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Perturbative solution to the time-dependent two-level problem and the validity of the Rosen-Zener conjecture

R. T. Robiscoe
Physics Department, Montana State University, Bozeman, Montana 59717

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We consider the time-dependent two-level problem of quantum mechanics, where the levels are coupled by a radio-frequency pulse with an arbitrary time-dependent envelope $V(t)$. We derive an approximate solution for the system's transition amplitude $P(\infty)$ which is correct to the third order of perturbation theory, and which applies to all pulses $V(t)$ with finite first and second moments which obey the following: $\lim t^3V(t)=0$, as $t\rightarrow\infty$. Our form of solution for $P(\infty)$ provides a criterion for judging the validity of a solution previously conjectured by Rosen and Zener, and it is generally useful for providing line-shape details in many cases of practical interest.

I. INTRODUCTION

A problem of continuing interest in quantum mechanics is to calculate the transition amplitude for a two-level system whose levels are coupled by a time-dependent interaction. With level amplitudes $S(t)$ and $P(t)$ interacting via a coupling pulse $U(t)\exp(i\nu t)$, which contains a rotating wave factor at frequency ν and an envelope function $U(t)$, the system is governed by the rate equations

$$\begin{aligned} i\dot{S} &= V^*(t)P\exp(i\Omega t)\ , \\ i\dot{P} &= V(t)S\exp(-i\Omega t)\ . \end{aligned} \tag{1}$$

Here $V(t)$ is the matrix element of the envelope function connecting the levels, and $\Omega=\omega_{sp}-\nu$ is the frequency off-resonance. For physical couplings, $V(t)$ vanishes as $t\rightarrow\pm\infty$, and one wishes to calculate the transition amplitude $P(\infty)$ for initial conditions: $S(-\infty)=1$, $P(-\infty)=0$. So far as we know, this can be done exactly for $\Omega\neq 0$ in only a few nontrivial cases: (1) $V(t)=$ const over some time interval and zero otherwise, (2) $V(t)\propto \operatorname{sech}(t/T)$, a case first solved by Rosen and Zener,[1] (3) a class of pulses asymmetric in time recently treated by Bambini and Berman.[2,3] Solutions for $P(\infty)$ for such physically interesting cases as Gaussian or Lorentzian pulse shapes apparently do not exist, at least not in terms of elementary functions.

In connection with estimating $P(\infty)$ for general pulses $V(t)$, Rosen and Zener[1] suggested the following solution (to within an arbitrary phase);

$$P(\infty)=[F(T,\Omega)/A]\sin A\ . \tag{2}$$

Here,

$$F(T,\Omega)=\int_{-\infty}^{\infty}V(t)\exp(-i\Omega t)dt$$

and is the pulse Fourier transform at frequency Ω, which depends also on the pulse width T, and $A=F(T,0)$ is the pulse area. Rosen and Zener showed that $P(\infty)$ of Eq. (2) is exact for the hyperbolic secant pulse, and they conjectured that this result held for "all nonsingular (coupling pulses), i.e., all functions which are continuous and whose first derivatives are continuous." The Rosen-Zener conjecture is also exact for all pulses on resonance, $\Omega=0$ [see Eq. (5) below], for all sufficiently narrow pulses [in the δ-function limit, see Eq. (35) below], and it holds approximately in the weak-coupling limit, $A\rightarrow 0$.[4] On the other hand, numerical solutions to Eqs. (1) show that the Rosen-Zener conjecture does not hold in general, although some expected features of $P(\infty)$ for Gaussian and Lorentzian pulses are divulged by use of Eq. (2).[2] What is lacking is an analytic criterion for deciding how good an approximation the Rosen-Zener conjecture is for a given pulse. More generally, one would like to solve Eqs. (1), at least approximately, for arbitrary coupling pulses $V(t)$ so as to determine how the actual transition amplitude $P(\infty)$ deviates from the Rosen-Zener conjecture. Such a solution should be of general utility in many spectroscopic applications.

In this paper we derive an approximate form for $P(\infty)$ which is valid for all pulses obeying the criterion $t^3V(t)\rightarrow 0$, as $t\rightarrow\pm\infty$. This limit excludes Lorentzian pulse shapes, but includes Gaussians, exponentials, etc. Our result for $P(\infty)$ is correct to the third order of perturbation theory, i.e., order A^3, and it reproduces several well-known results to this order.[5] Our form for $P(\infty)$ is given as a correction factor $f(\infty)$ times the solution of Eq. (2), so that the applicability of the Rosen-Zener conjecture may be judged by how closely $f(\infty)$ approaches unity. In Sec. II we discuss the nature of solutions for the transition amplitude $P(t)$ which resemble the Rosen-Zener conjecture. We show that there are no nontrivial pulses for which the conjecture holds at finite times, and we derive the differential equation for the correction factor $f(t)$. In Sec. III we derive a solution for $f(t)$ which is correct to terms of order A^2 and Ω^2. Our solution is given in terms of integrals over the first and second moments of the pulse distribution. In Sec. IV we check our result for $P(\infty)$ against various known solutions, apply it to several cases of physical interest, and show that certain couplings exist for which the Rosen-Zener conjecture is an excellent approximation. Section V is a brief summary of our results.

