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Nonadiabatic transitions through tilted avoided crossings

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NONADIABATIC TRANSITIONS THROUGH TILTED AVOIDED CROSSINGS[*]

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Abstract. We investigate the transition of a quantum wave-packet through a one-dimensional avoided crossing of molecular energy levels when the energy levels at the crossing point are tilted. Using superadiabatic representations, and an approximation of the dynamics near the crossing region, we obtain an explicit formula for the transition wave function. Our results agree extremely well with high precision ab-initio calculations.

Key words. nonadiabatic transitions, superadiabatic representations, asymptotic analysis, quantum dynamics, avoided crossings

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1. Introduction. The photo-dissociation of diatomic molecules is one of the paradigmatic chemical reactions of quantum chemistry. The basic mechanism is that a short laser pulse lifts the electronic configuration of the molecule into an excited energy state. The nuclei then feel a force due to the changed configuration of the electrons, and start to move according to the classical Born–Oppenheimer dynamics. Then, at some point in configuration space, the Born–Oppenheimer surfaces of the electronic ground state and first excited state come close to each other, leading to a partial breakdown of the Born–Oppenheimer approximation. As a result, with a certain small probability the electrons fall back into the ground state, facilitating the dissociation of the molecule into its atoms. This important mechanism is at the heart of many processes in nature, such as the photo-dissociation of ozone, or the reception of light in the retina [27]. For further details on the general mechanism we refer to [20].

The mathematical problem associated with photo-dissociation is to determine nonadiabatic transitions at avoided crossings in a two-level system, with one effective spatial degree of freedom. Thus, we study the system of partial differential equations

$$(1.1) \qquad \qquad i\varepsilon \partial_t \psi = H\psi,$$

with $\psi \in L^2(\mathbb{R}, \mathbb{C}^2)$, and

$$H = -\tfrac{\varepsilon^2}{2}\partial_x^2 \boldsymbol{I} + V(x).$$

Above, $\boldsymbol{I}$ is the 2×2 unit matrix, and, with σ_x and σ_z the Pauli matrices as defined in (3.2),

$$V(x) = X(x)\sigma_x + Z(x)\sigma_z + d(x)\boldsymbol{I} = \begin{pmatrix} Z(x) & X(x) \\ X(x) & -Z(x) \end{pmatrix} + d(x)\boldsymbol{I}$$

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is the real-symmetric potential energy matrix in the diabatic representation. Units are such that $\hbar = 1$ and the electron mass $m_{\mathrm{el}} = 1$. ε^2 is the ratio of electron and reduced nuclear mass, typically of the order 10^{-4}. The time scale is such that the nuclei (with position coordinate x) move a distance of order one within a time of order one. The motivation of (1.1) and its relevance for photo-dissociation is discussed further in [3].

There is a natural coordinate transformation of (1.1) that exploits the scale separation provided by the small parameter ε. The corresponding representation is called the adiabatic representation, and is given as follows: Let the unitary matrix $U_0(x)$ diagonalize $V(x)$ for each x. Using the same notation U_0, we define a unitary operator on $L^2(\mathbb{R}, \mathbb{C}^2)$ by $\psi_0(x) = (U_0\psi)(x) \equiv \psi(U_0(x))$. Then ψ_0 solves

$$(1.2) \qquad\qquad i\varepsilon\partial_t\psi_0 = H_0\psi_0,$$

with H_0 given to leading order by

$$(1.3) \qquad H_0 = -\frac{\varepsilon^2}{2}\partial_x^2\boldsymbol{I} + \begin{pmatrix} \rho(x) + d(x) & -\varepsilon\kappa_1(x)(\varepsilon\partial_x) \\ \varepsilon\kappa_1(x)(\varepsilon\partial_x) & -\rho(x) + d(x) \end{pmatrix}.$$

Here, $\rho = \sqrt{X^2 + Z^2}$ is half the energy level separation, and

$$\kappa_1 = \frac{Z'X - X'Z}{Z^2 + X^2}$$

is the adiabatic coupling element. A consequence of the choice of time scale in (1.2) is that solutions will oscillate with frequency $1/\varepsilon$. Thus the operator $\varepsilon\partial_x$ is actually of order one. However, we have still achieved a decoupling of the two energy levels in (1.3), up to errors of order ε, as long as $X^2(x) + Z^2(x) > 0$. Generically, this inequality is always true: assuming that the entries of V are analytic in the nuclear coordinate x, then eigenvalues of V do not cross [26], and so their difference $2\sqrt{X^2 + Z^2}$ remains positive. An avoided crossing is a (local or global) minimum of $\rho(x)$, which results in nonadiabatic transitions between the adiabatic energy levels.

The problem of photo-dissociation, or more generally of nonradiative decay, can now be formulated mathematically: assume that (1.2) is solved with an initial wave packet $\psi_{\mathrm{in}} \in L^2(\mathbb{R}, \mathbb{C}^2)$ that is fully in the upper adiabatic level (i.e., the second component of ψ_{in} is zero). This is the situation just after the laser pulse brings the electrons to their excited state. Assuming that the initial momentum is such that the wave packet travels past an avoided crossing, we wish to describe the second component of $\psi_0(x, t)$, to leading order, long after the avoided crossing has been passed. By doing this, we predict not only the probability of a molecule dissociating, but also the quantum mechanical properties (momentum and position distribution) of the resulting wave packet.

Solving the above problem, even numerically, is very difficult. The reason is that the energy levels $\pm\rho(x)$ are uniformly separated, and it is well known [12, 13, 17, 19] that then the transmitted wave packet is exponentially small in the parameter ε. This means that even for moderately small values of ε, we are trying to capture a very small effect. As an example, let us assume that the initial wave packet ψ_{in} has L^2-norm of order one, and that the parameters are such that the L^2-norm of the transmitted wave function is expected to be of order 10^{-6}, which we will later see is a fairly typical value. This means that any straightforward numerical method with an overall error of more than 10^{-6} will produce meaningless results, and thus if we were to apply a standard method (like Strang splitting) on the full equation (1.2), we would have

to use ridiculously small time steps. To make things worse, the solution is highly oscillatory. Thus, even though (1.2) is a system of just $1 + 1$ dimensional PDE's, it is not at all trivial to solve numerically. Efficient numerical methods to solve (1.2) will therefore require insight into the analytical structure of the equation.

In [2], we used superadiabatic representations in order to obtain such insight. We derive a closed-form approximation to the transmitted wave function at the transition point, which is highly accurate for general potential surfaces and initial wave packets whenever $d(x)$, the trace of the potential, is small, but deteriorates when $d(x)$ is moderate or large at the transition point. In general, it cannot be taken for granted in real world problems that $d(x)$ is small. Therefore, in this paper we treat a potential with an arbitrary trace. Our result is weaker than the one in [2]. While in the latter paper, we could allow arbitrary incoming wave functions as long as they were semiclassical, we essentially require the incoming wave packet to be either Gaussian or a generalized Hagedorn wave packet in the present work. However, in that case we still obtain a closed form expression for the transmitted wave function at the transition point, and the accuracy is as good as in [2].

The importance of nonadiabatic transitions has resulted in much effort to understand them. A simplification of the problem is to replace the nuclear degree of freedom by a classical trajectory. This approach is both long-established [28] and well understood [1, 11, 5] and leads to the well-known Landau–Zener formula for the transition probability between the electronic levels. This formula underpins a range of surface hopping models [25, 15, 14, 6]. Although these and other trajectory-based methods [24] yield reasonably accurate transition probabilities in the cases where they are applied, they are unable to accurately predict the shape of the transmitted wave packet [14]. More importantly, they seem to work well only when the transmitted wave packet is not too small. As an example, Fermanian Kammerer and Lasser [6] prove that the absolute error of their surface hopping algorithm is of the order at most $\varepsilon^{1/8}$, while numerical evidence suggests that the true error is closer to order $\varepsilon^{1/2}$. This is acceptable for them since they treat systems with several nuclear degrees of freedom, where generically the electronic adiabatic energy levels cross and transitions are of order one, provided the wave packet actually hits the crossing. In our case, where the energy levels generically stay separated, error margins of $\varepsilon^{1/2}$ completely obscure the exponentially small effect we are looking for, and are therefore not good enough. In this sense the one-dimensional problem is more difficult numerically than the moderately high-dimensional one, although of course very high dimensions pose their own significant difficulties. Yet another approach is the Zhu–Nakamura theory [18], which in a nonrigorous fashion strives to provide improved Landau–Zener rates based on the full quantum scattering theory of the problem, albeit in rather specialized situations. Once again only the transition probabilities are treated, and not the wave packet itself.

Due to the complexity of the full quantum-mechanical problem of transitions at avoided crossings, there are few existing mathematical approaches. The approach that is most relevant to our work is that of Hagedorn and Joye [13], where a formula is given (and proved) for the asymptotic shape of a nonadiabatic wave function in the scattering regime at an avoided crossing. Their formula looks quite different from ours, which is given in section 2, and it is too involved to display it here. See Theorem 5.1 of [13]. Of course, one would wish the formula of Hagedorn and Joye and our algorithm eventually lead to the same result, but the reality is more complicated. Indeed, we do not expect our results to agree with those of [13] in the asymptotic limit $\varepsilon \to 0$, since, as we explain below, our results rely on certain approximations

that are valid only when ε is small but not too small. Thus the algorithm we give is not asymptotically correct when $\varepsilon \to 0$ and all other parameters are fixed. On the positive side, it has the advantage of being trivial to implement and giving very good results in practice, while the formula of Hagedorn and Joye is not very well suited for numerical implementation. Moreover, there is evidence (given in the appendix of this paper) that our transition formula becomes correct in the limit when $\varepsilon \to 0$ and simultaneously the momentum of the incoming wave scales like $\varepsilon^{-\alpha}$ with $\alpha > 1/3$. It would be of great interest to compare our transition formula to the one of [13] in this case. However, the latter is too implicit and involved to easily do this.

It is important to note that for p_0 of the order $\varepsilon^{-\alpha}$ with α close to $1/3$, transitions are still beyond all orders in ε. Indeed, as explained in the next section, the order of magnitude for transitions is $\exp(-\frac{c}{p_0 \varepsilon})$, where p_0 is the incoming momentum. Thus the situation is very different from the cases treated in [9, 10], where the energy gap between the adiabatic surfaces is scaled such that transitions remain of order one. In [21], Rousse considers different scalings of the energy gap; however, those results are valid only up to errors of order $o(1)$ in ε. This means that no statement about the exponentially small transitions can be inferred from that paper.

Finally, let us remark that in applications all of the above asymptotic considerations are of somewhat secondary importance. ε and the other parameters of the model are dictated to us by the problem at hand, and for values of the order $\varepsilon = 10^{-2}$, which are fairly typical for the square root of the mass ratio between electrons and nuclei, whether an incoming momentum p_0 is of order $\varepsilon^{-1/3}$ or of order 1 is largely a matter of opinion. The good thing about the algorithm we propose is that it works well for a wide range of parameters. Indeed, we have found that it starts to really deteriorate only when either the transmitted wave packet becomes too large, or too small. In the first case, we are leaving the asymptotic regime, and it has to be expected that asymptotic methods do not work well. In the second case, it is already becoming very difficult to run reliable ab-initio dynamics to compare our results with, due to the oscillatory nature of the dynamics. Furthermore, the transition probabilities become so small that they are unlikely to be relevant for any practical application.

2. Computing the nonadiabatic transitions. In this section we will give a concise overview of our method for computing nonadiabatic transition wave functions, and explain the various parameters entering the final formula. The justification of our method, some extensions, and a numerical test will be given in the remainder of the paper.

The data of our problem consists of two parts, the potential energy matrix V and the initial wave function. More precisely, we assume that we are given $\rho(x)$ and $d(x)$ as in (1.3), and that ρ has a unique global minimum in the region of space that we are interested in. We choose the coordinate system such that this minimum occurs at $x = 0$, and we thus have

$$\rho(x) = \delta + \mathcal{O}(x^2), \qquad d(x) = d_0 + \lambda x + \mathcal{O}(x^2).$$

The transmitted wave function depends only on λ and ρ, but unfortunately the latter quantity does not enter in a simple way. Under the reasonable assumption that the matrix elements X and Z are analytic functions of x at least close to the real axis, then so is ρ^2. We write $\rho(q)^2 = \delta^2 + g(q)^2$, where g is analytic and $g(0) = 0$. Since g^2 is quadratic at 0, a Stokes line (a curve with $\text{Im}(\rho) = 0$) crosses the real axis perpendicularly, and, for small δ, extends into the complex plane to two complex

zeros of ρ, namely q_δ and q_δ^*. We define, for any complex z, the "natural scale" [1]

$$\tau(z) = 2 \int_0^z \rho(\xi) \, d\xi,$$

and write $\tau_\delta = \tau(q_\delta)$, where q_δ by convention is the complex zero with positive imaginary part. We write

$$\tau_{\mathrm{r}} = \mathrm{Re}\,(\tau_\delta), \qquad \tau_{\mathrm{c}} = \mathrm{Im}\,(\tau_\delta),$$

which are the two parameters that enter into the transition formula. When we are given ρ in a functional form, neither the computation of its complex zeroes nor of the complex line integral leading to τ_δ is a problem numerically, and can be carried out to any required accuracy. However, in the case of radiationless transitions, the potential energy surfaces are often only known approximately. As our final formula will depend very sensitively on the value of τ_δ, small errors in this quantity will lead to wrong predictions. This is not a fault of our method, but a general obstruction to any numerical method aiming to calculate small nonadiabatic transitions: Namely, since our formula below agrees very accurately with ab-initio computations, and depends very sensitively on τ_δ, getting ρ wrong will lead to wrong results regardless of the method used. In a way, it should not be too surprising that when looking for a very small effect, we need to get the data right with very high accuracy. But it does pose a serious practical challenge when trying to predict small nonadiabatic transitions.

As for the initial wave function, we first assume it to be initially concentrated in the upper electronic energy band. This means that we will consider (1.2) with initial condition $\psi_0(x,0) = (\phi_+(x,0),0)^T$. The restriction of this work, when compared to the case with $\lambda = 0$ considered in [2], is on the form of $\phi_+(x,0)$, which we require to be either Gaussian, or a finite linear combination of Gaussians, or a Hagedorn wave function. For the present exposition, we restrict to the case where it is Gaussian. The first step of our algorithm is straighforward.

Step 1. Solve the upper band adiabatic equation $i\varepsilon\partial_t\psi_+ = H^+\psi_+$, $\psi_+(0) = \phi_+(\cdot,0)$, where $H^+ = -\varepsilon^2\partial_x^2/2 + \rho(x) + d(x)$. This can be done either by direct Strang splitting, or using the theory of Hagedorn wave packets [16]. For a transition to occur, we need the wave packet to cross the transition region near $x = 0$, where ρ is minimal. So we monitor the expected position $\langle X \rangle = \int x|\psi_+(x)|^2 \, dx$ and stop the evolution when $\langle X \rangle = 0$, say at time t_0. Let us write $\phi(x) = \psi_+(x,t_0)$. ϕ is Gaussian up to errors of order ε [16] and centered at $x = 0$. Thus we have

$$(2.1) \qquad \widehat{\phi}^\varepsilon(k) = \exp\left(-\frac{c}{\varepsilon}(k - p_0)^2\right)$$

with parameters p_0 (the mean momentum) and c. Above, we used the semiclassical Fourier transform; cf. (3.8).

