Exact time-dependent solutions for a double-well model

2003 J. Phys. A: Math. Gen. 36 11643

(http://iopscience.iop.org/0305-4470/36/46/008)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **36** (2003) 11643–11653 PII: S0305-4470(03)66304-3

Exact time-dependent solutions for a double-well model

B L Burrows[1,3] **and M Cohen**[2]

[1] Mathematics Division, School of Computing, Staffordshire University, Beaconside Stafford, ST 15 0DG, UK
[2] Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel

Received 18 July 2003
Published 5 November 2003
Online at stacks.iop.org/JPhysA/36/11643

Abstract

Lie algebraic techniques are used to obtain *exact* solutions of the time-dependent Schrödinger equation for a model double-well potential with an applied, time-dependent, dipole field. The model potential consists of harmonic potentials in $x > 0$ and $x < 0$ with an interface region spanning the origin and the theory of the matching of the wavefunctions for the three different regions is examined in detail. The time-dependent solutions are shown to give rise to two independent types of charge transfer arising from a positional change in the wave packet due to the applied field and the change of shape of the wave packet due to interference effects.

PACS number: 03.65.Fd

1. Introduction

Double-well models have applications in many physical and chemical problems. For example, such a model has been used to explain the infrared spectrum in the H-F dimer in a uniform electric field (Bemish *et al* 1996), to model magnetic traps for Bose–Einstein condensates (Thomas and Wilson 2002), to model a radiation field used to localize an electron in one of the wells (Grossmann *et al* 1991a, 1992), and to treat the possibility of dissociation in intense laser fields (Ivanov *et al* 1995, Seideman *et al* 1995). We have previously obtained approximate analytical solutions for the stationary states of a generic symmetric double well (Burrows and Cohen 1998) and certain asymmetric and symmetric double wells (Burrows *et al* 1996, 1998) but it is of interest to obtain *exact time-dependent* solutions of the Schrödinger equation for a double-well *model*, in order to obtain insight into the main features of these physical and chemical problems. In this paper, we consider a model in which each separate well is described by a harmonic potential.

[3] Author to whom correspondence should be addressed.

Exact solutions are available for the stationary states of the symmetric double well with potential

$$V(x) = \tfrac{1}{2}(|x|^2 - a^2) \tag{1}$$

(see Merzbacher (1961)) and it is straightforward to generalize this to the asymmetric double-well potential

$$V(x) = \begin{cases} \frac{1}{2}(x+b)^2 + V_1 & x < 0 \\ \frac{1}{2}(x-a)^2 + V_2 & x > 0 \end{cases} \tag{2}$$

where $a, b > 0$ and V_1, V_2 are real constants.

These model potentials have a discontinuity, or a discontinuity of the derivative, at $x = 0$, whereas physical potentials are usually assumed analytic. However, we can construct analytic potentials which differ *infinitesimally* from (1) or (2) and lead essentially to the same physical and mathematical properties. Such a new potential is

$$\hat{V}(x) = V(x)u(L, x) \tag{3}$$

where $V(x)$ is given by (1) or (2) and $u(L, x)$ is a fairly good function of x in the sense defined by Lighthill (1958); that is a function which is everywhere differentiable any number of times and such that this and all its derivatives are $O(|x|^M)$ as $|x| \to \infty$ for some integer M. The required form of $u(L, x)$ is

$$u(L, x) = \begin{cases} 1 & |x| \geqslant \frac{1}{N} \\ s(x) & |x| < \frac{1}{N} \end{cases} \tag{4}$$

where $s(x)$ is chosen so that $u(L, x)$ is zero at $x = 0$ and all its derivatives are zero at $x = 0$, $\pm\frac{1}{N}$. The index L, which distinguishes $u(L, x)$ from the usual Heaviside function, denotes that such functions have been constructed by Lighthill (1958). There are many ways to construct $u(L, x)$, but one particular choice exploits the function

$$S(x) = \begin{cases} \exp(-1/(1-x^2)) & |x| \leqslant 1 \\ 0 & \text{otherwise} \end{cases} \tag{5}$$

which is zero and has all derivatives zero at $x = \pm 1$; the explicit form for $u(L, x)$ in this case is derived in the appendix. With this choice of $u(L, x)$ we take N sufficiently large so that $\hat{V}(x)$ differs infinitesimally from $V(x)$ and hence any physical insights from the two potentials are identical. However, $\hat{V}(x)$ is a fairly good function and consequently we may obtain a wavefunction which is also a fairly good function. In section 2 we review briefly the stationary state theory for these models, which will be used to specify the initial conditions in the time-dependent solutions.