II. ROSEN-ZENER-LIKE SOLUTIONS

In Eqs. (1) we consider S and P to be the initial and final levels, respectively, and we shall impose the following initial conditions: $S(-\infty)=1$, $P(-\infty)=0$. Then the desired transition amplitude $P(\infty)$ can be found from the solution to the decoupled differential equation

$$\ddot{P}+[i\Omega-(\dot{V}/V)]\dot{P}+V^2P=0 , \tag{3}$$

where we assume the pulse $V(t)$ is a real function. We implicitly assume that for any physical pulse $V(t)$ vanishes as $t\to\pm\infty$, and that it has a finite area and Fourier transform.

The components of the Rosen-Zener solutions of Eq. (2) originate, in a sense, from two quite different approximate solutions to Eq. (3). First, in the weak-coupling limit, where $|V| \ll |\Omega|$ and the last term in Eq. (3) can be neglected, we have

$$P(t)\simeq P(t_0)-iS(t_0)\int_{t_0}^{t} V(\tau)\exp(-i\Omega\tau)d\tau . \tag{4}$$

This is the result of standard first-order perturbation theory, and the appearance of a Fourier integral here indicates that such a factor is relevant in the asymptotic form for $P(\infty)$. The second factor in Eq. (2) is connected with the strong-coupling or on-resonance limit, i.e., $|V| \gg |\Omega| \to 0$, where we have

$$P(t)\simeq P(t_0)\cos\left[\int_{t_0}^{t} V(\tau)d\tau\right] -iS(t_0)\sin\left[\int_{t_0}^{t} V(\tau)d\tau\right] . \tag{5}$$

This solution is exact for all pulses $V(t)$ at resonance, $\Omega=0$; in this case, $P(\infty)=\sin A$, which is just the result of the Rosen-Zener solution of Eq. (2). Thus the $\sin A$ factor must also be important in the asymptotic form of $P(\infty)$.

These remarks suggest that a solution to Eq. (3) might profitably be sought in a Rosen-Zener-like form

$$P(t)=f(t)[\zeta(t)/\phi(t)]\sin\phi(t) , \tag{6}$$

where

$$\zeta(t)=\int_{-\infty}^{t} V(\tau)\exp(-i\Omega\tau)d\tau ,$$
$$\phi(t)=\int_{-\infty}^{t} V(\tau)d\tau .$$

As $t\to\infty$, $\zeta(t)$ and $\phi(t)$ become the Fourier transform F and pulse area A, respectively, which occur in Eq. (2), and $P(t)$ approaches the Rosen-Zener solution to the extent that $f(t)\to 1$. We shall devise a solution for the correction factor $f(t)$, which measures deviations from the Rosen-Zener conjecture, keeping in mind that we must have the following: (1) $f(\infty)=1$ at resonance, $\Omega=0$, when $\zeta=\phi$, and (2) $f(\infty)=1$ for the Rosen-Zener pulse $V(t)\propto \mathrm{sech}(t/T)$, when Eq. (2) is known to be an exact solution.

If we assume the correction factor $f(t)=$ const over its entire range, and substitute $P(t)$ of Eq. (6) into Eq. (3), then we get the residual equation

$$2(V/\phi)[V\exp(-i\Omega t)-\zeta V/\phi+\tfrac{1}{2}i\Omega\zeta] \times(\cos\phi-\phi^{-1}\sin\phi)=0 . \tag{7}$$

Any pulse V which satisfies this equation will have $P=(\zeta/\phi)\sin\phi$ as a solution for the transition amplitude. In fact, Eq. (7) is satisfied for *all* pulses V when either $\phi\to 0$ (order ϕ^2 negligible), $V\to 0$ (order V^2 negligible), or $\Omega=0$ (at resonance); this just repeats the content of Eqs. (4) and (5). The only pulse satisfying Eq. (7) identically is

$$V(t)=V(t_0)\exp[\tfrac{1}{2}i\Omega(t-t_0)] .$$

This shows that there are no nontrivial pulses which have a Rosen-Zener-like solution at finite times, not even the hyperbolic secant. Or, to say this differently, for all "interesting" pulses, the correction factor $f(t)$ in Eq. (6) must have a nontrivial time dependence.

