Transition probabilities for the three-level Landau-Zener model

1986 J. Phys. A: Math. Gen. 19 2061

(http://iopscience.iop.org/0305-4470/19/11/014)

J. Phys. A: Math. Gen. 19 (1986) 2061-2073. Printed in Great Britain

Transition probabilities for the three-level Landau–Zener model

C E Carroll and F T Hioe

Department of Physics, St John Fisher College, Rochester, New York 14618, USA

Received 28 October 1985

Abstract. A three-level model is used for an atom in which two transitions are driven by two laser beams, having constant amplitudes and detunings that are proportional to the time. Assuming that any two of the levels are unoccupied at large negative times, we obtain simple formulae for the occupation probabilities at large positive times. Our previous results and the early calculation of Landau and Zener are special cases of these general formulae.

1. Introduction

The Landau-Zener model is widely used in studying the dynamics of two-level quantum systems. The probability of a transition between the two levels was found by Landau (1932) and Zener (1932). They applied their model to transitions in diatomic molecules. More recently, this model has been applied to many physical topics, such as nuclear collisions (Abe and Park 1983) and impurities in semiconductors (Henry and Lang 1977). We seek to apply this model and its three-level generalisation to atomic or molecular systems driven by laser beams. This paper reports transition probabilities, and probabilities of no transition, calculated for the three-level driven-atom generalisation of the Landau-Zener model.

In the two-state model of an atom (or molecule), we assume that the transition is driven by a laser beam of constant amplitude, and that the detuning of the driving frequency is proportional to t, the time. If the atom is in a definite state at large negative time, and if the rotating-wave approximation is used, the calculation of Landau and Zener gives the probability that the atom is in the same state at large positive time. This two-state model will be called a two-level model, because we assume that each energy level corresponds to only one state.

In the three-level model, two transitions are driven by laser beams of constant amplitude, possibly derived from the same laser. We assume that the detunings of the two laser beams are both proportional to t. The transition probabilities and probabilities of no transition are found by generalising the Landau-Zener calculation. A complete set of calculated transition probabilities for this model is given in this paper. These probabilities are given by rather simple formulae, similar to the formula of Landau and Zener.

The assumption that the frequencies of the two laser beams pass through resonance at $t = 0$ might be replaced by an assumption that they pass through resonance at very different times. This allows calculation of transition probabilities by solving a sequence

0305-4470/86/112061+13$02.50

of two two-level problems. Such calculations are not considered in this paper; see Atabek *et al* (1984).

If the effect of one of the laser beams is negligible, our three-level model reduces to a two-level model, and the calculations of Landau and Zener are directly applicable. Their formula has been verified by an experiment with Rydberg states of lithium (Rubbmark *et al* 1981), and we hope that our three-level formulae can be verified by experiment.

Our model of a three-level atom driven by two laser beams is described in § 2, where we specify the assumptions used and write the Schrödinger equation. Section 3 describes the method of finding exact analytic solutions of the Schrödinger equation. The resulting final occupation probabilities are given in § 4, and the calculations are outlined in four appendices.

2. Driven atom and rotating-wave approximation

The three-level model of an atom driven by two laser beams is fully described in this section. We use the rotating-wave approximation, which permits elimination of optical frequency terms from the Hamiltonian and wavefunction. After this elimination, the Hamiltonian for this model is a linear function of t, the time, as is the Hamiltonian of the original Landau-Zener model.

Consider an experiment in which two laser beams drive two transitions in an atom. The driven transitions connect level 1 to level 2 and level 2 to level 3. We shall use a classical description of the two laser beams; the oscillating electric fields of the two beams appear as external fields in the Schrödinger equation for the atom. This means that we can write the Hamiltonian for the atom as a 3×3 matrix, with matrix elements $H_{11}, H_{22}, \ldots, H_{33}$. We assume that each laser beam drives only its own transition, and only when its frequency is near resonance. When its frequency is far from resonance, it has a negligible effect on the atom. Neglect of this effect will allow a simplification of our calculations.

In the 3×3 Hamiltonian matrix, as first written, the diagonal elements H_{11}, H_{22}, H_{33} are the atomic energy levels. The off-diagonal elements are proportional to the classical external fields that drive the transitions. The 1-3 transition is not driven by an applied oscillating field. Indeed, the electric dipole selection rules say that it cannot be driven. Hence

$$H_{13} = H_{31} = 0. \tag{1}$$

This is a significant simplification of the Hamiltonian matrix. The remaining off-diagonal elements oscillate at optical frequencies. Each of them contains terms in $\exp(\pm i\omega_L t)$, where ω_L is the frequency of the corresponding laser beam. One of these exponential terms represents a driving frequency that has the wrong sign, and it has little effect in driving the transition (Allen and Eberly 1975). We drop this ineffective term; this is the rotating-wave approximation. The errors involved in this approximation have been studied in detail (Bloch and Siegert 1940, Stevenson 1940, Shirley 1965), using the two-level model. If both transitions are driven by circularly polarised laser beams propagating along an external magnetic field, only one exponential function appears in each matrix element that is next to the main diagonal of the Hamiltonian matrix, and the rotating-wave approximation is not invoked. However, in this case,

we use a similar approximation, for we assume that each oscillating electric field is so weak that it drives only its own transition.

