Energy Level Crossings in Molecular Dynamics

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Summary. Energy level crossings are the landmarks that separate classical from quantum mechanical modeling of molecular systems. They induce non-adiabatic transitions between the otherwise adiabatically decoupled electronic level spaces. This review covers results on the analysis of propagation through level crossings of codimension two, a mathematical justification of surface hopping algorithms, and a spectral study of a linear isotropic system.

1 Introduction

Molecular systems are a prime example of a multiscale problem. The light electrons move rapidly, in a highly oscillatory fashion, while the nuclei, as the heavier parts of the molecule, move much slower. T his separation of mass and subsequently time and space scales is at the heart of Born-Oppenheimer approximation. It allows for a drastic reduction of problem size when dealing with molecular systems.

A quantum mechanical, non-relativistic description of a molecule is given by the molecular Schrödinger operator

$$H_{\mathrm{mol}} = -\sum_{j=1}^{N} \tfrac{1}{2M_j} \Delta_{q_j} - \sum_{j=1}^{n} \tfrac{1}{2} \Delta_{x_j} + \sum_{j<k} |x_j - x_k|^{-1} + \sum_{j<k} Z_j Z_k |q_j - q_k|^{-1} - \sum_{j,k} Z_k |x_j - q_k|^{-1},$$

where the vectors q and x denote the positions of N nuclei and n electrons, and M_j, Z_j denote mass and charge of the jth nucleus. For the simplicity of notation, one assumes that the nuclei have identical mass M and introduces a scale parameter

$$0 < \epsilon = \sqrt{1/M} \ll 1,$$

which is of the order 10^{-2}, typically. One rewrites the operator as

$$H_{\mathrm{mol}} = -\frac{\epsilon^2}{2}\Delta_q + H_{\mathrm{el}}(q),$$

where the electronic Hamiltonian $H_{\mathrm{el}}(q)$ acts, for a fixed nuclear configuration q, on the electronic degrees of freedom only.

The first step of Born-Oppenheimer approximation consists in solving the electronic eigenvalue problem for all nuclear configurations,

$$\forall q:\ H_{\mathrm{el}}(q)\chi(q,x) = E(q)\chi(q,x).$$

For the second step, one assumes that the electronic energy levels of interest are uniformly separated from the remainder of the electronic spectrum. That is, if one is interested in two levels $E^-(q)$ and $E^+(q)$,

$$\forall q:\ \mathrm{dist}(\{E^+(q), E^-(q)\}, \sigma(H_{\mathrm{el}}(q)) \setminus \{E^+(q), E^-(q)\}) > \delta$$

for some $\delta > 0$. Then, one looks for a diabatic basis $\{\widetilde{\chi}^{\pm}(q,x)\}$ of the electronic subspace $\mathrm{span}\{\chi^{\pm}(q,x)\}$, such that the mapping $q \mapsto \widetilde{\chi}^{\pm}(q,x)$ is smooth. If one replaces the Coulomb interactions inbetween nuclei, and between nuclei and electrons, by a mollified charge distribution, then the electronic Hamiltonian depends smoothly on X, which guarantees existence of a diabatic basis. A diabatic basis $\{\widetilde{\chi}^{\pm}(q,x)\}$ is expected to be different from the adiabatic basis $\{\chi^{\pm}(q,x)\}$ if the electron energy levels $E^{\pm}(q)$ have the same symmetry, see [LS06]. Given a diabatic basis, one builds a hermitian matrix

$$V(q) = \begin{pmatrix} V_{--}(q) & V_{-+}(q) \\ V_{+-}(q) & V_{++}(q) \end{pmatrix},$$

whose entries consists of the expectation values of the electronic Hamiltonian with respect to the diabatic basis functions,

$$V_{kl}(q) = \left\langle \widetilde{\chi}^k(q,\cdot), H_{\mathrm{el}}(q)\widetilde{\chi}^l(q,\cdot)\right\rangle_{L^2_{el}}, \qquad k,l \in \{-,+\}.$$

The Born-Oppenheimer Hamiltonian is then given as

$$H_{\mathrm{BO}} = -\frac{\epsilon^2}{2}\Delta_q + V(q).$$

It is a two-level Schrödinger operator acting only on the nucleonic degrees of freedom. Let $\widetilde{\chi}(q,x) = (\widetilde{\chi}^+(q,x), \widetilde{\chi}^-(q,x))^t$. If $\psi(q,t)$ is a solution of the time-dependent Born-Oppenheimer problem

$$i\epsilon\partial_t\psi = H_{\mathrm{BO}}\psi, \qquad \psi(q,0) = \psi_0(q), \tag{1.1}$$

then $\psi(q,t)\cdot\widetilde{\chi}(q,x)$ is an approximate solution of the full molecular problem

$$i\epsilon\partial_t\Psi = H_{\mathrm{mol}}\Psi, \qquad \Psi(q,x,0) = \psi_0(q)\cdot\widetilde{\chi}(q,x)$$

by an error of order ϵ as $\epsilon \to 0$, see [ST01].

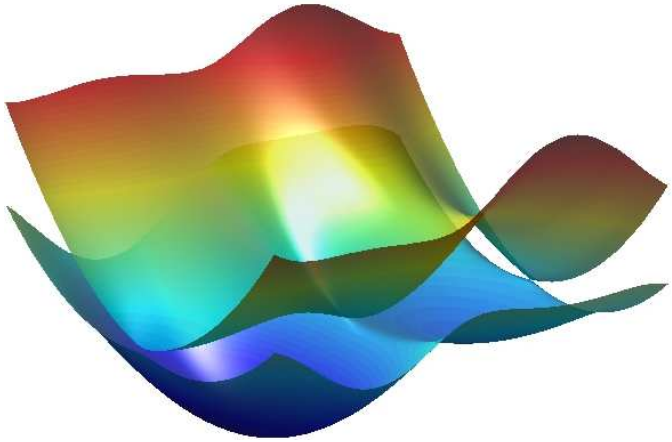

Fig. 1.1. The energy levels of the model for the cis-trans isomerization of retinal in rhodopsin of [HS00]. They cross, when the angular variable ϕ is approximately $\frac{\pi}{2}$ or $\frac{3\pi}{2}$, and the collective coordinate vanishes. In the plot, the abscissa corresponds to ϕ, the ordinate to y. The two local minima of the lower energy level are associated with the cis and the trans configuration of the molecule. (See page 694 for a colored version of the figure.)