Step 2. We now use the upper band wave function $\widehat{\phi}^\varepsilon$ at the transition point in order to generate a wave packet on the lower energy level. It is useful to recall that in [2, 3], we assumed $d = 0$ and were able to approximate the dynamics near the transition point by the free dynamics, leading to the formula

$$(2.2) \qquad \widehat{\phi^-}^\varepsilon(k) = 1_{\{k^2 > 4\delta\}} \frac{v + k}{2|v|} \, e^{i\frac{\tau_\delta}{2\delta\varepsilon}|k - v|} \, \widehat{\phi}^\varepsilon(v),$$

with $v = v(k) = \mathrm{sgn}(k)\sqrt{k^2 - 4\delta}$. This formula has been validated also for non-Gaussian incoming wave packets $\widehat{\phi}^\varepsilon$.

In the case where $d \neq 0$, the approximation of the true intraband dynamics by the free time evolution is no longer a good one, and the transition formula is considerably more involved. Put $n_0 = \frac{\tau_c}{\varepsilon k_0}$, where k_0 is part of the solution of the pair of equations

$$(2.3) \qquad k = \sqrt{\eta^2 + 4\delta}, \qquad \eta = k\left(1 - \frac{4c\delta(\eta - p_0)}{\tau_c}\right).$$

Again, the numerical value of n_0 is easy to obtain. In what follows, we will use the abbreviation

$$\eta^* = \eta^*(k) = \sqrt{k^2 - 4\delta}.$$

Now put

$$(2.4) \qquad \widehat{\phi_-}^\varepsilon(k) \approx \frac{1}{2\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} \exp\left[\frac{\alpha_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right]$$
$$\times (\eta^* + k) \, \mathrm{e}^{-\frac{\tau_c}{2\delta\epsilon}|k-\eta^*|} \, \mathrm{e}^{-\mathrm{i}\frac{\tau_r}{2\delta\epsilon}(k-\eta^*)} \, \mathrm{e}^{-\mathrm{i}\varphi(p_0)} \, \widehat{\phi}^\varepsilon(\eta^*)\chi_{k^2 > 4\delta},$$

with

$$\alpha_{1,0} = \frac{\mathrm{sgn}(k)\tau_\mathrm{c} + \mathrm{i}\tau_\mathrm{r} - \eta^* n_0\varepsilon - 4c\delta(\eta^* - p_0)}{2\delta\sqrt{\varepsilon}} + \frac{\sqrt{\varepsilon}}{k + \eta^*},$$

$$(2.5) \quad \alpha_{0,1} = -\frac{2(n_0+1)\varepsilon^{1/2}\lambda}{k + \eta^*}, \quad \alpha_{1,1} = -\mathrm{i}\eta^* + \frac{2(n_0+1)\lambda\varepsilon}{(k + \eta^*)^2},$$

$$\alpha_{2,0} = -\frac{2\delta n_0\varepsilon + \eta^{*2}}{8\delta^2} - c - \frac{\varepsilon}{2(k + \eta^*)^2}, \quad \alpha_{0,2} = -\mathrm{i}\frac{2\delta\lambda}{(k + \eta^*)} - \frac{2(n_0+1)\lambda^2\varepsilon}{(k + \eta^*)^2},$$

and

$$\varphi(p_0) = -\frac{(n_0+1)^2\varepsilon\lambda a_0\delta}{2(n_0+1)^2\lambda^2\varepsilon^2 + 2\delta^2 a_0^2} - \frac{1}{2}\arctan\left(\frac{a_0\delta}{(n_0+1)\varepsilon\lambda}\right) + \mathrm{sgn}(\lambda p_0)\frac{\pi}{4},$$

where above $a_0 = \sqrt{p_0^2 + 4\delta} + p_0$. While formula (2.4) is trival to implement on a computer and produces accurate results, it is not easy to interpret the various terms in a physically meaningful way. On the other hand, everything except the factor $\mathrm{e}^{-\mathrm{i}\varphi(p_0)}$ is obtained by plausible approximations and exact Gaussian computations. The latter factor, which is a constant phase shift, is more tricky. It is obtained by computing the phase in the case of an incoming Gaussian when the parameter c diverges, i.e., infinitely small momentum uncertainty, which gives $\varphi(p_0)$, and subtracting that. This fixes a discrepancy in the phase of the transmitted wave function between our formula without the factor and numerical ab-initio calculations, which is probably due to one of our approximations below being too crude. We do not know where the original inaccurate approximation has been made, or why the given recipe fixes it. Note, however, that the phase shift in question must be due to the dynamics not being free in the transition regime, as it vanishes when $\lambda \to 0$. There are other phase shifts in the transmitted wave function, a trivial one due to the energy gap and another one due to the fact that fast Fourier modes contribute more to the transition. These appear already in (2.2) and are well understood [13, 3].

Note $\varphi(p_0)$ is constant in both k and x and hence will not affect any quantum mechanical expectation values. It would, however, play a role when we consider interferences.

The final step of our algorithm is again straightforward.

Step 3. Solve the lower band adiabatic equation with initial condition ϕ_-, i.e. solve

$$\mathrm{i}\varepsilon\partial_t\psi_- = H^-\psi_-, \qquad \psi_-(t_0) = \phi_-(\cdot, t_0),$$

where $H^- = -\varepsilon^2\partial_x^2/2 - \rho(x) + d(x)$, and ϕ_- is the inverse semiclassical Fourier transform of $\widehat{\phi}_-^{\varepsilon}$. For times so large that ψ_- has support far away from the transition region, it describes the transmitted wave function of equation (1.2) with great accuracy; see section 6.

3. Evolution in the superadiabatic representations.

3.1. Superadiabatic representations. The key idea for deriving our transition formulae is to study the evolution in a suitable superadiabatic representation. For a careful discussion of the theory of those representations, we refer to [3]. Here we give only some intuition and the mathematical facts. The nth superadiabatic representation is implemented by a unitary operator U_n acting on $L^2(\mathbb{R}, \mathbb{C}^2)$, and its main property is that it diagonalizes the right-hand side of (1.1) up to errors of order ε^{n+1}. Thus, the adiabatic representation (1.3) is the zeroth superadiabatic representation, and in general,

$$H_n = U_n^{-1}HU_n = -\frac{\varepsilon^2}{2}\partial_x^2 \boldsymbol{I} + \begin{pmatrix} \rho(x) + d(x) & \varepsilon^{n+1}K_{n+1}^+ \\ \varepsilon^{n+1}K_{n+1}^- & -\rho(x) + d(x) \end{pmatrix},$$

where $K_n^{\pm}$ are the nth superadiabatic coupling elements. They are usually pseudo-differential operators, and so are the U_n. The useful consequence of switching to the superadiabatic representation is that now the evolution of the second component ψ_n^- of $\psi_n = U_n\psi$, subject to $\psi_n^-(-\infty) = 0$, is given by

$$(3.1) \qquad \psi_n^-(t) = -\mathrm{i}\varepsilon^n \int_{-\infty}^t \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}(t-s)H^-} K_{n+1}^- \, \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}sH^+} \, \phi \, \mathrm{d}s,$$

up to relative errors of order ε. Thus, provided we can control K_n^-, (3.1) gives the transmitted wave function in the nth superadiabatic representation to high precision.

There are some apparent problems with this idea. First, it is far from clear how we hope to control K_n^-. Second, the superadiabatic unitaries are, in general, very hard to calculate, and as such this formulation does not allow the adiabatic wave function to be easily obtained. Third, we have to decide which value of n we want to use. The sequence K_n^- is expected to be asymptotic in n, so after initially decaying rapidly (in an appropriate sense) it will start to grow beyond all limits when n is taken to infinity. The second problem above is resolved when we study the wave function in the scattering regime, well away from the avoided crossing. In this case, for potentials which are approximately constant, it is known that U_n and U_0 agree up to small errors depending on the derivatives of the potential [23], and (3.1) can be used to calculate the transmitted wave function. For the value of n, in [3] we showed for a special choice of parameters ρ, κ that there exists an "optimal" n for which $\psi_n^-(t)$ builds up monotonically, corresponding to a single transition. This n is given by the set of nonlinear equations (2.3) that we have seen in the previous section. We expect this set of equations to hold, in general, and have obtained very good results by using it here.

The problem of calculating K_n^- turns out to be reducible to a set of differential recursions, which we will now give. The discussion follows the one in [3] very closely,

the only difference being that we now include a nonzero trace $d(x)$ in the Hamiltonian. All the calculations and arguments are almost the same as in [3], so we will omit them.

We change from the spatial representation to the symbolic representation (see, e.g., [23]) by replacing x by $q \in \mathbb{R}$ and $i\varepsilon\partial_x$ by an independent variable $p \in \mathbb{R}$, where the factor ε takes into account the semiclassical scaling. We need to introduce some further notation: We rewrite the potential as

$$V(q) = \rho(q) \begin{pmatrix} \cos\left(\theta(q)\right) & \sin\left(\theta(q)\right) \\ \sin\left(\theta(q)\right) & \cos\left(\theta(q)\right) \end{pmatrix} + d(q) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},$$

which defines $\theta(q)$. It follows that the unitary transformation to the adiabatic representation is given by

$$U_0(q) = \begin{pmatrix} \cos\left(\frac{\theta(q)}{2}\right) & \sin\left(\frac{\theta(q)}{2}\right) \\ \sin\left(\frac{\theta(q)}{2}\right) & -\cos\left(\frac{\theta(q)}{2}\right) \end{pmatrix}.$$

Hence the Pauli matrices in the adiabatic representation are given by

$$\boldsymbol{\sigma}_{\mathrm{x}}(q) = U_0(q)\sigma_{\mathrm{x}}U_0(q), \quad \boldsymbol{\sigma}_{\mathrm{y}}(q) = U_0(q)\sigma_{\mathrm{y}}U_0(q), \quad \boldsymbol{\sigma}_{\mathrm{z}}(q) = U_0(q)\sigma_{\mathrm{z}}U_0(q),$$

where

$$(3.2) \qquad \sigma_{\mathrm{x}} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_{\mathrm{y}} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_{\mathrm{z}} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

and we have used that $U_0^* = U_0$.

Let $\mathbf{1}$ be the 2×2 identity matrix. A direct calculation confirms, with $\mathbf{1}$, the 2×2 identity matrix.

LEMMA 3.1. *We have*

$$\partial_q^n V(q) = a_n(q)\boldsymbol{\sigma}_{\mathrm{z}}(q) + b_n(q)\boldsymbol{\sigma}_{\mathrm{x}}(q) + c_n(q)\mathbf{1},$$

where $a_n(q)$, $b_n(q)$, and $c_n(q)$ are given by the recursions

$$(3.3) \qquad \begin{aligned} a_0(q) &= \rho(q), & a_{n+1}(q) &= a_n'(q) + \theta'(q)b_n(q), \\ b_0(q) &= 0, & b_{n+1}(q) &= b_n'(q) - \theta'(q)a_n(q), \\ c_0(q) &= d(q) & c_{n+1}(q) &= c_n'(q). \end{aligned}$$

We then have the following explicit recursion for the coupling elements.

THEOREM 3.2. *The Hamiltonian in the nth superadiabatic representation is given by*

$$H_n(\varepsilon, p, q) = \frac{p^2}{2}\mathbf{1} + \begin{pmatrix} \rho(q) + d(q) & \varepsilon^{n+1}\kappa_{n+1}^+(p,q) \\ \varepsilon^{n+1}\kappa_{n+1}^-(p,q) & -\rho(q) + d(q) \end{pmatrix} + \begin{pmatrix} \mathcal{O}(\varepsilon^2) & \mathcal{O}(\varepsilon^{n+2}) \\ \mathcal{O}(\varepsilon^{n+2}) & \mathcal{O}(\varepsilon^2) \end{pmatrix},$$

where

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

Setting $x_n(p,q) = \sum_{m=0}^n p^{n-m}x_n^m(q)$ with similar expressions for y_n, z_n, and w_n, the coefficients x_n^m to w_n^m are determined by the following recursive algebraic-differential equations:

$$(3.4) \qquad x_1^m = z_1^m = w_1^m = 0, \quad m = 0, 1, \qquad y_1^0 = -i\frac{\theta'(q)}{4\rho(q)}, \quad y_1^1 = 0$$

with

$$x_{n+1}^m = -\frac{1}{2\rho}\left(\frac{1}{i}(y_n^m)' - 2\sum_{j=1}^{\lfloor m/2 \rfloor}\frac{1}{(2i)^j}\binom{n+1-m+j}{j}(b_j z_{n+1-j}^{m-2j} - a_j x_{n+1-j}^{m-2j} + c_j y_{n+1-j}^{m-2j})\right)$$

for n odd, and

$$y_{n+1}^m = -\frac{1}{2\rho}\left(\frac{1}{i}\big((x_n^m)' - \theta' z_n^m\big)\right.$$
$$\left. - 2\sum_{j=1}^{\lfloor m/2 \rfloor}\frac{1}{(2i)^j}\binom{n+1-m+j}{j}\big(-a_j y_{n+1-j}^{m-2j} + b_j w_{n+1-j}^{m-2j} + c_j x_{n+1-j}^{m-2j}\big)\right),$$
$$0 = \frac{1}{i}\big((z_n^m)' + \theta' x_n^m\big) - 2\sum_{j=1}^{\lfloor m/2 \rfloor}\frac{1}{(2i)^j}\binom{n+1-m+j}{j}(b_j y_{n+1-j}^{m-2j} + a_j w_{n+1-j}^{m-2j} + c_j z_{n+1-j}^{m-2j}),$$
$$0 = \frac{1}{i}(w_n^m)' - 2\sum_{j=1}^{\lfloor m/2 \rfloor}\frac{1}{(2i)^j}\binom{n+1-m+j}{j}(a_j z_{n+1-j}^{m-2j} + b_j x_{n+1-j}^{m-2j} + c_j w_{n+1-j}^{m-2j})$$

for n even. The coefficients a_n to c_n are given by Lemma 3.1.

Proof. The proof is analogous to those of Theorem 3.4 and Proposition 3.5 of [3], with some easy alterations due to the presence of $d(x)$. □

We note that, as in the trace-free case in [3], $y_n^m = 0$ for all m when n is even and $x_n^m = z_n^m = w_n^m = 0$ for all m when n is odd. Furthermore, from the above equations, it is obvious that $x_n^m = y_n^m = z_n^m = w_n^m = 0$ for odd m.

We now have an explicit expression for κ_n^- and may therefore also calculate K_n^-, the superadiabatic coupling element, which is the Weyl quantization of the symbol κ_n^-:

$$K_n^\pm \psi(x) = \frac{1}{2\pi\varepsilon}\int_{\mathbb{R}^2} d\xi\, dy\, \kappa_n^\pm\left(\tfrac{x+y}{2}, \xi\right) e^{\frac{i}{\varepsilon}\xi(x-y)}\psi(y),$$

and from the recursions in Theorem 3.2, it is clear that

$$\kappa_n^\pm(p,q) = \sum_{j=0}^{n} p^j \kappa_{n,n-j}^\pm(q),$$

where the $\kappa_{n,n-j}^\pm$ can be calculated explicitly. Determining the asymptotics of this two-parameter recursion is a very tricky problem to which we have no solution. However, in the regime of large p (meaning, large incoming momentum) the sum is well approximated by the $j = n$ term. In the appendix, we give a rigorous estimate of the superadiabatic Hamiltonian and show that, when $p \gg \varepsilon^{-1/3}$, $\kappa_n^\pm$ is dominated by the term $p^n \kappa_{n,0}^\pm(q)$. This translates into large momentum for the incoming wave function. While these results certainly give rise to the hope that for large incoming momentum a rigorous asymptotic analysis is possible, there are still many obstacles to overcome: Just to mention two of them, the dependence of the error terms in Theorem 3.2 on n, p, and q needs to be controlled, as does the propagation of errors through the Weyl quantization below. A full asymptotic analysis of the regime $p \gg \varepsilon^{-1/3}$ is therefore still a work in progress. Here, we use the approximation of $\kappa_n^\pm(q,p)$ by $p^n \kappa_{n,0}^\pm(q)$

without further justification, and find that it gives good results even for relatively small values of p.