In generating the differential equation for $f(t)$ we shall adopt a dimensionless notation by defining a new independent variable $x=t/T$, where T is a scale time related to the pulse width. We also define

$$\alpha=\Omega T , \quad W(x)=TV(t=xT) . \tag{8}$$

Then, by substituting Eq. (6) into Eq. (3), we find

$$f''-b(x)f'=c(x)f , \tag{9}$$

where

$$b(x)=\frac{d}{dx}\ln[W\exp(-i\alpha x)/\zeta^2] +2W(\phi^{-1}-\cot\phi)$$

and

$$c(x)=\left[i\alpha+\frac{d}{dx}\ln(\zeta^2/\phi^2)\right]W(\phi^{-1}-\cot\phi)$$

with

$$\zeta(x)=\int_{-\infty}^{x}W(\xi)\exp(-i\alpha\xi)d\xi\ ,$$

$$\phi(x)=\int_{-\infty}^{x}W(\xi)d\xi\ .$$

Here, primes mean differentiation with respect to x. This equation is exact. In the next section we shall solve it to terms second order in the pulse area $A=\phi(\infty)$. Since $P(t)$ of Eq. (6) is already first order in A, this solution will provide a transition amplitude correct to order A^3, i.e., to the third order of perturbation theory.

III. SOLUTION FOR THE CORRECTION FACTOR

To solve Eq. (9) to requisite order, we first note that $c(x)$ is of order A^2 overall, since $W[(\phi)^{-1}-\cot\phi]\simeq W\phi/3\propto A^2$ as $\phi\rightarrow 0$. Similarly, the second term of $b(x)$ is of order A^2, while the first term is of order unity. Then, if we look for a solution for f in terms of a power series in A up to order A^2, we can approximate Eq. (9) as

$$f''-b(x)f'\simeq c(x)\ , \tag{10}$$

where

$$b(x)\simeq\frac{d}{dx}\ln[W\exp(-i\alpha x)/\zeta^2]$$

and

$$c(x)\simeq\tfrac{1}{3}W\phi\left[i\alpha+\frac{d}{dx}\ln(\zeta^2/\phi^2)\right]\ .$$

The first integral of this equation is

$$f'(x)\simeq\exp\left[\int_{x_0}^{x}b(\xi)d\xi\right]\left[f'(x_0)+\int_{x_0}^{x}\exp\left[-\int_{x_0}^{x'}b(\xi)d\xi\right]c(x')dx'\right]\ , \tag{11}$$

where x_0 is an arbitrary reference time. We set $f'(x_0)=0$ to avoid solutions $f(x)\neq 1$ when the resonance parameter $\alpha=0$. Then, choosing $f(x_0)=1$, $x_0\rightarrow-\infty$, and partial-integrating Eq. (11) against $[W\exp(-i\alpha\xi)/\zeta^2]d\xi=-d(1/\zeta)$, we find

$$\begin{aligned}f(x)\simeq 1+\tfrac{1}{3}\int_{-\infty}^{x}&\left[i\alpha+\frac{d}{d\xi}\ln(\zeta^2/\phi^2)\right]\\&\times[1-(\zeta/\zeta_x)]\zeta\phi\\&\times\exp(i\alpha\xi)d\xi\ ,\end{aligned} \tag{12}$$

where $\zeta_x=\zeta(x)$. This is the desired solution for the correction factor f in Eq. (6), correct to order A^2. We note that at resonance, $\alpha=0$ and $\zeta=\phi$, $f(x)\simeq 1$, as need be. In the rest of this section, we shall simplify this rather complicated expression for $f(x)$ to a form more suited for calculation. The principal simplification comes about by expanding the integral to terms of order α^2.

We first partial-integrate Eq. (12) against the $d\ln(\zeta^2/\phi^2)$ term. In the resulting integrals we expand the Fourier transform function $\zeta(x)$ as

$$W(x)=Ap(x)\ ,$$

where A equals pulse area and $\int_{-\infty}^{\infty}p(x)dx=1$; so

$$\begin{aligned}\zeta(x)&=A\int_{-\infty}^{x}p(\xi)\exp(-i\alpha\xi)d\xi\\&\simeq A[\lambda(x)-i\alpha\mu_1(x)-\tfrac{1}{2}\alpha^2\mu_2(x)]\ ,\end{aligned} \tag{13}$$

where

$$\lambda(x)=\int_{-\infty}^{x}p(\xi)d\xi\ ,$$

$$\mu_k(x)=\int_{-\infty}^{x}\xi^k p(\xi)d\xi\ .$$

This is possible only for pulses $p(x)$ whose first and second moments μ_k exist. For such pulses we then find—after some algebra—that as $x\rightarrow\infty$, the correction factor of Eq. (12) becomes

$$f(\infty)\simeq 1+\tfrac{1}{3}\alpha A^2(iK_1+\alpha K_2)\ ,$$

where

$$K_1=\int_{-\infty}^{\infty}\lambda^2(1-\lambda)dx+2\int_{-\infty}^{\infty}(2-3\lambda)p\mu_1dx$$