For polyatomic molecules, which consist of more than two nuclei, one has to expect the crossing of electron energy levels, that is the existence of nucleonic configurations q with $E^+(q) = E^-(q)$. These crossings, or more precisely, those with a crossing manifold of codimension two or higher,

$$\operatorname{codim}\{q \in \mathbb{R}^d;\, E^+(q) = E^-(q)\} \geq 2,$$

induce non-adiabatic transitions that are of leading order in ϵ as $\epsilon \to 0$: Denote the orthogonal eigenprojectors of the matrix $V(q)$ by $\Pi^{\pm}(q)$. There is a large set of initial data ψ_0 with

$$\Pi^{\pm}\psi_0 = 0 \qquad \text{and} \qquad \exists t > 0 : \Pi^{\pm}(e^{-iH_{\mathrm{BO}}t/\epsilon}\psi_0) = O(1), \quad \epsilon \to 0.$$

That is, the solution of the two-level system performs a non-adiabatic transition from the eigenspace associated with the eigenvalue $E^{\mp}(q)$ to the one associated with $E^{\pm}(q)$.

Non-adiabatic transitions are typically linked with ultrafast isomerization processes, radiationless decay, or molecular collisions. The most spectacular example of a femtosecond isomerization modelled by an electron level crossing, the cis-trans isomerization of retinal in rhodopsin, is the first step of vision, see [HS00]. Rhodopsin is the light-absorbing pigment of the rods, which are responsible for the acute, but coarse colorless vision. The model incorporates two electronic levels $E^-(q)$ and $E^+(q)$ and considers two nucleonic degrees of freedom $q = (\phi, y)$, an angular variable $\phi \in \mathbb{T}$ and a collective coordinate

$y \in \mathbb{R}$. The levels $E^{\pm}(q)$ cross twice, when $\phi \approx \frac{\pi}{2}$ or $\phi \approx \frac{3\pi}{2}$ and $y = 0$, see Fig. 1.1. The two local minima of $E^{-}(q)$ are associated with the cis and the trans configuration of the molecule; the lower steeper one represents the stable cis configuration and the higher flatter one the unstable trans configuration. Initially, the wave function is localized in the cis minimum. After photons excited the wave function vertically to the upper level $E^{+}(q)$, it runs down to approach the two crossing points and performs a non-adiabatic transition there, down to the trans minimum of the lower level $E^{-}(q)$. This isomerization is considered the first step in a chain of events that culminate in a change of the impulse pattern sent along the optic nerve.

Generally, physical models incorporate more than two nucleonic degrees of freedom. The numerical solution of Schrödinger equations with high dimensional configuration spaces, however, is a challenging task. A grid based representation of the wave function scales exponentially in the number of space dimensions. Since the wave function is highly oscillatory, with oscillations in space and time of about the order ϵ, a full grid based discretization in four space dimensions is still considered at the borderline of current computer power.

On the other hand, the wave function itself does not have any direct physical interpretation. Meaningful are quadratic quantities of the wave function like the position density or expectation values. A suitable vehicle for encoding quadratic quantities of a wave function $\psi \in L^2(\mathbb{R}^d, \mathbb{C}^2)$ is the associated Wigner function

$$W(\psi)(q,p) = (2\pi)^{-d} \int_{\mathbb{R}^d} e^{i\,y\cdot p} \psi(q - \tfrac{\epsilon}{2} y) \otimes \overline{\psi}(q + \tfrac{\epsilon}{2} y) dy, \qquad (q,p) \in \mathbb{R}^{2d},$$

which is a function on phase space $\mathbb{R}^{2d}$ taking values in the space of hermitian 2×2-matrices. We refer to Chapter 1.8 in [Fol89] for an exposition of the basic properties. Here, we will restrict ourselves to mentioning marginal distributions and the relation to expectation values.

Integration of the Wigner function with respect to momentum and position space result in position and momentum density, respectively,

$$\int_{\mathbb{R}^d} \operatorname{tr}\left(W(\psi)(q,p)\right) dp = |\psi(q)|^2, \quad \int_{\mathbb{R}^d} \operatorname{tr}\left(W(\psi)(q,p)\right) dq = (2\pi\epsilon)^{-d} \, |\widehat{\psi}(p/\epsilon)|^2.$$

Recall that Weyl quantization associates with a smooth, compactly supported function on phase space, $a \in C_0^\infty(\mathbb{R}^{2d}, \mathbb{C}^{2\times 2})$, a bounded operator $a(q, -i\epsilon\nabla_q)$ on the Hilbert space $L^2(\mathbb{R}^d, \mathbb{C}^2)$, whose action is defined by

$$a(q, -i\epsilon\nabla_q)\psi(q) = \int_{\mathbb{R}^{2d}} e^{i(q-y)\cdot p} a(\tfrac{1}{2}(q+y), \epsilon p)\psi(y) dy dp.$$

The expectation values of a Weyl quantized operator is encoded by the Wigner function, too:

$$\int_{\mathbb{R}^{2d}} \mathrm{tr}\left(W(\psi)(q,p)a(q,p)\right) dqdp = \langle \psi, a(q,-i\epsilon\nabla_q)\psi\rangle_{L^2}.$$