The asymptotics of the term $\kappa_{n,0}^-$ can be determined explicitly in the following generic case. Without loss of generality, we assume that the avoided crossing occurs at $x = 0$, specify the initial wave packet at $t = 0$, and write $\rho(q)^2 = \delta^2 + g(q)^2$, where g is analytic and $g(0) = 0$. As is standard in asymptotic analysis (see, e.g., [1]), the asymptotic behavior of $\kappa_{n,0}^-$ is determined by the complex zeros of ρ. Since g^2 is quadratic at 0, a Stokes line (a curve with $\mathrm{Im}(\rho) = 0$) crosses the real axis perpendicularly, and, for small δ, extends into the complex plane to two complex zeros of ρ, namely q_δ and q_δ^*. As argued by Berry and Lim [1], in the natural scale $\tau(q) = 2\int_0^q \rho(q)\mathrm{d}q$ and near $q = 0$, the adiabatic coupling function has the form $\kappa_1(q) = \frac{\mathrm{i}\rho(q)}{3}\big(\frac{1}{\tau(q)-\tau_\delta^*} - \frac{1}{\tau(q)-\tau_\delta} + \kappa_r(\tau(q))\big)$, with $\tau_\delta = \tau(q_\delta)$. In particular, κ_r has no singularities for $|\tau| < |\tau_\delta|$, and no singularities of order $\geqslant 1$ for $|\tau| \leqslant |\tau_\delta|$. As can be seen from Theorem 3.2, solving the recursions for κ_n^- requires taking high derivatives of κ_1. By the Darboux principle, the asymptotics are dominated by the complex singularities closest to the real axis, τ_δ and τ_δ^*. Hence, to leading order, we find

$$(3.5) \qquad \kappa_{n,0}^-(q) = \frac{\mathrm{i}^n}{\pi}\rho(q)(n-1)!\big(\frac{\mathrm{i}}{(\tau-\tau_\delta^*)^n} - \frac{\mathrm{i}}{(\tau-\tau_\delta)^n}\big).$$

Using the definition of the Weyl quantization, a direct calculation [3] shows

$$(3.6) \qquad K_{n,0}^- = \sum_{j=0}^n \binom{n}{j}\big(\tfrac{\varepsilon}{2\mathrm{i}}\big)^j \big(\partial_x^j \kappa_{n,0}^-(x)\big)(-\mathrm{i}\varepsilon\partial_x)^{n-j}.$$

3.2. Approximation of the adiabatic propagators. In order to determine a closed form approximation for (3.1), it is necessary to approximate the adiabatic propagators. This is in contrast to the situation in [3] where the model was chosen such that ρ is constant, and thus the adiabatic evolutions were trivial in Fourier space.

The first insight is that the operator $K_{n,0}^-$ given in (3.6) is sharply localized: $K_{n,0}^- f$ will only be significantly different from zero if either f or some of its derivatives have some support overlap with $\kappa_{n,0}^-$, which means they must be concentrated near the real solution of $\mathrm{Re}\,(\tau(q)) = \mathrm{Re}\,(\tau_\delta)$ that is closest to $q = 0$. We will refer to this solution as the transition point. In section 4.1 we will see that relevant values of n are of the order $1/\varepsilon$; furthermore, for large n we have $(1+x^2)^{-n} \approx \mathrm{e}^{-nx^2}$, and so $\kappa_{n,0}^-$ and its derivatives are concentrated in a $\sqrt{\varepsilon}$ neighborhood of the transition point. Since the time scale is chosen such that the semiclassical wave packets (which have width of order $\sqrt{\varepsilon}$) travel at speed of order one, the dominant transitions come from a time interval of order $\sqrt{\varepsilon}$ around the transition time, which we define to be the time when the expected position of the incoming wave packet crosses the transition point.

Let us pick a coordinate system so that that the transition time is $s = 0$. We cannot, however, choose the transition point to be at $x = 0$, since we have already fixed $x = 0$ to be the local minimum of ρ. On the other hand, one of our later calculations relies on the fact that the transition point is at least in a $\sqrt{\varepsilon}$ neighborhood of 0; see section 3.3. So from now on, we will always assume that the transition point does indeed have this property. This assumption can be justified by the observation that for sensible potentials, the real and imaginary parts of the complex zeroes of ρ are coupled, and are either both relatively small or both large. However, in the latter case, transitions tend to be so small that they are physically uninteresting. That said, it would, of course, be much preferable to be able to treat arbitrary transitions, but

we cannot do this yet. In what follows, we will always pretend that the transition point is $x = 0$, although for the calculation in the next paragraph this is not yet strictly necessary.

The above considerations allow us to replace the potential in the full adiabatic dynamics by its first Taylor approximation, as the following formal calculation shows. We take $H_1^{\pm} := -\varepsilon^2 \partial_x^2 / 2 \pm \delta + \lambda x$ and wish to show that $\mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H^{\pm}} - \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H_1^{\pm}}$ is small. We have

$$\mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H^{\pm}} - \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H_1^{\pm}} = \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H_1^{\pm}} \left(\mathrm{e}^{\frac{\mathrm{i}}{\varepsilon} s H_1^{\pm}} \, \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H^{\pm}} - 1 \right)$$

$$= \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H_1^{\pm}} \int_0^s \partial_r \left(\mathrm{e}^{\frac{\mathrm{i}}{\varepsilon} s H_1^{\pm}} \, \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H^{\pm}} \right) \mathrm{d}r$$

$$= \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H_1^{\pm}} \int_0^s \mathrm{e}^{\frac{\mathrm{i}}{\varepsilon} s H_1^{\pm}} \left(\tfrac{\mathrm{i}}{\varepsilon} (H_1^{\pm} - H^{\pm}) \right) \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s H^{\pm}} \, \mathrm{d}r.$$

We now note that $H_1^{\pm} - H^{\pm}$ is quadratic near $x = 0$ and hence the integrand is of order 1 in a $\sqrt{\varepsilon}$ neighborhood of zero. Hence the left-hand side is bounded by the length of the integration region $\sqrt{\varepsilon}$ and, to leading order, it suffices to replace (3.1) by

$$(3.7) \quad \psi_n^-(t) \approx -\mathrm{i}\varepsilon^n \, \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} t H^-} \int_{-\infty}^{t} \mathrm{e}^{\frac{\mathrm{i}}{\varepsilon} s (-\varepsilon^2 \partial_x^2 / 2 - \delta + \lambda x)} K_{n+1}^- \, \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s (-\varepsilon^2 \partial_x^2 / 2 + \delta + \lambda x)} \, \phi \, \mathrm{d}s,$$

where we have not altered the s-independent propagator.

We now find it convenient to switch to the Fourier representation by applying the semiclassical Fourier transform

$$(3.8) \qquad\qquad \widehat{f}^{\varepsilon}(k) = \frac{1}{\sqrt{2\pi\varepsilon}} \int_{\mathbb{R}} \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} k q} \, f(q) \, \mathrm{d}q = \frac{1}{\sqrt{\varepsilon}} \hat{f}\left(\tfrac{k}{\varepsilon}\right).$$

We define $\hat{K}_n$ through $\hat{K}_n \widehat{\psi}^{\varepsilon} = \widehat{K_n \psi}^{\varepsilon}$, and a direct calculation [3] gives

$$\hat{K}_{n,0}^{\pm} f(k) = \frac{1}{\sqrt{2\pi\varepsilon}} \int_{\mathbb{R}} \mathrm{d}\eta \, \widehat{\kappa_{n,0}^{\pm}}^{\varepsilon}(k - \eta) \left(\tfrac{\eta + k}{2}\right)^n f(\eta).$$

By Fourier transformation of both sides of (3.7), we see that $\widehat{\psi_n^-}^{\varepsilon}$ is given by a double integral:

$$\widehat{\psi_n^-}^{\varepsilon}(k, t)$$

$$\approx -\frac{\mathrm{i}\varepsilon^n}{\sqrt{2\pi\varepsilon}} \, \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} t \hat{H}^-(k)} \int_{-\infty}^{t} \mathrm{d}s \int_{\mathbb{R}} \mathrm{d}\eta \, \mathrm{e}^{\frac{\mathrm{i}}{\varepsilon} s \hat{H}_1^-(k)} \, \widehat{\kappa_{n+1,0}^-}^{\varepsilon}(k - \eta) \left(\tfrac{\eta + k}{2}\right)^{n+1} \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s \hat{H}_1^+(\eta)} \, \widehat{\phi}^{\varepsilon}(\eta),$$

where $\hat{H}_1^{\pm}$ ($\hat{H}^{\pm}$) are the approximate (exact) adiabatic propagators in momentum space.

By the Avron–Herbst formula, the approximate propagators are given exactly by

$$\mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s \hat{H}_1^{\pm}(k)} = \mathrm{e}^{-\mathrm{i}\frac{\lambda^2 s^3}{6\varepsilon}} \, \mathrm{e}^{\lambda s \partial_k} \, \mathrm{e}^{-\frac{\mathrm{i}}{2\varepsilon}((k^2 \pm 2\delta)s - \lambda k s^2)}.$$

In particular, we have

$$(3.9) \qquad \mathrm{e}^{\frac{\mathrm{i}}{\varepsilon} s \hat{H}_1^-(k)} = \mathrm{e}^{\frac{\mathrm{i}\lambda^2 s^3}{6\varepsilon}} \, \mathrm{e}^{-\lambda s \partial_k} \, \mathrm{e}^{\frac{\mathrm{i}}{2\varepsilon}(k^2 - 2\delta)s} \, \mathrm{e}^{\frac{\mathrm{i}}{2\varepsilon}\lambda k s^2},$$

$$\mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon} s \hat{H}_1^+(\eta)} = \mathrm{e}^{-\frac{\mathrm{i}\lambda^2 s^3}{6\varepsilon}} \, \mathrm{e}^{\lambda s \partial_\eta} \, \mathrm{e}^{-\frac{\mathrm{i}}{2\varepsilon}(\eta^2 - 2\delta)s} \, \mathrm{e}^{\frac{\mathrm{i}}{2\varepsilon}\lambda \eta s^2}.$$

In order to make use of these expressions we must understand the effects of the shift operators, where $e^{\lambda s \partial_k} f(k) = f(k + \lambda s)$. Using (3.9) in (3.7) we note that, due to the invariance of the integral under $\eta \mapsto \eta - \lambda s$, we may apply the η shift to the left with opposite sign. Hence $\widehat{\kappa_{n+1,0}^-}^\varepsilon (k - \eta)$ is unaffected and $(k+\eta)^{n+1} \mapsto (k + \eta - 2\lambda s)^{n+1}$.

Shifting the remaining propagator in k by $-\lambda s$, the remaining multiplicative parts of the propagators are given by

$$\exp\left[\tfrac{i}{2\varepsilon}\left([(k-\lambda s)^2 - 2\delta]s + \lambda(k-\lambda s)s^2 - (\eta^2 + 2\delta)s + \lambda\eta s^2\right)\right].$$

Simplifying this expression and inserting it into (3.7) gives

$$\widehat{\psi_n^-}^\varepsilon (k,t) \approx -\frac{i\varepsilon^n}{\sqrt{2\pi\varepsilon}}\, e^{-\frac{i}{\varepsilon} t \hat{H}_1^-(k)} \int_{-\infty}^t ds \int_{\mathbb{R}} d\eta \, (k+\eta - 2\lambda s)^{n+1} \widehat{\kappa_{n+1,0}^-}^\varepsilon (k-\eta)$$

$$(3.10) \qquad \times\, e^{\frac{i}{2\varepsilon}\left((k^2 - \eta^2 - 4\delta)s - (k-\eta)\lambda s^2\right)} \widehat{\phi}^\varepsilon(\eta).$$

3.3. Fourier transform of the coupling elements. In order to make use of (3.10), we require the Fourier transform of $\kappa_{n,0}^-$. Using (3.8) on (3.5) gives

$$\widehat{\kappa_{n,0}^-}^\varepsilon (k) = \frac{1}{\sqrt{2\pi\varepsilon}} \int e^{-\frac{i}{\varepsilon} kq} \frac{i^{n+1}}{\pi} \rho(q)(n-1)! \left[\frac{1}{\left(\tau(q) - \tau_\delta^*\right)^n} - \frac{1}{\left(\tau(q) - \tau_\delta\right)^n}\right] dq$$

$$= \frac{1}{\sqrt{2\pi\varepsilon}} \int e^{-\frac{i}{\varepsilon} kq(\tau)} \frac{i^{n+1}}{2\pi}(n-1)! \left[\frac{1}{\left(\tau - \tau_\delta^*\right)^n} - \frac{1}{\left(\tau - \tau_\delta\right)^n}\right] d\tau,$$

where we have used $d\tau = 2\rho(q)dq$.