To treat the time-dependent applications we solve the Schrödinger equation

$$\left(-\frac{1}{2}D^2 + \hat{V}(x) + \mathrm{i}p(t)D + q(t)x + r(t)\right)\psi = \mathrm{i}\frac{\partial\psi}{\partial t} \tag{6}$$

where $D = \frac{\mathrm{d}}{\mathrm{d}x}$. In the applications referred to earlier $p(t) = r(t) = 0$ and $q(t)$ would represent the electric or time-dependent laser field. However, the model easily generalizes to include the other terms. For example, in the case where p is a real constant and $r = -p^2/2$ we may rewrite (6) in the form

$$\left(\frac{1}{2}(\mathrm{i}D + p)^2 + \hat{V}(x) + xq(t)\right)\psi = \mathrm{i}\frac{\partial\psi}{\partial t} \tag{7}$$

and this would model a situation where the origin of the coordinates used (the origin moving with the system) has fixed momentum p with respect to some fixed origin. In section 3 we give an algebraic treatment of the time-dependent problem and in section 4 several examples are presented.

2. The stationary states of the harmonic double well

The time-independent Schrödinger equation for the double well is

$$\left(-\tfrac{1}{2}D^2 + \hat{V}(x)\right)\omega_r(x) = E_r\omega_r(x). \tag{8}$$

We examine the solutions in $x \geqslant \frac{1}{N}$ and $x \leqslant -\frac{1}{N}$ separately. The solutions in $|x| < \frac{1}{N}$ clearly depend on the detailed form of $u(L, x)$, but since N can be made as large as required, the solutions in this region need not be calculated explicitly. Taking the most general potential, (2), in $x \geqslant \frac{1}{N}$ we have

$$\left(-\tfrac{1}{2}D^2 + \tfrac{1}{2}(x-a)^2\right)\omega_r(x) = E_r\omega_r(x). \tag{9}$$

This can be treated algebraically by identifying

$$J_- = -\tfrac{1}{2}D^2 \qquad \text{and} \qquad J_+ = \tfrac{1}{2}X_1^2 = \tfrac{1}{2}(x-a)^2 \tag{10}$$

and we have the commutator $[D, X_1] = 1$ so that we may form the algebra $\{J_+, J_0, J_-\}$ where

$$[J_+, J_-] = 2J_0 \qquad [J_0, J_+] = J_+ \qquad [J_0, J_-] = -J_- \tag{11}$$

with

$$J_0 = \tfrac{1}{4}(X_1D + DX_1) \tag{12}$$

Thus to find the stationary states we need to solve

$$H\omega = (J_+ + J_-)\omega = E\omega \tag{13}$$

for the *restricted* range $x \geqslant \frac{1}{N}$, subject to the usual boundary conditions as $x \to \infty$ and $x \to \frac{1}{N}$. This implies that the eigenvalue is determined by matching the solutions from the separate regions.

Using

$$v = \exp(-\gamma J_+)\omega \tag{14}$$

we have

$$\exp(-\gamma J_+)H\exp(\gamma J_+)v = (J_+ + (J_- - 2\gamma J_0 - \gamma^2 J_+))v = Ev. \tag{15}$$

Choosing $\gamma = -1$ eliminates J_+ and leads to

$$(J_- + 2J_0)v = Ev \tag{16}$$

Theoretically, we can choose $\gamma = \pm 1$ but the choice $\gamma = -1$ leads to

$$\omega = \exp(-J_+)v = \exp\left(-\frac{X_1^2}{2}\right)v \tag{17}$$

and we obtain the correct asymptotic factor needed to ensure that the wavefunction vanishes as $x \to \infty$. We also require v to be analytic at $X_1 = 0$ and this implies that we may expand v in terms of the X_1^n (n a non-negative integer), which are eigenfunctions of J_0 with eigenvalues $\varepsilon_n = (2n+1)/4$. A further transformation of the form

$$v = \exp(-\gamma_1 J_-)v_1 \tag{18}$$

can be shown to lead to a divergent expansion in terms of X_1, unless E is restricted to a set of values that truncates the expansion of v_1. In order to match our solutions, we require E to be a free parameter. However, a convergent expansion may be obtained directly from (16) rather than using (18). We may write (16) in the form

$$hv = \left(-\tfrac{1}{2}D^2 + \tfrac{1}{2}(X_1D + DX_1)\right)v = Ev. \tag{19}$$

Since $h(D, X_1) = h(-D, -X_1)$ we see that the eigenfunctions of h are of definite parity. For even functions we write

$$v = y_1(X_1) = \left(a_0 + a_2 X_1^2 + a_4 X_1^4 + \cdots\right). \tag{20}$$

so that comparing coefficients of X_1^n leads to

$$a_{2n+2} = \frac{(4n + 1 - 2E)}{(2n + 1)(2n + 2)} a_{2n} \qquad n = 0, 1, 2, \ldots. \tag{21}$$

