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Partial Wigner Transforms and the Quantum-Classical Liouville Equation

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Abstract

In molecular dynamics applications there is a growing interest in mixed quantum-classical models. The *quantum-classical Liouville equation* (QCL) describes most atoms of the molecular system under consideration by means of a classical phase space density but an important, small portion of the system by means of quantum mechanics. The QCL is derived from the full quantum dynamical (QD) description by applying the Wigner transform to the "classical part" of the system only. We discuss the conditions under which the QCL model approximates the full QD evolution of the system. First, analysis of the asymptotic properties of the Wigner transform shows that solving the QCL yields a first order approximation of full quantum dynamics. Second, we discuss the adiabatic limit of the QCL. This discussion shows that the QCL solutions may be interpretated as classical phase space densities, at least near the adiabatic limit. Third, it is demonstrated that the QCL yields good approximations of *non-adiabatic quantum effects*, especially near so-called *avoided crossings* where most quantum-classical models fail.

1 Introduction

In molecular dynamics applications there is a growing interest in including quantum dynamical effects into the description of large molecular systems. Unfortunately, full quantum dynamical (QD) calculations for larger molecules are beyond the scope of simulations, today and in the next decades. Thus, typical molecular dynamics simulations describe the molecular motion by means of classical mechanics; quantum effects are considered only indirectly via parametrization of the force fields used [1]. In the *mixed quantum-classical approach* to this problem, an important (and mostly small) portion of the system is in fact described by the means of quantum mechanics while most atoms are still modelled classically.

The most prominent quantum-classical model is the so-called *time-dependent Born-Oppenheimer model* (BO), going back to the late 20's [8]. In this model, the quantally modelled subsystem is *adiabatically* coupled to the classical subsystem, i.e., the classical motion does *not* change the *populations* of the quantal energy levels of the molecule.[1] The literature contains an extensive discussion

[1] That is, the populations are assumed to be *adiabatic invariants* as in the well-known

concerning the conditions under which the BO model approximates the full QD evolution. In the mathematical literature, this discussion is based on the fact that, in many important situations, the Schrödinger equation governing the full QD evolution,

$$i\epsilon\, \partial_t \Psi \;=\; \left(-\tfrac{\epsilon^2}{2}\Delta_q \,+\, H(q)\right)\,\Psi, \tag{1}$$

is a singularly perturbed partial differential equation since ϵ is some small parameter that originates, e.g., from large mass differences between the particles in the molecular system (cf. Sec. 2 below). G. Hagedorn and others have demonstrated that —under certain "non-crossing"-conditions— the BO model is the *singular* or *adiabatic limit* of full QD for $\epsilon \to 0$, see, e.g., [13, 27, 35, 41]. "Non-crossing"-conditions exclude so-called *energy level crossings* or *intersections* between the potential energy surfaces[2] of the quantum subsystem.[3]

Thus, the BO model describes the adiabatic motion of the system. However, it leads to entirely wrong descriptions whenever *transitions* between the energy levels of the quantum system play an important role, i.e., when the molecular dynamics is significantly *non-adiabatic.* Such non-adiabatic transitions may be seen as *resonance effects* between the classical and quantum subsystems and occur whenever the *spectral gap* between the energy levels of the quantal subsystem becomes small enough in comparison to ϵ. The most important reasons for such resonances are (a) energy level crossings (zero spectral gap) and (b) so-called *avoided crossings* (small but non-vanishing spectral gaps; see the example in Sec. 6).

The possible effects of energy level crossings on the limit dynamics of full QD for $\epsilon \to 0$ have been analyzed in detail by means of matched asymptotics [23,24]. Effects of avoided crossings have been studied by asymptotic techniques under the assumption that the spectral gap is closing when ϵ tends to zero [25, 26]. These and other approaches [32] are modern rigorous contributions to more than 60 years of discussion of the well-known Landau-Zener formula [37,53,59] which allows to compute the asymptotic effect of avoided crossings in various specific situations.

Non-adiabatic deviations from adiabatic motion are not limited to the well-known electronic transitions in electronic relaxation processes or reactive molecular collisions. Other examples in realistic molecular systems are proton transfer processes in solution [4, 6, 22, 28, 29, 52, 54, 55] or in the active site of a protein [2, 47], electron diffusion in molten salts [51], or photo-induced effects in molecular systems [15, 36, 42, 48, 58]. In these examples the dynamics is only "mildly" non-adiabatic typically, i.e., it can be described with decisive, but rather "small" corrections to the adiabatic evolution. However, the mathematical results mentioned above do *not* suffice to describe most of these processes in detail, mainly because of two reasons: they cover rather specific situations only, and, as asymptotic results for $\epsilon \to 0$, they (in general) do *not* include all "higher order effects" that are relevant contributions due to the positive value of $\epsilon > 0$ associated with the molecular system of interest.

adiabatic theorem of quantum mechanics [7, 17, 18, 34].

[2]The *potential energy surfaces* or *energy levels* are given by the q-dependent eigenvalues of the (self-adjoint) Hamiltonian operator $H(q)$ occurring in (1); see Sec. 2.

[3]More precisely, most types of crossings must be excluded; some specific types (e.g., codimension 1 and non-transversal) do *not* effect the adiabatic motion [24].

Since, in most cases, the available *theoretical* results are not sufficient to describe molecular systems of real chemical interest correctly, a whole bunch of quantum-classical methods have been introduced in order to allow the *numerical* reproduction of the non-adiabatic corrections for $\epsilon > 0$. Some prominent methods have been discussed extensively, e.g., the so-called surface hopping method [3, 30, 55, 56], mean-field models like QCMD and TDSCF [9, 10, 21, 50], path integral oriented methods [12, 45, 46], or the semi-classical initial value representation [43, 44]. For each single of these methods the literature contains specific examples in which it reproduces the non-adiabatic effects correctly but also examples in which it fails to do so, cf. Part III of [5].

Recently, MARTENS and others introduced a novel density-matrix descriptions for the coupling between the quantum and classical subsystem based on the so-called *quantum-classical Liouville equation (QCL)* [33, 40]. In addition, MARTENS and coworkers also derived a deterministic particle method based on the QCL and applied it to certain examples with avoided crossings [16]. Unfortunately, these articles do not contain more than an intuitive derivation of the QCL and its numerical realizations.

Thus, a variety of quantum-classical methods is available. However, *rigorous* approximation results for these methods concerning non-adiabatic effects are extremely rare. This is the case, mainly because the necessary "higher order" corrections to the adiabatic limit are difficult to achieve, at least by means of the typical techniques like WKB expansions or matched asymptotics.

Herein, it is proposed to gain higher order expansions by means of the *Wigner transform* [57] and its asymptotic properties as studied by GÉRARD, MARKOWICH ET AL. in their remarkable article [20]. This will permit us to analyze the non-adiabatic behavior of the QCL: we will not only present a "first order" approximation result for different variants of the QCL (which can be generalized to higher orders, see Sec. 4) but will also demonstrate that the QCL allows to approximate non-adiabatic quantum effects near avoided crossings (Sec. 6). In this approach, the QCL will result from a *partial* Wigner transform [57] of the full Schrödinger equation of the system.

The present author expects that the primary importance of the QCL lies in the fact that it allows the construction of quantum-classical particle methods, either of deterministic character as in [16] or stochastic ones leading to surface-hopping-like techniques as studied in [33]. Therefore, it is important whether the QCL solution may be interpreted in terms of classical phase space densities. We will be able to justify this by studying the adiabatic limit of the QCL and exploiting the mathematical discussion concerning *Wigner measures* [19, 38, 39], see Sec. 5.

2 Quantum Dynamical Description

To simplify the notation we restrict our study to the case of a system with just two degrees of freedom $x \in \mathbb{R}^m$ and $q \in \mathbb{R}^d$ with significantly different associated masses, m and M. We suppose that the mass ratio $\epsilon^2 = m/M$ is a small parameter. After an appropriate rescaling [27], the time-dependent Schrödinger equation of this systems becomes

$$i\epsilon\,\partial_t \Psi \;=\; \left(-\tfrac{\epsilon^2}{2}\Delta_q \;+\; H(q)\right)\,\Psi. \tag{2}$$

$H = H(q)$ is a q-parametrized, selfadjoint Hamiltonian in the coordinate x, which in general is given by

$$H(q) \; = \; -\tfrac{1}{2}\Delta_x \, + \, V(x,q), \tag{3}$$

where $V = V(x,q)$ denotes the interaction potential of the system (cf. [27]). The term $-\epsilon^2\Delta_q/2$ denotes the kinetic energy operator in q-direction; in the following, we will often use the short notation $\mathcal{T} = -\epsilon^2\Delta_q/2$.

In general, the state space associated with the operator $H(q)$ for some fixed position q is $L^2(\mathbb{R}^m)$. Instead of working in $L^2(\mathbb{R}^m)$, we restrict ourselves to finite-dimensional Hilbert spaces (dimension N),[4] making H an $N \times N$ matrix. In the chemical literature, H is typically directly given in this form, since the chemical preparation of the model already includes the restriction to the subspace spanned by the interesting electronic states of the molecule. This is often called the *diabatic representation* of molecular quantum dynamics. Typically, the associated *diabatic Hamiltonian* H has real-valued entries $H_{kl}(q) = V_{kl}(q)$ that can be interpreted as *interaction potentials* between the electronic states considered. Furthermore, the diabatic Hamiltonian normally does *not* depend on ϵ. However, some specific situations require the Hamiltonian to be of the more general form $H(q) = H_0(q) + \epsilon H_1(q)$, see, e.g., [25, 26].

We assume that the matrix H inherits the self-adjointness of the original Hamiltonian, i.e., that $H(q)$ is some Hermitian matrix ($H(q) = H(q)^*$ for every position q, with * denoting the Hermitian transposition). We moreover always suppose in the following that $H = H(q)$ is an arbitrarily smooth (matrix-valued) function of q which is defined on the entire $\mathbb{R}^d$.

With H being a matrix, the solution $\Psi : \mathbb{R}^d \times \mathbb{R} \to \mathbb{C}^N$, $(q,t) \mapsto \Psi(q,t)$ of (2) is vector-valued. This solution describes what we call the full QD evolution of the system. Typically, a proper choice of the coordinate system allows to assume that the initial wavefunction $\Psi_I = \Psi(\cdot, t=0)$ is Gaussian in each component or arbitrarily smooth and rapidly decreasing.

