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Uniform Airy Approximation for Nonadiabatic Transitions in a Curve-Crossing Weak-Coupling Case

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Abstract: This work suggests a connection between Landau-Zener transition probabilities between two crossing potentials in the classically accessible WKB regime and Landau-Lifshitz transition probabilities in the classically inaccessible WKB regime. It is based on the uniform Airy (UAi) approximation which represents a generalization of quantum transition probabilities for linear crossing potentials with constant coupling. The performance of the UAi approximation is tested by comparison with distorted-wave probabilities for an exponential potential model and illustrated for potentials that determine the intersection of two \textit{ab initio} vibronic potential surfaces of the NO-Ar system.

Keyword: curve-crossing.

1 Introduction

In 1932 Landau determined the transition probability for a one-dimensional double-passage of the crossing of two weakly coupled potential curves [1]. This expression, traditionally called the Landau-Zener (LZ) transition probability $P^\text{LZ}$, includes the interference of two transition amplitudes under the condition
of large WKB phase differences for the motion between the crossing point and the turning points (we note that Zener [2] only considered a single passage of the crossing point and, therefore, did not consider the problem of interference; besides Landau, the latter had been studied by Stueckelberg [3]; the interference phenomenon was amply discussed e.g. in the Landau-Lifshitz (LL) textbook, i.e. Ref. [4], Sect. 90.7 Ch. 11).

For the case of a classically inaccessible crossing point, the counterpart of the LZ transition probability can be derived according to Sect. 51.6 Ch. 11 of Ref. [4] with referring to another article by Landau [5], where an expression for the probability is given within the exponential term only. The full expression for the transition probability, referred to here as $P_{LL}$, would have required the detailed specification of the integration contour or the analytic continuation of the LZ transition amplitude into the complex energy plane, from the classically accessible WKB region to the classically forbidden WKB region.

The two WKB probabilities, $P_{LZ}$ and $P_{LL}$, are separated on the energy axis $E$ by a non-WKB region, located near to the crossing energy $E_c$. The passage through this region requires the full solution of the quantum problem. One possibility to achieve this is the assumption of crossing linear (lin) potentials, for which the transition probability $P_{lin}^{Ai}$ can be expressed through the Airy (Ai) function (Ref. [4], Sect. 90, problem 3). Asymptotically, i.e. when $E$ is considerably higher or lower than $E_c$, this yields the respective LZ or LL expressions for crossing linear potentials, $P_{lin}^{LZ}$ or $P_{lin}^{LL}$. This allows for the possibility of a formulation of a uniform Airy (UAi) approximation of the probability, $P_{UAi}$, that interpolates between $P_{lin}^{LZ}$ or $P_{lin}^{LL}$ in the case of non-linear potentials through a properly modified expression for $P_{lin}^{Ai}$. This approach corresponds to other examples of applying the uniform approximation such as discussed e.g. in Refs. [6–9].

Our interest in a UAi approximation for crossing potentials was raised by recent applications of the Airy approximation to vibronic transitions in atom-molecule collisions [10, 11] and intersystem crossing in isolated molecules [12]. Accordingly, the presentation in this paper is arranged as follows. In Section 2 we consider the WKB transformation of LZ transition probabilities into LL transition probabilities. Section 3 is devoted to the formulation of a UAi approximation, bridging the gap between LZ and LL WKB expressions through a non-WKB region. Section 4 provides a test of the UAi approximation against the distorted-wave probability in a two-state exponential model and illustrates the convergence of UAi probabilities to its WKB asymptotics (i.e. to the LZ and LL limits) for ab initio potentials of an NO-Ar collision system. Section 5 concludes the article.
2 Analytic continuation of LZ transition probabilities into the classically forbidden WKB range

In the following, we consider crossing potential curves which represent the intersection of two vibronic potential energy surfaces (PESs) of the NO-Ar system along a “reaction coordinate” \( q \) that follows the minimal energy of the crossing line of two two-dimensional PESs \([10, 11]\). The nonadiabatic transition from the initial vibronic state \( A'', v=1 \) to the final state \( A', v=0 \) in this case is induced by weak Coriolis and spin-orbit interactions (see Figure 1). This figure also specifies the two WKB regions in which the crossing point is classically accessible (CAWKB) and classically forbidden (CFWKB), with turning points being well separated from the crossing point. The figure also shows a non-WKB region in which the turning points are close to the crossing point.

