Eigenvalue problem of the square of the pulse area for two-level systems

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(Received 27 December 1982)

This paper analyzes the dynamics of two-level systems from a new perspective. The notion of eigenvalues (EV) of the pulse area squared, which was introduced in a previous paper, is developed further. Integral expressions for the eigenvalues in terms of eigenfunctions are exhibited, and it is pointed out that these formulas also enable one to estimate EV variationally. Examples are given of how the method may be used to predict qualitative features of two-level spectra without solving equations of motion. Finally, an expression for the transition amplitude in terms of an eigenfunction expansion is derived. It is suggested that this expansion may be useful for both numerical determinations of transition probabilities and for analytic, variational calculations of these parameters. As an application, an expression for the transition probability at small detunings for a rather general class of coupling functions is derived, and its predictions compared to exact numerical calculations in a specific case.

I. INTRODUCTION

The study of the dynamics of a two-level atom coupled by an external, time-dependent field is more than 50 years old, but continues to be of interest to physicists.[1–10] This is the simplest, explicitly time-dependent problem in quantum mechanics, yet it represents an accurate approximation to a variety of actual systems in different physical contexts. Our purpose in writing the present paper is to deepen an approach to this problem first presented in a recent article.[9] This is the A^2 eigenvalue method.

With the exception of a few particular pulse shapes, closed-form solutions to two-level problems are not known.[2,4] Recently, Bambini and Berman[8] (BB) discovered a set of coupling functions for which the two-state equations of motion could be solved analytically. The hyperbolic secant of Rosen and Zener is a special case of their family.[2] All members of the class, with the exception of the hyperbolic secant, are temporally asymmetric. For these functions, Bambini and Berman found that there are no coupling strengths where P, the transition probability generated by the external potential, vanishes, unless the system frequency is resonant with the field.[8] This is in sharp distinction to the hyperbolic secant, where $P=0$ for pulse areas that are integral multiples of π, regardless of the detuning.[2] It is also known from numerical solutions, for example, that temporally symmetric pulses other than the hyperbolic secant possess pulse areas for which nonresonant transition probabilities vanish.[9]

The foregoing raised the question of whether it was true in general that symmetric pulses possess, and asymmetric pulses lack, nodes in the transition probability as a function of pulse area. Robinson addressed this question by reexpressing the equations of motion in terms of an eigenvalue (EV) problem for A^2, the square of the pulse area.[9] By determining under what conditions these EV were real or complex, it was possible to generalize the BB result[8] to all smooth pulses. I showed that the symmetric-asymmetric dichotomy is a consequence of the structure of the equations of motion for a two-level system, and was not peculiar to pulses of the BB type. My conclusions were that symmetric pulses always have nodes, but asymmetric pulses do not, except under over-determined circumstances.[9]

This generalization of BB rested upon some trivial properties of the EV which could be discerned by inspection. This was a much easier task than actually solving equations of motion. It is to the problem of calculating EV that I address my attention in the present paper. I shall point out how one may perform accurate, approximate calculations of those A^2 for which P vanishes, and present examples where this knowledge provides partial understanding of the spectra of two-level atoms. While more involved than determining whether or not A^2 is real, these EV calculations are still much simpler than the complete determination of the two-level amplitudes, especially since, in some cases, it may not be necessary to actually evaluate those integrals which appear in expressions for EV. One may be able to infer the relevant dependence of the spectrum on coupling potential parameters and detuning from the *form* of the integrals alone.

Finally, I shall demonstrate how to express transition amplitudes in terms of the eigenvalues and their associated eigenfunctions. This may prove useful in future numerical calculations where one wishes to determine the probability of absorption for a very large number of pulse areas. It also serves as the basis for variational estimates of transition probabilities.

II. THE EIGENVALUE PROBLEM AND ITS VARIATIONAL APPROXIMATION

For convenience, I review the basic theory. The time-dependent Schrödinger equation for a two-level system is a pair of coupled first-order equations for the state amplitudes a_1 and a_2. For real potentials, these are

$$i\dot{a}_1 = V(t)e^{i\Delta t}a_2 , \quad (1a)$$

$$i\dot{a}_2 = V(t)e^{-i\Delta t}a_1 , \quad (1b)$$

where we have set $\hbar = 1$, and made the rotating wave approximation. The detuning of the system from exact resonance is designated by Δ. Equations (1) are to be solved subject to the initial conditions that $a_1 = 1$, $a_2 = 0$ as $t \to -\infty$. They may be written as a pair of uncoupled second-order equations

$$\ddot{a}_1 - \left[\frac{\dot{V}}{V} + i\Delta \right] \dot{a}_1 + V^2 a_1 = 0 , \quad (2a)$$

$$\ddot{a}_2 - \left[\frac{\dot{V}}{V} - i\Delta \right] \dot{a}_2 + V^2 a_2 = 0 . \quad (2b)$$

Consider now only envelope functions which are of a single algebraic sign, a somewhat weaker restriction than that imposed in Ref. 9, where it was assumed that f varied smoothly. The imposed condition guarantees the single valuedness of the transformation $z = \int_{-\infty}^{t} f(t')dt' + \frac{1}{2}$, where f is the reduced envelope, $f(t) = V(t)/A$, and A is the pulse area defined as $A = \int_{-\infty}^{\infty} V(t)dt$. In the z plane Eqs. (2) become

$$a_1'' - \frac{i\Delta}{f} a_1' + A^2 a_1 = 0 , \quad (3a)$$

$$a_2'' + \frac{i\Delta}{f} a_2' + A^2 a_2 = 0 , \quad (3b)$$

where the prime denotes differentiation with respect to z. Recalling the transformation[9]

$$a_2 = b_2 \exp\left[-\frac{i}{2} \int_0^z \frac{dz'}{f(z')} \right] = b_2 \exp(-i\Delta t/2) ,$$

$$a_1 = b_1 \exp\left[+\frac{i}{2} \int_0^z \frac{dz'}{f(z')} \right] = b_1 \exp(+i\Delta t/2) ,$$

we obtain the normal form of Eqs. (3)

$$-b_1'' - \left[\frac{\Delta^2}{4f^2} - \frac{if'\Delta}{2f^2} \right] b_1 = A^2 b_1 , \quad (4a)$$

$$-b_2'' - \left[\frac{\Delta^2}{4f^2} + \frac{if'\Delta}{2f^2} \right] b_2 = A^2 b_2 . \quad (4b)$$