It is now that we need the transition point to be at or near $q = 0$. Provided this is so, we can use that ρ has a minimum δ at $q = 0$, and expand $q(\tau) = \frac{\tau}{2\delta} + \mathcal{O}(\tau^3)$. Note that no second order term is present. As the remainder of the integrand is concentrated in a $\sqrt{\varepsilon}$ neighborhood around $q = 0$, we keep only the first order term, giving

$$\widehat{\kappa_{n,0}^-}^\varepsilon (k) \approx \frac{1}{\sqrt{2\pi\varepsilon}} \int e^{-\frac{i}{2\delta\varepsilon} k\tau} \frac{i^{n+1}}{2\pi}(n-1)! \left[\frac{1}{\left(\tau - \tau_\delta^*\right)^n} - \frac{1}{\left(\tau - \tau_\delta\right)^n}\right] d\tau.$$

We now note that $\frac{1}{(\tau-\alpha)^n} = (-1)^{n-1}\frac{1}{(n-1)!}\partial_\tau^{n-1}\frac{1}{\tau-\alpha}$ and hence

$$\widehat{\kappa_{n,0}^-}^\varepsilon (k) \approx \frac{1}{\sqrt{2\pi\varepsilon}}\frac{i^{n+1}}{2\pi}(-1)^{n-1} \int e^{-\frac{i}{2\delta\varepsilon} k\tau} \partial_\tau^{n-1}\left[\frac{1}{\left(\tau - \tau_\delta^*\right)} - \frac{1}{\left(\tau - \tau_\delta\right)}\right] d\tau$$

$$= \frac{1}{\sqrt{2\pi\varepsilon}}\frac{i^{n+1}}{2\pi}(-1)^{n-1} \int e^{-\frac{i}{2\delta\varepsilon} k\tau} \partial_\tau^{n-1}\left[\frac{-2i\tau_c}{\left((\tau - \tau_r) + \tau_c^2\right)}\right] d\tau.$$

Using the identities $\widehat{f}^\varepsilon(k) = \frac{1}{\sqrt{\varepsilon}}\hat{f}\left(\frac{k}{\varepsilon}\right)$, $\widehat{\partial_\tau^n f}(k) = (ik)^n \hat{f}(k)$, $\widehat{f(x-a)}(k) = e^{-iak}\hat{f}(k)$, and the standard Fourier transform

$$\widehat{\frac{a}{x^2+a^2}}(k) = \sqrt{\tfrac{\pi}{2}}\, e^{-a|k|}$$

gives

$$\widehat{\kappa_{n,0}^-}^\varepsilon (k) \approx i\frac{\sqrt{2}\delta}{\sqrt{\pi\varepsilon}}\frac{1}{(2\delta)^n}\left(\frac{k}{\varepsilon}\right)^{n-1} e^{-\frac{\tau_c}{2\delta\varepsilon}|k|}\, e^{-i\frac{\tau_r}{2\delta\varepsilon}k},$$

where we have used $\tau_\delta = \tau_r + i\tau_c$. Inserting this formulation into (3.10) gives

$$\widehat{\psi_n^-}^\varepsilon(k,t) \approx -\frac{1}{4\pi\varepsilon} e^{-\frac{i}{\varepsilon}t\hat{H}^-(k)} \int_{-\infty}^t ds \int_{\mathbb{R}} d\eta\, (k+\eta)(1 - \tfrac{2\lambda s}{k+\eta})^{n+1}\big(\tfrac{k^2-\eta^2}{4\delta}\big)^n$$

$$(3.11) \qquad \times\ e^{-\frac{\tau_c}{2\delta\varepsilon}|k-\eta|}\ e^{-\frac{i\tau_r}{2\delta\varepsilon}(k-\eta)}\ e^{\frac{i}{2\varepsilon}\big((k^2-\eta^2-4\delta)s-(k-\eta)\lambda s^2\big)}\ \widehat{\phi}^\varepsilon(\eta).$$

4. Evaluation of the integral.

4.1. The choice of n. Equation (3.11) still depends on the parameter n, the order of the superadiabatic representation. For choosing n, we attempt to use the same argument that was employed in [3] in order to obtain universal transition histories. The idea then and now is that the modulus of the integrand in (3.11) depends on n, while the phase does not. We will thus try to choose n such that stationary phase and maximal modulus occur at the same point, making it possible to perform asymptotic analysis on the integral.

We recall the assumption that τ_r is small, and consider the imaginary part of the exponent. Indeed, we will set $\tau_r = 0$ in what follows. This simplifies the analysis and does not seem to greatly affect the accuracy of the final result. Differentiating the phase of (3.11) with respect to s and η gives

$$(4.1) \qquad\qquad (k^2 - \eta^2 - 4\delta) - 2\lambda(k - \eta)s = 0,$$

$$(4.2) \qquad\qquad\qquad\qquad -2\eta s - \lambda s^2 = 0.$$

Note that if $\lambda = 0$, then there is only one solution, namely $k^2 - \eta^2 = 4\delta$ and $s = 0$; this remains a solution if $\lambda \neq 0$.

For a simultaneous solution to (4.1) and (4.2) (i.e., stationary phase for both integrals) we require either $s = 0$ and $k^2 - \eta^2 - 4\delta = 0$, or $\lambda s = -2\eta$ and η the solution to $-5\eta^2 + 4k\eta + k^2 - 4\delta = 0$. In the second case, for $k = \mathcal{O}(1)$, we see that η and hence s are also of order 1. We have already discussed that we expect the significant transitions to occur only when $s = \mathcal{O}(\varepsilon^{1/2})$, and we therefore expect this solution to contribute only a negligible amount to the transmitted wave packet. So from the stationary phase condition, we obtain $s = 0$ and $k^2 - \eta^2 - 4\delta = 0$.

For the modulus, we assume the case of a Gaussian wave packet of the form (2.1). Differentiating the logarithm of the modulus with respect to η and s and equating to zero leads to the equations

$$(4.3) \qquad\qquad\qquad\qquad (n+1)\frac{2\lambda}{\eta + k - 2s} = 0,$$

$$(4.4) \qquad 2c(\eta - p_0) - \frac{\tau_c}{2\delta}\eta + n\varepsilon\frac{2\eta}{k^2 - \eta^2} - (n+1)\varepsilon\frac{2\lambda s}{(k+\eta)(k+\eta - 2\lambda s)} = 0.$$

Equations (4.1)–(4.4) cannot be solved simultaneously, which shows an interesting difference of the present case when compared to the nontilted case treated in [2] and [3]. To make progress, we argue that the choice of the optimal superadiabatic representation should depend only weakly on the trace λ of the potential. Therefore, we allow λ to vary as well as n, η, and s, and obtain the joint solution $s = \lambda = 0$, and n and η fulfilling $n = \frac{\tau_c}{\varepsilon k_0}$ with k_0 the solution of (2.3). In the future, we will always use this value of n, denoted n_0.

4.2. Rescaling. Recall that the wave packet moves a distance of order 1 in time of order 1, and, for a semiclassical wave packet, is of width of order $\varepsilon^{1/2}$. Hence for

times of order ε^γ with $\gamma < 1/2$, in position space, the wave function is localized well away from the transition region. It follows that there should be little contribution to the integral outside $s \in [-\varepsilon^\gamma, \varepsilon^\gamma]$ for $\gamma < 1/2$. We thus restrict the s-integral to this region.

We rewrite (3.11) as $\frac{1}{4\pi\varepsilon} \exp(-\frac{i}{\varepsilon} t \hat{H}^-(k)) \int_\mathbb{R} d\eta \int_{-\varepsilon^\gamma}^{\varepsilon^\gamma} ds\, g(k, \eta, s)$ with

$$g(\eta, k, s) = \exp\left[n \log\left(\frac{k^2 - \eta^2}{4\delta}\right) + \log(k + \eta) + (n+1)\log\left(1 - \frac{2\lambda s}{k + \eta}\right) - \frac{\tau_c}{2\delta\epsilon}|k - \eta| \right.$$
$$\left. - i\frac{\tau_r}{2\delta\epsilon}(k - \eta) + \frac{i}{2\varepsilon}\left[(k^2 - \eta^2 - 4\delta)s - \lambda(k - \eta)s^2\right]\right]\widehat{\phi}^\varepsilon(\eta).$$

We now note that, in order for the phase of the integrand to be stationary in s, we expect $\eta \approx \eta^* = \pm\sqrt{k^2 - 4\delta}$. For a semiclassical wave packet which has sufficient momentum to move past the avoided crossing, the choice of sign will correspond to the sign of the mean momentum of $\widehat{\phi}^\varepsilon$. For this choice of η^* to make sense, it is clear that we require $k^2 - 4\delta \geqslant 0$, and so introduce the cutoff function $\chi_{k^2 > 4\delta}$. The physical meaning of this cutoff is clear when one considers η to be the incoming momentum and k the outgoing momentum: Since the potential gap is 2δ, by energy conservation we have $k^2/2 = \eta^2/2 + 2\delta$, and since we require $\eta^2 > 0$ for the wave packet to move past the crossing, we have $k^2 > 4\delta$.

We now set $\eta = \tilde{\eta}\varepsilon^{1/2} + \eta^*$, where $\tilde{\eta}$ is of order 1 and rescale the s integral by $s = \tilde{s}\varepsilon^{1/2}$, which causes the domain of the $\tilde{s}$ integral to be at least of order 1, and tend to the whole of $\mathbb{R}$ as $\varepsilon \to 0$. Using $\int_\mathbb{R} d\eta \int_{-\varepsilon^\gamma}^{\varepsilon^\gamma} ds\, g(k, \eta, s) = \varepsilon \int_\mathbb{R} d\tilde{\eta} \int_{-\varepsilon^{\gamma - 1/2}}^{\varepsilon^{\gamma - 1/2}} d\tilde{s}\, g(k, \varepsilon^{1/2}\tilde{\eta} + \eta^*, \varepsilon^{1/2}\tilde{s})$, and removing the tildes from now on, we are interested in

(4.5)
$$g(\eta\varepsilon^{1/2} + \eta^*, k, \varepsilon^{1/2}s) = \exp\left[n \log\left(1 - \frac{\eta^2\varepsilon + 2\eta\eta^*\varepsilon^{1/2}}{4\delta}\right) + \log(k + \eta^* + \eta\varepsilon^{1/2}) \right.$$
$$+ (n+1)\log\left(1 - \frac{2\lambda s\varepsilon^{1/2}}{k + \eta^* + \eta\varepsilon^{1/2}}\right) - \frac{\tau_c}{2\delta\epsilon}|k - \eta^* - \eta\varepsilon^{1/2}| - i\frac{\tau_r}{2\delta\epsilon}(k - \eta^* - \eta\varepsilon^{1/2})$$
$$\left. + \frac{i}{2\varepsilon}\left[(-\eta^2\varepsilon - 2\eta\eta^*\varepsilon^{1/2})s\varepsilon^{1/2} - \lambda(k - \eta^* - \eta\varepsilon^{1/2})s^2\varepsilon\right]\right]\widehat{\phi}^\varepsilon(\varepsilon^{1/2}\eta + \eta^*).$$

We now discuss the evaluation of these two integrals.

4.3. The s integral. Since the wave function $\widehat{\phi}^\varepsilon$ is independent of s, we now aim to perform the s-integration explicitly. We now consider the regime where ε is small and k is of order 1. This is necessary as we wish to expand the logarithm term in powers of s, and require that $\frac{2\lambda s\varepsilon^{1/2}}{k + \eta^* + \eta\varepsilon^{1/2}} \ll 1$. This holds since, from the limits of integration, we see that at worst $s\varepsilon^{1/2} \sim \varepsilon^\gamma$ with $\gamma > 0$ and $\eta^* \sim k \sim \eta \sim 1$. Expanding to second order gives

(4.6)
$$\log\left(1 - \frac{2\lambda s\varepsilon^{1/2}}{k + \eta^* + \eta\varepsilon^{1/2}}\right) \approx -\frac{2\lambda s\varepsilon^{1/2}}{k + \eta^* + \eta\varepsilon^{1/2}} - \frac{2\lambda^2 s^2\varepsilon}{(k + \eta^* + \eta\varepsilon^{1/2})^2}.$$

In the small-ε limit, $\varepsilon^{\gamma - 1/2} \to \infty$, which, combined with the above expansion, reduces the s-integral to a Gaussian integral of the form

$$\int_\mathbb{R} \exp(\alpha s^2 + \beta s)ds = \sqrt{-\frac{\pi}{\alpha}}\exp\left(-\frac{\beta^2}{4\alpha}\right) \text{ for } \mathrm{Re}\,(\alpha) < 0.$$

In this case, we have

$$\alpha = -\frac{2(n+1)\lambda^2\varepsilon}{(k+\eta^*+\varepsilon^{1/2}\eta)^2} - \frac{\mathrm{i}\lambda}{2}(k-\eta^*) + \frac{\mathrm{i}\varepsilon^{1/2}\lambda}{2}\eta$$

(where $\mathrm{Re}\,(\alpha) < 0$) and

$$\beta = -\frac{2\lambda(n+1)\varepsilon^{1/2}}{k+\eta^*+\varepsilon^{1/2}\eta} - \mathrm{i}\eta^*\eta - \frac{\mathrm{i}\varepsilon^{1/2}}{2}\eta^2.$$

It therefore remains to calculate the integral over η:

$$
\begin{aligned}
\widehat{\psi_n^-}^\varepsilon&(k,t)\\
&= \frac{\chi_{k^2>4\delta}}{4\sqrt{\pi}\varepsilon}\,\mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}t\hat{H}^-(k)}\int_{\mathbb{R}}\mathrm{d}\eta\,\widehat{\phi}^\varepsilon(\varepsilon^{1/2}\eta+\eta^*)\Big(\tfrac{2(n+1)\lambda^2\varepsilon}{(k+\eta^*+\varepsilon^{1/2}\eta)^2}+\tfrac{\mathrm{i}\lambda}{2}(k-\eta^*)-\tfrac{\mathrm{i}\varepsilon^{1/2}\lambda}{2}\eta\Big)^{-1/2}\\
&\quad\times\exp\Big[n\log\big(1-\tfrac{\eta^2\varepsilon+2\eta\eta^*\varepsilon^{1/2}}{4\delta}\big)+\log(k+\eta^*+\eta\varepsilon^{1/2})\\
&\qquad\quad-\tfrac{\tau_c}{2\delta\epsilon}|k-\eta^*-\eta\varepsilon^{1/2}|-\mathrm{i}\tfrac{\tau_r}{2\delta\epsilon}(k-\eta^*-\eta\varepsilon^{1/2})\Big]\\
&\quad\times\exp\Big[-\Big(-\tfrac{2\lambda(n+1)\varepsilon^{1/2}}{k+\eta^*+\varepsilon^{1/2}\eta}-\mathrm{i}\eta^*\eta-\tfrac{\mathrm{i}\varepsilon^{1/2}}{2}\eta^2\Big)^2\\
&\qquad\quad\Big(-\tfrac{2(n+1)\lambda^2\varepsilon}{(k+\eta^*+\varepsilon^{1/2}\eta)^2}-\tfrac{\mathrm{i}\lambda}{2}(k-\eta^*)+\tfrac{\mathrm{i}\varepsilon^{1/2}\lambda}{2}\eta\Big)^{-1}\Big].
\end{aligned}
$$

For a general $\widehat{\phi}^\varepsilon$, we can say little else, and the integral must be computed numerically. However, in the important case where $\widehat{\phi}^\varepsilon$ is a Gaussian, we can derive a closed-form approximation, which is in excellent agreement with the full dynamics. The main idea is to approximate the integrand in (3.11) in such a way as to produce a Gaussian integral. The first hinderance to this comes from the log terms, which we now consider.

4.4. Expansion of log terms. Along with the expansion in (4.6), we have

$$\log(k+\eta^*+\eta\varepsilon^{1/2}) = \log(k+\eta^*)+\log\big(1+\tfrac{\eta\varepsilon^{1/2}}{k+\eta^*}\big) \approx \log(k+\eta^*)+\tfrac{\eta\varepsilon^{1/2}}{k+\eta^*}-\tfrac{\eta^2\varepsilon}{2(k+\eta^*)^2},$$
$$\log\big(1-\tfrac{\eta^2\varepsilon+2\eta\eta^*\varepsilon^{1/2}}{4\delta}\big) \approx -\tfrac{\eta^2\varepsilon+2\eta\eta^*\varepsilon^{1/2}}{4\delta}-\tfrac{1}{32\delta^2}(\eta^4\varepsilon^2+4\eta^3\eta^*\varepsilon^{3/2}+4\eta^2\eta^{*2}\varepsilon),$$

where we have once again used that $k,\eta^*,\eta\sim 1$.