Adiabatic Basis Whenever we consider the so-called *adiabatic basis* in the subsequent, let the following "non-crossing" assumption on the eigenspaces and eigenenergies of the zero order part H_0 of the q-parametrized $N \times N$ Hamiltonian $H = H_0 + \epsilon H_1$ be satisfied:

(A) For every $q \in \mathbb{R}^d$, $H_0(q)$ has N distinct eigenvalues $E_k(q)$ such that the ordering $E_1(q) < \ldots < E_N(q)$ does not depend on q.

This assumption guarantees that all eigenspaces of $H_0(q)$ are one-dimensional and that the eigenvalues $E_k = E_k(q)$ as well as the associated eigenfunctions $e_k = e_k(q)$ with

$$H_0(q)e_k(q) \; = \; E_k(q)e_k(q), \quad \|e_k(q)\| = 1, \qquad \forall k = 1, \ldots, N,$$

are smooth functions of q. This is a rather strong and thus convenient assumption. It can be substantially weakened in nearly all situations of interest in the following; we will give short comments on this question whenever appropriate.

[4]The reader may think of a finite dimensional subspace of the original state space. This subspace may, e.g., be associated with a suitable discretization in space.

In the chemical literature the orthonormal set $\{e_k(q)\}$ is often called the *adiabatic basis* with respect to the Hamiltonian $H = H(q)$. One often finds that the solution $\Psi = \Psi(q,t)$ of (2) is expanded in this adiabatic basis:

$$\Psi(q,t) \;=\; \sum_{k=1}^{N} \Phi_k(q,t)\; e_k(q). \tag{4}$$

Inserting this into (2) results in the following equation of motion for the vector $\Phi = (\Phi_k)$ of expansion coefficients:

$$\begin{aligned} i\epsilon\partial_t\Phi(q,t) \;&=\; E(q)\,\Phi(q,t) \,-\, \tfrac{\epsilon^2}{2}\Delta_q\Phi(q,t) \\ &\quad + \epsilon\mathcal{V}(q)\Phi(q,t) \,+\, \tfrac{\epsilon^2}{2}T(q)\,\Phi(q,t) \,-\, \epsilon^2\, C(q)\cdot D_q\Phi(q,t), \end{aligned} \tag{5}$$

where the matrix-valued functions E, T, and $\mathcal{V}$ (the *perturbing potential*), and the tensor-valued function C (the *coupling tensor*) are given by

$$\begin{array}{rclrcl} E(q) & = & \mathrm{diag}(E_k(q)) & & & \\ \mathcal{V}(q) & = & (\mathcal{V}_{kl}(q)) & \mathcal{V}_{kl} & = & \langle e_k(q)|H_1(q)e_l(q)\rangle \\ T(q) & = & (T_{kl}(q)) & T_{kl} & = & \langle e_k(q)|\Delta_q e_l(q)\rangle \\ C(q) & = & (C^j_{kl}(q)) & C^j_{kl} & = & \langle e_k(q)|D_{q_j}e_l(q)\rangle \\ & & \text{with} & (C\cdot D_q\Phi)_k & = & \sum_{j,l} C^j_{kl}\, D_{q_j}\Phi_l, \end{array} \tag{6}$$

where $\langle\cdot|\cdot\rangle$ denotes the scalar product in $L^2(\mathbb{R}^d)^N$. The first two terms on the RHS of (5) represent the evolution of the "wavefunction" $\Phi_k = \Phi_k(q,t)$ on the kth adiabatic energy surface, while the last three terms represent the *non-adiabatic couplings* between these surfaces. The definition of the coupling tensor C has the consequence that for all possible k, l, j:

$$\begin{aligned} C^j_{kl} \;&=\; \langle e_k|D_{q_j}e_l\rangle \;=\; -i\,\langle e_k, iD_{q_j}e_l\rangle \\ &=\; -i\,\left(\langle e_l|iD_{q_j}e_k\rangle^*\right) \;=\; -\left(C^j_{lk}\right)^*, \end{aligned} \tag{7}$$

i.e., a specific antisymmetry which we shortly denote $C^* = -C$ in the following.

In the adiabatic basis, the typical initial condition often has the following particularly simple form: All entries of $\Phi(\cdot, t=0)$ vanish excluding a single one, $\Phi_k(q, t=0)$, which is given by

$$\Phi_k(q,t=0) \;=\; \frac{1}{A_\epsilon}\,\exp\left(-\frac{1}{4\epsilon}(q-q_0)^2 \,-\, \frac{i}{\epsilon}p_0^T q\right), \tag{8}$$

with some normalization factor A_ϵ such that $\int |\Phi_0|^2 dq = 1$ for all $\epsilon > 0$, cf. [27,49].

3 The Wigner Transform

The typical approach to the reformation of a quantum dynamics in terms of classical phase space densities uses the well-known *Wigner transform* [57]. For the coordinate scalings used herein, this transform has to be defined as follows:

Definition 3.1 The transformation w_ϵ defined via

$$w^\epsilon(\psi,\phi)(q,p) \;=\; (2\pi)^{-d} \int_{R^d} \psi\left(q-\epsilon\frac{y}{2}\right)\,\phi^*\left(q+\epsilon\frac{y}{2}\right)\,\exp(ip^Ty)\,dy, \qquad (9)$$

for scalar functions $\psi,\phi:\mathbb{R}^d\to\mathbb{C}$, is called the Wigner transform of ψ and ϕ. For vector-valued arguments, e.g., for $\psi,\phi\in L^2(\mathbb{R}^d)^N$, the *Wigner matrix* is defined by

$$W^\epsilon(\psi,\phi)(q,p) \;=\; (2\pi)^{-d} \int_{R^d} \psi\left(q-\epsilon\frac{y}{2}\right)\otimes\phi^*\left(q+\epsilon\frac{y}{2}\right)\,\exp(ip^Ty)\,dy, \qquad (10)$$

where $\otimes$ defines the tensor product of vectors.

In the following, $\mathcal{S}'$ denotes the dual space to the space $\mathcal{S}$ of all rapidly decreasing functions.[5] The Wigner transform can be defined as a bilinear mapping from $\mathcal{S}'(\mathbb{R}^d)\times\mathcal{S}'(\mathbb{R}^d)$ to $\mathcal{S}'(\mathbb{R}^d\times\mathbb{R}^d)$ (in the scalar case) and also as a mapping from $\mathcal{S}(\mathbb{R}^d)\times\mathcal{S}(\mathbb{R}^d)$ to $\mathcal{S}(\mathbb{R}^d\times\mathbb{R}^d)$. For the cases considered herein, the following property will be of importance: If ψ and ϕ lie in some bounded subset of $L^2(\mathbb{R}^d)$, then (the family) $w^\epsilon(\psi,\psi)$ lies in some bounded subset of $\mathcal{S}'(\mathbb{R}^d)$ (Prop. 1.1 in [20]).

It is an immediate consequence of the definition that for scalar ψ,ϕ:

$$w^\epsilon(\psi,\phi) \;=\; w^\epsilon(\phi,\psi)^*. \qquad (11)$$

Thus, the Wigner transform $w^\epsilon(\psi,\psi)$ of ψ is real-valued.

The Wigner transform is of particular importance since it allows to reformulate quantum dynamical expectation values in terms of their classical counterparts. To understand this, let us first consider the *position densities* associated with the full quantum dynamical description and its Wigner transform:

3.1 Position Densities and Wigner Measures

Due to the typical interpretation of quantum mechanics, the wavefunction $\psi=\psi(q,t)$ corresponds to the position density $|\psi(q,t)|^2$, that is, the probability density for finding the corresponding quantum system in position q. One of the basic properties of the Wigner transform is that, for smooth functions ψ and ϕ:

$$\int_{\mathbb{R}^d} w^\epsilon(\psi,\phi)(q,p)\,dp \;=\; \psi(q)\,\phi(q)^*. \qquad (12)$$

Thus, the position density associated with the wavefunction $\psi=\psi(q)$ can alternatively be expressed by $\int w^\epsilon(\psi,\psi)dp$ with the immediate consequence that

$$\int_{\mathbb{R}^d}\int_{\mathbb{R}^d} w^\epsilon(\psi,\psi)(q,p)\,dqdp \;=\; \int_{\mathbb{R}^d}|\psi(q)|^2dq.$$

The last formulae seem to state that $w^\epsilon(\psi,\psi)$ might be nonnegative. However, $w^\epsilon(\psi,\psi)$ can have negative values and only its Huisimi transform (the convolution with two narrow Gaussians in the position and momentum space, see [39]) is a pointwise nonnegative function. Despite this, $w^\epsilon(\psi,\psi)$ is often interpreted as a probability density in phase space. Under certain conditions this is justified, at least in the limit $\epsilon\to 0$:

[5]We will use the notations $\mathcal{S}$ and $\mathcal{S}'$ with respect to functions living on different definition domains; if not explicitly stated the exact meaning should be clear from the context.

PROPOSITION 3.2 *([19] and [20], Prop. 1.3) Let (ψ_ϵ) be some bounded family in $L^2(\mathbb{R}^d)^N$ of vector-valued functions. Let W^0 be the limit of the Wigner matrices $W^\epsilon(\psi_{\epsilon_k}, \psi_{\epsilon_k})$ of some subsequence (ψ_{ϵ_k}). Then, W_0 is a nonnegative matrix-valued measure,*[6] *called the* Wigner measure.

3.2 Weyl Operators and Expectation Values

Let D_q denote the derivative with respect to q and let us now consider some pseudo-differential operator $A(q, \epsilon D_q)$ related to the symbol $A = A(q,p) \in \mathcal{S}'(\mathbb{R}^d \times \mathbb{R}^d)$ and defined via

$$(A(q, \epsilon D_q)u)(q) \;=\; \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \int_{\mathbb{R}^d} A(q, \epsilon\xi)\, u(\xi)\, \exp(i(q-y)^T\xi)\, d\xi\, dy, \qquad (13)$$

for $u \in \mathcal{S}(\mathbb{R}^d)$. One can easily generalize this definition for matrix-valued symbols; as a simple example for matrix-valued pseudo-differential operators, consider the Hamiltonian

$$\mathcal{H}(q, \epsilon D_q) \;=\; -\frac{\epsilon^2}{2}\Delta_q \;+\; H(q)$$

associated with the full Schrödinger equation (2) from Sec. 2. The corresponding matrix-valued symbol is $\mathcal{H}(q,p) = |p|^2/2 + H(q)$.