The LZ transition probability in the CAWKB region is given by

\[
P^{LZ}(E) = \frac{8\pi V^2 \sqrt{\mu / 2}}{\hbar \Delta F \sqrt{E - E_c}} \sin^2(\Phi^r(E) + \pi / 4) \Theta(E - E_c)
\]

(1)

Fig. 1: Intersection of two vibronic PESs for the NO-Ar system along the reaction coordinate \( q \), see text.
where $\Theta(E - E_c)$ is the step function, $V$ is the coupling matrix element (assumed to be independent of $E$), and $\mu$ is the effective mass for motion along the reaction coordinate; $\Delta F$ is the difference of slopes of the two potentials at the crossing point and $\Phi$(E) is the interference phase. The latter was first introduced by Landau [1] who suggested that the transition probability in practical applications can be averaged over fast interference oscillations. This leads to an expression for the double-passage probability which is a simple example of the “surface-hopping” (SH) approach [13] with the probability

$$P_{LZ}^{SH}(E) = \langle P_{L}^{12}(E) \rangle_{\Phi} = \frac{4\pi V^2 \sqrt{\mu/2}}{\hbar \Delta F} \sqrt{E - E_c}$$  \hspace{1cm} (2)$$

It should be emphasized that the lack of a dependence of the interference phase on the coupling matrix element [at the r.h.s. of Eq. (1)] is a property of weak coupling. This feature considerably simplifies the subsequent presentation in comparison to the general case (which was discussed in Refs. [6, 8, 9]; we note that the Stueckelberg expression for the double-passage transition probability on p. 49 of Ref. [3] even in the weak-coupling limit does not give the correct expression for the interference phase).

The r.h.s. of Eq. (1) [and its SH counterpart in Eq. (2)] diverges at $E \rightarrow E_c$; this is related to the divergence of CAWKB wave functions near to turning points which approach the crossing point. In this respect, the satisfactory performance of Eq. (1) can be interpreted as the condition for $\Phi$(E) to be sufficiently large. Another restriction for the applicability of Eq. (1) lies in the requirement that the linear approximation for the potentials near to the crossing point (i.e. in the region of nonadiabatic transitions) does not contradict the general non-linear character of the potentials far from the crossing point. This condition imposes a restriction on the energy difference $E - E_c$ at $E > E_c$.

The phase $\Phi$(E) is expressed through the classical action integrals in the CAWKB region. Since, in the following, we use a more general phase function $\Phi(E)$ across the non-WKB and CFWKB regions, we define $\Phi(E)$ for all values of $E$ in the complex energy plane by

$$\Phi(E) = \sqrt{2\mu E - V_1(q)} dq - \sqrt{2\mu E - V_2(q)} dq$$  \hspace{1cm} (3)$$

where $q$ is the reaction coordinate, $q_{t1}$, $q_{t2}$ are the turning points, and $q_c$ corresponds to the crossing point. One should note that the r.h.s. of Eq. (3) can be represented as an integral along a contour that leads from the turning point to
the crossing point on the initial potential curve and, then, from the crossing point to the turning point on the final potential curve (the two parts of the contour in Figure 1 are indicated by red and blue arrows).