In order to produce a Gaussian integral, it is necessary to make a number of justifiable approximations. Expanding $(k+\eta^*+\varepsilon^{1/2}\eta)^{-p}$, $p=1,2$ in (4.6) around $\eta\varepsilon^{1/2}=0$ and neglecting terms of order larger than ε in all three logarithm expansions reduces them to

(4.7)
$$\log\big(1-\tfrac{2\lambda s\varepsilon^{1/2}}{k+\eta^*+\eta\varepsilon^{1/2}}\big) \approx -\tfrac{2\lambda s\varepsilon^{1/2}}{k+\eta^*}+\tfrac{2\lambda s\varepsilon\eta}{(k+\eta^*)^2}-\tfrac{2\lambda^2 s^2\varepsilon}{(k+\eta^*)^2},$$
$$\log(k+\eta^*+\eta\varepsilon^{1/2}) \approx \log(k+\eta^*)+\tfrac{\eta\varepsilon^{1/2}}{k+\eta^*}-\tfrac{\eta^2\varepsilon}{2(k+\eta^*)^2},$$
$$\log\big(1-\tfrac{\eta^2\varepsilon+2\eta\eta^*\varepsilon^{1/2}}{4\delta}\big) \approx -\tfrac{\eta^2\varepsilon+2\eta\eta^*\varepsilon^{1/2}}{4\delta}-\tfrac{\eta^2\eta^{*2}\varepsilon}{8\delta^2}.$$

Note that all three expansions now contain terms of at most order two in s and η and thus are of the form required for a Gaussian integral.

4.5. Explicit closed form. One final simplification is necessary to obtain a Gaussian integral: Equation (4.5) still contains the third order terms, namely $\frac{i\varepsilon^{1/2}}{2}\eta^2 s$ and $\frac{i\lambda}{2\varepsilon^{1/2}}\eta s^2$. But here we recall that the stationary phase argument required $s = 0$, and in the scaled variables also $\eta = 0$. This allows us to remove the above terms: Not only are these terms already the highest order in ε, but since we expect the main contribution to the integral to come from the region around $(s, \eta) = (0,0)$, the effects of these terms is negligible.

Inserting the expansions (4.7) into (4.5), ignoring the third order terms in s and η, and setting $\widehat{\phi}^\varepsilon(\eta)$ to be the Gaussian $\widehat{\phi}^\varepsilon(\eta) = \exp(-\frac{c}{\varepsilon}(\eta - p_0)^2)$ gives, for η sufficiently small,

$$g(k, \eta\varepsilon^{1/2} + \eta^*, \varepsilon^{1/2}s) = \exp(\alpha_{2,0}\eta^2 + \alpha_{1,0}\eta + \alpha_{1,1}\eta s + \alpha_{0,1}s + \alpha_{0,2}s^2),$$

with the $\alpha_{i,j}$ given in (2.5). Note that the $\mathrm{sgn}(k)$ in $\alpha_{1,0}$ is necessary if we wish to deal with negative momenta: For $k > 0$, we have $k - \eta^* > 0$ and hence, for small ε, $k - \eta^* - \varepsilon^{1/2}\eta > 0$. Therefore $|k - \eta^* - \varepsilon^{1/2}\eta| = |k - \eta^*| - \varepsilon^{1/2}\eta$. However, for $k < 0$ we have $k - \eta^* - \varepsilon^{1/2}\eta < 0$ and $|k - \eta^* - \varepsilon^{1/2}\eta| = |k - \eta^*| + \varepsilon^{1/2}\eta$.

Gaussian integration now gives

$$(4.8) \quad \int_\mathbb{R} \int_\mathbb{R} \mathrm{d}\eta \, \mathrm{d}s \; g(k, \eta\varepsilon^{1/2} + \eta^*, \varepsilon^{1/2}s)$$

$$= \frac{2\pi}{\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} \exp\left[\frac{\alpha_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}} \right],$$

which holds for $\mathrm{Re}\left(\frac{\alpha_{1,1}^2}{\alpha_{2,0}} - 4\alpha_{0,2}\right) > 0$.

We now check that the above constraint $\mathrm{Re}\left(\frac{\alpha_{1,1}^2}{\alpha_{2,0}} - 4\alpha_{0,2}\right) > 0$ is satisfied for a suitable parameter regime. For ease of analysis, we note that n_0 is approximately given by $\tau_c/(\varepsilon\sqrt{p_0^2 + 4\delta}) = \mathcal{O}(\varepsilon^{-1})$. Taking ε to be small, to leading order we find

$$\alpha_{2,0} = -\frac{n_0\varepsilon}{4\delta} - \frac{n_0\eta^{*2}\varepsilon}{8\delta^2} - c \approx -\frac{\tau_c}{4\delta\sqrt{p_0^2+4\delta}} - \frac{\tau_c\eta^{*2}}{8\delta^2\sqrt{p_0^2+4\delta}} - c,$$

$$\alpha_{1,1} = -i\eta^* + \frac{2n_0\varepsilon\lambda}{(k+\eta^*)^2} \approx -i\eta^* + \frac{2\tau_c\lambda}{(k+\eta^*)^2\sqrt{p_0^2+4\delta}},$$

$$\alpha_{0,2} = -i\frac{2\delta\lambda}{(k+\eta^*)} - \frac{2(n_0+1)\lambda^2\varepsilon}{(k+\eta^*)^2} \approx -i\frac{2\delta\lambda}{(k+\eta^*)} - \frac{2\tau_c\lambda^2}{(k+\eta^*)^2\sqrt{p_0^2+4\delta}}.$$

Note that the real part of $-4\alpha_{0,2}$ is nonnegative, so we need only check the sign of $\mathrm{Re}(\alpha_{1,1}^2/\alpha_{2,0})$. Using $\alpha_{1,1}^2 = -\eta^{*2} + \frac{4\tau_c^2\lambda^2}{(k+\eta^*)^4(p_0^2+4\delta)} - i\frac{4\tau_c\lambda\eta^*}{(k+\eta^*)^2\sqrt{p_0^2+4\delta}}$ gives

$$\mathrm{Re}\left(\frac{\alpha_{1,1}^2}{\alpha_{2,0}} - 4\alpha_{0,2}\right) \geqslant \frac{8\delta^2}{(k+\eta^*)^4\sqrt{p_0^2+4\delta}} \left[\frac{\eta^{*2}(k+\eta^*)^4(p_0^2+4\delta) - 4\tau_c^2\lambda^2}{8\delta^2 c\sqrt{p_0^2+4\delta} + 2\delta\tau_c + \tau_c p_0^2} \right].$$

Since $\tau_c > 0$, this is clearly positive when p_0 is sufficiently large. Hence the regime of interest is ε small and p_0 large. We then have

$$\widehat{\psi_n^-}^\varepsilon(k, t) \approx e^{-\frac{i}{\varepsilon}t\hat{H}^-} \frac{1}{2\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} \exp\left[\frac{\alpha_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}} \right]$$

$$(4.9) \qquad \times (\eta^* + k) \, e^{-\frac{c}{\varepsilon}(\eta^* - p_0)^2} \; e^{-\frac{\tau_c}{2\delta\epsilon}|k-\eta^*|} \; e^{-i\frac{\tau_r}{2\delta\epsilon}(k-\eta^*)} \, \chi_{k^2 > 4\delta},$$

with the $\alpha_{i,j}$ as given in (2.5).

We note that setting $\lambda = 0$ gives $\alpha_{0,1} = \alpha_{0,2} = 0$ and $\alpha_{1,1} = \mathrm{i}\eta^*$, and returns the n-independent form (see [3])

$$\widehat{\psi_n^-}^\varepsilon (k,0) \approx \frac{(\eta^*+k)}{2|\eta^*|}\, \mathrm{e}^{-\frac{c}{\varepsilon}(\eta^*-p_0)^2}\, \mathrm{e}^{-\frac{\tau_c}{2\delta\epsilon}|k-\eta^*|}\, \mathrm{e}^{-\mathrm{i}\frac{\tau_r}{2\delta\epsilon}(k-\eta^*)}\, \chi_{k^2>4\delta}.$$

4.6. Asymptotics of $\alpha_{i,j}$. We now show that, under suitable assumptions, the $\alpha_{i,j}$ given in (2.5) may be somewhat simplified. Note that $n_0 = \mathcal{O}(\varepsilon^{-1})$ and so $\alpha_{2,0} = \mathcal{O}(1)$ and $\alpha_{1,0} = \mathcal{O}(\varepsilon^{-1/2})$. However, the two terms which come from the n-independent prefactor $k+\eta$ in (3.11) are of lower order than the remaining terms in the respective $\alpha_{i,j}$, and, hence, for small ε may safely be neglected. From the point of view of exponential asymptotics this is completely natural, one would normally fix the slowly varying terms (i.e., independent of ε, and in this case of n) at the stationary value of the integrand. For clarity, we now have

$$\alpha_{2,0} = -\frac{n_0\varepsilon}{4\delta} - \frac{n_0\eta^{*2}\varepsilon}{8\delta^2} - c, \qquad \alpha_{1,0} = -\frac{n_0\eta^*\varepsilon^{1/2}}{2\delta} - \frac{2c(\eta^*-p_0)}{\varepsilon^{1/2}} + \frac{\mathrm{sgn}(k)\tau_c}{2\delta\varepsilon^{1/2}} + \mathrm{i}\frac{\tau_r}{2\delta\varepsilon^{1/2}}.$$

One additional simplification is possible when p_0 is large and the wave function is quickly decaying (i.e., c is also large). In this case the modulus of the integrand is negligible unless η^* is close to p_0. For such a range, using $n_0 \approx \tau_c/(\varepsilon\sqrt{p_0^2+4\delta})$ shows that the first three terms in $\alpha_{1,0}$ above are all negligible. Further, if the potential is symmetric, $\tau_r = 0$ and we may use the approximation $\alpha_{1,0} = 0$. In addition, in this limit, and with the assumption that λ is not too large, we see that the second terms in each of $\alpha_{1,1}$ and $\alpha_{0,2}$ in (2.5) are negligible. To conclude, for ε small, p_0 and c large, and λ not too large, we have

$$\alpha_{2,0} \approx -\frac{\tau_c(2\delta+\eta^{*2})}{8\delta^2\eta^*} - c, \quad \alpha_{1,0} \approx \frac{\mathrm{i}\tau_r}{2\delta\sqrt{\varepsilon}}, \quad \alpha_{1,1} \approx -\mathrm{i}\eta^*,$$
$$\alpha_{0,1} \approx -\frac{2\lambda}{\sqrt{\varepsilon}(k+\eta^*)\eta^*}, \quad \alpha_{0,2} \approx -\frac{\mathrm{i}2\delta\lambda}{(k+\eta^*)}.$$

4.7. Additional phase shift. While testing the formula (4.9) against ab-initio numerics, we found a discrepancy by a phase shift which, in the region where the wave function has significant magnitude, is constant in k. We believe that this effect comes from one of the approximations detailed above, but have currently been unable to determine its exact cause. For many applications this phase shift is unimportant. Since it is constant in k, all expected values of observables are correctly reproduced by (4.9) in the case of a single Gaussian wave packet. Where the phase shift begins to matter is for interference phenomena, and when considering a superposition of Gaussians (see below) such that their centers are at significantly different locations in k; then the phase shift will not be constant in k anymore, and we will get wrong predictions for position expected values.

It is therefore desirable to have a method of removing this effect of the approximations. We now describe a heuristic method which has proven to be effective for a wide range of potentials and initial Gaussian wave packets. Consider (4.9) for $\lambda \neq 0$ and the wave function normalized by a prefactor $\sqrt{c/(\pi\varepsilon)}$. Note that if $\lambda = 0$, the following argument is invalid. However, setting $\lambda = 0$ in (4.9) we see that the phase depends only on τ_r, which agrees with that of [2] and the corresponding numerics.

We are going to consider the phase of the transmitted wave function in the limit $c \to \infty$, i.e., the incoming wave packet approximating a δ-function at $\eta = p_0$. Since the numerical phase shift is independent of k, we need to choose a value of k at which to

evaluate this phase. In the classical picture, from energy conservation we see that the the transmitted wave packet should be approximately a δ-function at $k = \sqrt{p_0^2 + 4\delta}$, and hence we consider this value of k, where the sign of the square root is chosen to match that of p_0.

We are therefore interested in

$$\widehat{\psi_n^-}^\varepsilon(\sqrt{p_0^2 + 4\delta}, 0) \approx \frac{\sqrt{c}}{\sqrt{\pi\varepsilon}} \frac{1}{2\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} \exp\left[\frac{\alpha_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right]$$
$$\times a_0\, e^{\frac{-\tau_c}{2\delta\varepsilon}|b_0|}\, e^{\frac{-i\tau_r}{2\delta\varepsilon}b_0}\, \chi_{k^2 > 4\delta},$$

where $a_0 = \sqrt{p_0^2 + 4\delta} + p_0$ and $b_0 = \sqrt{p_0^2 + 4\delta} - p_0$. We now investigate the phase of this wave packet when $c \to \infty$ and note that there are contributions from both the square root and the exponent.

We write $\alpha_{2,0} = \beta_{2,0} - c$, and, since $\eta^* = p_0$, this is the only term that depends on c. Consider first the prefactor

$$\frac{\sqrt{c}}{\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} = \frac{\sqrt{c}}{\sqrt{4(\beta_{2,0} - c)\alpha_{0,2} - \alpha_{1,1}^2}} = \frac{1}{\sqrt{-4\alpha_{0,2} + \frac{1}{c}(4\beta_{2,0}\alpha_{0,2} - \alpha_{1,1}^2)}}$$

$$(4.10) \qquad \overset{c\to\infty}{\to} \frac{1}{\sqrt{-4\alpha_{0,2}}}.$$

For the exponent, we have

$$\frac{\alpha_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}} = \frac{(\beta_{2,0} - c)\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4(\beta_{2,0} - c)\alpha_{0,2}}$$
$$= \frac{-\alpha_{0,1}^2 + \frac{1}{c}(\beta_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1})}{4\alpha_{0,2} + \frac{1}{c}(\alpha_{1,1}^2 - 4\beta_{2,0}\alpha_{0,2})}$$

$$(4.11) \qquad \overset{c\to\infty}{\to} -\frac{\alpha_{0,1}^2}{4\alpha_{0,2}}.$$

It remains to determine the phases of (4.10) and (4.11). We write $\alpha_{1,0} = \beta_{1,0}$, $\alpha_{1,1} = \beta_{1,1} + i\gamma_{1,1}$, $\alpha_{0,1} = \beta_{0,1}$, and $\alpha_{0,2} = \beta_{0,2} + i\gamma_{0,2}$, with $\beta_{i,j}, \gamma_{i,j} \in \mathbb{R}$. For (4.10), we note that $-\alpha_{0,2} = -(\beta_{0,2} + i\gamma_{0,2}) =: r\, e^{i\theta}$, where $\theta = \arctan(\frac{\gamma_{0,2}}{\beta_{0,2}})$, giving the phase of (4.10) as $-\frac{1}{2}\arctan(\frac{\gamma_{0,2}}{\beta_{0,2}})$. Using that $\gamma_{0,2} = -\lambda b_0/2$, $\beta_{0,2} = -2(n_0 + 1)\lambda^2\varepsilon/a_0^2$, and $a_0 b_0 = 4\delta$, we have $-\frac{1}{2}\arctan(\frac{a_0\delta}{(n_0+1)\varepsilon\lambda})$.