The last identity, combined with the theorem of Calderón-Vaillancourt that asserts that the operator norm of $a(q,-i\epsilon\nabla_q)$ is bounded by a finite sum of sup-norms of derivatives of a, allows one to view the Wigner function as a distribution,

$$W(\psi):\ a \mapsto \int_{\mathbb{R}^{2d}} \mathrm{tr}\left(W(\psi)(q,p)a(q,p)\right) dqdp.$$

Let ψ be the solution of the two-level system (1.1). If one considers the Wigner matrix $W(\psi)$ with respect to an eigenbasis of the eigenvalues $E^{\pm}(q)$, the diagonals of the matrix $W(\psi)$ show a much more favorable behavior as compared to the highly oscillatory wave function ψ. In the semiclassical limit $\epsilon \to 0$ the diagonals can approximately be described by classical transport and a non-adiabatic transfer of weight between them, see Theorem 2.2 below. Hence, level populations, that is

$$\|\Pi^{\pm}\psi(t)\|_{L^2}^2 = \int_{\mathbb{R}^{2d}} \Pi^{\pm}(q) W(\psi(t))(q,p)\Pi^{\pm}(q) dqdp$$

or other quadratic quantities related to the projected wave functions $\Pi^{\pm}\psi(t)$, can be computed efficiently, even in high dimensional situations.

2 Analysis of the dynamics

The mathematical analysis of time-dependent two-level Schrödinger systems

$$i\epsilon\partial_t\psi^\epsilon = \left(-\tfrac{\epsilon^2}{2}\Delta_q + V(q)\right)\psi^\epsilon, \qquad \psi^\epsilon(0) = \psi_0^\epsilon \in L^2(\mathbb{R}^d,\mathbb{C}^2) \tag{2.1}$$

with crossing eigenvalues has been pioneered by Hagedorn [Hag94]. For time-reversible molecular systems the potential matrix is real-symmetric,

$$V(q) = w(q)\mathrm{Id} + \begin{pmatrix} v_1(q) & v_2(q) \\ v_2(q) & -v_1(q)\end{pmatrix}, \tag{2.2}$$

where $w, v_1, v_2 \in C^\infty(\mathbb{R}^d,\mathbb{R})$ are smooth, real-valued functions with decay properties guaranteeing the essential self-adjointness of the Hamilton operator

$$H = -\tfrac{\epsilon^2}{2}\Delta_q + V(q).$$

Denoting $v(q) = (v_1(q), v_2(q))^t$, the matrix $V(q)$ has the eigenvalues

$$w(q) \pm \sqrt{v_1(q)^2 + v_2(q)^2} = w(q) \pm |v(q)|.$$

The crossing manifold $\{q \in \mathbb{R}^d;\, v(q) = 0\}$ of coinciding eigenvalues has codimension two if one assumes

$$v(q) = 0 \quad \Rightarrow \quad \operatorname{rank} Dv(q) = 2,$$

where $Dv(q) = (\nabla_q v_1(q), \nabla_q v_2(q))$. These crossings are called conical intersections in the chemical physics literature, see [DYK04]. They seem to be the most commonly studied type of level crossings.

The mathematical results on the dynamics near conical intersections rely on the smallness of the semiclassical parameter $0 < \epsilon \ll 1$, giving dynamical descriptions that are asymptotic with respect to $\epsilon \to 0$. They fall into three groups: the propagation of Gaussian wave packets [Hag94], of two-scale Wigner measures [FG02, FG03, Fer03, FL03], and of Wigner functions [LT05, FL06]. Resolving the non-adiabatic transitions at the crossing manifold, all approaches rely on some kind of normal form, which in its essence is the Landau-Zener operator [Zen32]

$$-i\epsilon\partial_s + \begin{pmatrix} s & \gamma \\ \gamma & -s \end{pmatrix}, \qquad \gamma \in \mathbb{R}.$$

In the framework of microlocal analysis, that is, locally in phase space, normal forms for generic level crossings have been derived by Fermanian Kammerer and Gérard [FG02, FG03]. T he microlocal normal forms of Colin de Verdière [CdV03, CdV04] even allow for superpolynomial error estimates.

2.1 Heuristics

An intuitive, but *non-rigorous* argument that shows the Landau-Zener operator to essentially gear the dynamics through conical intersections has been given for the linear isotropic potential

$$V(q) = \begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix} \tag{2.3}$$

by Teufel and the second author [LT05]. We will adapt these heuristics to general conical intersections in the following. We note, that they result in an explicit formula for the gap γ, which will be a crucial ingredient of the effective asymptotics and the subsequent numerical algorithm that we aim for.

The Schrödinger operator H is the semiclassical Weyl quantization of the matrix-valued symbol

$$\mathbb{R}^{2d} \to \mathbb{R}^{2\times 2}, \quad (q,p) \mapsto \tfrac{1}{2}|p|^2 + V(q).$$

Given its eigenvalues

$$\mathbb{R}^{2d} \to \mathbb{R}, \quad (q,p) \mapsto \tfrac{1}{2}|p|^2 + w(q) \pm |v(q)|$$

one associates the two Hamiltonian systems

$$\dot{q} = p, \qquad \dot{p} = -\nabla_q w(q) \mp \frac{Dv(q)v(q)}{|v(q)|} \tag{2.4}$$

and the corresponding classical flows $\Phi_{\pm}^t$, which are well-defined away from the crossing manifold.