On the real energy axis, $\Phi(E)$ can then be represented as

$$
\Phi(E) = \Phi^>(E) + i\Phi^<(E)
$$

$$
\Phi^>(E) = |\Phi(E)| \Theta(E - E_c)
$$

$$
\Phi^<(E) = -|\Phi(E)| \Theta(E_c - E)
$$

with $\Phi^>(E) \geq 0$ and $\Phi^<(E) \leq 0$. If $E$ is close to $E_c$, i.e. when $q_{t1}, q_{t2}$ are close to $q_c$, one can use the linear approximation to the potentials

$$
V_1(q) \rightarrow V_{\text{lin}}(q) = E_c - F_1(q - q_c),
$$

$$
V_2(q) \rightarrow V_{\text{lin}}(q) = E_c - F_2(q - q_c)
$$

such that Eq. (4) with $\Phi(E) \rightarrow \Phi_{\text{lin}}(E)$ become

$$
\Phi_{\text{lin}}(E) = (3/2)[(E - E_c)/E_{\text{lin}}]^{3/2} = \Phi^>_{\text{lin}}(E) - i\Phi^<_{\text{lin}}(E)
$$

$$
\Phi^>_{\text{lin}}(E) = (3/2)[(E - E_c)/E_{\text{lin}}]^{3/2} \Theta(E - E_c)
$$

$$
\Phi^<_{\text{lin}}(E) = -(3/2)[(E_c - E)/E_{\text{lin}}]^{3/2} \Theta(E_c - E)
$$

$$
E_{\text{lin}} = (\hbar^2 / 2\mu)^{1/3} (F_1F_2)^{-2/3} (\Delta F)^{2/3}
$$

$\Phi_{\text{lin}}(E)$ here is the first term of an expansion of $\Phi(E)$ in powers of $E - E_c$. Figure 2 shows graphs of $|\Phi(E)|$ and $|\Phi_{\text{lin}}(E)|$ as a function of the scaled energy $\varepsilon = E/E_c$ (for the potentials of Figure 1 with $E_c/k_B = 5250$ K and $\mu = 9.43$ amu [10, 11]). This figure also specifies the non-WKB range defined by the condition $|\Phi(E)| < 1$ (for a justification of this condition, see Section 4), and a plot of the real-valued monotonically decreasing positive function $f(\varepsilon) = \Phi(\varepsilon)/\Phi_{\text{lin}}(\varepsilon)$.

An important feature of the energy dependence of the LZ transition amplitude $A_{\text{LZ}}(E) \propto \sqrt{\Omega_{\text{LZ}}(E)}$ is its similarity to the coordinate dependence of the WKB wave function in the field of a linear potential. Therefore, the analytic continuation of $A_{\text{LZ}}(E)$ into the complex $E$ plane, from the classically allowed WKB region to the classically forbidden WKB region along a contour circumventing the point $E_c$, can be accomplished analogous to that for WKB wave functions (as described in Ch. 7, Sect. 47 of Ref. [4]). One of the oscillating exponentials in $A_{\text{LZ}}(E)$ for $E > E_c$ here exponentially decays with increasing $|E - E_c|$ while the other one is lost (see Sect. 47 of Ref. [4]). This feature, the “Stokes phenomenon”, is described in detail, e.g. in Refs. [13–16].
On the basis of the foregoing discussion one obtains the following expression for the LL transition probability

$$p^{\text{lin}}(E) = \frac{2\pi V^2}{\hbar \Delta F} \sqrt{\frac{\mu}{2}} \exp(2\Phi^c(E))$$

(7)

If $\Phi^c(E)$ and $\Phi^c(E)$ in Eqs. (1) and (7) are replaced by $\Phi^c_{\text{lin}}(E)$ and $\Phi^c_{\text{lin}}(E)$, the respective expressions for $P^\text{lin}_{\text{lin}}(E)$ and $P^\text{lin}_{\text{lin}}(E)$ represent the WKB asymptotes of the quantum expression for the transition probability between linear potentials. This will be further elaborated in Section 3.

