Non-adiabatic transitions in two-state curve crossing systems
A study of a semiclassical Magnus approximation

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The transition amplitudes for passage through a potential curve crossing are calculated by means of the first order Magnus approximation to the coupled equations in the momentum representation, together with a semiclassical mapping prescription. The cases of potentials with similar or different slopes at the crossing point require a different treatment: for similar slopes the semiclassical Magnus approximation is practically identical with the exponential uniform distorted wave approximation (EUDWBA); for slopes with different signs a new probability conserving approximation is obtained, which differs from the EUDWBA and leads to a substantial improvement of the transition probabilities in the weak and intermediate coupling region. The present approximation can easily be extended to multi-state crossings.

1. INTRODUCTION

Since the fundamental work of Landau [1], Zener [2] and Stueckelberg [3] on the two-state curve crossing problem numerous papers have been devoted to this subject (see, for instance, Nikitin [4, 5], Child [6] and references therein). But despite the considerable amount of work on this simple problem, numerical comparisons between the various approximations and exact computations are surprisingly rare. In a recent article by Baer and Child [7], which was motivated by quantum mechanical studies of non-adiabatic chemical reactions [8], several distorted wave approximations are compared with Landau–Zener and exact results. It was found that the uniform (Airy) distorted wave Born approximation (UDWBA) [9], improved by using exponential techniques (EUDWBA) [10], fitted the exact results quite well for weak coupling, whereas the agreement was poor for intermediate coupling. For strong coupling the distorted wave type approximations are clearly inadequate. In all cases the Landau–Zener (LZ) approximations [4–7, 11] turned out to be equal or superior to the UDWBA or EUDWBA results, with the exception of the threshold and sub-threshold region, where the LZ approximation used in [7] breaks down completely. (It should be noted, however, that the LZ treatment can be extended to the sub-threshold region by complex trajectory techniques [12, 13].) The poor agreement between the EUDWBA and exact results found in [7] is surprising and differs from findings for other problems.
It is the aim of the present study to discuss a different approach to curve crossing problems, which makes use of the Magnus approximation and semiclassical mapping techniques. Two levels of approximation are clearly distinguished. The first is the solution of a simple reference system, which can be solved in a good approximation; this reference system is the well known linear crossing/constant coupling model, which is discussed in the following section. The remaining problem is to construct the mapping from the realistic system to the reference model; a simple mapping procedure is suggested in §3. The paper concludes with a discussion of the relation between the present approximation and the EUDWBA.

2. The two-state linear model

The two-state system,
\[ \frac{\hbar^2}{2m} \frac{d^2 \psi_1}{dR^2} + [E - V_1(R)]\psi_1(R) = V_{12}(R)\psi_2(R), \]
\[ \frac{\hbar^2}{2m} \frac{d^2 \psi_2}{dR^2} + [E - V_2(R)]\psi_2(R) = V_{21}(R)\psi_1(R), \]
with linear diabatic potentials
\[ V_i(R) = -F_i(R - R_c) \quad (i = 1, 2) \] (2)
in the following we assume \( F_1 > 0 \) without loss of generality and constant coupling
\[ V_{12}(R) = V_{21}(R) = A = \text{const.}, \] (3)
considered in this section is one of the best studied curve crossing problems [1–6]. The adiabatic potentials are
\[ V_+(R) = V(R) + \frac{1}{2}(\Delta F^2(R - R_c)^2 + 4A^2)^{1/2}, \]
\[ V_-(R) = V(R) - \frac{1}{2}(V_1 + V_2), \]
\[ \Delta F = F_1 - F_2 \]
and the non adiabatic coupling in the adiabatic representation is a Lorentzian
\[ \langle \psi_1^{\text{ad}} | \frac{d}{dR} | \psi_2^{\text{ad}} \rangle = g_0[1 + (R - R_c)^2/(\Gamma/2)^2]^{-1}, \] (5)
with width \( \Gamma = 4A/\Delta F \) [14].

