

Approximate solutions to two-level transition and surface-ion neutralisation problems

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys. A: Math. Gen. 23 1101

(<http://iopscience.iop.org/0305-4470/23/7/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 01/06/2010 at 10:03

Please note that [terms and conditions apply](#).

Approximate solutions to two-level transition and surface-ion neutralisation problems

B L Burrows[†] and A T Amos[‡]

[†] Department of Mathematics, Staffordshire Polytechnic, Beaconside, Stafford ST18 0AD, UK

[‡] Department of Mathematics, University of Nottingham, Nottingham NG7 2RD, UK

Received 30 March 1989

Abstract. Approximate analytical solutions for the dynamical variation of a two-level system with a time-dependent pulse potential are introduced. These approximations are based on the replacement of the potential by a series of step functions and, in principle, can be as accurate as required. The method is extended to many-level transition problems such as those which arise in the theory of surface-ion neutralisation

1. Introduction

The dynamics of a two-level system coupled by an external time-dependent field is a problem which has been of importance for at least 50 years (Rosen and Zener 1932) and in which there has been a considerable revival of interest recently.

The problem can be described by the two equations

$$\frac{da_1}{dt} = -iV(t)e^{i\alpha t}a_2, \quad \frac{da_2}{dt} = -iV(t)e^{-i\alpha t}a_1, \quad (1)$$

where $a_1 = 1$ and $a_2 = 0$ as $t \rightarrow -\infty$ and where $V(t)$ is a pulse potential. By the term pulse potential we mean a real, non-negative, sectionally continuous function which, for large $|t|$, decreases monotonically to zero, and for which

$$\int_{-\infty}^{\infty} V(t) dt < \infty. \quad (2)$$

These equations arise in any semiclassical two-state calculation coupled by such a potential and in two-state quantum problems in which the levels are coupled by a nearly resonant oscillating field so that the anti-resonant component can be neglected.

It is possible to treat the two-state problem numerically using standard techniques for solving systems of differential equations such as Runge-Kutta or predictor-corrector methods. However, interest has also been shown in analytical solutions by many authors including Bambini and Berman (1981), Robinson and Berman (1983), Bambini and Lindberg (1984), Robinson (1984, 1985a, 1985b), Hioe (1984), Carroll and Hioe (1986). In general, the class of pulses considered analytically is restricted, and most of the solutions are for pulses which are symmetric with respect to the origin, although recently a few calculations have been made for non-symmetric pulses. Furthermore, the solutions are given in terms of hypergeometric functions and, in most cases, further analysis is necessary to examine the shape and magnitude of the probability amplitudes a_1 and a_2 .

Equations (1) can be generalised to an n -level problem. One particular example of current interest is in the theory of surface-ion neutralisation (SIN). For a review and references see Amos *et al* (1989). Experimentally, a positive ion is scattered from a solid surface and, in the process, may gain an electron from the solid, thus becoming neutralised. Theoretically this can be modelled using an Anderson–Newns Hamiltonian within the Hartree or Hartree–Fock approximation (Blandin *et al* 1976, Bloss and Hone 1978). This leads to a one-electron Schrödinger equation for the molecular orbitals $|\psi_j(t)\rangle$ of the system with a time-dependent one-electron Hamiltonian of the form:

$$\mathcal{H}(t) = \varepsilon_0|0\rangle\langle 0| + \sum_{k=1}^n \varepsilon_k|\chi_k\rangle\langle\chi_k| + \sum_{k=1}^n v_k V(t)(|0\rangle\langle\chi_k| + |\chi_k\rangle\langle 0|) \quad (3)$$

where $|0\rangle$ and ε_0 are the vacant orbital and orbital energy of the incoming ion, $|\chi_k\rangle$ and ε_k ($k = 1, \dots, n$) are the initial states and energy levels of the solid band with which the ion interacts. The final term in (3) is the interaction potential, which involves terms such as $v_k V(t)$, representing the interaction between $|0\rangle$ and $|\chi_k\rangle$, which is assumed to be the product of a constant v_k , depending on $|\chi_k\rangle$ and a time-dependent potential $V(t)$ independent of $|\chi_k\rangle$. The exact form of $V(t)$ is not known precisely but, since it should increase from zero to a maximum as the ion approaches the surface and then fall away to zero again as the ion is scattered, it should be a pulse-like potential and should satisfy (2).