Equation (3a) is to be solved subject to the initial conditions $a_2(-\frac{1}{2}) = 0$, $a_2'(-\frac{1}{2}) = -iAe^{i\phi}$, ϕ real but arbitrary. For certain A^2, which we designate A_n^2, the EV of Eqs. (3b) or (4b), $a_2(\frac{1}{2})$ also vanishes. Now the A_n^2 are real if $f(t)$ is temporally symmetric, while they are ordinarily complex for asymmetric potentials and $\Delta \neq 0$.[9] We designate the eigenfunctions corresponding to A_n^2 as a_{2n} and b_{2n}, respectively, in the representations of Eqs. (3) and (4). I shall restrict the remainder of the discussion to potentials that are symmetric in the time (and in z).

Equation (4b) resembles a one-dimensional, time-independent Schrödinger equation for a particle moving under the influence of a complex "potential." Because of the non-Hermiticity of the operator that plays the role analogous to the Hamiltonian, there may be a lack of familiarity among physicists as to which integrals express the orthogonality of eigenfunctions, of how to calculate expectation values, etc. A brief discussion of these properties is given by Morse and Feshbach,[11] and we summarize the relevant portions for the convenience of the reader.

The operators

$$-\frac{d^2}{dz^2} - \left[\frac{\Delta^2}{4f^2} + \frac{if'\Delta}{2f^2} \right] ,$$

$$-\frac{d^2}{dz^2} - \left[\frac{\Delta^2}{4f^2} - \frac{if'\Delta}{2f^2} \right] ,$$

have eigenfunctions, respectively, b_n and $\bar{b}_n$, with eigenvalues A_n^2 and A_n^{*2}. These form a complete, biorthogonal set, where the orthogonality condition is

$$\int_{-1/2}^{1/2} \bar{b}_n^* b_m dz = 0, \quad m \neq n .$$

If the b_n are normalized according to

$$\int_{-1/2}^{1/2} \bar{b}_n^* b_n dz = 1 ,$$

the eigenfunctions form a complete biorthonormal set, and the eigenvalues may be expressed as expectation values.

In general, if L is a non-Hermitian operator, its eigenfunctions and those of L^* are not complex conjugates of each other. In the present case, $\bar{b}_n = b_n^*$, so that the orthonormality condition is $\int (\bar{b}_n)^* b_m dz = \delta_{mn} = \int b_n b_m dz$.

As I have indicated, the discussion will be restricted to the case of temporally symmetric pulses. A_n^2 is given by

$$A_n^2 = -\int_{-1/2}^{1/2} b_n'' b_n dz - \int_{-1/2}^{1/2} b_n^2 \left[\frac{\Delta^2}{4f^2} + \frac{if'\Delta}{2f^2} \right] dz . \quad (5)$$

If b_n is exact, the expression in Eq. (5) gives A_n^2 without error. One may also interpret Eq. (5) as a variational principle for the square of the pulse area eigenvalue, with b_n a trial function containing adjustable parameters. If b_n is allowed to be arbitrarily flexible, the Euler-Lagrange equation that is generated is just Eq. (4b). If b_n is a function of a finite number of parameters, Eq. (5) provides a variational approximation for the eigenvalues of (4b). One may also write the variational principle in terms of the function $\tilde{a}_n = \tilde{b}_n \exp(-i\Delta t/2)$ as

$$A_n^2 = \frac{-\int_{-1/2}^{1/2} \tilde{a}_n'' \tilde{a}_n e^{i\Delta t} dz - i\Delta \int_{-1/2}^{1/2} \frac{\tilde{a}_n \tilde{a}_n'}{f} e^{i\Delta t} dz}{\int_{-1/2}^{1/2} \tilde{a}_n^2 e^{i\Delta t} dz} , \quad (6)$$

or, integrating the first term by parts

$$A_n^2 = \frac{\int_{-1/2}^{1/2} \tilde{a}_n'^2 e^{i\Delta t} dz}{\int_{-1/2}^{1/2} \tilde{a}_n^2 e^{i\Delta t} dz} , \quad (7)$$

where the tilde indicates an unnormalized eigenfunction. Note that the quadratic factors involve the squares of a_n and its derivative, and are not squares of absolute values.

III. APPLICATION OF THE EIGENVALUE METHOD

In this section, I shall demonstrate how the eigenvalue method can be useful in helping to predict the qualitative dependence of two-level spectra on the parameters of the coupling potential. I shall address the question of the validity of the Rosen-Zener conjecture[2] for temporally symmetric pulses and small detunings.

When Rosen and Zener solved the two-level system for the hyperbolic secant coupling pulse, they found a very simple expression for the transition probability as a function of detuning and pulse area, namely,

$$P=2\pi\,|\,\tilde{V}(\Delta)\,|^2\frac{\sin^2 A}{A^2}\,, \tag{8}$$

where $\tilde{V}$ is the Fourier transform of $V(t)=Af(t)$.[2] They surmised that Eq. (8) might be true for all smooth coupling functions, provided that the Fourier transform of the actual potential is used in place of that of the hyperbolic secant.[2] This is an attractive idea, since Eq. (8) does hold for all coupling potentials on resonance, and off resonance in the limit where first-order perturbation theory is valid. It is now known that their suggestion is incorrect. It is manifestly false for temporally asymmetric potentials[8,9] and has been explicitly shown not to apply to symmetric pulses at large detunings for couplings other than the hyperbolic secant, where asymptotically exact expressions have been derived.[10] Since it does hold for $\Delta=0$, however, one might expect a region of approximate validity of the conjecture for symmetric pulses at small detunings. I shall establish that this is indeed the case, in the sense that corrections are $O(\Delta^2)$ for many, but not all, $f(t)$. Some preliminary analysis is necessary before we arrive at the role the eigenvalue method plays in this.

