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Clotilde Fermanian Kammerer and Caroline Lasser

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1. Introduction : an example, a model for pyrazine.

The dynamics of the molecule pyrazine $C_4H_4N_2$ is described in [13] by a two-level Schrödinger equation

$$i\partial_t\psi(q,t) = H_{\text{pyr}}\,\psi(q,t), \quad \psi(\cdot,0) = \psi_0 \in \mathbf{L}^2(\mathbf{R}^3,\mathbf{C}^2),$$

$$H_{\text{pyr}} = \sum_{j=1}^{3} \frac{\omega_j}{2}\left(-\partial_j{}^2 + q_j{}^2\right)\mathrm{Id} + \begin{pmatrix} E_1 + \sum_{j=1}^{2}\kappa_j^{(1)} q_j & \lambda q_3 \\ \lambda q_3 & E_2 + \sum_{j=1}^{2}\kappa_j^{(2)} q_j \end{pmatrix}.$$

$$\begin{array}{cccc} \omega_1 = 0.126 & \omega_2 = 0.074 & \omega_3 = 0.118 & \\ E_1 = 3.94 & E_2 = 4.84 & \lambda = 0.2623 & \\ \kappa_1^{(1)} = 0.037 & \kappa_2^{(1)} = -0.105 & \kappa_1^{(2)} = -0.254 & \kappa_2^{(2)} = 0.149 \end{array}$$

The wave function $\psi(q,t)$ itself does not have any direct physical interpretation, while the position density

$$n(q,t) = |\psi(q,t)|^2 = \mathrm{tr}\int_{\mathbf{R}^3} W^\varepsilon\left(\psi(t)\right)(q,p)\mathrm{d}p$$

is the probability of finding the molecule in the configuration q at time t. We are interested in asymptotic descriptions and algorithms for the time evolution of quadratic quantitites of the wave function like the position density $n(q,t)$. We consider a larger class of equations which contains the special case of the pyrazine model.

2. More general models

In the framework of time-dependent Born-Oppenheimer approximation, G. Hagedorn rigorously derived and classified N-level Schrödinger systems for molecular

propagation through electron energy level crossings [9]. The wave function $\psi^\varepsilon(q,t)$ satisfies a Schrödinger equation

$$\begin{cases} i\varepsilon\partial_t\psi^\varepsilon(q,t) = \left(-\frac{\varepsilon^2}{2}\Delta_q + V(q)\right)\psi^\varepsilon(q,t), \\ \psi^\varepsilon(\cdot,0) = \psi_0^\varepsilon \in L^2(\mathbf{R}^d, \mathbf{C}^N). \end{cases} \tag{1}$$

Here ε is a small positive parameter,

$$0 < \varepsilon := \sqrt{\frac{\text{electronic mass}}{\text{average mass of the nuclei}}} \ll 1,$$

and $N \in \{2,4\}$. Under certain genericity conditions, G. Hagedorn derives matrix potentials $V(q)$, which are either diagonal or have eigenvalues of non-constant multiplicity. In the first case, the study reduces to N decoupled scalar Schrödinger equations, which is classic. We focus on the second type of potentials with eigenvalue crossings. They are of the form

$$V(q) = v(q)\mathrm{Id} + V_\ell\left(\phi(q)\right), \quad \ell \in \{2,3,5\},$$

with $v \in \mathcal{C}^\infty(\mathbf{R}^d, \mathbf{R})$ and $\phi \in \mathcal{C}^\infty(\mathbf{R}^d, \mathbf{R}^\ell)$ satisfying

$$\mathrm{d}\phi \text{ of maximal rank on } \{\phi = 0\}.$$

The matrix $V_\ell(\phi(q))$ has two eigenvalues of non-constant multiplicity and is one of the four different forms:

- **Codimension two crossing**: $V_2(\phi) = \begin{pmatrix} \phi_1 & \phi_2 \\ \phi_2 & -\phi_1 \end{pmatrix}$,
- **Codimension three crossing**: $V_3(\phi) = \begin{pmatrix} \phi_1 & \phi_2 + i\phi_3 \\ \phi_2 - i\phi_3 & -\phi_1 \end{pmatrix}$,

$$\text{or } V_{3'}(\phi) = \begin{pmatrix} \begin{pmatrix} \phi_1 & \phi_2 + i\phi_3 \\ \phi_2 - i\phi_3 & -\phi_1 \end{pmatrix} & \mathbf{0} \\ \mathbf{0} & \begin{pmatrix} \phi_1 & \phi_2 - i\phi_3 \\ \phi_2 + i\phi_3 & -\phi_1 \end{pmatrix} \end{pmatrix},$$

- **Codimension five crossing**:

$$V_5(\phi) = \begin{pmatrix} \phi_0\,\mathbf{1} & \begin{pmatrix} \phi_1 + i\phi_2 & \phi_3 + i\phi_4 \\ -\phi_3 + i\phi_4 & \phi_1 - i\phi_2 \end{pmatrix} \\ \begin{pmatrix} \phi_1 - i\phi_2 & -\phi_3 - i\phi_4 \\ \phi_3 - i\phi_4 & \phi_1 + i\phi_2 \end{pmatrix} & -\phi_0\,\mathbf{1} \end{pmatrix}.$$

One observes that the Hamiltonian of the pyrazine model can be rewritten as

$$H^\varepsilon_{\mathrm{pyr}} = -\tfrac{\varepsilon^2}{2}\Delta_q + v(q)\mathrm{Id} + V_2\left(\phi(q)\right)$$

with $\varepsilon = 0.074$, while $v(q)$ and $\phi(q)$ are a quadratic and a linear function with coefficients of order one. Hence, the model falls into the class of codimension 2 crossings.

