Contents

To do:

- Background reading: [Hag98]
- Numerics: [FGL09]
- Tunneling paper: [GHJ10] - Are they also doing a projection? Or they have an explicit expression for the transition of Hagedorn wavepackets?
- Lubich review: [Lub08] - splitting scheme, hyperbolic cross set, Gaussian quadrature rules
- Numerical integration: [Bou17]; Gaussian quadrature rules
- Non-adiabatic transitions near avoided crossings: [BGH12] - this is a fully numerical approach, i.e. just extending the Dirac-Frenkel variational approximation.
- Propagation of wavepackets for conical intersections [FLR20]
- Hagedorn wavepackets as eigenfunctions of the Harmonic oscillator

1 Hagedorn Semiclassical Wavepackets

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The superadiabatic formulas of equation ... allow us to to effectively reduce a coupled systems of two PDEs to two uncoupled PDEs, within the error made by the approximation of the transmitted wavepacket. In this framework, the numerical challenge stems from solving the one level BO dynamics efficiently. In the literature there are various approaches for doing this, often revolving around Gaussian basis sets. I actually do not know about any methods, this is something to look into. In this chapter we explore an approach which is rather unknown within the Chemistry community and absent from any QMD commercial or open-source software package. It consists in evolving a set of parametrised orthogonal basis functions, known as Hagedorn wavepackets. Precisely, these are the d-dimensional equivalent of Hermite polynomials, eigenfunctions of the Harmonic oscillator [reference]. When the potential is quadratic one has to evolve only the set of parameters according to a system of ODEs. For more general potentials, one accounts for the non-quadratic remainder term by applying the Dirac-Frenkel variational principle; this leads to a set of integrals involving the non-quadratic remainder term [reference]. Our contribution consists in merging the Superadiabatic formula with this classical evolution of the Hagedorn wavepackets. In Section 1 we introduce the Hagedorn wavepackets and their properties as outlined in [Hag98]. In Section 2 we address the projection of the transmitted wavepacket back onto an Hagedorn basis. The nature of these integrals is similar to the ones encountered in accounting the non-quadratic terms of the quadratic potential.

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1.1 Hagedorn's parametrization

To do list:

- Why is it exact for a quadratic potential (metaplectic transformation?) - (similar to egorov theorem)
- what does $e^{-iH/t}$ do qualitatively? (exponentiation of 1st order derivative is translation)
- How does the variance of the wavepacket evolve in time? Can you draw any qualitative conclusions about when the support spreads out fast vs slow?

Consider a complex semi-classical Gaussian wavepacket in the following form

$$\varphi_0^\epsilon(\boldsymbol{x}) := (\pi\epsilon)^{-\frac{d}{4}}(\det \boldsymbol{Q})^{-\frac{1}{2}} \exp\left(\frac{i}{2\epsilon}(\boldsymbol{x}-\boldsymbol{q})^T \boldsymbol{P}\boldsymbol{Q}^{-1}(\boldsymbol{x}-\boldsymbol{q}) + \frac{i}{\epsilon}\boldsymbol{p}^T(\boldsymbol{x}-\boldsymbol{q})\right) \tag{1.1}$$

Here on we will follow the notational convention as in [Bou17] to denote the set of parameters as $\Pi := (\boldsymbol{q}, \boldsymbol{p}, \boldsymbol{Q}, \boldsymbol{P})$. The matrix $\mathbb{C}^{d\times d} \ni \boldsymbol{C} := \boldsymbol{P}\boldsymbol{Q}^{-1}$ is complex symmetric with positive definite imaginary part. The matrices $\boldsymbol{P}$ and $\boldsymbol{Q}$ must satisfy further properties as enunciated in the following Lemma.

Lemma 1.1 ([Hag98]) *Two square matrices* $\boldsymbol{Q}, \boldsymbol{P} \in \mathbb{C}^{d\times d}$ *satisfy the following relations*

$$\begin{aligned} \boldsymbol{Q}^T\boldsymbol{P} - \boldsymbol{P}^T\boldsymbol{Q} &= 0 \\ \boldsymbol{Q}^*\boldsymbol{P} - \boldsymbol{P}^*\boldsymbol{Q} &= 2i\boldsymbol{I}_d \end{aligned} \tag{1.2}$$

if and only if $\boldsymbol{Q}$ *and* $\boldsymbol{P}$ *are invertible and* $\boldsymbol{C} = \boldsymbol{P}\boldsymbol{Q}^{-1}$ *is complex symmetric with positive definite imaginary part. Moreover,* $\Im(\boldsymbol{C}) = (\boldsymbol{Q}\boldsymbol{Q}^*)^{-1}$.

($\Rightarrow$) Suppose b.w.o.c. that Q is not invertible. Then $\det(\boldsymbol{Q}) = 0 = \det(\boldsymbol{Q}^*)$ which leads to a contradiction when taking the determinant of both sides of the second equation in (1.2). Similarly for $\boldsymbol{P}$.
Multiplying the first equation in (1.2) by $\boldsymbol{Q}^{-1}$ on the right we get $\boldsymbol{Q}^T\boldsymbol{P}\boldsymbol{Q}^{-1} = \boldsymbol{P}^T \Rightarrow \boldsymbol{P}\boldsymbol{Q}^{-1} = (\boldsymbol{Q}^T)^{-1}\boldsymbol{P}^T = (\boldsymbol{P}\boldsymbol{Q}^{-1})^T$ and therefore $\boldsymbol{C}$ is complex symmetric. Show positive definiteness: $\boldsymbol{x}^T\Im(\boldsymbol{C})\boldsymbol{x} = \langle \boldsymbol{x}, \Im(\boldsymbol{C})\boldsymbol{x}\rangle > 0 \;\forall\; \boldsymbol{x} \in \mathbb{R}^n$
($\Leftarrow$)

Lemma ... gives a sufficient and necessary condition for two matrices $\boldsymbol{Q}, \boldsymbol{P}$ to yield such a matrix $\boldsymbol{C}$ (?) and also a method(?) to construct two desired such matrices. Given a complex symmetric matrix, how to decompose into such P, Q. Is there a trivial decomposition involving say the identity matrix. However, is there a decomposition which requires a least number of wavepackets such that the error in the norm (or another statistic/observable) is less than some tolerance value?

The fact that $\Im(\boldsymbol{C}) = (\boldsymbol{Q}\boldsymbol{Q}^*)^{-1}$ justifies why the normalisation factor of the complex Gaussian depends on $\boldsymbol{Q}$ alone. The reason why Hagedorn's

parametrisation is useful will become clearer when we will look at the dynamics. It is then useful to compare it to what one obtains when this parametrisation is not made.

1.2 Lowering and Raising operators

- Eigenvalues and eigenvectors of the d-dimensional Harmonic oscillator
- Commutator relations...
- This is background reading
- the properties of the raising and lowering operators and then used to derive a recurrence relation for

1.2.1 Recursive relation for Hagedorn wavepackets

For a given parameter set Π with matrices $\boldsymbol{P}, \boldsymbol{Q}$ satisfying Lemma 1.1, a Schauder orthonormal basis for $L^2_{\mathbb{C}}(\mathbb{R}^d, \mathcal{B}(\mathbb{R}^d), \lambda^d)$ can be constructed with the basis vectors $\Phi := \{\varphi_k[\Pi]\}_{k\in\mathbb{N}^d}$ satisfying the following recursive relation

$$\varphi_0^\epsilon := \varphi_0^\epsilon[\Pi](\boldsymbol{x})$$
$$\boldsymbol{Q}\left(\sqrt{k_j+1}\varphi^\epsilon_{k+\langle j\rangle}\right)_{j=1}^d = \sqrt{\frac{2}{\epsilon}}(\boldsymbol{x}-\boldsymbol{q})\varphi_k^\epsilon - \overline{\boldsymbol{Q}}\left(\sqrt{k_j}\varphi_{k-\langle j\rangle}\right)_{j=1}^d \tag{1.3}$$

Exercise: derive recurrence relation

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1.3 Semiclassical dynamics

1.3.1 Quadratic potential

Consider a one level TDSE with a quadratic potential $V(\boldsymbol{x})$ and $\varphi_k^\epsilon[\Pi]$ as initial condition, for some $k \in \mathbb{N}^d$. Then, Hagedorn showed that the solution is fully described in terms of a system of ordinary differential equations for the parameter set Π, that is

$$\dot{\boldsymbol{q}} = \boldsymbol{p} \tag{1.4}$$

$$\dot{\boldsymbol{p}} = -\nabla V(\boldsymbol{q}) \tag{1.5}$$

$$\dot{\boldsymbol{P}} = -\nabla^2 V(\boldsymbol{q})\boldsymbol{Q} \tag{1.6}$$

$$\dot{\boldsymbol{Q}} = \boldsymbol{P} \tag{1.7}$$

$$S(t) = \int_0^t \frac{|\boldsymbol{p}(s)|^2}{2} - V(\boldsymbol{q}(s))ds \tag{1.8}$$

where $e^{-\frac{i}{\epsilon}S(t)}$ is a multiplicative global phase factor. To do: understand the equation of motion and descripe what happens from a qualitative perspective.

Can it be proven using Baker-Campbell-Hausdorf formula? First for φ_0 and then generally using the properties of the raising and lowering operators as in..[reference].

Since $\left[-\frac{\epsilon^2}{2}\Delta, V\right] = \frac{\epsilon^2}{2}\Delta(V) = \frac{\epsilon^2}{2}c$ where $c \in \mathbb{R}$, the Baker-Campbell-Hausdorf

formula yields

$$\begin{aligned}\varphi_0(x,t) &= e^{-\frac{i}{\epsilon}tH}\varphi_0(x,0)\\ &= e^{i\frac{\epsilon}{2}t\Delta}e^{-\frac{i}{\epsilon}tV}e^{i\frac{\epsilon}{4}tc}\varphi_0(x,0)\\ &= \cdots\end{aligned} \tag{1.9}$$

1.3.2 Cubic potentials

Why can we not modify the system of ODEs describing the evolution of the parameter set Π such that the result also holds for cubic potentials? If we think of what would happen if we had a tunnelling situation, then the tunnelled wavepacket would have to be described by a different set of parameters or even a different linear combination of Hagedorn wavepackets. this is an informal answer. But perhaps there is a modification if the potential is a polynomial of only even degrees, but this will not be very useful from a practical perspective.

1.3.3 Non-quadratic potentials

I have chosen perhaps the non standard convention of conjugating the second entry which will entail having to put the basis vectors in the second entry when doing the projection, I think the convention is to conjugate the first entry - to check

Let $W(x)$ denote the non-quadratic term of the potential and consider a linear combination of Hagedorn wavepackets as initial condition, that is $\psi(x,0) = \sum_{k\in\mathcal{K}} c_k\varphi_k^\epsilon[\Pi]$ subject to $\sum_{k\in\mathcal{K}}|c_k|^2 = 1$. Since $W(x) \neq 0$, we seek an approximate solution $\psi_\mathcal{K}(x,t) := e^{\frac{i}{\epsilon}S(t)}\sum_{k\in\mathcal{K}} c_k(t)\varphi_k^\epsilon[\Pi]$ such that

the residual between the exact solution $\psi(x,t)$ and $\psi_{\mathcal{K}}(x,t) \in span(\{\varphi_k\}_{k\in\mathcal{K}})$ is minimised (see the illustration in Figure ...). In [Lub08] this is formalised via the so-called Dirac-Frenkel variational approximation principle which results in finding $\frac{d}{dt}c_k$ such that projecting the residual on the time derivative would be a weaker requirement - you can be orthogonal to a line in a plane but not to the all plane. and we want to be orthogonal to the all subspace since we are already using those basis sets

$$\left\langle -\frac{i}{\epsilon}H\psi_{\mathcal{K}} - \partial_t\psi_{\mathcal{K}}, \varphi_k \right\rangle = 0 \qquad \forall\ k \in \mathcal{K} \tag{1.10}$$

Expanding the above equation we have

$$\sum_{l\in\mathcal{K}} \left\langle -\frac{i}{\epsilon}Hc_l e^{\frac{i}{\epsilon}S(t)}\varphi_l - \partial_t(c_l e^{\frac{i}{\epsilon}S(t)}\varphi_l), \varphi_k \right\rangle = 0 \tag{1.11}$$

and since

$$\begin{aligned} Hc_l e^{\frac{i}{\epsilon}S(t)}\varphi_l &= (H-W)(c_l e^{\frac{i}{\epsilon}S(t)}\varphi_l) + W(c_l e^{\frac{i}{\epsilon}S(t)}\varphi_l) \\ \partial_t(c_l e^{\frac{i}{\epsilon}S(t)}\varphi_l) &= \dot{c}_l e^{\frac{i}{\epsilon}S(t)}\varphi_l - c_l\frac{i}{\epsilon}(H-W)e^{\frac{i}{\epsilon}S(t)}\varphi_l \end{aligned} \tag{1.12}$$

by the orthonormality property of the Hagedorn wavepackets we have

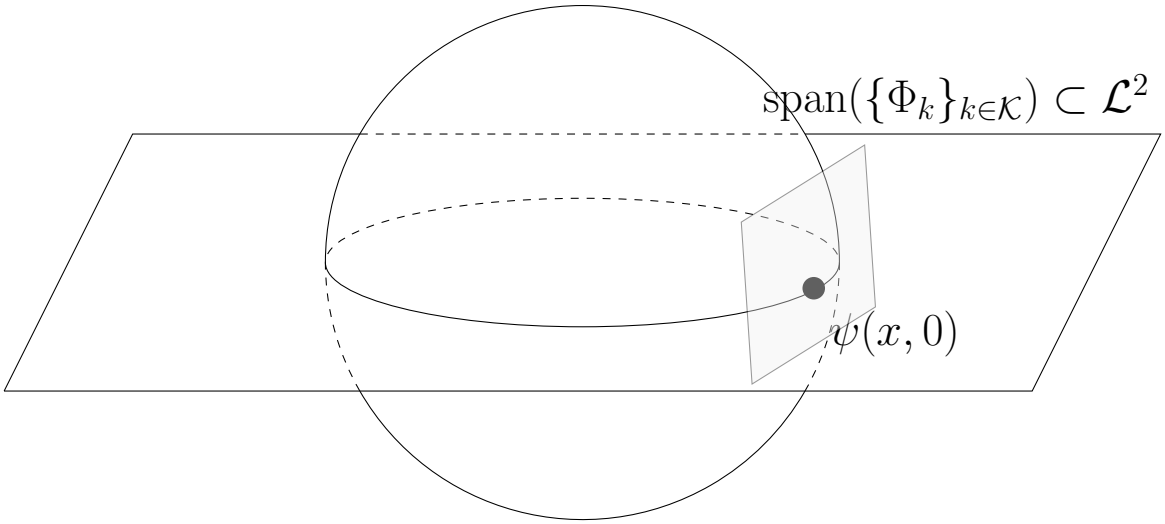
$$\dot{c}_l = \sum_{l\in\mathcal{K}} -\frac{i}{\epsilon}c_l \langle W\varphi_l, \varphi_k\rangle \tag{1.13}$$

so that $\boldsymbol{c}(t) := (c_k(t))_{k\in\mathcal{K}}$ satisfy the following differential equation

$$i\epsilon\dot{\boldsymbol{c}}(t) = \boldsymbol{F}(t)\boldsymbol{c}(t) \tag{1.14}$$

with $\boldsymbol{F}_{kl}(t) = \langle W\varphi_l, \varphi_k\rangle = \overline{\boldsymbol{F}_{lk}}$.