The rotating-wave approximation is associated with a simple time-dependent unitary transformation that removes optical frequency terms from the Hamiltonian and wavefunction. See Einwohner *et al* (1976) for the N-level formulation of this transformation. Due to (1), their transformation is applicable to our case. We assume that the amplitude of each optical frequency applied field is constant; these constants appear in off-diagonal elements of the Hamiltonian matrix. The time-dependent unitary transformation removes the factors of $\exp(\pm i\omega_L t)$, and gives us a Hamiltonian matrix in which off-diagonal elements are constant. The unitary matrix used in this transformation is diagonal. This means that it does not change the numbering of the three levels, nor the condition (1).

The diagonal elements of the Hamiltonian matrix are changed by this time-dependent unitary transformation. It replaces each atomic energy level on the diagonal by the detuning of one of the laser frequencies or by a linear combination of the two detunings. These diagonal matrix elements should include a factor of Planck's constant, but we set $\hbar = 1$ and measure frequencies in radians per unit time. Since we assume detunings proportional to t, the Schrödinger equation for the atom has the form

$$i\frac{d}{dt}\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} 2r_1 t & -\frac{1}{2}\Omega_{12} & 0 \\ -\frac{1}{2}\Omega_{12} & 2r_2 t & -\frac{1}{2}\Omega_{23} \\ 0 & -\frac{1}{2}\Omega_{23} & 2r_3 t \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}. \tag{2}$$

Here, a_1, a_2, a_3 are the amplitudes for the three atomic states or atomic levels. The Rabi frequencies are Ω_{12} and Ω_{23}; each of them is twice the product of a transition dipole moment and the corresponding optical frequency field amplitude. The corresponding detunings are

$$2(r_1 - r_2)t \qquad \text{and} \qquad 2(r_2 - r_3)t. \tag{3}$$

We assume that the amplitude of each optical frequency field is entirely independent of t, so that Ω_{12} and Ω_{23} are constants. Although it is necessary to turn the laser beams on at an early time and turn them off at a late time, we omit this time dependence from the mathematical model, because the laser beams have negligible effects when their detunings are large. This physical argument is supported by the analytic solutions of (2).

The limiting cases of this model must be mentioned. If either of the Rabi frequencies, Ω_{12} and Ω_{23}, is set equal to zero, we have a simple case to which the calculations of Landau and Zener are applicable. If both Rabi frequencies are non-zero and the three coefficients r_1, r_2, r_3 do not have distinct values, we have a resonant case in which one of the detunings (3) vanishes or the sum of the two detunings vanishes. In the resonant cases, we may not claim that the effects of the two laser beams become negligible as $t \to \pm\infty$. In each resonant case, the occupation probabilities of two or three atomic states can oscillate indefinitely as $t \to \pm\infty$. Rather than abandon our assumption of strictly constant Rabi frequencies, we shall calculate those few transition probabilities, and probabilities of no transition, that exist in resonant cases.

The experiment proposed in this section is based on detunings proportional to t. Such detunings might be produced by varying the laser frequencies, but it seems simpler to use the Stark or Zeeman shifts to vary the differences of atomic energy levels. Furthermore, it may be possible to derive the two laser beams from one laser.

The ground state of the atom could be any of the three atomic states in our model. One may assume that the atom is initially in its ground state, but this does not affect our calculations.

3. Solution of Schrödinger equation

To calculate occupation probabilities for the three levels at large positive times, we shall use integral representations of the solutions of (2). This section points out the significant parameters in (2), shows that the resonant cases appear as boundaries between six non-resonant cases and indicates what integral representations are applicable in the resonant and non-resonant cases.

The transformation leading to (2) can be arranged so that r_1, r_2 or r_3 vanishes, or so that $r_1+r_2+r_3$ has any desired value. Alternatively, a simple transformation that increases the Hamiltonian by t times the unit matrix can be constructed separately. Such a transformation multiplies the wavefunction by an overall factor of $\exp(iCt^2)$, where C is any real constant, without changing any occupation probability or expectation value. This means that the differences (3) are the physical quantities represented on the main diagonal of the Hamiltonian matrix. We have a resonant case if r_1-r_2 or r_2-r_3 or r_1-r_3 vanishes. In the non-resonant cases, each of these differences is positive or negative, and six combinations of signs are possible. Only one of these six combinations was treated in our earlier paper (Carroll and Hioe 1985). Of course, the Landau-Zener calculation is applicable to a limiting case of our model.