The analysis of scalar Schrödinger equation shows, that it is impossible to study directly the time-evolution of the position density $n^\varepsilon(q,t) = |\psi^\varepsilon(q,t)|^2$. Indeed, the oscillations of $\psi^\varepsilon(q,t)$ have to be taken into account, and one has to work in the space of *positions and momenta* (q,p): the phase space $\mathbf{R}^d_q \times \mathbf{R}^d_p$. Therefore, one studies the Wigner transform of $\psi^\varepsilon(q,t)$ (see [16])

$$W^\varepsilon(\psi^\varepsilon(t))(q,p) = (2\pi)^{-d} \int_{\mathbf{R}^d} \psi^\varepsilon\Big(q - \frac{\varepsilon}{2}v, t\Big) \otimes \overline{\psi}^\varepsilon\Big(q + \frac{\varepsilon}{2}v, t\Big)\, \mathrm{e}^{i\, v\cdot p}\, \mathrm{d}v.$$

This quantity plays the role of a generalized probability density in phase space. One recovers the position density $n^\varepsilon(q,t)$ by

$$n^\varepsilon(q,t) = \mathrm{tr} \int_{\mathbf{R}^d} W^\varepsilon\left(\psi^\varepsilon(t)\right)(q,p)\, \mathrm{d}p.$$

3. Description of the Wigner transform

We first introduce some notation. We denote by $\lambda^\pm$ the eigenvalues of the matrix $V(q)$

$$\lambda^\pm(q) = v(q) \pm |\phi(q)|$$

and by $\Pi^\pm(q)$ the associated eigenprojectors. Any point $(q,p) \in \mathbf{R}^{2d}$ in phase space with $\phi(q) = 0$ is called a *crossing point*. At such points, $\lambda^+(q) = \lambda^-(q)$: the eigenvalues $\lambda^\pm$ cross, and the eigenprojectors present a conical singularity. Then, we consider the classical flow

$$\Phi^t_\pm : \mathbf{R}^{2d} \to \mathbf{R}^{2d}, \quad \Phi^t_\pm(q_0,p_0) = \Big(q^\pm(t), p^\pm(t)\Big)$$

associated to the Hamiltonian curves of $\lambda^\pm(q) + \frac{|p|^2}{2}$.

Outside the crossing, the dynamics of the Wigner transform shows two different features. The off-diagonal blocks of $W^\varepsilon(\psi^\varepsilon(t))$ are highly-oscillatory both in phase space and time and have a time average of order ε:

$$\int_0^T \int_{\mathbf{R}^{2d}} W^\varepsilon(\psi^\varepsilon(t))(q,p)\, a(q,p)\, \mathrm{d}q\, \mathrm{d}p = O(\varepsilon)$$

for all $T > 0$ and observables $a \in \mathcal{C}^\infty_0(\mathbf{R}^{2d}, \mathbf{C}^{N,N})$ such that

$$a = \Pi^+ a \Pi^- + \Pi^- a \Pi^+, \quad \mathrm{supp}(a) \subset \mathbf{R}^{2d} \setminus \{\phi = 0\}.$$

The diagonal blocks are well approximated in terms of classical transport:

$$\int_{\mathbf{R}^{2d}} \Big(W^\varepsilon(\psi^\varepsilon(t)) - W^\varepsilon(\psi^\varepsilon_0) \circ \Phi^{-t}_\pm\Big)(q,p)\, a(q,p)\, \mathrm{d}q\, \mathrm{d}p = O(\varepsilon) \tag{2}$$

for all times $t \in [0,T]$ such that the classical trajectories do not pass the crossing set $\{\phi = 0\}$ and all observables $a \in \mathcal{C}^\infty_0(\mathbf{R}^{2d}, \mathbf{C}^{N,N})$ such that

$$a = a^\pm \Pi^\pm, \quad a^\pm \in \mathcal{C}^\infty_0(\mathbf{R}^{2d} \setminus \{\phi = 0\}, \mathbf{C}).$$

Introducing the *Born-Oppenheimer function*

$$W^\varepsilon_{\mathrm{BO}}(t) := \Pi^+ W^\varepsilon\left(\psi_0^\varepsilon\right)\Pi^+ \circ \Phi_+^{-t} + \Pi^- W^\varepsilon\left(\psi_0^\varepsilon\right)\Pi^- \circ \Phi_-^{-t},$$

one may rewrite (2) as

$$\int_{\mathbf{R}^{2d}} (W^\varepsilon(\psi^\varepsilon(t)) - W^\varepsilon_{\mathrm{BO}}(t))(q,p)\, a(q,p)\, \mathrm{d}q\, \mathrm{d}p = O(\varepsilon)$$

for all $t \in [0,T]$ such that the trajectories do not pass the crossing and $a \in \mathcal{C}_0^\infty(\mathbf{R}^{2d}, \mathbf{C}^{N,N})$ such that

$$a = a^+\Pi^+ + a^-\Pi^-, \quad a^\pm \in \mathcal{C}_0^\infty(\mathbf{R}^{2d} \setminus \{\phi = 0\}, \mathbf{C}).$$

Such a description for the dynamics outside the crossing is well-established (see [8] or [14], for example).