The *Weyl operator* associated with the pseudo-differential operator $A(q, \epsilon D_q)$ is defined via

$$(A^W(q, \epsilon D_q)u)(q) \;=\; \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \int_{\mathbb{R}^d} A\left(\frac{q+y}{2}, \epsilon\xi\right)\, u(\xi)\, e^{i(q-y)^T\xi}\, d\xi\, dy. \qquad (14)$$

Whenever A is a sum of two expressions that depend on q and on p only, respectively, we find

$$A(q,p) \;=\; a(q) + b(p) \quad \Rightarrow \quad A^W(q, \epsilon D_q) \;=\; A(q, \epsilon D_q).$$

For other observables, the Weyl operator and the corresponding pseudo-differential operator are different. However, even in these cases one can often evaluate the symbol A associated with some given Weyl operator A^W (or find an asymptotic expansion in terms of ϵ; cf. Appendix A).

Let now $\langle\cdot,\cdot\rangle$ denote the duality bracket between $\mathcal{S}'$ and $\mathcal{S}$. A quantum *observable* is a self-adjoint Weyl-operator with associated symbol $A \in \mathcal{S}'$. The quantal expectation value of the observable $A^W(\cdot, \epsilon D_q)$ with respect to the quantum state $\psi \in \mathcal{S}$ is given by

$$\langle A^W(\cdot, \epsilon D_q)\rangle_\psi = \langle \psi | A^W(\cdot, \epsilon D_q)\psi\rangle,$$

while the expectation value of the associated classical observable A with respect to the Wigner transform $w^\epsilon(\psi,\psi)$ of ψ can be written as

$$[A]_{w^\epsilon(\psi)} \;=\; \langle w^\epsilon(\psi,\psi), A\rangle \;=\; \int_{\mathbb{R}^d} \int_{\mathbb{R}^d} A(q,p)\, w^\epsilon(\psi,\psi)(q,p)\, dq\, dp.$$

[6] That is, for any $z \in \mathbb{C}^N$, we have $z^* W^0 z \geq 0$.

Consequently, the general identity

$$\langle\psi|A^W\phi\rangle \;=\; \langle w^\epsilon(\psi,\phi),A\rangle, \quad \text{for } \psi,\phi\in\mathcal{S},\, A\in\mathcal{S}' \text{ or } \psi,\phi\in\mathcal{S}',\, A\in\mathcal{S}, \tag{15}$$

guarantees that $[A]_{w^\epsilon(\psi)} = \langle A^W\rangle_\psi$, i.e., we can compute quantal expectation values via classical expectation values of the Wigner transform. This relation is particularly simple whenever A is the sum of some function of q only and some function of p only:

$$A(q,p) \;=\; a(q)+b(p) \quad \Rightarrow \quad \langle A(\cdot,\epsilon D_q)\rangle_\psi \;=\; [A]_{w^\epsilon(\psi)}. \tag{16}$$

For matrix-valued operators, the expectation values are defined via the corresponding traces, i.e., if $\Psi = \Psi(q)$ is some vector-valued wavefunction and $A^W(q,\epsilon D_q)$ some (self-adjoint) matrix-valued Weyl operator, the expectation value is given by

$$\langle A^W\rangle_\Psi \;=\; \int \operatorname{tr}\left\{A^W(\cdot,\epsilon D_q)\Psi\otimes\Psi^*\right\}dq.$$

If $A = A(q,p)$ is the associated matrix-valued symbol, we have the identity

$$\int \operatorname{tr}\left\{A^W(\cdot,\epsilon D_q)\Psi\otimes\Psi^*\right\}dq \;=\; \int_{\mathbb{R}^d}\int_{\mathbb{R}^d}\operatorname{tr}\left\{A\,W^\epsilon(\Psi,\Psi)\right\}dq\,dp. \tag{17}$$

3.3 Asymptotic Properties

In the sequel we will be interested in studying the asymptotic expansion of the action of some pseudo-differential operator under the Wigner transform. Therefore, we will frequently make use of the following

Assumption 3.3 *Suppose that A is smooth matrix-valued symbol, i.e., $A\in C^\infty(\mathbb{R}^d\times\mathbb{R}^d)^{n\times n}$ such that, for some $M\geq 0$ and every multi-index $\alpha\in\mathbb{N}^d\times\mathbb{N}^d$,*

$$|D^\alpha_{(q,p)}A(q,p)| \;\leq\; C_\alpha(1+|p|)^M,$$

componentwise.

For symbols satisfying this assumption the following asymptotic expansion is valid:

Lemma 3.4 *([20], Prop. 1.4) Let $\{\cdot,\cdot\}$ denote the classical* Poisson bracket,[7] *and suppose that the matrix-valued symbol $\mathcal{B}$ satisfies Assumption 3.3. Then, for vector-valued ψ,ϕ lying in some bounded subset of $L^2(\mathbb{R}^d)^N$ we have*

$$\begin{aligned} W^\epsilon(\mathcal{B}^W(\cdot,\epsilon D_q)\psi,\phi) &= \mathcal{B}W^\epsilon(\psi,\phi) + \tfrac{\epsilon}{2i}\{\mathcal{B},W^\epsilon(\psi,\phi)\}+\epsilon^2R_\epsilon \\ W^\epsilon(\psi,\mathcal{B}^W(\cdot,\epsilon D_q)\phi) &= W^\epsilon(\psi,\phi)\mathcal{B}^* + \tfrac{\epsilon}{2i}\{W^\epsilon(\psi,\phi),\mathcal{B}^*\}+\epsilon^2Q_\epsilon \end{aligned} \tag{18}$$

with R_ϵ, Q_ϵ being bounded in $\mathcal{S}'$.

Lemma 3.4 will be our main working tool. The reader might notice that the results of [31], Sec. 18.5, allow to calculate the next terms in the expansions, too.

[7] That is, for smooth functions $\psi=\psi(q,p)$ and $\phi=\phi(q,p)$ write $\{\psi,\phi\} = D_p\psi(q,p)\cdot D_q\phi(q,p) - D_q\psi(q,p)\cdot D_p\phi(q,p)$. For matrix-valued arguments, the order is relevant.

Remark 3.5 Closer inspection of the proof in [20] reveals that the action of R_ϵ (and of Q_ϵ respectively) is more precisely characterized by the following: there is some family $\{r_\epsilon\} \subset \mathcal{S}$, being bounded in $\mathcal{S}$, such that the reminder R_ϵ in (18) satisfies

$$\langle R_\epsilon, A\rangle \;=\; \langle A^W r_\epsilon^W \psi|\phi\rangle \tag{19}$$

for any matrix-valued symbol $A \in \mathcal{S}$.

The symbol $\mathcal{T}(p) = |p|^2/2$ associated to the kinetic energy operator $\mathcal{T} = -\epsilon^2 \Delta_q/2$ satisfies Ass. 3.3, such that, due to Lemma 3.4, the action of $\mathcal{T}$ under the Wigner transform is given by

$$W^\epsilon(\mathcal{T}\psi, \psi) \;=\; \frac{1}{2}p^2 W^\epsilon(\psi,\psi) \;+\; \frac{\epsilon}{2i}\,p\cdot D_q W^\epsilon(\psi,\psi) + \mathcal{O}(\epsilon^2).$$

But straightforward computations reveal that *exactly*

$$W^\epsilon\left(\mathcal{T}\psi, \psi\right) \;-\; W^\epsilon\left(\psi, \mathcal{T}\psi\right) \;=\; -i\epsilon\, p\cdot D_q W^\epsilon(\psi,\psi), \tag{20}$$

i.e., that the above $\mathcal{O}(\epsilon^2)$-error term vanishes for this specific difference.

4 Quantum-Classical Liouville Equation

We will consider q to be the "classical" coordinate and x to have significant "quantum" nature. Thus, we are interested in some description of the system in which the distribution in q is modelled by a kind of classical phase space density while the other degree of freedom is modelled quantally, i.e., in our formulation by some vector-valued wave-"function" Ψ or the corresponding *density matrix* $\Psi \otimes \Psi^*$.

4.1 Partial Wigner Transform

To this end, we will apply the Wigner transform to the vector-valued solution $\Psi^\epsilon = \Psi^\epsilon(q,t)$ of (2).[8] In contrast to the typical application of Wigner transforms in quantum theory, we apply the Wigner transform to the q-coordinate only, leaving the "quantum nature" in the other degree of freedom untouched: This leads to the *Wigner matrix*

$$\mathcal{W}^\epsilon(q,p,t) \;=\; W^\epsilon(\Psi^\epsilon(\cdot,t), \Psi^\epsilon(\cdot,t))(q,p). \tag{21}$$

Because of (11), this Wigner matrix $\mathcal{W}^\epsilon$ is a Hermitian matrix.

In order to determine the equation of motion governing $\mathcal{W}^\epsilon$, we have to introduce the formal notation

$$K_\epsilon^\pm(q,p) \;=\; (2\pi)^{-d} \int_{R^d} \exp(ip^T y)\, H(q \,\pm\, \epsilon y/2)\, dy,$$

denoting some operator for which the convolution with matrix-valued functions $\rho = \rho(q,p)$ is defined by

$$\left(K_\epsilon^\pm * \rho\right)(q,p,t) \;=\; \int_{\mathbb{R}^d} K_\epsilon^\pm(q, p-\eta)\, \rho(q,\eta,t)\, d\eta.$$

[8]The super-index is often used to indicate that we are concerned with a family of solutions depending on the parameter ϵ.

Using this notation, simple explicit computations reveal that the evolution of the Wigner density matrix ρ^ϵ defined by (21) is given by the following *Wigner equation*

$$\partial_t \mathcal{W}^\epsilon \;=\; -p\cdot D_q \mathcal{W}^\epsilon \;-\; \frac{i}{\epsilon}\left(K_\epsilon^- * \mathcal{W}^\epsilon \;-\; \mathcal{W}^\epsilon * K_\epsilon^+\right), \tag{22}$$

with initial values given by the Wigner density matrix $\mathcal{W}_I^\epsilon = W^\epsilon(\Psi_I^\epsilon, \Psi_I^\epsilon)$ associated with the initial wavefunction Ψ_I^ϵ.