2.1. The momentum representation

The linear crossing/constant interaction model can be discussed conveniently in the momentum representation [4, 6, 15], where the system of coupled second order differential equations (1) reduces to coupled first-order equations. After removing the diagonal coupling by an interaction-like transformation and introduction of dimensionless variables and parameters these coupled equations take the particularly simple form
\[ i \frac{d}{d\tau} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} 0 & g(\tau) \\ g^*(\tau) & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}, \] (6 a)
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valid for forces with the same sign \((F_1 F_2 > 0)\) or

\[
i \frac{d}{d\tau} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} 0 & g^*(\tau) \\ -g(\tau) & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}
\]

(6b)

for forces with different signs \((F_1 F_2 < 0)\); \(g(\tau)\) is given by

\[
g(\tau) = \exp \left\{ -i \left( \frac{8\tau^3}{3\beta^2} - 2\epsilon \tau \right) \right\}.
\]

(7)

The dimensionless parameters \(\epsilon\) and \(\beta\) are defined as

\[
\epsilon = \frac{\Delta F}{2AF},
\]

(8)

\[
\beta = \frac{4A}{\hbar} \left( \frac{mA}{F\Delta F} \right)^{1/2},
\]

(9)

with \(F = \left| F_1 F_2 \right|^{1/2}\), and the dimensionless variable \(\tau\) is related to the wavenumber \(k\) by

\[
\tau = A k / F.
\]

(10)

For further reference we note that

\[
\epsilon \beta^{2/3} = E/\epsilon_0,
\]

(11)

with

\[
\epsilon_0 = \left( \frac{\hbar^2 F^4}{2m\Delta F^2} \right)^{1/3}.
\]

(12)

Introducing the \(\tau\)-evolution operator \(U(\tau)\) by

\[
\begin{pmatrix} a_1(\tau) \\ a_2(\tau) \end{pmatrix} = U(\tau) \begin{pmatrix} a_1(-\infty) \\ a_2(-\infty) \end{pmatrix}
\]

(13)

equations (6a, b) read

\[
i \frac{d}{d\tau} U = A_\pm U,
\]

(14)

with \(\pm = \text{sign} \ (F_1 F_2)\) and

\[
A_+ = \begin{pmatrix} 0 & g \\ g^* & 0 \end{pmatrix}, \quad A_- = \begin{pmatrix} 0 & g^* \\ -g & 0 \end{pmatrix}.
\]

(15)

Equation (14) has to be solved with the boundary condition \(U(-\infty) = I\). It should be noted that \(\det U\) is a conserved quantity in (14)

\[
\det U(\tau) = 1.
\]

(16)

Obviously we have \(A_\pm^\dagger = \pm A_\pm\), that is \(A_\pm\) is hermitian and \(U\) is unitary in this case \((|a_1|^2 + |a_2|^2 = \text{const})\), whereas \(A\) is anti-hermitian \((|a_1|^2 - |a_2|^2 = \text{const})\).

For the positive case \((F_1 F_2 > 0)\) we have complete analogy with time evolution; in fact, with the introduction of a mean classical trajectory governed by the force \(F = (F_1 F_2)^{1/2}\), equation (14) can be written as a time evolution equation. This concept breaks down, however, for forces with different sign, where this
concept of a mean trajectory is meaningless. The transition probabilities for $F_1F_2 > 0$ are given simply by

$$
\begin{align*}
P_{+}^{11} &= |a_1(+\infty)|^2 = |U_{11}(+\infty)|^2 \quad \text{(reflection)}, \\
P_{+}^{21} &= |a_2(+\infty)|^2 = |U_{21}(+\infty)|^2 \quad \text{(transition)},
\end{align*}
$$

(initial state 1; $a_i(-\infty) = \delta_{i1}$).