comment on the kind of system you obtained above intuitively and how you would go about solving it efficiently. What are the properties of the block matrix F



Would the approximation then have necessarily smaller norm...? only if you do the projection and do not increment the number of basis functions

I suppose one would diagonalise $\boldsymbol{F}$ since it is a symmetric matrix and obtain a fully decoupled system. So what is this Kryloc space about - see Lubich

Different choices for $\mathcal{K}$ have been investigated in [Lub08] together with the related computational challenges. A numerical scheme (order...) based on the splitting method for solving the system of equations (1.4) - (1.7) can be found in [Lub08] while an higher order method in [BG20]

1.3.4 Computing the weights for non-quadratic potentials

Why are we actually doing this? are we sure there is an actual advantage?

In this section we address the computation of the (time dependent) block matrix $\boldsymbol{F}$. Its entries are d-dimensional integrals which must be solved at

each time step Check numerical scheme

$$\langle W\varphi_l, \varphi_k\rangle = \int_{\mathbb{R}^d} W(x)\varphi_l\bar{\varphi}_k dx \tag{1.15}$$

In [Bou17] the evaluation of these integrals has been addressed through (sparse) quadrature methods We investigate alternative numerical (and asymptotic) integration methods. Firstly, by making use of the recursive relation (...) we reduce the evaluation of the integrals to the computation of $\boldsymbol{F}_{00}$ and its higher order moments. This should not come as a surprise since the Hagedorn wavepackets are polynomials multiplied by a Gaussians. Let us re-write (ref recursive relation) as follows At some point I will consider translating everything to the origin

$$\left(\sqrt{k_j+1}\varphi^\epsilon_{k+\langle j\rangle}\right)_{j=1}^d = \sqrt{\frac{2}{\epsilon}}\boldsymbol{Q^{-1}}\left((\boldsymbol{x}-\boldsymbol{q})_j\varphi^\epsilon_k\right)_{j=1}^d - \boldsymbol{Q^{-1}}\overline{\boldsymbol{Q}}\left(\sqrt{k_j}\varphi^\epsilon_{k-\langle j\rangle}\right)_{j=1}^d \tag{1.16}$$

Let $\boldsymbol{K}$ denote the diagonal matrix with diagonal entries $\boldsymbol{K}_{jj} = k_j$ for $j \in \{1, ..., d\}$. Then, multiplying each side of the equality by $(\boldsymbol{K}+\boldsymbol{I}_d)^{-\frac{1}{2}}$ yields

$$\begin{aligned}\left(\varphi^\epsilon_{k+\langle j\rangle}\right)_{j=1}^d =& \sqrt{\frac{2}{\epsilon}}(\boldsymbol{K}+\boldsymbol{I}_d)^{-\frac{1}{2}}\boldsymbol{Q^{-1}}\left((\boldsymbol{x}-\boldsymbol{q})_j\varphi^\epsilon_k\right)_{j=1}^d + \\ &- (\boldsymbol{K}+\boldsymbol{I}_d)^{-\frac{1}{2}}\boldsymbol{Q^{-1}}\overline{\boldsymbol{Q}}\boldsymbol{K}^{\frac{1}{2}}\left(\varphi^\epsilon_{k-\langle j\rangle}\right)_{j=1}^d\end{aligned} \tag{1.17}$$

Letting $\boldsymbol{A} = \sqrt{\frac{2}{\epsilon}}(\boldsymbol{K}+\boldsymbol{I}_d)^{-\frac{1}{2}}\boldsymbol{Q}^{-1}, \boldsymbol{B} = (\boldsymbol{K}+\boldsymbol{I}_d)^{-\frac{1}{2}}\boldsymbol{Q}^{-1}\overline{\boldsymbol{Q}}\boldsymbol{K}^{\frac{1}{2}}$ we can re-write the above expression more coincisely as

$$\left(\varphi^\epsilon_{k+\langle j\rangle}\right)_{j=1}^d = \boldsymbol{A}\left((\boldsymbol{x}-\boldsymbol{q})_j\varphi^\epsilon_k\right)_{j=1}^d - \boldsymbol{B}\left(\varphi^\epsilon_{k-\langle j\rangle}\right)_{j=1}^d \tag{1.18}$$

Multiplying both sides by $W\overline{\varphi_l}$ (a scalar valued function) and integrating over $\mathbb{R}^d$ yields

$$\Big(\langle\varphi^\epsilon_{k+\langle j\rangle}, W\varphi^\epsilon_l\rangle\Big)_{j=1}^d = \boldsymbol{A}\Big(\langle(\boldsymbol{x}-\boldsymbol{q})_j\varphi^\epsilon_k, W\varphi^\epsilon_l\rangle\Big)_{j=1}^d - \boldsymbol{B}\Big(\langle\varphi^\epsilon_{k-\langle j\rangle}, W\varphi^\epsilon_l\rangle\Big)_{j=1}^d \tag{1.19}$$

Hence, in order to compute $\langle\varphi^\epsilon_{k+\langle j\rangle}, W\varphi^\epsilon_l\rangle$ we need the higher order moment of the previous Hagedorn wavepacket $\langle(\boldsymbol{x}-\boldsymbol{q})_j\varphi^\epsilon_k, W\varphi^\epsilon_l\rangle$. In a similar manner, we can derive a recurrence relation for these higher order terms. By defining the diagonal matrix $\boldsymbol{Y}$ with entries $\boldsymbol{Y}_{jj} = (\boldsymbol{x}-\boldsymbol{q})_j$ and multiplying both sides of equation (1.18) gives

$$\boldsymbol{Y}^p\Big(\varphi^\epsilon_{k+\langle j\rangle}\Big)_{j=1}^d = \boldsymbol{Y}^p\boldsymbol{A}\Big((\boldsymbol{x}-\boldsymbol{q})_j\varphi^\epsilon_k\Big)_{j=1}^d - \boldsymbol{Y}^p\boldsymbol{B}\Big(\varphi^\epsilon_{k-\langle j\rangle}\Big)_{j=1}^d \tag{1.20}$$

The diagonal matrix $\boldsymbol{Y}^p$ does not commute with $\boldsymbol{A}$ unless the latter is also diagonal and so we have that the higher order moments depend on the higher order cross term moments

$$\begin{aligned}\Big((\boldsymbol{x}-\boldsymbol{q})^p_j\varphi^\epsilon_{k+\langle j\rangle}\Big)_{j=1}^d &= \boldsymbol{Y}^p\Big(\sum_{i=1}^d \boldsymbol{A}_{j,i}(\boldsymbol{x}-\boldsymbol{q})_i\varphi^\epsilon_k\Big)_{j=1}^d - \boldsymbol{Y}^p\Big(\sum_{i=1}^d \boldsymbol{B}_{j,i}\varphi^\epsilon_{k-\langle i\rangle}\Big)_{j=1}^d \\ &= \Big(\sum_{i=1}^d \boldsymbol{A}_{j,i}(\boldsymbol{x}-\boldsymbol{q})^p_j(\boldsymbol{x}-\boldsymbol{q})_i\varphi_k\Big)_{j=1}^d - \Big(\sum_{i=1}^d \boldsymbol{B}_{j,i}(\boldsymbol{x}-\boldsymbol{q})^p_j\varphi_{k-\langle i\rangle}\Big)_{j=1}^d\end{aligned} \tag{1.21}$$

Now, repeating the same process as before, multiplying by the scalar $W\overline{\varphi_l}$ on both sides and integrating over $\mathbb{R}^d$ yields

$$\begin{aligned}&\Big(\langle(\boldsymbol{x}-\boldsymbol{q})^p_j\varphi_{k+\langle j\rangle}, W\varphi_l\rangle\Big)_{j=1}^d = \\ =&\Big(\sum_{i=1}^d \boldsymbol{A}_{j,i}\langle(\boldsymbol{x}-\boldsymbol{q})^p_j(\boldsymbol{x}-\boldsymbol{q})_i\varphi_k, W\varphi_l\rangle\Big)_{j=1}^d - \Big(\sum_{i=1}^d \boldsymbol{B}_{j,i}\langle(\boldsymbol{x}-\boldsymbol{q})^p_j\varphi_{k-\langle i\rangle}, W\varphi_l\rangle\Big)_{j=1}^d\end{aligned} \tag{1.22}$$

which now leads to finding an additional recurrence relation for the cross terms/moments. Note that equation (1.19) is just equation (1.22) with $p = 0$. We can write out the general expression. Letting $\alpha \in \mathbb{N}^d$, we then have

$$\begin{aligned}\left(\left\langle (\boldsymbol{x}-\boldsymbol{q})_j^p \prod_{s=1}^{d} (\boldsymbol{x}-\boldsymbol{q})_s^{\alpha_s} \varphi_{k+\langle j\rangle}, W\varphi_l \right\rangle\right)_{j=1}^{d} &= \\ = \left(\sum_{i=1}^{d} \boldsymbol{A}_{j,i} \left\langle (\boldsymbol{x}-\boldsymbol{q})_j^p \prod_{s=1}^{d} (\boldsymbol{x}-\boldsymbol{q})_s^{\alpha_s} (\boldsymbol{x}-\boldsymbol{q})_i \varphi_k, W\varphi_l \right\rangle\right)_{j=1}^{d} &+ \\ - \left(\sum_{i=1}^{d} \boldsymbol{B}_{j,i} \left\langle (\boldsymbol{x}-\boldsymbol{q})_j^p \prod_{s=1}^{d} (\boldsymbol{x}-\boldsymbol{q})_s^{\alpha_s} \varphi_{k-\langle i\rangle}, W\varphi_l \right\rangle\right)_{j=1}^{d} &\end{aligned} \tag{1.23}$$

Note that we have kept l fixed above, the reason being that we can use the conjugate symmetry property to fill in the other entries. This is to be argued better but ultimately, it should be clear that we can construct the block matrix $\boldsymbol{F}$ from knowledge of $\boldsymbol{F}_{00}$ and its higher order terms alone. $[./\text{main}_h agedorn.tex] subfile samsmath pgfplots$

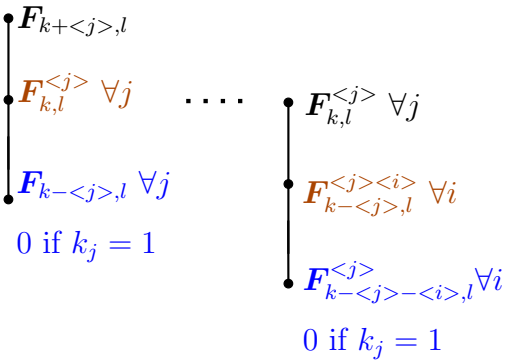
1.4 Numerical integration for the Hagedorn coefficients

Hence, we are interested in computing the following integrals involving φ_0^ϵ. Translate center to origin: $\boldsymbol{y} = \boldsymbol{x} - \boldsymbol{q}$

$$\left\langle \prod_{i=1}^{d} \boldsymbol{y}_i^{\alpha_i} \varphi_0^\epsilon, W(\boldsymbol{y}+\boldsymbol{q})\varphi_0^\epsilon \right\rangle = \int_{\mathbb{R}^d} \prod_{i=1}^{d} \boldsymbol{y}_i^{\alpha_i} W(\boldsymbol{y}+\boldsymbol{q}) |\varphi_0^\epsilon|^2 d\boldsymbol{y} \tag{1.24}$$

1.5 Algorithmic implementation

SKIP THIS SECTION FOR THE MOMENT. THE PRIORITY LIES WITH THE NUMERICAL EVALUATION OF THE INTEGRALS **NOTE THAT**



the direction should not matter w.r.t.

direction?

Figure 1: recursion impleentation

THE SECOND TERM IS ZERO FOR K=0 There are two approaches that we can consider with regards to the numerical implementation: **static** and **adaptive**. In the static approach the basis set is fixed at all times while for the adaptive approach basis vectors are added until the L2 norm is within some prescribed tolerance of 1. We investigate the latter approach together where the index set is the hyperbolic cross set

1.5.1 Static

Here, we fix the basis set $\mathcal{K} \subset \mathbb{N}$ throughout the dynamics. This means that each time step we need to build the block matrix.