and

$$\begin{aligned}K_2=-\int_{-\infty}^{\infty}(\lambda^2+2p\mu_1)(1-\lambda)x\,dx+\int_{-\infty}^{\infty}(2-3\lambda)p\mu_2dx-\int_{-\infty}^{\infty}\mu_1\lambda\,dx-5\int_{-\infty}^{\infty}p\mu_1^2dx\\+\mu_{1\infty}\int_{-\infty}^{\infty}(\lambda^2+6p\mu_1)\lambda\,dx\ ,\end{aligned} \tag{14}$$

where $\mu_{1\infty}=\mu_1(\infty)$. The correction coefficients K_1 and K_2, both real, determine the phase and magnitude of $f(\infty)$, respectively. They can be simplified considerably by further partial integrations. In any case, $f(\infty)$ is now correct up to terms of order α^2 and A^2.

For the first integral in K_1 we write

$$\int_{x=-\infty}^{x=+\infty} \lambda^2(1-\lambda)dx = \lambda^2(1-\lambda)x \,|_{x=-\infty}^{x=+\infty} - \int_{x=-\infty}^{x=+\infty} x\, d[\lambda^2(1-\lambda)] \; . \tag{15}$$

As $x \to \pm\infty$, $\lambda \to 1$ or 0, and the integrated term vanishes if $x^2p(x)$ vanishes as $x \to \infty$. This is already necessary for the existence of the second moment in Eq. (13). For the new integral in Eq. (15) we note that $d\lambda = p\,dx$, and $d\mu_1 = x\,d\lambda$. A further partial integration then yields

$$\int_{-\infty}^{\infty} \lambda^2(1-\lambda)dx = \mu_{1\infty} + 2\int_{-\infty}^{\infty}(1-3\lambda)p\mu_1 dx \; . \tag{16}$$

This result allows us to write the first correction coefficient of Eq. (14) as

$$K_1 = \mu_{1\infty} + 6\int_{-\infty}^{\infty}(1-2\lambda)p\mu_1 dx \; , \tag{17}$$

which is reasonably compact. For the case of symmetric pulses, $p(-x)=p(x)$, the overall first moment vanishes, i.e., $\mu_{1\infty}=0$, and in the integrand both p and μ_1 are even functions of x while $(1-2\lambda)$ is odd, so that K_1 vanishes identically. Thus for symmetric pulses there are no lowest-order phase corrections to the Rosen-Zener transition amplitude.

Simplification of K_2 of Eq. (14) requires more work. By methods similar to those of Eqs. (15) and (16) we find for the first term in K_2

$$\int_{-\infty}^{\infty} \lambda^2(1-\lambda)x\,dx = \tfrac{1}{2}\mu_{2\infty} + \int_{-\infty}^{\infty}(1-3\lambda)p\mu_2 dx \; , \tag{18}$$

where $\mu_{2\infty} = \mu_2(\infty)$ is the overall second moment of the pulse distribution, and this result holds, provided that $x^3p(x) \to 0$ as $x \to \infty$. For the second term in K_2, we note $d\mu_1 = xp\,dx$, so that

$$2\int_{x=-\infty}^{x=+\infty} p\mu_1(1-\lambda)x\,dx = \int_{x=-\infty}^{x=+\infty}(1-\lambda)d\mu_1^2 = \int_{x=-\infty}^{x=+\infty} p\mu_1^2 dx \; , \tag{19}$$

where the integrated term vanishes without restriction. This term will combine with the fourth integral in K_2 of Eq. (14). We next combine the third integral in K_2 with the first term of the last integral to get

$$\int_{x=-\infty}^{x=+\infty}(\mu_{1\infty}\lambda^2-\mu_1)\lambda\,dx = (\mu_{1\infty}\lambda^2-\mu_1)\lambda x \,|_{x=-\infty}^{x=+\infty} - \int_{x=-\infty}^{x=+\infty} x\,d[(\mu_{1\infty}\lambda^2-\mu_1)\lambda] \; . \tag{20}$$

The integrated term vanishes at the upper limit if $x^3p(x) \to 0$ as $x \to \infty$; it vanishes at the lower limit if $x^2p(x) \to 0$ as $x \to (-)\infty$, which is necessary for the existence of the second moment. For the new integral we need

$$\int_{-\infty}^{\infty} \lambda^2 px\,dx = \mu_{1\infty} - 2\int_{-\infty}^{\infty} p\mu_1\lambda\,dx \; ,$$
$$\int_{-\infty}^{\infty} p\mu_1 x\,dx = \tfrac{1}{2}\mu_{1\infty}^2 \; , \tag{21}$$
$$\int_{x=-\infty}^{x=+\infty} \lambda x\,d\mu_1 = \mu_{2\infty} - \int_{-\infty}^{\infty} p\mu_2 dx \; ,$$

all of which hold without restriction. The integral on the left-hand side of Eq. (20) can then be written as

$$\mu_{2\infty} - \int_{-\infty}^{\infty} p\mu_2 dx - \tfrac{5}{2}\mu_{1\infty}^2 + 6\mu_{1\infty}\int_{-\infty}^{\infty} p\mu_1\lambda\,dx \; . \tag{22}$$