3 Airy- and uniform Airy approximations

Quantum transition probabilities in the case of linear potentials, $P^\text{lin}_{\text{lin}}(E)$, are expressed through the Airy function (see Ref. [4], Sect. 90, problem 3) by

$$P^\text{lin}_{\text{lin}}(E) = 4\pi \frac{V^2}{E^2_{\text{lin}}} \frac{F F}{(\Delta F)^2} \text{Ai}^2 \left( \frac{E - E_{\text{lin}}}{E^2_{\text{lin}}} \right)$$

(8)

where $E_{\text{lin}}$ is defined in Eq. (6). The argument of the Airy function here can be expressed through the phase $\Phi_{\text{lin}}$ via Eq. (5). Since the value of the coupling
matrix element $V$, in the comparison of $P^{\mathrm{Ai}}(E)$ with $P^{\mathrm{LZ}}(E)$ and $P^{\mathrm{LL}}(E)$, is not essential, it is convenient to use probability ratios defined by $R^{\mathrm{Ai}}(E) = P^{\mathrm{Ai}}(E) / P^{\mathrm{Ai}}(E_c)$, $R^{\mathrm{LZ}}(E) = P^{\mathrm{LZ}}(E) / P^{\mathrm{Ai}}(E_c)$, and $R^{\mathrm{LL}}(E) = P^{\mathrm{LL}}(E) / P^{\mathrm{Ai}}(E_c)$. The energy dependence of the probability ratios is then expressed through $\Phi^{\mathrm{lin}}(E)$ and $\Phi(E)$. In this way one obtains the explicit expressions

$$R^{\mathrm{Ai}}_{\mathrm{lin}}(E) = N\mathrm{Ai}^2 \{-[3\Phi^{\mathrm{lin}}_{\mathrm{lin}}(E)/2]^{2/3}\}$$  \hspace{1cm} (9)

$$R^{\mathrm{LZ}}(E) = (N / \pi)[3\Phi^{\mathrm{lin}}_{\mathrm{lin}}(E)/2]^{-1/3}\sin^2(\Phi^{\mathrm{lin}}(E) + \pi/4)$$  \hspace{1cm} (10)

$$R^{\mathrm{LL}}(E) = (N/4\pi)[-3\Phi^{\mathrm{lin}}_{\mathrm{lin}}(E)/2]^{-1/3}\exp(2\Phi^{\mathrm{lin}}(E))$$  \hspace{1cm} (11)

$$R^{\mathrm{LZH}}_{\mathrm{lin}} = (N/2\pi)[3\Phi^{\mathrm{lin}}_{\mathrm{lin}}(E)/2]^{-1/3}.$$  \hspace{1cm} (12)

where $N = \mathrm{Ai}^{-2}(0) = 7.735$. One should note that $\Phi^{\mathrm{lin}}_{\mathrm{lin}}$ enters Eqs. (10)–(12) because of the linear approximation of the potentials near to the crossing point [but not over the full region from the crossing point to the turning points, such as this is the case for Eq. (9)]. In order to describe the passage of $R^{\mathrm{Ai}}_{\mathrm{lin}}(E)$ to its asymptotic limit, it is convenient to introduce two auxiliary functions $R^{\mathrm{LZ}}_{\mathrm{lin}}$ and $R^{\mathrm{LL}}_{\mathrm{lin}}$ defined by

$$R^{\mathrm{LZ}}_{\mathrm{lin}}(E) = R^{\mathrm{LZ}}(E)_{\Phi = \Phi^{\mathrm{lin}}_{\mathrm{lin}}}$$

$$R^{\mathrm{LL}}_{\mathrm{lin}}(E) = R^{\mathrm{LL}}(E)_{\Phi = \Phi^{\mathrm{lin}}_{\mathrm{lin}}}$$

which, for $|\Phi^{\mathrm{lin}}_{\mathrm{lin}}| \gg 1$, represent the WKB asymptotes of $R^{\mathrm{Ai}}_{\mathrm{lin}}(E)$.