Writing the molecular orbital in the form

$$|\Psi_j(t)\rangle = a_{0j}(t) e^{-i\varepsilon_0 t}|0\rangle + \sum_{k=1}^n a_{kj}(t) e^{-i\varepsilon_k t}|\chi_k\rangle \quad (4)$$

and substituting into the time-dependent Schrödinger equation leads to the set of equations (Davison *et al* 1986, Amos *et al* 1989)

$$\begin{aligned} \dot{a}_{0j}(t) &= -i \sum_{k=1}^n v_k V(t) e^{i\omega_k t} a_{kj}(t) \\ \dot{a}_{kj}(t) &= -i v_k V(t) e^{-i\omega_k t} a_{0j}(t) \quad k = 1 \dots n \end{aligned} \quad (5)$$

where $\omega_k = \varepsilon_0 - \varepsilon_k$ and subject to the initial conditions

$$a_{0j}(-\infty) = 0 \quad a_{kj}(-\infty) = \delta_{kj}. \quad (6)$$

Equations (5) and (6) are generalised forms of (1). The quantity of interest is the probability of neutralisation which, allowing for spin, is given by

$$P(\infty) = 2 \sum_{i=1}^p |a_{0j}(\infty)|^2 \quad (7)$$

where p is the number of doubly occupied orbitals. There have been many papers which have estimated the value of P for various systems and have considered its dependence on such physical parameters as the ion's speed and the bandwidth of the solid. However, although there have been a few attempts to calculate $P(\infty)$ by solving (5) numerically (Muda and Hanawa 1980, McDowell 1982, Grimley *et al* 1983, Sulston *et al* 1988a) in the main, theoretical treatments of the problem has relied on making various approximations (Blandin *et al* 1976, Bloss and Hone 1978, Brako and Newns 1981, Sulston *et al* 1988b).

In this paper, we describe how a particular set of approximate solutions to (1) and (5) can be found for any pulse potential $V(t)$ satisfying (2). These approximate solutions are obtained by considering a set of N subintervals $\{[t_{n-1}, t_n], n = 1, \dots, N\}$ within each of which $V(t)$ is replaced by a constant potential λ_n , so that the equation of motion becomes very simple. Consequently, the solutions are expressed in terms of sinusoidal functions in the various intervals and so the approximation is actually the composition of a number of analytic solutions valid in these intervals. The composite solution is forced to be continuous by imposing this as a requirement at $t = t_n$ for all n , but the derivatives change discontinuously at these division points in most examples. As we shall show, at least for the two-level case, it is an almost trivial exercise to obtain these approximate solutions, and the algorithm can be used on the simplest microcomputer. Since, within each interval, the solution has analytic form, we believe the method we describe has both qualitative and quantitative advantages.

2. The analytic approximation

We first discuss how we approximate $V(t)$. Equation (2) implies that to within any given error ϵ we can find a T such that $V(t)$ may be ignored in $|t| > T$. For $|t| < T$ we use a series of N step functions, and so we write

$$V(t) \approx \hat{V}(t) = \sum_{n=0}^{N-1} \lambda_n (u(t_n) - u(t_{n+1})) \tag{8}$$

with $t_0 = -T$ and $t_N = T$ and where $u(t_n)$ is the Heaviside step function, which is zero for $t < t_n$ and unity for $t \geq t_n$. A method of solving the time-independent Schrödinger equation for bound-state problems, by approximating a scalar potential in a similar way, has been introduced by Canosa and de Oliveira (1970). Our assumption is that, by suitable choice of T and the parameters $\{t_n, \lambda_n\}$, the error $|V(t) - \hat{V}(t)|$ can be made as small as desired. In practice, we wish to use as few intervals as possible and, for the two-level problem, a maximum of 24 are used. The $\{t_n\}$, which define these, were chosen so that there was a fairly uniform change in $|V(t_{n+1}) - V(t_n)|$ for all n . The λ_n were taken to be the mean values[†] of $V(t)$ in the interval, i.e.