For the (4.11) we have $-\frac{\beta_{0,1}^2}{4(\beta_{0,2} + i\gamma_{0,2})} = -\frac{\beta_{0,1}^2(\beta_{0,2} - i\gamma_{0,2})}{4(\beta_{0,2}^2 + \gamma_{0,2}^2)}$. Hence, using that $\beta_{0,1} = 2(n_0 + 1)\varepsilon^{1/2}\lambda/a_0$, this phase is given by $-\frac{(n_0+1)^2\varepsilon\lambda a_0\delta}{2(n+1)^2\lambda^2\varepsilon^2 + 2\delta^2 a_0^2}$, and the total phase by

$$-\frac{(n_0 + 1)^2\varepsilon\lambda a_0\delta}{2(n_0 + 1)^2\lambda^2\varepsilon^2 + 2\delta^2 a_0^2} + \frac{1}{2}\arctan\left(-\frac{a_0\delta}{(n_0 + 1)\varepsilon\lambda}\right) - \frac{\tau_r}{2\delta\varepsilon}b_0.$$

One further adjustment seems to be necessary. One would expect that the phase is continuous in λ, and we know that for $\lambda = 0$, the phase is $-\frac{\tau_r}{2\delta\varepsilon}b_0$. However, the limit of the λ-dependent terms in above expression is $-1/2\arctan(\text{sgn}(\lambda)\,\text{sgn}(a_0)\infty) = -\text{sgn}(\lambda)\,\text{sgn}(p_0)\pi/4$, and hence we take the phase shift to be

$$(4.12) \qquad \varphi(p_0) = -\frac{(n_0 + 1)^2\varepsilon\lambda a_0\delta}{2(n_0 + 1)^2\lambda^2\varepsilon^2 + 2\delta^2 a_0^2} - \frac{1}{2}\arctan\left(\frac{a_0\delta}{(n_0 + 1)\varepsilon\lambda}\right) + \text{sgn}(\lambda p_0)\frac{\pi}{4},$$

which seems to give very good numerical results for a wide range of all parameters.

To summarize, we now have an explicit closed form for the transmitted wave packet given an initial Gaussian of the form (2.1),

$$\widehat{\psi_n^-}^\varepsilon (k,t) \approx e^{-\frac{i}{\varepsilon}t\hat{H}^-} \frac{1}{2\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} \exp\left[\frac{\alpha_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right]$$

(4.13)
$$\times (\eta^* + k)\, e^{-\frac{\tau_c}{2\delta\epsilon}|k-\eta^*|}\, e^{-i\frac{\tau_r}{2\delta\epsilon}(k-\eta^*)}\, e^{-i\varphi(p_0)}\, \widehat{\phi}^\varepsilon(\eta^*)\chi_{k^2>4\delta},$$

with $\varphi(p_0)$ as given in (4.12) and the $\alpha_{i,j}$ as in (2.5), or, alternatively, with the simplifications from section 4.6. n_0 is given as indicated in (2.3). We thus have finished the justification of the algorithm given in section 2.

4.8. Phase shift for large momentum. For large momentum, we use the approximations $a_0 = 2p_0$ and $n_0 = \tau_c/(\varepsilon p_0)$ and get the phase shift $\varphi(p_0)$ as $\varphi(p_0) \approx -\frac{1}{\varepsilon}\frac{\tau_c^2\lambda\delta p_0}{\tau_c^2\lambda^2+4\delta^2 p_0^4} - \frac{1}{2}\arctan(\frac{4p_0^2\delta}{\tau_c\lambda}) + \mathrm{sgn}(\lambda p_0)\frac{\pi}{4}$ Note that if $p_0 \to \infty$, then $\varphi(p_0) \to 0$. More concretely, we are interested in the rate at which it goes to zero when we write p_0 in terms of ε. Letting $p_0 = \varepsilon^{-\alpha}$ gives

$$\varphi \approx -\frac{1}{\varepsilon}\frac{\tau_c^2\lambda\delta}{\tau_c^2\lambda^2\varepsilon^{1+\alpha} + 4\delta^2\varepsilon^{1-3\alpha}} - \frac{1}{2}\arctan\left(\frac{4\varepsilon^{-2\alpha}\delta}{\tau_c\lambda}\right) + \mathrm{sgn}(\lambda p_0)\frac{\pi}{4}.$$

Hence if $\alpha > 1/3$, we see that $\varphi(\varepsilon^{-\alpha}) \to 0$ as $\varepsilon \to 0$. We note that this value of $1/3$ is the same value as that for which we have rigorous bounds on the errors; cf. the appendix.

From this analysis, it appears that the phase shift is a consequence of taking momenta that are too small (or equivalently, ε that are too large).

5. Non-Gaussian incoming wave functions.

5.1. Extension to Hagedorn wave functions. We note that a general Hagedorn wave function [8] in one dimension is a Hermite polynomial multiplied by a Gaussian. By linearity of the integral, it is sufficient to consider the case $\widehat{\phi}^\varepsilon(\eta) = \eta^p \exp\left(-c(\eta - p_0)^2/\varepsilon\right)$, $p \in \mathbb{N}$. We perform the same rescaling as in section 4.2 and note that the monomial prefactor becomes $(\eta\varepsilon^{1/2} + \eta^*)^p = \sum_{j=0}^p \binom{p}{j}(\eta\varepsilon^{1/2})^j\eta^{*(p-j)}$. Using the same arguments as above, we obtain for each j the integral

$$\int_{\mathbb{R}}\int_{\mathbb{R}} d\eta ds\, (\varepsilon^{1/2}\eta)^j \exp(\alpha_{2,0}\eta^2 + \alpha_{1,0}\eta + \alpha_{1,1}\eta s + \alpha_{0,1}s + \alpha_{0,2}s^2).$$

We now note that $\partial_{\alpha_{1,0}}^j \exp(\alpha_{1,0}\eta) = \eta^j \exp(\alpha_{1,0}\eta)$ and since differentiation with respect to $\alpha_{1,0}$ commutes with the integral, we have

$$\int_{\mathbb{R}}\int_{\mathbb{R}} d\eta\, ds\, (\varepsilon^{1/2}\eta)^j \exp(\alpha_{2,0}\eta^2 + \alpha_{1,0}\eta + \alpha_{1,1}\eta s + \alpha_{0,1}s + \alpha_{0,2}s^2)$$

$$= \varepsilon^j \partial_{\alpha_{1,0}}^j \frac{2\pi}{\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} \exp\left[\frac{\alpha_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right]$$

$$= \varepsilon^j \frac{2\pi}{\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} \exp\left[\frac{\alpha_{2,0}\alpha_{0,1}^2}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right] \partial_{\alpha_{1,0}}^j \exp\left[\frac{\alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right].$$

In more generality, we wish to compute $\partial_\alpha^j f$ where $f = \exp(-a\alpha^2 + b\alpha) = \exp(-\frac{2a}{2}(\alpha - \frac{b}{2a})^2 + \frac{b^2}{4a})$. It is clear that this will be f multiplied by a scaled and

shifted Hermite polynomial. In fact, we have $\partial_\alpha^j f = (-\sqrt{2a})^j H_j\left(\sqrt{2a}(\alpha - \frac{b}{2a})\right)f$, where H_j is the probabilist's Hermite polynomial of order j (namely chosen such that the coefficient of the leading order is 1).

In our case, we have $a = -\frac{\alpha_{2,0}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}$ and $b = -\frac{\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}$, giving $\frac{b}{2a} = \frac{\alpha_{0,1}\alpha_{1,1}}{2\alpha_{0,2}}$. Hence (3.11) with $\widehat{\phi}^\varepsilon(\eta) = \eta^p \exp\left(-c(\eta - p_0)^2/\varepsilon\right)$ is given by

$$
\begin{aligned}
\widehat{\psi_n^-}^\varepsilon(k,t) \approx{}& e^{-\frac{i}{\varepsilon}t\hat{H}^-(k)} \frac{\chi_{k^2>4\delta}}{2\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} \exp\left[\frac{\alpha_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right] \\
&\times (\eta^* + k)\, e^{-\frac{c}{\varepsilon}(\eta^* - p_0)^2}\, e^{-\frac{\tau_c}{2\delta\epsilon}|k-\eta^*|}\, e^{-i\frac{\tau_r}{2\delta\epsilon}(k-\eta^*)} \\
&\times \sum_{j=0}^p \binom{p}{j} \varepsilon^j \eta^{*(p-j)} \left(\frac{2\alpha_{0,2}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right)^{j/2} \\
&\times H_j\left[\left(\frac{2\alpha_{0,2}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right)^{1/2} \left(\alpha_{1,0} - \frac{\alpha_{0,1}\alpha_{1,1}}{2\alpha_{0,2}}\right)\right],
\end{aligned}
$$

with the $\alpha_{i,j}$ as given in (2.5).

Using the identity $H_p(x+y) = x^p \sum_{j=0}^p \binom{p}{j} x^{-j} H_j(y)$, with $x = \frac{\eta^*}{\varepsilon}\left(\frac{2\alpha_{0,2}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right)^{-1/2}$, and $y = \left(\frac{2\alpha_{0,2}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right)^{1/2}\left(\alpha_{1,0} - \frac{\alpha_{0,1}\alpha_{1,1}}{2\alpha_{0,2}}\right)$ gives

$$
\begin{aligned}
\widehat{\psi_n^-}^\varepsilon(k,t) \approx{}& e^{-\frac{i}{\varepsilon}t\hat{H}^-(k)} \frac{\chi_{k^2>4\delta}}{2\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} \exp\left[\frac{\alpha_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right] \\
&\times (\eta^* + k)\, e^{-\frac{c}{\varepsilon}(\eta^* - p_0)^2}\, e^{-\frac{\tau_c}{2\delta\epsilon}|k-\eta^*|}\, e^{-i\frac{\tau_r}{2\delta\epsilon}(k-\eta^*)}\, \varepsilon^p \left(\frac{2\alpha_{0,2}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right)^{p/2} \\
&\times H_j\left[\frac{\eta^*}{\varepsilon}\left(\frac{2\alpha_{0,2}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right)^{-1/2} \right. \\
&\left. + \left(\frac{2\alpha_{0,2}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right)^{1/2} \left(\alpha_{1,0} - \frac{\alpha_{0,1}\alpha_{1,1}}{2\alpha_{0,2}}\right)\right].
\end{aligned}
$$

We are interested in the leading order behavior with respect to ε. From (2.5) and using $n_0 = \mathcal{O}(\varepsilon^{-1})$ we see that $\alpha_{2,0}, \alpha_{1,1}, \alpha_{0,2}$ are all $\mathcal{O}(1)$ whilst $\alpha_{1,0}$ and $\alpha_{0,1}$ are $\mathcal{O}(\varepsilon^{-1/2})$. Hence $\frac{2\alpha_{0,2}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}} = \mathcal{O}(1)$ and $\alpha_{1,0} - \frac{\alpha_{0,1}\alpha_{1,1}}{2\alpha_{0,2}} = \mathcal{O}(\varepsilon^{-1/2})$, which, in particular, shows that the prefactor is $\mathcal{O}(\varepsilon^n)$ whilst the argument of the Hermite polynomial is $\mathcal{O}(\varepsilon^{-1})$. Thus, to leading order, only the highest power of the Hermite polynomial contributes, giving

$$
\begin{aligned}
\widehat{\psi_n^-}^\varepsilon(k,t) \approx{}& e^{-\frac{i}{\varepsilon}tH^-} \frac{1}{2\sqrt{4\alpha_{2,0}\alpha_{0,2} - \alpha_{1,1}^2}} \exp\left[\frac{\alpha_{2,0}\alpha_{0,1}^2 + \alpha_{0,2}\alpha_{1,0}^2 - \alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2 - 4\alpha_{2,0}\alpha_{0,2}}\right] \\
&\times (\eta^* + k)\, e^{-\frac{c}{\varepsilon}(\eta^* - p_0)^2}\, e^{-\frac{\tau_c}{2\delta\epsilon}|k-\eta^*|}\, e^{-i\frac{\tau_r}{2\delta\epsilon}(k-\eta^*)}\, \eta^{*p}\chi_{k^2>4\delta},
\end{aligned}
$$

which is precisely (4.9) with the Gaussian replaced by $\eta^p \exp(-c(\eta - p_0)^2/\varepsilon)$.

We note that the error in this closed form is expected to be of order $\sqrt{\varepsilon}$. Whilst this could be improved by taking further terms in the expansion, in the following we choose to concentrate on the case of a wave packet which has been decomposed into a linear combination of Gaussians. The main reason for this is the heuristic phase correction which is discussed in section 4.7. From numerical studies, we see that this works well only for Gaussian wave packets, and without this correction, the relative error between the formula and the "exact" numerical wave packet is of the order of 10%, compared to an error of around 2% for a Gaussian wave packet with the phase correction.

5.2. General wave packets as superpositions of Gaussians. Due to the strong reliance on the wave packet being a Gaussian in the preceding discussion, formula (4.9) is not immediately applicable to general wave packets. However, we propose a simple algorithm which allows use of (4.9) in many cases of chemical interest.

The main idea is that we can decompose such a wave packet into Gaussians. Whilst for a general semiclassical wave packet this may be very difficult, for systems of chemical interest we suggest that this is, in fact, relatively straightforward. For a given two-level system, the potential energy surface around the minimum of the ground state will be approximately quadratic, and hence the ground state may be taken to be a Gaussian. When excited to the upper level, it remains Gaussian and has mean momentum zero. It has been shown by Hagedorn [7] that, under suitable regularity assumptions on the wave packet, and physically realistic assumptions on the potential, the wave packet at time t is approximated up to errors of $\mathcal{O}(\varepsilon^{1/2})$ by another Gaussian, whose coefficients can be found by solving a system of ODEs. Hence, in particular, the wave packet at the crossing point can be taken to be a Gaussian, which introduces errors of order $\mathcal{O}(\varepsilon^{1/2})$. Note that up to this point we are studying one-level dynamics, and so absolute errors are as good as relative errors.

For a more general wave packet, or to obtain higher-order accuracy, the results of [7] suggest decomposing the wave packet into Hagedorn wave packets, which, for sufficiently regular wave packets, allows arbitrary accuracy. In general, if the original wave packet is formed from a linear combination of the first J Hagedorn wave packets, the ODEs must be solved for $J + 3\ell - 3$ Hagedorn wave packets to get an error of $\mathcal{O}(\varepsilon^{\ell/2})$. Thus, for nearly Gaussian initial wave packets, one needs very few Hagedorn wave packets to get very small errors. In order to apply our phase shift, it would be necessary to decompose these low-order Hagedorn wave packets into Gaussians. As the Hagedorn wave packets are given in their very specific functional form, this is significantly more straightforward than decomposing a general semiclassical wave packet into Gaussians. This process should be aided by the fact that the mean momentum of the initial wave packet is zero, and hence we do not need to fit highly oscillatory phases.

From now on, we assume that we have decomposed the initial wave packet into Gaussians. We now evolve each Gaussian using Hagedorn dynamics [16] on the upper level until the mean position of the wave packet coincides with the crossing point (which we choose without loss of generality to be at $x = 0$). We then transform into Fourier space (which can be done analytically), giving a wave packet of the form

$$(5.1) \qquad \sum_{j=1}^{N} A_j \exp\left(-\frac{(p-p_i)^2}{\sigma_j^2 \varepsilon}\right) \exp\left(\mathrm{i}\frac{px_j}{\varepsilon}\right),$$

where in position space x_j is the offset from the crossing point.

We now need to deal with the fact that the Gaussians reach the crossing point at different times. We first note that, for small ε, this should be a small effect for semiclassical wave packets: Since the wave packet is localized in a $\sqrt{\varepsilon}$ neighborhood of zero in position space, we have $x_j = \mathcal{O}(\sqrt{\varepsilon})$. As discussed in section 3.2, on a $\sqrt{\varepsilon}$ neighborhood of the origin and for times of order $\sqrt{\varepsilon}$, the dynamics are well approximated by the explicit propagators (3.9). Since the wave packets move with the speed of order one, this is still the region of interest and we may simply insert the complex Gaussian into (3.11).