We may write a perturbation series for the transition amplitude

$$a_2(\infty)=\sum_{k=0}^{\infty}(-1)^k a_2^{(2k+1)}\,, \tag{9a}$$

$$\begin{aligned} a_2^{(1)}&=-i\int_{-\infty}^{\infty}V(t_1)e^{-i\Delta t_1}dt_1\,,\\ a_2^{(2k+1)}&=-i\int_{-\infty}^{\infty}V(t_1)e^{-i\Delta t_1}\\ &\quad\times\prod_{j=2}^{2k+1}\int_{-\infty}^{t_{j-1}}V(t_j)e^{\Delta i(-1)^j t_j}dt_j\,. \end{aligned} \tag{9b}$$

This series converges absolutely for all A finite.[10] For symmetric pulses, each term in Eq. (9b) is a pure imaginary (see Appendix C), so that one may replace the exponential factors in the integrals by cosines, so that the $a_2^{(2k+1)}$ are all invariant under a change of sign in Δ. It is convenient to rewrite Eq. (9a) in the form

$$R=\frac{a_2}{a_2^{(1)}}=1+\frac{\sum_{k=1}^{\infty}(-1)^k a_2^{(2k+1)}}{a_2^{(1)}}\,. \tag{10}$$

The ratio of the amplitudes $a_2/a_2^{(1)}=R$ is similarly an even function of the detuning. If a representation of R as a power series in Δ exists, it is clear that only even powers of the detuning are present. In general then, if R is differentiable with respect to Δ, at $\Delta=0$, we may write $R(\Delta)=R(\Delta=0)+O(\Delta^2)$. Since $R(\Delta=0)=(\sin A)/A$ for arbitrary coupling potentials, we immediately find that if the derivative with respect to Δ of R at $\Delta=0$ exists, then the Rosen-Zener conjecture is valid with a correction term of order Δ^2, i.e.,

$$a_2(\Delta)=\frac{\sin A}{A}a_2^{(1)}(\Delta)+O(\Delta^2)\,. \tag{11}$$

One can easily show that a sufficient condition for R to be differentiable at resonance is that $\tilde{V}(\omega)$, the Fourier transform of $V(t)$ be differentiable at $\omega=0$. Recalling that third- and higher-order terms of the perturbation expansion may be written in the frequency domain,[9] in terms of $\tilde{f}(\omega)$, the Fourier transform of $f(t)$, we have

$$a_2^{(2k+1)}=\lim_{\lambda\to 0}\frac{1}{(2\pi)^{k-1/2}}\int_{-\infty}^{\infty}d\omega_2\cdots d\omega_{2k+1}\tilde{f}\left[\sum_{j=2}^{2k+1}\omega_j-\Delta\right]\prod_{j=2}^{2k+1}\left[\frac{\tilde{f}(\omega_j)}{\sum_{l=j}^{2k+1}\{\omega_l-i\lambda+\frac{1}{2}[1+(-1)^{l+1}]\Delta\}}\right]. \tag{12}$$

Making the change of variable $\Delta\nu_j=\omega_j$,

$$a_2^{(2k+1)}=\lim_{\lambda\to 0}\frac{1}{(2\pi)^{k-1/2}}\int_{-\infty}^{\infty}d\nu_2\cdots d\nu_{2k+1}\tilde{f}\left[\Delta\left[\sum_{j=2}^{2k+1}\nu_j-1\right]\right]\prod_{j=2}^{2k+1}\left[\frac{\tilde{f}(\Delta\nu_j)}{\sum_{l=j}^{2k+1}\{\nu_l-i\lambda+\frac{1}{2}[1+(-1)^{l+1}]\}}\right]. \tag{13}$$

The derivative of the transition amplitude with respect to Δ contains factors proportional to $f'(\Delta\nu)$. Since if $f'(0)$ exists, it is zero by symmetry, the leading correction will be of second order.

The foregoing implies that if the first derivative of the Fourier transform does not exist at zero detuning, the leading correction to the Rosen-Zener conjecture will be first order in $|\,\Delta\,|$. An exception will occur if the contribution to the linear terms in the derivatives of a_2 and $a_2^{(1)}$ exactly cancel. Intuitively, the possibility of this happening seems to be remote, but it would be useful if one could nonlaboriously verify the presence of linear corrections.

The variational method for calculating the eigenvalues provides an opportunity to check the dependence at small detunings of the corrections to the Rosen-Zener conjecture, since these will manifest themselves in EV shifts. The presence of an eigenvalue shift proportional to Δ cannot be the signature of quadratic corrections to the expression for the transition amplitude.

As an example, we examine the case of the Lorentzian, whose Fourier transform, $\tilde{f}=e^{-|\Delta|}/\sqrt{2\pi}$ is manifestly nondifferentiable at $\Delta=0$. At resonance, the first node in the transition amplitude occurs, of course, for a pulse area of π. For the purpose at hand, it is sufficient to demonstrate that, for small Δ, there is a linear correction in this first eigenvalue. The resonant normalized eigenfunction is $\sqrt{2}/[\pi(1+t^2)]^{1/2}$. Off resonance, we choose a trial unnormalized eigenfunction of the form

$$\tilde{a}_T=e^{-i\Delta t}\frac{1}{(1+t^2)^{1/2}}\frac{1}{1+\alpha^2t^2}\;. \tag{14}$$

[The factor $(1+\alpha^2t^2)^{-1}$ is needed to render one of the integrals in Eq. (7) convergent. No such factor is required on resonance, since inverse powers of f are removed when a is differentiated with respect to time.] We have thus constructed a single-parameter trial function. In general then, our variational estimate of A^2 will be a function of α and Δ. If we were interested in maximizing the accuracy of the calculation of the EV, we would optimize with respect to α. In the present case, it is much simpler and sufficient to perform a nonoptimal calculation by evaluating the integrals, passing to the limit of $\alpha\to 0$, and retaining only terms linear in Δ. The results for the integration are given in Appendix A. I find that the smallest A^2 that corresponds to a vanishing transition probability is given by

$$A^2=\pi^2\frac{1+3|\Delta|}{1+|\Delta|}\;. \tag{15}$$

It turns out, incidentally, that this crude trial function gives a result that is a surprisingly accurate approximation to the eigenvalue. For $\Delta=0.1$, Yeh and Berman[12] have performed numerical calculations of the transition amplitude for a Lorentzian pulse as a function of pulse area. Their values are exhibited in Table I. To within the author's ability to interpolate, the eigenvalue deduced from the table is in exact agreement with that calculated from Eq. (15).

