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NON-ADIABATIC TRANSITIONS IN MULTIPLE DIMENSIONS∗

V.BETZ †, B.GODDARD‡, AND TIM HURST§

Abstract. We consider non-adiabatic transitions in multiple dimensions, which occur when the
Born-Oppenheimer approximation breaks down. We present a general, multi-dimensional algorithm
which can be used to accurately and efficiently compute the transmitted wavepacket at an avoided
crossing. The algorithm requires only one-level Born-Oppenheimer dynamics and local knowledge
of the potential surfaces. Crucially, in contrast to many standard methods in the literature, we
calculate the whole wavepacket, including its phase, rather than simply the transition probability.
We demonstrate the excellent agreement with full quantum dynamics for a range of examples in
two dimensions. We also demonstrate surprisingly good agreement for a system with a full conical
intersection.

Key words. time-dependent Schrödinger equation, non-adiabatic transitions, superadiabatic
representations.

AMS subject classifications. 35Q40, 81V55

1. Introduction. Many computations in quantum molecular dynamics rely on
the Born-Oppenheimer Approximation (BOA) [13], which utilises the small ratio $\epsilon^2$
of electronic and reduced nuclear masses to replace the electronic degrees of freedom
with Born-Oppenheimer potential surfaces. When these surfaces are well separated,
the BOA further reduces computational complexity by decoupling the dynamics to
individual surfaces.

However, there are many physical examples (see e.g. [15],[16],[35] and [40]) where
the Born-Oppenheimer surfaces are not well separated (known as an avoided crossing)
or even have a full intersection. In these regions the BOA breaks down, and the
coupled dynamics must be considered; when a wavepacket travels over a region where
the surfaces are separated by a small but non-vanishing amount, a chemically crucial
portion of the wavepacket can move to a different energy level via a non-adiabatic
transition. The existence of the small parameter $\epsilon$ introduces several challenges when
attempting to numerically approximate the dynamics. First, and independently of the
existence of an avoided or full crossing, the wavepacket oscillates with frequency $1/\epsilon$
and hence a very fine computational grid is required. Furthermore, in the region of an
avoided crossing, the dynamics produce rapid oscillations and, in turn, cancellations
in the wavepacket; the transmitted wavepacket very close to the crossing is $O(\epsilon)$,
but in the scattering regime the transmission is exponentially small. It is therefore
necessary to travel far from the avoided crossing (in position space) with a small time-
step to accurately calculate the phase, size and shape of the transmitted wavepacket.

In order to calculate the exponentially small wavepacket, one must ensure that the

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†Fachbereich Mathematik, Technische Universität Darmstadt, 64289 Darmstadt, Germany
(betz@mathematik.tu-darmstadt.de, http://www.mathematik.tu-darmstadt.de/~betz/).
‡School of Mathematics and the Maxwell Institute for Mathematical Sciences, University of Edin-
burgh, Edinburgh, UK, EH9 3FD (b.goddard@ed.ac.uk, http://www.maths.ed.ac.uk/~bgoddard/).
§Maxwell Institute for Mathematical Sciences, School of Mathematics, University of Ed-
inburgh, Edinburgh, UK, EH9 3FD (t.hurst@sms.ed.ac.uk, http://www.maxwell.ac.uk/migsaa/
people/tim-hurst).
absolute errors in a given numerical scheme are also exponentially small, or they will
swamp the true result. Finally, the number of gridpoints in the domain increases
exponentially as the dimension of the system increases. Thus standard numerical
algorithms quickly become computationally intractable.

Many efforts have been made to avoid computational expense by approximating
the transmitted wavepacket while avoiding the coupled dynamics. **Surface hopping
algorithms** discussed in [41, 33, 37, 29, 39, 23, 34, 36, 17, 18, 31, 4, 3] approximate
the transition using classical dynamics, where the **Landau-Zener transition rate** [42],
[30] is sometimes used to determine the size of the transmitted wavepacket. This
method has enjoyed some success, and has been applied to higher dimensional systems
(in particular see [31, 4]). However, the full transmitted quantum wavepacket is not
always calculated; phase information is lost, although surface hopping approaches have
been considered which try to incorporate phase information [21, 32, 14, 27, 24, 26].
Such information is crucial when considering systems with interference effects, e.g.
ones in which the initial wavepacket makes multiple transitions through an avoided
crossing. In contrast, in [10] and [7], a formula is derived to accurately approximate
the full transmitted wavepacket, in one dimension, using only decoupled dynamics.
The formula has been applied to a variety of examples with accurate results, including
the transmitted wavepacket due to photo-dissociation of sodium iodide [9].

In this paper we construct a method to apply the formula derived in [10] and
[7] to higher dimensional problems. We set up the problem, state assumptions, and
the main result and algorithm in Section 2. Our derivation is motivated by the
derivation of the formula in one dimension [10], which we outline in Section 3 and
extend to d dimensions in Section 4. In Section 5 we create a d-dimensional formula
for systems in which near the avoided crossing, when the derivatives of the adiabatic
potential surfaces are slowly varying in all but the direction in which the wavepacket
is travelling. We then extend this result via a simple algorithm to obtain a general
\(d\)-dimensional formula. We provide some examples and results in Section 6 and note
conclusions and future work in Section 7.

2. Set-up and Main Results. We consider the evolution of a semiclassical
wavepacket \(\psi : \mathbb{R}^d \to \mathbb{C}^2\) at time \(t\), \(\psi = \left( \psi_1(x, t), \psi_2(x, t) \right)\), governed by the equation:

\[
\frac{i\varepsilon}{\partial t} \psi(x, t) = H\psi(x, t),
\]

where \(\varepsilon^2\) is the ratio between an electron and the reduced nuclear mass of the molecule,
i.e. \(\varepsilon \ll 1\) and \(H\) is a Hamiltonian operator. This system is derived after a standard
rescaling of a full two level Schrödinger equation involving the kinetic and potential
terms between electrons and nuclei, which for example is given in [20]. We use the
\(\varepsilon\)-scaled Fourier transform to transform the wavepackets \(\psi_1, \psi_2\) and operators such as
\(H\) into momentum space:

**Definition 2.1.** In \(d\) dimensions the wavepacket \(f : \mathbb{R}^d \to \mathbb{C}\) in scaled momen-
tum space is given using the \(\varepsilon\)-scaled Fourier transform

\[
\hat{f}^\varepsilon(k) = \frac{1}{(2\pi \varepsilon)^{d/2}} \int_{\mathbb{R}^d} f(x) \exp \left( -\frac{i}{\varepsilon} k \cdot x \right) dx.
\]

For any (sufficiently nice) function \(f : \mathbb{R}^d \to \mathbb{C} \in L^2(\mathbb{R}^d)\), the \(\varepsilon\)-scaled Fourier
transform \(\hat{A}^\varepsilon\) of an operator \(A\) is given by

\[
\hat{A}^\varepsilon f^\varepsilon(k, t) := \hat{A} f^\varepsilon(k, t) = \frac{1}{(2\pi \varepsilon)^{d/2}} \int_{\mathbb{R}^d} A f(x, t) \exp \left( -\frac{i}{\varepsilon} k \cdot x \right) dx.
\]
We also define the Weyl quantization [2] in multiple dimensions, which is used throughout this paper.