The problems arise when classical trajectories reach a crossing point. Then, the approximation of the Wigner transform by $W^\varepsilon_{\mathrm{BO}}$ is no longer valid and there are non-adiabatic transitions between the levels. The energy propagated until the crossing on one level may pass (partially or utterly) on the other level. This phenomenon is well-known since the works of Landau and Zener in the 30's ([10] and [17]) and has been precisely studied in the case of Gaussian wave packet propagation by G. Hagedorn [9]. For initial data, which are less specific than Gaussian wave packets, the evolution of weak limits of the Wigner transform (which are called *Wigner measures*) has been studied in [4] and [5] for general 2×2 systems and in [3] for all of Hagedorn's models. The algorithm we present here makes extensive use of ideas and methods introduced in these articles.

In addition to

$$\mathrm{d}\phi \ \text{ of maximal rank on } \ \{\phi = 0\}, \tag{3}$$

we suppose

$$\mathrm{d}\phi(q)p \neq 0 \ \text{ on } \ \{\phi = 0\} \tag{4}$$

in the zone we study. These assumptions guarantee that the crossing points are *generic* in the sense of [5] (see also [1], [2] and [3]). The latter assumption (4) especially implies existence of a unique classical trajectory passing through the crossing point for each level. Then, the transition depends on how the wave function $\psi^\varepsilon(q,t)$ concentrates on these ingoing trajectories with respect to the scale $\sqrt{\varepsilon}$: our algorithm relies on the understanding of this mechanism as stated in [3]. We begin by describing previous results.

4. Previous results

Theoretical chemists have designed innumerous algorithms for propagation through electron level crossings. J. Tully's surface hopping algorithm of the fewest switches [15] seems to be among the most popular approaches. The first algorithm of this type with a rigorous mathematical derivation has been proposed in [11] for a codimension

two crossing with $\phi(q) = q$, $q \in \mathbf{R}^2$. This model has very specific features (see [6]). In particular, all the classical trajectories are included in the set

$$I = \{q \wedge p = 0\}.$$

The proof given in [11] relies on the analysis of Wigner measures of $\psi^\varepsilon(q,t)$. The underlying idea is, that if one is able to calculate the Wigner measure at time t, one has an approximate value of the Wigner transform according to the following diagram

$$\begin{array}{ccc} \psi_0^\varepsilon,\, W^\varepsilon(\psi_0^\varepsilon) & \overset{\text{Schrödinger, Heisenberg eq.}}{\longrightarrow} & \psi^\varepsilon(t),\, W^\varepsilon(\psi^\varepsilon(t)) \\ \downarrow^{\varepsilon\to 0} & & \downarrow^{\varepsilon\to 0} \\ \mu_0 & \overset{?}{\longrightarrow} & \mu(t) \end{array}$$

However, the sole knowledge of μ_0 is not enough to calculate Wigner measures $\mu(t)$ at later times t. As said before, one needs to know how the data concentrates at the scale $\sqrt{\varepsilon}$ on all the classical trajectories which enter the crossing set. In the special setting $\phi(q) = q$, $q \in \mathbf{R}^2$, knowledge about $\sqrt{\varepsilon}$-concentration on I is enough, since I contains all these trajectories. One uses the two-scale Wigner measure ν_0 associated with the concentration of ψ_0^ε on I for the scale $\sqrt{\varepsilon}$.

Two-scale Wigner measures are weak limit points of two-scale Wigner transforms

$$W^\varepsilon_{(2)}\left(\psi^\varepsilon(t)\right)(q,p,\eta) = W^\varepsilon\left(\psi^\varepsilon(t)\right)(q,p) \otimes \delta\left(\eta - \frac{q \wedge p}{\sqrt{\varepsilon}}\right),$$

which act on smooth functions $a = a(q,p,\eta)$, which are compactly supported in the variables (q,p) uniformly with respect to η and satisfy symbol type estimates in the variable η. They have been first introduced by L. Miller in [12]. Observe that one can recover the Wigner transform by projecting the two-scale Wigner transform on (q,p)-space. As for Wigner measures, the diagonal blocks of two-scale Wigner measures $\nu(t)$ propagate along classical trajectories:

$$\Pi^\pm \nu(t) \Pi^\pm = \Pi^\pm \nu_0 \Pi^\pm \circ \Phi_\pm^{-t}$$

for times t such that the trajectories do not pass the crossing. Setting $\nu^\pm := \Pi^\pm \nu \Pi^\pm$, the measures $\nu^\pm$ have traces on both sides of the crossing set and the outgoing traces $\nu^\pm_{out}$ are related with the ingoing ones $\nu^\pm_{in}$ through a *Landau-Zener formula* [4]:

$$\begin{pmatrix} \nu^+_{out} \\ \nu^-_{out} \end{pmatrix} = \begin{pmatrix} 1 - T(p,\eta) & T(p,\eta) \\ T(p,\eta) & 1 - T(p,\eta) \end{pmatrix} \begin{pmatrix} \nu^+_{in} \\ \nu^-_{in} \end{pmatrix}; \text{ with } T(p,\eta) = \exp\left(-\pi \frac{|\eta|^2}{|p|^3}\right).$$