Since the Airy approximation is valid only for the linear approximation of the potentials in Eq. (4), it does not guarantee that the WKB asymptotes of $R^{\mathrm{Ai}}_{\mathrm{lin}}(E)$ smoothly pass into $R^{\mathrm{LZ}}_{\mathrm{lin}}(E)$ and $R^{\mathrm{LL}}_{\mathrm{lin}}(E)$. This passage, for increasing $|E - E_c|$, is characterized by an increasing divergence between $\Phi(E)$ and $\Phi_{\mathrm{lin}}(E)$. Nonetheless, the expressions of Eqs. (10) and (13) suggest a possibility to define an Airy-based uniform approximation for the probability ratio $R^{\mathrm{UAi}}(E)$ which would satisfactorily describe the energy dependence of the transition probability across a wide energy range.

The UAi approximation provides a continuous passage from $R^{\mathrm{Ai}}_{\mathrm{lin}}(E)$ to $R^{\mathrm{UAi}}_{\mathrm{lin}}(E)$ at energies far from the energy of the crossing point, conserving the linear character of crossing potentials near to the crossing point. The former is achieved by the change of the argument of the Airy function and the latter by introducing correction factors in front of the Airy function. In this way one transforms $R^{\mathrm{Ai}}_{\mathrm{lin}}(E)$ from Eq. (10) to $R^{\mathrm{UAi}}_{\mathrm{lin}}(E)$:
\begin{equation}
R^{\text{UAi}}(E) = N \left( \Phi(E) / \Phi_{\text{lin}}(E) \right)^{1/3} \text{Ai}^2 \left\{ -\left[ 3\Phi(E) / 2 \right]^{2/3} \right\} \tag{14}
\end{equation}

The phases $\Phi_{\text{lin}}(E)$ and $\Phi(E)$ in Eq. (14) are either positive real (for $E \geq E_c$) or negative imaginary (for $E \leq E_c$), such that the respective argument of the Airy function is negative or positive and the ratio of the phases in the pre-exponential factor is positive. For not too large values of $\Phi(E)$, when $\Phi(E)$ is close to $\Phi_{\text{lin}}(E)$, the expression $R^{\text{UAi}}(E)$ in Eq. (15) reduces to $R^{\text{Ai}}_{\text{lin}}(E)$, while, for the case of sufficiently large $\Phi(E)$, $R^{\text{UAi}}(E)$ approaches $R^{\text{li}}_{\text{lin}}(E)$ or $R^{\text{li}}_{\text{lin}}(E)$. In intermediate cases, $R^{\text{UAi}}(E)$ provides a uniform interpolation between the two WKB regimes across a non-WKB regime at energies $E$ close to $E_c$. The final expression for the UAi probabilities reads

\begin{equation}
P^{\text{UAi}}(E) = \frac{4\pi^2}{N} \frac{V^2}{E_{\text{lin}}^2} \frac{F_{1}\overline{F}_2}{(\Delta E)^2} R^{\text{UAi}}(E) \tag{15}
\end{equation}

The factor in front of $R^{\text{UAi}}(E)$ in Eq. (15) contains only parameters of the crossing point.

There are three conditions for the applicability of the UAi approximation:
(i) a small transition probability;
(ii) WKB motion in the field of the nonlinear potentials;
(iii) a consistency of LZ modeling with a linear crossing in the field of nonlinear potentials.

The conditions (i)–(iii) are most consistently formulated in terms of a characteristic length $a_1$ of the potential $V_1(q)$, the ratio of slopes $F_2/F_1$ in the linear limit and the characteristic WKB parameter $\xi_c$. These quantities are defined as

\begin{equation}
a_1 = E_c / F_1, \quad F_2 / F_1 = 1 + \delta, \quad \xi_c = \sqrt{2\mu E_c a_1 / \hbar}, \tag{16}
\end{equation}

Using scaled energies

\begin{equation}
e = E / E_c, \quad \epsilon_{\text{lin}} = E_{\text{lin}} / E_c = (\xi_c \delta / (1 + \delta))^{-2/3}, \quad \nu = V / E_c, \tag{17}
\end{equation}

the conditions (i)–(iii) are now formulated as
(i) \( (4\pi^2 / N)(\nu / \epsilon_{\text{lin}}^2)((1 + \delta) / \delta^2) << 1 \) \tag{18}
(ii) \( \xi_c \sqrt{\epsilon} >> 1 \) \tag{19}
(iii) \( \sqrt{\epsilon} / \xi_c \delta << 1 \) \tag{20}