As a first step, one formally inserts a classical trajectory $(q(t), p(t))$ of one of the Hamiltonian systems into the trace-free part of the symbol of the full operator, obtaining the purely time-dependent problem

$$i\epsilon\dot{\phi}(t) = \begin{pmatrix} v_1(q(t)) & v_2(q(t)) \\ v_2(q(t)) & -v_1(q(t)) \end{pmatrix} \phi(t). \tag{2.5}$$

Such systems show non-adiabatic transitions in the region, where the gap between the eigenvalues is minimal (see e. g. [Bor98, HJ04, BT05]). A necessary condition for the gap between the eigenvalues to become minimal along the chosen trajectory is

$$\tfrac{d}{dt}|v(q(t))|^2 = 0.$$

This condition is satisfied if the trajectory passes the hypersurface

$$S = \left\{(q,p) \in \mathbb{R}^{2d};\, Dv(q)p \cdot v(q) = 0\right\}.$$

Let $\alpha \in [-1, 1]$ be an angle to be determined later. A conjugation by the half-angle rotation matrix

$$\begin{pmatrix} \cos\frac{\alpha}{2} & -\sin\frac{\alpha}{2} \\ \sin\frac{\alpha}{2} & \cos\frac{\alpha}{2} \end{pmatrix}$$

transforms problem (2.5) to

$$i\epsilon\dot{\phi}(t) = \begin{pmatrix} (\cos\alpha, \sin\alpha)^t \cdot v(q(t)) & (\cos\alpha, \sin\alpha)^t \wedge v(q(t)) \\ (\cos\alpha, \sin\alpha)^t \wedge v(q(t)) & -(\cos\alpha, \sin\alpha)^t \cdot v(q(t)) \end{pmatrix} \phi(t),$$

where $x \wedge y = x_1y_2 - x_2y_1$ denotes the symplectic product of the two vectors $x, y \in \mathbb{R}^2$. Assuming that the chosen trajectory passes the hypersurface of minimal gap through the point (q_*, p_*) at time $t = 0$, one linearizes,

$$v(q(t)) = v(q_*) + tDv(q_*)p_* + O(t^2).$$

Aiming at a Landau-Zener problem with the diagonals linearly depending on time and the off-diagonals constant, one chooses the rotation angle as

$$\alpha = \arccos\left(\frac{\nabla_q v_1(q_*) \cdot p_*}{|Dv(q_*)p_*|}\right) = \arcsin\left(\frac{\nabla_q v_2(q_*) \cdot p_*}{|Dv(q_*)p_*|}\right).$$

Since $Dv(q_*)p_* \cdot v(q_*) = 0$, the linearized system then reads as

$$i\epsilon\dot{\phi}(t) = \begin{pmatrix} t|Dv(q_*)p_*| & \frac{Dv(q_*)p_* \wedge v(q_*)}{|Dv(q_*)p_*|} \\ \frac{Dv(q_*)p_* \wedge v(q_*)}{|Dv(q_*)p_*|} & -t|Dv(q_*)p_*| \end{pmatrix} \phi(t).$$

If $|Dv(q_*)p_*| \gg 0$, one sets a new semiclassical parameter $\tilde{\epsilon} = \epsilon/|Dv(q_*)p_*|$, and obtains the Landau-Zener problem

$$i\tilde{\epsilon}\dot{\phi}(t) = \begin{pmatrix} t & \gamma \\ \gamma & -t \end{pmatrix} \phi(t)$$

with gap

$$\gamma = \frac{Dv(q_*)p_* \wedge v(q_*)}{|Dv(q_*)p_*|^2}.$$

Let $\phi^{\pm}(t)$ denote the components of the vector $\phi(t)$ with respect to the eigenbasis of the Landau-Zener matrix, and put $\phi^{\pm}(\pm\infty) = \lim_{t\to\pm\infty} \phi^{\pm}(t)$. If

$$\begin{pmatrix} \phi^+(-\infty) \\ \phi^-(-\infty) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{or} \qquad \begin{pmatrix} \phi^+(-\infty) \\ \phi^-(-\infty) \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

then

$$\begin{pmatrix} |\phi^+(+\infty)|^2 \\ |\phi^-(+\infty)|^2 \end{pmatrix} = \begin{pmatrix} 1-T & T \\ T & 1-T \end{pmatrix} \begin{pmatrix} |\phi^+(-\infty)|^2 \\ |\phi^-(-\infty)|^2 \end{pmatrix}$$

with a transition rate

$$T \sim \exp\Big(-\frac{\pi}{\tilde{\epsilon}}\gamma^2\Big), \qquad \tilde{\epsilon} \to 0.$$

In particular, the Landau-Zener rate T exhibits that the non-adiabatic transitions are of leading order in $\tilde{\epsilon}$ if the chosen trajectory experiences a gap γ that is of order $\sqrt{\tilde{\epsilon}}$.

Remark 2.1. We note that even though the time-dependent problem (2.5) we started with is formulated just in terms of the position coordinate $q(t)$, the resulting Landau-Zener problem has a gap γ that depends on phase space information, namely the point (q_*, p_*) at which the trajectory attains the minimal gap between the eigenvalues $w(q) \pm |v(q)|$.

2.2 Branching process

The heuristics motivates the following definition of random trajectories and a corresponding Markov process for effectively describing the dynamics through conical intersections.

One attaches to points $(q,p) \in \mathbb{R}^{2d}$ in phase space a label -1 or $+1$, indicating reference to the eigenvalue $w(q) - |v(q)|$ or $w(q) + |v(q)|$. Moreover, one chooses a positive number $R > 0$, defining the set

$$\big\{(q,p) \in \mathbb{R}^{2d};\, |v(q)| \le R\sqrt{\epsilon}\big\}$$

as a distinguished tubular neighborhood of the crossing manifold. For labelled phase space points $(q,p,j) \in \mathbb{R}^{2d} \times \{-1,+1\}$, one sets

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

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

$$|v(q^j(t))| > R\sqrt{\epsilon} \qquad \text{or} \qquad Dv(q^j(t))p^j(t) \cdot v(q^j(t)) \neq 0.$$

A jump from j to $-j$ occurs with probability

$$T(q_*,p_*) = \exp\left(-\frac{\pi}{\epsilon}\frac{(Dv(q_*)p_* \wedge v(q_*))^2}{|Dv(q_*)p_*|^3}\right) \tag{2.6}$$

whenever $\Phi_j^t(q,p)$ hits the manifold of minimal gap

$$S = \left\{(q,p) \in \mathbb{R}^{2d};\ Dv(q)p \cdot v(q) = 0\right\}.$$

at time t in a point $(q_*,p_*) \in S$ with $|v(q_*)| \leq R\sqrt{\epsilon}$.