The idea is now to propagate the diagonal parts of the Wigner transform along classical trajectories and to apply the ε-dependent transition coefficient

$$T^\varepsilon(q,p) = T\left(p, \frac{q \wedge p}{\sqrt{\varepsilon}}\right) = \exp\left(-\frac{\pi}{\varepsilon} \frac{|q \wedge p|^2}{|p|^3}\right),$$

as soon as the trajectories reach their *minimal distance* from the crossing set, which is easy to check since $q \cdot p = 0$ at such a point. This ε-dependent propagation of the

initial Wigner transform is correct in the limit $\varepsilon \to 0$, assuming that the initial data has only one two-scale Wigner measure [11].

Two questions arise: How does such an asymptotic description carry over to more general crossings ? What is the convergence rate with respect to ε ?

The extension of the algorithm to more general crossings is not straightforward. Indeed, for general geometries the classical trajectories touching the crossing set are *not* contained in a submanifold of phase space $\mathbf{R}^d_q \times \mathbf{R}^d_p$. Previous normal forms results ([1], [2], [5]) only yield local existence of such a submanifold in the whole space-time phase space $\mathbf{R}^{d+1}_{(q,t)} \times \mathbf{R}^{d+1}_{(p,\tau)}$, and there are no explicit equations. To obtain a convergence rate, another proof has to be deviced without actually passing to the limit $\varepsilon \to 0$.

Here, we now propose a generalization of the algorithm which allows to overcome these two difficulties. The proof of the convergence rate is sketched below and is presented in detail in [7].

5. The asymptotic description

We follow the formalism of [11]. The general idea is the same: propagation along classical trajectories and transitions near the crossing set. But we introduce two modifications:

- a more general criterium for applying the transitions. We check, whether we are close enough to the crossing set, that is at a distance $R\sqrt{\varepsilon}$ where $R > 0$ is a fixed positive number. Then, inside the set $\{|\phi(q)| \leq R\sqrt{\varepsilon}\}$ the transitions occur as before, when trajectories reach their minimal distance from the crossing set $\{\phi = 0\}$, i.e. when

$$\mathrm{d}\phi(q)p \cdot \phi(q) = 0.$$

- a transition coefficient $T^\varepsilon(q,p) = T(f(q,p)/\sqrt{\varepsilon})$ with

$$f(q,p) = |\mathrm{d}\phi(q)p|^{-1/2}\, \pi_\ell(q,p)\phi(q),$$

  where $\pi_\ell(q,p)$ is the orthogonal projection from $\mathbf{R}^\ell$ on the hyperplane normal to the non-zero vector $\mathrm{d}\phi(q)p$ (for the Euclidian structure of $\mathbf{R}^\ell$). For the case of codimension two crossings, $\pi_2(q,p)\phi(q) = \mathrm{d}\phi(q)p \wedge \phi(q)/|\mathrm{d}\phi(q)p|$. The hypersurface $\{f(q,p) = 0\}$ is tangent to the set of all the incoming and outgoing trajectories at the crossing set up to order 1.

It is our aim now to generalize the Born-Oppenheimer function $W^\varepsilon_{\mathrm{BO}}(t)$ by encorporating the ε-dependent non-adiabatic transition rates T^ε.

First, one defines a *Markov process*. One considers the random trajectories

$$\mathcal{T}^{(q,p,j)}_{\varepsilon,R} :\ [0,+\infty) \to \mathbf{R}^{2d} \times \{-1,+1\}$$

such that $\mathcal{T}_{\varepsilon,R}^{(q,p,j)} = \Big(\Phi_j^t(q,p), j\Big)$ as long as

$$\Big|\phi(\Phi_j^t(q,p))\Big| > R\sqrt{\varepsilon} \quad \text{or} \quad \mathrm{d}\phi\Big(q^j(t)\Big)\, p^j(t)\cdot\phi\Big(q^j(t)\Big) \neq 0.$$

A jump from j to $-j$ occurs with probability $T^\varepsilon(q^j(t), p^j(t))$,

$$T^\varepsilon(q,p) = \exp\left(-\frac{\pi}{\varepsilon}\frac{\Big|\pi_\ell(q,p)\phi(q)\Big|^2}{\Big|\mathrm{d}\phi(q)p\Big|}\right),$$

whenever $\Phi_j^t(q,p)$ hits the jump manifold

$$S = \Big\{\mathrm{d}\phi(q)p\cdot\phi(q) = 0,\ |\phi(q)| \leq R\sqrt{\varepsilon}\Big\}.$$