**Definition 2.2.** For a symbol \( H(\varepsilon, \mathbf{p}, \mathbf{q}) \), given a test function \( \psi \), we define the Weyl quantization of \( H \) by

\[
(W_{\varepsilon}H\psi)(x) = \frac{1}{(2\pi\varepsilon)^d} \int_{\mathbb{R}^{2d}} d\xi d\gamma H(\varepsilon, \xi, \frac{1}{2}(x + y))e^{\frac{i}{\varepsilon}(\xi \cdot (x-y))} \psi(y).
\]

The Hamiltonian in (2.1) is given by [7]

\[
H(x) = -\frac{\varepsilon^2}{2} \nabla_x^2 I + V(x) + d(x)I,
\]

where

\[
V(x) = \begin{pmatrix} Z(x) & X(x) \\ X(x) & -Z(x) \end{pmatrix}
\]

and \( d(x) \) is the part of the potential operator with non-zero trace. In general \( V(x) \) can be given by a Hermitian matrix, but as noted in [5], any Hermitian \( V(x) \) can be transformed into real symmetric form. This is known as the diabatic representation of the system. We define \( V_1 = Z(x) + d(x) \) and \( V_2 = -Z(x) + d(x) \) as the two diabatic potentials, with the diabatic coupling element as the off-diagonal element \( V_{12} = X(x) \). It is useful to define \( \theta(x) = \tan^{-1}\left(\frac{X(x)}{Z(x)}\right) \), so that we can write the polar decomposition of (2.5):

\[
\cos(\theta(x)) = \frac{Z(x)}{\sqrt{X(x)^2 + Z(x)^2}}, \quad \sin(\theta(x)) = \frac{X(x)}{\sqrt{X(x)^2 + Z(x)^2}}.
\]

Then, defining \( \rho(x) = \sqrt{X(x)^2 + Z(x)^2} \), gives

\[
V(x) = \rho(x) \begin{pmatrix} \cos(\theta(x)) & \sin(\theta(x)) \\ \sin(\theta(x)) & -\cos(\theta(x)) \end{pmatrix}.
\]

Consider the unitary matrix \( U_0 \) which diagonalises the potential operator \( V(x) \):

\[
U_0(x) = \begin{pmatrix} \cos(\frac{\theta(x)}{2}) & \sin(\frac{\theta(x)}{2}) \\ -\sin(\frac{\theta(x)}{2}) & -\cos(\frac{\theta(x)}{2}) \end{pmatrix}.
\]

If we define \( \psi_0(x, t) = \begin{pmatrix} \psi^+(x, t) \\ \psi^-(x, t) \end{pmatrix} = U_0(x)\psi(x, t) \), then we arrive at the adiabatic Schrödinger equation

\[
i\varepsilon \partial_t \psi_0(x, t) = H_0\psi_0(x, t).
\]

Here \( H_0 = U_0H U_0^{-1} \) is given by

\[
H_0(x) = -\frac{\varepsilon^2}{2} \nabla_x^2 I + \left( \frac{\rho(x) + d(x) + \varepsilon^2 \|\nabla_x \theta(x)\|^2}{2} \right) - \varepsilon \nabla_x \theta(x) \cdot (\varepsilon \nabla_x) - \frac{\varepsilon^2}{8} \frac{\|\nabla_x \theta(x)\|^2}{\varepsilon^2} - \rho(x) + d(x) + \varepsilon^2 \|\nabla_x \theta(x)\|^2.
\]
The adiabatic potential surfaces are given by the diagonal entries of the adiabatic potential matrix to leading order,

\[ V_U(x) = \rho(x) + d(x), \quad V_L(x) = -\rho(x) + d(x), \]

where \( V_U \) is the upper adiabatic potential surface, and \( V_L \) is the lower adiabatic potential surface. The off-diagonal entries of (2.12) are coupling terms, which are negligible when the two adiabatic surfaces are well separated. An avoided crossing occurs when two adiabatic surfaces become close to one another, and the coupling terms have a non-negligible effect. Note that, as we are considering semiclassical wavepackets, derivatives are of order \( 1/\varepsilon \) and hence the leading order off-diagonal elements are of order \( \varepsilon \).

For a more precise definition of an avoided crossing, we direct the reader to [22] (although it should be noted that the precise meaning of avoided crossing does vary in the literature), but for the purposes of this paper we will work with a definition of an avoided crossing with respect to the wavepacket. We define the centre of mass of the wavepacket \( \psi^\pm \) at time \( t \) by

\[ \mathbf{x}_{\text{COM}}(t) = \frac{\int_{\mathbb{R}^n} d\mathbf{x} |\psi^\pm(\mathbf{x}, t)|^2}{\int_{\mathbb{R}^n} d\mathbf{x} |\psi^\pm(\mathbf{x}, t)|^2}, \]

and the centre of momentum of \( \psi^\pm \) as

\[ \mathbf{p}_{\text{COM}}(t) = \frac{\int_{\mathbb{R}^n} d\mathbf{p} |\psi^\pm(\mathbf{p}, t)|^2}{\int_{\mathbb{R}^n} d\mathbf{p} |\psi^\pm(\mathbf{p}, t)|^2}. \]

**Definition 2.3.** Let \( V_U \) and \( V_L \) be the adiabatic surfaces defined in (2.12) such that \( V_U(x) - V_L(x) = 2\rho(x) \). A wavepacket \( \psi^\pm \) on the upper/lower level is said to reach an avoided crossing at time \( t \) when \( \rho(x_{\text{COM}}(t)) \) reaches a local minimum of \( \rho \) along its trajectory. Furthermore, we say that the avoided crossing is tilted when, near the avoided crossing, the non-symmetric part \( d(x) \) of \( V_U \) and \( V_L \) can be written as \( d(x) = \mathbf{\lambda} \cdot x + O(\|x\|^2) \), where \( \mathbf{\lambda} \) is non-zero in the direction \( \mathbf{p}_{\text{COM}}(t) \).

We note that, at an avoided crossing, the derivative couplings in (2.11) are non-negligible, and it is in such regions that we expect the transitions between the adiabatic states to occur. In the following we consider only cases in which the avoided crossing is of dimension zero, either due to the nature of the potential energy surfaces, or the path of the wavepacket. In cases where the dimension is higher, for example, when the wavepacket travels along a ‘seam’ of avoided crossings, we expect the method to break down. For the case of ‘tilted’ crossings in 1D, we refer the reader to [8] and note that we will soon make the assumption that \( \|\mathbf{\lambda}\| \) is small in the direction of \( \mathbf{p}_{\text{COM}} \), and thus not treat the ‘tilted’ case here.

We will assume that the initial wavepacket is purely on the upper level, \( \psi^0(x) = (\psi^0_+)(x) \) and, without loss of generality, that the centre of mass of the wavepacket in position space reaches an avoided crossing of height \( 2\delta \) at position \( x_0 \) at time \( t_{ac} \), and is moving in the direction of \( q_0 \). The adiabatic representation approximates the wavepacket transmitted through an avoided crossing to leading order by the perturbative solution [38]

\[ \psi^0_0(x, t) = -i\varepsilon \int_{-\infty}^{t} e^{-\frac{i}{\varepsilon}(t-s)H^-(x)}\kappa_1^-(x) \cdot (\varepsilon\partial_x e^{-\frac{i}{\varepsilon}sH^+(x)} \psi^0_+(x)) ds, \]
where

\[
H^\pm(x) = -\frac{\varepsilon^2}{2} \nabla_x^2 \pm \rho(x) + d(x), \quad \kappa^\pm_1(x) = \pm \frac{\partial_x \theta(x)}{2}.
\]

The perturbative solution in the adiabatic representation does not offer much explanation as to the properties of the transmitted wavepacket. For instance, the constructed wavepacket at first looks to be \(O(\varepsilon)\). However due to the adiabatic coupling operator \(\kappa^\pm_1\), fast oscillations and cancellations between upper and lower transmissions occur near the avoided crossing, so that far from in position space the crossing the transmitted wavepacket is much smaller than the transition at the crossing point (Figure 1). For this reason, the transmitted wavepacket is better approximated using the perturbative solution from the \(n^{th}\) superadiabatic representation [10], for some optimal choice of \(n\). The \(n^{th}\) superadiabatic representation is produced by creating and applying unitary pseudodifferential operators \(U_n\), such that the off-diagonal elements of the potential operator have prefactor \(\varepsilon^{n+1}\), and the diagonal elements are the same to leading order as in the adiabatic representation. Existence of such operators is discussed in [10]. The Hamiltonian \(H_n\) in the \(n^{th}\) superadiabatic representation is
given by

\[
H_n(x) = -\frac{\varepsilon^2}{2} \nabla_x^2 I + \left( \begin{array}{cc} \rho(x) + d(x) + O(\varepsilon^2) & \varepsilon^{n+1}K^+_n \varepsilon^{-n+1} \rho(x) + d(x) + O(\varepsilon^2) \\ \varepsilon^{n+1}K^-_n + \varepsilon^{-n+1} \rho(x) + d(x) + O(\varepsilon^2) \end{array} \right),
\]

for some pseudodifferential coupling operators \(K^\pm_n\), which are of order one. The perturbative solution in the \(n^{th}\) superadiabatic representation is then given by

\[
\psi^-_n(x,t) = -i\varepsilon^n \int_{-\infty}^{t} e^{-\frac{i}{\varepsilon} (t-s)H^-(x)} K^-_{n+1}(x)e^{-\frac{i}{\varepsilon} sH^+(x)} \psi_0^+(x) \, ds,
\]

Direct computation of the pseudodifferential operators \(K_{n+1}\) and \(U_n\) is recursive in \(n\) (see Section 4), and leads to very complex operators, so we cannot produce a practical numerical scheme directly using superadiabatic representations. However we will use

\[
\text{Fig. 1: The total mass of wavepacket } \psi^-(x) \text{ on the lower potential surface against time } t, \text{ for the system described in Example 6.1 with parameters in } (6.7). \text{ The centre of mass of the wavepacket reaches the avoided crossing at } t = 2.
\]
superadiabatic representations to construct a simple and accurate algorithm.