Similarly for odd functions

$$v = y_2(X_1) = \left(a_1 X_1 + a_3 X_1^3 + \cdots\right) \tag{22}$$

with

$$a_{2n+3} = \frac{(4n + 3 - 2E)}{(2n + 2)(2n + 3)} a_{2n+1} \qquad n = 0, 1, \ldots. \tag{23}$$

The functions $y_1(X_1)$ and $y_2(X_1)$ are parabolic cylinder functions and we may form the combination

$$\omega_+(x) = A \exp\left(-X_1^2/2\right)(y_1(X_1) + \lambda_+ y_2(X_1)) \tag{24}$$

where A is an arbitrary constant and

$$\lambda_+ = -\frac{\sqrt{2}\Gamma((1 - \nu)/2)}{\Gamma(-\nu/2)} \qquad \text{where} \qquad \nu = E - \frac{1}{2}. \tag{25}$$

With this choice of λ_+, $\omega_+(x)$ is finite as X $\to \infty$; see Merzbacher (1961). We have then calculated $\omega = \omega_+(x)$ for $x > \frac{1}{N}$; we now *define* $\omega_+(x)$ so that $\omega = \omega_+(x)$ also for $0 < x < \frac{1}{N}$.

A similar analysis can be carried out for $x < -\frac{1}{N}$ where now $X_2 = (x + b)$ leading to

$$\omega_-(x) = B \exp\left(-X_2^2/2\right)(y_1(X_2) + \lambda_- y_2(X_2)) \tag{26}$$

with an arbitrary constant B and

$$\lambda_- = \frac{\sqrt{2}\Gamma((1 - \nu)/2)}{\Gamma(-\nu/2)} \qquad E = \nu + \frac{1}{2} \tag{27}$$

to ensure that $\omega_-(x)$ is finite as $X_2 \to -\infty$ and $\omega = \omega_-(x)$ for $x < 0$. To find the eigenvalue E we may use the continuity conditions at $x = 0$:

$$\omega_-(0) = \omega_+(0) \qquad \omega'_-(0) = \omega'_+(0). \tag{28}$$

These conditions imply that

$$F(E) = \omega_+(0)\omega'_-(0) - \omega_-(0)\omega'_+(0) = 0 \tag{29}$$

and, in practice, this equation is solved to obtain E. Since

$$F(E) = \lim_{N\to\infty} \left\{ \omega_+\left(\frac{1}{N}\right) \omega'_-\left(-\frac{1}{N}\right) - \omega_-\left(-\frac{1}{N}\right) \omega'_+\left(\frac{1}{N}\right) \right\} \tag{30}$$

by choosing N sufficiently large we can find E to any desired accuracy using the solutions in $|x| \geqslant \frac{1}{N}$. Given the value of E, equations (28) determine the ratio of A to B and the wavefunctions are unique up to an arbitrary normalization constant.

3. The time-dependent problem

We now consider the solution of (6) separately in $x \geqslant \frac{1}{N}$ and $x \leqslant -\frac{1}{N}$. For $x \geqslant \frac{1}{N}$ we have

$$\left(-\frac{1}{2}D^2 + \frac{1}{2}X_1^2 + \mathrm{i}p(t)D + q(t)X_1 + r_1(t)\right)\psi = H\psi = \mathrm{i}\frac{\partial\psi}{\partial t} \tag{31}$$

where $X_1 = (x - a)$ and $r_1(t) = r(t) + aq(t) + V_2$. Let

$$\psi = \exp(\beta D)\exp(\alpha X_1)\phi = U\phi \tag{32}$$

where α and β are functions of t. We have that

$$\mathrm{i}\frac{\partial\psi}{\partial t} = \mathrm{i}\{\dot{\beta}DU\phi + U\dot{\alpha}X_1\phi + U\dot{\phi}\} \tag{33}$$

where the dot denotes differentiation with respect to t. Using the Campbell–Hausdorff expansion we obtain

$$\mathrm{i}\{\dot{\beta}(D+\alpha)\phi + \dot{\alpha}X_1\phi + \dot{\phi}\} = U^{-1}HU\phi = \left(-\tfrac{1}{2}(D+\alpha)^2 + \tfrac{1}{2}(X_1 - \beta)^2\right.$$
$$\left. + \mathrm{i}p(t)(D+\alpha) + q(t)(X_1 - \beta) + r_1(t)\right)\phi. \tag{34}$$