The obvious first step toward solving (2) is to write it in terms of dimensionless variables. However, the amplitudes a_1, a_2 and a_3 are already dimensionless and the introduction of a dimensionless time does not seem worthwhile. The transition probabilities must depend on dimensionless parameters derived from (2), and the integral representations used in the six non-resonant cases prompt us to define two dimensionless parameters

$$p=\frac{(\Omega_{12})^2}{16(r_1-r_2)} \qquad \text{and} \qquad q=\frac{(\Omega_{23})^2}{16(r_2-r_3)}. \tag{4}$$

Here, we assume that Ω_{12} and Ω_{23} are real, so that p and q are real; the relative phases of a_1, a_2, a_3 can always be chosen so that Ω_{12} and Ω_{23} are real. A third dimensionless parameter is $(r_1-r_2)/(r_2-r_3)$, the ratio of the two detunings, (3). This parameter is of lesser importance, and we do not assign a special symbol to it. The remaining dimensionless parameters in (2) are unphysical parameters that cannot appear in calculated transition probabilities. For example, $r_1/(\Omega_{12})^2$ is a dimensionless parameter; it can be given an arbitrary value (unless $\Omega_{12}=0$) by using the simple transformation mentioned in the previous paragraph. The transition probabilities can depend only on the three dimensionless parameters we have mentioned. But in resonant cases, one of the denominators in (4) can vanish. This causes no difficulty; we shall not use any definition that involves a division by zero.

In the exact analytic solutions of (2), each component of the wavefunction is proportional to an integral along a certain path in the complex plane. Although each integral representation can be verified by substitution into (2), the methods used to find these integral representations are outlined in appendix 1. We assume that neither Ω_{12} nor Ω_{23} is zero, because the Landau-Zener calculation is applicable if either is

zero. If the three coefficients r_1, r_2 and r_3 have distinct values, there are six possible orderings of the three values along the real axis, and these are the six non-resonant cases mentioned above. They are treated briefly in appendix 2, which explains that we do two separate calculations rather than six. In the resonant cases, the values of r_1, r_2, and r_3 are not distinct. If $r_1 = r_2 = r_3$, all three occupation probabilities oscillate as $t \to \pm\infty$, and no limits can be calculated. If $r_1 = r_2 \neq r_3$, then the occupation probabilities of levels 1 and 2 can oscillate with frequency Ω_{12} as $t \to \pm\infty$. This case and the case of $r_1 \neq r_2 = r_3$, which is similar, are treated in appendix 3. If $r_1 = r_3 \neq r_2$, then the occupation probabilities of levels 1 and 3 can oscillate as $t \to \pm\infty$, although the oscillations become slower and slower as $|t|$ increases. This case is treated in appendix 4. We find that if $r_j = r_k$ and $j \neq k$ then we must assume that levels j and k are both unoccupied at large negative times.

Using the integral representations shown in appendices 2, 3 and 4, we can write the general solution of (2) in any particular case. We impose the initial condition that one of the three levels is occupied with unit probability in the limit as $t \to -\infty$, and we use each level in turn as the initial level, provided the behaviour of the general solution as $t \to -\infty$ allows this. These initial conditions lead to the following results.

4. Resulting final occupation probabilities

The transition probability calculated by Landau and Zener is given by a simple formula, involving the exponential function and the single dimensionless parameter of their model. The transition probabilities for our three-level model are similarly simple. They involve exponential functions but no square roots or higher transcendental functions. Furthermore, they involve only p and q, the dimensionless parameters defined by (4). If p and q are constant, the transition probabilities do not depend on $(r_1 - r_2)/(r_2 - r_3)$, the third dimensionless parameter. This is the other simple feature of the transition probabilities given by our model.

The initial condition for solution of (2) involves limits as $t \to -\infty$, and the transition probabilities are limits of occupation probabilities as $t \to +\infty$. Because of these limits, the transition probabilities can be discontinuous functions of $r_1 - r_2$ and $r_2 - r_3$, the two coefficients appearing in (3). Discontinuities appear in figure 1, where we plot the two calculated transition probabilities as functions of r_3. The discontinuities appear at $r_3 = r_1$, where the sum of the two detunings is zero at all times, and at $r_3 = r_2$, where one of the detunings is zero at all times. The transition probabilities plotted in figure 1 are not defined at these points; only a few final occupation probabilities can be calculated in the resonant cases.

We postpone listing the results for resonant cases, and assume that the coefficients r_1, r_2 and r_3 have distinct values. Then the three final occupation probabilities are simply quadratic polynomials in

$$P = \exp(-2\pi|p|) \qquad \text{and} \qquad Q = \exp(-2\pi|q|). \tag{5}$$

The three-level atom can be in any of its three levels at large negative times, and there are six possibilities for the signs of the two detunings (3) and their sum. This means that there are many cases to be covered. Table 1 is a concise collection of the results for all these cases.