Finally, by combining the results of Eqs. (18)–(22), we can write the second correction coefficient of Eq. (14) in the simpler form

$$K_2 = \tfrac{1}{2}(\mu_{2\infty} + \mu_{1\infty}^2) - 6\int_{-\infty}^{\infty}(\mu_1 - 2\lambda\mu_{1\infty})p\mu_1 dx - 3\mu_{1\infty}^2 \; . \tag{23}$$

This holds for all pulses $p(x)$ whose first and second moments exist, and which satisfy the criterion $x^3p(x) \to 0$ as $x \to \infty$.

For symmetric pulses, $p(-x)=p(x)$, $\mu_{1\infty}=0$, and K_2 becomes

$$K_2 = \tfrac{1}{2}\mu_{2\infty} - 12\int_0^{\infty} \mu_1^2 p\,dx \; . \tag{24}$$

In this case, the phase correction coefficient $K_1=0$, as we have remarked above, and the correction factor for the Rosen-Zener transition amplitude is simply

$$f(\infty) \simeq 1 + \tfrac{1}{3}K_2\alpha^2A^2 \; , \tag{25}$$

to lowest order. It is in this form that we shall check $f(\infty)$ against known results. Note that $K_1=K_2=0$, i.e., $f(\infty)=1$, is a necessary (but not sufficient) condition for the Rosen-Zener form of Eq. (2) to exactly solve the problem at hand.

In this section we have solved Eq. (9) for the correction factor $f(t)$ up to terms of order A^2 and α^2. The principal result is $f(\infty)$ of Eq. (14), with the coefficients K_1 and K_2 given by Eqs. (17) and (23). For symmetric pulses $K_1=0$ and K_2 is given by Eq. (24). We shall now apply these results.

IV. COMPARISON WITH KNOWN RESULTS

At this point our solution for the transition amplitude for the general two-level problem of Eqs. (1) can be written as

$$P(\infty) = f(\infty)[F(T,\Omega)/A]\sin A \; . \tag{26}$$

A is the area under the coupling pulse $V(t)$, F is the pulse Fourier transform, and $f(\infty)$ is the correction factor calculated above. The last two factors in $P(\infty)$ comprise the Rosen-Zener conjecture of Eq. (2), while $f(\infty)$ determines deviations from that form. Since our result for $f(\infty)$ holds to terms of order A^2 and Ω^2 for all pulses with first and second moments obeying the condition $\lim_{t\to\infty} t^3 V(t)=0$, then our solution for $P(\infty)$ applies to such pulses under the same conditions, and is valid to third order in A. Consequently, the factor $\sin A$ in Eq. (26) is reliable only to order A^3, i.e., $\sin A \simeq A(1-\frac{1}{6}A^2)$, valid to 5% up to $A=1.4$. With this proviso we shall retain $\sin A$ as a factor. Comparison with standard theory is not readily possible,[5] but we can compare our solution with cases where $P(\infty)$ is known. We find agreement between our result and known results in all cases.

A. Rectangular pulse

A physically unrealizable but often used model of coupling is provided by the so-called rectangular pulse, i.e., in normalized form

$$p(x)=\begin{cases}\beta, & -\frac{1}{2}\beta \le x \le +\frac{1}{2}\beta\\ 0, & \text{otherwise.}\end{cases} \tag{27}$$

Here β is a parameter which can be varied to change the pulse height and width. The exact transition amplitude is known in this case, it is[6]

$$P_R(\infty)=(2\beta A/\alpha)[Q^{-1}\sin(Q\alpha/2\beta)] \tag{28}$$

with

$$Q=[1+(2\beta A/\alpha)^2]^{1/2},$$

where A is the pulse area and $\alpha=\Omega T$ is the resonance parameter. If we expand the square bracket to terms of order A^2 and α^2 we find

$$P_R(\infty)\simeq(2\beta A/\alpha)[1-\tfrac{1}{360}(\alpha A/\beta)^2-\tfrac{1}{6}A^2]\times\sin(\alpha/2\beta). \tag{29}$$

If our form for $P(\infty)$ in Eq. (26) is correct, it must reproduce this result.