In [7], where a formula approximating the transmitted wavepacket in one dimension is constructed, five assumptions are made:

(A1) The avoided crossing is ‘flat’, i.e. \( ||\lambda|| \) in Definition 2.3 is small (in the direction of \( p_{\text{COM}}(t_{ac}) \)) compared to the energy gap, \( 2\delta \). This approximation can be removed in 1D [8], but the resulting algorithm is more complicated; we will pursue the multidimensional version of this in future work.

(A2) The momentum of the wavepacket near the avoided crossing is sufficiently large. Furthermore, by a coordinate rotation we can assume without loss of generality that the momentum is concentrated in the first dimension. This allows the quantum symbol of the coupling operator \( K_{n+1} \) to be approximated by its highest order polynomial term, as discussed in Section 4.

(A3) The first order Taylor approximation of the adiabatic (Born-Oppenheimer) energy surfaces near \( x_0 \) leads to a dynamics that is a good approximation of the true dynamics near \( x_0 \), i.e. we can write the adiabatic propagators near the avoided crossing as

\[
H^\pm \approx -\frac{\varepsilon^2}{2} \nabla_x^2 \pm \delta + \lambda \cdot x, \tag{2.19}
\]

(A4) The width of the wavepacket is \( O(\varepsilon) \). For the 1D case, it has been shown[9] that, by the linearity of the Schrödinger equation, we can consider wider wavepackets through a slicing method. We expect this to also hold in higher dimensions.

(A5) The functions \( \rho \) and \( \theta \) are analytic in a strip containing the real axis.

In the multidimensional derivation we will make one additional assumption:

(A6) The adiabatic potential surfaces near the avoided crossing point vary slowly in all but the direction of \( p_{\text{COM}}(t_{ac}) \).

We are now ready to state the main result of this paper. Under the assumptions (A2) to (A6), we approximate the transmitted wavepacket at the avoided crossing point using the formula:

\[
\hat{\psi}_{-\varepsilon}^-(k, t) = e^{-\frac{i}{\varepsilon} t \hat{H}^-} \nu(k_1) + k_1 - \frac{1}{2} \hat{\nu}(k_1) \hat{\nu}(k_1 + \frac{2\pi}{\varepsilon}) e^{\frac{i}{2\varepsilon} \hat{\nu}(k_1)} \times \chi_{k_1^2 > 4\delta^2 \hat{\phi}_{-\varepsilon}^+ (\nu(k_1), k_2, \ldots, k_d)}, \tag{2.20}
\]

where \( \xi, \nu, \tau_c \) and \( \tau_e \) are the \( d \)-dimensional analogues of those quantities defined in one dimension in (D1) to (D4), and are discussed in Section 4 and Section 5. Here, as described precisely in Algorithm 2.4 below, \( \hat{\phi}_{+} \) is the wavepacket on the upper level at the avoided crossing.

We outline the method through which (2.20) may be used to compute the transmitted wavepacket using only one-level dynamics via the following algorithm and 2D diagrams available in Figure SM1:

\textbf{Algorithm 2.4.}

\begin{enumerate}
\item \textbf{(B1)} Begin with an initial wave packet \( \psi^{0,+}(x) \) on the upper adiabatic energy surface, far from the crossing in position space, with momentum such that \( \rho(x_{\text{COM}}(t)) \) will attain a minimum value (Figure SM1a).
\item \textbf{(B2)} Evolve \( \psi^{0,+}(x) \) on the upper level, i.e. under the BOA, until its centre of mass reaches a local minimum at time \( t_{ac} \). Define
\end{enumerate}

\[
\phi^+(x) := e^{-\frac{i}{\varepsilon} t_{ac} \hat{H}^+(x)} \psi^{0,+}(x). \tag{2.21}
\]
(B3) Divide up the full $d$-dimensional space into $d$-dimensional strips parallel to $\mathbf{p}_{\text{COM}}(t_{ac})$. The width of the strips in all directions perpendicular to $\mathbf{p}_{\text{COM}}(t_{ac})$ should be of the order of the width of the transition region (along $\mathbf{p}_{\text{COM}}(t_{ac})$) in the optimal superadiabatic basis. In practice we restrict these strips to the region of space where the wavepacket has significant mass.

(B4) On each strip, replace the true potential energy matrix by an approximation that is flat perpendicular to the direction of $\mathbf{p}_{\text{COM}}(t_{ac})$. In practice, we take the potential along $\mathbf{p}_{\text{COM}}(t_{ac})$ in the middle of the strip and replicate it in the directions perpendicular to $\mathbf{p}_{\text{COM}}(t_{ac})$. Note in particular that the new potential may be different for each strip.

(B5) Compute the transmitted wavepacket on the lower level for each strip by applying the formula (2.20) along $\mathbf{p}_{\text{COM}}$ (Figure SM1c) and sum them together:

$$\hat{\psi}^{-\varepsilon}(k, t_{ac}) = \sum_{j=1}^{n} \hat{\psi}_{j}^{-\varepsilon}(k, t_{ac})$$

(B6) Evolve the transmitted wavepacket away from the avoided crossing on the lower level, say to time $t_{ac} + s$, using the BOA (Figure SM1e):

$$\hat{\psi}^{-\varepsilon}(k, t_{ac} + s) = e^{-i \varepsilon s \hat{H}^{-\varepsilon}} \hat{\psi}^{-\varepsilon}(k, t_{ac})$$

To summarise, we have derived an algorithm for approximating the transmitted wavepacket for an avoided crossing in any dimension, which only requires one-level dynamics, and local information about the adiabatic electronic surfaces, i.e. $\delta$ and $\tau_{cz}$. The dependence on the $n^{th}$ superadiabatic representation is also removed due to cancellations in the derivation. This seems peculiar to the case where (A1) applies and is not expected to be true in general. A similar method can be used to determine transmitted wavepackets from lower to upper levels. While we note that when the dimension of the system is large, we still require a high dimensional discretization for simulation of the one-level dynamics. However, methods (e.g. [28]) which improve performance of one-level dynamics can be applied to significantly reduce computational cost. In the following section, we derive Algorithm 2.4 and provide numerical examples. We note that for a particular asymptotic limit in one dimension, error bounds have been constructed for this approximation [10], but for general $\mathbf{p}_{\text{COM}}, \varepsilon$ only empirical estimates are available.

3. Motivation: Approximating the transmitted wavepacket in one dimension. The formula is derived in one dimension using the superadiabatic perturbative solution (2.18) by

(C1) Finding algebraic recursive differential equations to calculate the quantum symbol $\kappa_{n+1}^\pm$, where $K_{n+1}^\pm$ is the Weyl quantisation of $\kappa_{n+1}^\pm$.

(C2) Introducing by a change of variables $\hat{\kappa}^\pm(\tau(q)) = \kappa_{n+1}^\pm(q)$, where

$$\tau(q) = 2 \int_{0}^{q} \rho(r) \, dr,$$

which is the natural scale discussed in [5]) then approximating $\hat{\kappa}_{n+1}^\pm$ in an analogous way to the time-adiabatic case in [11].

(C3) Applying the Avron-Herbst formula [1] to $H^\pm \approx \frac{\varepsilon^2}{2} \partial_x^2 \pm \delta + \lambda x$ by using (A3).