The EV method is also of value in establishing certain characteristics of the spectrum for potentials whose Fourier transforms are differentiable at $\Delta=0$. I have previously shown that the leading correction term to the Rosen-Zener conjecture is of order Δ^2 by means of a perturbation expansion for the transition amplitude. That is,

$$a_2=-i\sqrt{2\pi}\tilde{V}(\Delta)\left[\frac{\sin A}{A}+O(\Delta^2)\right]. \tag{16}$$

An important question that remains is whether or not the coefficient of Δ^2 remains small for all pulse areas, or whether for sufficiently large A^2, it grows and eventually dominates over the term $(\sin A)/A$. Since the Rosen-Zener surmise is exact in the limit where first-order perturbation theory is valid, the leading correction term in the coefficient of Δ^2 is proportional to A^2, and so that it is trivially true that, for small Δ, one may use the Rosen-Zener expression for transition amplitudes with impunity, provided that one is in a regime of interaction strengths where third-order theory would be correct. Our goal is to go further than this level of approximation. We again use our variational method for estimating A^2 eigenvalues to show, approximately, that the coefficient of Δ^2 does not grow with A^2 relative to $(\sin A)/A$ so that the smallness of the Δ^2 coefficient applies to general theories, not just those correct to third order.

TABLE I. Transition probability $|a_2(\infty)|^2$ for a Lorentzian pulse, $V=(A/\pi)(1+t^2)^{-1}$ at detuning $\Delta=0.1$.

Pulse area A	Transition probability $\|a_2(\infty)\|^2$
0.1π	0.077
0.2π	0.282
0.3π	0.546
0.4π	0.782
0.5π	0.911
0.6π	0.892
0.7π	0.731
0.8π	0.483
0.9π	0.229
1.0π	0.050
1.1π	0.002
1.2π	0.093
1.3π	0.286
1.4π	0.511
1.5π	0.689

Again, let us choose a trial function which reduces to the known resonant $\tilde{a}_n$,

$$\tilde{a}_T=e^{-i\Delta t}\sin\left[n\pi\int_{-\infty}^{t}f(t')dt'\right]\phi(\alpha,t)\;.$$

The factor $\phi(\alpha,t)$ assumes the role of guaranteeing convergence that $1/(1+\alpha^2t^2)$ did in the specific case of the Lorentzian. If the Fourier transform $\tilde{f}(\omega)$ has a vanishing derivative at zero detuning, the eigenvalue will be of the form $n^2\pi^2-s^2\Delta^2$ where the limit $\alpha\to 0$ is taken after the integrals are performed. We obtain

$$A_n^2=\frac{\int_{-\infty}^{\infty}e^{-i\Delta t}dt\left[n^2\pi^2f(t)\cos^2\left[n\pi\int_{-\infty}^{t}f(t')dt'\right]-\frac{\Delta^2}{2f}\right]}{\int_{-\infty}^{\infty}e^{-i\Delta t}dtf(t)\sin^2\left[n\pi\int_{-\infty}^{t}f(t')dt'\right]}\;. \tag{17}$$

For $n\to\infty$ (large pulse areas), we replace $\sin^2 n\pi z, \cos^2 n\pi z$ by their averages, so that the correction terms in the eigenvalue expression become independent of n. That is, the correction terms do not depend on pulse area to the extent that the variational approximation is valid, i.e., the roots of $a_2/a_2^{(1)}$ are all displaced essentially the same. This could hardly be so if the full correction term grew strongly with pulse area. Robiscoe[3] has recently studied this question perturbatively through third order. He also gives an expression for the leading term of the Δ^2 correction.

I checked my conclusion by performing calculations of the transition amplitude as a function of detuning and pulse area for the potential,

$$V=A\frac{\pi}{2T}\operatorname{sech}^2\frac{\pi t}{T}\ , \tag{18}$$

the square of the hyperbolic secant. For this potential, the equations of motion Eq. (2) can be solved analytically,[13] although no simple formula for a_2 analogous to Eq. (8) for the Rosen-Zener linear hyperbolic secant[2] has been derived. Our results indicate that for $\operatorname{sech}^2\pi t/T$, the Rosen-Zener conjecture is an accurate approximation, at least for pulse areas up to 6π and $\Delta T<2\pi$. (If one wished to solve this problem perturbatively for $A=6\pi$, a series of about 50 terms would be required for convergence, so that it is evident that the smallness of Δ^2 correction persists beyond low order.)