In the case of a static basis set throughout the dynamics, we can consider pre-computing all higher order cross terms moments involving φ_{00} or compute them as we go along when needed. The latter approach is definitely the

one to take in the adaptive case.

Filling the first diagonal entry of $\boldsymbol{F}$ is straightforward

$$\boldsymbol{F} = \begin{bmatrix} F_{00} & \begin{bmatrix} \dots \end{bmatrix} \\ \begin{bmatrix} \dots \end{bmatrix} \begin{bmatrix} \dots \end{bmatrix} \dots \\ \begin{bmatrix} \dots \end{bmatrix} \begin{bmatrix} \dots \end{bmatrix} \\ \dots \quad \dots \end{bmatrix} \tag{1.25}$$

Then, we can proceed filling $\boldsymbol{F}$ along the columns, i.e. fix $l = 0$, which is in analogy to moving along the axes on the n-dimensional lattice through the recurrence relation. Let $k = (0, ..., 0)$ and $\langle j \rangle = (0, ..., 1, ..., 0)$ In order to compute $F_{00+\langle j \rangle 0}$ I need $\langle (x - q)_j \varphi_0, W\varphi_0$, the first moment.

$$\boldsymbol{F} = \begin{bmatrix} F_{00} & \begin{bmatrix} \dots \end{bmatrix} \\ \begin{bmatrix} F_{00+\langle j \rangle 0} \end{bmatrix}_{j=1}^{d} \begin{bmatrix} \dots \end{bmatrix} \dots \\ \begin{bmatrix} \dots \end{bmatrix} \begin{bmatrix} \dots \end{bmatrix} \\ \dots \quad \dots \end{bmatrix} \tag{1.26}$$

We can now move one step more along the axes of the d-dimensional lattice to compute $F_{00+\langle j \rangle 0+\langle j \rangle 0}$ where we now need the moments $\langle (\boldsymbol{x} - \boldsymbol{q})_j \varphi_1, W\varphi_0 \rangle)_{j=1}^{d}$ which need the cross terms moments $\langle (\boldsymbol{x} - \boldsymbol{q})_j (\boldsymbol{x} - \boldsymbol{q})_i \varphi_0, W\varphi_0 \rangle$ and need to figure out more generally about $F_{00+\sum_{i=1}^{n} \langle j \rangle 0}$ for some n.

$$\boldsymbol{F} = \begin{bmatrix} F_{00} & \begin{bmatrix} \dots \end{bmatrix} \\ \begin{bmatrix} F_{00+\langle j \rangle 0} \end{bmatrix}_{j=1}^{d} & \begin{bmatrix} \dots \end{bmatrix} \\ \begin{bmatrix} F_{00+\langle j \rangle 0+\langle j \rangle 0} \end{bmatrix}_{j=1}^{d} \begin{bmatrix} \dots \end{bmatrix} \\ \dots \quad \dots \end{bmatrix} \tag{1.27}$$

Since the block matrix is Hermitian/self-adjoint and we have built the first column, we have implicitly built the first row.

$$\boldsymbol{F} = \begin{bmatrix} F_{00} & \left[\overline{F_{00+\langle j \rangle 0}} \right]_{j=1}^{d} \\ \left[F_{00+\langle j \rangle 0} \right]_{j=1}^{d} & \left[\dots \right] \\ \left[F_{00+\langle j \rangle 0+\langle j \rangle 0} \right]_{j=1}^{d} & \left[\dots \right] \\ \dots & \dots \end{bmatrix} \tag{1.28}$$

Now we can fill in the 2nd column

$$\boldsymbol{F} = \begin{bmatrix} F_{00} & \left[\overline{F_{00+\langle 1 \rangle 0}} \quad \overline{F_{00+\langle 2 \rangle 0}} \quad \dots \quad \overline{F_{00+\langle d \rangle 0}} \right] & \\ \begin{bmatrix} F_{00+\langle 1 \rangle 0} \\ F_{00+\langle 2 \rangle 0} \\ \dots \\ F_{00+\langle d \rangle 0} \end{bmatrix} & \begin{bmatrix} F_{01+\langle 1 \rangle 0} \\ F_{01+\langle 2 \rangle 0} \\ \dots \\ F_{01+\langle d \rangle 0} \end{bmatrix} & \dots \\ \begin{bmatrix} F_{10+\langle 1 \rangle 0} \\ F_{10+\langle 2 \rangle 0} \\ \dots \\ F_{10+\langle d \rangle 0} \end{bmatrix} & \begin{bmatrix} F_{11+\langle 1 \rangle 0} \\ F_{11+\langle 2 \rangle 0} \\ \dots \\ F_{11+\langle d \rangle 0} \end{bmatrix} & \\ \dots & \dots & \end{bmatrix} \tag{1.29}$$

1.5.2 Adaptive

Fixing the basis set throughout the dynamics might not be such a good idea especially one case about preserving conserved quantities such as the norm within some prescribed tolerance $\mathcal{TOL}$. One may consider a larger set than necessary at time zero to begin with but requires some educated guessing about how many basis function are necessary. It would more convenient to consider an adaptive approach.

1. Decompose initial condition at time zero by augmenting the set $\mathcal{K}$ with basis functions until $|\sum_{k\in\mathcal{K}}|c_k|^2 - 1| <= \mathcal{TOL}$

2. When updating coefficients/projecting the transmitted wavepacket repeat at the same process as in 1 perhaps filling up the set using the unit cube or this hyperbolic set.

Example: 1d

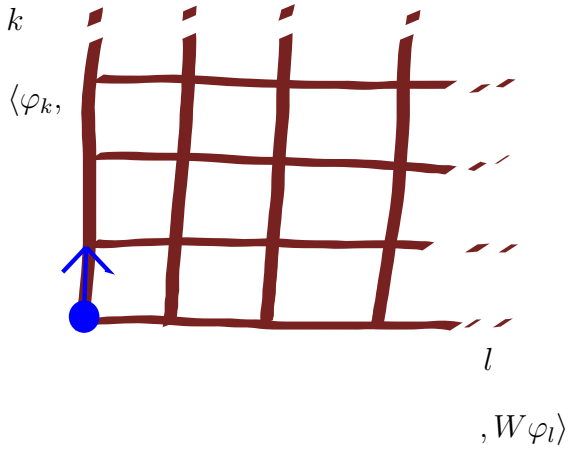


Figure 2: Integral recursion: d=1

(the blue denotes the things we have to compute) (enphasise that one of the terms in the recursion relation will have always been pre-computed - but do we use it anywhere else)

Also othe than the moments you will have access to all the results since you need to then exponentiate the matrix

Let us first start by fixing $l = 0$ and understand how the recursion for $\langle \varphi_k, W\varphi_0 \rangle$ unfolds so as to better the pattern (also translate so that $q = 0$).
$\langle \varphi_0, W\varphi_0 \rangle$ (given)
$\langle \varphi_1, W\varphi_0 \rangle \leftarrow \langle x\varphi_0, W\varphi_0 \rangle$ (i.e. the first "moment" of the previous one)
$\langle \varphi_2, W\varphi_0 \rangle \leftarrow \langle \varphi_0, W\varphi_0 \rangle$, $\langle x\varphi_1, W\varphi_0 \rangle \leftarrow \langle x^2\varphi_0, W\varphi_0 \rangle$
$\langle \varphi_3, W\varphi_0 \rangle \leftarrow \langle \varphi_1, W\varphi_0 \rangle$, $\langle x\varphi_2, W\varphi_0 \rangle \leftarrow \langle x\varphi_0, W\varphi_0 \rangle$, $\langle x^2\varphi_1, W\varphi_0 \rangle \leftarrow \langle x^3\varphi_0, W\varphi_0 \rangle$
$\langle \varphi_k, W\varphi_0 \rangle \leftarrow$ (already computed staff) $\langle x^k\varphi_0, W\varphi_0 \rangle$
Still to answer the question of whether I use the moments at any other stage — use Hermitian property...

presumably k 0 involves x2 moment -¿ check - already computed

This means I need to focus only on the integrals involving φ_0

Now it obviously does make perfect sense. But then is there really an advantage...? because essentially you are computing the integral of a polynomial against a gaussian but the polynomial is simplified essentially.. I suppose it would depend on whether you can approximate these integral more easily since you do know the "polynomials" in your integral...
Essentially all it is is that we do know the monomials explicitly, all that has be done really is "hide" the constants and the rescaling (I mean they are polynomials)

2 Computation of observables

How would we be computing the observables of interest...? [./main$_h$*agedorn.tex*]*subfilesamsmath*

3 Non-adiabatic transitions: avoided crossings

Need to discuss [**GHJ10**] which is about applying a similar method but in the context of tunneling Still need to look at the work of Hagedorn for gap size shrinking with $\sqrt{\epsilon}$ but also the the work by Olivier using normal local forms in the context of avoided crossings. Hagedorn wavepacket dynamics in the context of avoided crossings has been previously investigated by Bourquin et al. in [BGH12] The authors extend the one level algorithm outlined in [Lub08] to the multilevel case: the potential matrix $V(\boldsymbol{x})$ is splitted into a diagonal quadratic term and the non-quadratic remainder, with the non-adiabatic coupling terms occupying the off-diagonal entries. The same dirac-Frenkel variational principle reported in Section ... can be applied to yield a similar set of equations for the update of the coefficients as in equation (...) but now it also envolves the coupling terms. Details of the numerics regarding the computation of these integrals can be found in [Bou17]. Here we consider incorporating the Superadiabatic formulae outlined in section ... into the (one level) Hagedorn dynamics framework. A similar approach was also considered in [BGH12] by implementing the one dimensional transition formula derived in [HJ05] through JWKB analysis but with no concrete implementation given the impractility of the formula (analytic continuation - needs to be explained

better). eventually will need a comparison of the numerical results beside a description of advantages/disadvantages Since the transmitted wavepacket is expressed in momentum space, We will now denote the parameter set as $\hat{\Pi} := \{p, q, P, Q\}$ as a reminder.

Initial condition

Consider the following initial condition corresponding to one of the adiabatic subspaces

$$\hat{\psi}^{\pm}(\xi, 0) := \sum_{k \in \mathcal{K}} c_k^{\pm}(0) \varphi_k^{\epsilon}[\hat{\Pi}^{\pm}(0)](\xi) \tag{3.1}$$

where $c_k^{\pm} \in \mathbb{C}$ $\xi \in \mathbb{R}^d$ and the index set $\mathcal{K} \subset \mathbb{N}^d$. Let t_c denote the time at which the avoided crossing is detected. The wavepacket at time t_c is given by

$$\hat{\psi}^{\pm}(\xi, t_c) = \exp\left(-\frac{i}{\epsilon} S^{\pm}(t_c)\right) \sum_{k \in \mathcal{K}} c_k^{\pm}(t_c) \varphi_k^{\epsilon}[\hat{\Pi}^{\pm}(t_c)](\xi) \tag{3.2}$$

The projection onto a Hagedorn basis set at the avoided crossing for the transmitted wavepacket requires the following steps:

1. **Change of basis/co-ordinates** for the Hagedorn wavepackets such that a coordinate axis is parallel to $p(t_c)$, the mean momentum of the wavepacket at the time of the avoided crossing (and keep same orientation)

2. **Compute the new parameter set** for p, P, Q likely change p but keep the same P and Q

3. **Project the transmitted wavepackets onto the new basis set.**

[./main$_h$*agedorn.tex*]*subfilesamsmath*

3.1 Change of co-ordinates

The aim is to apply the one dimensional Superadiabatic formula to parallel strips of the incoming wavepacket in the direction of the mean momentum at the crossing. hence the gap should depend on the directions orthogonal to the mean momentum To this end, we firstly rotate the co-ordinate axes such that one co-ordinate lies parallel to p_c. Hence, we want a matrix R satisfying

- $Rp_c = (\|p_c\|, 0, ..., 0)$ - align momentum vector with one axis
- $R^T = R^{-1}$ (orthogonality)
- $\det(R) = 1$ (keep the same orientation of the basis)

We construct it by applying the Gram-Schmidt process to the vector $\frac{p_c}{\|p_c\|}$, i.e. we form an orthonormal basis $\{r_1 = \frac{p_c}{\|p_c\|}, r_2, ..., r_d\}$. Stacking this vectors into a matrix R as rows yields the desired rotation matrix R, that is

$$R = \begin{bmatrix} \frac{p_c^T}{\|p_c\|} \\ r_2^T \\ \dots \\ r_d^T \end{bmatrix} \tag{3.3}$$

If $\det(R) = -1$ then multiply its last column by -1. (There is also another way of doing it called Householder reflection which is computationally cheaper

Applying the change of coordinates to the wavepacket at the crossing yields

$$\hat{\psi}^{\pm}(\tilde{\xi}, t_c) = \exp\left(-\frac{i}{\epsilon}S^{\pm}(t_c)\right) \sum_{k \in \mathcal{K}} c_k^{\pm}(t_c)\varphi_k^{\epsilon}[\hat{\Pi}^{\pm}(t_c)](R^T\tilde{\xi}) \tag{3.4}$$