We assume that condition (18) is satisfied for sufficiently small coupling matrix elements $\nu$ (weak coupling limit). The conditions (19) and (20) define an energy window $(w)$, $\epsilon \in \epsilon_w$ as
\[
\xi_c^{-2} \ll \varepsilon \ll \xi_c^2 \delta^2
\] (21)

within which the UAi approach is expected to provide a good approximation to accurate results. This window will be particularly wide when \( \xi_c \gg 1 \). We, therefore, consider the inequality \( \xi_c \gg 1 \) as a necessary condition for a satisfactory performance of the UAi approximation across a wide energy range.

With Eqs. (16) and (17), the dependence of the phase \( \Phi \) on the energy \( E \) and a collection of other parameters \( \Gamma \) can be written in reduced form as

\[
\Phi(E, \Gamma) = \xi_c \phi(\varepsilon, \gamma) \quad \text{where} \\
\phi(\varepsilon, \gamma) = \int_0^{\rho_1} \sqrt{\varepsilon - v_1(\rho, \gamma)} d\rho - \int_0^{\rho_2} \sqrt{\varepsilon - v_2(\rho, \gamma)} d\rho
\] (22)

Here, \( \rho = (q - q_c)/a \) and \( \gamma \) denote dimensionless parameters that do not include \( \varepsilon \). In the linear approximation, the set \( \gamma \) reduces to a single parameter \( \delta \), such that Eq. (21) becomes

\[
\Phi_{\text{lin}}(E, \Gamma) = \xi_c \phi_{\text{lin}}(\varepsilon, \delta) \big|_{\gamma=\delta}, \\
\phi_{\text{lin}}(\varepsilon, \delta) \big|_{\gamma=\delta} = (2\delta / 3(1+\delta))(\varepsilon - 1)^{3/2}
\] (23)

One can avoid complex-valued phases by transforming them into a real-valued function \( f(\varepsilon) = \phi(\varepsilon)/\phi_{\text{lin}}(\varepsilon) \). In terms of this variable, Eq. (14) reads

\[
R^{\text{UAi}}(\varepsilon) = N f^{1/3}(\varepsilon) A \left\{ -\frac{\varepsilon - 1}{\varepsilon_{\text{lin}}^{2/3}} f^{2/3}(\varepsilon) \right\}
\] (24)

The graph of \( f(\varepsilon) \) is shown in Figure 2.

4 Test of the UAi approximation and the convergence of UAi probabilities to their WKB asymptotes

A test of the accuracy of the UAi approximation and a clarification of its range of applicability is obtained by comparing \( R^{\text{UAi}}(\varepsilon) \) with its accurate counterpart calculated for model potentials. As an example, one can choose an exponential (exp) model which employs exponential functions for repulsive potentials (see Ref. [11]) and the coupling. In scaled variables, it assumes the form

\[
v_1(\rho) = \exp(-\rho) \\
v_2(\rho) = (1+\delta)\exp(-\rho) - \delta \\
v_{12}(\rho) = v\exp(-\rho)
\] (25)
The phase functions $\Phi^{\exp(>)}$ and $\Phi^{\exp(<)}$ for the potentials in Eq. (27) are

$$
\Phi^{\exp(>)}(\varepsilon) = \xi_c \left[ 2\sqrt{\varepsilon} \ln \sqrt{\varepsilon + \sqrt{-1}} - 2\sqrt{\varepsilon + \delta} \ln \left( \frac{\sqrt{\varepsilon + \delta} + \sqrt{-1}}{\sqrt{1 + \delta}} \right) \right] \Theta(\varepsilon - 1),
$$

$$
\Phi^{\exp(<)}(\varepsilon) = \xi_c \left[ 2\sqrt{\varepsilon} \arctan \left( \frac{1 - \varepsilon}{\varepsilon} \right) - 2\sqrt{\varepsilon + \delta} \arctan \left( \frac{1 - \varepsilon}{\varepsilon + \delta} \right) \right] \Theta(1 - \varepsilon)
$$

Then Eq. (14), with $\Phi \to \Phi^{\exp(\cdot)}$, defines the quantity $R^{\text{UAi}}_{\text{exp}}(\varepsilon)$.