The randomized evolution $\mathcal{T}^{(q,p,j)}(t)$ defines a Markov process. The associated backwards semi-group $\mathcal{L}^t$ is given by its action on a class of continuous scalar-valued functions $a = a(q,p,j)$ satisfying suitable boundary conditions at the manifold of minimal gap S,

$$\mathcal{L}^t a(q,p,j) := \mathbf{E}^{(q,p,j)} a\big(\mathcal{T}^{(q,p,j)}(t)\big),$$

see [LT05, FL06]. This definition naturally extends to matrix-valued functions of the form $a = a^+\Pi^+ + a^-\Pi^-$ with $a^\pm \in C_0^\infty(\mathbb{R}^{2d} \setminus S, \mathbb{C})$, that is, to functions that commute with the potential matrix V. By duality, the semigroup acts on Wigner functions also,

$$\mathcal{L}^t W(\psi) : \ a \mapsto \int_{\mathbb{R}^{2d}} \mathrm{tr}\left(W(\psi)(q,p)(\mathcal{L}^t a)(q,p)\right) dqdp.$$

Theorem 2.2 ([LT05, FL06]). *Let $(\psi_0^\epsilon)_{\epsilon>0}$ be a bounded sequence in $L^2(\mathbb{R}^d,\mathbb{C}^2)$ such that $\Pi^-\psi_0^\epsilon = 0$ and there exists $\delta > 0$ with*

$$\lim_{\epsilon\to 0} \int_{S_\delta} |W(\psi_0^\epsilon)(q,p)|\, dqdp = 0,$$

where $S_\delta = \{(q,p) \in \mathbb{R}^{2d};\ |v(q)|, |Dv(q)p \cdot v(q)| \leq \delta\}$. Let V be a matrix with conically intersecting eigenvalues as given in (2.2). Suppose, that $q \mapsto |v(q)|$ is convex, and that $Dv(q)\nabla w(q) \cdot v(q) \leq 0$ for all $q \in \mathbb{R}^d$.

Then, for all $T > 0$, the solution $\psi^\epsilon(t)$ of the Schrödinger equation (2.1) with initial data $\psi^\epsilon(0) = \psi_0^\epsilon$ satisfies

$$\begin{aligned}\sup_{t\in[0,T]} \int_{\mathbb{R}^{2d}} &\left(W(\psi^\epsilon(t)) - \mathcal{L}^t W(\psi_0^\epsilon)\right) a(q,p)\, dqdp \\ &= O(R^{-1}) + O(R^3\sqrt{\epsilon}) + O(\sqrt{\epsilon}\,|\ln\epsilon|)\end{aligned}$$

for all $a = a^+\Pi^+ + a^-\Pi^-$ with $a^\pm \in C_0^\infty(\mathbb{R}^{2d} \setminus S, \mathbb{C})$.

Remark 2.3. Note, that the error is minimal as $R = \epsilon^{-1/8}$ and is of order $\epsilon^{1/8}$.

Remark 2.4. The assumptions on the potential $V(q)$ guarantee that minus-trajectories issued from the upper level never meet the crossing again. Hence, the system dealt with does not show any interlevel interferences, which could not be resolved by merley working on the diagonal of the Wigner matrix.

Remark 2.5. The assumptions on the initial data $(\psi_0^\epsilon)_{\epsilon>0}$ ensure that the wave function does not localize near the manifold of minimal gap and the crossing manifold initially. This is due to the semigroup encorporating only an effective treatment of the non-adiabatic transitions, which becomes valid when the solution has passed by the crossing and the manifold of minimal gap.

In [LT05], Theorem 2.2 has been proven for the linear isotropic potential (2.3) with an error of $o(1)$ as $\epsilon \to 0$. The proof for general potentials providing the error bound with respect to ϵ and R is given in [FL06]. It falls into two parts: Away from the crossing, there is only classical transport. One shows by semiclassical Weyl calculus that the error of propagation is of order $O(R^{-1}) + O(\sqrt{\epsilon})$. Near the crossing, non-adiabatic transitions become relevant. For proving the correctness of the asymptotic transition rates one resorts to a refined version of the microlocal normal form of [CdV03].

2.3 Surface hopping algorithm

The semigroup $\mathcal{L}^t$ suggests a numerical algorithm that can be seen as a rigorous counterpart to the surface hopping algorithms of chemical physics. Such algorithms have been introduced by Tully and Preston in [TP71] for studies of molecular collisions. To our knowledge Theorem 2.2 is the first mathematically rigorous justification for such an approach. For high dimensional problems in photochemistry surface hopping seems to be one of the most popular algorithms employed. We refer to the review [ST05] as a pointer to the vast chemical literature on algorithms of this type.

A numerical realization of the semigroup $\mathcal{L}^t$ is achieved by the following steps: one projects the initial wave function to the energy levels and computes the associated Wigner functions. After sampling the Wigner functions, one propagates along the classical trajectories of the Hamiltonian systems (2.4) and opens up a new trajectory on the other level whenever a trajectory passes through the hypersurface of minimal gap. When splitting up, the weight associated with the trajectories is distributed according to the Landau-Zener transition coefficient (2.6).

[LST06] thoroughly validates this algorithm for systems with linear isotropic potentials. Figure 2.1 shows the relative error of level populations for the following test case: the initial data are Gaussian wave packets associated with the upper level localized at a distance of $5\sqrt{\epsilon}$ from the crossing with average momentum of order one. The time evolution stops at time $t = 10\sqrt{\epsilon}$.