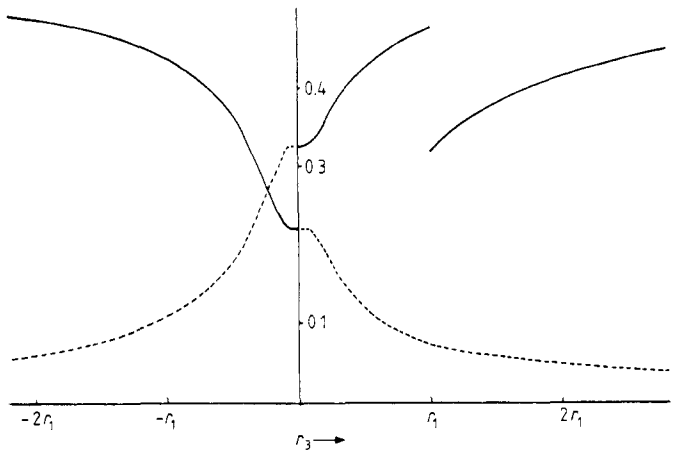

Figure 1. Transition probabilities calculated for an atom that is in state 1, with unit probability, at large negative times. The transition probabilities are the occupation probabilities of states 2 and 3 at large positive times. Full curve: probability of transition from 1 to 2; broken curve: probability of transition from 1 to 3. We assume $(\Omega_{12})^2 = (\Omega_{23})^2 = r_1 - r_2 > 0$, and plot the transition probabilities as functions of r_3. We assume $r_2 = 0$, which simplifies the labels on the abscissa, without causing any further loss of generality.

Table 1. Final occupation probabilities for the non-resonant cases. The initial condition is that one of the three levels is certainly occupied in the limit as $t \to -\infty$. The three possible initial levels correspond to the three columns. The final occupation probabilities for the nth level appear as the nth row in the appropriate matrix. Hence, the probabilities of no transition appear as diagonal matrix elements. P and Q are defined by (5) and the matrices are symmetric.

Initial occupation probabilities 1, 0, 0	Initial occupation probabilities 0, 1, 0	Initial occupation probabilities 0, 0, 1
Cases of $r_2 > r_1 > r_3$ and $r_3 > r_1 > r_2$		
$(1-Q+PQ)^2$	$Q(1-P)(1+PQ)$	$Q(1-P)(1-Q)$
$Q(1-P)(1+PQ)$	P^2Q^2	$(1-Q)(1+PQ)$
$Q(1-P)(1-Q)$	$(1-Q)(1+PQ)$	Q^2
Cases of $r_1 > r_2 > r_3$ and $r_3 > r_2 > r_1$		
P^2	$(1-P)(P+Q)$	$(1-P)(1-Q)$
$(1-P)(P+Q)$	$(1-P-Q)^2$	$(1-Q)(P+Q)$
$(1-P)(1-Q)$	$(1-Q)(P+Q)$	Q^2
Cases of $r_1 > r_3 > r_2$ and $r_2 > r_3 > r_1$		
P^2	$(1-P)(1+PQ)$	$P(1-P)(1-Q)$
$(1-P)(1+PQ)$	P^2Q^2	$P(1-Q)(1+PQ)$
$P(1-P)(1-Q)$	$P(1-Q)(1+PQ)$	$(1-P+PQ)^2$

Table 2. Probability of no transition in the cases of $r_1 = r_2 \neq r_3$ and $r_1 \neq r_2 = r_3$. Either p or q is defined; see (4). The initial occupation probabilities must be as in the middle column in order to have definite limits as $t \to -\infty$. Although two occupation probabilities oscillate indefinitely as $t \to +\infty$, the probability of no transition can be calculated.

Resonant case	Initial occupation probabilities for levels 1, 2 and 3	Probabilility of no transition
$r_1 = r_2$	0, 0, 1	$\exp(-4\pi\|q\|)$
$r_2 = r_3$	1, 0, 0	$\exp(-4\pi\|p\|)$

Table 3. Final occupation probabilities for the resonant case in which the sum of the two detunings is always zero. Here, $r_1 = r_3 \neq r_2$. Both p and q are defined; see (4).

Level	Initial occupation probability	Final occupation probability
1	0	$\dfrac{(\Omega_{12})^2}{(\Omega_{12})^2+(\Omega_{23})^2}[1-\exp(-4\pi\|p\|-4\pi\|q\|)]$
2	1	$\exp(-4\pi\|p\|-4\pi\|q\|)$
3	0	$\dfrac{(\Omega_{23})^2}{(\Omega_{12})^2+(\Omega_{23})^2}[1-\exp(-4\pi\|p\|-4\pi\|q\|)]$

If $\Omega_{23} = 0$, then $Q = 1$ and the results shown in table 1 simplify somewhat; they agree with the result of Landau and Zener. The case of $\Omega_{12} = 0$, which gives $P = 1$, is similar.