This is a case where the Rosen-Zener conjecture is expected *not* to work, because neither the pulse nor its derivatives are continuous. Indeed, the correction factor $f(\infty)$ differs from unity. From Eq. (24) we calculate

$$\mu_{2\infty}=\int_{-\infty}^{\infty} x^2 p(x)dx=1/12\beta^2,$$
$$\int_0^{\infty}\mu_1^2 p\, dx=1/240\beta^2;$$
$$K_2=\tfrac{1}{2}\mu_{2\infty}-12\int_0^{\infty}\mu_1^2 p\,dx=-1/120\beta^2, \tag{30}$$

and $f(\infty)$ is given by Eq. (25). With the pulse Fourier transform

$$F=A\int_{-\infty}^{\infty}p(x)\exp(-i\alpha x)dx$$
$$=(2\beta A/\alpha)\sin(\alpha/2\beta), \tag{31}$$

we find that the solution of Eq. (26) is

$$P(\infty)\simeq(2\beta A/\alpha)[1-\tfrac{1}{360}(\alpha A/\beta)^2]\times A^{-1}(\sin A)\sin(\alpha/2\beta). \tag{32}$$

To terms of order A^3, this is just the same as the exact solution of Eq. (29), since $A^{-1}\sin A\simeq 1-\frac{1}{6}A^2$, to lowest order in A. Thus, in the case of the rectangular pulse, our solution for $P(\infty)$ reproduces the exact result, term by term, to the requisite order.

In passing, we note that in the δ-function limit here, i.e., $\beta\to\infty$, both the exact solution of Eq. (28) and our $P(\infty)$ become $P(\infty)=\sin A$, which is the exact form of the Rosen-Zener conjecture in this case.

B. Rosen-Zener pulse

The Rosen-Zener pulse, which suggested this formalism, is given by

$$p(x)=\operatorname{sech}\pi x, \tag{33}$$

in normalized form. For this pulse it is known that Eq. (2) is an exact solution for the transition amplitude. This means that our correction factor $f(\infty)$ can have no A dependence in this case; we must have $K_1=K_2=0$. K_1 does vanish by symmetry, and in K_2 we can easily calculate $\mu_{2\infty}=\frac{1}{4}$. But we must also evaluate $\int \mu_1^2 p\, dx$, over the first moment function

$$\mu_1(x)=\int_{-\infty}^{x}\xi p(\xi)d\xi$$
$$=(1/\pi^2)\int_{-\infty}^{\pi x}(y/\cosh y)dy. \tag{34}$$

This integral cannot be expressed in terms of elementary functions, and so we must resort to numerical methods. By numerical integration we have shown that for the Rosen-Zener pulse, K_2 of Eq. (24) is less than 5×10^{-6}, and is consistent with zero.[7] Thus, our result for $P(\infty)$ agrees with the Rosen-Zener conjecture in this case.

C. Narrow pulses: The δ-function limit

For very narrow pulses, with widths $T \ll 1/|\Omega|$, we can pass to the δ-function limit $p(x)=\delta(x)$, and immediately calculate that $K_1=K_2=0$, $F=A$. In this limit our formalism thus gives

$$P(\infty)=\sin A. \tag{35}$$

This is the same as the result of the Rosen-Zener conjecture in this case, and both results reproduce the known solution. In fact, in this limit, *all* solutions to the two-level problem must become indistinguishable from one another. If we think of the limit as being approached by a pulse of height $V(0)\rightarrow\infty$ and width $T\rightarrow 0$ in such a way that the pulse area $A\sim TV(0)=$ const, then the resonance parameter we have used, namely, $\alpha=\Omega T$, must vanish and Eq. (35) for $P(\infty)$ also must reduce to the on-resonance result. It does, and this provides another check on the correctness of our results.

D. Gaussian pulse

A Gaussian pulse shape is often used to model the output of a nearly monochromatic pulsed laser.[8] This provides the coupling

$$p(x)=(\beta/\pi)^{1/2}\exp(-\beta x^2)\ , \tag{36}$$

which is normalized, i.e., $\int_{-\infty}^{\infty}p(x)dx=1$, and which contains an adjustable height-width parameter β. No solution is known for the transition amplitude $P(\infty)$ induced by this pulse. Our formalism provides an approximate form for $P(\infty)$ by calculation of the quantities

$$\mu_{2\infty}=\int_{-\infty}^{\infty}x^2p(x)dx=1/2\beta\ ,$$
$$\int_0^{\infty}\mu_1^2p\,dx=1/8\beta\pi\sqrt{3}\ ;$$
$$K_2=\tfrac{1}{2}\mu_{2\infty}-12\int_0^{\infty}\mu_1^2p\,dx=(-)k/\beta\ , \tag{37}$$

where

$$k=\tfrac{1}{4}[(6/\pi\sqrt{3})-1]=0.025\,664\ .$$

This gives the correction factor $f(\infty)$ of Eq. (25), and with the Fourier transform

$$F=A\int_{-\infty}^{\infty}p(x)\exp(-i\alpha x)dx$$
$$=A\exp(-\alpha^2/4\beta) \tag{38}$$

the transition amplitude is

$$P(\infty)\simeq[1-\tfrac{1}{3}(k/\beta)\alpha^2A^2]$$
$$\times\exp(-\alpha^2/4\beta)\sin A\ . \tag{39}$$

This approximation improves as the pulse narrows, i.e., for increasing β.

