $\bar{u}_1$. Taking these elements to be equal to some common normalizing constant, we find that subsequent elements satisfy the relationship

$$\begin{aligned} u_2&=-\bar{u}_2, \\ u_3&=\bar{u}_3, \\ &\vdots \\ u_m&=(-1)^{m+1}\bar{u}_m. \end{aligned}$$

In particular, if the components of U are all positive, then the components of $\bar{U}$ alternate in sign.

The foregoing construction demonstrates that the components u_m and $\bar{u}_m$ of the eigenvectors corresponding to eigenvalues $+\lambda$ and $-\lambda$ have the same magnitude:

$$|u_m|=|\bar{u}_m|.$$

This equality holds for any real symmetric tridiagonal null-diagonal matrix and thus it applies to any sequence of Rabi frequencies. As a corollary, sums such as Eq. (13) vanish. For let the eigenvalues be numbered

$$\lambda_{+1}, \lambda_{-1}=-\lambda_{+1}, \lambda_{+2}, \lambda_{-2}=-\lambda_{+2}, \ldots.$$

Then because $|U_n^{(+m)}|=|U_n^{(-m)}|$ the sum reads, in part,

$$\sum_m \frac{|U_n^{(m)}|^2}{\lambda_m} = \frac{|U_n^{(+1)}|^2}{\lambda_{+1}} + \frac{|U_n^{(-1)}|^2}{\lambda_{-1}} + \cdots$$

$$= \frac{|U_n^{(+1)}|^2}{\lambda_{+1}} - \frac{|U_n^{(+1)}|^2}{\lambda_{+1}} + \cdots = 0 .$$

Thus the detunings d_1 and d_2 of Eq. (13) vanish identically for any Rabi-frequency sequence.

ACKNOWLEDGMENTS

We are indebted to Dr. David Eimerl and to Dr. Ann Greenbaum for proving the symmetry property of Appendix B. Work performed under the auspices of the U. S. Department of Energy at Lawrence Livermore Laboratory under Contract No. W-7405-Eng-48.

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