In the resonant cases, we assume that Ω_{12} and Ω_{23} are non-zero. If $r_1 = r_2 = r_3$, no occupation probability approaches a limit as $t \to -\infty$ or $+\infty$. If $r_1 = r_2 \neq r_3$, then the occupation probabilities of levels 1 and 2 oscillate when $|t|$ is large, unless they both vanish. We assume that only level 3 is occupied at large negative times and calculate the probability of no transition, which is Q^2. This result and a similar result for the case of $r_1 \neq r_2 = r_3$ are displayed in table 2. We notice that the calculated probabilities are again quadratic polynomials in P or Q, whichever is defined. In the remaining resonant case, $r_1 = r_3 \neq r_2$. Again, the occupation probabilities can oscillate indefinitely as $t \to -\infty$. We must assume that the atom is initially in level 2. The final occupation probabilities are shown in table 3. Since $(\Omega_{12})^2/(\Omega_{23})^2 = -p/q$ holds in this case, the final occupation probabilities could be written as functions of p and q only.

5. Conclusion

We have studied a three-level model for an atom in which two transitions are driven by laser beams of constant amplitude. A generalisation of the Landau-Zener model was obtained by assuming that both detunings are proportional to t. The transition

probabilities, and probabilities of no transition, have been calculated in every case where these limits exist.

Acknowledgment

This work was partially supported by the Division of Chemical Sciences, US Department of Energy, under grant no DE-FG02-84ER13243.

Appendix 1. Integral representations

We can find exact analytic solutions of (2) by making each component of the wavefunction proportional to an integral along a certain path in the complex plane. The integrands can be found by a Laplacian method, described in some textbooks. They can also be found by the method of Demkov (1966), unless the coefficients r_1, r_2 and r_3 have distinct values. Since this paper is mainly concerned with the case of three distinct values, we do not describe the application of Demkov's method. After construction of the integral representations, further calculations lead to tables 1, 2 and 3. These calculations are described in separate appendices.

Using (2) and eliminating a_2 and a_3, we find the differential equation for a_1

$$\begin{aligned} \mathrm{d}^3a_1/\mathrm{d}t^3 + 2\mathrm{i}(r_1+r_2+r_3)t\,\mathrm{d}^2a_1/\mathrm{d}t^2 + \{&-4(r_1r_2+r_2r_3+r_3r_1)t^2 \\ &+ 2\mathrm{i}(2r_1+r_2) + \tfrac{1}{4}[(\Omega_{12})^2+(\Omega_{23})^2]\}\,\mathrm{d}a_1/\mathrm{d}t \\ &+ \{-8\mathrm{i}r_1r_2r_3t^3 - 4r_1(2r_2+r_3)t \\ &+ \tfrac{1}{2}\mathrm{i}[(\Omega_{12})^2r_3+(\Omega_{23})^2r_1]t\}a_1 = 0. \end{aligned} \tag{A1.1}$$

The coefficients that appear here are odd and even polynomials in t, alternately. This circumstance, and the concise treatment of the two-level case by Wannier (1965), lead us to use

$$x = t^2 \tag{A1.2}$$

as a new independent variable. This gives

$$\begin{aligned} x\,\mathrm{d}^3a_1/\mathrm{d}x^3 + [\mathrm{i}(r_1+r_2+r_3)x + \tfrac{3}{2}]\,\mathrm{d}^2a_1/\mathrm{d}x^2 + \{&-(r_1r_2+r_2r_3+r_3r_1)x \\ &+ \tfrac{1}{2}\mathrm{i}(3r_1+2r_2+r_3) + \tfrac{1}{16}[(\Omega_{12})^2+(\Omega_{23})^2]\}\,\mathrm{d}a_1/\mathrm{d}x \\ &+ \{-\mathrm{i}r_1r_2r_3x - \tfrac{1}{2}r_1(2r_2+r_3) + \tfrac{1}{16}\mathrm{i}[(\Omega_{12})^2r_3+(\Omega_{23})^2r_1]\}a_1 = 0 \end{aligned}$$

in which the polynomials are linear in x. A known method, attributed to Laplace, will give integral representations of two or more solutions; see Burkill (1962) or Morse and Feshbach (1953). Forsyth (1888) describes this method, and cites several authors other than Laplace.

To solve the equation

$$(c_nx+d_n)y^{(n)}(x) + \ldots + (c_1x+d_1)y'(x) + (c_0x+d_0)y(x) = 0 \tag{A1.3}$$

we let $C(z) = c_nz^n + \ldots + c_1z + c_0$ and $D(z) = d_nz^n + \ldots + d_1z + d_0$.