We now choose α and β to eliminate the terms linear in X_1 and D,

$$-\alpha + \mathrm{i}p = \mathrm{i}\dot{\beta} \qquad \text{and} \qquad -\beta + q = \mathrm{i}\dot{\alpha} \tag{35}$$

and such that $\alpha(0) = \beta(0) = 0$. Writing

$$\mathbf{z} = \begin{pmatrix}\beta\\ \alpha\end{pmatrix} \tag{36}$$

we have

$$\dot{\mathbf{z}} = -\mathrm{i}M\mathbf{z} + \mathbf{d} \tag{37}$$

where

$$M = \begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix} \qquad \text{and} \qquad \mathbf{d} = \begin{pmatrix}p\\ -\mathrm{i}q\end{pmatrix}. \tag{38}$$

The solution of (37) may be written formally as

$$\mathbf{z} = \int_0^t \exp(-\mathrm{i}M(t-x))\,\mathbf{d}(x)\,\mathrm{d}x \tag{39}$$

where

$$\exp(-\mathrm{i}Mt) = \begin{pmatrix}\cos(t) & -\mathrm{i}\sin(t)\\ -\mathrm{i}\sin(t) & \cos(t)\end{pmatrix} \tag{40}$$

leading to

$$\beta = \int_0^t (p(x)\cos(t-x) - q(x)\sin(t-x))\,\mathrm{d}x. \tag{41}$$

Since we assume that p and q are real functions then β is real and consequently α is purely imaginary. Writing $\alpha = \mathrm{i}\delta$ with δ real, (34) reduces to

$$\mathrm{i}\frac{\partial\phi}{\partial t} = \left(-\frac{1}{2}D^2 + \frac{1}{2}X_1^2 + G_1(t)\right)\phi \tag{42}$$

where $G_1(t) = -p\delta - \beta q + r_1 + \dot{\beta}\delta + \frac{1}{2}(\beta^2 + \delta^2)$ is a real function. A further transformation of the form

$$\Psi = \exp\left\{-\mathrm{i}\int_0^t G_1(t')\,\mathrm{d}t'\right\}\phi \tag{43}$$

leads to the solution expressed in the concise form

$$\psi(x,t) = \exp(\beta(t)D)\exp(\mathrm{i}\delta(t)X_1)\exp\left\{\mathrm{i}\int_0^t G_1(t')\,\mathrm{d}t'\right\}\Psi(x,t) \tag{44}$$

where

$$\mathrm{i}\frac{\partial\Psi}{\partial t} = \left(-\frac{1}{2}D^2 + \frac{1}{2}X_1^2\right)\Psi \tag{45}$$

and the initial conditions are preserved so that $\Psi(x,0) = \phi(x,0) = \psi(x,0)$. A similar analysis in $x \leqslant \frac{1}{N}$ gives

$$\psi(x,t) = \exp(\beta(t)D)\exp(\mathrm{i}\delta(t)X_2)\exp\left\{\mathrm{i}\int_0^t G_2(t')\,\mathrm{d}t'\right\}\Psi(x,t) \tag{46}$$

where now $X_2 = (x+b)$ and $G_2(t) = G_1(t) - (b+a)q(t) + V_1 - V_2$. In order to complete the solution we need to specify the initial conditions. From the form of (45) and its analogue for $x \leqslant -\frac{1}{N}$ the initial conditions of Ψ and hence ψ may be expressed in terms of the stationary states of the harmonic double well examined in section 2, so that

$$\psi(x,0) = \Psi(x,0) = \sum_r a_r\omega_r(x) \tag{47}$$

and

$$\Psi(x,t) = \sum_r \exp(-\mathrm{i}E_r t)a_r\omega_r(x) \tag{48}$$

which is a fairly good function of x over the infinite range $(-\infty,\infty)$.

Defining $G(t)$ to be the phase factor for all t, so that in particular

$$(X, G(t)) = \begin{cases}(X_1, G_1(t)) & x \geqslant \frac{1}{N}\\ (X_2, G_2(t)) & x \leqslant -\frac{1}{N}\end{cases} \tag{49}$$

we have

$$\psi(x,t) = \exp(\beta(t)D)\exp(\mathrm{i}\delta(t)X)\exp\left\{\mathrm{i}\int_0^t G(t')\,\mathrm{d}t'\right\}\sum_r \exp(-\mathrm{i}E_r t)a_r\omega_r(x). \tag{50}$$

Note that although there is a significant phase change over the range $|x| \leqslant \frac{1}{N}$, nevertheless by choosing N as large as required the effect on $\Psi(x,t)$ is insignificant. It is well known that such phase changes can occur at interfaces between different regions (Levy–Leblond 1987). We emphasize that equation (50) implies that for all $|x| \geqslant \frac{1}{N}$

$$|\psi(x,t)|^2 = \left|\sum_r \exp(-\mathrm{i}E_r t)a_r\omega_r(x+\beta(t))\right|^2 \tag{51}$$

and this simple expression is all that is required for most physical and chemical analysis. If the initial condition is a single eigenstate, $\omega_m(x)$ say, then

$$|\psi(x,t)|^2 = |\omega_m(x+\beta(t))|^2 \tag{52}$$

and the wave packet essentially moves position, driven by $\beta(t)$, but the shape of the initial stationary state wavefunction is unchanged. In the more general case in (51), in addition to this effect, there is the usual time-dependent interference between the stationary states so that the wave packet will change in shape as well as position.