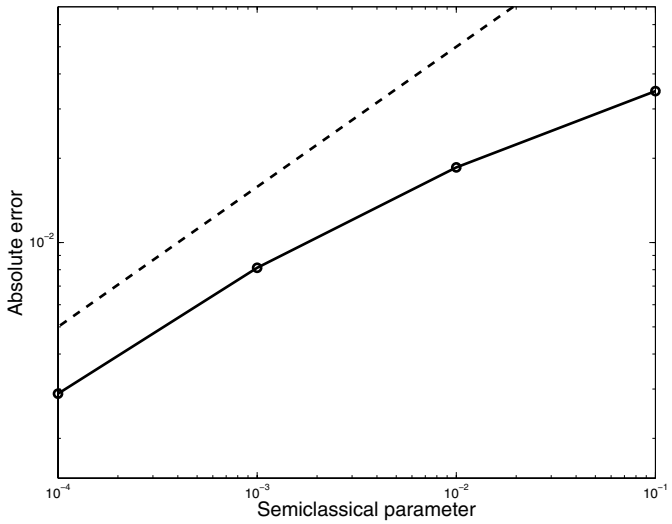

Fig. 2.1. The absolute error of the surface hopping algorithm versus a Strang splitting scheme for level populations with respect to the semiclassical parameter ϵ. The dashed line is the function $\frac{1}{2}\sqrt{\epsilon}$, while the solid line is the absolute error for the final populations on the two levels.

The level populations $\|\Pi^{\pm}\psi(t)\|_{L^2}^2$ are computed by the rigorous surface hopping algorithm as well as by a numerically converged Strang splitting scheme. As a function of the semiclassical parameter, the resulting absolute error is bounded by $\frac{1}{2}\sqrt{\epsilon}$. All the other experiments of [LST06] show a comparable error of order $\sqrt{\epsilon}$, indicating, that the $\epsilon^{1/8}$ error bound of Theorem 2.2 is not sharp.

3 Spectral study

Mathematically rigorous spectral studies of operators with crossing eigenvalues have aimed at resolvent estimates [Jec0303, Jec05] and bounds on the number of resonances [Néd96, Néd01, Néd03]. More explicit, quantitative investigations showing a clear spectral fingerprint of non-adiabatic origin have been undertaken by Avron and Gordon in the zero energy regime [AG00a, AG00b]. Complementarily to these results, the joint work of the second author with Fujiié and Nédélec [FLN06] deals with Bohr-Sommerfeld conditions for energies bounded away from zero.

The common model operator of [AG00a, AG00b, FLN06] has a linear isotropic potential matrix with conically intersecting eigenvalues,

$$H = -\epsilon^2 \Delta_q + V(q) = -\epsilon^2 \Delta_q + \begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix}.$$

Its scalar counterparts are the one-level operators

$$H^{\pm} = -\epsilon^2 \Delta_q \pm |q|.$$

The upper level operator H^+ has a confining potential, which is bounded from below by zero and increases to infinity as $|q| \to \infty$. Hence, H^+ has purely discrete spectrum with strictly positive eigenvalues (see Theorems XIII.47 and XIII.67 in [RS78]). The lower level operator H^- has a repulsive potential. Its commutator with the generator of dilations $D = \frac{1}{2i}(q \cdot \nabla_q + \nabla_q \cdot q)$ is positive,

$$[H^-, iD] = -2\Delta_q + |q|,$$

and yields a global Mourre estimate. Hence, H^- has purely absolutely continuous spectrum (see Corollary 4.10 in [CF*87]). The full operator H, however, inherits the purely absolutely continuous spectrum of H^-, while echoing the discrete spectrum of H^+ with resonances close to the real axis.

The resonances of the operator H are defined by complex dilation (see Theorem 2.1 in [Néd96]). They are the eigenvalues $E \in \mathbb{C}$ of the complex scaled Hamiltonian

$$H_\theta = -\epsilon^2 e^{-2i\theta} \Delta_q + e^{i\theta} V(q),$$

which is a non-selfadjoint operator with discrete spectrum in the lower half-plane independent of the dilation parameter $\theta \in]0, \frac{\pi}{3}[$.

Remark 3.1. For a large class of scalar Schrödinger operators, resonances defined by complex dilation have been identified with the poles of a suitable continuation of the resolvent or of the scattering matrix. The underlying physical picture is that of a slowly decaying state, whose life-time is set by the imaginary part of the resonance. We refer to Chapter 8 in [CF*87], Chapter 16 in [HS96], or the review [Zwo99] as introductory reading for the theory of resonances.

A resonance E of H is determined by solving $H\psi = E\psi$ in the distributional sense and validating decay and regularity properties of the dilated resonant state $q \mapsto \psi(e^{-i\theta} q)$. One uses the radial symmetry in $V(q)$ to reduce the partial differential operator H to a direct sum of ordinary differential systems: the operator P is unitarily equivalent to

$$\bigoplus_{\nu \in \mathbb{Z} + \frac{1}{2}} H_\nu(r, -i\epsilon\partial_r; \epsilon), \qquad H_\nu(r, \rho; \epsilon) = \begin{pmatrix} r^2 - \rho & \epsilon\nu/r \\ \epsilon\nu/r & r^2 + \rho \end{pmatrix}, \tag{3.1}$$

where $(r, \rho) \in \mathbb{R}^+ \times \mathbb{R}$. Nédélec [Néd96] has derived this equivalence by a Fourier transformation, a change to polar coordinates $(r, \phi) \in \mathbb{R}^+ \times \mathbb{T}$, a conjugation by the half-angle rotation matrix

$$\begin{pmatrix} \cos\frac{\phi}{2} & -\sin\frac{\phi}{2} \\ \sin\frac{\phi}{2} & \cos\frac{\phi}{2} \end{pmatrix},$$

and a final Fourier series ansatz in the angular variable ϕ. A similar decomposition labelled by half-integers has been obtained by Avron and Gordon [AG00a, AG00b], using the commutation relation of H with an angular momentum operator L,

$$[H, L] = 0, \qquad L = q \wedge (-i\epsilon\nabla_q) + \tfrac{1}{2}\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}.$$

Both decompositions share the fact, that the half-integer labelling turns the conical intersection $q \mapsto \pm|q|$ into a family of avoided crossings. However, while in [AG00a, AG00b] the ordinary differential systems are solved in the zero energy regime in terms of generalized hypergeometric functions, the aim of [FLN06] is an explicit asymptotic analysis ($\epsilon \to 0$) of non-zero energies by means of an exact WKB method.