Then, one defines the associated *backwards semi-group* $\mathcal{L}_{\varepsilon,R}^t$ by its action on a class of continuous scalar-valued functions $a = a(q,p,j)$ satisfying suitable boundary conditions at the jump manifold S,

$$(\mathcal{L}_{\varepsilon,R}^t)a(q,p,j) := \mathbf{E}^{(q,p,j)}a\Big(\mathcal{T}_{\varepsilon,R}^{(q,p,j)}(t)\Big).$$

This definition naturally extends to matrix-valued functions of the form $a = a^+\Pi^+ + a^-\Pi^-$, $a^\pm \in \mathcal{C}_0^\infty(\mathbf{R}^{2d}\setminus S, \mathbf{C})$ and then by duality also to Wigner transforms,

$$\mathcal{L}_{\varepsilon,R}^t W^\varepsilon(\psi):\ a \mapsto \mathrm{tr}\int_{\mathbf{R}^{2d}}\Big(W^\varepsilon(\psi)(q,p)(\mathcal{L}_{\varepsilon,R}^t a)(q,p)\Big)\,\mathrm{d}q\,\mathrm{d}p.$$

In analogy to the Born-Oppenheimer function $W_{\mathrm{BO}}^\varepsilon(t)$, we define the *Landau-Zener function*

$$W_{\mathrm{LZ}}^{\varepsilon,R}(t) := \mathcal{L}_{\varepsilon,R}^t\, W^\varepsilon(\psi_0^\varepsilon)$$

and have the following theorem.

Theorem 1. *Let $\psi^\varepsilon(t)$ be the solution of the Schrödinger equation (1).*
Suppose that assumptions (3) and (4) are satisfied, that $\mathrm{d}\phi(q)\nabla v(q)\cdot\phi(q) \leq 0$, and that the map $q \mapsto |\phi(q)|^2$ is convex.
Suppose moreover that $(\psi_0^\varepsilon)_{\varepsilon>0}$ is uniformly bounded in $L^2(\mathbf{R}^d, \mathbf{C}^N)$ such that

$$(a) \qquad \Big\|\Pi^-\psi_0^\varepsilon\Big\|_{L^2(\mathbf{R}^d,\mathbf{C}^N)} = \eta^\varepsilon \to 0 \quad as \quad \varepsilon\to 0,$$
$$(b) \qquad \exists\delta > 0,\ \ \mu_0\left(\{|\phi(q)| < \delta\}\right) = 0.$$

Then, for all $T > 0$

$$\sup_{t\in[0,T]}\int_{\mathbf{R}^{2d}}\Big(W^\varepsilon\left(\psi^\varepsilon(t)\right) - W_{\mathrm{LZ}}^{\varepsilon,R}(t)\Big)(q,p)a(q,p)\mathrm{d}q\,\mathrm{d}p$$
$$= O(\eta^\varepsilon) + O\Big(\frac{1}{R}\Big) + O\Big(R^3\sqrt{\varepsilon}\Big) + O\Big(\sqrt{\varepsilon}\,|\ln\varepsilon|\Big).$$

for all $a = a^+\Pi^+ + a^-\Pi^-$ with $a^\pm \in \mathcal{C}_0^\infty(\mathbf{R}^{2d}\setminus S, \mathbf{C})$.

The assumptions made on the potential $V(q) = v(q)\mathrm{Id} + V_\ell(\phi(q))$ in particular imply that the minus trajectories issued from crossing points never meet the crossing again. Hence, they cannot interfer with trajectories on the plus level. The non-degenericity assumption (3) is easily checked a priori globally, while assumption (4) can be numerically verified at each transition as a test of validity of the algorithm.

The assumption (b) on the initial data ψ_0^ε ensures that we do not deal with the crossing set at $t = 0$ but only after a finite time. Then, assumption (a) together with the properties of the minus trajectories yields that the Wigner transform propagated until a crossing point on the minus level is of lower order. This could be weakened by simply assuming that the incoming two-scale Wigner measures are singular at any crossing point (as assumed in [5] for example), but such a condition does not fit with our aim of giving an ε-dependent dynamical description.

6. Scheme of the proof

The proof consists in two steps: proving the propagation in the zone $\{|\phi(q)| > R\sqrt{\varepsilon}\}$, then studying the transitions in the zone $\{|\phi(q)| \leq R\sqrt{\varepsilon}\}$.

6.1. Propagation outside the transition zone

Here, the Landau Zener function reduces to the Born-Oppenheimer one, and the usual strategy applies. One works separately with each level and, for studying the level $+$, one defines

$$I(t) := \mathrm{tr} \int_{\mathbf{R}^{2d}} W^\varepsilon(\psi^\varepsilon(t)(q,p))\, \Pi^+(q)\, a^+(q,p) \mathrm{d}q\mathrm{d}p$$

for a^+ with $\mathrm{supp}(a^+) \subset \{|\phi(q)| > R\sqrt{\varepsilon}\}$. One writes $I(t)$ in terms of pseudo-differential operators

$$I(t) = \Big((a^+\Pi^+)^W(q, -i\varepsilon\nabla_q)\psi^\varepsilon(t)\ ,\ \psi^\varepsilon(t) \Big)_{L^2}\,,$$

where we denote by $c^W(q, -i\varepsilon\nabla_q)$ the semi-classical pseudo-differential operator of a symbol $c = c(q,p)$ with Weyl quantification. Then, we observe that

$$\frac{\mathrm{d}\, I}{\mathrm{d}t}(t) = \frac{1}{i\varepsilon} \Big(\Big[(a^+\Pi^+)^W(q, -i\varepsilon\nabla_q)\ ,\ -\tfrac{\varepsilon^2}{2}\Delta_q + V(q) \Big] \psi^\varepsilon(t)\ ,\ \psi^\varepsilon(t) \Big)_{L^2}\,.$$