$$\lambda_n = \frac{1}{t_{n+1} - t_n} \int_{t_n}^{t_{n+1}} V(t) dt \tag{9}$$

since they are the minimum values of

$$G(\lambda) = \int_{t_n}^{t_{n+1}} (\lambda - V(t))^2 dt. \tag{10}$$

For the cases we have examined, this seemed to lead to a quite satisfactory approximation to $V(t)$, but other criteria may be better for different pulse shapes. Note, however, that to ensure convergence as the number of intervals is increased, we require

$$\min_{[t_n, t_{n+1}]} V(t) \leq \lambda_n \leq \max_{[t_n, t_{n+1}]} V(t) \tag{11}$$

which is, of course, satisfied by (9).

[†] Numerical approximations to these will suffice when their exact values are not expressible in terms of elementary functions.

Turning now to the equations of motion (1), we introduce the substitutions

$$a_1 = \phi_1 e^{i\alpha t/2} \quad a_2 = \phi_2 e^{-i\alpha t/2} \tag{12}$$

so that, in matrix form, the equations become

$$\dot{\phi}(t) = -i\mathbf{A}(t)\phi(t) \tag{13}$$

with

$$\phi = \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} \quad \mathbf{A} = \begin{bmatrix} \frac{1}{2}\alpha & V(t) \\ V(t) & -\frac{1}{2}\alpha \end{bmatrix}$$

where $\phi_2 = 0$ and $\phi_1 = \exp(-\frac{1}{2}i\alpha t)$ as $t \rightarrow -\infty$. Thus we take $\phi_2(-T) = 0$ and

$$\phi_1(-T) = \cos \frac{1}{2}\alpha T + i \sin \frac{1}{2}\alpha T. \tag{14}$$

Similarly, equations (5) can be put in the form of (13) with

$$\phi = \begin{bmatrix} a_{0j} \\ a_{1j} \exp(i\omega_1 t) \\ \vdots \\ a_{nj} \exp(i\omega_n t) \end{bmatrix} \quad \mathbf{A} = \begin{bmatrix} 0 & v_1 V(t) & \dots & v_n V(t) \\ v_1 V(t) & -\omega_1 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ v_n V(t) & 0 & \dots & -\omega_n \end{bmatrix}. \tag{15}$$

We now approximate $V(t)$ by the series of step functions as in (8), so that in the subinterval $[t_r, t_{r+1}]$, (13) becomes

$$\dot{\phi}(t) = -i\mathbf{A}_r\phi \tag{16}$$

where \mathbf{A}_r is obtained by replacing $V(t)$ in \mathbf{A} by λ_r , so that \mathbf{A}_r is a constant matrix. The solution of (16) is

$$\phi(t) = \exp[-i\mathbf{A}_r(t - t_r)]\phi(t_r) \tag{17}$$

where $\phi(t_r)$ is obtained from the solution in the previous subinterval $[t_{r-1}, t_r]$. Therefore,

$$\phi(t_N) = \left(\prod_{r=0}^{N-1} \exp[-i\mathbf{A}_r(t_{r+1} - t_r)] \right) \phi(t_0). \tag{18}$$

A more useful form for computation is

$$\phi(t_N) = \left(\prod_{r=0}^{N-1} \mathbf{U}_r \mathbf{D}_r \mathbf{U}_r^+ \right) \phi(t_0) \tag{19}$$

where \mathbf{D}_r is the diagonal matrix whose j th element is

$$\exp[-i\nu_{rj}(t_{r+1} - t_r)]$$

where the $\{\nu_{rj}\}$ are the eigenvalues of \mathbf{A}_r and the columns of \mathbf{U}_r are the corresponding eigenvectors.