(C4) Applying a stationary phase argument (with small $\lambda$) to evaluate the remaining integral.
Following this derivation leads to an approximation of the transmitted wavepacket in scaled momentum space, far from the avoided crossing in momentum space:

\[ \hat{\psi}^- (k, t) = e^{\frac{\nu k^2}{2}} e^{\frac{\nu k^2}{2} t} e^{-\frac{\nu}{2} (k - \nu k)(k_0 + \nu k)} e^{-\frac{\pi \nu}{2} (k - \nu k) |k - \nu k|} \chi_{k^2 > 4\delta} \hat{\phi}^+ (\nu(k)) , \]

where

- \( \chi_{k^2 > 4\delta} \) (which is one when \( k^2 > 4\delta \) and zero otherwise) relates to (classical) energy conservation: kinetic energy from the potential energy difference between two levels must be gained by the wavepacket.

- \( \nu(k) = \text{sgn}(k)(\sqrt{k^2 - 4\delta}) \), the initial momentum a classical particle would need to have momentum \( k \) after falling down a potential energy difference of \( 2\delta \), i.e. the distance between the potential surfaces at the avoided crossing, which shifts the wavepacket in momentum space. This arises naturally; it is often enforced in surface hopping algorithms.

- The indicator function \( \chi_{k^2 > 4\delta} \) is extended to the complex plane.

The constructed formula (3.2) allows us to approximate the size and shape of the transmitted wave packet due to an avoided crossing, and avoid computing expensive coupled dynamics. The method for applying the algorithm is as follows:

**Algorithm 3.1 (1D version of Algorithm 2.4).**

(\( t^c2 := \tau_r + it_c = 2 \int_0^\infty \rho(q) dq \), where \( q^2 \in \mathbb{C} \) is the closest value to the local minimum of \( \rho \) such that \( \rho(q^{c2}) = 0 \), when \( \rho \) is extended to the complex plane. The prefactor \( e^{-\frac{\pi \nu}{2} |k(k_0 - k)|} \) determines the size of the transmitted wavepacket. In [20], we show that under appropriate approximations of the momentum and potential surfaces, this prefactor is comparable to the Landau-Zener transition prefactor used in surface hopping algorithms such as in [4]. An additional change in phase occurs due to \( \tau_r \), which is present when the potential is not symmetric about the avoided crossing.

**Algorithm 3.1 (1D version of Algorithm 2.4).**

(\( E1 \) Begin with an initial wave packet \( \psi_0^+ \) on the upper adiabatic energy surface, far from the crossing in position space, with momentum such that the wave packet will cross the minimum of \( \rho \) (Figure 2a).

(\( E2 \) Evolve \( \psi_0^+ \) according to the BOA on the upper adiabatic level until the centre of mass is at the avoided crossing, at time \( t_{ac} \) (Figure 2b),

(\( E3 \) Apply the one dimensional formula to the \( \varepsilon \)-Fourier transform of the wave packet at the crossing (Figure 2c):

\[ \hat{\psi}^- (k, t_{ac}) = \frac{\nu(k) + k}{2\nu(k)} e^{-\frac{\nu}{2} (k - \nu k)(k_0 + \nu k)} e^{-\frac{\pi \nu}{2} |k - \nu k|} \chi_{k^2 > 4\delta} \hat{\phi}^+ (\nu(k)) , \]

(\( E4 \) Evolve the transmitted wave packet far away enough from the crossing in position space, say to time \( t_{ac} + s \), using the BOA (Figure 2d): \( \hat{\psi}^- (x, t_{ac} + s) = e^{\frac{\pi \nu}{2}} \hat{\psi}^- (x, t_{ac}) \).

Applications of the one dimensional formula have been widely successful on a variety of examples. In addition to the sodium iodide example [9] already mentioned,
Fig. 2: Application of the 1D formula for a particular system discussed in [7]. The centre of mass of the associated wavepacket (inset) is represented by a black point on either the upper (blue) and lower (red) adiabatic potential surfaces.

tilted avoided crossings have been examined, and a formula developed which in contrast is dependent on $n$. The formula has also been successfully applied to model interference effects in multiple transitions [20].

Finally, the above derivation can also be modified for reverse transitions (from lower to upper surface). If we consider an initial wavepacket $\psi_0^-$ far from the avoided crossing in position space on the lower energy level, the above algorithm can be applied analogously, where to approximate the wavepacket transmitted to the upper level, (3.4) is replaced by

$$\hat{\psi}^+(k, t_{ac}) = \frac{\nu(k)}{2|\nu(k)|} e^{-\frac{i}{2}\nu(k)(x_0 + \frac{2\delta}{k})} e^{-\frac{i}{2\delta}(k-\nu(k))}\frac{k}{\nu(k)} e^{-\frac{i}{2\delta}(k-\nu(k))} e^{-\frac{i}{\delta}(\nu(k), t_{ac})},$$

(3.5) where $\nu(k) = \text{sgn}(k)\sqrt{k^2 + 4\delta}$ contributes a loss of momentum due to the potential
4. Coupling operators in higher dimensions. The first step in deriving (3.2) in [10] was to approximate the superadiabatic coupling operators $K_{n+1}^\pm$. We now consider these operators in higher dimensions. We restrict the calculations here to two dimensions for clarity, but they can easily be adapted to $d$ dimensions.

**Lemma 4.1.** In two dimensions, $\kappa_{n+1}^\pm$ is given by

$$\kappa_{n+1}^\pm(p, q) = -2\rho(q)(x_{n+1}(p, q) \pm y_{n+1}(p, q)).$$

where $x_{n+1}(p, q), y_{n+1}(p, q)$ are given by the following algebraic recursive differential equations (where we omit the arguments of symbols to ease notation):

$$x_1 = z_1 = w_1 = 0, \quad y_1 = -\frac{i}{4\rho}(p \cdot \nabla q \theta).$$

and

$$y_n = 0, \ n \ even, \ x_n = z_n = w_n = 0, \ n \ odd,$$

where $\rho = \rho(q)$. For $n$ odd, we have

$$x_{n+1} = -\frac{1}{2\rho}\left[\frac{1}{i}(p \cdot \nabla q y_n) - 2\sum_{j=1}^{n} \frac{1}{(2i)^j j!} \sum_{|\alpha|=j} \partial_p^\alpha (b_{\alpha}(z_{n+1-j} - a_{\alpha} x_{n+1-j}))\right],$$

and for $n$ even

$$y_{n+1} = -\frac{1}{2\rho}\left[\frac{1}{i}(p \cdot \nabla q x_n) - z_n(p \cdot \nabla q \theta)\right]$$

$$- 2\sum_{j=1}^{n} \frac{1}{(2i)^j j!} \sum_{|\alpha|=j} \partial_p^\alpha (-a_{\alpha} y_{n+1-j} + b_{\alpha} w_{n+1-j})\right],$$

where $\alpha \equiv (\alpha_1, \alpha_2), \ \partial_p^\alpha = \partial_p^\alpha_1 \partial_p^\alpha_2$, and $a_{\alpha} = a_{\alpha}(q), b_{\alpha} = b_{\alpha}(q)$ depend only on $q$, and are given by the recursions

$$a_0 = \rho(q), \ b_0 = 0,$$

$$a_{(\alpha_1+1, \alpha_2)} = \partial_{q_1} a_{(\alpha_1, \alpha_2)} + (\partial_{q_1} \theta) b_{(\alpha_1, \alpha_2)}, \ b_{(\alpha_1+1, \alpha_2)} = \partial_{q_1} b_{(\alpha_1, \alpha_2)} - (\partial_{q_1} \theta) a_{(\alpha_1, \alpha_2)},$$

$$a_{(\alpha_1, \alpha_2+1)} = \partial_{q_2} a_{(\alpha_1, \alpha_2)} + (\partial_{q_2} \theta) b_{(\alpha_1, \alpha_2)}, \ b_{(\alpha_1, \alpha_2+1)} = \partial_{q_2} b_{(\alpha_1, \alpha_2)} - (\partial_{q_2} \theta) a_{(\alpha_1, \alpha_2)}.$$
The result of Lemma 4.1 shows that \(x_n, y_n, z_n, w_n\) can be written as polynomials in \(p\) of order \(n\), as the recursive definitions involve finite products, derivatives and sums of the initial \(x_0, y_0, z_0, w_0\), which are polynomials in \(p\). We therefore write

\[(4.8)\quad x_n(p, q) = \sum_{m=0}^{n} \sum_{k=0}^{m} p_1^k p_2^{m-k} x_n^{k,m-k}(q),\]

for some \(x_n^{k,m-k}(q)\), and similarly for \(y_n, z_n, w_n\). For a given \(j\), we write \(\alpha_j = (\alpha, j-\alpha)\) for each \(\alpha \leq j\).