Hence, one analyses the commutator

$$K = \frac{1}{i\varepsilon} \Big[(a^+\Pi^+)^W(q, -i\varepsilon\nabla_q)\ ,\ -\tfrac{\varepsilon^2}{2}\Delta_q + V(q) \Big]\,.$$

In particular, even if Π^+ is smooth in the zone $\{|\phi(q)| > R\sqrt{\varepsilon}\}$, one has to consider its behavior when $|\phi(q)|$ becomes small. More precisely, using that for all multi-indices α there are constants $C, C' > 0$ such that

$$\partial_q^\alpha \Pi^+(q) \leq \frac{C}{|\phi(q)|^{|\alpha|}} \leq \frac{C'}{(R\sqrt{\varepsilon})^{|\alpha|}},$$

one obtains

$$\frac{\mathrm{d}}{\mathrm{d}t}I(t) = \frac{1}{i\varepsilon}\left(\left(\left\{a^+\ ,\ \tfrac{|p|^2}{2}+\lambda^+\right\}\Pi^+\right)^W(q,-i\varepsilon\nabla_q)\psi^\varepsilon(t)\ ,\ \psi^\varepsilon(t)\right)_{L^2} + O(\sqrt{\varepsilon}) + O\left(\frac{1}{R}\right).$$

Hence the contribution to the error term is of order

$$O(\sqrt{\varepsilon}) + O\left(\frac{1}{R}\right).$$

6.2. Transitions in the crossing zone

The first step consists in a microlocalization in space-time variables: we work near some time t_0 in a small interval such that the random trajectories involved have only one jump. Moreover, we work near the characteristic set

$$\Sigma = \left\{\left(\tau + \tfrac{|p|^2}{2} + v(q)\right)^2 = |\phi(q)|^2\right\}.$$

In this zone, we use Colin de Verdière's normal forms. Thanks to a change of symplectic coordinates (a change of variables in the phase space $\mathbf{R}^{d+1}_{(q,t)} \times \mathbf{R}^{d+1}_{(p,\tau)}$ compatible with the geometry) and a corresponding change of the wave function given by a Fourier integral operator, one reduces to a simpler system, for which the transition rates can be calculated explicity. However, the theorems as stated in [1] and [2] were not enough for our purpose: we had to perform a generalization to codimension 5 crossings and compute some quantities precisely in order to come back to our initial system of coordinates.

We give below the generalized version of the normal form theorem. We consider classical trajectories in space-time variables

$$\left(q^\pm(t), t, p^\pm(t), \tau = -v(q^\pm(t)) - \tfrac{|p^\pm(t)|^2}{2} \pm |\phi(q^\pm(t))|\right).$$

We denote by $J^{\pm,in}$ (resp. $J^{\pm,out}$) the set of all the trajectories for the level $\pm$ which enter the crossing (resp. come out of the crossing). Then one can prove (see [5] and [3]), that

$$J = J^{+,in} \cup J^{-,out} \ \text{ and } \ J' = J^{-,in} \cup J^{+,out}$$

are smooth submanifolds of the space-time phase space.

Theorem 2. (Y. Colin de Verdière, 2003 – Extended version).
Consider $\rho_0 = (q_0, t_0, p_0, \tau_0 = -v(q_0) - \frac{|p_0|^2}{2})$ such that $\phi(q_0) = 0$ and that (3) and (4) hold near ρ_0. Then, there exists a local canonical transform κ from a neighborhood of ρ_0 into some neighborhood Ω of 0,

$$\kappa : (q, t, p, \tau) \mapsto (s, z, \sigma, \zeta), \quad \kappa(\rho_0) = 0.$$

There exists a Fourier integral operator K associated with κ and a matrix-valued symbol $A_\varepsilon = A_0 + \varepsilon A_1 + \varepsilon^2 A_2 + ...$ such that

$$v^\varepsilon = K\mathrm{op}_\varepsilon(A_\varepsilon)\psi^\varepsilon$$

satisfies microlocally in Ω

$$\frac{\varepsilon}{i}\partial_s v^\varepsilon = V_\ell\left(s, \tilde{z} + \gamma_\varepsilon^W(z, -i\varepsilon\nabla_z)\right)\, v^\varepsilon + O(\varepsilon^\infty) \tag{5}$$

with $z = (\tilde{z}, z')$*, where* $\tilde{z} \in \mathbf{R}^{\ell-1}$ *are the coordinates of* $|\mathrm{d}\phi(q)p|^{-1/2}\pi_\ell(q,p)\phi(q)$ *in an orthonormal basis of the hyperplane normal to* $\mathrm{d}\phi(q)p \in \mathbf{R}^\ell$ *up to* $O(|\phi(q)|^2)$*.*