For the negative case ($F_1F_2 < 0$) the situation is somewhat more complicated, because the momentum space amplitudes $a_i(+\infty)$, $a_2(+\infty)$ can no longer be considered as the probability amplitudes of the final state. The final state is characterized by the initial conditions $a_i(-\infty) = 1$ and $a_2(+\infty) = 0$ (that is no flux in channel 2 incident from the left). The transition probabilities in this case are [4, 6]

$$
\begin{align*}
P_{-}^{11} &= |a_1(+\infty)|^2 = |1/U_{22}(+\infty)|^2 \quad \text{(reflection)}, \\
P_{-}^{21} &= |a_2(-\infty)|^2 = |-U_{21}(+\infty)/U_{22}(+\infty)|^2 \quad \text{(transition)},
\end{align*}
$$

which can be obtained from

$$
\begin{pmatrix}
a_1(+\infty) \\
0
\end{pmatrix} = U(+\infty) 
\begin{pmatrix}
1 \\
a_1(-\infty)
\end{pmatrix}
$$

and det $U = 1$. The total probability $P_{-}^{11} + P_{-}^{21}$ is, of course, equal to one, because $|a_1(+\infty)|^2 - |a_2(+\infty)|^2 = |a_1(-\infty)|^2 - |a_2(-\infty)|^2 = 1$.

### 2.2. The Magnus approximation

The usual approach [4, 6] to a solution of the equations (6 a, b) is a conversion of the two first order equations into a single second order equation for $a_1$ or $a_2$. Various limiting forms can be extracted from this differential equation, which are valid for various combinations of the parameters $\epsilon$ and $\beta$ in (7). A general closed form solution has unfortunately not been found even for this simplistic linear model, so that one has to rely on approximate solutions for this reference system.

In the limit $\beta \to 0$ (weak adiabatic coupling limit) we find [4]

$$
P_{-}^{21} = \pi^2 \beta^{4/3} A i^2 (-\epsilon^{2/3}).
$$

Other limiting expressions are valid for large values of $\beta$ and/or large values of $\epsilon$ (for a discussion of the various approximations see Nikitin [4] and Delos and Thorson [16]). Typically the region $\beta \leq 1$ and $|\epsilon\beta^{2/3}| \leq 1$ (intermediate coupling and energies close to the transition region) is not covered by the approximations. In the following the Magnus approximation is investigated for the linear curve crossing system.

The Magnus expansion [17, 18] for the system

$$
i \frac{d}{d\tau} U = A U
$$

is

$$
U(\tau) = \exp \{-i\Omega(\tau)\},
$$

where $\Omega(\tau)$ is expanded as a series of repeated commutators of $A$, $\Omega = \Omega^{(1)} +$
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\( \Omega^{(a)} + \ldots \), with

\[ \Omega^{(1)}(\tau) = \int_{\tau_0}^{\tau} A(\tau') d\tau', \]
\[ \Omega^{(2)}(\tau) = -\frac{1}{2} \int_{\tau_0}^{\tau} d\tau' \int_{\tau_0}^{\tau} d\tau'' [A(\tau'), A(\tau'')] \]

(see, for instance, Pechukas and Light [18]). It is well known, [18] that for hermitian \( A \) an arbitrary truncation of the Magnus expansion gives a unitary evolution operator \( U \). For anti-hermitian \( A \) each commutator in the Magnus expansion is also anti-hermitian and therefore the Magnus expansion gives a hermitian \( U \)-operator by truncating the series anywhere. The conservation of \( \det U \) is also guaranteed by the Magnus expansion. From the relation [17]

\[ \det U(\tau) = \exp \left\{ -i \int \text{Tr} A(\tau') d\tau' \right\} \]

we note that the first order Magnus approximation gives the exact \( \tau \)-dependence of \( \det U \) (the higher order terms give no contribution to \( \text{Tr} \Omega \) in (22), because a commutator is traceless). For a discussion of the convergence behaviour of the Magnus expansion see [18]. Basically there are two extremes where the first order approximation is sufficient, the diametrical cases of a constant \( A \) and a sudden (impulsive) \( \tau \)-dependence. In the following we confine ourselves to a first order treatment. This leads immediately to

\[ \Omega^{(1)}(\tau) = \begin{pmatrix} 0 & G(\tau) \\ G^*(\tau) & 0 \end{pmatrix}, \quad \Omega^{(2)}(\tau) = \begin{pmatrix} 0 & G^*(\tau) \\ -G(\tau) & 0 \end{pmatrix}, \]

with

\[ G(\tau) = \int_{-\infty}^{\tau} g(\tau') d\tau' = \int_{-\infty}^{\tau} \exp \left\{ \frac{i}{4} G_{-2} \right\} d\tau'. \]