The accurate weak-coupling counterpart of $R^{\text{UAi}}_{\text{exp}}(\varepsilon)$ can be expressed through the distorted wave (DW) transition probabilities $P^{\text{DW}}_{\text{exp}}(\varepsilon)$ as $R^{\text{DW}}_{\text{exp}}(\varepsilon) = P^{\text{DW}}_{\text{exp}}(\varepsilon) / P^{\text{DW}}_{\text{exp}}(\varepsilon)_{|\varepsilon = 1}$. The transition probabilities $P^{\text{DW}}_{\text{exp}}(\varepsilon)$, as calculated by Mies [17], are expressed through the hypergeometric function that, beside $\varepsilon$, contains also parameters $\delta$ and $\xi_c$. One expects that $R^{\text{DW}}_{\text{exp}}(\varepsilon)$, with $\varepsilon$ in the energy window $\varepsilon_w$ (i.e. for $\varepsilon \in \varepsilon_w$), would correspond to $R^{\text{UAi}}_{\text{exp}}(\varepsilon)$, i.e.

$$
R^{\text{DW}}_{\text{exp}}(\varepsilon)_{|\varepsilon \in \varepsilon_w} = R^{\text{UAi}}_{\text{exp}}(\varepsilon)
$$

Using the Olver approach [18], Umanskii [19] simplified the expression for $P^{\text{exp}}_{\text{exp}}(\varepsilon)$ under two conditions that correspond to the lower and upper boundaries of the energy window, i.e. he derived an analytical expression for $P^{\text{exp}}_{\text{exp}}(\varepsilon)_{|\varepsilon \in \varepsilon_w}$ (see Eqs. (42a) and (42b) of Ref. [19]). An analysis of the latter shows that it is indeed equivalent to $P^{\text{UAi}}_{\text{exp}}(\varepsilon)$, though in different nomenclature. This indicates that $R^{\text{exp}}_{\text{exp}}(\varepsilon)_{|\varepsilon \in \varepsilon_w}$ is described by the UAi approximation for $\varepsilon \in \varepsilon_w$ as it should be in the general case. On the other hand, for $\varepsilon \notin \varepsilon_w$ (i.e. for $\varepsilon$ outside $\varepsilon_w$), $R^{\text{DW}}_{\text{exp}}(\varepsilon)$ deviates from $R^{\text{UAi}}_{\text{exp}}(\varepsilon)$ in a model-specific manner, reflecting the breakdown of the WKB condition and the assumption of a coordinate-independent coupling (which, according to Eq. (25), depends on $\rho$). This shows the limitations of the performance of the UAi approximation in this specific case.

The convergence of UAi probabilities to its WKB asymptotics, i.e. to the LZ and LL limits, is illustrated here by comparing $R^{\text{UAi}}_{\text{exp}}(\varepsilon)$, $R^{\text{LZ}}_{\text{exp}}(\varepsilon)$, $R^{\text{LZSH}}_{\text{exp}}(\varepsilon)$, and $R^{\text{LL}}_{\text{exp}}(\varepsilon)$ for the potentials of intersection of two two-dimensional \textit{ab initio} PESs along the reaction coordinate of an NO-Ar collision system [11]. According to Ref. [11], the parameters $\xi_c$ and $\delta$ of this system are about 10 and 0.3. They define the energy window $\varepsilon$ for the application of the UAi approximation as