Obviously, we can repeat the same procedure for the adiabatic representation (5) of QD, that is, we can also consider the *adiabatic density matrix* $\mathcal{W}^{\mathrm{ad},\epsilon}$, i.e., the partial Wigner transform of the solution Φ^ϵ of (5):

$$\begin{aligned}
\mathcal{W}^{\mathrm{ad},\epsilon}(q,p,t) \;&=\; W^\epsilon(\Phi^\epsilon(\cdot,t),\Phi^\epsilon(\cdot,t))(q,p) \\
&=\; \tfrac{1}{(2\pi)^d}\int_{R^d} \Phi^\epsilon\left(q-\epsilon\tfrac{y}{2}\right)\otimes\Phi^{\epsilon *}\left(q+\epsilon\tfrac{y}{2}\right)\,\exp(ip^Ty)\,dy.
\end{aligned} \tag{23}$$

Since the adiabatic basis $e_k = e_k(q)$ depends on q, it is, at least at first glance, not clear which is the relation between the two Wigner density matrices $\mathcal{W}^\epsilon$ and $\mathcal{W}^{\mathrm{ad},\epsilon}$. But application of Lemma 3.4 yields the following:

Corollary 4.1 *Suppose that the family $\{\Psi_\epsilon\}$ of solutions of (2) lies in some bounded subset of $L^2(\mathbb{R}^d)^N$. Then, the two families of Wigner matrices $\mathcal{W}^\epsilon = W^\epsilon(\Psi_\epsilon,\Psi_\epsilon)$ and $\mathcal{W}^{\mathrm{ad},\epsilon} = W^\epsilon(\Phi_\epsilon,\Phi_\epsilon)$ are related via*

$$\mathcal{W}^\epsilon \;=\; \sum_{k,l=1}^N \left(\mathcal{W}_{kl}^{\mathrm{ad},\epsilon} \;+\; \frac{i\epsilon}{2}\left([C, D_p\mathcal{W}^{\mathrm{ad},\epsilon}]_+\right)_{kl}\right)\, e_k\otimes e_l^* \;+\; \epsilon^2 R_\epsilon, \tag{24}$$

where R_ϵ is bounded in $\mathcal{S}'$, and $[C, D_p\mathcal{W}^{\mathrm{ad},\epsilon}]_+ = \sum_j [C^j, D_{p_j}\mathcal{W}^{\mathrm{ad},\epsilon}]_+$.

Proof: By applying Lemma 3.4 to (4), we find the following:

$$\begin{aligned}
\mathcal{W}^\epsilon \;&=\; \sum_{k,l=1}^N W^\epsilon(\Phi_k^\epsilon e_k, \Phi_l^\epsilon e_l) \\
&=\; \sum_{k,l=1}^N \Big(e_k\otimes W^\epsilon(\Phi_k^\epsilon,\Phi_l^\epsilon e_l) \;-\; \frac{\epsilon}{2i} D_q e_k \otimes D_p W^\epsilon(\Phi_k^\epsilon,\Phi_l^\epsilon e_l)\Big) \;+\; \epsilon^2 R_\epsilon \\
&=\; \sum_{k,l=1}^N \Big(\mathcal{W}_{kl}^{\mathrm{ad},\epsilon}\, e_k\otimes e_l^* \;-\; \frac{\epsilon}{2i} D_p\mathcal{W}_{kl}^{\mathrm{ad},\epsilon}\cdot D_q e_k\otimes e_l^* \\
&\qquad\qquad +\; \frac{\epsilon}{2i} D_p\mathcal{W}_{kl}^{\mathrm{ad},\epsilon}\, e_k\otimes D_q e_l^*\Big) \;+\; \epsilon^2 R_\epsilon,
\end{aligned}$$

where R_ϵ is bounded in $\mathcal{S}'$. Moreover, we have (using the notation introduced above)

$$D_p\mathcal{W}^{\mathrm{ad},\epsilon}\cdot D_q e_k \;=\; \sum_{n=1}^d D_{p_n}\mathcal{W}^{\mathrm{ad},\epsilon}\sum_{j=1}^N \langle e_j | D_{q_n} e_k\rangle\, e_j \;=\; D_p\mathcal{W}^{\mathrm{ad},\epsilon}\cdot\sum_{j=1}^N C_{jk}\, e_j.$$

Inserted above, this yields (together with $C = -C^*$):

$$\begin{aligned}
\mathcal{W}^\epsilon \;&=\; \sum_{k,l=1}^N \mathcal{W}_{kl}^{\mathrm{ad},\epsilon}\; e_k\otimes e_l^* \\
&\quad -\tfrac{\epsilon}{2i}\sum_{k,l,j=1}^N \left(C_{kj}\cdot D_p\mathcal{W}_{jl}^{\mathrm{ad},\epsilon} \;+\; C_{jl}\cdot D_p\mathcal{W}_{kj}^{\mathrm{ad},\epsilon}\right)\, e_k\otimes e_l^* \;+\; \epsilon^2 R_\epsilon
\end{aligned}$$

from which the assertion follows. ∎

4.2 First Order Approximations

We now want to find *asymptotic expansions* of the equations of motion governing $\mathcal{W}^\epsilon$ and $\mathcal{W}^{\mathrm{ad},\epsilon}$. In order to handle the two representations of QD (equations (2) and (5)) simultaneously, we consider the following general Schrödinger equation

$$i\epsilon\partial_t\Psi^\epsilon \;=\; -\frac{\epsilon^2}{2}\Delta_q\Psi^\epsilon \;+\; \mathcal{E}_\epsilon(q)\,\Psi^\epsilon \;-\; \epsilon\, C(q)\cdot(\epsilon D_q)\Psi^\epsilon, \tag{25}$$

where $\mathcal{E}_\epsilon(q) = \sum_{j=0}^2 \epsilon^j \mathcal{E}_j(q)$ is Hermitian matrix-valued and $C = C(q)$ may be some smoothly q-dependent, real-valued tensor as C in (5), which satisfies the antisymmetry relation $C^* = -C$ in the sense of (7). Thus, $\mathcal{E}_0 = H_0$, $\mathcal{E}_1 = H_1$, $\mathcal{E}_2 = 0$, and $C = 0$ lead to (2), while $\mathcal{E}_0 = E$, $\mathcal{E}_1 = \mathcal{V}$, $\mathcal{E}_2 = T/2$, and $C \neq 0$ yield (5).

Let us denote the operator on the RHS of (25) by the Weyl operator

$$\mathcal{H}^W(q,\epsilon D_q) \;=\; -\frac{\epsilon^2}{2}\Delta_q \;+\; \underbrace{\mathcal{E}_\epsilon \;-\; \epsilon\, C\cdot(\epsilon D_q)}_{=\mathcal{B}^W(q,\epsilon D_q)}. \tag{26}$$

Since $\mathcal{H}^W$ and $\mathcal{B}^W$ are no longer simple sums of terms depending on q or ϵD_q only, it is not automatically clear which symbols are associated with them. But due to the results presented in Appendix A, the symbols can be computed and are given by

$$\mathcal{H}(q,p) \;=\; \frac{1}{2}|p|^2 \;+\; \underbrace{\mathcal{E}_\epsilon(q) \;-\; i\epsilon\, C(q)\cdot p \;+\; \frac{\epsilon^2}{2} D_q\cdot C(q)}_{=\mathcal{B}(q,p)}, \tag{27}$$

where $D_q\cdot C$ is matrix-valued with entries $(D_q\cdot C)_{kl} = \sum_j D_{q_j} C^j_{kl}$.

We will have to make the following technical assumptions on the general Hamiltonian $\mathcal{H}^W$:

(B1) $\mathcal{H}^W$ is essentially self-adjoint on $L^2(\mathbb{R}^d)^N$.

(B2) Its symbol $\mathcal{H}$ satisfies Assumption 3.3 (uniformly for all $0 < \epsilon < \epsilon_0$).[9]

These assumption are valid for a rather wide range of interaction potentials defining the original quantum Hamiltonian H. They allow to prove the following

THEOREM 4.2 *Let $\Psi^\epsilon = \Psi^\epsilon(q,t)$ be the solution of (25) with (uniformly) normalized initial conditions $\Psi^\epsilon(t=0)$.[10] Moreover, let $\mathcal{W}^\epsilon = W^\epsilon(\Psi^\epsilon,\Psi^\epsilon)$ denote the corresponding partial Wigner transform. Then, the evolution of $\mathcal{W}^\epsilon =$*

[9]Due to (27) this implies that $\mathcal{H} \in \mathcal{S}^2(\mathbb{R}^d\times\mathbb{R}^d)$ uniformly with the consequence that the Sobolev space $H^2(\mathbb{R}^d)$ is in the domain of $\mathcal{H}^W$.

[10]That is, for all values of ϵ, the family of initial conditions is lying on the unit sphere in $L^2(\mathbb{R}^d)^N$, cf. (8).

$\mathcal{W}^\epsilon(q,p,t)$ is governed by the following equation of motion:

$$\begin{aligned}\partial_t \mathcal{W}^\epsilon(q,p,t) \;&=\; -\tfrac{i}{\epsilon}\left[\mathcal{E}_0(q)+\epsilon\mathcal{E}_1(q)-i\epsilon p\cdot C(q)\,,\,\mathcal{W}^\epsilon(q,p,t)\right]_- \\ &\quad -p\cdot D_q\mathcal{W}^\epsilon(q,p,t)+\tfrac{1}{2}\left[D_q\mathcal{E}_0(q),D_p\mathcal{W}^\epsilon(q,p,t)\right]_+ \\ &\quad +\epsilon R_\epsilon,\end{aligned} \tag{28}$$

where the family of functions $R_\epsilon = R_\epsilon(q,p,t)$ is uniformly (in ϵ and t) bounded in $\mathcal{S}'$ and $[\cdot,\cdot]_\pm$ denotes the usual commutator and anti-commutator, i.e., $[A,B]_\pm = AB \pm BA$ for two square matrices A, B.

Additionally, we exactly have $R_\epsilon \equiv 0$ whenever $\mathcal{E}_1 = \mathcal{E}_2 \equiv 0$, $C \equiv 0$, and $\mathcal{E}_0$ is linear in q componentwise.