IV. AN EIGENFUNCTION EXPANSION FOR TRANSITION AMPLITUDES

As noted above, the set of functions b_n (or, equivalently, a_n) is complete. Accordingly, one may use it as a basis for expanding unknown functions. In particular, if b_2 is the solution to Eq. (4b) for a value of A^2 that does not correspond to an eigenvalue, we may express this function in terms of the eigenfunctions in the range $-\frac{1}{2}\le z<\frac{1}{2}$. The transition amplitude $b_2(\frac{1}{2})$ may be deduced from the expansion by standard mathematical procedures. This approach may prove more efficient, for example, than direct solution in calculating transition amplitudes numerically, if one wishes to find transition probabilities for a very large number of pulse areas, since the amount of numerical work will depend on the number of eigenfunctions needed for convergence, not on the number of pulse areas to be analyzed. The formal methodology is strongly reminiscent of the R-matrix approach to scattering theory.[14]

Let b_n represent an eigenfunction that is normalized to unity. The expansion of b_2 may be written

$$b_2(z)=\sum \alpha_n b_n(z)=\sum b_n(z)\int b_n(z')b_2(z')dz'\ . \tag{19}$$

The equations of motion for b_n, b_2 are

$$-b_2''-\left[\frac{if'\Delta}{2f^2}+\frac{\Delta^2}{4f^2}\right]b_2=A^2b_2\ , \tag{20a}$$

$$-b_n''-\left[\frac{if'\Delta}{2f^2}+\frac{\Delta^2}{4f^2}\right]b_n=A_n^2b_n\ . \tag{20b}$$

Multiply Eq. (20a) by b_n, Eq. (20b) by b_2, subtract and integrate over all allowed z. This yields

$$-(b_2''b_n-b_2b_n'')=(A^2-A_n^2)b_2b_n\ , \tag{21a}$$

$$-(b_2'b_n-b_2b_n')\,|_{z=-1/2}^{z=+1/2}=(A^2-A_n^2)\int_{-1/2}^{1/2}b_z(z)b_n(z)dz\ , \tag{21b}$$

a result obtained from Green's theorem. We have, for the boundary conditions $b_2(-\frac{1}{2})=b_n(-\frac{1}{2})=b_n(+\frac{1}{2})=0$,

$$\begin{aligned}\alpha_n&=\frac{b_2(\frac{1}{2})b_n'(\frac{1}{2})}{A^2-A_n^2}\ ,\\ b_2(z)&=\sum_n \alpha_n b_n(z)\\ &=b_2(\tfrac{1}{2})\sum_n\frac{b_n'(\frac{1}{2})b_n(z)}{A^2-A_n^2}\ ,\\ b_2(\tfrac{1}{2})&=\frac{b_2(z)}{\sum_n[b_n'(\frac{1}{2})b_n(z)/(A^2-A_n^2)]}\ .\end{aligned} \tag{22}$$

Equation (22) holds for all pulse areas, so that it is valid in the limit of weak potential strengths where first-order perturbation theory holds. If we designate $b_2^{(1)}(z)=Ac_2(z)$, the first-order approximation to $b_2(z)$, then

$$c_2(\tfrac{1}{2})=\frac{c_2(z)}{\sum_n[b_n'(\frac{1}{2})b_n(z)/(-A_n^2)]}\ . \tag{23}$$

Now for sufficiently early times, first-order perturbation theory holds for all pulse areas, so that

$$\begin{aligned}b_2(\tfrac{1}{2})&=\lim_{z\to-1/2}\frac{Ac_2(z)}{\sum_n[b_2'(\frac{1}{2})b_n(z)/(A^2-A_n^2)]}\\ &=\lim_{\substack{z\to-1/2\\ z'\to+1/2}}b_2^{(1)}(\tfrac{1}{2})\frac{\sum_n[b_n(z)b_n'(z')/-A_n^2]}{\sum_n[b_n(z)b_n'(z')/(A^2-A_n^2)]}\ .\end{aligned} \tag{24}$$

We may approach Eq. (24) from two perspectives. For numerical calculations, it clearly provides an alternative to a direct solution of the equations of motion. Instead of solving Eq. (3) anew for each pulse area, one solves for a sufficient number of eigenfunctions and eigenvalues to obtain convergence in Eq. (24). This procedure yields the transition amplitude for all pulse areas at once, and, if it is desired to obtain answers for a large number of coupling strengths, is much more efficient than repetitive, direct solutions.

Equation (24) also leads to an approximation scheme for $b_2(\frac{1}{2})$. The summations are very closely related to Green's functions. That is, the Green's function $G(\lambda,z,z')$ is defined by

$$G(\lambda,z,z')=\sum_n\frac{b_n(z)b_n(z')}{\lambda-A_n^2}\ , \tag{25}$$

so that Eq. (24) for $b_2(\frac{1}{2})$ may be written

$$b_2(\tfrac{1}{2})=b_2^{(1)}(\tfrac{1}{2})\lim_{\substack{z\to-1/2\\ z'\to+1/2}}\left[\frac{\frac{\partial}{\partial z'}G(0,z,z')}{\frac{\partial}{\partial z'}G(A^2,z,z')}\right]\ . \tag{26}$$

The Green's function satisfies the equation

$$\left[-\frac{d^2}{dz^2}-\frac{\Delta^2}{4f^2}-\frac{if'\Delta}{2f^2}-\lambda\right]G=-\delta(z-z') . \qquad (27)$$

It is, of course, at least as difficult to solve Eq. (27) for $G(\lambda,z,z')$ exactly as it is to solve Eq. (3). However, there exist variational principles that enable one to approximate Green's functions.[15] If G and G_T represent the Green's function and a trial estimate, respectively, with $\Delta G=G-G_T$, then

$$G=2G_T+\int_{-1/2}^{1/2}dz''[G_T(\lambda,z,z'')(L-\lambda)G_T(\lambda,z'',z')] +O((\Delta G)^2) , \qquad (28)$$

where L is the operator on the left side of Eq. (4b).

As a simple application of Eq. (28), I present an expression for the transition amplitude at small detunings for pulse shapes that are symmetric in time, and whose Fourier transforms are differentiable at zero frequency. At $\Delta=0$, the eigenvalues $A_n^2=n^2\pi^2$, while, for small detunings, it is shown in Appendix B that they are given by $A_n^2=n^2\pi^2-s^2\Delta^2$, where the shift parameter s is approximately independent of n, and is a function of the pulse shape. For the hyperbolic secant of Rosen and Zener, $s=0$, while for the rectangular pulse, s is rigorously independent of n and there are no correction terms of higher order than second in Δ. It is shown in Appendix D that the transition amplitude for this case is approximately given by

$$b_2=b_2^{(1)}\{[\sin(A^2+\Delta^2s^2)^{1/2}]/(A^2+\Delta^2s^2)^{1/2}\}(\Delta s)/\sin\Delta s , \qquad (29)$$

a formula which is exact for the hyperbolic secant and rectangular pulses and for all symmetric pulses with differentiable Fourier transforms in the weak coupling regime. To test its usefulness in other cases, I have compared its predictions with the numerical calculations of Yeh and Berman[12] for the case of the envelope function $f(t)=(\pi/2)\text{sech}^2\pi t$, at detuning $\Delta=4$. The results, which are presented in Table II, show remarkably good agreement, especially considering that the detuning parameter, $\Delta/2\pi$, is not vanishingly small compared to unity. We note that the range of pulse areas in the table is entirely outside the weak coupling regime.