Applying the rescaling as described in section 4.2 gives an extra term in the exponent in (4.5) of the form $\mathrm{i}x_j(\eta^* + \varepsilon^{1/2}\eta)/\varepsilon$. The η^* term combines with the Gaussian term in η^* to give the wave packet evaluated at η^* as before. The remaining term provides a contribution of the form $\mathrm{i}x_j/\varepsilon^{1/2}$ to $\alpha_{1,0}$ in (2.5).

It is now easy to see that in the small ε limit this term is negligible. Since $x_j = \mathcal{O}(\sqrt{\varepsilon})$ we see that the new term in $\alpha_{1,0}$ is order one. In contrast, the dominant terms in $\alpha_{1,0}$ are of order $\varepsilon^{-1/2}$ and one may apply (4.9) directly to the complex Gaussian.

We note that for the values of ε under consideration in the numerics, ignoring this correction increases the relative error by the order of 0.1%, which is quite significant given the high accuracy of the final formula. In the implementation of the non-Gaussian wave packet below, we therefore included the additional term $\mathrm{i}x_j/\varepsilon^{1/2}$ in the expression for $\alpha_{0,1}$.

The above analysis suggests a simple and efficient algorithm for calculating the form of the transmitted wave packet, even if not of Gaussian form, given an initial wave packet $\psi_{-\infty}$ located well away from the transition point in position space.

1. Decompose the initial wave packet into a linear combination of Gaussians, as described above.
2. Evolve the initial wave packet on the upper BO level using Hagedorn dynamics until its center of mass reaches the transition point. This can either be pre-determined by finding the point at which the two energy levels are closest, or, as would be required in higher dimensions, by monitoring the energy gap at the center of mass over time and determine its minimum.
3. Transform the resulting wave packet into momentum space, giving a linear combination of complex Gaussians as in (5.1).
4. Apply formula (2.4) to each complex Gaussian in turn and take the corresponding linear combination.
5. Evolve the resulting transmitted wave packet using the BO dynamics on the lower level, until the center of mass reaches the scattering region.

Assuming that the energy levels become constant in the scattering regime, the computed wave packet will agree up to small errors with that computed using the full coupled dynamics.

In practice the formula is more accurate for narrow Gaussians (since this improves a number of the approximations including the choice of fixed n_0 and the heuristic phase shift) and thus it may be worth constraining the variances of the Gaussians. Since the application of the formula is cheap (simply multiplications in Fourier space over a region in which the modulus of the wave packet is significant—comparable to one time step in uncoupled BO dynamics) and steps (2–4) scale linearly with the number of Gaussians, increasing the number of Gaussians whilst decreasing their variances would be a reasonable approach to increase accuracy.

It is important to realize that, although this algorithm performs a molecular dynamics calculation using Gaussian wave packets, it does not share the obstructions of

most Gaussian-based methods (see, e.g., [22]). These occur mainly due to the Gaussians being not orthogonal, and the resulting ill-conditioning of various matrices under time evolution. Since our Gaussians are evolved independently, transmitted at the crossing point, and resummed on the lower level, we do not encounter such problems. In higher dimensions, the use of Hagedorn dynamics rather than simple grid-based methods is almost compulsory, as such naïve methods are computationally intractable.

6. Numerics. We now compare the results of formula (2.4) to those of high-precision fully coupled numerics. For ease of demonstration, we set the transition point to be at $x = 0$ and $t = 0$ and choose to specify the wave packet ϕ as a linear combination of complex Gaussians in momentum space at the crossing time. This simplifies the implementation of the above algorithm, as $\widehat{\phi}^\varepsilon$ is already in the required form. Further, we set $\varepsilon = 1/50$, which gives reasonably small transition probabilities, whilst still enabling the "exact" calculations to be performed. Note that, when transformed to position space, both examples have mean position zero.

To begin both the full numerics and the implementation of the above algorithm, we evolve ϕ on the upper BO surface to large negative time (i.e., to a position where the potentials are essentially flat) to give a good approximation $\phi_{-T} \approx \psi_{-\infty}$.

The full numerics were performed using a symmetric Strang splitting in MATLAB with initial condition ϕ_{-T}, which is run to a time $t_* > 0$, where once again the potentials are essentially flat. In particular, for times $t > t_*$, the lower component $\|\psi_0^-(t)\|$ is constant. We then evolve $\psi_0^-(t_*)$ backwards in time to $t = 0$ and compare its Fourier transform to formula (2.4). The calculation was performed on a grid with 16,384 points in both the position ($[-40, 40]$) and corresponding momentum ($[-12.87, 12.87]$) spaces, with $T = t_* = 4$ and 1,000 time steps. Doubling both the number of space and time gridpoints produces a wave function which differs from this computation by around 0.01% in the L^2 norm, and hence we take the numerical simulation to be "exact."

We choose $Z = \alpha \tanh(x) + \beta x^2 / \cosh(x)$, $X = \delta$, and $d = \lambda \tanh(x)$. For these choices, δ and λ correspond to their earlier use, the ratio α^2/δ determines the second derivative of ρ at the transition point, and β primarily affects the asymmetry of the potential. In particular, $\beta = 0$ gives $\tau_r = 0$. We set $\alpha = 0.5$, $\beta = -0.4$, $\delta = 0.5$, and $\lambda = 1$. This leads to the two potential surfaces given in Figure 1, with $\tau_\delta = -0.16611 + 0.53772i$, which can be easily calculated numerically.

The first wave packet we treat is given by the complex Gaussian $A \exp\big(-c(p - p_0)^2/(2\varepsilon)\big)$, with $p_0 = 5$, $c = 1/(2\sigma^2)$, $\sigma = \sqrt{2}$, and A chosen such that the wave packet is normalized in L^2. The second case we consider is a linear combination of three complex Gaussians of the form (5.1) where $|A_j| = A$, $j = 1, 2, 3$, which, in turn, is chosen to normalize the wave packet. The remaining parameters are given, with $c = 1/(2\sigma^2)$, by

A_j	p_j	σ_j	x_j
A	5.00	1.414	-0.0238
A	5.15	1.664	0.0186
$-A$	4.90	0.714	0.0328

Results of the numerical calculations, and comparison with the results obtained via formula (2.4), are given in Figure 2 for the Gaussian case, and Figure 3 for the non-Gaussian case. In both cases, the relative error is less than 2% over the full interval where the transmitted wave function is essentially supported. The transition probability $\|\psi^-\|^2$ in both cases is of the order 10^{-5} (3.03×10^{-5} and 3.48×10^{-5} for the
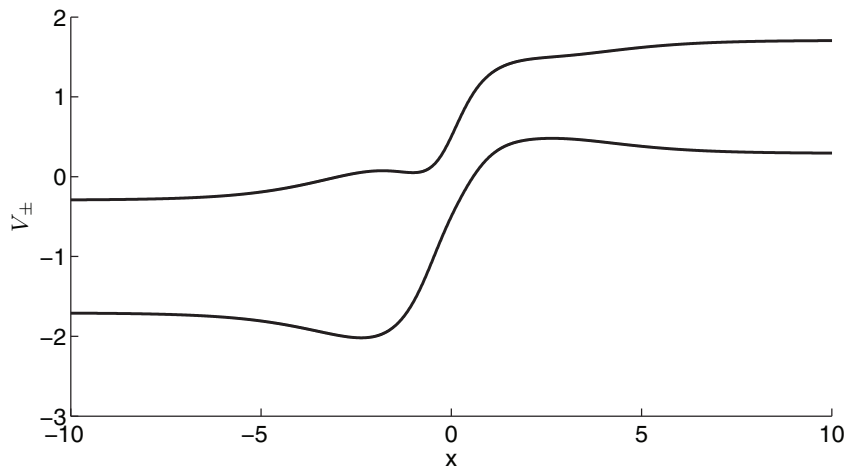
FIG. 1. *The two adiabatic energy surfaces $V_\pm = \pm\rho(x) + d(x)$ with $\rho(x) = \sqrt{X^2(x) + Z^2(x)}$. $Z = \alpha \tanh(x) + \beta x^2/\cosh(x)$, $X = \delta$, $d = \lambda \tanh(x)$, with the parameters $\alpha = 0.5$, $\beta = -0.4$, $\delta = 0.5$, and $\lambda = 1$. Note that the avoided crossing (minimum of the energy gap) is at $x = 0$.*

Gaussian and non-Gaussian cases, respectively). In addition to these two examples, we have tested a wide range of parameters for both the potentials and semiclassical wave functions, and all results are good to within a few percent. They deteriorate only when ε (and thus also $\|\psi^-\|$) becomes too large and we leave the adiabatic regime, or when p_0 (and thus also $\|\psi^-\|$) gets too small and our many approximations requiring that p_0 is suitably large break down. In particular, the relative error is less than a few percent when the transition probability is in the range 10^{-2}–10^{-15}.

Appendix A. Rigorous asymptotic estimates for high incoming momenta. In this section we show rigorously that when $p \gg \varepsilon^{-1/3}$, the off-diagonal element $\kappa_n^\pm(p, q)$ of the superadiabatic Hamiltonian is dominated by its highest order in p, i.e., the term $p^n \kappa_{n,0}^\pm(q)$. We will also restrict our attention to the case where $\rho(q)$ is constant.

We introduce a family of norms, first used in [5], that will be useful in what follows. For $\tau_{\mathrm{c}} > 0$ and $I \subset \mathbb{R}$, we define

$$(A.1) \qquad \|f\|_{(I,\alpha,\tau_{\mathrm{c}})} := \sup_{t \in I} \sup_{k \geqslant 0} \left|\partial^k f(t)\right| \frac{\tau_{\mathrm{c}}^{\alpha+k}}{\Gamma(\alpha + k)} \leqslant \infty$$

for a function $f \in C^\infty$ on the real line. We also define

$$F_{\alpha,\tau_{\mathrm{c}}}(I) = \left\{ f \in C^\infty(I) : \|f\|_{(I,\alpha,\tau_{\mathrm{c}})} < \infty \right\}.$$

When τ_{c} and I are fixed, we will simply write $\|\cdot\|_{(\alpha)}$ and F_α. In [4] we prove

$$(A.2) \qquad \sup_{q \in I} \left|\partial^k f(q)\right| \leqslant \frac{\Gamma(\alpha + k)}{\tau_{\mathrm{c}}^{\alpha+k}} \|f\|_{(I,\alpha,\tau_{\mathrm{c}})} \quad \forall k \geqslant 0,$$

$$(A.3) \qquad \|f'\|_{(I,\alpha+1,\tau_{\mathrm{c}})} \leqslant \|f\|_{(I,\alpha,\tau_{\mathrm{c}})},$$

$$(A.4) \qquad \left\|\int_s^t f(r)\, \mathrm{d}r\right\|_{(I,\alpha-1,\tau_{\mathrm{c}})} \leqslant \max\left\{ \frac{(\alpha-1)|t-s|}{\tau_{\mathrm{c}}}, 1 \right\} \|f\|_{(\alpha)},$$

$$(A.5) \qquad \|fg\|_{(I,\alpha+\beta,\tau_{\mathrm{c}})} \leqslant B(\alpha,\beta) \|f\|_{(I,\alpha,\tau_{\mathrm{c}})} \|g\|_{(I,\beta,\tau_{\mathrm{c}})},$$

where $B(\alpha,\beta) = \Gamma(\alpha)\Gamma(\beta)/\Gamma(\alpha + \beta)$ is the Beta function.
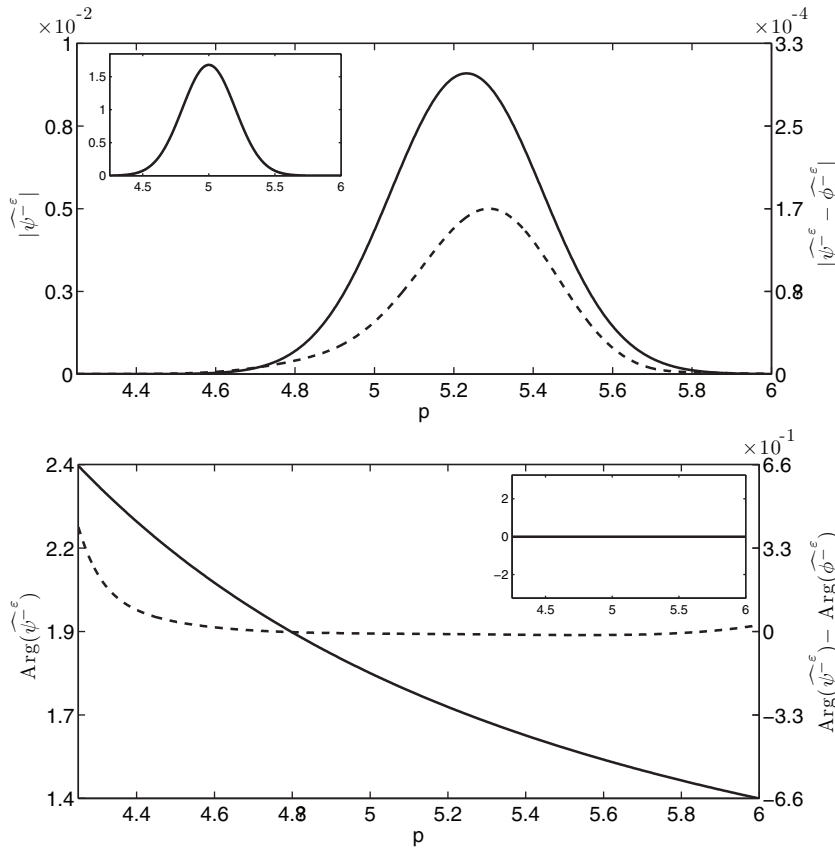
FIG. 2. *Top: The absolute value of the transmitted wave packet $\widehat{\psi^-}^{\,\varepsilon}$ as given by (2.4) (solid, left axis) and the error as compared to the numerical solution $\widehat{\phi^-}^{\,\varepsilon}$ computed as described using the fully coupled dynamics (dashed, right axis). Inset is the initial Gaussian wave packet in momentum space at the transition time. Bottom: As in the top plot but showing the argument (phase) of the wave packets.*

We will now estimate the n-norm of the $\kappa_{n,m}^{\pm}$. Without further loss of generality we take $\rho = 1/2$.