The exponentiation in (22) can be done analytically and we find for \( F_1F_2 > 0 \)

\[ U_+(\tau) = \begin{pmatrix} \cos |G| & -iG^* \sin |G| \\ -iG^* \sin |G| & \cos |G| \end{pmatrix} \]

(28a)

and for \( F_1F_2 < 0 \)

\[ U_-(\tau) = \begin{pmatrix} \cosh |G| & -iG^* \sinh |G| \\ iG^* \sinh |G| & \cosh |G| \end{pmatrix} \]

(28b)

The transition probabilities are therefore

\[ P_{+1} = \cos^2 G(\pm \infty), \quad P_{-1} = \sin^2 G(\pm \infty), \]
\[ P_{-1} = \frac{1}{\cosh^2 G(\pm \infty)}, \quad P_{-1} = \tanh^2 G(\pm \infty), \]

with

\[ g(\pm \infty) = \pi \beta^{3/3} \text{Ai} (-\epsilon \beta^{3/3}). \]

Note that the total probability is conserved.
Both results for $P^{a_1}$ reduce in the weak coupling limit to the first order perturbation result (20). A comparison of the first order Magnus transition probabilities $P^{a_{+1}}$ (that is for forces with the same sign) and exact calculations is shown in figure 1 for the case $\beta = 0.5$. The exact values are taken from [16]. The Magnus approximation is in good agreement with the exact curve and gives a considerable improvement over the simple first order perturbation formula (20), which gives transition probabilities larger than one in this case. For larger values of $\beta$ the agreement between exact and first order Magnus results gets worse, and higher order approximations must be used. Similar results were found for $P^{a_{-1}}$ (that is for forces with different signs). A discussion of this case is given at the end of the following section.

3. General (non-linear) potentials

The two-state linear model is of course not the main objects of interest in the present study. The guiding idea behind the discussion of the linear model is to use it as a reference model for more general situations. This generates the question of the optimal mapping between a realistic curve crossing system and the linear model, that is how can the parameters $F_1$, $F_2$, $\mu$ of the linear reference model be determined from the system under consideration? The simplest mapping is of course the naive choice that $F_1$, $F_2$ and $\mu$ are the slopes of the potentials and the coupling at the crossing point; needless to say, this choice yields rather poor results. A more elaborate mapping was suggested by Delos and Thorson [16], whose choice was motivated by considerations of the classical trajectories. We would like to suggest a different kind of mapping, which is closely related to several semiclassical extensions of Landau–Zener type transition probabilities, which were derived for the linear model and then extended to other situations (see, for instance, [4–6] and references therein).
Let us first discuss the meaning of the quantities appearing in the first order Magnus approximation (to simplify the discussion we confine ourselves to the case of potentials intersecting with different slopes \(F_1F_2<0\) in this section, unless otherwise stated). We have zero transmission probability (complete reflection) at the zeros of the Airy function. It is now observed \([6]\) that the argument \(\beta^{2/3}\) of the Airy function is directly related to the phase integral

\[
\Phi = \int_{R_i}^{R_e} k_1(R)dR + \int_{R_e}^{R_i} k_2(R)dR. \tag{31}
\]

A short calculation gives \(\epsilon \beta^{2/3} = (\frac{3}{2} \Phi)^{2/3}\), so that the zeros of the transmission probability are closely connected with resonances in the upper diabatic well \(V = \max (V_1, V_2)\).