Proof: Differentiation of the definition of $\mathcal{W}^\epsilon$ yields

$$i\epsilon\partial_t\mathcal{W}^\epsilon \;=\; W^\epsilon\left(i\epsilon\partial_t\Psi^\epsilon,\Psi^\epsilon\right) \;-\; W^\epsilon\left(\Psi^\epsilon,i\epsilon\partial_t\Psi^\epsilon\right). \tag{29}$$

Inserting the equation of motion (25) governing Ψ^ϵ, each of the two terms on the RHS of (29) can be handled by applying Lemma 3.4:[11]

$$\begin{aligned}W^\epsilon\left(i\epsilon\partial_t\Psi^\epsilon,\Psi^\epsilon\right) \;&=\; W^\epsilon\left(-\frac{\epsilon^2}{2}\Delta_q\Psi^\epsilon,\Psi^\epsilon\right) \;+\; W^\epsilon\left(\mathcal{B}^W\Psi^\epsilon,\Psi^\epsilon\right) \\ &=\; W^\epsilon\left(-\frac{\epsilon^2}{2}\Delta_q\Psi^\epsilon,\Psi^\epsilon\right) \;+\; \mathcal{B}\,\mathcal{W}^\epsilon \;+\; \frac{\epsilon}{2i}\left\{\mathcal{B},\mathcal{W}^\epsilon\right\} + \epsilon^2\tilde{R}_\epsilon,\end{aligned}$$

where $\tilde{R}_\epsilon$ is bounded in $\mathcal{S}'$. Inserting this together with equation (20) into (29), we find

$$i\epsilon\partial_t\mathcal{W}^\epsilon \;=\; -i\epsilon\, p\cdot D_q\mathcal{W}^\epsilon \;+\; \left(\mathcal{B}\mathcal{W}^\epsilon-\mathcal{W}^\epsilon\mathcal{B}^*\right) \;+\; \frac{\epsilon}{2i}\left(\{\mathcal{B},\mathcal{W}^\epsilon\}-\{\mathcal{W}^\epsilon,\mathcal{B}^*\}\right)+\epsilon^2\bar{R}_\epsilon,$$

where $\bar{R}_\epsilon$ is again bounded in $\mathcal{S}'$. Using the explicit representation (27) of the symbol $\mathcal{B}$ and the antisymmetry of C, we easily compute that

$$\begin{aligned}\mathcal{B}\mathcal{W}^\epsilon-\mathcal{W}^\epsilon\mathcal{B}^* \;&=\; \left[\mathcal{E}_0+\epsilon\mathcal{E}_1,\mathcal{W}^\epsilon\right]_- \;-\; i\epsilon\left[p\cdot C,\mathcal{W}^\epsilon\right]_- \;+\; \epsilon^2 r_{1,\epsilon} \\ \{\mathcal{B},\mathcal{W}^\epsilon\}-\{\mathcal{W}^\epsilon,\mathcal{B}^*\} \;&=\; -D_q\mathcal{E}_0\cdot D_p\mathcal{W}^\epsilon - D_p\mathcal{W}^\epsilon\cdot D_q\mathcal{E}_0 + \epsilon r_{2,\epsilon},\end{aligned}$$

where again $r_{1,\epsilon}$ and $r_{2,\epsilon}$ are bounded in $\mathcal{S}'$. Putting all this together, we end up with

$$\begin{aligned}\partial_t\mathcal{W}^\epsilon \;&=\; -p\cdot D_q\mathcal{W}^\epsilon \;-\; \frac{i}{\epsilon}\left[\mathcal{E}_0+\epsilon\mathcal{E}_1,\mathcal{W}^\epsilon\right]_- \;-\; \left[p\cdot C,\mathcal{W}^\epsilon\right]_- \\ &\quad +\frac{1}{2}\left[D_q\mathcal{E}_0,D_p\mathcal{W}^\epsilon\right]_+ \;+\; \epsilon^2 R_\epsilon,\end{aligned}$$

where $R_\epsilon = \bar{R}_\epsilon + r_{1,\epsilon} + r_{2,\epsilon}$ is bounded in $\mathcal{S}'$.

Explicit calculations concerning the error terms associated with $\mathcal{B}$ show that $R_\epsilon \equiv 0$ whenever $\mathcal{E}_1 = \mathcal{E}_2 \equiv 0$, $C \equiv 0$, and the second derivative of $\mathcal{E}_0$ vanishes, i.e., if $\mathcal{E}_0$ is linear in q componentwise. $\square$

We are now interested in studying the properties of the solution of (28) with the reminder R_ϵ set to zero.

[11] Assumption (A1) implies that the evolution of (25) is unitary, so that $\|\Psi^\epsilon(t)\|_2 = \|\Psi^\epsilon(t=0)\|_2$ in $L^2(\mathbb{R}^d)^N$. Thus, Lemma 3.4 can be applied since $\Psi^\epsilon = \Psi^\epsilon(t)$ lies in some bounded subset of $L^2(\mathbb{R}^d)^N$.

DEFINITION 4.3 Let the assumption of Thm. 4.2 be valid and $\epsilon > 0$. The equation

$$\begin{aligned} \partial_t \rho^\epsilon(q,p,t) &= -\tfrac{i}{\epsilon}\left[\mathcal{E}_0(q) + \epsilon\mathcal{E}_1(q) - i\epsilon p \cdot C(q)\,,\, \rho^\epsilon(q,p,t)\right]_- \\ &\quad -p \cdot D_q \rho^\epsilon(q,p,t) + \tfrac{1}{2}\left[D_q\mathcal{E}_0(q), D_p\rho^\epsilon(q,p,t)\right]_+ , \end{aligned} \tag{30}$$

with initial conditions $\rho^\epsilon(t=0) = W^\epsilon({\Psi^\epsilon}_I, {\Psi^\epsilon}_I)$ given by the initial conditions $\Psi^\epsilon(t=0) = {\Psi^\epsilon}_I$ of the Schrödinger equation (25), is called the *quantum-classical Liouville equation (QCL)*; we refer to its solution $\rho^\epsilon = \rho^\epsilon(q,p,t)$ as to the *QCL solution*. We sometimes express the QCL in the form $i\epsilon\partial_t\rho^\epsilon = \mathcal{L}_\epsilon\rho^\epsilon$; the operator $\mathcal{L}_\epsilon$ being defined via the RHS of (30) is called the *QCL operator*.

REMARK 4.4 The special case $R_\epsilon \equiv 0$ for $\mathcal{E}_1 = \mathcal{E}_2 \equiv 0$, $C \equiv 0$, and linear $\mathcal{E}_0$, shows that the QCL reproduces the well-known Landau-Zener formula for the nonadiabatic redistribution of populations in a two-state quantum system which passes through an avoided crossing. This can be seen as follows: According to its original derivation by ZENER [59], this formula holds, if $\mathcal{E}_1 = \mathcal{E}_2 \equiv 0$, $C \equiv 0$ and (a) the transition zone of the avoided crossing is small, (b) H_0 is componentwise linear in this transition zone, and (c) the off-diagonal entries of H_0 are small enough compared to the kinetic energy of the system. Thus, the fact that the QCL is identical to the Wigner equation for $\mathcal{E}_1 = \mathcal{E}_2 \equiv 0$, $C \equiv 0$, and linear $\mathcal{E}_0 = H_0$, demonstrates that the QCL embodies the full QD effects in exactly the case satisfying the conditions for ZENER's derivation. Obviously, this is not a rigorous mathematical statement, but its rigorous justification is a severe problem (see [25, 26]) and not the aim of this article.

Expectation Values Next, the question will be addressed to which accuracy the QCL solution allows to compute the expectation value of an observable associated with some matrix-valued symbol A. Therefore, one should remember that the expectation value of an observable $A \in \mathcal{S}(\mathbb{R}^d \times \mathbb{R}^d)$ with respect to some density matrix $\rho \in \mathcal{S}'$ is given by

$$\langle \rho, A \rangle = \int_{\mathbb{R}^d}\int_{\mathbb{R}^d} \mathrm{tr}(\rho A^*)\, dp\, dq.$$

We will show that the expectation values $\langle \rho^\epsilon, A\rangle$ computed due to the QCL solution ρ^ϵ are $\mathcal{O}(\epsilon)$-approximations of the expectation values $\langle W^\epsilon(\Psi^\epsilon, \Psi^\epsilon), A\rangle$ computed due to the Wigner transform of the full QD solution Ψ^ϵ.

For any fixed ϵ, the QCL operator $\mathcal{L}_\epsilon$ generates the semigroup $\mathcal{U}_\epsilon(t)$, i.e., the QCL solution can be written as $\rho^\epsilon(t) = \mathcal{U}_\epsilon(t)\rho^\epsilon(0)$. Due to the assumptions on the Hamiltonian $\mathcal{H}^W$ above, the semigroup $\mathcal{U}_\epsilon(t)$ maps $\mathcal{S}$ to $\mathcal{S}$, and $\mathcal{S}'$ to $\mathcal{S}'$. The special properties of the $\mathcal{E}_k$ and of C imply that, for every $\epsilon > 0$,

$$\langle \mathcal{U}_\epsilon(t)\rho, A\rangle = \langle \rho, A\,\mathcal{U}_\epsilon(-t)\rangle, \qquad \text{for all } A \in \mathcal{S}, \rho \in \mathcal{S}'. \tag{31}$$

This insight leads to the following

THEOREM 4.5 *Suppose that the assumptions of Thm. 4.2 are valid and that a finite time span $[0, T]$ of interest is given. Let the solutions of the Schrödinger equation (25) be denoted by Ψ^ϵ and the solution of the QCL (30) by ρ^ϵ. Then,* *for any observable $A \in \mathcal{S}(\mathbb{R}^d \times \mathbb{R}^d)$ there exists some constant C such that for all $\epsilon > 0$ and for all $t \in [0,T]$:*

$$|\langle W^\epsilon(\Psi^\epsilon, \Psi^\epsilon), A\rangle \, - \, \langle \rho^\epsilon, A\rangle| \, < \, C\,\epsilon. \tag{32}$$

Proof: Due to (28) and Thm. 4.2, we can express the Wigner matrices of the QD solutions Ψ^ϵ in the form

$$W^\epsilon(\Psi^\epsilon, \Psi^\epsilon)(t) \, = \, \rho^\epsilon(t) \, - \, i\,\epsilon \int_0^t \mathcal{U}_\epsilon(t-s)\, R_\epsilon(s)\, ds,$$

which (together with (31)) yields

$$\langle W^\epsilon(\Psi^\epsilon, \Psi^\epsilon), A\rangle \, - \, \langle \rho^\epsilon, A\rangle \, = \, -i\,\epsilon \int_0^t \langle R_\epsilon(s), A\mathcal{U}_\epsilon(s-t)\rangle.$$

which implies the assertion since R_ϵ is bounded in $\mathcal{S}'$.[12] ∎

As a consequence of this theorem and equation (15), the QCL solution ρ^ϵ allows to compute the quantal expectation values with respect to the QD solutions $\Psi^\epsilon = \Psi^\epsilon(q,t)$ due to

$$\int_{\mathbb{R}^d} \mathrm{tr}\left\{A^W \Psi^\epsilon \otimes (\Psi^\epsilon)^*\right\} \, dp\, dq \, = \, \langle \rho^\epsilon, A\rangle \, + \, \mathcal{O}(\epsilon)$$

for all quantum observables A^W given by symbols $A \in \mathcal{S}(\mathbb{R}^d \times \mathbb{R}^d)$.