Standard techniques in the theory of linear differential equations (see, for example, Cesari 1963, Coddington and Levinson 1955) can be used to show that $\phi(t_N)$ will tend to the exact solution $\phi(\infty)$ as the difference between the approximate and real potential tends to zero, the error being related to the modulus of this difference integrated over $(-\infty, \infty)$. Consequently, increasing the number of intervals will decrease the overall error, and so the method is inherently stable. We note that any phase errors arising from the approximation are unimportant since the quantities of physical interest involve moduli only.

3. The two-level problem

To illustrate the method we consider two examples of a two-level problem. Firstly we use the Lorentzian pulse

$$V(t) = \frac{\Delta}{\pi} \frac{1}{1+t^2} \tag{20}$$

with $\alpha = 0.1$, which has been investigated by a number of authors. We take $T = 20$ and $N = 23$ to represent the pulse in the step-function form of (8), the division points $\{t_n\}$ being listed in table 1. Applying (18), we can then obtain values for $|\phi_2(T)|^2$, which corresponds to the probability that at $t = \infty$, the system has transferred to the state originally unoccupied. These values are compared in table 1 with numerical results obtained by Yeh and Berman (quoted in Robinson 1984) and with accurate Runge-Kutta numerical results. The agreement between the numerical results and our results is very satisfactory.

We now consider the example of the non-symmetric pulse

$$V(t) = \begin{cases} 0.1 e^{5t} & t < 0 \\ 0.1 e^{-6t} & t \geq 0 \end{cases} \tag{21}$$

when $\alpha = 1$. The pulse $V(t)$ is small so that we have truncated by ignoring $V(t)$ for $|t| > 2 = T$. In table 2 we list the values of the real and imaginary parts p_1 and p_2 , q_1 and q_2 of ϕ_1 and ϕ_2 at $t = 2$ obtained using the 10, 6 and 4 points given in the table. These points were chosen, as in the last example, to give a uniformly small variation

Table 1. Example calculations for Lorentzian pulses with various values of Δ . The points used are $\pm 20, \pm 10, \pm 5, \pm 3, \pm 2, \pm 1.25, \pm 1.0, \pm 0.8, \pm 0.6, \pm 0.5, \pm 0.4$ and ± 0.2 .

Δ	$ \phi_2(T) ^2$	$ a_2(\infty) ^{2\dagger}$	Runge-Kutta‡
0.1π	0.079	0.077	0.078
0.5π	0.920	0.911	0.919
π	0.034	0.050	0.040
1.5π	0.747	0.680	0.734

† Yeh and Berman, as quoted in Robinson (1984).

‡ Obtained using 1600 points in the interval $[-20, 20]$.

Table 2. The non-symmetric pulse calculations†.

	Ten-point calculation	Six-point§ calculation	Four-point‡ calculation	Runge-Kutta calculation		
				200 points	1200 points	4000 points
$p_1(2)$	0.540	0.540	0.540	0.531	0.538	0.540
$q_1(2)$	-0.841	-0.841	-0.841	-0.846	-0.846	-0.841
$p_2(2)$	0.030	0.028	0.022	0.031	0.030	0.030
$q_2(2)$	-0.018	-0.015	-0.011	-0.018	-0.018	-0.018

† All values are given correct to three decimal places.

‡ The points used are $\pm 2, \pm 0.1$.

§ The points used are $\pm 2, \pm 0.1$ and ± 0.25 .

|| The points used are $\pm 2, \pm 0.1, \pm 0.25, \pm 0.8$ and ± 0.05 .

in $V(t)$ from a tabulation of values of $V(t)$. Thus, for example, using four points in $|t| < 2$ gives three intervals for which the variation is approximately 0.05. The number of points can be increased using this strategy so that the difference between the approximate and correct potential becomes as small as is felt necessary. Our results are compared with Runge-Kutta values using 200, 1200 and 4000 equally spaced points in $|t| < 2$.

The table illustrates how convergence can be tested by increasing the number of intervals used. The slow convergence of the Runge-Kutta method is almost certainly due to the fact that the points used are evenly spaced, whereas for a pulse potential the density of points should be larger near the peak of the pulse. Clearly a numerical method can be constructed with this feature, but the simple analytical approximation used here suffices.