We want to show that the properties satisfies by the matrices Q,P are still satiied. Since the φ_k^ϵ's obey recurrence relation (1.3) we only need to consider the change of coordinates for φ_0^ϵ

$$\begin{aligned}
\varphi_0^\epsilon[\hat{\Pi}](\tilde{\xi}) &\propto \exp\left(\frac{i}{2\epsilon}(R^T\tilde{\xi}-p)^T QP^{-1}(R^T\tilde{\xi}-p)+\frac{i}{\epsilon}q^T(R^T\tilde{\xi}-p)\right)\\
&= \exp\left(\frac{i}{2\epsilon}(R^T(\tilde{\xi}-Rp))^T QP^{-1}R^T(\tilde{\xi}-Rp)+\frac{i}{\epsilon}q^TR^T(\tilde{\xi}-Rp)\right)\\
&= \exp\left(\frac{i}{2\epsilon}(\tilde{\xi}-Rp)^T RQP^{-1}R^T(\tilde{\xi}-Rp)+\frac{i}{\epsilon}(Rq)^T(\tilde{\xi}-Rp)\right)\\
&= \exp\left(\frac{i}{2\epsilon}(\tilde{\xi}-Rp)^T RQ(RP)^{-1}(\tilde{\xi}-Rp)+\frac{i}{\epsilon}(Rq)^T(\tilde{\xi}-Rp)\right)
\end{aligned} \tag{3.5}$$

where we have made use of the transposition rules in each equality. Perhaps expected, a rotation of the co-ordinate axes yields a new parameter set $\hat{\Pi}' = \{Rp, Rq, RP, RQ\}$ for the family of Hagedorn wavepackets. Indeed, the matrices RP and RQ still satisfy the symplectic properties of Lemma 1.1 since

$$\begin{aligned}
&(RP)^T(RQ)-(RQ)^T(RP)=\\
&P^TR^TRQ-Q^TR^TRP=\\
&P^TQ-Q^TP=0
\end{aligned} \tag{3.6}$$

and similarly

$$\begin{aligned}
&(RP)^*(RQ)-(RQ)^*(RP)=\\
&P^*R^*RQ-Q^*R^*RP=\\
&P^*R^TRQ-Q^*R^TRP=\\
&P^*Q-Q^*P=2iI_d
\end{aligned} \tag{3.7}$$

3.2 Superadiabatic transition

We address the application of the Superadiabatic formula to an Hagedorn wavepacket. Consider an incoming Hagedorn wavepacket at the crossing $\hat{\psi}^{\pm}(\xi, t_c) = e^{\frac{i}{\epsilon}S(t)}\varphi_k^{\epsilon}[\hat{\Pi}(t_c)]$. If we were to apply the Superadiabatic formula to the co-ordinate in the direction of the momentum, say ξ_1 then we would obtain

$$\hat{\psi}^{\mp}(t_c) = -e^{\frac{i}{\epsilon}S(t)}\Theta(\xi_1^2 - 4\delta)\frac{\xi_1 + v}{2|v|}e^{i\tau_c|\xi_1 - v|/(2\delta\epsilon)}\varphi_k^{\epsilon}[\hat{\Pi}](\tilde{\xi}) \tag{3.8}$$

where $v = \mathrm{sgn}(\xi_1)\sqrt{\xi_1^2 - 4\delta}, \delta = \rho(x_c)$ and $\tilde{\xi} = (v, \xi_2, ...)$ correct the formula so as to account the differences for the hopping depending on which level it lies The application of the formula in this form works well enough for the slice of the wavepacket sitting on the center of mass but clearly not for the ones orthogonal to it. For instance, suppose the wavepacket were to cross with its center of mass directly over a conical intersection. Then, we would have $\delta = 0$ so that the all incoming wavepacket gets transmitted. This would obviously yield incorrect results; we need to modify the one dimensional formula for each slice giving a different δ for each.

Alternative

A better alternative would be to let the gap depend on each slice and therefore on the directions orthogonal to ξ_1. This should correspond to the following

$$\begin{aligned}\hat{\psi}^{\mp}(t_c) = &-e^{\frac{i}{\epsilon}S(t)}\Theta(\|\xi\|^2 - 4\rho(x_{c_1}, \xi_2, \xi_3, ...)) \\ &\times \frac{\|\xi\| + v}{2|v|}e^{i\tau_c\frac{|\|\xi\| - v|}{2\rho(x_{c_1}, \xi_2, ...)\epsilon}}\varphi_k^{\epsilon}[\hat{\Pi}](\tilde{\xi})\end{aligned} \tag{3.9}$$

where $v = \mathrm{sgn}(\xi_1)\sqrt{\|\xi\|^2 - 4\rho(x_{c_1}, \xi_2, ...)}$ and $\tilde{\xi} = (v, \xi_2, ...)$ $[./\mathrm{main}_h agedorn.tex]subfilescomment$ $biber, style = alphabetic, sorting = ynt]biblatexHagedorn.bib$

3.3 Projecting onto Hagedorn basis

Upon detection of the avoided crossing and application of the transmission formula, the transmitted wavepacket $\hat{\psi}^{\mp}$ needs to be projected back onto a Hagedorn basis set $\Phi[\hat{\Pi}'] = \{\varphi_l[\hat{\Pi}']\}_{l\in\mathcal{L}}$ in order for it to be evolved away from the crossing using Hagedorn dynamics. Since $\Phi[\hat{\Pi}']$ is an orthonormal set, the closest point in its linear span to the transmitted wavepacket is given by

$$P_{\Phi}\hat{\psi}^{\mp} := \sum_{l\in\mathcal{L}} \left\langle \frac{\hat{\psi}^{\mp}}{\|\hat{\psi}^{\mp}\|}, \varphi_l[\hat{\Pi}'] \right\rangle \varphi_l[\hat{\Pi}'] \tag{3.10}$$

and it is unique since a linear subspace is convex. The coefficients $a_l := \left\langle \frac{\hat{\psi}^{\mp}}{\|\hat{\psi}^{\mp}\|}, \varphi_l[\hat{\Pi}'] \right\rangle$ are known as Fourier coefficients. The parameters $\hat{\Pi}$ for the new sub-basis set may take different values than the ones for the incoming wavepacket so as to minimise the number of Fourier coefficients a_l needed to represent the transmitted wavepacket.

3.3.1 Different parameter set Π

Constant eigenvalues - do it for the general case

Given the considerations outlined in the previous subsection we consider a different parameter set for the Hagedorn basis corresponding to the transmitted wavepacket. More precisey we change the entry of the momentum parameter p corresponding to the direction of motion of the wavepacket at the crossing, $\{p, q, P, Q\} \mapsto \{p', q, P, Q\}$ where $p'_i = p_i \ \forall\ 1 < i \leq d$ while

$$\begin{aligned} p'_1 &= \langle \xi\hat{\psi}^{\mp}(\xi_1), \hat{\psi}^{\mp}(\xi_1)\rangle \\ &= ... \end{aligned} \tag{3.11}$$

The Fourier coefficients are then given by

$$\begin{aligned} a_l &= \left\langle \frac{\hat{\psi}^{\mp}}{\|\hat{\psi}^{\mp}\|}, \varphi_l[\hat{\Pi}'] \right\rangle \\ &= \frac{1}{\|\hat{\psi}^{\mp}\|} \left\langle \sum_{k\in\mathcal{K}} c_k^{\pm}(t_c) f(\xi_1, \nu(\xi_1); \delta) \varphi_k^{\epsilon}[\hat{\Pi}_{t_c}^{\pm}](\tilde{\xi}), \varphi_l^{\epsilon}[\hat{\Pi}'](\xi) \right\rangle \\ &= \frac{1}{\|\hat{\psi}^{\mp}\|} \sum_{k\in\mathcal{K}} c_k^{\pm}(t_c) \left\langle f(\xi_1, \nu(\xi_1); \delta) \varphi_k^{\epsilon}[\hat{\Pi}_{t_c}^{\pm}](\tilde{\xi}), \varphi_l^{\epsilon}[\hat{\Pi}'](\xi) \right\rangle \end{aligned} \tag{3.12}$$

where

$$f(\xi_1, \nu(\xi_1); \delta) = \exp\left(-\frac{i}{\epsilon} S^{\pm}(t_c)\right) \sin\left(\frac{\pi\gamma}{2}\right) \operatorname{sgn}(\xi_1) \Theta(\xi_1^2 - 4\delta) \left(1 + \frac{\xi_1}{\nu(\xi_1)}\right) \exp\left[-\frac{q_c}{\epsilon}|\xi_1 - \nu(\xi_1)|\right]$$

and

$$\tilde{\xi} = (\nu(\xi_1), \xi_2, ..., \xi_d)$$

It is actually convenient to define

$$a_{kl} := \left\langle f(\xi_1, \nu(\xi_1); \delta) \varphi_k^{\epsilon}[\hat{\Pi}_{t_c}^{\pm}](\tilde{\xi}), \varphi_l^{\epsilon}[\hat{\Pi}'](\xi) \right\rangle$$

so that

$$a_l = \frac{1}{\|\hat{\psi}^{\mp}\|} \sum_{k\in\mathcal{K}} c_k^{\pm}(t_c) a_{kl}$$

Following the same approach as for the update of the coefficients stemming from the variational approximation, computation of the coefficients requires solving integrals of the following form

$$kd \tag{3.13}$$

Under the integral sign, the product of the two Gaussians is given by

$$= \exp\left[\frac{i}{2\epsilon}(\tilde{\xi}-p)^T QP^{-1}(\tilde{\xi}-p) + \frac{i}{\epsilon}q^T(\tilde{\xi}-p) - \frac{q_c}{\epsilon}|\xi_1 - \nu(\xi_1)|\right] \exp\left[\overline{\frac{i}{2\epsilon}(\xi-p')^T QP^{-1}(\xi-p') + \frac{i}{\epsilon}q^T(\xi-p')}\right] d\xi \tag{3.14}$$

We can simplify the argument in the exponential term further. Consider the real and imaginary matrix decomposition $QP^{-1} = R + iI$ where R and I are symmetric since QP^{-1} is, and let

$$\tilde{a} = [\nu(\xi_1) - p_1, 0, ..., 0] \qquad a = [\xi_1 - p_1', 0, ..., 0] \qquad b = [0, \xi_2 - p_2, ..., \xi_d - p_d] \tag{3.15}$$

. Then,

$$
\begin{aligned}
&\frac{i}{2\epsilon}\overline{(\tilde{a}+b)^T(R+iI)(\tilde{a}+b)+\frac{i}{\epsilon}q^T(\tilde{a}+b)-\frac{q_c}{\epsilon}|\xi_1-\nu(\xi_1)|}+\\
&+\frac{i}{2\epsilon}(a+b)^T(R+iI)(a+b)+\frac{i}{\epsilon}q^T(a+b)=\\
&-\frac{1}{2\epsilon}\left[(\tilde{a}+b)^TI(\tilde{a}+b)+(a+b)^TI(a+b)+2q_c|\xi_1-\nu(\xi_1)|\right]\\
&+\frac{i}{2\epsilon}\left[(\tilde{a}+b)^TR(\tilde{a}+b)-(a+b)^TR(a+b)+2q^T(\tilde{a}-a)\right]=\\
&-\frac{1}{2\epsilon}\left[\tilde{a}^TI\tilde{a}+a^TIa+2b^TIb+(\tilde{a}^T+a^T)Ib+b^TI(\tilde{a}+a)+2q_c|\xi_1-\nu(\xi_1)|\right]\\
&+\frac{i}{2\epsilon}\left[\tilde{a}^TR\tilde{a}-a^TRa+(\tilde{a}^T-a^T)Rb+b^TR(\tilde{a}-a)+2q_1(\tilde{a}_1-a_1))\right]=\\
&-\frac{1}{2\epsilon}\left[\tilde{a}^TI\tilde{a}+a^TIa+2b^TIb+2(\tilde{a}^T+a^T)Ib+2q_c|\xi_1-\nu(\xi_1)|\right]\\
&+\frac{i}{2\epsilon}\left[\tilde{a}^TR\tilde{a}-a^TRa+2(\tilde{a}^T-a^T)Rb+2q_1(\tilde{a}_1-a_1)\right]=\\
&-\frac{1}{2\epsilon}\left[I_{11}(\tilde{a}_1^2+a_1^2)+2b^TIb+2(\tilde{a}_1+a_1)\sum_{j=2}^{d}I_{1,j}b_j+2q_c|\xi_1-\nu(\xi_1)|\right]\\
&+\frac{i}{2\epsilon}\left[R_{11}(\tilde{a}_1^2-a_1^2)+2(\tilde{a}_1-a_1)\sum_{j=2}^{d}R_{1,j}b_j+2q_1(\tilde{a}_1-a_1)\right]=\\
&-\frac{1}{2\epsilon}\left[I_{11}(\tilde{a}_1^2+a_1^2)+2b^TIb+2(\tilde{a}_1+a_1)\sum_{j=2}^{d}I_{1,j}b_j+2q_c|\xi_1-\nu(\xi_1)|\right]\\
&+\frac{i}{2\epsilon}\left[R_{11}(\tilde{a}_1^2-a_1^2)+2(\tilde{a}_1-a_1)\left(q_1+\sum_{j=2}^{d}R_{1,j}b_j\right)\right]
\end{aligned}
\tag{3.16}
$$

We investigate different attempts to solving the integral for the Fourier coefficients. For each approach there is a convenient way of re-writing the integral.