Remark 4.6 We have to accept the restriction to observables induced by symbols from $\mathcal{S}$, since we decided to consider the Wigner matrices as distributions from $\mathcal{S}'$. The main reason for this decision lies in the fact that, in the limit $\epsilon \to 0$, typical initial conditions like (8) lead to δ-like Wigner matrices. Whenever one can guarantee that $W^\epsilon(\Psi^\epsilon, \Psi^\epsilon)$ remains in some bounded subset of $\mathcal{S}$, one may allow for observables associated to polynomially growing symbols. But even the restriction to $\mathcal{S}$ is no serious limitation: For Hamiltonians satisfying Assumptions (B1) and (B2), initial conditions like (8), and finite time intervals, the QD solution remains to be exponentially small outside of some sufficiently large compact subset K of the position space $\mathbb{R}^d$. Thus, we may neglect the exponentially small error introduced by replacing an observable associated to some symbol $A \in C^\infty$ by the observable associated to the symbol $\varphi \cdot A \in \mathcal{S}$, where φ is some smooth, compactly supported function with $\varphi|_K \equiv 1$.

4.3 QCL in Diabatic and Adiabatic Basis

Suppose that the diabatic Hamiltonian $H(q) = H_0(q) + \epsilon H_1(q)$ satisfies the assumptions (A1) and (A2). Then, the *diabatic QCL* reads

$$\begin{aligned} \partial_t \rho(q,p,t) \;\; &= \;\; -\tfrac{i}{\epsilon}\,[H(q), \rho(q,p,t)]_- \\ &\quad\; -p \cdot D_q \rho(q,p,t) \, + \, \tfrac{1}{2}\,[D_q H_0(q), D_p \rho(q,p,t)]_+ \, . \end{aligned} \tag{33}$$

[12] In the proof of Thm. 4.2, the reminder R_ϵ resulted from applications of Lemma 3.4. Thus, the terms $\langle R_\epsilon, A\mathcal{U}_\epsilon\rangle$ can be expressed as in (19) in Rmk. 3.5. This implies the required uniform bound since the L^2-norm of Ψ^ϵ is independent of t and ϵ and the $(A\mathcal{U}_\epsilon)^W$ and r_ϵ^W resulting from the application of (19) are bounded in the operator norm in L^2 uniformly in ϵ (cf. [31], Lemma 18.6.1).

REMARK 4.7 The reader might notice that, *for the diabatic QCL*, the statements of Thms. 4.2 and 4.5 are valid even if energy level crossings or *not* excluded.

Analogously, if the adiabatic Hamiltonian $E(q)+\epsilon(\mathcal{V}(q)-C\cdot(\epsilon D_q))$ satisfies the assumptions (A1) and (A2), the equation

$$\begin{aligned}\partial_t \rho^{\mathrm{ad},\epsilon}(q,p,t) \;&=\; -\tfrac{i}{\epsilon}\left[\,E(q)+\epsilon\,(\mathcal{V}(q)-ip\cdot C(q))\;,\;\rho^{\mathrm{ad},\epsilon}(q,p,t)\right]_- \\ &\quad -p\cdot D_q\rho^{\mathrm{ad},\epsilon}(q,p,t)\;+\;\tfrac{1}{2}\left[D_qE(q),D_p\rho^{\mathrm{ad},\epsilon}(q,p,t)\right]_+ .\end{aligned} \tag{34}$$

is called the *adiabatic QCL*.

Total Energy The total energy observable associated with the Wigner transform $W^\epsilon(\Psi^\epsilon,\Psi^\epsilon)$ of the diabatic QD solution Ψ^ϵ is given by

$$\mathcal{H}^{\mathrm{dia}}(q,p) \;=\; \frac{1}{2}|p|^2 \;+\; H(q).$$

The associated expectation value is conserved along the evolution, i.e.,

$$\int \mathrm{tr}\,(\mathcal{H}^{\mathrm{dia}}\,W^\epsilon(\Psi^\epsilon,\Psi^\epsilon))\;dp\,dq \;=\; \mathrm{const.}$$

The solution ρ of (33) also conserves this magnitude, but *only if* $H=H_0$.

Due to (27), the total energy observable associated with the *exact* Wigner transform $W^\epsilon(\Phi^\epsilon,\Phi^\epsilon)$ of the QD solution Φ^ϵ in adiabatic basis is given by

$$\mathcal{H}^{\mathrm{ad}}(q,p) \;=\; \frac{1}{2}|p|^2 \;+\; E(q)\;+\;\epsilon\;(\mathcal{V}(q)-i\epsilon\,C(q)\cdot p)\;+\;\frac{\epsilon^2}{2}D_q\cdot C(q),$$

with the property that

$$\int \mathrm{tr}\,\{\mathcal{H}^{\mathrm{ad}}\,W^\epsilon(\Phi^\epsilon,\Phi^\epsilon)\}\;dp\,dq \;=\; \mathrm{const.}$$

This total energy expectation value is *not* conserved along the evolution of the adiabatic QCL (in contrast to the observations for the diabatic QCL); the associated expectation value $\int \mathrm{tr}\,\{\mathcal{H}^{\mathrm{ad}}\,\rho^{\mathrm{ad},\epsilon}\}\;dp\,dq$ is conserved up to order $\mathcal{O}(\epsilon)$ only.

Energy Level Populations In order to discuss nonadiabatic effects we have to introduce the notion of "energy level populations" for the different types of description. To this end, let $\mathcal{P}_j=\mathcal{P}_j(q)$ denote the orthonormal projection onto energy level j, which (under the assumptions of Sec. 2) is given by $\mathcal{P}_j = e_j(q)\otimes e_j(q)^*$. In the full QD and Wigner description the population of level j is defined by

$$\theta^\epsilon_j(t)=\int |\langle e_j(q)|\Psi^\epsilon(q,t)\rangle|^2 dq \;=\; \int \mathrm{tr}\,(\mathcal{P}_j(q)\,W^\epsilon(\Psi^\epsilon,\Psi^\epsilon)(q,p,t))\;dqdp. \tag{35}$$

The analogous definitions for the adiabatic and diabatic representations are

$$\theta^{\mathrm{dia}}_j(t) \;=\; \int \mathrm{tr}\,\{\mathcal{P}_j(q)\,\rho(q,p,t)\}\;dqdp, \tag{36}$$

$$\theta^{\mathrm{ad}}_j(t) \;=\; \int \rho^{\mathrm{ad},\epsilon}_{jj}(q,p,t)\,dqdp. \tag{37}$$

The relation between the θ^{ad}_j and the full QD populations $\int |\Phi_j|^2\,dq$ is discussed in Sec. 5 and illustrated in Sec. 6.

5 Adiabatic Limit of the QCL

For the sake of simplicity we directly use the adiabatic basis to discuss the adiabatic limit of the QCL. To this end, we turn back to the Schrödinger equation (5) in this basis: Let Φ^ϵ denote the family of solutions, and $\mathcal{H} = \mathcal{H}(q,p)$ the matrix-valued symbol of the associated Hamiltonian $\mathcal{H}^W$ (given by (26) with $\mathcal{E}_0 = E$, $\mathcal{E}_1 = \mathcal{V}$, $\mathcal{E}_2 = T$, and $C \neq 0$) which is again supposed to satisfy assumptions (B1) and (B2) given on page 11.

The eigenvalues of the zero order part $\mathcal{E}_0 = E$ of the Hamiltonian are exactly the eigenenergies $E_k = E_k(q)$, $k = 1,\ldots,N$, which are supposed to satisfy Assumption (A) on page 4. The corresponding eigenvectors are the unit vectors u_k, $k = 1,\ldots,N$, of the coordinate directions (with entries $u_{k,j} = \delta_{kj}$ where δ denotes the Kronecker symbol).

Finally, let the family of initial conditions $\Phi_I^\epsilon = \Phi^\epsilon(\cdot, t=0)$ be bounded in $L^2(\mathbb{R}^d)^N$ and suppose that ρ_I^0 is the *unique* Wigner measure of the family (Φ_I^ϵ) (cf. Prop. 3.2) and that it satisfies

$$\operatorname{tr}\rho_I^0\left(\mathbb{R}^d\times\mathbb{R}^d\right) \;=\; \limsup_{\epsilon\to 0}\int_{\mathbb{R}^d}|\Phi_I^\epsilon|^2 dq. \tag{38}$$

This condition allows a trivial physical interpretation and is satisfied for initial conditions like (8) that are typical for applications in physical chemistry.[13]

Under these conditions, the following theorem holds:

THEOREM 5.1 *The solutions $\rho^{0,k} = \rho^{0,k}(q,p,t)$ of the classical Liouville equations*

$$\partial_t\rho^{0,k} \;=\; -p\cdot D_q\rho^{0,k} \;+\; D_qE_k\cdot D_p\rho^{0,k} \tag{39}$$

with initial conditions given by the diagonal entries of ρ_I^0, i.e., by $\rho^{0,k}(0) = \rho^0_{I,kk}$, are continuously t-dependent positive measures on $\mathbb{R}^d\times\mathbb{R}^d$. The family of Wigner matrices $\mathcal{W}^\epsilon = \mathcal{W}^\epsilon(q,p,t)$ associated with the family of solutions Φ^ϵ, and the family of solutions $\rho^{\mathrm{ad},\epsilon}$ of the adiabatic QCL (34), both, converge weak-$*$ in $L^\infty(\mathbb{R},\mathcal{S}')$ to the (diagonal) matrix-valued measure

$$\rho^0 \;=\; \sum_{k=1}^N \rho^{0,k}\; u_k\otimes u_k^T, \tag{40}$$

and the corresponding position densities $\Phi^\epsilon\otimes(\Phi^\epsilon)^*$ converge in $L^\infty(\mathbb{R},\mathcal{S}')$ weak-$*$ to $\int_{\mathbb{R}^d}\rho^0(\cdot,dp,\cdot)$. Furthermore, the diagonal entries of the Wigner matrices $\mathcal{W}^\epsilon$ and the diagonal entries of the solution $\rho^{\mathrm{ad},\epsilon}$ of the adiabatic QCL converge locally uniformly with respect to t:

$$\mathcal{W}^\epsilon_{kk}\to\rho^{0,k} \quad\text{and}\quad \rho^{\mathrm{ad},\epsilon}_{kk}\to\rho^{0,k}. \tag{41}$$

Proof: The asserted weak-$*$ convergences are corollaries to Thm. 6.1 in [20] (the additional correction on the RHS of the limit equation (6.10) in [20] vanishes in our special case). The assertion concerning the uniform convergence

[13] It can be checked without explicit reference to the Wigner matrix ρ_I^0: Sec. 1 in [20] contains equivalent conditions in the form of direct conditions on the decay of Φ_I^ϵ and its Fourier transform.

follows along the same line of argument as in [10, 11, 20], since the diagonal entries of $[E,\rho]_- = [\mathcal{E}_0,\rho]_-$ vanish so that the time derivatives $\partial_t \mathcal{W}^\epsilon_{kk}$ and $\partial_t \rho^{\mathrm{ad},\epsilon}_{kk}$ of the diagonal entries are bounded in $L^\infty(\mathbb{R}, \mathcal{S}'(\mathbb{R}^d \times \mathbb{R}^d))$. ∎

Theorem 5.1 demonstrates, that the highly oscillatory parts in the adiabatic QCL (34) (i.e., the first term on its RHS) *do not* contribute to the limit dynamics, but embody oscillatory corrections to the adiabatic behavior.

The scalar functions $\rho^{0,k} = \rho^{0,k}(q,p,t)$ are classical phase space distributions that are transported along the energy surfaces $E_k = E_k(q)$ according to the classical Liouville equation (39). Thus, the total mass $\theta^0_k = \int \rho^{0,k}(dq,dp,\cdot)$ of each $\rho^{0,k}$ is conserved — it is nothing but the population of the corresponding energy level. Thus, along the limit solution, the populations are constant. In addition, the uniform convergence stated in (41) guarantees that the family of energy level populations given by the QCL solution $\rho^{\mathrm{ad},\epsilon}$ converges uniformly to these constants:

$$\theta^{\mathrm{ad}}_j(t) \;=\; \int \rho^{\mathrm{ad},\epsilon}_{kk}(q,p,t)\,dp\,dq \;\to\; \theta^0_k, \qquad \text{for } \epsilon \to 0.$$

Thus, the QCL populations come out to be *adiabatic invariants*, i.e., they converge to constants in the adiabatic limit, exactly as in the alternative approaches to the adiabatic limit of QD [10, 11, 13, 27, 41]. As a consequence, the relation between the QCL populations θ^{ad}_j and the populations $\theta^\epsilon_j = \int |\Phi^\epsilon_j|^2\,dq$ in full QD comes out to be of the form

$$\theta^{\mathrm{ad}}_j \;=\; \theta^\epsilon_j \;+\; o(1). \tag{42}$$

Remark 5.2 Concerning the spectrum of the zero order part of the Hamiltonian, weaker assumptions than the "non-crossing"-assumption A are possible (cf. [20], Sec. 6).

Remarks 5.3

1. The application of the general Thm. 6.1 in [20] to the *diabatic* QCL yields the analogous adiabatic limit. To achieve this, some assumption excluding energy level crossings as, e.g., Assumption A is required.
2. In the diabatic case, the diagonal entries of the Wigner matrices do *not* converge uniformly as in the adiabatic case. Consider, e.g., the q-independent Hamiltonian

$$H(q) = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \qquad \text{with eigenvalues } E_1 = 0 \text{ and } E_2 = 2.$$

Then, the diagonal entries of the diabatic QCL solution for initial conditions ρ_I are given by

$$\begin{aligned}
\rho_{11}(q,p,t) &= \frac{1}{2}(1+\cos\frac{2it}{\epsilon})\rho_{I,11}(q-pt,p) \\
&\qquad + \frac{1}{2}(1-\cos\frac{2it}{\epsilon})\rho_{I,22}(q-pt,p) \\
\rho_{22}(q,p,t) &= \frac{1}{2}(1-\cos\frac{2it}{\epsilon})\rho_{I,11}(q-pt,p) \\
&\qquad + \frac{1}{2}(1+\cos\frac{2it}{\epsilon})\rho_{I,22}(q-pt,p),
\end{aligned}$$

with (only) weak-$*$ convergence in both cases.

6 Nonadiabatic Effects

Up to now we only discussed the adiabatic limit behavior and the asymptotic approximation properties of the different versions of the QCL. We observed that the QCL may allow to reproduce Landau-Zener-like redistributions of populations in full QD (see Rmk. 4.4). However, the question remains to which extent and with which precision the reproduction of nonadiabatic effects in QD may be possible whenever the parameter ϵ is small but not arbitrarily small. In this section we will compare the nonadiabatic effects in the QCL and the QD solutions of a generic example.

6.1 An Avoided Crossing Example

In the subsequent, let us consider the particularly simple test case where the quantum subsystem can be described as a two state system and the classical subsystem is one-dimensional. Thus, $q \in \mathbb{R}^1$ and the full Schödinger equation has the form:

$$i\epsilon\,\dot{\Psi} \;=\; \left(-\tfrac{\epsilon^2}{2}\Delta_q \,+\, H(q)\right)\,\Psi, \tag{43}$$

with $H = H(q)$ denoting the 2×2 hermitian matrix:

$$H(q) = \begin{pmatrix} V_1(q) & c \\ c & V_2(q) \end{pmatrix}.$$

The wavefunction $\Psi \in L^2(\mathbb{R}) \times L^2(\mathbb{R})$ consists of two components $\Psi = (\Psi_1, \Psi_2)^T$, each of which a function in q and t.

Herein, we choose the potentials to be $V_1(q) = q^2$ and $V_2(q) = 1/|q|$. The interpretation is as follows: V_1 describes a harmonic bond, V_2 a repulsive potential, and c a weak coupling between these two (electronic) configurations. We choose $\epsilon = 0.01$ which is a suitable scaling for electrons. In the following we set $c = 0.1$. For the choices made, Fig. 1 shows the energy eigenvalues $E_1 = E_1(q)$ and $E_2 = E_2(q) < E_1(q)$ of $H(q)$ and the corresponding off-diagonal entry C_{12} of the coupling tensor C. Notice that there is some "transition zone" around $q = 1$ where the gap between the two energy levels is minimal and the coupling tensor entry significantly large.

We are interested in the following initial condition: Let $e_1 = e_1(q)$ be the eigenvector to E_1, $q_0 = 0.4$ and $p_0 = 1$. Then the initial wavefunction is centered at q_0 with momentum expectation p_0 and the energy level E_1 is occupied only, i.e.,

$$\Psi(q, t=0) \;=\; \tfrac{1}{A}\exp\left(-\tfrac{1}{4\epsilon}(q-q_0)^2 \,-\, \tfrac{i}{\epsilon}p_0^T q\right)\,\cdot\, e_1(q). \tag{44}$$

Figure 2 illustrates the full quantum dynamical solution of (43) for the initial condition given. We observe that the centers of the two components Ψ_1 and Ψ_2 of the wavefunction diverge when crossing the transition zone. The motion of each of these two centers is governed by the Born-Oppenheimer solutions on

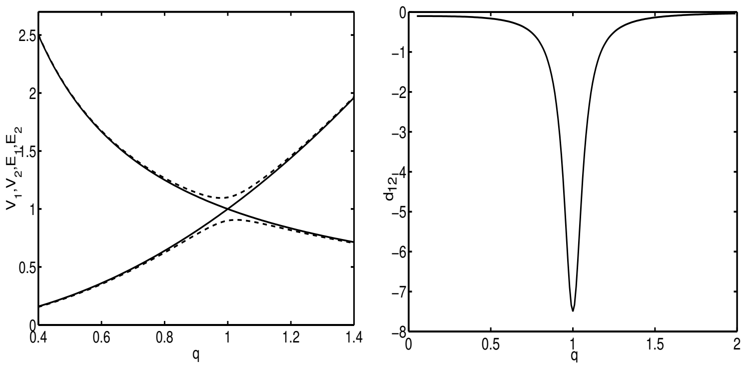

Figure 1: **(a)** Potentials V_1 and V_2 (*solid lines*) and energy levels E_1 and E_2 (*dashed lines*) versus q. **(b)** Non-Adiabatic coupling matrix element C_{12} versus q

the corresponding[14] energy levels E_1 and E_2 (cf. Fig. 2). We can conclude that the non-adiabatic effect of the transition zone induces some significant population of the initially unoccupied energy level whereas the motion outside of the transition zone is governed by classical dynamics on the energy levels and induces the observed divergence.