$$
10^{-2} \ll \varepsilon \ll 10
$$

This corresponds to lower and upper limits of the collision energy of about 100 K and several 1000 K. This window, thus, includes the experimental conditions of all available studies of NO-Ar collisions.
The values of $R_{UAi}(\varepsilon)$, $R_{LZ}(\varepsilon)$, $R_{LZSH}(\varepsilon)$, and $R_{LL}(\varepsilon)$ were calculated from the appropriate equations of Section 2 where the phases $\Phi_{\text{lin}}(E)$ and $\Phi(E)$ were determined numerically with Eq. (2) along the reaction coordinate [11]. Graphs of these functions are shown in Figure 3 (linear ordinate scale) and Figure 4 (logarithmic ordinate scale). In both figures the red arrows indicate the width of the first Stueckelberg maximum which, for $E_c/k_B = 5250$ K, is about 6000 K. $R_{UAi}(\varepsilon)$ in Figure 4 provides a smooth interpolation between two WKB limits, $R_{LL}(\varepsilon)$ and $R_{LZ}(\varepsilon)$, at $\varepsilon = \varepsilon_c = 0.5$ and at (and above) $\varepsilon = \varepsilon_c = 1.9$ respectively. The interpolation covers well the energy window defined by Eq. (28), and it roughly corresponds to the phases $|\Phi(\varepsilon)|$, $\Phi(\varepsilon) < 1$ of Figure 2. Interestingly, the asymmetry of the points $\varepsilon_c$ and $\varepsilon_c'$ with respect to the crossing energy $\varepsilon_c = 1$ corresponds to the asymmetry of the function $|\Phi(\varepsilon)|$ with respect to the same energy. $R_{UAi}(\varepsilon)$, thus, provides a general description of the UIAi probability $P_{UAi}(\varepsilon)$ across a wide energy range. The extension of energies to values outside the energy windows requires the specification of the coordinate dependence of the coupling matrix element. The first-order transition probability then loses the important feature that the energy dependence is completely defined by the factor $R_{UAi}(\varepsilon)$ which, irrespective of the coupling, is specified by the coordinate dependence of the diabatic potentials.

Fig. 3: Probability ratios $R_{UAi}$, $R_{LZ}$, and $R_{LZSH}$, as a function of the reduced energy $\varepsilon = E/E_c$, see Section 4.
In the investigation of nonadiabatic tunneling effects in NO-Ar collisions in Ref. [11], we have used the so-called generalized Airy (GAi) approximation, for which the function $R^{\text{GAi}}(E)$, for $E < E_c$, was defined as

$$R^{\text{GAi}}(E)_{E < E_c} = \text{Nexp}[2\Phi^<(E) - 2\Phi^<_{\text{lin}}(E)] \text{Ai}^2 \{-[3\Phi^<_{\text{lin}}(E)/2]^{2/3}\}$$  \hspace{1cm} (29)

A numerical comparison of the expressions for $R^{\text{UAi}}(E)_{E < E_c}$ and $R^{\text{GAi}}(E)_{E < E_c}$ from Eqs. (14) and (29), shows that the UAi and GAi probabilities are very close to each other in the CFWKB region. The results of Ref. [11], therefore, are also valid for the UAi approach.

5 Conclusions

The calculation of transition probabilities for curve-crossing systems, under the condition of weak-coupling, represents a particularly simple problem, since interferences arising from double passage of the coupling region do not depend on the coupling strength and are determined only by motion in uncoupled crossing potentials. Under this condition, the Landau WKB expression for curve-crossing...
transition probabilities can be extended such that the gap between classically accessible and classically forbidden WKB regimes is bridged. The interpolation between the two limits across a non-WKB region can be described by the uniform Airy approximation. It is based on a quantum solution of the problem for crossing linear potentials and an analytic continuation of the transition amplitude beyond the linear expression for complex-valued interference phases. The latter are calculated with classical action integrals, from the crossing points to the turning points and for energies above and below the crossing-point energy. We finally mention that the uniform Airy approximation complements other models (which were termed the Nikitin, Demkov, Kummer, and noncrossing parabolic models in Ref. [15]).

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References