Consider for example

\[(4.9)\quad \partial_{\alpha}^\alpha x_{n+1-j} = \sum_{m=j}^{n+1-j} \sum_{k=\alpha}^{m} k! \frac{(m-k)!}{(m-k-j+\alpha)!} p_1^{k-\alpha} p_2^{m-k-j+\alpha} x_{n+1-j}(q),\]

where by a direct calculation

\[(4.10)\quad \mathcal{A}(p, q) := \sum_{j=1}^{n} \frac{1}{(2i)!} \sum_{\alpha=0}^{j} a_{\alpha} \partial_{\alpha}^\alpha \sum_{m=j}^{n+1-j} \sum_{k=\alpha}^{m} k! \frac{(m-k)!}{(m-k-j+\alpha)!} p_1^{k-\alpha} p_2^{m-k-j+\alpha} x_{n+1-j}(q),\]

we now want to switch the order of summation. We note that, for an arbitrary \(B\),

\[
\sum_{j=1}^{\left\lfloor \frac{n+1}{2} \right\rfloor} \sum_{c=0}^{n+1-c-j} B_{c,j} = \sum_{c=0}^{n+1} \sum_{j=1}^{\left\lfloor \frac{n+1}{2} \right\rfloor} B_{c,j},
\]
which can be shown directly (note that the terms where \( c = 0, c = 1 \) are zero). Using this, we finally have that

\[
A = \sum_{c=0}^{n+1} \sum_{b=0}^{n+1-c} p_1^b p_2^{n+1-c-b} \tag{4.11}
\]

\[
\times \sum_{j=1}^{\lfloor \frac{n+1-c}{2} \rfloor} \frac{a_{\alpha_j} (b+\alpha)(n+1-c-j-b)}{(2i)^j j! b! (n+1-c-b)!} x_j^{b+\alpha, (n+1-c-j)-(b+\alpha)}(q). \tag{4.12}
\]

Importantly, \( p_1 \) and \( p_2 \) have been extracted from two of the summations. Note that (4.11) reduces to the 1D result in [10] for \( p_2 \) and \( p_1 \), by taking \( b = 0 \) and \( \alpha = 0 \), or \( j - \alpha = 0 \) and \( n + 1 - c - b = 0 \) respectively. We then obtain the following result.

**PROPOSITION 4.2.** The coefficients \( x_n^{A,B}(q) \) to \( w_n^{A,B}(q) \) are determined by the following algebraic-differential recursive equations. We have (omitting arguments of symbols for ease of notation):

\[
x_1^{A,B} = z_1^{A,B} = w_1^{A,B} = 0, \quad A + B \in \{0, 1\}, \tag{4.13}
\]

\[
y_1^{0,0} = y_1^{1,1} = 0, \quad y_1^{1,0} = -\frac{i}{4\rho} \partial_{\theta_1} \theta, \quad y_1^{0,1} = -\frac{i}{4\rho} \partial_{\theta_2} \theta. \tag{4.14}
\]

Further, when \( n \) is odd,

\[
x_n^{A,B} = \frac{1}{2\rho} \left[ \frac{1}{i} \left( \partial_{\theta_1} y_n^{A-1,B} + \partial_{\theta_2} y_n^{A,B-1} \right) - 2 \sum_{j=1}^{\lfloor \frac{n+1-(A+B)}{2} \rfloor} \sum_{\alpha=0}^{j} \frac{1}{(2i)^j j!} \right]
\]

\[
\times \frac{(A+\alpha)!}{A!} \frac{(B+j-\alpha)!}{B!} \left( b_{\alpha_j} z_{n+1-j}^{A+\alpha,B+j-\alpha} - a_{\alpha_j} y_{n+1-j}^{A+\alpha,B+j-\alpha} \right) \] \tag{4.15}

When \( n \) is even, we have

\[
y_n^{A,B} = \frac{1}{2\rho} \left[ \frac{1}{i} \left( \partial_{\theta_1} y_n^{A-1,B} + \partial_{\theta_2} y_n^{A,B-1} \right) - (z_n^{A-1,B} \partial_{\theta_1} \theta + z_n^{A,B-1} \partial_{\theta_2} \theta) \right]
\]

\[
- 2 \sum_{j=1}^{\lfloor \frac{n+1-(A+B)}{2} \rfloor} \sum_{\alpha=0}^{j} \frac{1}{(2i)^j j!} \frac{(A+\alpha)!}{A!} \frac{(B+j-\alpha)!}{B!} \times \left( -a_{\alpha_j} y_{n+1-j}^{A+\alpha,B+j-\alpha} + b_{\alpha_j} y_{n+1-j}^{A+\alpha,B+j-\alpha} \right) \] \tag{4.16}

\[
0 = \frac{1}{i} \left( \partial_{\theta_1} z_n^{A-1,B} + \partial_{\theta_2} z_n^{A,B-1} \right) + (z_n^{A-1,B} \partial_{\theta_1} \theta + z_n^{A,B-1} \partial_{\theta_2} \theta) \right]
\]

\[
- 2 \sum_{j=1}^{\lfloor \frac{n+1-(A+B)}{2} \rfloor} \sum_{\alpha=0}^{j} \frac{1}{(2i)^j j!} \frac{(A+\alpha)!}{A!} \frac{(B+j-\alpha)!}{B!} \times \left( b_{\alpha_j} z_{n+1-j}^{A+\alpha,B+j-\alpha} + a_{\alpha_j} z_{n+1-j}^{A+\alpha,B+j-\alpha} \right), \]
\[(4.17)\quad 0 = \frac{1}{i}((\partial_{q_1} w_n^{A-1,B} + \partial_{q_2} w_n^{A,B-1})
- 2 \sum_{j=1}^{(|n+1-(A+B)|)} \sum_{\alpha=0}^{j} \frac{1}{(2i)^j j! A! B!} \times (a_{\alpha,j} x_n^{A+\alpha,B+j-\alpha} + b_{\alpha,j} x_n^{A+\alpha,B+j-\alpha})).
\]

**Proof.** We substitute (4.8) into the results of Lemma 4.1 and compare coefficients in powers of \(p_1, p_2\) on either side, using (4.11).

As with the coefficients \(x_n\) and \(y_n\) in (4.1), \(\kappa_{n+1}^\pm\) has polynomial form:

\[(4.18)\quad \kappa_{n+1}^\pm(p, q) = \sum_{m=0}^{n} \sum_{j=0}^{m} p_1^j p_2^{m-j} \kappa_{n+1}^{(j,m-j)\pm}(q).
\]

Here we apply assumption (A2): \(\kappa_{n+1}^\pm \approx p_1^n \kappa_{n+1}^{(n,0)\pm}(q)\). In the one dimensional case this has been shown to be accurate for sufficiently large \(p\), but in practice holds for much smaller values. By directly constructing the Weyl quantisation of \(p_1^n \kappa_{n+1}^{(n,0)\pm}(q)\) as in [10, pg. 3570], we see that the effect of the coupling operator is negligible outside a small region near the avoided crossing, determined by the small parameter \(\varepsilon\) which shows that it is reasonable to take the leading term in \(\kappa_{n+1}^\pm\). The 2D algebraic differential recursive equations then reduce to the one dimensional case in [10]:

\[(4.19)\quad x_{n+1}^{1,0} \approx \frac{i}{2\rho} (\partial_{q_1} y_{n+1}^{0,0}),
\]

To ease notation, redefine \(x_{n+1} = x_{n+1}^{1,0}\), and similar for \(y_{n+1}, z_{n+1}\). It is unclear what the analogue of (3.1), introduced initially in [6] for the time-adiabatic case, would be for multidimensional systems. We introduce the natural scaling in the first dimension

\[(4.20)\quad \tau(q) = 2 \int_{0}^{q} \rho(r, q_2) dr.
\]