We wish to point out that the approximate analytical solutions obtained in this way do have a particularly simple form. As an illustration of this, we can write the solution in the interval $[-0.1, -0.05]$ for the 10-point calculation as

$$\phi(t) = e^{i\mu(t+0.1)} b_1 + e^{-i\mu(t+0.1)} b_2 \tag{22}$$

where $\mu = 0.5047$ and $-\mu$ are the eigenvalues of A_3 and b_1 and b_2 are constant vectors related to the eigenvectors of A_3 and $\phi(-0.1)$.

We note that the analytical solutions are continuous at the interval points but not differentiable. This is not a serious disadvantage, however, since we are free to choose the data points arbitrarily so that approximations to the derivatives can be obtained at any point.

We now examine the accuracy of the approximations. Equation (13) may be written in the form of integral equations

$$\begin{aligned} \phi_1(t) &= -i \int_{-\infty}^t e^{-i\alpha(t-x)/2} V(x) \phi_2(x) dx + e^{-i\alpha t/2} \\ \phi_2(t) &= -i \int_{-\infty}^t e^{i\alpha(t-x)/2} V(x) \phi_1(x) dx. \end{aligned} \tag{23}$$

Now, the definition of $V(t)$ implies that for any given error ϵ we can find $-T_1$ such that

$$\int_{-\infty}^t V(t) dt < \epsilon \quad \text{for } t < -T_1. \tag{24}$$

Consequently, since $|\phi_k(x)| \leq 1$

$$\left| \int_{-\infty}^t e^{i\alpha(t-x)/2} V(x) \phi_k(x) dx \right| < \epsilon \quad \text{for } t < -T_1, k = 1 \text{ or } 2 \tag{25}$$

which shows that truncation is always possible for any given tolerance and a similar argument shows that, for $t > T > T_1$,

$$|\phi_k(t) - \phi_k(T)| < \epsilon \quad k = 1, 2. \tag{26}$$

The last result implies that we can always estimate the asymptotic values to any given accuracy (using $\phi_k(T) \approx \phi_k(\infty)$). Furthermore, whatever definition of integration is used (Riemann or Lebesgue), by choosing $\max|t_{n+1} - t_n|$ sufficiently small and λ_n satisfying (6), we can ensure that

$$\int_{-T}^T |V - \hat{V}| dt < \epsilon \tag{27}$$

for any given error ϵ . This shows that in principle it is always possible to replace V by \hat{V} in (8) or (23), with the consequent errors in ϕ_1 and ϕ_2 being as small as required.

4. A many-level system: SIN

The potential function most frequently used in theoretical treatments of SIN problems is

$$V(t) = V_0 e^{-\mu|t|} \tag{28}$$

where V_0 and μ are constants. The constant μ is proportional to the speed of the ion and values of about 0.1–0.2 au correspond to slow ions with larger values around 10 au corresponding to fast ions. Values used for V_0 tend to be in the range 0.25–1.0 au.

It should be stressed that the exact form of $V(t)$ is not precisely known. Equation (28) is used because it has the overall shape and properties intuitively expected of the correct potential. In view of the highly approximate nature of the potential used, detailed quantitative results have little validity and the major interest is the qualitative behaviour of the neutralisation probability $P(\infty)$, obtained from the solutions of (15) via (7).

To approximate $V(t)$ by $\hat{V}(t)$, as in (8), we use N subintervals (N odd) symmetrically placed with respect to the origin so that $t_0, \dots, t_{(N-1)/2}$ are negative, and $t_n = -t_{N-n}$. Thus $\hat{V}(t)$ will be an even function of t . We take $t_0 = -T$, with T to be determined, and $t_n = \mu^{-1} \log(1 - 2n/N + 1)$ ($n = 1, \dots, \frac{1}{2}(N-1)$). This ensures that, in all subintervals except the extreme outer intervals and the central one, $V(t)$ increases or decreases by the same amount. We have examined other choices for the $\{t_n\}$, but have found none which prove better overall for a range of values of the parameters. The λ_n are chosen as in (9). An analysis of the error in the fit, as measured by (10), for the interval $[t_1, t_{N-1}]$, shows that it is $O(\mu^{-1}N^{-2})$. Thus, for large values of μ (fast ions), a reasonable fit can be found with a small number of intervals, whereas for smaller values of μ a larger number of intervals may be required.