TABLE II. Transition probability $|a_2(+\infty)|^2$ for the pulse $f=(\pi/2)\text{sech}^2\pi t$ at detuning $\Delta=4$.

Pulse area A	$\lvert a_2(\infty)^2\rvert$ (exact)[a]	$\lvert a_2(\infty)^2\rvert$ [Eq. (29)]
$4/\pi$	0.269	0.273
$6/\pi$	0.245	0.248
$8/\pi$	0.068	0.069
$16/\pi$	0.295	0.311

[a]Numerical calculations of Yeh and Berman (Ref. 12).

V. SUMMARY

I have developed the ideas of eigenvalues of pulse area squared in two-level systems introduced in a previous paper, pointing out the existence of a variational principle for estimating these quantities. Examples have been given where knowledge of the dependence of the eigenvalues on potential and detuning parameters may assist one in understanding the qualitative behavior of two-level spectra. First, using noneigenvalue methods, I showed that if the derivative of the Fourier transform of a symmetric potential with respect to detuning does not exist at $\Delta=0$, the small-detuning correction to the Rosen-Zener conjecture is linear in Δ, unless cancellation of the nondifferentiability between exact and first-order transition amplitudes occurs. I then proceed via eigenvalue methods to show that this cancellation does not occur in the case of a Lorentzian potential. Similarly, the eigenvalue method was used to demonstrate that the quadratic correction to the Rosen-Zener conjecture that exists in the case of potentials with Fourier transforms that are differentiable with respect to Δ remains small for large pulse areas. Thus, the low-detuning form of the conjecture applies more generally than to the coupling regime where the two leading terms of perturbation theory suffice.

Furthermore, since the zeros of the transition amplitude as a function of A^2 occur for $A^2=n^2\pi^2+O(\Delta^2)$, it is clear that the nodes considered as a function of A are

$$n\pi[1+O(\Delta^2)/n^2\pi^2]^{1/2}\simeq n\pi+O(\Delta^2)/2n\pi ,$$

i.e., the shift in the position of the roots with A decreases as $1/n$.

Finally, I demonstrated that transition amplitudes could be expressed in terms of the A^2 eigenvalues and their corresponding eigenfunctions, and derived the relevant expansion. This expansion may be used both in numerical calculations of $b_2(\frac{1}{2})$, and in analytic, variational approximations. A simple application of the latter is presented for the case of a symmetric pulse whose Fourier transform is differentiable at zero frequency.

ACKNOWLEDGMENTS

The author is indebted to Dr. A. Bambini and Professor P. R. Berman for valuable discussions. He would also like to thank Professor Berman for his and S. Yeh's numerical calculations of transition probabilities given in the tables. This work was supported by the Office of Naval Research.

APPENDIX A: VARIATIONAL CALCULATION OF THE SMALL DETUNING DEPENDENCE OF THE EV FOR A LORENTZIAN PULSE

In this appendix, I shall use Eq. (7) to calculate, for a Lorentzian pulse, the shift due to detuning of the value of the EV. I calculate displacement of the node in transition probability that occurs at $A^2=\pi^2$ on resonance.

The unnormalized eigenfunction for $\Delta=0$ is

$$\tilde{a}=\sin\left[\pi\int_{-\infty}^{t}f(t')dt'\right]=\frac{1}{(1+t^2)^{1/2}}\ .$$

I base the trial functions for the slightly off-resonant case on this function, choosing

$$\tilde{a}=\frac{e^{-i\Delta t}}{(1+t^2)^{1/2}(1+\alpha^2t^2)}\ . \tag{A1}$$

The $e^{-i\Delta t}$ factor mimics the Rosen-Zener eigenfunction. We shall later pass to the limit $\alpha\to 0$. The contribution $(1+\alpha^2t^2)^{-1}$ makes every integral which appears in Eq. (7) convergent under all definitions. The omission of this factor renders one of the integrals divergent in the ordinary sense, although it is expressible in terms of delta functions. I prefer to retain this convergence factor partially because an analogous feature is employed in the next appendix, where integrals are not explicitly performed, and where it is desired that ambiguities related to convergence not arise.

The time derivative of the trial function for small Δ is

$$\dot{\tilde{a}}=\frac{e^{-i\Delta t}}{1+\alpha^2t^2}\left[\frac{-i\Delta}{(1+t^2)^{1/2}}-\frac{t}{(1+t^2)^{3/2}}\right]+O(\alpha)\ . \tag{A2}$$

Terms proportional to α will not be carried any further.

The integrands of numerator and denominator become, respectively,

$$N=\frac{e^{i\Delta t}\dot{\tilde{a}}^2}{f}=\pi\frac{e^{-i\Delta t}}{(1+\alpha^2t^2)^2}\left[-\Delta^2+\frac{2i\Delta t}{1+t^2}+\frac{t^2}{(1+t^2)^2}\right]\ , \tag{A3}$$

$$D=e^{i\Delta t}\tilde{a}^2f=\frac{1}{\pi}\frac{e^{-i\Delta t}}{(1+\alpha^2t^2)^2}\left[\frac{1}{(1+t^2)^2}\right]\ , \tag{A4}$$

where we recall $f=(1/\pi)(1+t^2)^{-1}$.