If we assume that $\alpha_1, \ldots, \alpha_n$ the zeros of $C(z)$, are all distinct, so that $D(z)/C(z)$ can be written in the form

$$\frac{D(z)}{C(z)} = d_0 + \frac{k_1}{z-\alpha_1} + \ldots + \frac{k_n}{z-\alpha_n}$$

then a solution of (A1.3) can be written as

$$y(x) = \int_C \exp[(x+k_0)z](z-\alpha_1)^{k_1-1} \ldots (z-\alpha_n)^{k_n-1}\, dz$$

where the contour C is chosen so that

$$\exp[(x+k_0)z](z-\alpha_1)^{k_1} \ldots (z-\alpha_n)^{k_n}$$

vanishes at both ends.

In our case the integral representation is

$$a_1 = \int (z+ir_1)^{-1+ip}(z+ir_2)^{-1/2-ip+iq}(z+ir_3)^{-iq} \exp(zt^2)\, dz \qquad \text{(A1.4)}$$

assuming that r_1, r_2 and r_3 have three distinct values. The parameters p and q are defined by (4). A similar calculation gives a similar integral representation for a_3. The integrands used for a_1 and a_3 have three branch points, at $-ir_1$, $-ir_2$ and $-ir_3$. In appendix 2, we shall use a path of integration that encloses one, and only one, of these branch points.

For the two-level model, or Landau-Zener model, Wannier (1965) writes one component of the two-component wavefunction as $t^{-1/2}$ times the Whittaker function. Whittaker (1903) defined this function by an integral similar to (A1.4), but with only two branch points. The path of integration in this definition encloses one branch point but not the other. We have solved the three-level problem simply by using a third branch point.

If the values of r_1, r_2 and r_3 are not distinct, the calculations are simpler. Use of (A1.2) is not desirable. We can use the simple transformation mentioned early in § 3 to make at least two of the coefficients r_1, r_2 and r_3 vanish. Then (A1.1) has the form of (A1.3). The resulting integral representations are used in appendices 3 and 4. If $r_1 = r_2 = r_3$, we can make all the diagonal elements of the matrix in (2) vanish, so that solutions of (2) are easily found.

Appendix 2. Non-resonant cases

Here, we assume that the values of r_1, r_2 and r_3 are distinct. This is to say that the two coefficients in (3) are non-zero, and the sum of the two detunings vanishes only at $t = 0$. In integrands such as that in (A1.4), the three branch points are distinct. We draw a branch line to the left from each branch point; it is on or parallel to the negative real z axis. The path of integration has ends far to the left in the z plane, where $|\exp(zt^2)|$ is negligible. It does not cross any branch line. It encloses one and only

one branch point and it goes around the branch point in the usual counterclockwise direction. The same path of integration is used in each component of the vector

$$V_j = \begin{pmatrix} iN_j(\Omega_{12}/8)\int (z+ir_1)^{-1+ip}(z+ir_2)^{-1/2-ip+iq}(z+ir_3)^{-iq}\exp(zt)^2\,dz \\ \tfrac{1}{2}tN_j\int (z+ir_1)^{ip}(z+ir_2)^{-1/2-ip+iq}(z+ir_3)^{-iq}\exp(zt^2)\,dz \\ iN_j(\Omega_{23}/8)\int (z+ir_1)^{ip}(z+ir_2)^{-1/2-ip+iq}(z+ir_3)^{-1-iq}\exp(zt^2)\,dz \end{pmatrix}. \tag{A2.1}$$

The subscript j, which is 1, 2 or 3, serves to distinguish the three paths of integration; the path used for V_j encloses $-ir_j$ and no other branch point. The normalisation constant N_j will be determined shortly. Using partial integration, one verifies that (A2.1) is a solution of (2). This verification does not go through if $t=0$ and one of the integrals in (A2.1) diverges if $t=0$. Consideration of this difficulty is postponed.

We assume that t is real. Wannier (1965) uses large complex values of t to find the transition probability for the two-level case, but such a calculation seems entirely impractical for the three-level case. We also assume that Ω_{12} and Ω_{23} are positive. The relative phases of a_1, a_2 and a_3 can be adjusted so that Ω_{12} and Ω_{23} are positive, except in the simple case where one of them vanishes.

The three solutions of (2) that we call V_1, V_2 and V_3 have simple behaviours as $t\to\pm\infty$. In the z plane, the neighbourhood of $-ir_j$ determines the behaviour of V_j when $|t|$ is large, and one component of the vector is dominant. This leads to a simple computation of the normalisation constants N_j. For example, if $r_2>r_1>r_3$

$$N_1=\frac{\exp[\pi(q-\frac{1}{2}p)]}{[\pi\sinh(\pi|p|)]^{1/2}} \qquad N_2=\frac{\exp[\frac{1}{2}\pi(q-p)]}{[\pi\cosh(\pi p-\pi q)]^{1/2}} \qquad N_3=\frac{\exp(\frac{1}{2}\pi q)}{[\pi\sinh(\pi q)]^{1/2}}$$

and $t\to\pm\infty$ gives

$$V_1\sim\begin{pmatrix} \exp\{-ir_1t^2-i(p-q)\ln[(r_2-r_1)t^2]-iq\ln[(r_1-r_3)t^2]+i\arg[\Gamma(ip)]+\frac{1}{4}i\pi\} \\ 0 \\ 0 \end{pmatrix}.$$