The symbol γ_ε *with* $\gamma_\varepsilon(z,\zeta) \in \mathbf{R}^{\ell-1}$ *satisifies* $(\gamma_\varepsilon)_{|\tilde{z}=0} = 0$*.*

Moreover,

$$J \cup J' = \Sigma \cap \{\tilde{z} = 0\} = \{\sigma^2 = s^2, \tilde{z} = 0\},$$

$$J^{\pm,in} = \{\sigma \mp s = 0, \tilde{z} = 0, s \leq 0\}, \qquad J^{\pm,out} = \{\sigma \pm s = 0, \tilde{z} = 0, s \geq 0\}.$$

The end of the proof relies on a scattering result for the model problem (5), which is proved in [5] (Proposition 7). This result describes the solutions of the model problem (5) for $s > 0$ (after the crossing) in terms of their form for $s < 0$ (before the crossing). The precise information contained in Theorem 2 allows us to come back to the initial coordinates and to prove the convergence rate of the algorithm.

At this stage of the proof we crucially use, that the assumptions made on $v(q)$ and $\phi(q)$ ensure, that the minus trajectories arising from a crossing point never come back to the crossing set. Therefore, when some energy is carried out of the crossing, the incoming energy for the level minus only comes from the propagation of the initial energy for the same level and thus is of order $O(\eta^\varepsilon)$. This not only explains the $O(\eta^\varepsilon)$ in the error term but is also crucial for the approach in terms of Wigner transforms. Indeed, if the energy carried into the crossing by the minus trajectories is not negligible, there might be interferences between both levels, which cannot be described by a linear function of the Wigner transform for each level.

Finally, the last error term is $\sqrt{\varepsilon}\ln\varepsilon$. It comes from commutation relations with operators of the form

$$\left|\frac{s}{\sqrt{\varepsilon}}\right|^{i\Gamma_\varepsilon\Gamma_\varepsilon^*}, \qquad \Gamma_\varepsilon = \frac{1}{\sqrt{\varepsilon}}\left(\tilde{z} + \gamma_\varepsilon^W(z, -i\varepsilon\nabla_z)\right),$$

which appear in the scattering result for the model problem (5).

7. The algorithm

An algorithmic realization of $W_{\mathrm{LZ}}^{\varepsilon,R}(t)$ can be achieved along the following lines:

1. One projects the initial data ψ_0^ε on the two levels, $\psi_{0,\pm}^\varepsilon := \Pi^\pm\psi_0^\varepsilon$, and computes the ε-scaled Fourier transform of $\psi_{0,\pm}^\varepsilon$, that is $(\mathcal{F}^\varepsilon\psi_{0,\pm}^\varepsilon)(p) = \widehat{\psi_{0,\pm}^\varepsilon}(p/\varepsilon)$.

2. One samples position and momentum densities on both levels, that is $|\psi_{0,\pm}^\varepsilon(q)|^2$ and $|(\mathcal{F}^\varepsilon\psi_{0,\pm}^\varepsilon)(p)|^2$, and obtains pairs of sampling points $(q_\pm, p_\pm) \in \mathbf{R}^{2d}$ in phase space.

   For these points one computes the Wigner transforms $W^\varepsilon(\psi_{0,\pm}^\varepsilon)(q_\pm, p_\pm)$.

3. One propagates the points $(q_\pm, p_\pm)$ according to the classical flows $\Phi^t_\pm$.

   When $|\Phi^t_\pm(q_\pm, p_\pm)| \leq R\sqrt{\varepsilon}$ and $\mathrm{d}\phi(q^\pm(t))p^\pm(t) \cdot \phi(q^\pm(t)) = 0$, one multiplies by one minus the transition rate,

   $$W^\varepsilon(\psi^\varepsilon_{0,\pm})(q_\pm, p_\pm) \quad \curvearrowright \quad \Big(1 - T^\varepsilon(q^\pm(t), p^\pm(t))\Big) W^\varepsilon(\psi^\varepsilon_{0,\pm})(q_\pm, p_\pm).$$

   Moreover, one opens up a trajectory on the other level with starting point $\Phi^t_\pm(q_\pm, p_\pm)$ and associated weight $T^\varepsilon(q^\pm(t), p^\pm(t))W^\varepsilon(\psi^\varepsilon_{0,\pm})(q_\pm, p_\pm)$.

   This procedure is continued until some final time $T > 0$.

4. One ends with a lot of particles $(q_\pm(T), p_\pm(T))$ on both levels with associated weights $w(q_\pm(T), p_\pm(T))$. From these, one computes approximations to quadratic quantities of the projected wave function like

   $$\Big|\Pi^\pm(q^\pm(T))\psi^\varepsilon(q^\pm(T), T)\Big|^2 \approx \sum_{p_\pm(t)} w(q_\pm(T), p_\pm(T)) \,\mathrm{vol}_{p_\pm(T)},$$

   where $\mathrm{vol}_{p_\pm(T)}$ denotes the volume element associated with the point $p_\pm(T)$.

Below we give pictures obtained for a linear codimension two crossing with $v(q) = 0$, $\phi(q) = q$ and semi-classical parameter $\varepsilon = 0.01$. The initial data are microlocalized on the upper level on a point (q_0, p_0). The three rows of plots show the propagated level densities $|\Pi^\pm(q)\psi^\varepsilon(q, t)|^2$ for times $t = 0$, $t = 2\sqrt{\varepsilon}$ and $t = 4\sqrt{\varepsilon}$.