The integral representation of a_{kl} is given by

$$\begin{aligned}
a_{kl} \propto & \int_{\mathbb{R}^d} \operatorname{sgn}(\xi_1)\Theta(\xi_1^2 - 4\delta)\left(1 + \frac{\xi_1}{\nu(\xi_1)}\right) P_k[\hat{\Pi}^{\pm}_{t_c}](\tilde{\xi})\overline{P_l[\hat{\Pi}'](\xi)}\times \\
& \exp\left\{-\frac{1}{2\epsilon}\left[I_{11}(\tilde{a}_1^2 + a_1^2) + 2b^T I b + 2(\tilde{a}_1 + a_1)\sum_{j=2}^{d} I_{1,j}b_j + 2q_c|\xi_1 - \nu(\xi_1)|\right]\right\} \\
& \exp\left\{\frac{i}{2\epsilon}\left[R_{11}(\tilde{a}_1^2 - a_1^2) + 2(\tilde{a}_1 - a_1)\left(q_1 + \sum_{j=2}^{d} R_{1,j}b_j\right)\right]\right\} d\xi \\
= & \int_{\mathbb{R}^{d-1}} \exp\left\{-\frac{1}{\epsilon}\left[b^T I b\right]\right\} \int_{\mathbb{R}} \operatorname{sgn}(\xi_1)\Theta(\xi_1^2 - 4\delta)\left(1 + \frac{\xi_1}{\nu(\xi_1)}\right) P_k[\hat{\Pi}^{\pm}_{t_c}](\tilde{\xi})\overline{P_l[\hat{\Pi}'](\xi)} \\
& \times \exp\left\{-\frac{1}{2\epsilon}\left[I_{11}(\tilde{a}_1^2 + a_1^2) + 2(\tilde{a}_1 + a_1)\sum_{j=2}^{d} I_{1,j}b_j + 2q_c|\xi_1 - \nu(\xi_1)|\right]\right\} \\
& \exp\left\{\frac{i}{2\epsilon}\left[R_{11}(\tilde{a}_1^2 - a_1^2) + 2(\tilde{a}_1 - a_1)\left(q_1 + \sum_{j=2}^{d} R_{1,j}b_j\right)\right]\right\} d\xi_1 d\xi_{d-1}
\end{aligned} \tag{3.17}$$

The proportionality constant is $\exp\left(-\frac{i}{\epsilon}S^{\pm}(t_c)\right)\sin(\frac{\pi\gamma}{2})$ Have the resulting integral here

We also note that I is real symmetric and so diagonalizable

3.4 Approximation error by Hagedorn basis

A natural question that arises as we approximate the transmitted wavepacket $\hat{\psi}^-$ with a Hagedorn basis is the following:

1. How large $|\mathcal{K}|$ should be such that the L^2 error (or better the relative error) is less than $\mathcal{TOL}$?

2. If the incoming wavepacket is a Hagedorn wavepacket of order k then the largest coefficient for the projection of Superadiabatic formula should

still coincide with c_k and so could I better choose the Hagedorn basis?

We can perhaps answer the first question using Theorem 1.2 in [Lub08] about approximation of Scwhartz functions by Hermite basis which is the equivalent to the 1d Hagedorn basis. We report the statement of the Theorem here below.

Theorem 3.1 *Approximation by Hermite functions Let ... Then,*

$$\|f - P_k f\| \leq (K(K-1)\dots(k-s+1))^{-1/2}\|A^s f\| \tag{3.18}$$

We can turn this result into an inequality for the relative error simply by multiplying both sides by $\|f\|$. In a numerical implementation we would like to estimate a-priori the number of wavepackets needed in the approximation for some desired tolerance. There is probably more than one way to do this:

1. if you know $\|f\|$ you can probably increment the values of k until you have reached some desired accuracy

2. use Theorem above by either estimating $\|A^s f\|$ for $s = K$ or compute it numerically (although you would have K to play around with)
   Also bear in mind that our transmitted wavepacket is not a Schwartz function - although this space is dense in L^2 so that you can not write it as a limit of such functions and then pass to the limit ? commutativity could be a problem?

I am going to consider the same example as in [Lub08] to numerically demonstrate the theorem and the importance of changing the parameter set for the transmitted wavepacket projection - although it'd be nice to come up with my own example, perhaps a modified version of it

3.5 d-dimensional case

Solution of the inner most nasty integral in ξ_1 may then allow us to solve the remaining $d-1$ dimensional integral explicitly

3.5.1 Monte Carlo Integration

(Ignore global phase factor for the moment)

We find it convenient to re-write a_{kl} in terms of complex coefficients as follows (we will use this form in other parts of the projection section)

$$\begin{aligned}
a_{kl} &= \sin\left(\frac{\pi\gamma}{2}\right)\int_{\mathbb{R}^{d-1}}\exp\left[-\frac{1}{\epsilon}b^T I b\right]\int_{\mathbb{R}}\mathrm{sgn}(\xi_1)\Theta(\xi_1^2-4\delta)\left(1+\frac{\xi_1}{\nu(\xi_1)}\right)P_k[\hat{\Pi}^{\pm}_{t_c}](\tilde{\xi})\overline{P_l[\hat{\Pi}'](\xi)}\times \\
&\qquad \exp\left[-\frac{1}{2\epsilon}\left(\alpha\tilde{a}_1^2+\overline{\alpha}a_1^2+\beta\tilde{a}_1+\overline{\beta}a_1+2q_c|\xi_1-\nu(\xi_1)|\right)\right]d\xi_1 d\xi_{d-1} \\
&= \int_{\mathbb{R}^{d-1}}\exp\left[-\frac{1}{\epsilon}b^T I b\right]\int_{\mathbb{R}}\mathrm{sgn}(\xi_1)\Theta(\xi_1^2-4\delta)\left(1+\frac{\xi_1}{\nu(\xi_1)}\right)P_k[\hat{\Pi}^{\pm}_{t_c}](\tilde{\xi})\overline{P_l[\hat{\Pi}'](\xi)}\times \\
&\qquad \exp\Bigg[-\frac{1}{2\epsilon}\Big(\alpha(\nu(\xi_1)-p_1)^2+\overline{\alpha}(\xi_1-p_1')^2+\beta(\nu(\xi_1)-p_1)+\overline{\beta}(\xi_1-p_1') \\
&\qquad +2q_c|\xi_1-\nu(\xi_1)|\Big)\Bigg]d\xi_1 d\xi_{d-1}
\end{aligned} \tag{3.19}$$

We spot a Gaussian term in the integral which would be suitable for numerical integration via MC.

$$a_{kl} = \int_{\mathbb{R}^{d-1}} \exp\left[-\frac{1}{\epsilon} b^T I b\right] \int_{\mathbb{R}} \mathrm{sgn}(\xi_1)\Theta(\xi_1^2 - 4\delta)\left(1 + \frac{\xi_1}{\nu(\xi_1)}\right) P_k[\hat{\Pi}^{\pm}_{t_c}](\tilde{\xi})\overline{P_l[\hat{\Pi}'](\xi)} \times$$
$$\exp\left[-\frac{1}{2\epsilon}\Big(\alpha(\nu(\xi_1) - p_1)^2 + \beta(\nu(\xi_1) - p_1) + \overline{\beta}(\xi_1 - p_1') + iR_{11}(\xi_1 - p_1')^2 + 2q_c|\xi_1 - \nu(\xi_1)|\Big)\right.$$
$$\exp\left[-\frac{I_{11}}{2\epsilon}(\xi_1 - p_1')^2\right] d\xi_1 d\xi_{d-1} \tag{3.20}$$

where

$$\alpha = I_{11} - iR_{11} \qquad \beta = -i2q_1 + 2\sum_{j=2}^{d}(I_{1,j} - iR_{1,j})b_j \tag{3.21}$$

We can use a Monte Carlo estimator so that

$$a_{kl} = \lim_{N\to\infty} \sum_{n=0}^{N} \mathrm{sgn}(\xi_n)\Theta(\xi_n^2 - 4\delta)\left(1 + \frac{\xi_n}{\nu(\xi_n)}\right)$$
$$\exp\left[-\frac{1}{2\epsilon}\Big(\alpha(\nu(\xi_n) - p_1)^2 + iR_{11}(\xi_n - p_1')^2 + 2q_c|\xi_n - \nu(\xi_n)|\Big)\right] \times$$
$$\int_{\mathbb{R}^{d-1}} P_k[\hat{\Pi}^{\pm}_{t_c}](\nu(\xi_n), \xi_2, ..., \xi_d)\overline{P_l[\hat{\Pi}'](\xi_n, \xi_2, ..., \xi_d)}$$
$$\exp\left[-\frac{1}{\epsilon}(b^T I b)\right] \tag{3.22}$$

To do:

- integral is incomplete but we get the idea
- will loose efficiency of samples when checking $\Theta(....)$
- there is some normalisation constant missing
- inner integral should be solvable since I is diagonalizable

3.5.2 Taylor expansion + Gaussian Integrals

We will consider this approach once we have an expression for the k^{th} order polynomials. For the moment jump to the section on one dimensional integration which consists in the same approach and not much will change for this situation since we will be able to solve the remaining $d-1$ integrals exactly.

3.5.3 One dimension - principle of stationary phase

Could think of solvin inner integral using an asymptotic expansion and then see whether the resulting $d-1$ integral could be solved exactly...?
In this case we want to re-write the integral in a form such that the imaginary term in the exponent is explicit. For $d = 1$, the polynomials reduce to Hermite polynomials. The integral is of the form

$$\int_{\mathbb{R}} f(\xi;\delta) \exp\left[\frac{i}{2\epsilon} g(\xi;\delta)\right] d\xi \tag{3.23}$$

where

$$
\begin{aligned}
f(\xi;\delta) &= \mathrm{sgn}(\xi_1)\Theta(\xi_1^2 - 4\delta)\left(1 + \frac{\xi_1}{\nu(\xi_1)}\right) p_k[\Pi](\nu(\xi))p_l[\Pi'](\xi) \\
&\quad \exp\left[-\frac{1}{2\epsilon}(2I_{11}\xi_1^2 + 2\xi_1(-I_{11}p_1' + \sum_{j=2}^{d} I_{1,j}b_j) + 2\nu(\xi_1)(-p_1 I_{11} + \sum_{j=2}^{d} I_{1,j}b_j))\right] \\
&\quad \exp\left[I_{11}(-4\delta + p_1^2 + {p_1'}^2) - 2(p_1 + p_1')(\sum_{j=2}^{d} I_{1,j}b_j) + q_c|\xi_1 - \nu(\xi_1)|\right] \\
g(\xi;\delta) &= 2\nu(\xi_1)(\sum_{j=2}^{d} R_{1,j}b_j + q_1 - R_{11}p_1) - 2\xi_1(\sum_{j=2}^{d} R_{1,j}b_j + q_1 - R_{11}p_1') \\
&\quad R_{11}(-4\delta + p_1^2 - {p_1'}^2) + 2\left(q_1 + \sum_{j=2}^{d} R_{1,j}b_j\right)(-p_1 + p_1')
\end{aligned}
\tag{3.24}
$$

If you approximate $\nu(\xi_1)$ then you would be able to say something about the frequency of the oscillations

For $d = 1$, the polynomials reduce to the Hermite polynomials We can re-write the oscillator more succintly as

$$g(\xi_1;\delta) = \alpha\nu(\xi_1) + \beta\xi_1 + \gamma$$

where

$$
\begin{aligned}
\alpha &= 2(q_1 + \sum_{j=2}^{d} R_{1,j}b_j - Rp_1) \\
\beta &= 2(-q_1 - \sum_{j=2}^{d} R_{1,j}b_j + Rp_1') \\
\gamma &=
\end{aligned}
\tag{3.25}
$$

and $g(\xi)$ has a stationary point on $(2\sqrt{\delta}, \infty)$ at ξ_1^* that solves

$$\begin{aligned} &\frac{\alpha\xi_1}{\sqrt{\xi_1^2 - 4\delta}} + \beta = 0 \\ &\Leftrightarrow \xi_1^* = \sqrt{\frac{-4\beta^2\delta}{\alpha^2 - \beta^2}} \end{aligned} \tag{3.26}$$

where $\alpha^2 - \beta^2 \leq 0$ with equality when ....

The stationary point is non-degenerate so should be able to re-write in quadratic form via a change of variables

The frequency depends on the ration δ/ϵ Change of variables...? $f(\xi)$ is not smoothed but can be smoothed...?

$$\begin{aligned} \int_{\mathbb{R}} \operatorname{sgn}(\xi_1)\Theta(\xi_1^2 - 4\delta) \left(1 + \frac{\xi_1}{\nu(\xi_1)}\right) g(\xi_1, \nu(\xi_1)) \times \\ \exp\left[-\frac{1}{2\epsilon}\left(\alpha\tilde{a}_1^2 + \overline{\alpha}a_1^2 + \beta\tilde{a}_1 + \overline{\beta}a_1 + 2q_c|\xi_1 - \nu(\xi_1)|\right)\right] d\xi_1 \end{aligned} \tag{3.27}$$

4 Numerical Integration

In one dimension, the projection integral to reconstruct the transmitted wavepacket in terms of the Hagedorn basis set can be written in the following form

$$I_{lk} := \int_{-\infty}^{+\infty} f(x)k(x)dx \tag{4.1}$$

where $k(x)$ and $f(x)$ are called the weight function and .. respectively. where we have made the change of variables ... Integrals of this form can be solved rather efficiently using Gauss-Hermite quadrature rules. The idea behind .. and all other types of Gauss quadrature is to approximate the integral with a weighted sum

$$I_{lk} \approx \sum_{i=i}^{N} w_i f(x_i) \tag{4.2}$$

where $\{w_i\}_{i=1}^{N}$ and x_i are called the weights and the nodes of the quadrature rule respectively. The nodes could be set a priori for example in situations where they are given to us and so we are only left to determine the weights. Otherwise these can be determined. The general idea behind these methods is that the quadrature rule should be exact for a class of polynomials up to a certain degree which is determined by the number of nodes N.

4.1 Approximation error for Gauss-Hermite quadrature rule

A natural question that arises is the following: how many points do I need such that the relative error in the computation of c_k is a below a certain a tolerance value. in [Lub08] it simply stated that the error in the quadrature rule

is $\mathcal{O}(M^{-}r)$ where $r > 1$ (why r=1 not allowed) satisfies $\|c_k\| \leq C(1+k)^{-r}$. In words, the coefficients of the Hermite expansions decay obeying that bound for some $C \in \mathbb{R}$.

The example for $f(x)$ we will be considering is both instructive as an example for the order of convergence properties of this result but also given the fact that the integrals we are interested involve other Gaussian functions but also may involve oscillatory term - this is something which could be approached in different ways: purely imaginary PQ^{-1}, a new rule for a different weight?, turn into stationary phase-integrals. The following example indeed demonstrates the difficulties that arise as the function becomes highly oscillatory and how the oscillatory term affects the rate of convergence (but what about the constants?)