We now consider the asymptotic regions, $t < t_1$ and $t > t_{N-1}$. When $N > 1$, we choose $t_0 = -T$, $t_N = T$ and $\lambda_0 = \lambda_N$ with

$$\lambda_N(T - t_{N-1}) = \int_{t_{N-1}}^{\infty} V_0 e^{-\mu t} dt \tag{29}$$

so as to preserve the asymptotic area under the curve and

$$\lambda_N^2(T - t_{N-1}) = \int_{t_{N-1}}^{\infty} V_0^2 e^{-2\mu t} dt \tag{30}$$

so as to preserve the area under the square of $V(t)$ in the asymptotic region. This leads to the values $\lambda_N = V_0/N + 1$ and $T = t_{N-1} + 2\mu^{-1}$. For $N = 1$, $\lambda_1 = V_0/2$ and $T = 2\mu^{-1}$. Consequently the error in fitting $\hat{V}(t)$ to $V(t)$ in the asymptotic region as measured by

$$\int_{-\infty}^{t_1} [V(t) - \hat{V}(t)]^2 dt + \int_{t_{N-1}}^{\infty} [V(t) - \hat{V}(t)]^2 dt \tag{31}$$

will be $O(\mu^{-1}N^{-2})$, just as for the central region $[t_1, t_{N-1}]$.

With the choices described above, all the $\{\lambda_i\}$ turn out to be independent of μ and, therefore, so do the matrices \mathbf{A}_r in (16). This leads to a considerable simplification if neutralisation probabilities have to be computed for a range of values for μ , because the eigenvectors and eigenvalues of \mathbf{A}_r , used to form the matrices in (19), have to be computed once and once only.

The term resonant charge transfer is usually applied to SIN processes in which the solid band is wide and the energy of the valence orbital of the scattered ion is close to or actually lies within the energy band of the solid. Quasi-resonance is applied to the case where the participating band is narrow, such as the core band of a metal or the valence band of an alkali halide solid, and where the energy of the valence orbital lies outside the band. We now present two sets of calculations to illustrate the use of our method for both of these situations.

We follow most authors in this area by modelling the solid as a tight-binding one-dimensional array of M atoms with tight-binding parameters α and β . We take $\alpha = -0.1$ au and use two values for β , $\beta = -0.125$ au and $\beta = -0.0125$ au. Since the band width is $4|\beta|$, the former choice of β corresponds to a wide band (resonant charge transfer) and the latter to a narrow band (quasi-resonant charge transfer). We use $V_0 = 0.5$ au for the interactive strength and, for the valence level of the ion, $\epsilon_0 = -0.2$ au so that in the wide-band case it lies within the band, while for the narrow-band quasi-resonant case it lies well below the band. Numerical calculations using the Runge-Kutta-Merson method have been made for these systems and can be regarded as effectively exact values for comparison.

Firstly we demonstrate that our method can give values in agreement with the 'exact' Runge-Kutta-Merson values provided N , the number of intervals used in (8), is taken large enough. This is shown in tables 3 and 4. The number of intervals required depends significantly on the parameter μ^{-1} , as would be expected. For μ^{-1} small (fast ions) rather few intervals are needed, but to get accurate values when μ^{-1} is large (slow ions) as many as 200 have to be used. However, even for slow ions, qualitatively reasonable results are obtained for $N = 19$.

Table 3. Effect on neutralisation probability of number of intervals (narrow-band case).

μ^{-1}	Calculated values of $P(T)$				Runge-Kutta-Merson value $P(\infty)$
	$N = 7$	$N = 11$	$N = 19$	$N = 199$	
1	0.694	—	—	—	0.693
3	0.025	0.027	0.029	—	0.032
10	0.267	0.076	0.015	0.035	0.036

Table 4. Effect on neutralisation probability of increasing of intervals (wide-band case).