The phase integral \(\Phi\) determines the oscillatory behaviour of the transition probabilities; the magnitude is essentially determined by the usual Landau-Zener exponent

\[
\delta = \frac{\beta}{8\epsilon^{1/2}} = \frac{A^2}{\hbar |v| \Delta F} \tag{32}
\]

(\(v\) is the velocity at the crossing point). This can immediately be verified from equations (20) or (30) using the asymptotic expression for the Airy function (note that the argument of the Airy function is proportional to \(\hbar^{-2/3}\)). A short calculation shows that \(\delta\) is related to the phase integral between the complex intersection points \(R, \bar{R}\) of the adiabatic potentials (4) or more precisely to the phase difference between the upper and lower adiabatic surface \([6, 12, 13]\), which for the linear model is given approximately by

\[
\Theta_{LM} = \int_R^{R^*} \{k_+(R) - k_-(R)\} dR = \int_R^{R^*} \frac{k_+^2 - k_-^2}{k_+ + k_-} dR \\
= \frac{2}{\hbar v} \int_R^{R^*} \{\Delta F^2(R - R_c)^2 + 4A^2\}^{1/2} dR = 2\pi \delta, \tag{33}
\]

where \(k_+ + k_-\) is approximated by the wavenumber at the crossing point. This suggests the use of the phase integrals \(\Phi\) and \(\Theta\) as the basic mapping quantities to determine the parameters \(\epsilon\) and \(\beta\) of the linear reference model. It was found numerically that this mapping prescription works very well. A computationally much more convenient recipe, however, is a separate mapping of the phase integrals

\[
\Phi_1 = \int_{R_i}^{R_e} k_1(R)dR \quad \text{and} \quad \Phi_2 = \int_{R_e}^{R_i} k_2(R)dR
\]

appearing in equation (31), thus determining the slopes \(F_1\) and \(F_2\) of the linear reference model

\[
F_i = \frac{(8m)^{1/2} E^{3/2}}{3\hbar \Phi_i} \quad (i = 1, 2). \tag{34}
\]

The phase integral \(\Theta\) for the system under consideration is then approximated in the same manner as the phase integral (33) for the reference model, with the additional assumption that the potential difference \(\Delta V = V_2 - V_1\) and the coupling \(V_{12}\) are slowly varying in the range of integration and can be approximated by their
behaviour near the crossing point $R_c$

$$\Theta \approx \frac{2}{\hbar |v|} \int_{R_c}^{R} \left\{ \Delta V^2 + 4V_{12}^2 \right\}^{1/2} dR$$

$$\approx \frac{2}{\hbar |v|} \int_{R_c}^{R} \left\{ \Delta F_c^2 (R - R_c)^2 + 4V_{12}^2(R_c) \right\}^{1/2} dR$$

$$= \frac{2\pi V_{12}^2(R_c)}{\hbar |v| \Delta F_c}.$$  \hspace{1cm} (35)

The mapping $\Theta = \Theta_{LM}$ leads to the simple relation

$$A = \left[ \frac{\Delta F}{\Delta F_c} \right]^{1/2} V_{12}(R_c),$$  \hspace{1cm} (36)

where $\Delta F_c$ is the difference of the potential slopes at the crossing point. (Note that $A = V_{12}(R_c)$ at the energy of the crossing point.)

The simple mapping prescription suggested above was tested for several systems, for which exact results are available, and generally good agreement was found. Typical examples are shown in figures 2 and 3. In figure 2 several approximations are compared for a system recently studied by Baer and Child [7]. The potentials are $V_1(R) = V_0 \exp (-aR)$, $V_2(R) = V_0 \exp (+aR)$ ($V_0 = 0.1$ eV, $a = 2\text{Å}^{-1}$) and $V_{12}(R) = 0.05$ eV. The reduced mass is 1.905 u and the energy is measured from the potentials at infinity. The semiclassical Magnus approximation is in reasonable agreement with the exact results taken from [7]. (Note that the coupling $A$ for the reference model is energy dependent, even if $V_{12}$ is constant!) Also shown in figure 2 are the exponential uniform distorted wave approximation (UDWBA) and a modified Landau–Zener approximation [4–7] (these curves are also taken from [7]). The semiclassical Magnus approximation is clearly superior to the UDWBA (the uniform distorted wave approximation without exponential correction yields rather poor results with probabilities larger than one [7], which are not shown in figure 2 and roughly of the same quality as Landau–Zener approximation.