Let

$$f(x;b) := \exp\left\{-\frac{x^2}{2} + i\sqrt{2}bx\right\} \tag{4.3}$$

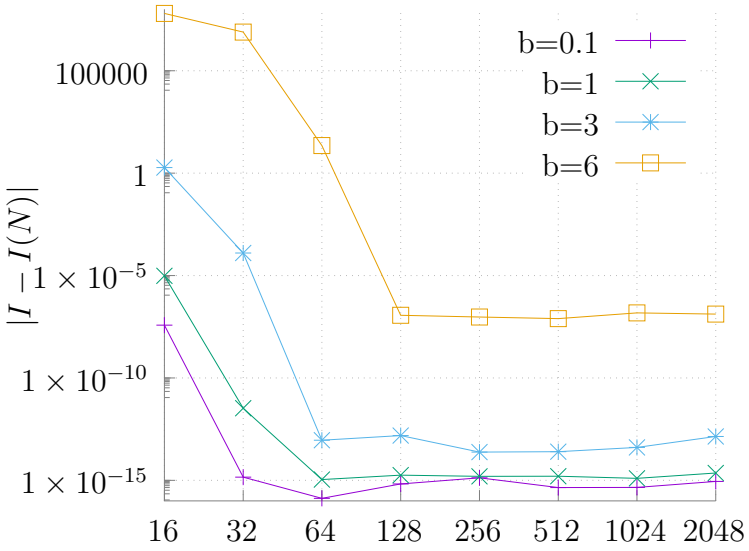
where $b \in \mathbb{R}$ will be taken to be non-negative for convenience. For an Hermite basis of the form (...) the coefficients in the expansion are given by

$$c_k = \pi^{1/4} \exp\left\{-\frac{b^2}{2}\right\} \frac{i^k b^k}{\sqrt{k!}} \tag{4.4}$$

from which we have $|c_k| = C\frac{b^k}{\sqrt{k!}}$ where $C = \pi^{1/4}\exp\left\{-\frac{b^2}{2}\right\}$. The aim is to find an $r > 1$ -independent of k- such that $|c_k| \leq D(1+k)^{-r}$ for some $C \in \mathbb{R}$ - this condition is such that the result about convergence holds. Equivalently, find r and $D \in \mathbb{R}$ such that

$$1 < r \leq -\frac{1}{D}\frac{\log(b^k/\sqrt{k!})}{\log(1+k)} \tag{4.5}$$

1. if $b < 1$, then $k = 1$ leads to the largest value on the RHS



4.2 Gaussian Hermite Quadrature

We have been running simple tests on functions such as $1, x, x^2$

1. Explain Gaussian quadrature rule and how it differs from more standard quadrature methods- say Riemann sums for example - rectangles of the same width, Simpson..

2. Comment on the theory - when is it accurate, exact,

3. Test the method on Hagedorn wavepackets - say they should satisfy the orthogonality condition How many points does the theory require for it to be exact?

4. Talk about the evaluation of the polynomial using the efficient recurrence relation. Perhaps the derivation you have written avoids the issue of stability? to look into

5. There is something to comment about the quadrature rule. The points and the weights depend only on the number of nodes. Are these always symmetric about zero and are so the weights?

Let φ_k have the parameter set ... Consider the following integrals

$$\begin{aligned} I_{lk} &:= \int_{\mathbb{R}} \varphi_k \bar{\varphi}_l dx \\ &= \int_{\mathbb{R}} P_k(x) \bar{P}_l(x) |\varphi_0|^2 dx \\ &= \int_{\mathbb{R}} P_k(x) \bar{P}_l(x) \exp\left(-\frac{1}{2\epsilon} x^2\right) dx \end{aligned} \tag{4.6}$$

where the Hagedorn wavepackets are normalised. do a change of variable to yield the desired form $\int_{\mathbb{R}} f(x)dx$. In this case $f(x)$ is a polynomial of degree $k+l$ so how many points does the theory say I would require?

5 Numerical results

5.1 Constant eigenvalues

As our first example we consider the case of constant eigenvalues. By considering the potential matrix in the form of equation ... we can arbitrarily choose the form of $\rho(x)$. The trace is zero in this case. Given that the eigenvalues are constant we know that the evolution of the parameters suffices to describe the one level dynamics exactly, that is the initial coefficients do not

change over time. In this way we remove any potential sources of error from numerical integration. We consider the same system as in [reference Ben's paper] with ....

5.1.1 Initial condition

The initial condition is given at the crossing (not an avoided crossing nor a conical intersection but simply where the coupling term $\theta'(x)$ peaks ?) by

$$\begin{aligned}\hat{\psi}^{+}(\xi, t_c) &= (2\pi\epsilon)^{-1/4} \exp\left\{-\frac{(\xi - p_0)^2}{4\epsilon}\right\} \\ &= \varphi_0^{\epsilon}\left[\Pi\right](\xi)\end{aligned} \tag{5.1}$$

where $\Pi = \left[p_0, 0, \sqrt{2}, \frac{i}{\sqrt{2}}\right]$ Application of the Superadiabatic formula yields

$$\begin{aligned}\hat{\psi}^{-}(\xi, t_c) = \sin\left(\frac{\pi}{2\gamma}\right) \Theta(\xi^2 - 4\delta) \frac{v + \xi}{2|v|} \times \\ \exp\left\{-iq_c \frac{|\xi - v|}{2\delta\epsilon}\right\} \varphi_0^{\epsilon}\left[\Pi\right](v)\end{aligned} \tag{5.2}$$

I would have a graph here showing the incoming wavepacket and the transmitted wavepacket The question now is how to project the transmitted wavepacket onto an Hagedorn basis $\{\varphi_k\}_{k\in\mathcal{K}}$ with parameters $\Pi' = \left[p_0', 0, \sqrt{2}, \frac{i}{\sqrt{2}}\right]$ In particular, how large should $\mathcal{K}$ be in order for the L^2 (relative) error to be less than $\mathcal{TOL}$. The integrals we need to compute are

$$c_k = \int_{\mathbb{R}} \hat{\psi}^{-}(\xi, t_c) H_k \varphi_0^{\epsilon}[\Pi'](\xi) d\xi \tag{5.3}$$

where if solved with Gauss-Hermite quadrature we must have $f(x) = ..$ and $w(x) = \varphi_0^{\epsilon}[\Pi']$ what I would do is verify that the general formula you have derived in the previous section yields the same result that you obtain by doing it explicitly

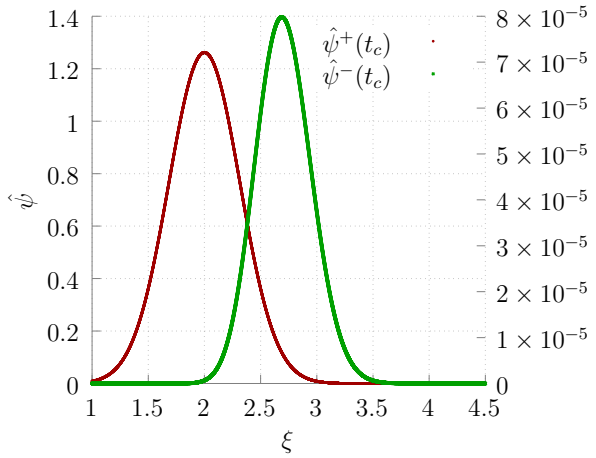


Figure 3: ..

References

[Hag98] George A Hagedorn. "Raising and Lowering Operators for Semiclassical Wave Packets". In: *Annals of Physics* 269.1 (Oct. 1998), pp. 77–104. ISSN: 00034916. DOI: 10.1006/aphy.1998.5843. URL: https://linkinghub.elsevier.com/retrieve/pii/S0003491698958432 (visited on 03/27/2021).

[HJ05] George A. Hagedorn and Alain Joye. "Determination of Non-Adiabatic Scattering Wave Functions in a Born-Oppenheimer Model". In: *Annales Henri Poincaré* 6.5 (Oct. 2005), pp. 937–990. ISSN: 1424-0637, 1424-0661. DOI: 10.1007/s00023-005-0231-y. URL: http://link.springer.com/10.1007/s00023-005-0231-y (visited on 03/05/2021).

[Lub08] Christian Lubich. *From Quantum to Classical Molecular Dynamics: Reduced Models and Numerical Analysis*. In collab. with Euro-

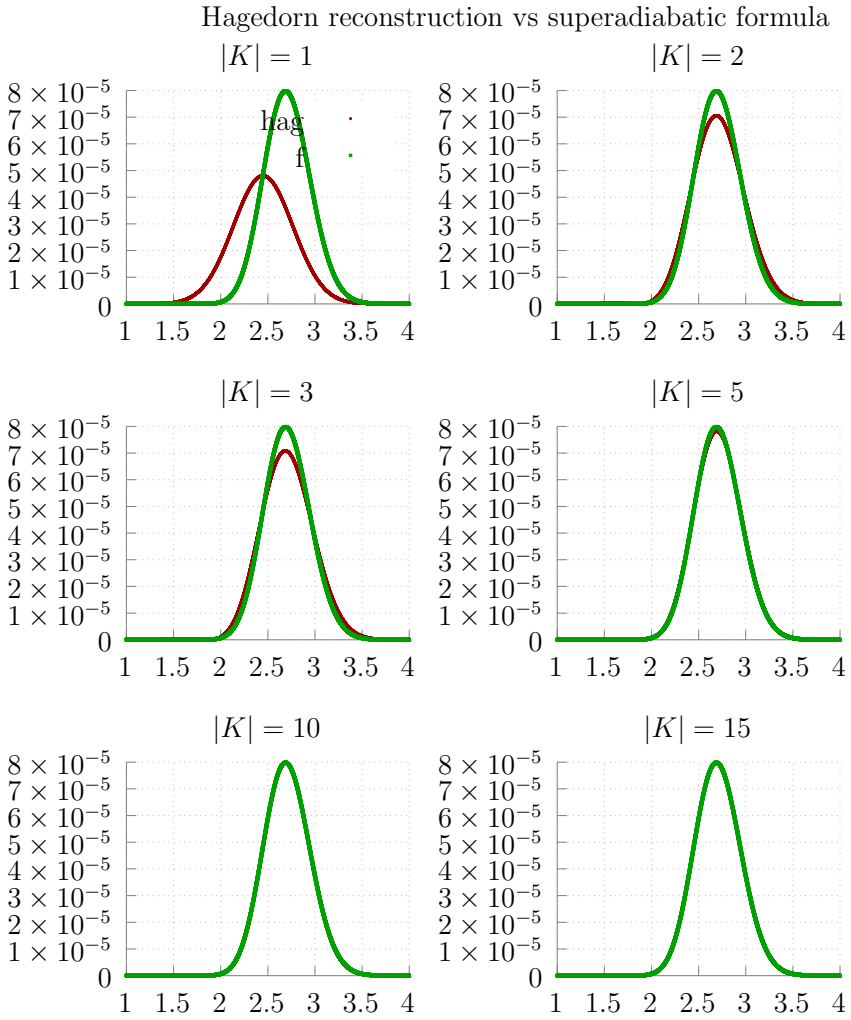


Figure 4: ..

pean Mathematical Society. Zurich Lectures in Advanced Mathematics. Zürich, Switzerland: European Mathematical Society, 2008. ISBN: 978-3-03719-067-8.

[BGT09] Volker Betz, Benjamin D. Goddard, and Stefan Teufel. "Superadiabatic Transitions in Quantum Molecular Dynamics". In: *Proceed-*

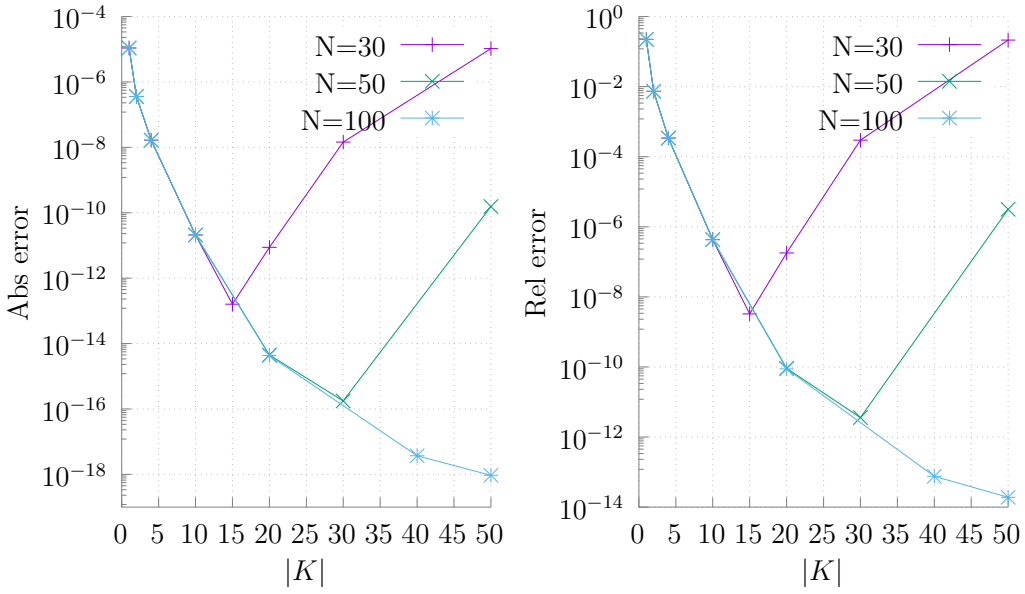


Figure 5: ..

ings of the Royal Society A: Mathematical, Physical and Engineering Sciences 465.2111 (Nov. 8, 2009), pp. 3553–3580. ISSN: 1364-5021, 1471-2946. DOI: 10.1098/rspa.2009.0337. URL: https://royalsocietypublishing.org/doi/10.1098/rspa.2009.0337 (visited on 03/28/2021).