Defining \(\tilde{f}(\tau(q)) = f(q)\) the recursive relations (4.19) then become

\[(4.21)\quad \tilde{x}_{n+1}^0 = i\tilde{y}_{n+1}^0, \quad \tilde{y}_{n+1}^0 = i(\tilde{x}_{n+1}^0 + \tilde{\theta}^r z_{n+1}^0), \quad 0 = (\tilde{z}_{n+1}^0 + \tilde{\theta}^r \tilde{x}_{n+1}^0),
\]

where \(\tilde{\theta}^r = \frac{d}{d\tau(q_1, q_2)} \tilde{\theta}\). These recursive equations also occur in [11], where they are solved in one dimension, under the assumption that

\[(4.22)\quad \frac{d}{d\tau} \tilde{\theta}(\tau) = \frac{i\gamma}{\tau - \tau^c(z)} - \frac{i\gamma}{\tau - \tau^c(z)} + \tilde{\theta}'(\tau),
\]

where \(\tau^c(z)\) is a first order complex singularity of \(\tilde{\theta}\), and \(\tilde{\theta}'\) has no singularities closer to the real axis than \(\tau^c(z)\). If the avoided crossing occurs at 0, we can write \(\rho^2(q) = \delta^2 + g(q)^2\), for some analytic function \(g\) such that \(g(0) \approx 0\), and \(g^2\) is quadratic in the
neighbourhood of \( q = 0 \). Therefore a Stokes line (i.e. a curve with \( \text{Im}(\rho) = 0 \)) crosses the real axis perpendicularly [25], and following this line leads to a pair of complex conjugate points \( q^\pm, \bar{q}^\pm \) which are complex zeros of \( \rho \). Defining \( \tau^\pm = \tau(q^\pm) \), it is shown in [6] that first order complex singularities of the adiabatic coupling function arise at these complex zeros. This derivation is still valid in our case, for each \( q_2 \).

The recursive algebraic differential equations solved in [11] then give us \( \kappa_n^\pm \) to leading order:

\[
\kappa_n^-(q) \approx \kappa_{n,0}^-(q) := \frac{i^n}{n!} \rho(q)^{(n-1)!} \left( \frac{i}{(\tau(q) - \tau^-(q_2))^n} - \frac{i}{(\tau(q) - \tau^+(q_2))^n} \right).
\]

It is clear that the results of this section can be extended to higher dimensions, by assuming the direction of travel of the wavepacket is in the first dimension. We will now use this observation to design an algorithm for multi-dimensional transitions using only the 1D transition formula.

5. Multi-dimensional formula derivation. The derivation of a multidimensional formula, under the assumptions above, follows similarly to the one dimensional case. We want to approximate the pseudodifferential operator \( K_n \), which is given by the Weyl quantisation of \( \kappa_n \). The polynomial form of \( \kappa_n \) allows us to simplify the Weyl quantisation as follows.

**Proposition 5.1.** Let \( \kappa(p, q) = g(q) \prod_{i=1}^d p_i^{A_i} \), for \( A_i \in \mathbb{N} \). Then

\[
(\hat{W}_v \kappa \psi)(k) = \frac{1}{(2\pi\varepsilon)^{d/2}} \int_{\mathbb{R}^d} \hat{g}(k - \eta) \prod_{i=1}^d \left( k_i + \eta_i \right)^{A_i} \hat{\psi}(\eta) \, d\eta.
\]

**Proof.** The proof is a multi-dimensional extension of [7, Lemma 4.1]. Firstly, using that \( \psi(y) = (2\pi\varepsilon)^{-d/2} \int_{\mathbb{R}^d} d\eta \hat{\psi}(\eta) \exp(i(\eta \cdot y)/\varepsilon),

\[
(\hat{W}_v \kappa \psi)(x) = \frac{1}{(2\pi\varepsilon)^d} \int_{\mathbb{R}^{2d}} d\xi \, dy \left( \prod_{i=1}^d \xi_i^{A_i} \right) g \left( \frac{x + y}{2} \right) e^{i\varepsilon(x \cdot y)} \psi(y),
\]

Now define \( \tilde{y}_i = (x_i + y_i)/2, i = 1, \ldots, d. \) Then

\[
(\hat{W}_\xi \kappa \psi)(x) = \frac{2^d}{(2\pi\varepsilon)^{d/2}} \int_{\mathbb{R}^{2d}} d\xi \, d\tilde{y} \eta \left( \prod_{i=1}^d \xi_i^{A_i} \right) g(\tilde{y}) \psi(x + (2\xi - y) \cdot (\eta - \xi)),
\]

\[
= \frac{2^d}{(2\pi\varepsilon)^d} \int_{\mathbb{R}^{2d}} d\xi \, d\eta \left( \prod_{i=1}^d \xi_i^{A_i} \right) e^{i\varepsilon(x \cdot (2\xi - \eta))} \psi(\eta) \tilde{y}^\varepsilon(2(\xi - \eta)).
\]

We perform a second change of variables \( \tilde{\xi}_i = 2\xi_i \) and find

\[
(\hat{W}_\xi \kappa \psi)(x) = \frac{1}{(2\pi\varepsilon)^d} \int_{\mathbb{R}^{2d}} d\tilde{\xi} \, d\eta \left( \prod_{i=1}^d \left( \frac{\tilde{\xi}_i}{2} \right)^{A_i} \right) e^{i\varepsilon(x \cdot (\xi - \eta))} \hat{\psi}(\eta) \tilde{y}^\varepsilon(\xi - 2\eta).
\]
We apply the scaled Fourier transform to both sides of this equation:

\[
(\mathcal{W}_\varepsilon \hat{\psi}^\varepsilon(k) = \frac{1}{(2\pi\varepsilon)^d} \int_{\mathbb{R}^d} d\xi d\eta \int dx \left( \prod_{i=1}^d \left( \frac{\xi_i}{\varepsilon} \right)^{A_i} \right) e^{\frac{i}{\varepsilon}(\xi \cdot (\xi - \eta - k))} \hat{\psi}^\varepsilon(\eta) \hat{\psi}^\varepsilon(\xi - 2\eta).
\]

Using that \((2\pi\varepsilon)^{-d} \int dx \exp(i(a \cdot x)/\varepsilon) = \delta(a)\) allows us to directly compute the \(x\) integral, giving (5.1).

Next we linearise the dynamics near the avoided crossing. By (A3), to leading order, the uncoupled propagators in (2.16) can be approximated by

\[
(5.2) \quad H_1^\pm = -\frac{\varepsilon^2}{2} \nabla_x^2 \pm \lambda \cdot x.
\]

Then, by the fundamental theorem of calculus,

\[
(5.3) \quad e^{\frac{i}{\varepsilon} s H_1^-} - e^{\frac{i}{\varepsilon} s H_1^+} = \left\{ \left[ \int_0^s e^{\frac{i}{\varepsilon} t (H_1^- - H_1^+)} e^{-\frac{i}{\varepsilon} t H_1^\pm} dt \right] e^{\frac{i}{\varepsilon} s H_1^\pm} \right\}
\]

Since \(H_1^+ - H_1^-\) is quadratic near zero, the integrand in (5.3) is of order 1 in an \(\varepsilon\)-neighbourhood of zero. Outside of this region the coupling function provides a negligible result, as seen in the one dimensional case [10]. We also use the \(d\)-dimensional Avron-Perelomov formula [1], which shows that

\[
(5.4) \quad e^{\frac{i}{\varepsilon} s H_1^-} = e^{-\frac{|\lambda|^2 s^2}{2\varepsilon}} e^{i\lambda \cdot \partial_k} e^{-\frac{i}{\varepsilon}(\|k\|^2 + 2\varepsilon s - (\lambda \cdot k) s^2)}.
\]