Terms in $1/t$ and powers of $1/t$ are not shown here. It is clear that V_1 is correctly normalised when $|t|$ is sufficiently large. Since it satisfies (2), the Schrödinger equation, when $t\neq 0$, it is correctly normalised when $t\neq 0$. The asymptotic form of V_2 at large $|t|$ is similar, except that the second component is dominant. In V_3, the third component is dominant when $|t|$ is large. This means that V_1, V_2 and V_3 are normalised and orthogonal when $|t|$ is sufficiently large. The Schrödinger equation (2) is used to show that they are normalised and orthogonal when $t\neq 0$.

We now have a complete set of orthonormal vectors V_j, although the normalisation constants N_j have to be computed in each of the six cases. The vectors V_1, V_2 and V_3 satisfy (2) when $t\neq 0$, which makes them quite useful as basis vectors for describing solutions of (2). Since the middle component of (A2.1) is discontinuous at $t=0$, these basis vectors are not themselves the desired solutions of (2). The general solution of (2) can be written as $A_1V_1+A_2V_2+A_3V_3$, where the coefficients A_1, A_2, A_3 are time dependent only because of the difficulty at $t=0$. We write the general solution more explicitly as $A_1(\pm)V_1+A_2(\pm)V_2+A_3(\pm)V_3$, where the ambiguous sign is the sign of t. The general solution is continuous at $t=0$, of course. Continuity of the

three components of the wavefunction gives three linear equations to determine $A_1(+)$, $A_2(+)$ and $A_3(+)$ in terms of $A_1(-)$, $A_2(-)$ and $A_3(-)$, or vice versa. Solving these equations will give the unitary matrix that relates the basis vectors for $t>0$ to the basis vectors for $t<0$. This unitary matrix is just the S matrix, because the initial condition, applied at large negative t, implies that two of the coefficients $A_1(-)$, $A_2(-)$ and $A_3(-)$ are zero. Each final occupation probability is the absolute square of an $A_j(+)$ or of an element of the S matrix.

The linear equations to determine the S matrix can be written out after we calculate the limits of V_j as $t\to 0$, from above and from below. These limits involve beta functions times hypergeometric functions. Hypergeometric functions of two different arguments appear, but the two arguments are positive and their sum is unity. A standard formula can be used to write the equations for the S matrix in terms of hypergeometric functions of the same argument. Because of differences in the three parameters of the hypergeometric function, we have four different hypergeometric functions at this stage. The Wronskian of an ordinary linear second-order differential equation is used to find a useful relation among these four hypergeometric functions. Then the hypergeometric functions, the beta functions and the complex numbers can be eliminated from the linear equations for the S matrix, which turns out to be real and symmetric. The square roots drop out when final occupation probabilities are calculated, and we find the simple results shown in table 1.

A more detailed account of this lengthy calculation was given by Carroll and Hioe (1985), but only for the case of $r_1>r_2>r_3$. The case of $r_1<r_2<r_3$ can be obtained by interchanging the labels 1 and 3 or by using the time-reversal transformation to change the signs of r_1, r_2 and r_3. In (2), one may replace a_1, a_2 and a_3 by their complex conjugates and also change the signs of i, t, r_1, r_2 and r_3; this leaves (2) unchanged. This transformation and the simple interchange of 1 and 3 can be used to avoid treating all six of the non-resonant cases. Only two of them have to be treated explicitly, starting with calculation of N_1, N_2 and N_3. If the two detunings in (3) have the same sign, we can use the calculation in our earlier paper. To treat the case of opposite signs in (3), the whole lengthy calculation has to be repeated.

Appendix 3. One detuning is zero

If $r_1=r_2\neq r_3$, we assume $r_1=r_2=0$, to find a solution of (A1.1), and then remove this assumption. The exact solution of (2) has the form

$$a_1=\frac{\Omega_{12}\Omega_{23}}{8[\pi(r_1-r_3)]^{1/2}}\int (z-\tfrac{1}{2}\Omega_{12})^{-1+iq}(z+\tfrac{1}{2}\Omega_{12})^{-1+iq}\exp\left(-\frac{iz^2}{4(r_1-r_3)}-izt-ir_1t^2\right)dz$$

$$a_2=\frac{-\Omega_{23}}{4[\pi(r_1-r_3)]^{1/2}}\int z(z-\tfrac{1}{2}\Omega_{12})^{-1+iq}(z+\tfrac{1}{2}\Omega_{12})^{-1+iq}\exp\left(-\frac{iz^2}{4(r_1-r_3)}-izt-ir_1t^2\right)dz$$