[FGL09] Erwan Faou, Vasile Gradinaru, and Christian Lubich. "Computing Semiclassical Quantum Dynamics with Hagedorn Wavepackets". In: *SIAM Journal on Scientific Computing* 31.4 (Jan. 2009), pp. 3027–3041. ISSN: 1064-8275, 1095-7197. DOI: 10.1137/080729724. URL: http://epubs.siam.org/doi/10.1137/080729724 (visited on 03/06/2021).

[GHJ10] V. Gradinaru, G. A. Hagedorn, and A. Joye. "Tunneling Dynamics and Spawning with Adaptive Semiclassical Wave Packets". In: *The Journal of Chemical Physics* 132.18 (May 14, 2010), p. 184108. ISSN: 0021-9606, 1089-7690. DOI: 10.1063/1.3429607. URL: http://aip.scitation.org/doi/10.1063/1.3429607 (visited on 04/08/2021).

[BGH12] Raoul Bourquin, Vasile Gradinaru, and George A. Hagedorn. "Non-Adiabatic Transitions near Avoided Crossings: Theory and Numerics". In: *Journal of Mathematical Chemistry* 50.3 (Mar. 2012), pp. 602–619. ISSN: 0259-9791, 1572-8897. DOI: 10.1007/s10910-011-9827-2. URL: http://link.springer.com/10.1007/s10910-011-9827-2 (visited on 03/27/2021).

[Bou17] Raoul Bourquin. "Numerical Algorithms for Semiclassical Wavepackets". In: 2017. DOI: 10.3929/ethz-b-000183094.

[BGH19] V. Betz, B. D. Goddard, and Tim Hurst. "Nonadiabatic Transitions in Multiple Dimensions". In: *SIAM Journal on Scientific Computing* 41.5 (Jan. 2019), B1011–B1033. ISSN: 1064-8275, 1095-7197. DOI: 10.1137/18M1188756. URL: https://epubs.siam.org/doi/10.1137/18M1188756 (visited on 03/28/2021).

[BG20] Sergio Blanes and Vasile Gradinaru. "High Order Efficient Splittings for the Semiclassical Time–Dependent Schrödinger Equation". In: *Journal of Computational Physics* 405 (Mar. 2020), p. 109157. ISSN: 00219991. DOI: 10.1016/j.jcp.2019.109157.

URL: https://linkinghub.elsevier.com/retrieve/pii/S0021999119308629 (visited on 05/20/2021).

[FLR20] Clotilde Fermanian-Kammerer, Caroline Lasser, and Didier Robert. *Propagation of Wave Packets for Systems Presenting Codimension 1 Crossings*. Aug. 25, 2020. arXiv: 2001.07484 [math-ph]. URL: http://arxiv.org/abs/2001.07484 (visited on 06/28/2021).

Appendices

Some Appendix

A Transmitted Wavepacket

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A.1 Transmitted wavepacket

We can now apply the transmission formula of equation ... for the two cases of constant and non-constant eigenvalues

A.1.1 Constant eigenvalues

The transmitted wavepacket is given by [BGT09]

$$\begin{aligned}\hat{\psi}^{\mp}(\xi, t_c) &= \exp\left(-\frac{i}{\epsilon}S^{\pm}(t_c)\right)\sin\left(\frac{\pi\gamma}{2}\right)\times \\ &\quad \operatorname{sgn}(\xi_1)\Theta(\xi_1^2-4\delta)\left(1+\frac{\xi_1}{\nu(\xi_1)}\right)\exp\left(-\frac{q_c}{\epsilon}|\xi_1-\nu(\xi_1)|\right)\times \\ &\quad \sum_{k\in\mathcal{K}} c_k^{\pm}(t_c)\varphi_k^{\epsilon}[\hat{\Pi}^{\pm}(t_c)](\nu(\xi_1),\xi_2,...,\xi_d) \\ &\quad = \exp\left(-\frac{i}{\epsilon}S^{\pm}(t_c)\right)\sin\left(\frac{\pi\gamma}{2}\right)\times \\ &\quad \operatorname{sgn}(\xi_1)\Theta(\xi_1^2-4\delta)\left(1+\frac{\xi_1}{\nu(\xi_1)}\right)\exp\left(-\frac{q_c}{\epsilon}|\xi_1-\nu(\xi_1)|\right)\times \\ &\quad \varphi_0^{\epsilon}[\hat{\Pi}^{\pm}(t_c)](\nu(\xi_1),\xi_2,...,\xi_d)\sum_{k\in\mathcal{K}} c_k^{\pm}(t_c)p_k(\nu(\xi_1),\xi_2,...,\xi_d)\end{aligned} \tag{A.1}$$

- At least for Gaussian wavepackets with "large enough" momentum, the effect of the cut-off function should be "negligible" as a result of the exponential decay. Is this still the case as the order of the Hagedorn wavepacket increases...? The variance of φ_k^{ϵ} scales with k...

A.1.2 Non-constant + tilted crossings

The transmitted wavepacket is given by [BGH19]

$$\begin{aligned}\hat{\psi}^{\mp}(\xi, t_c) &= \exp\left(-\frac{i}{\epsilon}S^{\pm}(t_c)\right)\times \\ &\quad \Theta(\xi_1^2-4\delta)\frac{\nu(\xi_1)+\xi_1}{2|\nu(\xi_1)|}\exp\left(-\frac{\tau_c}{2\delta\epsilon}|\xi_1-\nu(\xi_1)|\right)\exp\left(-\frac{i\tau_r}{2\delta\epsilon}(\xi_1-\nu(\xi_1))\right)\times \\ &\quad \sum_{k\in\mathcal{K}} c_k^{\pm}(t_c)\varphi_k^{\epsilon}[\hat{\Pi}^{\pm}(t_c)](\nu(\xi_1),\xi_2,...,\xi_d)\end{aligned} \tag{A.2}$$

Is there an actual mismatch between the formulas for the constant eigenvalue and the general case? That is, why does the sin prefactor disappear for the general case? Also, I would think the formula is invariant to the direction of the jump between levels..? The derivation was done from up to down but intuitively thing should not change...?

B Proof of concept for choosing different parameter set in the projection

Given that we can obtain the results numerically, it is questionable whether this is needed or not Here we try to determine/justify whether it is at all numerically convenient to change the parameters $\hat{\Pi}$ for the transmitted wavepacket and thus reduce the number of coefficients needed to represent the wavepacket in the Hagedorn basis. This is motivated by the knowledge we have regarding the momentum shift.

Since this is only a proof of concept, let us consider the simplest complex Gaussian wavepacket for our incoming wavepacket with $P = 1, Q = i$. Furthermore, we are interested in the dependence of the Fourier coefficients with respect to a relative shift δ in the mean momentum of the transmitted wavepacket and so we find it convenient to consider deviations δ from $p = 0$. We also consider the location of the avoided crossing to be at $q = 0$ presumably for the dynamics one can always relocate the avoided crossing to zero by translating the center of mass - however this would then now work for on the fly dynamics? and thus removing oscillatory

terms from the integral. More precisely we are interested in computing $c_k(\delta) = \langle \varphi_0^\epsilon[\delta,0,1,i](\xi), \varphi_k^\epsilon[0,0,1,i](\xi)\rangle$. The φ_k's for this choice of parameters can be generated from the recurrence relation (1.3) in momentum space If I make an ansatz about the polynomial gaussian relation, it should give a recurrence relation for the polynomials only I would guess that one can do this by first doing the translation to $p = 0$ and then re-introducing the translation after the tablulation

$$\begin{aligned}
\varphi_0^\epsilon(\xi) &= (\pi\epsilon)^{-\frac{1}{4}} \exp\left(-\frac{\xi^2}{2\epsilon}\right) \\
\varphi_{k+1}^\epsilon &= \sqrt{\frac{2}{\epsilon(k+1)}}\xi\varphi_k^\epsilon - \sqrt{\frac{k}{k+1}}\varphi_{k-1} \\
&= \ldots \\
\varphi_1^\epsilon(\xi) &= \sqrt{\frac{2}{\epsilon}}\xi\varphi_0^\epsilon, \quad \varphi_2^\epsilon(\xi) = \left(\sqrt{\frac{2}{\epsilon^2}}\xi^2 - \frac{1}{\sqrt{2}}\right)\varphi_0^\epsilon \\
\varphi_3^\epsilon(\xi) &= \left(\frac{2}{\sqrt{3\epsilon^3}}\xi^3 - \frac{3}{\sqrt{3\epsilon}}\xi\right)\varphi_0^\epsilon, \quad \varphi_4^\epsilon(\xi) = \left(\frac{1}{\epsilon^2}\sqrt{\frac{2}{3}}\xi^4 - \frac{\sqrt{6}}{\epsilon}\xi^2 + \sqrt{\frac{3}{8}}\right)\varphi_0^\epsilon
\end{aligned} \tag{B.1}$$

If we let $a_n(\delta) = \langle \varphi_0^\epsilon[\delta,0,1,i](\xi), \xi^n\varphi_0^\epsilon[0,0,1,i](\xi)\rangle$ we can then re-write the coefficients more succintly as

$$\begin{aligned}
c_1(\delta) &= \sqrt{\frac{2}{\epsilon}}a_1(\delta), \quad c_2(\delta) = \sqrt{\frac{2}{\epsilon^2}}a_2(\delta) - \frac{1}{\sqrt{2}}a_0(\delta) \\
c_3(\delta) &= \frac{2}{\sqrt{3\epsilon^3}}a_3(\delta) - \frac{3}{\sqrt{3\epsilon}}a_1(\delta), \quad c_4(\delta) = \frac{1}{\epsilon^2}\sqrt{\frac{2}{3}}a_4(\delta) - \frac{\sqrt{6}}{\epsilon}a_2(\delta) + \sqrt{\frac{3}{8}}
\end{aligned} \tag{B.2}$$

The polynomials need to check... would they have had complex coefficients if we had a complex valued P, in higher dimension are they linear combinations

of monomials or they have cross terms? are the Hermite polynomials but I still need to get the coefficients right...? Given the form the wavepackets we only need to consider the integral for a monomial ξ^n as a prefactor,

$$\begin{aligned}
a_n(\delta) =&(\pi\epsilon)^{-\frac{1}{2}} \int_{\mathbb{R}} \xi^n \exp\left[-\frac{1}{2\epsilon}\left(\xi^2 + (\xi-\delta)^2\right)\right] d\xi \\
=&(\pi\epsilon)^{-\frac{1}{2}} \int_{\mathbb{R}} \xi^n \exp\left[-\frac{1}{2\epsilon}\left(2\xi^2 - 2\xi\delta + \delta^2\right)\right] d\xi \\
=&(\pi\epsilon)^{-\frac{1}{2}} \exp\left[-\frac{\delta^2}{2\epsilon}\right] \int_{\mathbb{R}} \xi^n \exp\left[-\frac{1}{\epsilon}\left(\xi^2 - \xi\delta\right)\right] d\xi \\
=&(\pi\epsilon)^{-\frac{1}{2}} \exp\left[-\frac{\delta^2}{2\epsilon}\right] \int_{\mathbb{R}} \epsilon^n \frac{d^n}{d\delta^n} \exp\left[-\frac{1}{\epsilon}\left(\xi^2 - \xi\delta\right)\right] d\xi \\
=&(\pi\epsilon)^{-\frac{1}{2}} \exp\left[-\frac{\delta^2}{2\epsilon}\right] \epsilon^n \frac{d^n}{d\delta^n} \int_{\mathbb{R}} \exp\left[-\frac{1}{\epsilon}\left(\xi^2 - \xi\delta\right)\right] d\xi \\
=&(\pi\epsilon)^{-\frac{1}{2}} (\pi\epsilon)^{\frac{1}{2}} \epsilon^n \exp\left[-\frac{\delta^2}{2\epsilon}\right] \frac{d^n}{d\delta^n} \exp\left[\frac{\delta^2}{4\epsilon}\right] \\
=&\epsilon^n \exp\left[-\frac{\delta^2}{2\epsilon}\right] \frac{d^n}{d\delta^n} \exp\left[-\frac{(i(2\epsilon)^{-\frac{1}{2}}\delta)^2}{2}\right] \\
=&\epsilon^n \exp\left[-\frac{\delta^2}{2\epsilon}\right] \exp\left[\frac{\delta^2}{4\epsilon}\right] (-i)^n (2\epsilon)^{-n/2} H_n\left(i\frac{\delta}{\sqrt{2\epsilon}}\right) \\
=&\epsilon^n \exp\left[-\frac{\delta^2}{4\epsilon}\right] (-i)^n (2\epsilon)^{-n/2} H_n\left(i\frac{\delta}{\sqrt{2\epsilon}}\right)
\end{aligned}$$

(B.3)

where we have used the a known identity for the Gaussian integral and the probabilists' Hermite polynomials $H_e(x) = ...$

- $a_0(\delta) = c_0(\delta)$
- $a_0(0) = c_0(0) = 1$ as expected

- Checked the first few but the following plot will also serve as a sanity check
- This makes clearer Hagedorn and Joye's claim that the leading order is a Gaussian
- If we consider the c_n's it does seem as if the dependence on the higher order basis vectors is in ascending order as we increase δ up to a certain point
- It is intuitively clear why it depends on the ratio between the momentum shift and the variance $\mathcal{O}(\epsilon)$
- The coefficients are real because we have chosen $q = 0$
- We know that the mean momentum shift is at least $2\sqrt{\delta}$ from conservation of energy