Table 1. Successive approximations to the lowest energy states of the symmetric double well with $a = 2.5$.

N	Ground state energy	First excited state energy
10	0.499 594 09	0.500 248 55
15	0.499 765 95	0.500 197 97
20	0.499 775 45	0.500 195 45
30	0.499 775 66	0.500 195 41

4. Example calculations

First we consider a symmetric double well with $a = b = 2.5$. To illustrate the analysis we will consider four different time-dependent forcing terms $p(t)$ and $q(t)$:

(a) $p = 0$, $q(t) = t\exp(-t)$ which models a pulsed potential field;
(b) $p = 0$, $q(t) = \sin(t)\exp(-t)$ which models an oscillating pulse potential;
(c) $p = 0$, $q(t) = \sin(t)$ which models an oscillating, periodic, field;
(d) p a constant and $q(t) = t\exp(-t)$ which models a pulse potential applied to a system moving with fixed momentum with respect to a fixed frame.

Note that $q(0) = 0$ in all cases so we are not considering a discontinuous impulsive field.

The solutions of (35) in these cases are as follows:

$$\begin{aligned}
&\text{(a)}\quad \alpha(t) = \tfrac{1}{2}\mathrm{i}(t\ \exp(-t) - \sin(t)) \qquad \beta(t) = \tfrac{1}{2}(t\exp(-t) + \exp(-t) - \cos(t))\\
&\text{(b)}\quad \alpha(t) = \tfrac{1}{5}\mathrm{i}(3\sin(t)\exp(-t) + \cos(t)\exp(t) - \cos(t) - 2\sin(t))\\
&\qquad \beta(t) = \tfrac{1}{5}(\sin(t)\exp(-t) + 2\cos(t)\exp(-t) - 2\cos(t) + \sin(t))\\
&\text{(c)}\quad \alpha(t) = -\tfrac{1}{2}\mathrm{i}t\sin(t) \qquad \beta(t) = \tfrac{1}{2}(\sin(t) - t\cos(t))\\
&\text{(d)}\quad \alpha(t) = \tfrac{1}{2}\mathrm{i}(t\exp(-t) - \sin(t) + 2p - p\cos(t))\\
&\qquad \beta(t) = \tfrac{1}{2}(t\exp(-t) + \exp(-t) - \cos(t) + p\sin(t)).
\end{aligned} \tag{53}$$

All of these solutions are asymptotically periodic, so that if the initial condition is described by a single eigenstate then eventually the wave packet moves periodically whilst retaining its shape. If we consider a symmetric double well described by (1) with $a = 2.5$ then the ground state has approximate energy 0.499 775 66 and the wavefunction is symmetrically distributed in the two wells. Table 1 gives an indication of the rate of convergence of the two lowest eigenvalues of this system with increasing N.

In figure 1 we illustrate $|\psi(x, 0)| = |\omega_0(x)|$ (light curve) and $|\psi(x, t_0)| = |\omega_0(x + \beta(t_0))|$ (dark curve) where $\beta(t) = \frac{1}{2}(t\exp(-t) + \exp(-t) - \cos(t))$ (case (a) above) and $t_0 = 2.4$. The initial form of $|\psi(x, 0)|$ has peaks at $x = \pm 2.5$ and the entire wave packet has moved in the positive x direction at $t_0 = 2.4$. The maximum displacement of 0.594 589 466 8 occurs at $t_1 = 2.990\,735\,230$ but asymptotically the displacement is ± 0.5. Similar behaviour is attained from all of the four potentials considered which have asymptotic periodicity or complete periodicity in case (c).