Then

\[
(5.5) \quad \hat{\psi}^\varepsilon_n(k, t) \approx -i\varepsilon^n e^{-\frac{i}{\varepsilon} t H_1^-} \int_{-\infty}^t ds e^{-\frac{|\lambda|^2 s^2}{2\varepsilon}} e^{i\lambda \cdot \partial_k} e^{-\frac{i}{\varepsilon}(\|k\|^2 + 2\varepsilon s - (\lambda \cdot k) s^2)} K_n^{\varepsilon n+1} 
\]

\[
\times e^{-\frac{|\lambda|^2 s^2}{6\varepsilon}} e^{i\lambda \cdot \partial_k} e^{-\frac{i}{\varepsilon}(\|k\|^2 + 2\varepsilon s - (\lambda \cdot k) s^2)} \hat{\phi}^\varepsilon_n(k) ds.
\]

Using Proposition 5.1 for the coupling function shows that

\[
\hat{\psi}^\varepsilon_n(k, t) \approx -i\varepsilon^n \frac{e^n}{(2\pi\varepsilon)^d/2} e^{-\frac{i}{\varepsilon} t H_1^-} \int_{-\infty}^t ds e^{-\frac{|\lambda|^2 s^2}{6\varepsilon}} e^{i\lambda \cdot \partial_k} e^{-\frac{i}{\varepsilon}(\|k\|^2 + 2\varepsilon s - (\lambda \cdot k) s^2)} 
\]

\[
\times \int_{\mathbb{R}^d} d\eta \left\{ \sum_{A_{i=1}=1, i=1, \ldots, d}^{n+1} K_{n+1}^- (k - \eta) \left( \prod_{i=1}^d \left( \frac{k_i + \eta_i}{2} \right)^{A_i} \right) \right\} 
\]

\[
\times e^{-\frac{|\lambda|^2 s^2}{6\varepsilon}} e^{i\lambda \cdot \partial_k} e^{-\frac{i}{\varepsilon}(\|\eta\|^2 + 2\varepsilon s - (\lambda \cdot \eta) s^2)} \hat{\phi}^\varepsilon_n(\eta),
\]

where \(A = (A_1 \ldots A_d)\). The operator \(e^{i\lambda \cdot \partial_k}\) is a shift operator, so \(e^{i\lambda \cdot \partial_k} f(k) = f(k + \lambda s)\). Instead of applying the shift operator to the right, we use the fact that the integral is invariant under the transform \(\eta \mapsto \eta - \lambda s\) to apply it to the left: in this case \(f(\eta)e^{-\frac{i}{\varepsilon}(\lambda \cdot \eta)} = f(\eta - \lambda s)\). The following transformations take place in the integrand:

\[
\hat{\psi}^\varepsilon_n(k - \eta) \mapsto \hat{\psi}^\varepsilon_n(k - \eta), \quad k + \eta \mapsto k + \eta - 2\lambda s,
\]

\[
e^{-\frac{i}{\varepsilon}(\|k\|^2 + 2\varepsilon s - (\lambda \cdot k) s^2)} \mapsto e^{-\frac{i}{\varepsilon}(\|k - \lambda s\|^2 + 2\varepsilon s - (\lambda \cdot (k - \lambda s)) s^2)}.
\]
Rearranging gives
\[ \widetilde{\psi}_n^\pm(k, t) \approx -i \frac{\varepsilon^n}{(2\pi \varepsilon)^{d/2}} e^{\frac{i}{\varepsilon} \hat{H} \cdot z} \] \[ \times \int_{-\infty}^t \int_{R^d} ds \, d\eta \left\{ \sum_{A, B = 1}^{n+1} \kappa_{n+1}^{\pm} \left( k - \eta \right) \left( \prod_{i=1}^{d} \left( \frac{k_i + \eta_i - 2\lambda_i s}{2} \right)^A_i \right) \right\} \] \[ \times \hat{\phi}_{\pm}^\pm(\eta) \exp \left\{ \frac{i}{2\varepsilon} \left[ (||k||^2 - ||\eta||^2 - 4\delta) s - (\lambda \cdot (k - \eta)) s \right]^2 \right\}. \]

We approximate \( \kappa_{n+1}^{\pm} \) with (4.23), then calculate the scaled Fourier transform:
\[ \kappa_{n, 0}^\pm(k) = \frac{(n-1)!}{(2\pi \varepsilon)^{d/2}} \int_{R^d} \rho(q) \left[ \frac{i}{\tau(q) - \tau^{\pm}(q^{d-1})} \right]^n - \frac{i}{\tau(q) - \tau^{\pm}(q^{d-1})} \right] e^{-i\varepsilon k \cdot q} \, dq, \]
where \( q^{d-1} = (q_2, ..., q_d) \). Using (A6) \( \rho(q) \approx \rho(q_1) \) and consequently \( \tau(q) = \tau(q_1) \), \( \tau^{\pm}(q^{d-1}) = \tau^{\pm}(q_2, ..., q_d) \). Therefore the Fourier transform in all other dimensions produces a Dirac function, \( \frac{1}{\sqrt{2\pi \delta(k)}} e^{-i\frac{k}{\delta(k)} x} dx = \sqrt{2\pi \delta(k)} \). As \( \tau(q) \approx \tau(q_1) \), we only need to consider the one dimensional case. This is discussed in [10]. A simple extension to \( d \) dimensions therefore shows that
\[ \kappa_{n, 0}^\pm(k) = \frac{i}{\sqrt{2\pi \varepsilon}} \left( \frac{k_1}{2\varepsilon} \right)^{n-1} e^{-i\varepsilon^{\frac{k_1}{\varepsilon}} e^{-i\varepsilon^{\frac{k_1}{\varepsilon}}} \sqrt{2\pi \varepsilon^{(d-1)}} \delta(k_2, ..., k_d). \]

We insert (5.7) into (5.6), and rearrange to find
\[ \widetilde{\psi}_n^\pm(k, t) = \frac{1}{4\pi \varepsilon} e^{-\frac{i}{\varepsilon} \hat{H} \cdot z} \int_0^\infty ds \int_{R^d} d\eta_1 \left( \frac{k_1^2 - \eta_1^2}{4\delta} \right)^n \left( 1 - 2\lambda_1 s \right) \] \[ \times e^{-i\varepsilon^{\frac{(k_1 - \eta_1)}{2\varepsilon}}} e^{-\varepsilon^{\frac{(k_1 - \eta_1)}{2\varepsilon}}} \] \[ \times \left\{ \int_{R^{d-1}} d\eta_{2d} \hat{\phi}_{\pm}^\mp(\eta) e^{\frac{i}{\pi} \left[ (||k||^2 - ||\eta||^2 - \lambda \cdot (k - \eta)) s \right]} \delta(k_2 - \eta_2, ..., k_{d} - \eta_{d}) \right\}. \]

By the identity \( f(x) = \int_0^\infty \delta(x - a) f(a) \, da \), the integral in the dimensions 2, ..., \( d \) can be evaluated to find
\[ \widetilde{\psi}_n^\pm(k, t) = \frac{1}{4\pi \varepsilon} e^{-\frac{i}{\varepsilon} \hat{H} \cdot z} \int_0^\infty ds \int_{R^d} d\eta_1 \left( \frac{k_1^2 - \eta_1^2}{4\delta} \right)^n \left( 1 - 2\lambda_1 s \right) \] \[ \times e^{-i\varepsilon^{\frac{(k_1 - \eta_1)}{2\varepsilon}}} e^{-\varepsilon^{\frac{(k_1 - \eta_1)}{2\varepsilon}}} \] \[ \times \hat{\phi}_{\pm}^\mp(\eta_1, k_2, ..., k_{d}) e^{\frac{i}{\pi} \left[ (||k||^2 - ||\eta||^2 - 4\delta) s - \lambda \cdot (k_1 - \eta_1) s \right]} \]
\[ \] \[ (5.8) \]

By (A1), \( \lambda_1 \) is small and so can be neglected, so that
\[ \widetilde{\psi}_n^\pm(k, t) = \frac{1}{4\pi \varepsilon} e^{-\frac{i}{\varepsilon} \hat{H} \cdot z} \int_0^\infty ds \int_{R^d} d\eta_1 \left( \frac{k_1^2 - \eta_1^2}{4\delta} \right)^n e^{-i\varepsilon^{\frac{(k_1 - \eta_1)}{2\varepsilon}}} e^{-\varepsilon^{\frac{(k_1 - \eta_1)}{2\varepsilon}}} \]
\[ \times \hat{\phi}_{\pm}^\mp(\eta_1, k_2, ..., k_{d}) e^{\frac{i}{\pi} \left[ (||k||^2 - ||\eta||^2 - 4\delta) s \right]}. \]

This manuscript is for review purposes only.
6. Numerical results. We perform the algorithm on a selection of examples, and compare it to the two level 'exact' computation, where the Strang splitting method is used. For all examples we consider two wavepackets given in momentum space by:

\[
\tilde{\psi}_0(p) = \frac{1}{N_\phi} \exp \left( -\frac{\|p - p_0\|^2}{2\varepsilon} \right) \exp \left( -i \frac{(p - p_0) \cdot x_0}{\varepsilon} \right),
\]

\[
\tilde{\phi}(p) = \frac{1}{N_\phi} \exp \left( -\frac{\|p - p_0\|^6}{2\varepsilon} \right) \exp \left( -i \frac{(p - p_0) \cdot x_0}{\varepsilon} \right),
\]

where \(N_\alpha\) are normalisation constants. To ensure that the wavepacket has sufficient momentum to travel through the avoided crossing, we choose to define the wavepackets at the avoided crossing point, then evolve backwards in time away from the avoided crossing using one level dynamics, before evolving forwards and applying the formula.