μ^{-1}	Calculated values of $P(T)$			Runge-Kutta-Merson value $P(\infty)$
	$N = 7$	$N = 11$	$N = 199$	
1	0.682	—	—	0.681
5	0.784	0.799	0.790	0.790
10	0.921	0.902	0.875	0.876

The calculations reported in tables 3 and 4 assumed a chain of 20 atoms ($M = 20$) was sufficient to represent the solid. This assumption is tested in table 5, and it is clear that even with $M = 10$ quite satisfactory results are obtained. Thus large values of M are not required to give a good representation of the band. In table 5 we consider also the case $M = 1$. Since this can be regarded as taking the limit $\beta = 0$, it is not surprising that the $M = 1$ results cannot be applied to the wide band, but clearly do correspond to the narrow band. What is surprising is that, for the narrow band, taking $M = 1$ gives remarkably good results.

Obviously the smaller the values used for M and N , the faster and more efficient is our numerical method. It seems worthwhile, therefore, to examine how well the results given by using small values of these parameters compare qualitatively with the 'exact' results based on the exponential. However, it turns out to be necessary to treat narrow bands and wide bands quite differently.

In order to obtain results with the correct qualitative behaviour for a wide band, we find it is necessary to take reasonably large values of M so as to give a good representation of the band. A suitable choice for M depends not only on the band width but, also, and we stress this point, on the value of μ . For $\beta = -0.125$ and μ in the range 0.1-1.0, $M = 20$ is certainly sufficient but, for smaller values of μ , M should be increased. Therefore, for wide bands, we have only the option of using small values of N to produce a fast and efficient numerical procedure. To examine whether this can provide sufficiently accurate results, we have made calculations with $N = 1$ and $N = 3$, in both cases taking $M = 20$. In table 6, the results are compared with 'exact' numerical values.

Table 5. Effect on neutralisation probability of increasing number of states M (with $N = 3$).

μ^{-1}	Narrow band		Wide band		$M = 1$
	$M = 10$	$M = 20$	$M = 10$	$M = 20$	
1	0.695	0.696	0.683	0.681	0.696
3	0.019	0.018	0.599	0.597	0.010
10	0.742	0.743	0.925	0.924	0.729

Table 6. Ionisation probabilities for the wide-band case with $M = 20$.

μ^{-1}	Calculated values of $P(T)$		Runge-Kutta-Merson value $P(\infty)$
	$N = 1$	$N = 3$	
1	0.690	0.681	0.680
2	0.862	0.873	0.882
3	0.588	0.597	0.538
4	0.931	0.803	0.733
5	0.657	0.752	0.790
6	0.722	0.796	0.678
7	0.876	0.850	0.757
8	0.568	0.886	0.846
9	0.852	0.918	0.852
10	0.736	0.924	0.876

The table shows that, initially, there is a fairly precise fit of both $N = 1$ and $N = 3$ to the numerical results. However, only the $N = 3$ approximation gives a good qualitative fit as μ decreases. Both the 'exact' results and the $N = 3$ case give an initial oscillation followed by values approaching 1 as μ decreases. This is to be expected on the basis of the wide-band approximation used by many authors.

As we pointed out earlier, the exact form of the interaction potential for the SIN process is not known and the exponential most often used is just a qualitative approximation to it. Consequently, the purpose of calculations based on (28) is simply to establish the qualitative behaviour of the neutralisation probability as a function of the parameters of the system, particularly ion speed as represented by the parameter μ . Some attempts have been made to use simpler potentials, in particular a constant potential in an interval about $t = 0$ with zero potential outside the interval; in effect this is our method with $N = 1$. However, table 6 shows that this gives unreliable results. Fortunately the case $N = 3$, which is almost as simple, does give results in good qualitative agreement with those based on the exponential function. Since the results with $N = 3$ are quick and easy to obtain, it would seem advantageous in future SIN calculations of scattering from wide bands to replace the exponential potential by the $N = 3$ approximation to it.