$$a_3=\tfrac{1}{2}[\pi(r_1-r_3)]^{-1/2}\int (z-\tfrac{1}{2}\Omega_{12})^{iq}(z+\tfrac{1}{2}\Omega_{12})^{iq}\exp\left(-\frac{iz^2}{4(r_1-r_3)}-izt-ir_1t^2\right)dz$$

where q is given by (4) and the same path of integraition is used in all three integrals. Three independent solutions can be obtained by altering the branch lines and the path of integration. The branch lines that we shall use are rays that run downward from $z=\pm\frac{1}{2}\Omega_{12}$, parallel to the negative imaginary axis. The path of integration will run off to ∞ in two opposite quadrants of the complex plane. If $r_1>r_3$, the normalisation

factor of $[\pi(r_1-r_3)]^{-1/2}$ that appears here is correct; if $r_1<r_3$, a normalisation factor of $[\pi(r_3-r_1)]^{-1/2}\exp(2\pi q)$ should be used instead. An overall phase factor in this solution depends on what units of frequency are used; the reader may prefer a solution in dimensionless form.

If t is large and negative, the path of integration for this solution can be deformed to run through the saddle point at $z\simeq -2(r_1-r_3)t$ and stay away from the branch lines. In the limit as $t\to-\infty$, this solution gives zero occupation probabilities for levels 1 and 2. As $t\to+\infty$, the occupation probabilities of levels 1 and 2 oscillate indefinitely, and the occupation probability of level 3 approaches the limit shown in table 2. If $r_1\neq r_2=r_3$, we may exchange the labels 1 and 3 rather than repeating this calculation.

Appendix 4. Sum of detunings is zero

In the remaining case, $r_1=r_3\neq r_2$. Some exact solutions of (2) have the form

$$a_1=\frac{\Omega_{12}}{4[\pi(r_1-r_2)]^{1/2}}\int z^{-1+2i(p-q)}\exp\left(-\frac{iz^2}{4(r_1-r_2)}-izt-ir_1t^2\right)dz$$

$$a_2=\frac{-1}{2[\pi(r_1-r_2)]^{1/2}}\int z^{2i(p-q)}\exp\left(-\frac{iz^2}{4(r_1-r_2)}-izt-ir_1t^2\right)dz$$

$$a_3=\frac{\Omega_{23}}{4[\pi(r_1-r_2)]^{1/2}}\int z^{-1+2i(p-q)}\exp\left(-\frac{iz^2}{4(r_1-r_2)}-izt-ir_1t^2\right)dz$$

where the same path of integration is used in all three integrals. This integral representation gives two independent solutions of (2). The third solution has $a_2=0$, while a_1 and a_3 are constant multiples of $\exp(-ir_1t^2)$. To obtain definite occupation probabilities in the limit as $t\to-\infty$, we ignore the third solution and use the negative imaginary axis as the branch line. The path of integration runs off to ∞ in two opposite quadrants. If $r_1>r_2$, the normalisation factor written in front of these integrals is correct; if $r_1<r_2$, it must be changed. If t is large and negative, the path of integration can go through the saddle point at $z\simeq-2(r_1-r_2)t$ and stay away from the branch point at $z=0$. This gives the initial occupation probabilities shown in table 3. Further calculation gives the final occupation probabilities shown in table 3.

References

Abe Y and Park J Y 1983 *Phys. Rev.* C **28** 2316

Allen L and Eberly J H 1975 *Optical Resonance and Two-Level Atoms* (New York: Wiley)

Atabek O, Lefebvre R and Jacon M 1984 *J. Chem. Phys.* **81** 3874

Bloch F and Siegert A 1940 *Phys. Rev.* **57** 522

Burkill J C 1962 *The Theory of Ordinary Differential Equations* (London: Oliver and Boyd) p 60

Carroll C E and Hioe F T 1985 *J. Opt. Soc. Am.* B **2** 1355

Demkov Yu N 1966 *Dokl. Akad. Nauk* **166** 1076 (*Sov. Phys.-Dokl.* **11** 138)

Einwohner T H, Wong J and Garrison J C 1976 *Phys. Rev.* A **14** 1452

Forsyth A R 1888 *A Treatise on Differential Equations* (London: MacMillan) § 135ff

Henry C H and Lang D V 1977 *Phys. Rev.* B **15** 989

Landau L 1932 *Phys. Z. Sowj.* **2** 46

Morse P M and Feshbach H 1953 *Methods of Theoretical Physics* (New York: McGraw-Hill) p 606

Rubbmark J R, Kash M M, Littman M G and Kleppner D 1981 *Phys. Rev.* A **23** 3107
Shirley J H 1965 *Phys. Rev.* **138** B979
Stevenson A F 1940 *Phys. Rev.* **58** 1061
Wannier G H 1965 *Physics* **1** 251
Whittaker E T 1903 *Bull. Am. Math. Soc.* **10** 125
Zener C 1932 *Proc. R. Soc.* A **137** 696