The wave packet changes shape if the initial condition is a sum of eigenstates and we now examine this for the double well given in (1), with $a = 2.5$, where initially we have

$$\psi(x, 0) = \frac{1}{\sqrt{2}}(\omega_0(x) + \omega_1(x)) \tag{54}$$

which, for a suitable choice of phase, corresponds to an electron localized in $x > 0$. The eigenvalue for the first excited state is 0.500 195 41, which is nearly degenerate with the

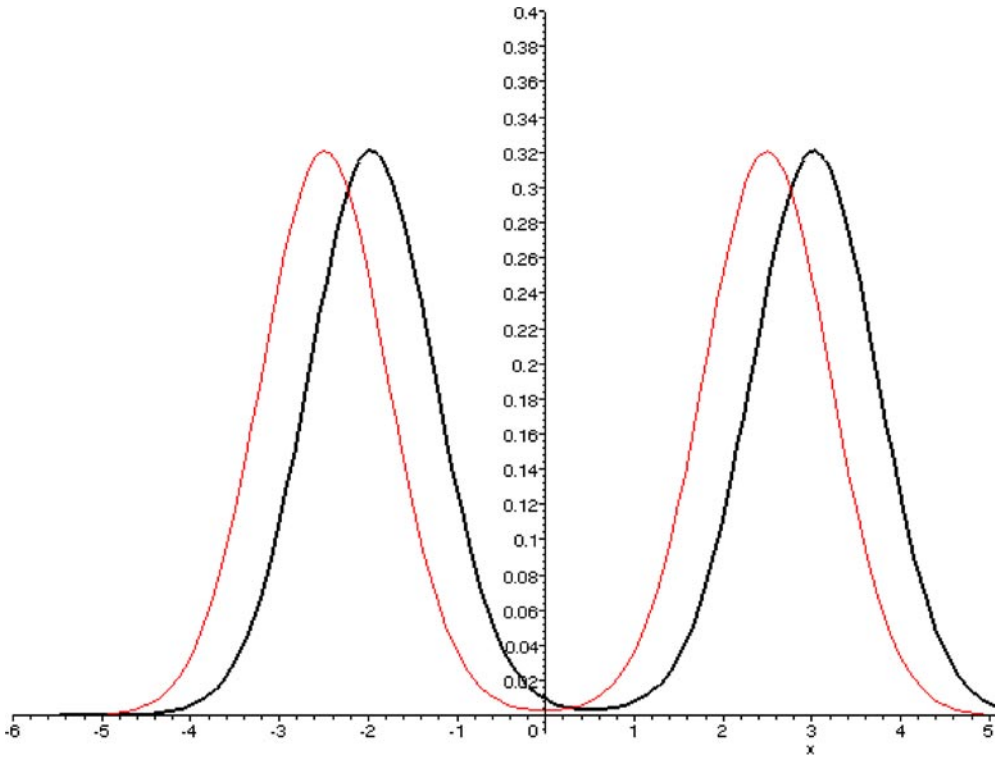

Figure 1. The symmetric well ($a = 2.5$, $V_1 = V_2 = 0$) using $\beta(t) = \frac{1}{2}(t\exp(-t) + \exp(-t) - \cos(t))$, where the initial wavefunction (light curve) is the ground state wavefunction.

ground state, so that in the absence of a field, charge transfer to $x < 0$ occurs only after a long time interval.

At any time t we have

$$|\psi(x,t)|^2 = \tfrac{1}{2}(|\omega_0(x+\beta(t))|^2 + |\omega_1(x+\beta(t))|^2 + 2\cos(\Delta t)\omega_0(x+\beta(t))\omega_1(x+\beta(t))) \tag{55}$$

where $\Delta = (E_1 - E_0)$.

Now changing $p(t)$ and $q(t)$ to $V_0\,p(t)$ and $V_0\,q(t)$ respectively merely changes α and β by a factor V_0. We may choose this factor so that

$$\beta\left(\frac{\pi}{4\Delta}\right) = 1. \tag{56}$$

In figure 2 we illustrate the initial waveform (light curve) and the waveform for $t = \frac{\pi}{4\Delta}$ (dark curve). The latter is such that the major peak has moved to the right along the x-axis but the waveform has changed shape and there is spread into the region $x < 0$.

Finally, we consider a calculation using an asymmetric well whose potential is given by the more general form (2) with $b = 2.5$, $a = 0.1$, $V_1 = -0.1$ and $V_2 = 0$. The ground state energy is 0.497 185 08 and the wavefunction is almost entirely localized in the deeper left well. This is illustrated in figure 3 (light curve with a peak of $|\psi(x,t)|^2$ at $x = -2.5$). We may use case (a) above to construct