PROPOSITION A.1. *Assume $\rho = 1/2$. For an interval $I \subset \mathbb{R}$, assume $\theta' \in F_1(I)$ and $c_1 = d' \in F_1(I)$. Let x_n^m, y_n^m, z_n^m, and w_n^m be defined by the recursion given in Theorem 3.2. Then we have the following.*

(a) *$x_n^m \in F_n(I)$ for any interval I, and the same holds for the other coefficients.*
(b) *Assume further that $|I| \leqslant \min\{\tau_c / \|\theta'\|_{(1)}, \tau_c / \|\theta'\|_{(1)}^2\}$. Then, for every $\alpha > 1/2$ there exists $C_\alpha > 0$ such that for all m, n we have*

$$\|x_n^m\|_{(I,n,\tau_c)}, \|y_n^m\|_{(I,n,\tau_c)} \leqslant C_\alpha \frac{\Gamma(n + \alpha m)}{\Gamma(n)}$$

and

$$\|z_n^m\|_{(I,n,\tau_c)}, \|w_n^m\|_{(I,n,\tau_c)} \leqslant \frac{2C_\alpha}{\|\theta'\|_{(1)}} \frac{\Gamma(n + \alpha m)}{\Gamma(n)}.$$

Proof. We will proceed inductively. First, consider a_n, b_n as given in Lemma 3.1. We claim that a_n and b_n are in F_n, with $\|a_n\|_{(n)}, \|b_n\|_{(n)} \leqslant \|\theta'\|_{(1)} (n+1)/2$. Indeed,
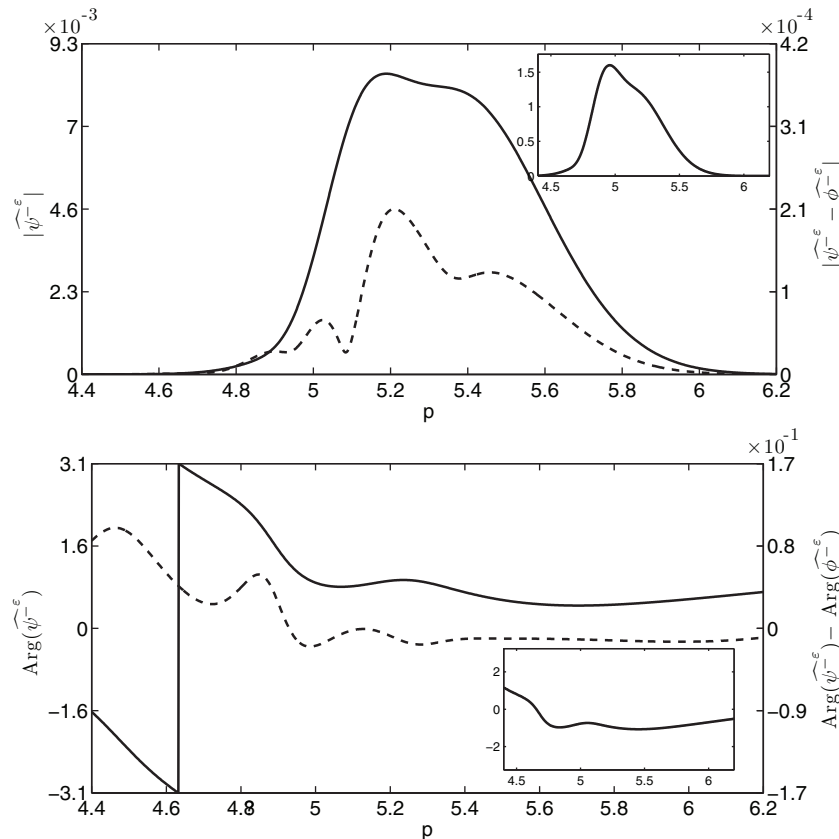
FIG. 3. *As Figure* 2 *but for the non-Gaussian wave packet described in the text.*

let $A_n = a_n + \mathrm{i}b_n$. Then (3.3) implies $A_{n+1} = A'_n + \mathrm{i}\theta' A_n$, and since both a_n and b_n are real valued, we have $\|a_n\|_{(n)} \leqslant \|A_n\|_{(n)}$ and $\|b_n\|_{(n)} \leqslant \|A_n\|_{(n)}$. Now using (A.3) and (A.5) above, we find

$$\|A_{n+1}\|_{(n+1)} \leqslant \|A_n\|_{(n)} \left(1 + \frac{1}{n}\|\theta'\|_{(1)}\right) \leqslant \cdots \leqslant \prod_{j=1}^{n}\left(1 + \frac{1}{j}\right)\|A_1\|_{(1)}.$$

Now $\|A_1\|_{(1)} = \frac{1}{2}\|\theta'\|_{(1)} < \infty$, and $\prod_{j=1}^{n}(1 + 1/j) = \prod_{j=1}^{n}(j+1)/j = n+1$, which proves the claim. Trivially, we also have $\|c_n\|_{(n)} \leqslant \|c_1\|_{(1)}$. From the recursions in Theorem 3.2 it now follows that $x_n^m \in F_n$ for all n and m, and also for all other coefficients. It remains to give bounds on the actual size of the norms. For $m = 0$, the bounds claimed in (b) were given in [5, cf. Theorem 2]. Now let us assume that the claim (b) holds up to $m - 2$ (remember that for odd m everything is zero), and up to n. Let us write

$$S_n^m := \sum_{j=1}^{\lfloor m/2 \rfloor} \frac{1}{(2\mathrm{i})^j}\binom{n+1-m+j}{j}(b_j y_{n+1-j}^{m-2j} - a_j w_{n+1-j}^{m-2j} + c_j z_{n+1-j}^{m-2j}).$$

Then

$$\|S_n^m\|_{(n+1)} \leqslant \sum_{j=1}^{\lfloor m/2 \rfloor} \frac{1}{2^j} \frac{\Gamma(n+2-m+j)}{\Gamma(n+2-m)\Gamma(j+1)} \frac{\Gamma(n+1-j)\Gamma(j)}{\Gamma(n+1)}$$
$$\times \left(\|b_j\|_{(j)} \left\|y_{n+1-j}^{m-2j}\right\|_{(n+1-j)} + \|a_j\|_{(j)} \left\|w_{n+1-j}^{m-2j}\right\|_{(n+1-j)} \right.$$
$$\left. + \|c_j\|_{(j)} \left\|z_{n+1-j}^{m-2j}\right\|_{(n+1-j)} \right)$$
$$\leqslant C_\alpha c_0 \left(1 + \frac{4}{\|\theta'\|_{(1)}} \right) \sum_{j=1}^{\lfloor m/2 \rfloor} \frac{1}{2^j} \frac{j+1}{j}$$
$$\frac{\Gamma(n+2-m+j)\Gamma(n+1-j)\Gamma(n+1+\alpha m-(1+2\alpha)j)}{\Gamma(n+2-m)\Gamma(n+1)\Gamma(n+1-j)}.$$

Here, $c_0 = \max\{\|\theta'\|_{(1)}/2, \|d'\|_{(1)}\}$. Clearly, the fraction of Gamma functions with $j = 1$ is the largest of all, and thus the factor $1/2^j$ allows us to estimate the sum through twice its first term, giving

$$\|S_n^m\|_{(n+1)} \leqslant C_\alpha \tilde{C} \frac{(n+2-m)\Gamma(n+\alpha m-2\alpha)}{\Gamma(n+1)},$$

where $\tilde{C}$ does not depend on n or m. The same holds for all the other sums appearing in Theorem 3.2. Using the recurrence relation there, we have

$$\left\|y_{n+1}^m\right\|_{(n+1)} \leqslant \|x_n^m\|_{(n)} + \frac{\|\theta'\|_{(1)}}{n} \|z_n^m\|_{(n)} + C_\alpha \tilde{C} \frac{(n+2-m)\Gamma(n+\alpha m-2\alpha)}{\Gamma(n+1)}$$
$$\leqslant C_\alpha \left(\frac{\Gamma(n+\alpha m)}{\Gamma(n)} + 2\frac{\Gamma(n+\alpha m)}{\Gamma(n+1)} + \tilde{C}\frac{(n+2-m)\Gamma(n+\alpha m-2\alpha)}{\Gamma(n+1)} \right)$$
$$= C_\alpha \frac{\Gamma(n+1+\alpha m)}{\Gamma(n+1)} \left(\frac{n+2}{n+1+\alpha m} + \tilde{C}\frac{(n+2-m)\Gamma(n+\alpha m-2\alpha)}{\Gamma(n+1+\alpha m)} \right).$$

The last term in the bracket above is $\mathcal{O}((n+\alpha m)^{-2\alpha})$, and as $\alpha > 1/2$, it vanishes faster than $1/n$. The first term in the bracket, on the other hand, is at most $\frac{n+2}{n+2+(2\alpha-1)} \leqslant 1 - \frac{2\alpha-1}{n}$, as $m \geqslant 2$. Thus the bracket becomes smaller than one for large enough n. By choosing C_α so large that the induction hypothesis holds up to this n, we have shown the induction step for y_{n+1}^m. The argument for x_n^m is similar and simpler. As for z_n^m, we have

$$\left\|z_n^{m'}\right\|_{(n+1)} \leqslant \frac{1}{n} \|\theta'\|_{(1)} \|x_n^m\|_{(n)} + C_\alpha \tilde{C} \frac{(n+2-m)\Gamma(n+\alpha m-2\alpha)}{\Gamma(n+1)},$$

and using (A.4), we see that

$$\|z_n^m\|_{(n)} \leqslant C_\alpha \frac{|I|}{q_c} \left(\|\theta'\|_{(1)} \|x_n^m\|_{(n)} + \tilde{C}\frac{(n+2-m)\Gamma(n+\alpha m-2\alpha)}{\Gamma(n)} \right)$$
$$\leqslant C_\alpha \frac{\Gamma(n+\alpha m)}{\Gamma(n)} \left(1 + \tilde{C}\frac{(n+2-m)\Gamma(n+\alpha m-2\alpha)}{\Gamma(n+\alpha m)} \right).$$

The last bracket will be bounded by 2 for large enough n, and so the same reasoning as above shows the induction step for z_n^m. The proof for w_n^m is similar and simpler. $\quad\square$

By piecing together intervals as given in Proposition A.1(b), and using (A.2), we obtain the following.

COROLLARY A.2. *For any compact interval I and any $\alpha > 1/2$, there exists a constant C such that*

$$\sup_{q \in I} |x_n^m(q)| \leqslant C \frac{\Gamma(n + \alpha m)}{\tau_{\mathrm{c}}^n},$$

and the same for z_n^m.

We can now give asymptotic shape of the coupling functions $\kappa_n^{0,\pm}$ for high momenta. It is clear that choosing p large enough will suffice to counter the growth of the coefficients as given in Corollary A.2. To obtain precise statements, let us first note that by choosing

$$\text{(A.6)} \qquad n = \frac{\tau_{\mathrm{c}}}{\varepsilon p},$$

we obtain

$$\text{(A.7)} \qquad \varepsilon^n p^n x_n^0(q) = 2\mathrm{i}\sqrt{2\varepsilon}\pi\tau_{\mathrm{c}} \sin(\pi\gamma/2)\, \mathrm{e}^{-\frac{\tau_{\mathrm{c}}}{\varepsilon p}}\, \mathrm{e}^{-\frac{q^2}{2\varepsilon p \tau_{\mathrm{c}}}}\, \mathrm{e}^{\frac{\mathrm{i}}{\varepsilon p}q}\, (1 + \mathcal{O}((\varepsilon p)^{1/2-\delta})).$$

This follows directly from the results in [4, 5]. Recall also that under the assumptions $\theta' \in F_1$ and $\rho = 1/2$, we have $p^n x_n^0 \sim p^n \frac{(n-1)!}{\tau_{\mathrm{c}}^n}$ at its maximum. We will now specify the regime of p for which this is also the leading order behavior.

PROPOSITION A.3. *Assume $\rho = 1/2$, $\theta \in F_1$, $d' \in F_1$, and $I \subset \mathbb{R}$ is compact. Assume further that $p = \varepsilon^{-\beta}$, with $1/3 < \beta < 1$. Then there exists $\delta > 0$ such that for all $n \leqslant \frac{\tau_{\mathrm{c}}}{p\varepsilon}$, we have*

$$\varepsilon^n \sum_{m=1}^{n} p^{n-m} x_n^m(q) = \varepsilon^n p^n \frac{(n-1)!}{\tau_{\mathrm{c}}^n} \mathcal{O}(\varepsilon^\delta).$$

Proof. By Corollary A.2 and Stirlings formula, we have

$$\left| \frac{\tau_{\mathrm{c}}^n}{p^n(n-1)!} \sum_{m=1}^{n} p^{n-m} x_n^m(q) \right| \leqslant \sum_{m=1}^{n} \frac{\Gamma(n + \alpha m)}{\Gamma(n)p^m} \leqslant c \sum_{m=1}^{n} \frac{(n + \alpha m)^{n+\alpha m}\, \mathrm{e}^{-\alpha m}}{n^n p^m}$$

for any $\alpha > 1/2$. Clearly, this is largest for the maximal value $n = \frac{\tau_{\mathrm{c}}}{p\varepsilon}$, so it suffices to treat this case. Inserting $\varepsilon = p^{-1/\beta}$ into $n = \frac{\tau_{\mathrm{c}}}{p\varepsilon}$ gives

$$p = \tau_{\mathrm{c}}^{-\frac{\beta}{1-\beta}} n^{\frac{\beta}{1-\beta}}.$$

Thus

$$\frac{(n+\alpha m)^{n+\alpha m}}{n^n p^m} \leqslant \frac{(n+\alpha m)^{n+\alpha m}}{n^{n+\frac{\beta}{1-\beta}m}} \tau_{\mathrm{c}}^{\frac{\beta}{1-\beta}m}$$

$$= \exp\left((n+\alpha m)\ln(n+\alpha m) - \left(n + \frac{\beta}{1-\beta}m \right)\ln(n) + m\frac{\beta}{1-\beta}\ln\tau_{\mathrm{c}} \right).$$

Now when $\beta > 1/3$, we can pick $\alpha > 1/2$ such that $\beta/(1-\beta) > \alpha$, and the exponent becomes negative for large enough n, and all $m < n$. The factor $\mathrm{e}^{-\alpha m}$ in the sum

above then guarantees summability up to $m = n$ without losing more than a constant, and the proof is finished. $\square$

Together with (A.7), the previous result immediately gives the following.

COROLLARY A.4. *We make the same assumptions as in Proposition* A.3, *and put* $n = \frac{\tau_c}{p\varepsilon}$. *Then*

$$(A.8) \qquad \kappa_n^{0,\pm}(p,q) = \mp 2\mathrm{i}\sqrt{2\varepsilon}\pi\tau_c \sin(\pi\gamma/2)\,\mathrm{e}^{-\frac{\tau_c}{\varepsilon p}}\,\mathrm{e}^{-\frac{q^2}{2\varepsilon p\tau_c}}\,\mathrm{e}^{\frac{\mathrm{i}}{\varepsilon p}q}\,(1 + \mathcal{O}(\varepsilon^\delta)),$$

for some $\delta > 0$.

This result, even if only derived for the special case $\rho = 1/2$, strongly suggests that for $p \gg \varepsilon^{-1/3}$ the asymptotic transitions should be governed by the off-diagonal elements of the form given in (A.8). We want to reemphasize, however, that ultimately it is not the asymptotic shape of the coupling functions we are interested in, but rather the shape of the time-dependent transmitted wave function. To obtain the latter rigorously, many further error estimates are necessary; these are not easy and constitute current work in progress. Curiously, the neat form (A.8) does not seem well suited for this task: Namely, in order to obtain the transmitted wave function, we will either need to solve the Wigner equation, or translate back into the language of operators using the Weyl quantization. In both cases, it is inconvenient that (A.8) contains terms of the form $\mathrm{e}^{-q^2/(\varepsilon p)}$, since these are in none of the usual symbol classes. There is no theory, and worse, no calculus for dealing with such symbols. This is why for our numerical approach we chose *not* to apply optimal truncation until the very end. Instead we did a Weyl quantization for finite n, solved the corresponding PDE, and decided in the end how large n should be. It is likely that any rigorous error estimates on the transmitted wave function would need to use the same strategy.

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