In practice the initial wavepacket can be given in any initial location, provided it is far enough from the avoided crossing to be unaffected by coupling effects.

To compare the formula results to exact calculations we use the \(L^2\)-relative error:

\[
E_{\text{rel}}(\psi_1, \psi_2) = \max \left( \frac{\|\psi_1 + \psi_2\|}{\|\psi_1\|}, \frac{\|\psi_1 + \psi_2\|}{\|\psi_2\|} \right),
\]

Where \(\|\cdot\|\) is the standard \(L^2\)-norm. For comparison to other algorithms which do not calculate phase, it is also beneficial to consider the relative absolute error

\[
E_{\text{abs}}(\psi_1, \psi_2) = \max \left( \frac{\|\psi_1 - \psi_2\|}{\|\psi_1\|}, \frac{\|\psi_1 - \psi_2\|}{\|\psi_2\|} \right),
\]

or the relative mass error

\[
E_{\text{mass}}(\psi_1, \psi_2) = \max \left( \frac{\|\psi_1\|}{\|\psi_2\|}, \frac{\|\psi_2\|}{\|\psi_1\|} \right) - 1.
\]
Example 6.1. Consider the diabatic potential matrix

\[
V(x) = \begin{pmatrix}
\tanh(x_1) & \delta \\
\delta & -\tanh(x_1)
\end{pmatrix}.
\]

This is a direct extension of a one dimensional problem, and as there is no dependence in \(x_2\), the assumptions made in the derivation in Section 5 are exactly valid, if the direction of the wavepacket is independent of \(p_2\). The lower surface is given by \(V_L = -V_U\). The upper adiabatic surface is shown in Figure 3a. We take parameters

\[
\{\varepsilon, \delta, p_0, x_0\} = \left\{ \frac{1}{30}, \frac{1}{2}, (6, 1), (0, 0) \right\}.
\]

Using a mesh of \(2^{13} \times 2^{13}\) points on the domain \([-20, 20]^2\), starting at time 0, we evolve the wavepacket back to time -2 with time-step \(1/(50\|p_0\|)\), then evolve forwards to time 2, applying the algorithm, and compare to the exact calculation. For the Gaussian wavepacket \(\psi\), \(E_{r\text{rel}} = 0.0151, E_{r\text{abs}} = 0.0151, \text{ and } E_{r\text{mass}} = 0.0016\). For non-Gaussian \(\phi\) \(E_{r\text{rel}} = 0.0389, E_{r\text{abs}} = 0.0387, \text{ and } E_{r\text{mass}} = 0.0023\). The result of the formula and corresponding error are shown in Figures 4 and 5.

Example 6.2. We consider the diabatic potential matrix described in [14]

\[
V(x) = \begin{pmatrix}
\frac{x_1}{\sqrt{x_2^2 + \delta^2}} & \sqrt{x_2^2 + \delta^2} \\
-\frac{x_1}{\sqrt{x_2^2 + \delta^2}} & -x_1
\end{pmatrix},
\]

which is a modified Jahn-Teller diabatic potential, where the conical intersection is replaced with an avoided crossing with gap \(2\delta\). The upper adiabatic surface is shown in Figure 3b. We use parameters

\[
\{\varepsilon, \delta, p_0, x_0\} = \left\{ \frac{1}{30}, 0.5, (5, 2), (0, 0) \right\},
\]

a mesh of \(2^{13} \times 2^{13}\) points on the domain \([-40, 40]^2\), we start at time 0, and evolve backwards with time-step \(1/(50\|p_0\|)\) to time -20/\(\|p_0\|^2\), then forwards to 20/\(\|p_0\|^2\),
we find $E_{\text{rel}} = 0.0351$, $E_{\text{abs}} = 0.0304$, and $E_{\text{mass}} = 0.0029$ using Gaussian initial wavepacket $\psi_0$, and $E_{\text{rel}} = 0.0679$, $E_{\text{abs}} = 0.0616$, and $E_{\text{mass}} = 0.0033$ for non-Gaussian initial wavepacket $\phi$. Figures 6 and 7 display the result of the formula compared to the exact calculation. We now use the parameters

$$\{\varepsilon, \delta, p_0, x_0\} = \left\{ \frac{1}{30}, 0, (5, 0), (0, 0.5) \right\}.$$  

In addition, we included the sign of $x_2$ in the off-diagonal elements of $V(x)$, which then gives the standard Jahn-Teller Hamiltonian. However, let us stress that non-adiabatic transitions must be exactly the same for the Hamiltonian with and without the sign included. The reason is that by that choice, we have just chosen a
different diabatic representation, but the (unique) adiabatic representation remains the same. It is an advantage of our method, which only uses the adiabatic energy surfaces, that it is insensitive to such a change. The Jahn-Teller Hamiltonian has a conical intersection. We have chosen momentum such that the centre of mass of the wavepacket does not cross the intersection. We evolve back to $-25/\|p_0\|^2$ with a time-step of $1/(50\|p_0\|)$, then evolve forwards to $25/\|p_0\|^2$ using the algorithm, and compare with the exact calculation. Then $E_{\text{rel}} = 0.0638, E_{\text{abs}} = 0.0550$, and $E_{\text{mass}} = 0.0309$ for initial wavepacket of form $\psi_0$ and $E_{\text{rel}} = 0.1511, E_{\text{abs}} = 0.0850$, and $E_{\text{mass}} = 0.0604$ for $\phi$, the transmitted wavepacket and error is given in Figure 6. Although the relative error is large in this final calculation, the absolute error and mass error shows that the algorithm has performed well, given that it is not designed for systems where $\delta$ is small or vanishing. Figure 9 also shows that the shape of the wavepacket is still well approximated qualitatively.
We note that the relative and absolute error in Example 6.2 differ, while in Example 6.1 they are the same. We believe this is due to a change in phase when $\rho$ is not flat in $q_2$, so the error due to the modification of the potential surface for each strip is larger.

Fig. 8: As in Figure 6, but with parameters (6.10).

Fig. 9: As in Figure 8, but with initial wavepacket (6.2).

7. Conclusions and Future Work. In this paper we have constructed an algorithm which can be used to approximate the transmitted wavepacket in non-adiabatic transitions in multiple dimensions, by constructing a formula based on the one dimensional result in [7], and appealing to the linearity of the Schrödinger equation to decompose the dynamics onto strips with potentials that are constant in all but one direction. Presented examples in two dimensions show similar accuracy to one dimensional analogues, and are accurate in the phase, which is beyond the capability of standard surface hopping models.

Correctly approximating the phase of the wavepacket becomes important when more than one transition takes place. In [20] various one dimensional examples of

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multiple transitions are explored using the formula, with accurate results. In future work we will consider multiple transitions in two dimensions using the algorithm. This will involve taking into account the effect of geometric phase [12] due to multiple avoided crossings, as well as constructing an approximation of the wavepacket which remains on the upper level after a transition has taken place. We also will compare the results of the algorithm considered in this paper with other algorithms designed to approximate non-adiabatic transitions, e.g. [19].

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