For the narrow band, we find almost the exact opposite of the wide-band conclusions. It appears, as is suggested by table 5, that a small value of M , even as small as $M = 1$ when the problem becomes a two-level one, is usually sufficient. On the other hand, quite large values of N are sometimes needed to obtain the correct qualitative behaviour, particularly when μ is small. This is shown in table 7, where results for $M = 1$ and several choices for N are listed and compared with 'exact' numerical results obtained for $M = 20$. For large μ , all the calculations are in reasonable agreement, but for small μ it is highly inadvisable to attempt to use low values for N , since only with $N = 19$ and $N = 99$ are results obtained comparable to the 'exact' ones.

Table 7. Neutralisation probabilities for the narrow-band case with $M = 1$ and various N values.

μ^{-1}	Calculated values of $P(T)$					Runge-Kutta-Merson value $P(\infty)^\dagger$
	$N = 3$	$N = 5$	$N = 11$	$N = 19$	$N = 99$	
1.57	0.955	0.954	0.954	0.954	0.955	0.956
3.14	0.001	0.000	0.000	0.000	0.000	0.009
4.71	0.691	0.601	0.553	0.554	0.577	0.590
6.28	0.063	0.045	0.008	0.000	0.000	0.010
7.85	0.630	0.350	0.187	0.192	0.282	0.319
9.42	0.208	0.231	0.040	0.000	0.005	0.008

\dagger Computed with $M = 20$.

The neutralisation probabilities in table 7 are computed for μ^{-1} equal to multiples of $\frac{1}{2}\pi$ where the Rosen-Zener approximation (Amos *et al* 1986) suggests $P(\infty)$ has alternating maxima and minima ($P(\infty) = 0$). This is more or less the case with the 'exact' results, which clearly show oscillatory behaviour with the amplitude of the oscillations decreasing with increasing μ^{-1} . The same properties are found for the $N = 19$ and $N = 99$ results, but those for small values of N do not reproduce the correct qualitative behaviour.

References

- Amos A T, Davison S G and Sulston K W 1986 *Phys. Lett. A* **118** 471
Amos A T, Sulston K W and Davison S G 1989 *Adv. Chem. Phys.* **76** p 335
Bambini A and Berman P R 1981 *Phys. Rev. A* **23** 2496
Bambini A and Lindberg M 1984 *Phys. Rev. A* **30** 794
Blandin A, Nourtier A and Hone D 1976 *J. Physique* **37** 369
Bloss W and Hone D 1978 *Surf. Sci.* **72** 277
Brako R and News D M 1981 *Surf. Sci.* **108** 253
Canosa J and de Oliveira R G 1970 *J. Comp. Phys.* **5** 188
Carroll C E and Hioe F T 1986 *J. Phys. A: Math. Gen.* **19** 3579
Cesari L 1963 *Asymptotic Behavior and Stability Problems in Ordinary Differential Equations* (Berlin: Springer)
Coddington E A and Levinson N 1955 *Theory of Ordinary Differential Equations* (New York: McGraw-Hill)
Davison S G, Sulston K W and Amos A T 1986 *J. Electroanal. Chem.* **204** 173
Grimley T B, Jyothei Bhasu V C and Sebastian K L 1983 *Surf. Sci.* **124** 305
Hioe F T 1984 *Phys. Rev. A* **30** 2100
McDowell H K 1982 *J. Chem. Phys.* **77** 3263
Muda Y and Hanawa T 1980 *Surf. Sci.* **97** 283
Robinson E J 1984 *Phys. Rev. A* **29** 1665
—— 1985a *J. Phys. B: At. Mol. Phys.* **18** L657
—— 1985b *J. Phys. B: At. Mol. Phys.* **18** 3687
Robinson E J and Berman P R 1983 *Phys. Rev. A* **27** 1022
Rosen N and Zener C 1932 *Phys. Rev.* **40** 502
Spalberg M R, Los J and Devdariani A Z 1986 *Chem. Phys.* **103** 253
Sulston K W, Amos A T and Davison S G 1988a *Chem. Phys.* **124** 411
—— 1988b *Surf. Sci.* **197** 555