$|P(\infty)|^2$, as a function of the frequency parameter $\alpha=\Omega T$, gives the line shape for the induced transition. In the present case, the line half-width at half maximum, for small values of pulse area A, is

$$\Delta\alpha\simeq 1.177\sqrt{\beta}(1-\tfrac{2}{3}kA^2)\ . \tag{40}$$

The line is thus narrower than would be expected on the basis of an estimate by the Rosen-Zener conjecture alone (where we would have $k=0$). Interestingly, the line narrowing becomes more pronounced as the pulse power level is increased, within the limits of our approximation. Such a "power-sharpening" effect has been noted before in connection with line-shape theories which deal with fine details of the coupling pulse.[9]

E. Exponential pulse

To treat an example of a pulse which is asymmetric in time we look at the exponential

$$p(x)=\begin{cases}0, & x<0\\ \beta\exp(-\beta x), & x\geq 0\ .\end{cases} \tag{41}$$

Such a pulse represents level coupling provided by a quickly decaying transient. An exact solution for $P(\infty)$ is possible in this case.[3] Our calculation gives a simple but useful approximation to $P(\infty)$, which now depends on the general forms for K_1 and K_2 in Eqs. (17) and (23). In turn, these depend on

$$\mu_{1\infty}=1/\beta\ ,\quad \mu_{2\infty}=2/\beta^2\ ;$$
$$\lambda=1-\exp(-y)\ , \tag{42}$$
$$\mu_1=\beta^{-1}[1-(1+y)\exp(-y)]\ ,$$

for this pulse, with $y=\beta x$. The K integrals are easy, and we find

$$K_1=1/6\beta\ ,\quad K_2=1/18\beta^2\ . \tag{43}$$

With these, the correction factor $f(\infty)$ is given by Eq. (14). To get $P(\infty)$ of Eq. (26) we also need the Fourier transform

$$F=A\int_{-\infty}^{\infty}p(x)\exp(-i\alpha x)dx$$
$$=A\beta/(\beta+i\alpha)\ . \tag{44}$$

Then the desired approximation for the transition amplitude is

$$P(\infty)\simeq[1+\tfrac{1}{3}iK_1\alpha A^2+\tfrac{1}{3}K_2\alpha^2A^2]$$
$$\times\beta\sin A/(\beta+i\alpha)\ , \tag{45}$$

where K_1 and K_2 are given in Eqs. (43). The approximation again improves as the pulse narrows, i.e., as β increases. In forming the line-shape function $|P(\infty)|^2$ for the present pulse we note that while K_1 controls the phase of $f(\infty)$, it does not affect its magnitude since, to order A^2,

$$|f(\infty)|^2\simeq 1+\tfrac{2}{3}K_2\alpha^2A^2\ . \tag{46}$$

This is true of *all* pulses in the present order of approximation. Then the line-shape function corresponding to Eq. (45) is

$$|P(\infty)|^2\simeq[1+\tfrac{1}{27}(\alpha A/\beta)^2]$$
$$\times(\beta\sin A)^2/(\alpha^2+\beta^2)\ . \tag{47}$$

This line is nearly Lorentzian, with half width $\Delta\alpha = \beta[1+(A^2/27)]$, and it is power broadened by the correction term in A^2.

F. Composite pulses

As we noted after Eq. (25), a necessary (but not sufficient) condition for the Rosen-Zener conjecture of Eq. (2) to be an exact solution for the transition amplitude is that the correction coefficients obey $K_1 = K_2 = 0$. This condition is satisfied identically, as it must be, for the Rosen-Zener pulse of Eq. (33). We can ask whether this is unique: Is $p(x) = \text{sech}(\pi x)$ the only nontrivial pulse for which $K_1 = K_2 = 0$? The answer is no, as we now show by constructing a composite pulse whose K coefficients vanish. Although such pulses do not necessarily have $P(\infty)$ of Eq. (2) as an exact solution for the transition amplitude, they will follow that form quite closely, since the first correction term will be of order A^5. More importantly, the existence of such pulses indicates that there is a large class of couplings for which the Rosen-Zener form of $P(\infty)$ is an excellent approximation.