The present approximation gives a good approximation below and close to the threshold region and reproduces the amplitudes quite well, whereas the modified Landau–Zener approximation gives a better prediction of the position of the zero transmission probabilities [7]. This small phase shift is mainly due to the restriction to a first order treatment of the Magnus expansion for the linear reference model (compare the small phase shift in figure 1) and not a consequence of the semiclassical mapping.

It is, of course, of great interest to compare the present approximation with the UDWBA. A short calculation shows that, with the mapping equation (34), $G(+\infty)$ in equation (30) is identical with the UDWBA amplitude (see, for instance equation (19) of [7]), that is in the weak coupling (perturbation) limit the present approximation agrees with the UDWBA. We regard this as support for our quite empirical choice of the semiclassical mapping. (A more general study of the mapping of systems of differential equations is presently under way and will be published elsewhere.) Therefore the basic difference between the UDWBA approximation and the present semiclassical first order Magnus approach is due to the different exponential approximations used; for
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Figure 2. Transition probabilities for exponential potentials with different slopes ($F_1 F_2 < 0$) [7]: exact results; exponential uniform DWBA; Landau–Zener results (all taken from [7]); semiclassical first order Magnus approximation (present work).

Figure 3. Transition probabilities for a system with nonconstant coupling [13] (see text): exact results [13]; Landau–Zener type approximation [13]; semiclassical first order Magnus approximation (present work).

systems with the same sign of forces at the crossing point equation (29 a) agrees with the EUDWBA formula [7, 10], whereas the present approach yields a different formula (29 b) for the potentials intersection with different signs of slopes. This leads to a substantial improvement of the transition probabilities for larger values of the coupling.

As a final example of the semiclassical Magnus approximation figure 3 shows results for a system with nonconstant coupling recently studied by Laing et al. [13]. The diabatic potentials are $V_\nu(R) = V_0 (1 - (-1)^\nu \tanh(\beta R/2))$ ($\nu = 1, 2$) and
\[ V_{12}(R) = V \exp (-\alpha R^2) \] with \( V_0 = 0.5 \text{ eV}, V = 0.1 \text{ eV}, \beta = 20 \text{ Å}^{-1}, \alpha = 20 \text{ Å}^{-2} \) and reduced mass \( m = 4.18 \text{ u} \) (the \( \hbar = 1 \) units used in [13] have been converted for convenience). The solid line is the exact result and the open circles represent a semiclassical Landau–Zener type formula [13]. Figure 3 demonstrates that the present approximation (dashed line) is clearly superior to the semiclassical treatment of [13] and, in addition, much more convenient in practical computations.

**Conclusions**

It has been demonstrated that the Magnus expansion together with a semiclassical mapping prescription leads to a useful approximation for curve crossing problems in the intermediate coupling region. The semiclassical Magnus approximation turns out to be identical to the exponential uniform distorted wave approximation (EUDWBA) for the case of diabatic potentials with similar slopes at the turning point. For different signs of the forces a new formula has been derived, which differs from the EUDWBA expression and leads to a remarkable improvement of the approximation. The admittedly quite empirical semiclassical mapping prescription in the present article demands, of course, a more rigorous derivation. The general semiclassical mapping of systems of differential equations is currently being investigated; the results will be published elsewhere.

Finally it should be pointed out that, in contrast to other approaches, the semiclassical Magnus approximation can easily be extended to multistate systems, because nothing in the analysis presented in §§ 2 and 3 depends on the two-state nature of the system.

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**References**