$$\beta(t) = V_0\tfrac{1}{2}(t\exp(-t) + \exp(-t) - \cos(t)) \tag{57}$$

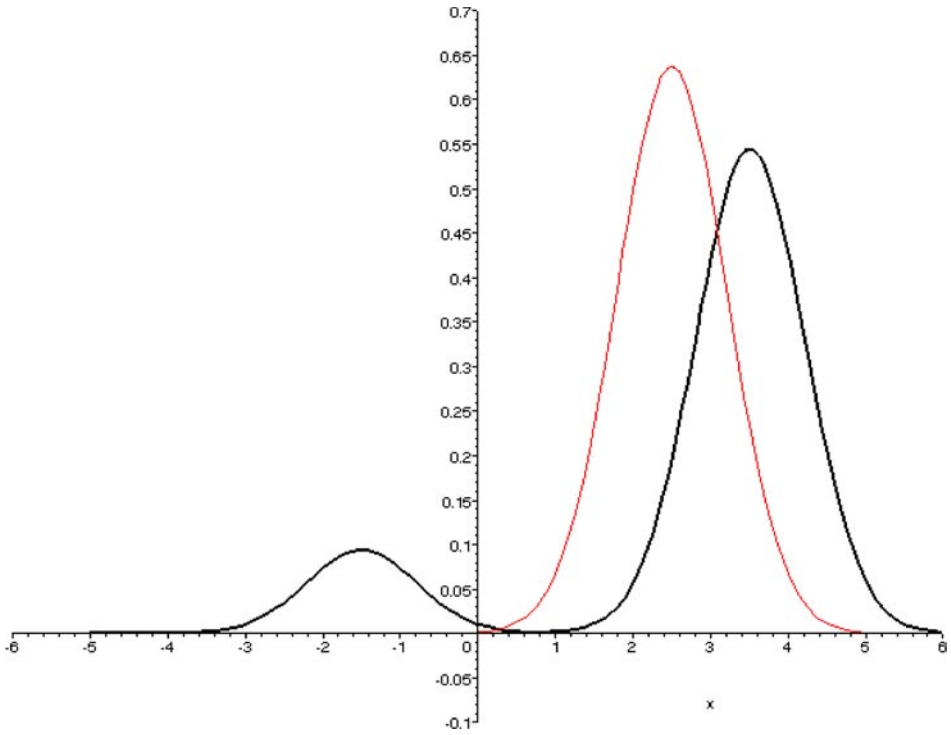

Figure 2. The symmetric double well ($a = 2.5$, $V_1 = V_2 = 0$) using $\beta(t) = \frac{1}{2}(t\exp(-t) + \exp(-t) - \cos(t))$, where the initial wavefunction (light curve) is a combination of the lowest two eigenstates.

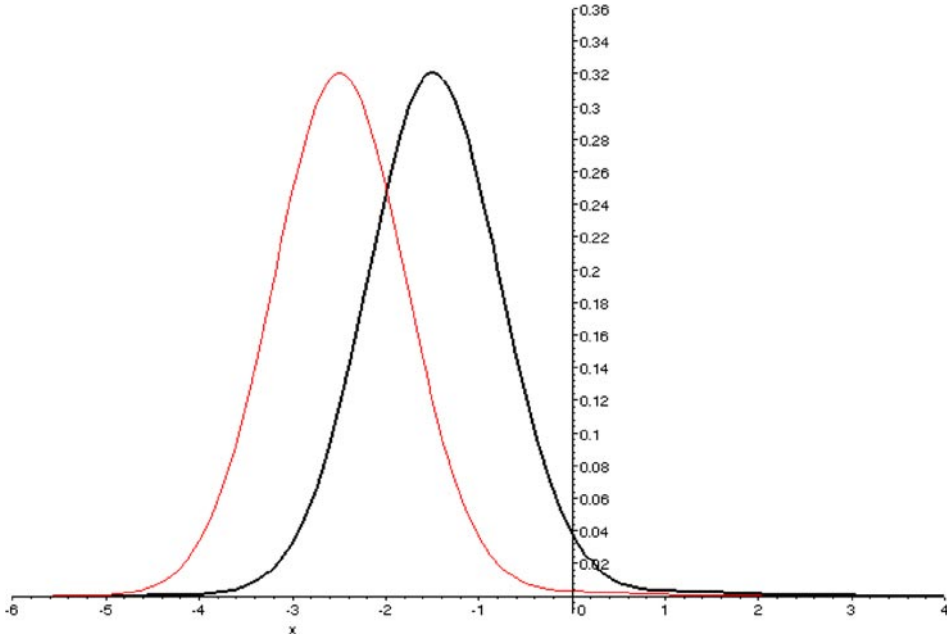

Figure 3. The asymmetric double well ($b = 2.5$, $a = 0.1$, $V_1 = -0.1$ and $V_2 = 0$) using $\beta(t) = V_0\ \frac{1}{2}(t\exp(-t) + \exp(-t) - \cos(t))$, $V_0 = 5.062\ 316\ 385$, where the initial wavefunction (light curve) is the ground state wavefunction.

so that $\beta(t_1) = 1$. Since $t_1 = 2.990\,735\,230$ then

$$V_0 = 3.01(0.594\,589\,466\,8)^{-1} = 5.062\,316\,385. \tag{58}$$

In figure 3 we illustrate that the wave packet retains its shape and moves to the right with a small but significant probability in the shallow right well (see the dark curve in figure 3). The corresponding maximum value of the pulse potential $q(t)$ is $1.862\,322\,123$ at $t = 1$ and therefore the applied field is not small. This illustrates that the theory developed is valid for fields of arbitrary magnitude and would be especially useful for fields that cannot be treated perturbatively.