According to the decomposition (3.1) one associates with a resonance E of H an angular momentum number $\nu \in \mathbb{Z} + \frac{1}{2}$ if E corresponds to a distributional solution of the ordinary differential problem

$$H_\nu(r, -i\epsilon\partial_r; \epsilon)u = Eu,$$

such that $r \mapsto u(e^{-i\theta}r)$ satisfies appropriate boundary conditions as $r \to 0$ and $r \to +\infty$. Consider $E \in]a, b[$ for positive numbers $0 < a < b$. If $\epsilon > 0$ is sufficiently small, the energy surface

$$\left\{(r, \rho) \in \mathbb{R}^+ \times \mathbb{R};\ \det\left(H_\nu(r, \rho; \epsilon) - E\right) = 0\right\}$$

consists of two connected curves, a closed simple one and one being unbounded. Let $A_\nu(E, \epsilon)$ be the action associated with the closed curve,

$$A_\nu(E, \epsilon) = 2\int_{r_0}^{r_1} \sqrt{\det(H_\nu(r, 0; \epsilon) - E)}\, dr,$$

where $0 < r_0 < r_1$ are the first and second positive zero of the mapping $r \mapsto \det(H_\nu(r, 0; \epsilon) - E)$, and the square root is taken positive. As a function of E, the action $A_\nu(E, \epsilon)$ is extended analytically into a complex neighborhood of the interval $]a, b[$. The first result is the following Bohr-Sommerfeld type quantization condition of resonances with fixed angular momentum.

Theorem 3.2 ([FLN06]). *Let $E_0 > 0$ and $\nu \in \mathbb{Z} + \frac{1}{2}$ be given. Then there exist $\delta > 0$, $\epsilon_0 > 0$, and a function $c(E, \epsilon) : \{(E, \epsilon) \in \mathbb{C}\times]0, \epsilon_0[;\ |E - E_0| < \delta\} \to \mathbb{C}$ with $c(E, \epsilon) \to 0$ uniformly in E as $\epsilon \to 0$, such that E is a resonance of $H = -\epsilon^2\Delta_q + V(q)$ with angular momentum ν if and only if (E, ϵ) satisfies the following quantization condition:*

$$\sqrt{\frac{\pi\epsilon}{2}}\, \nu\, e^{-i\pi/4}\, E^{-3/4}\, e^{iA_\nu(E,\epsilon)/\epsilon} + 1 = c(E, \epsilon). \tag{3.2}$$

To our knowledge, Theorem 3.2 is the first Bohr-Sommerfeld quantization condition for a Schrödinger system with crossing eigenvalues. The prefactor before the exponential of the action carrying the second scale $\sqrt{\epsilon}$ is a clear signature of non-adiabaticity, stemming from a connection formula involving the Landau-Zener problem

$$i\epsilon\partial_r u = \begin{pmatrix} r & -\gamma \\ \overline{\gamma} & -r \end{pmatrix} u, \qquad \gamma = \epsilon\tfrac{\nu}{\sqrt{2}}E^{-3/4} + O(\epsilon^2). \tag{3.3}$$

For the proof of Theorem 3.2, the exact WKB method of Gérard and Grigis [GG88] is extended from scalar Schrödinger equations to a class of 2×2 first order differential systems, covering the case $H_\nu(r, -i\epsilon\partial_r; \epsilon)u = Eu$. The exact WKB solutions are of the form

$$u(r) = e^{\pm iz(r)/\epsilon} w(r), \qquad z(r) = \int_{r_*}^{r} \sqrt{\det(H_\nu(s, 0; \epsilon) - E)}\, ds.$$

They are locally defined away from turning points, which are the zeros of the mapping $r \mapsto \det(H_\nu(r, 0; \epsilon) - E)$. For $E \in]a, b[$, there are three positive turning points $r_0 < r_1 < r_2$, where r_0 tends to zero, while r_1 and r_2 coalesce at $\sqrt{E}$ as $\epsilon \to 0$.

For obtaining global solutions, one connects the exact WKB solutions at the turning points, using the good ϵ-asymptotics of the amplitude vector w. More precisely, one constructs an exact solution, which vanishes at the origin, and represents it after several connection procedures as a linear combination of solutions with controlled behavior at infinity. For $r \to +\infty$, there is a fundamental system of solutions $u_\infty^\pm$, such that $r \mapsto u_\infty^+(e^{-i\theta}r)$ is exponentially growing and $r \mapsto u_\infty^-(e^{-i\theta}r)$ exponentially decaying. The quantization formula (3.2) corresponds to the condition that the connection coefficient of the exponentially growing solution u_∞^+ vanishes.

The origin is a regular singular point of the equation $H_\nu(r, -i\epsilon\partial_r; \epsilon)u = Eu$ with indices $\pm\nu$. Moreover, the first turning point r_0 tends to zero as $\epsilon \to 0$. One constructs an exact WKB solution in a small complex neighborhood of the origin, which corresponds to the index $+\nu$. Studying the two parameter asymptotics of this solution as $(r, \epsilon) \to (0, 0)$, one encounters the same difficulties as in the context of the Langer modification for the radial Schrödinger equation, see also [FR00]. The $o(1)$ error estimate in Theorem 3.2 originates just from here. The rest of the proof gives better control on the convergence rate.