We may evaluate $\int_{-\infty}^{\infty}N\,dt$ and $\int_{-\infty}^{\infty}D\,dt$ in the complex plane, choosing contours that include the real axis and are closed by semicircles, whose contributions to the integral vanish, in the upper (lower) half-plane for negative (positive) detuning. The results are

$$\int D\,dt=\frac{1}{2\pi}(1+|\Delta|)$$

and

$$\int N\,dt=\frac{\pi}{2}(1+|3\Delta|)\ .$$

I have omitted the effect of poles at $t=\pm i/\alpha$ which make contributions proportional to $e^{-|1/\alpha|}\to 0$. Thus the variational approximation for the EV is

$$A^2=\pi^2\frac{1+3|\Delta|}{1+|\Delta|}\ , \tag{A5}$$

which contains a correction term to the resonant eigenvalue that is manifestly linear in the detuning.

APPENDIX B: ON THE APPROXIMATE CONSTANCY OF THE Δ^2 CORRECTION TERM TO THE EV

In this appendix, I shall apply the variational method, Eq. (7), to symmetric pulses whose Fourier transforms are differentiable at $\Delta=0$. This will demonstrate that the term in the expression for the EV quadratic in the detuning is approximately independent of pulse area.

At resonance, the eigenvalue and unnormalized eigenfunction, for "quantum number" n are $n^2\pi^2$ and $\sin[n\pi\int_{-\infty}^{t}f(t')dt']$. We choose the nonresonant trial eigenfunction to be

$$\tilde{a}=\phi(\alpha,t)\sin\left[n\pi\int_{-\infty}^{t}f(t')dt'\right]e^{-i\Delta t}\ .$$

Then

$$\dot{\tilde{a}}=e^{-i\Delta t}\phi(\alpha,t)\left[-i\Delta\sin\left[n\pi\int_{-\infty}^{t}f(t')dt'\right]+n\pi f\cos\left[n\pi\int_{-\infty}^{t}f(t')dt'\right]\right]\ ,$$

where ϕ is a convergence factor equal to unity for finite time, $\to 0$ as $|t|\to\infty$. Integrals whose integrands contain derivatives of ϕ are neglected. The integrands become

$$N=\frac{\dot{\tilde{a}}^2}{f}e^{i\Delta t}=[\phi(\alpha,t)]^2e^{-i\Delta t}\left[-\frac{\Delta^2}{f}\sin^2\left[n\pi\int_{-\infty}^{t}f(t')dt'\right]-i\Delta n\pi\sin\left[2\pi n\int_{-\infty}^{t}f(t')dt'\right]+n^2\pi^2f(t)\cos^2\left[n\pi\int_{-\infty}^{t}f(t')dt'\right]\right]\ , \tag{B1}$$

$$D=\tilde{a}^2fe^{i\Delta t}=[\phi(\alpha,t)]^2f(t)e^{-i\Delta t}\sin^2\left[n\pi\int_{-\infty}^{t}f(t')dt'\right]\ . \tag{B2}$$

Integrating the second term in the numerator by parts, and combining it with the third term, we have

$$\int_{-\infty}^{\infty}N\,dt=\int_{-\infty}^{\infty}e^{-i\Delta t}dt\left[n^2\pi^2f(t)\cos^2\left[n\pi\int_{-\infty}^{t}f(t')dt'\right]-\frac{\Delta^2}{2f}\right][\phi(\alpha,t)]^2\ .$$

The second integral is independent of n. If we replace the factor $\cos^2[n\pi\int_{-\infty}^{t}f(t'dt']$, in the first integral by its average value of $\frac{1}{2}$, and make a similar substitution for $\sin^2[\pi n\int_{-\infty}^{t}f(t')dt']$ in the denominator, the eigenvalue becomes $n^2\pi^2+O(\Delta^2)$, where the $O(\Delta^2)$ term is independent of n. This approximation clearly improves with increasing n. We also note that the scheme of replacing the squares of the sinusoidal function by their averages gives the exact eigenvalue on resonance.

We have assumed that f is of a single algebraic sign. If this is true, and if the ansatz of replacing the squares of sinusoidal functions by their averages is valid, the shift in the eigenvalue from its resonant value is negative semidefinite. That is, the zeros off resonance occur for pulse areas that are never larger than the corresponding zeros at resonance. This differs from the Lorentzian case, whose nonresonant transition probability nodes occur for larger pulse areas than do the resonant nodes.

APPENDIX C: PROOF THAT THE TRANSITION AMPLITUDE IN A TWO-LEVEL SYSTEM DRIVEN BY A SYMMETRIC PULSE IS PURELY IMAGINARY

It was shown in a previous paper[10] that the perturbation expansion for the transition amplitude in a two-level system

$$ia_2 = \int_{-\infty}^{\infty} V(t)e^{-i\Delta t}dt - \int_{-\infty}^{\infty} V(t)e^{-i\Delta t}dt \int_{-\infty}^{t} V(t')e^{+i\Delta t'}dt \int_{-\infty}^{t'} V(t'')e^{-i\Delta t''}dt'' + \cdots , \tag{C1}$$

is convergent for finite pulse areas. Therefore, if we show that each individual term on the right-hand side is real, a_2 will be imaginary and unchanged by reversing the sign of Δ. Accordingly, if $(da_2/d\Delta)\,|_{\Delta}=0$ exists, it will vanish.

For $V(t)=V(-t)$, the first-order term, $\int_{-\infty}^{\infty} V(t)e^{-i\Delta t}dt$, is clearly real. We shall indicate how to demonstrate the reality of the term

$$\int_{-\infty}^{\infty} V(t)e^{-i\Delta t}dt \int_{-\infty}^{t} V(t')e^{+i\Delta t'}dt' \int_{-\infty}^{t'} V(t'')e^{-i\Delta t''}dt'' .$$

The method used may readily be extended to fifth- and higher-order contributions.