Let $p_0(x)$ be a known, symmetric pulse with K coefficients: $K_1 = 0$, $K_2 = K_{20} \neq 0$. Add a narrow pulse at the origin to form the composite

$$p(x) = ap_0(x) + (1-a)\delta(x) , \tag{48}$$

where the parameter a is to be found, and $p(x)$ is normalized if $p_0(x)$ is. Since $p(x)$ is symmetric it will have $K_1 = 0$. Its K_2 value can be calculated in terms of K_{20}, a, and the moments associated with $p_0(x)$. Using Eq. (24) we find

$$K_2 = \tfrac{1}{2} a\mu_{2\infty}^{(0)}(Aa^2 - Ba + 1) ,$$

where

$$B = 24\mu_{10}^2(0)/\mu_{2\infty}^{(0)} , \tag{49}$$

$$A = (2K_{20}/\mu_{2\infty}^{(0)}) + B - 1 .$$

Here, $\mu_{2\infty}^{(0)} = \int_{-\infty}^{\infty} x^2 p_0(x)dx$ and $\mu_{10}(0) = \int_{-\infty}^{0} xp_0(x)dx$. This K_2 value vanishes for real values of a if the quadratic form in square brackets has real roots. This requires $B^2 \geq 4A$, or

$$[12\mu_{10}^2(0) - \mu_{2\infty}^{(0)}]^2 \geq 2K_{20}\mu_{2\infty}^{(0)} , \tag{50}$$

which is possible for any pulse $p_0(x)$ with $K_{20} \leq 0$, such as the Gaussian of Eq. (37). For such pulses the composite of Eq. (48) provides a class of couplings for which $K_1 = K_2 = 0$, and for which the Rosen-Zener conjecture is exact up to order A^5.

In this section, we have compared our result for the transition amplitude $P(\infty)$ with various known results. The most detailed comparison is in the case of a rectangular pulse, where the term by term agreement between our $P(\infty)$ and the exact solution shows that the "arithmetic" of our calculation is correct. Our $P(\infty)$ also shows the expected behavior for a hyperbolic secant pulse, and for very narrow pulses. Next, we have calculated $P(\infty)$ for the physically interesting cases of Gaussian and exponential transient pulses. The Gaussian result is new, insofar as a solution for $P(\infty)$ is not known in this case, and both results provide quantitatively useful details of the transition line-shape function $|P(\infty)|^2$. Finally, we have constructed examples of composite pulses for which the Rosen-Zener conjecture for $P(\infty)$ is an exact solution within the present approximation. For such pulses, $P(\infty)$ is given by Eq. (2) and correct is up to terms fifth order in the pulse area A. This suggests a large class of couplings for which the Rosen-Zener $P(\infty)$ is an excellent approximation.

V. SUMMARY

To summarize, we have calculated the approximate form of the transition amplitude $P(\infty)$ for the time-dependent two-level problem, where the levels are coupled by a quite general class of pulses $V(t)$. Our solution for $P(\infty)$ is correct up to the third order of perturbation theory, i.e., up to terms third order in the pulse area $A = \int_{-\infty}^{\infty} V(t)dt$, and it applies to all pulse distributions $V(t)$ which have finite first and second moments and which obey $\lim_{t\to\infty} t^3 V(t) = 0$. Our result for $P(\infty)$ is given as the product of two factors: (1) a form of solution previously conjectured by Rosen and Zener and (2) a correction factor $f(\infty)$ which is calculable in terms of integrals over the pulse distribution. The extent to which $f(\infty)$ differs from unity provides a criterion for judging the validity of the Rosen-Zener conjecture, and its general form provides a useful approximation to $P(\infty)$ in many cases of practical interest.

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[1]N. Rosen and C. Zener, Phys. Rev. 40, 502 (1932).
[2]A. Bambini and P. R. Berman, Phys. Rev. A 23, 2496 (1981). The Bambini-Berman pulses include the Rosen-Zener pulse as a special case.
[3]It has been pointed out to the author that an exact solution is also possible for an exponential pulse. See A. D. Wilson and H. Friedmann, Chem. Phys. 23, 105 (1977).
[4]B. G. Skinner, Proc. Phys. Soc. London 77, 551 (1961).
[5]The (symbolic) formulation of third-order time-dependent perturbation theory appears in standard references, such as Sec. 74 of A. S. Davydov, *Quantum Mechanics,* edited by D. ter Haar (Pergamon, New York, 1965). So far as we know, however, an *explicit* calculation to third order for the general two-level problem does not appear in the literature.
[6]From Eq. (26) of R. T. Robiscoe, Phys. Rev. A 17, 247 (1978).
[7]We are indebted to our colleague, J. E. Drumheller, for devising and running the computer program.
[8]D. J. Bradley and G. H. C. New, Proc. IEEE 62, 313 (1974); J. Wiedmann and A. Penzkofer, Opt. Commun. 30, 107 (1979).
[9]See Appendix IV of W. E. Lamb, Jr., Phys. Rev. 85, 259 (1952).