8. Conclusion

We finish by one word about the limitation of our asymptotic description and the resulting algorithm. One observes for the pyrazine model, that the assumption $d\phi(q)\nabla v(q) \cdot \phi(q) \leq 0$ made in Theorem 1 is not satisfied. Hence, one has to expect that trajectories issued onto the minus level come back to the crossing set and possibly interfer with trajectories on the plus level. If those interferences are too strong, the proposed algorithm fails. This defect motivates the analysis of situations, where the approach of just propagating the diagonal blocks of the Wigner function is not enough for a correct approximation of the dynamics, which is a challenging question for further work.

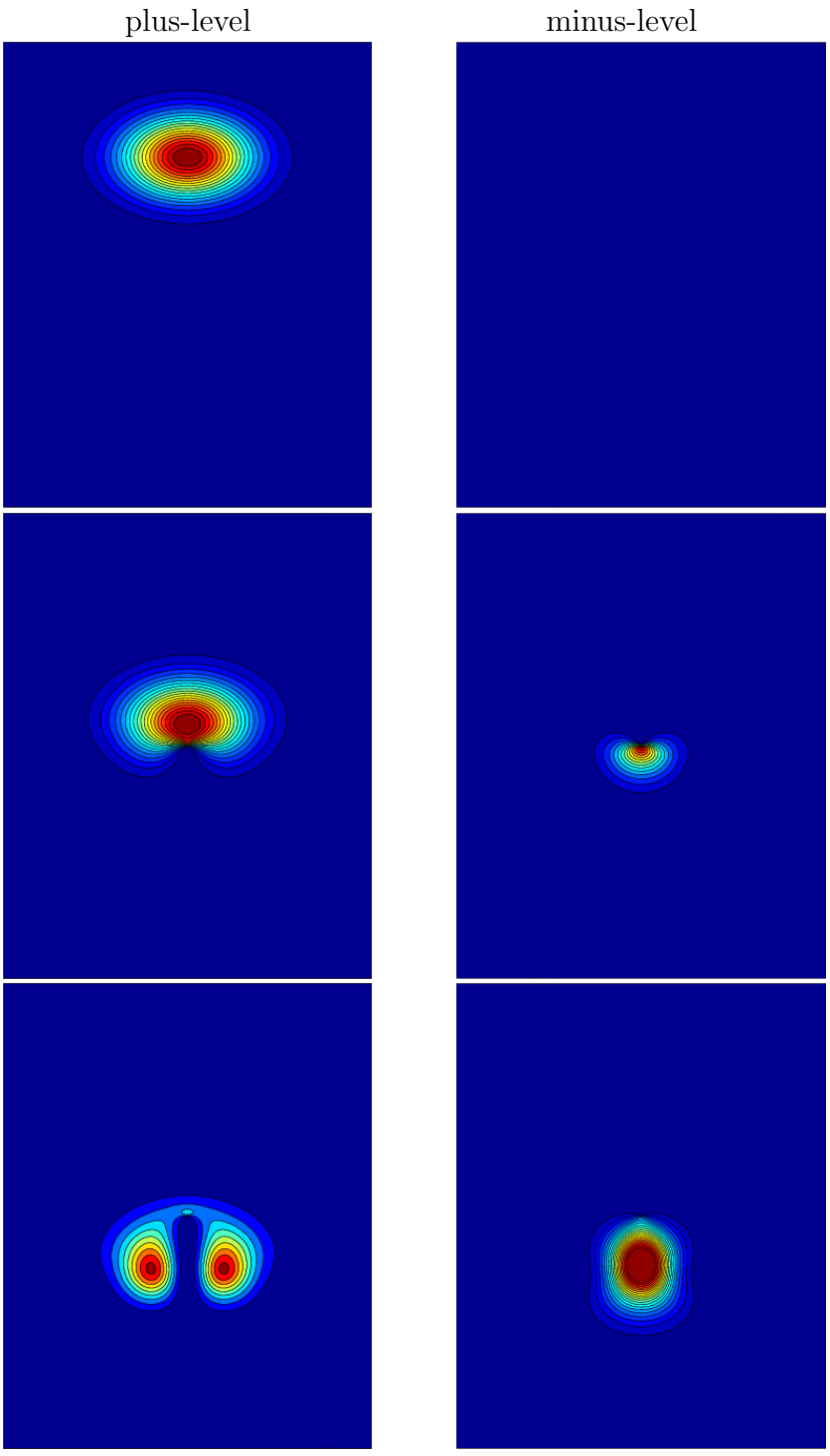

Figure 1: Propagation through a linear codimension two crossing for $\varepsilon = 0.01$.

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Université de Cergy-Pontoise, Mathématiques, 2 avenue Adolphe Chauvin, BP 222, Pontoise, 95 302 Cergy-Pontoise cedex, France.
Clotilde.Fermanian@math.u-cergy.fr

Freie Universität Berlin, Arnimallee 3, 14195 Berlin, Deutschland.
classer@math.fu-berlin.de