Robinson and Berman[10] showed that the terms in the perturbation series could be explicitly written in the frequency domain. The third-order term $ia_2^{(3)}$, is proportional to

$$I_3 = \lim_{\lambda\to 0} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\tilde{f}(\Delta y_1)\tilde{f}(\Delta y_2)\tilde{f}[\Delta(y_1+y_2-1)]}{(y_1-1-i\lambda)(y_1+y_2-i\lambda)} dy_1 dy_2 , \tag{C2}$$

where, for $f(t)$ temporally symmetric, the Fourier transform $\tilde{f}(\omega)$, is real for all ω. Using the identity

$$\lim_{\epsilon\to 0} \int \frac{\phi(x)dx}{x-x_0\mp i\epsilon} = P\int \frac{\phi(x)}{x-x_0} \pm i\pi\phi(x_0) , \tag{C3}$$

and integrating with respect to y_1

$$\begin{aligned} I_3 = {} & \int_{-\infty}^{\infty} dy_2 P \int_{-\infty}^{\infty} dy_1 \frac{\tilde{f}(\Delta y_1)\tilde{f}(\Delta y_2)\tilde{f}[\Delta(y_1+y_2-1)]}{(y_1-1)(y_1+y_2)} \\ & + \lim_{\lambda\to 0} i\pi \int_{-\infty}^{\infty} dy_2 \tilde{f}(\Delta)[\tilde{f}(\Delta y_2)]^2 \left[\frac{1}{1+y_2-i\lambda} - \frac{1}{1+y_2+i\lambda} \right] , \end{aligned} \tag{C4}$$

where the P for the first integral should be understood to indicate that the integration excludes the neighborhoods of both $y_1=1$ and $y_1=-y_2$. This first term contains only real factors and is manifestly real. If, in the terms proportional to $i\pi$, we partition both contributions according to Eq. (C3), the principal value portions exactly cancel, leaving only a contribution proportional to $2(i\pi)^2[\tilde{f}(\Delta)]^3$, which is also obviously real.

That the transition amplitude is inherently imaginary has been explicitly shown to be true for all symmetric pulses, whether or not the perturbation expansion converges.[16]

APPENDIX D: EVALUATION OF THE TRANSITION AMPLITUDE FOR A SYMMETRIC PULSE WITH DIFFERENTIABLE FOURIER TRANSFORM BY THE GREEN'S FUNCTION METHOD. SMALL-DETUNING CASE

In this appendix, I derive an approximate formula for the small-detuning transition amplitude for a two-level system driven by a pulse whose shape is temporally symmetric and whose Fourier transform is differentiable at zero frequency. I shall use Eq. (26) to obtain $b_2(\frac{1}{2})$, estimating the Green's function from the variational principle, Eq. (28).

As a preliminary, it is convenient to write down the Green's function $G_0(\lambda,z,z')$ for the case of $\Delta=0$, in terms of its eigenfunction expansion, and in explicit form as well. These are, respectively,

$$G_0 = 2\sum \frac{\sin[n\pi(z-\frac{1}{2})]\sin[n\pi(z'-\frac{1}{2})]}{\lambda-n^2\pi^2} , \tag{D1}$$

$$G_0 = \frac{\sin[\sqrt{\lambda}(z_< + \frac{1}{2})]\sin[\sqrt{\lambda}(z_> - \frac{1}{2})]}{\sqrt{\lambda}\sin\sqrt{\lambda}} . \tag{D2}$$

We choose the following form for the trial Green's function

$$G_T=e^{-i\Delta(t+t')/2}\phi(\alpha,t)\phi(\alpha,t')\left[\sum_n a_n \frac{\sin[n\pi(z-\frac{1}{2})]\sin[n\pi(z'-\frac{1}{2})]}{\int_{-1/2}^{1/2} e^{-i\Delta t''}\sin^2[n\pi(z''-\frac{1}{2})]dz''}\right], \tag{D3}$$

where a_n is an adjustable parameter, and $\phi(\alpha,t)$ is a convergence factor with the property that it is unity at finite times and approaches zero sufficiently rapidly as $t\rightarrow\pm\infty$ to rid integrands of any divergences. We assume, in performing parts integrations, that integrands which contain derivatives of ϕ may be neglected.

This trial function is then substituted into Eq. (28), and optimized with respect to the a_n. The integrals are evaluated by making an ansatz similar to that of Appendix B—squares of trigonometric functions are replaced by their average values, and products of trigonometric functions of arguments $n\pi z, m\pi z, m\neq n$, are neglected. With these assumptions, we find

$$a_n=(\lambda-\widetilde{A}_n^2)^{-1}, \tag{D4}$$

where $\widetilde{A}_n^2$ is the approximate eigenvalue calculated in Appendix B, given, to quadratic terms in the detuning, by $\widetilde{A}_n^2=n^2\pi^2-s^2\Delta^2$. The shift parameter, as indicated previously, is approximately independent of n. It does, of course, depend on the particular pulse shape. The Green's function is given by

$$G=\sum_n \frac{e^{-i\Delta(t+t')/2}\phi(\alpha,t)\phi(\alpha,t')\sin[n\pi(z-\frac{1}{2})]\sin[n\pi(z'-\frac{1}{2})]}{N_n(\lambda-n^2\pi^2+s^2\Delta^2)}, \tag{D5}$$

where the normalizing factor

$$N_n=\int_{-1/2}^{1/2}\phi^2(\alpha,t'')e^{-i\Delta t''}\sin^2[n\pi(z''-\tfrac{1}{2})]dz''=N$$

is independent of n in our approximation, and will drop out when the ratio given in Eq. (28) is calculated. The Green's function of Eq. (D5) has the explicit form

$$G=\frac{N}{2}\phi(\alpha,t)\phi(\alpha,t')e^{-i\Delta(t+t')/2} \times\frac{\sin\bar{A}(z_<+\frac{1}{2})\sin\bar{A}(z_>-\frac{1}{2})}{\bar{A}\sin\bar{A}}, \tag{D6}$$

where $\bar{A}=(\lambda+s^2\Delta^2)^{1/2}$. If $G(0,z,z')$, $G(A^2,z,z')$ are differentiated with respect to z', and one passes to the limit $z\rightarrow-\frac{1}{2}, z'\rightarrow+\frac{1}{2}$ as in Eq. (26), we obtain Eq. (29).

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