2.1 One dimensional case

(Ignore global phase factor for the moment) In one dimension the a_{kl} becomes

$$a_{kl} = \sin\left(\frac{\pi\gamma}{2}\right) \int_{\mathbb{R}} \operatorname{sgn}(\xi_1)\Theta(\xi_1^2 - 4\delta) \left(1 + \frac{\xi_1}{\nu(\xi_1)}\right) P_k[\hat{\Pi}^{\pm}_{t_c}](\tilde{\xi})\overline{P_l[\hat{\Pi}']}(\xi)\times$$
$$\exp\Bigg[-\frac{1}{2\epsilon}\Big(\alpha(\nu(\xi_1) - p_1)^2 + \overline{\alpha}(\xi_1 - p_1')^2 + \beta(\nu(\xi_1) - p_1) + \overline{\beta}(\xi_1 - p_1')$$
$$+ 2q_c|\xi_1 - \nu(\xi_1)|\Big)\Bigg] d\xi_1 \tag{2.4}$$

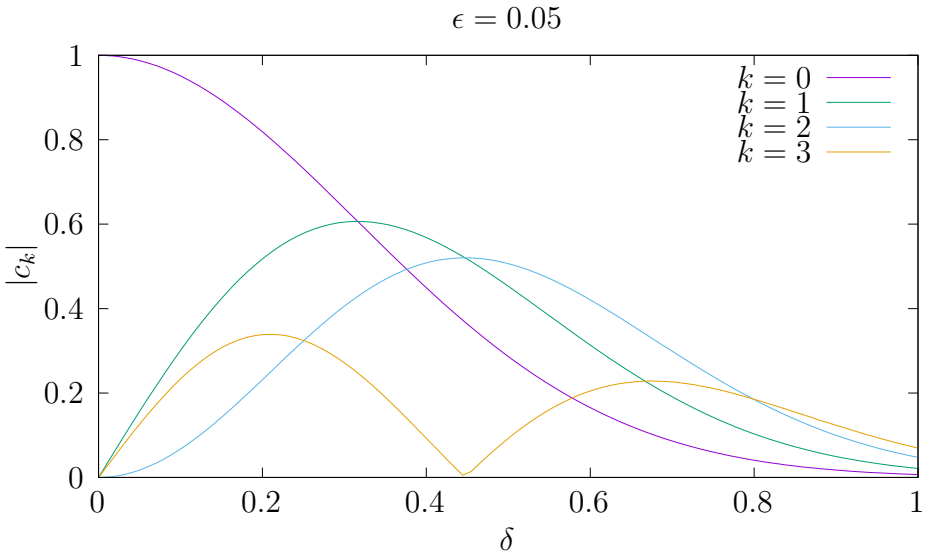

Figure 6: c_k is the coefficient corresponding to the projected Gaussian onto the k^{th} Hagedorn wavepacket.

where

$$\alpha = I_{11} - iR_{11} \qquad \beta = -i2q_1 \tag{2.5}$$

and (see attached written notes)

$$\begin{aligned} P_k[\Pi](x)\varphi_0 = \sqrt{k!}\left(\frac{i}{2\epsilon}\right)^k \sum_{\substack{j=0 \\ j\equiv k(\text{mod}2)}}^{k} \frac{(i\epsilon Q^* P^*/2)^{(k-j)/2}}{j!(\frac{k-j}{2})!} \times \\ \times \left(\sum_{r=0}^{j}\binom{j}{r}\left(P^*(x-q)+Q^*p\right)^r\left(Q^* i\epsilon d_x\right)^{j-r}\right)\varphi_0 \end{aligned} \tag{2.6}$$

so that

$$P_k[\Pi](x) = \sqrt{k!}\left(\frac{i}{2\epsilon}\right)^k \sum_{\substack{j=0 \\ j\equiv k(\mathrm{mod}2)}}^{k} \frac{(i\epsilon Q^* P^*/2)^{(k-j)/2}}{j!(\frac{k-j}{2})!}\times$$
$$\times\left(\sum_{r=0}^{j}\binom{j}{r}\left(P^*(x-q)+Q^*p\right)^r\left(Q^*i\epsilon\right)^{j-r}\sum_{l=0}^{\lfloor j-r\rfloor}\sum_{s=0}^{j-r-2l}\binom{j-r-2l}{s}\right.$$
$$\left.\times\left(i\epsilon PQ^{-1}(x-q)\right)^{j-r-2l-s}\left(\frac{i}{\epsilon}p\right)^s\left(i\epsilon PQ^{-1}\right)^l\frac{(j-r)!}{l!(j-r-2l)!}2^{-l}\right) \tag{2.7}$$

- there is an extra parity condition on j which you are missing
- Polynomial has degree k and so we would need at most $k+1$ terms in the summation. So how can we go about simplifying the expression further, perhaphs using properties of P, Q from Lemma 1.1 and a bit of manipulation
- The expression can most likely be simplified further - for the moment we will just going to use it to see if it is at least correct
- verify expression reduces to Hermite polynomial for particular parameter values
- Plot result from expression against one from recurrence relation
- Start by considering $k = 0$ for ease so only one subsitution
- You should be able to evaluate the second term recursively

Before attempting any simplification we will start by considering the a_{0l}'s with $\hat{\Pi}' = \{P = 1, Q = i, q = 0, p = p'\}$ for which

Example

In certain sense we can already comment on the dependence of the ... based on the proof concept in one of previous sections

$$\begin{aligned} P_l[\hat{\Pi}'](\xi) &= \sqrt{k!}\left(\frac{i}{2\epsilon}\right)^k \sum_{\substack{j=0 \\ j\equiv k(\mathrm{mod}2)}}^{k} \frac{(\epsilon/2)^{(k-j)/2}}{j!(\frac{k-j}{2})!} \times \sum_{r=0}^{j}\binom{j}{r}\epsilon^j i^j \left(-\frac{1}{\epsilon}(\xi - p')\right)^r \\ &\times \left(\sum_{l=0}^{\lfloor j-r \rfloor}\left(-\frac{1}{\epsilon}(\xi - p')\right)^{j-r-2l}\left(-\frac{1}{\epsilon}\right)^l 2^{-l}\frac{(j-r)!}{l!(j-r-2l)!}\right) \\ &= \sqrt{k!}\left(\frac{1}{2\epsilon}\right)^k \sum_{\substack{j=0 \\ j\equiv k(\mathrm{mod}2)}}^{k} \frac{(\epsilon/2)^{(k-j)/2}}{(\frac{k-j}{2})!}\epsilon^j i^{j+k} \times \sum_{r=0}^{j}\frac{1}{r!} \\ &\times \sum_{l=0}^{\lfloor j-r \rfloor}(-2\epsilon)^{-l}\frac{1}{l!(j-r-2l)!}\left(-\frac{1}{\epsilon}(\xi - p')\right)^{j-2l} \end{aligned} \tag{2.8}$$

Perhaps it is easier to consider the cases where k is even or odd

The i dependence cancels since k, j have the same parity

since this should reduce to the expression for the Hermite polynomials except some ϵ With regards to the integral, let us first consider the case $k = 0$

$$\begin{aligned} a_{0l} = \int_{\mathbb{R}} \mathrm{sgn}(\xi_1)\Theta(\xi_1^2 - 4\delta)\left(1 + \frac{\xi_1}{\nu(\xi_1)}\right)\overline{P_l[\hat{\Pi}'](\xi)} \times \\ \exp\left[-\frac{1}{2\epsilon}\Big((\nu(\xi_1) - p_1)^2 + (\xi_1 - p_1')^2 + 2q_c|\xi_1 - \nu(\xi_1)|\Big)\right] d\xi_1 \end{aligned} \tag{2.9}$$

As we have argued the polynomials will be real valued in this case.

If we Taylor expand $\tilde{a}_1 = \nu(\xi_1) - p_1$ about p_1' to first order we have,

$$\tilde{a}_1 = \text{sgn}(\xi_1)\sqrt{\xi_1^2 - 4\delta} - p_1 = \text{sgn}(\xi_1)\sum_{n=0} ...$$
$$= \text{sgn}(\xi_1)\left(\sqrt{{p_1'}^2 - 4\delta} - p_1 + \frac{p_1'}{\sqrt{{p_1'}^2 - 4\delta}}(\xi - p_1') + ...\right)$$

i.e. of the form $\alpha + \beta(\xi_1 - p_1')$ the remainder can also be formulated as an integral - which one is most convenient and assume the wavepacket's momentum is large and positive . Further, with expanding $\nu(\xi_1)$ using the binomial theorem

$$\nu(\xi_1) = \text{sgn}(\xi_1)\sqrt{\xi_1^2 - 4\delta} = \xi_1\sqrt{1 - \frac{4\delta}{\xi_1^2}} = \xi_1\sum_{n=0}^{\infty} ...$$
$$= \xi_1(1 - \frac{2\delta}{\xi_1^2} - \frac{2\delta^2}{\xi_1^4} + ...) = \xi_1 - \frac{2\delta}{\xi_1} - \frac{2\delta^2}{\xi_1^3} + ...$$

yields - "contribution to integral comes from positive axis" - is the integration known over half domain

$$
\begin{aligned}
a_{0l} &\approx 2\exp\left[-\frac{1}{2\epsilon}(\alpha^2+p_1'-p_1-\alpha)\right]\int_{\mathbb{R}}\overline{P_l[\hat{\Pi}'](\xi)}\times \\
&\qquad \exp\left[-\frac{1}{2\epsilon}\Big((\beta^2+1)(\xi_1-p_1')^2+(2\alpha\beta+\beta+1)(\xi_1-p_1')\Big)\right]d\xi_1 \\
&= 2\exp\left[-\frac{1}{2\epsilon}(\alpha^2+p_1'-p_1-\alpha)\right]\int_{\mathbb{R}}\overline{P_l[\hat{\Pi}'](u+p_1')}\times \\
&\qquad \exp\left[-\frac{1}{2\epsilon}\Big(\gamma u^2+\zeta u\Big)\right]du \\
&= 2\exp\left[-\frac{1}{2\epsilon}(\alpha^2+p_1'-p_1-\alpha)\right]\sqrt{k!}\left(\frac{1}{2\epsilon}\right)^k\sum_{\substack{j=0\\ j\equiv k(\mathrm{mod}2)}}^{k}\frac{(\epsilon/2)^{(k-j)/2}}{(\frac{k-j}{2})!}\epsilon^j i^{j+k}\times\sum_{r=0}^{j}\frac{1}{r!} \\
&\times\sum_{l=0}^{\lfloor j-r\rfloor}(-2\epsilon)^{-l}\frac{1}{l!(j-r-2l)!}\left(-\frac{1}{\epsilon}\right)^{j-2l}\int_{\mathbb{R}}u^{j-2l}\exp\left[-\frac{1}{2\epsilon}\Big(\gamma u^2+\zeta u\Big)\right]du
\end{aligned}
\tag{2.10}
$$

The integral above can be solved as

$$
\begin{aligned}
&\int_{\mathbb{R}}-(2\epsilon)^{j-2l}\frac{d^{j-2l}}{d\zeta}\exp\left[-\frac{1}{2\epsilon}\Big(\gamma u^2+\zeta u\Big)\right]du \\
&=-(2\epsilon)^{j-2l}\frac{d^{j-2l}}{d\zeta}\int_{\mathbb{R}}\exp\left[-\frac{1}{2\epsilon}\Big(\gamma u^2+\zeta u\Big)\right]du \\
&=-(2\epsilon)^{j-2l}\sqrt{\frac{\pi}{\gamma}}\frac{d^{j-2l}}{d\zeta}\exp\left[\frac{\zeta^2}{4\gamma}\right]
\end{aligned}
\tag{2.11}
$$

and the derivatives once again give rise to Hermite polynomials

I still need to get round to test it

I can always consider smoothing the cut-off function with a bump function and take the limit outside...?

Change of variables –¿ Asymptotic expansion via stationary phase principle This would work only in 1d as there is no stationary point in d¿1

Changing range of integration

Consider

$$\int_{2\sqrt{\delta}}^{\infty} f(\xi) \exp\left[-\frac{i}{2\epsilon}()\right] d\xi \tag{2.12}$$

3 Transmitted wavepacket recurrence relation derivation

We have

$$\Big(\langle(\tilde{\boldsymbol{\xi}}-\boldsymbol{q})_j^p f(\tilde{\boldsymbol{\xi}})\tilde{\varphi}_{k+\langle j\rangle}, \varphi_l\rangle\Big)_{j=1}^d =$$
$$=\Big(\sum_{i=1}^d \boldsymbol{A}_{j,i}\langle(\tilde{\boldsymbol{\xi}}-\boldsymbol{q})_j^p(\tilde{\boldsymbol{\xi}}-\boldsymbol{q})_i f(\tilde{\boldsymbol{\xi}})\tilde{\varphi}_k, \varphi_l\rangle\Big)_{j=1}^d - \Big(\sum_{i=1}^d \boldsymbol{B}_{j,i}\langle(\tilde{\boldsymbol{\xi}}-\boldsymbol{q})_j^p f(\tilde{\boldsymbol{\xi}})\tilde{\varphi}_{k-\langle i\rangle}, \varphi_l\rangle\Big)_{j=1}^d \tag{3.1}$$

and then proceeding in a similar manner as before for the higher order cross terms. Now, let k be fixed and l vary giving

$$\Big(\langle f(\tilde{\boldsymbol{\xi}})\tilde{\varphi}_k, (\boldsymbol{\xi}-\boldsymbol{q})_j^p\varphi_{l+\langle j\rangle}\rangle\Big)_{j=1}^d =$$
$$=\Big(\sum_{i=1}^d \boldsymbol{A}_{j,i}\langle f(\tilde{\boldsymbol{\xi}})\tilde{\varphi}_k, (\boldsymbol{\xi}-\boldsymbol{q})_j^p(\boldsymbol{\xi}-\boldsymbol{q})_i\varphi_l\rangle\Big)_{j=1}^d - \Big(\sum_{i=1}^d \boldsymbol{B}_{j,i}\langle f(\tilde{\boldsymbol{\xi}})\tilde{\varphi}_k, (\boldsymbol{\xi}-\boldsymbol{q})_j^p\varphi_{l-\langle i\rangle}\rangle\Big)_{j=1}^d \tag{3.2}$$

and then for the higher moments similarly.