At $r = \sqrt{E}$, the second and third turning points r_1 and r_2 coalesce as $\epsilon \to 0$. The connection formula at this double turning point is calculated using a microlocal reduction to a normal form. Microlocally near $(r, \rho) = (\sqrt{E}, 0)$, the equation $H_\nu(r, -i\epsilon\partial_r; \epsilon)u = Eu$ looks like the Landau-Zener problem (3.3). A further reduction step leads to the saddle-point problem

$$r(-i\epsilon\partial_r)u = \tfrac{|\gamma|^2}{2}u.$$

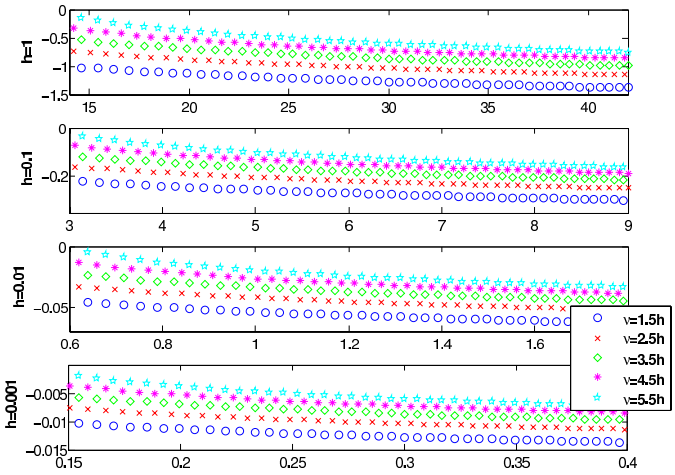

Fig. 3.1. Resonances of the model operator $H = -\epsilon^2 \Delta_q + V(q)$. The parameter k lies in $\{11, 12, \ldots, 60\}$, while ν is chosen in $\{1.5, 2.5, \ldots, 5.5\}$. The semiclassical parameter ϵ varies from 10^{-3} to 1. (See page 694 for a colored version of the figure.)

For this problem exact microlocal connection formulas are known [CP94, Ram96] and one has to lift them to the exact WKB solutions. The second scale $\sqrt{\epsilon}$ in the quantization condition (3.2) originates from this connection.

An asymptotic study (Proposition 8.2 in [FLN06]) of the action yields

$$A_\nu(E, \epsilon) = \tfrac{4}{3} E^{3/2} + \pi \nu \epsilon + O(\epsilon^2 |\ln \epsilon|) \qquad (\epsilon \to 0).$$

Plugging this expansion into the Bohr-Sommerfeld condition (3.2), one is motivated to define the following family of almost horizontal sequences:

$$\Gamma_\nu(a, b; \epsilon) = \Big\{ \lambda \in \mathbb{C};\ \lambda = \lambda_{k\nu} \epsilon - i\, \tfrac{3}{8} \Big(\epsilon \ln \tfrac{1}{\epsilon} - \epsilon \ln \tfrac{\pi \nu^2}{2 \lambda_{k\nu} \epsilon} \Big), \\ k \in \mathbb{Z} \text{ s.t. } \lambda_{k\nu} \epsilon \in]a, b[\Big\}$$

with

$$\lambda_{k\nu} = \tfrac{3\pi}{16}(8k - 4\nu + 5) \qquad (k \in \mathbb{Z},\ \nu \in \mathbb{Z} + \tfrac{1}{2}).$$

Since $\lambda_{k\nu} \epsilon \in]a, b[$, the second term of the imaginary part of $\lambda \in \Gamma_\nu(a, b; \epsilon)$ is of $O(\epsilon)$ and smaller than the first term $-\frac{3}{8} \epsilon \ln \frac{1}{\epsilon}$. Hence, $\Gamma_\nu(a, b; \epsilon)$ is an almost horizontal sequence in the lower half-plane with distance of $O(\epsilon \ln \frac{1}{\epsilon})$ from the real axis. The asymptotic distribution of resonances with real part in the positive interval $]a, b[$ reads as follows:

Theorem 3.3 ([FLN06]). *Let $N \in \mathbb{N}$ and $0 < a < b$ be given. Then there is $\epsilon_0 > 0$ and a positive function $c :]0, \epsilon_0[\to \mathbb{R}^+$ with $c(\epsilon) = o(\epsilon)$ as $\epsilon \to 0$ such that for each $\lambda \in \bigcup_{\nu \le N} \Gamma_\nu(a, b; \epsilon)$ there exists one and only one resonance of $H = -\epsilon^2 \Delta_q + V(q)$ within the set $\big\{ E \in \mathbb{C};\ |E - \lambda^{2/3}| < c(\epsilon) \big\}$.*

The plots in Fig. 3.1 illustrate the distorted lattice of resonances given by Theorem 3.3. The larger the angular momentum number ν is taken, the closer the resonance is to the real axis and the longer the life time of the corresponding resonant states will be. This observation is in wonderful agreement with the dynamical properties of the operator P. The one-level operators $H^{\pm}$ induce Hamiltonian systems conserving angular momentum $q \wedge p = q_1 p_2 - q_2 p_1$, which also encodes how close classical trajectories arrive near the crossing manifold $\{q = 0\}$. On the one hand, a high angular momentum number ν of a resonance mirrors a periodic orbit of the upper level with high angular momentum. Such orbits in turn imply existence of localized quasimodes and long-living resonant states. On the other hand, small angular momentum numbers ν correspond to orbits close to the crossing manifold. Close to the crossing, non-adiabatic transitions to the unbounded motion of the minus-system are possible. In this regime shorter life-times and resonances far away from the real axis have to be expected.

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