Acknowledgments

One of us (BLB) would like to thank EPSRC for support through the travel grant GR/S26439/01 and Hebrew University for their hospitality.

Appendix. Improved potentials

Let

$$S(y) = \begin{cases} \exp\{-1/(1-y^2)\} & |y| \leqslant 1 \\ 0 & |y| > 1. \end{cases} \tag{A1}$$

Then it is easy to establish that

$$S(\pm 1) = 0 \tag{A2}$$

and

$$S^4(m)(\pm 1) = 0 \tag{A3}$$

for all derivatives $S^{(m)}(y)$ (see Lighthill (1958)). The function

$$s_+(x) = \int_0^x S(2Ny-1)\,\mathrm{d}y \Big/ \int_0^{1/N} S(2Ny-1)\,\mathrm{d}y \tag{A4}$$

is such that $s_+(0) = 0$ and $s_+\left(\frac{1}{N}\right) = 1$. Furthermore

$$As_+^{(m)}(x) = (2N)^{m-1}S^{(m-1)}(2Nx-1), \qquad A = \int_0^{1/N} S(2Ny-1)\,\mathrm{d}y \qquad (m = 1, 2\ldots) \tag{A5}$$

so that $s_+^{(m)}(0) = s_+^{(m)}\left(\frac{1}{N}\right) = 0$. Similarly

$$s_-(x) = \int_0^x S(2Ny-1)\,\mathrm{d}y \Big/ \int_0^{-1/N} S(2Ny-1)\,\mathrm{d}y \tag{A6}$$

is such that $s_-(0) = 0$, $s_-\left(-\frac{1}{N}\right) = 1$ and $s_-^{(m)}(0) = s_-^{(m)}\left(-\frac{1}{N}\right) = 0$.

We now define

$$u(L,x) = \begin{cases} 1 & x \geqslant \frac{1}{N} \\ s_+(x) & 0 \leqslant x \leqslant \frac{1}{N} \\ s_-(x) & -\frac{1}{N} \leqslant x \leqslant 0 \\ 1 & x \leqslant -\frac{1}{N} \end{cases} \tag{A7}$$

which is continuous and has continuous derivatives of all orders. Now since $V(x)$ satisfies the conditions for a fairly good function except at $x = 0$, we have that $\hat{V}(x) = V(x)u(L, x)$ also satisfies these conditions for $x \neq 0$. Also since

$$\lim_{x>0, x\to 0} \hat{V}(x) = \lim_{x<0, x\to 0} \hat{V}(x) = 0 \tag{A8}$$

$\hat{V}(x)$ is continuous at $x = 0$. A similar analysis establishes that all derivatives of $\hat{V}(x)$ are continuous and zero at $x = 0$. Consequently $\hat{V}(x)$ is a fairly good function.

References

Bemish R J, Chan M C and Miller R E 1996 *Chem. Phys. Lett.* **251** 182
Burrows B L and Cohen M 1998 *Chem. Phys. Lett.* **295** 389
Burrows B L, Cohen M and Feldmann T 1996 *Mol. Phys.* **88** 611
Burrows B L, Cohen M and Feldmann T 1998 *Can. J. Phys.* **76** 129
Grossmann F, Dittrich T, Jung P and Hanggi P 1991a *Z. Phys. B Condens. Matter* **84** 315
Grossmann F, Dittrich T, Jung P and Hanggi P 1991b *Phys. Rev. Lett.* **67** 516
Grossmann F and Hanggi P 1992 *Europhys. Lett.* **18** 571
Invanov M, Seideman T, Corkum P, Ilkov F and Deitrich P 1995 *Phys. Rev. Lett.* **75** 2819
Levy-Leblond J M 1987 *Phys. Lett.* A **125** 441
Lighthill M J 1958 *Introduction to Fourier Analysis and Generalised Functions* (Cambridge: Cambridge University Press)
Merzbacher E 1961 *Quantum Mechanics* (New York: Wiley)
Seidman T, Ivanov M and Corkman P 1995 *Phys. Rev. Lett.* **75** 2819
Thomas N R and Wilson A C 2002 *Phys. Rev.* A **65** 063406