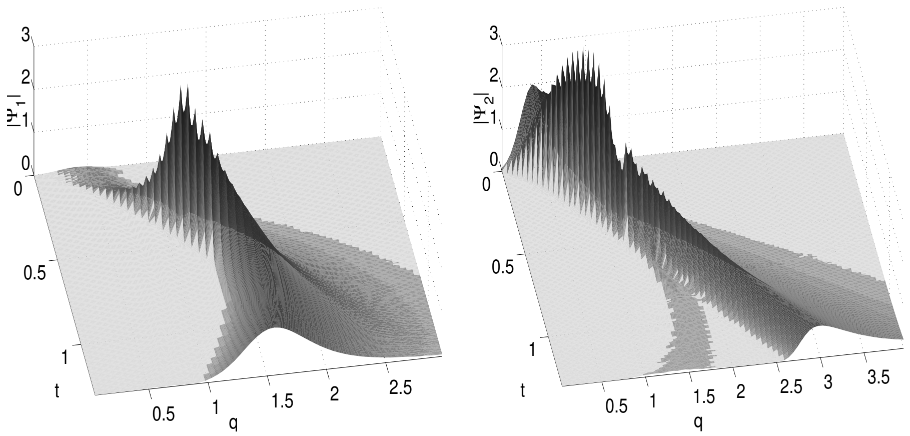

Figure 2: Avoided Crossing Example: Evolution of the full QD wavepacket in q and t for parameter $\epsilon = 0.01$. Absolute value of **(a)** Ψ_1 and **(b)** Ψ_2

6.2 Deterministic Integrator for the Adiabatic QCL

In the subsequent, a deterministic integrator for the adiabatic QCL will be constructed based on some finite-difference-like spatial discretization of the corresponding phase space and on a Trotter-splitting in time. This methods is introduced *only* to compute a reliable, highly accurate numerical solution of the

[14]Away from the transition zone, the eigenvectors of H are approximately given by the two unit vectors.

QCL, *not* to establish a competitive numerical solver for such equations of motion.[15] The QCL should rather be seen as the *starting point* for the derivation of quantum-classical particle methods, either of deterministic character as in [16] or in stochastic form as variants of the surface-hopping technique.

In order to propagate the adiabatic QCL equation (34), we use the following decomposition of its RHS:

$$\begin{aligned} \partial_t \rho^{\mathrm{ad}} &= \underbrace{[pC, \rho^{\mathrm{ad}}]_-}_{=\hat{C}\rho^{\mathrm{ad}}} \underbrace{- \frac{i}{\epsilon}[E, \rho^{\mathrm{ad}}]_-}_{=-\frac{i}{\epsilon}\hat{E}\rho^{\mathrm{ad}}} + L\rho^{\mathrm{ad}}, \\ L &= -p \cdot D_q + \frac{1}{2}\,[D_q E, D_p\,]_+, \end{aligned}$$

with the following obvious physical interpretations: $\hat{C}$ represents the *exchange between the energy levels*, $\hat{E}$ the *oscillatory phase effects*, and L embodies the *transport on the level surfaces.*

For stepsizes $\tau = \mathcal{O}(\epsilon)$, we may approximate the QCL evolution $\rho^{\mathrm{ad}} = \rho^{\mathrm{ad}}(t)$ by the following Trotter splitting up to order $\mathcal{O}(\epsilon)$:

$$\rho^{\mathrm{ad}}(\tau) \approx \rho_1^{\mathrm{ad}} = \exp(\tau L)\, \exp(\tau \hat{C})\, \exp(-\frac{i\tau}{\epsilon}\hat{E})\, \rho^{\mathrm{ad}}(0).$$

For the sake of simplicity, we restrict ourselves to the case $N = 2$, i.e., we consider two energy levels only. Moreover, we assume that the eigenvectors $e_k = e_k(q)$ of $H = H(q)$ are real-valued,[16] so that the coupling matrix C is zero on the diagonal:

$$C(q) = \begin{pmatrix} 0 & C_{12}(q) \\ -C_{12}(q) & 0 \end{pmatrix} \quad \Rightarrow \quad p \cdot C(q) = \begin{pmatrix} 0 & \gamma \\ -\gamma & 0 \end{pmatrix}, \quad \text{with } \gamma = \gamma(q,p) = p \cdot C_{12}(q).$$

Under these conditions we can easily find numerical realizations for each of the three subproblems:

1: The oscillatory phase effects do not change the diagonal entries of ρ^{ad}:

$$\exp(-\frac{i\tau}{\epsilon}\hat{E})\rho^{\mathrm{ad}} = \begin{pmatrix} \rho_{11}^{\mathrm{ad}} & \exp(\frac{-i\tau}{\epsilon}(E_2 - E_1))\rho_{12}^{\mathrm{ad}} \\ \text{c.c.} & \rho_{22}^{\mathrm{ad}} \end{pmatrix}.$$

2: The exchange between the energy levels is generated by a rotation by the angle $\tau\gamma(q,p)$:

$$\begin{aligned} \exp(\tau\hat{C})\rho^{\mathrm{ad}} &= \exp(\tau p \cdot C)\, \rho^{\mathrm{ad}}\, \exp(-\tau p \cdot C) \\ &\quad \text{with} \quad \exp(\tau p \cdot C) = \begin{pmatrix} cos(\tau\gamma) & \sin(\tau\gamma) \\ \sin(-\tau\gamma) & \cos(\tau\gamma) \end{pmatrix}. \end{aligned}$$

[15] Based on the technique introduced herein, numerical integration of the QCL definitely produces more computational effort than numerical integration of the full Schrödinger equation itself.

[16] This is always possible if H itself is real-valued.

3: The transport on the level surfaces requires an approximation of the Hamiltonian flow Φ_{kl}^{τ} on the surfaces $E_{kl} = (E_k + E_l)/2$:

$$\eta = \exp(\tau L)\rho^{\rm ad} \quad \Rightarrow \quad \eta_{kl}(q,p) = \rho_{kl}^{\rm ad}\left(\Phi_{kl}^{-\tau}(q,p)\right),$$

which is realized via the well-known Verlet discretization $\tilde{\Phi}_{kl}^{-\tau}$ of $\Phi_{kl}^{-\tau}$ given by

$$\tilde{\Phi}_{kl}^{-\tau}(q,p) = (q_1, p_1) \quad \text{with} \quad \begin{cases} q_{12} &= q - \tau p/2 \\ p_1 &= p + \tau D_q E_{kl}(q_{12}) \\ q_1 &= q_{12} - \tau p_1 \end{cases}.$$

In order to realize this step, we have to introduce some (spatial) discretization of the interesting phase space volume. We will herein choose a uniform grid with nodes (q_j, p_r). Let $\rho^{\rm ad}$ be given on the grid and let $\tilde{\rho}^{\rm ad}$ denote the linear interpolation of $\rho^{\rm ad}$ between the nodes. Then, the new values on the nodes are computed via

$$\eta_{kl}(q_j, p_r) = \tilde{\rho}_{kl}^{\rm ad}(\tilde{\Phi}_{kl}^{-\tau}(q_j, p_r)).$$

6.3 QCL Solution of the Avoided Crossing Example

The initial state given in (44) implies the following initial condition for the adiabatic QCL evolution:

$$\rho_{11}^{\rm ad}(q,p,0) = \frac{1}{\pi\epsilon}\exp\left(-\frac{(q-q_0)^2}{2\epsilon}\right)\exp\left(-\frac{2(p-p_0)^2}{\epsilon}\right), \quad \rho_{22}^{\rm ad}(0) = \rho_{12}^{\rm ad}(0) \equiv 0.$$

In order to approximate the solution $\rho^{\rm ad} = \rho^{\rm ad}(t)$ of (34) numerically, the integration scheme explained in Sec. 6.2 above was applied based on a highly accurate box discretization of the interesting phase space volume.[17] The resulting energy level populations (see (37)) are illustrated in comparison with the exact QD populations in Fig. 3 below. Obviously, the QCL solution allows an intriguing reproduction of the nonadiabatic effects in full QD.

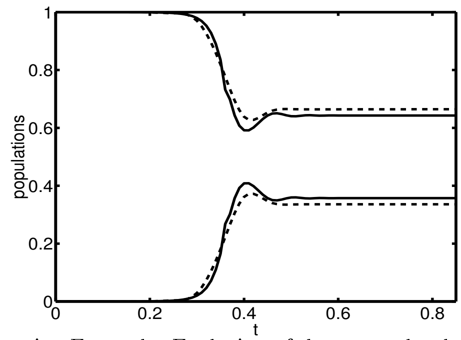

Figure 3: Avoided Crossing Example: Evolution of the energy level populations for $\epsilon = 0.01$. Solid lines: QD; dashed lines: QCL.

[17]The (q,p)-volume $[0.01, 4] \times [-1, 4]$ was divided into 1000×500 nodes. The stepsize of the Trotter splitting was set to $\tau = \epsilon/10$.

In order to compare the QCL solution with the QD solution, we first examine the QCL position densities defined by

$$Q_{jj}^{\mathrm{ad}}(q,t) \;=\; \int \sum_{k,l=1}^{N} \rho_{kl}^{\mathrm{ad}}(q,p,t)\, e_k^j(q) \cdot e_l^j(q)\; dp,$$

where e_k^j denotes the jth component of the eigenvalue e_k. The numerical approximations of the Q_{jj}^{ad} are shown in Fig. 4. Comparison with Fig. 2 (QD solution) shows that even details of the full quantum evolution can be reproduced by the QCL dynamics. To allow a detailed inspection of the slight differences visible, Fig. 5 shows some snapshots of the QCL and QD distributions. It becomes clear, that the most significant differences between the QCL and QD densities are differences in the width of the distributions.

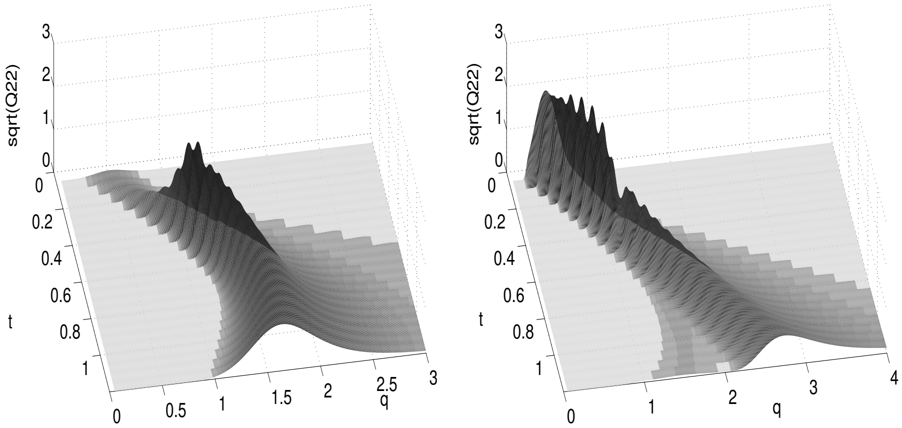

Figure 4: Avoided Crossing Example: QCL position densities. Square root of the absolute value of **(a)** Q_{11}^{ad} and **(b)** Q_{22}^{ad} versus q and t. To be compared with the QD position densities shown in Fig. 2.

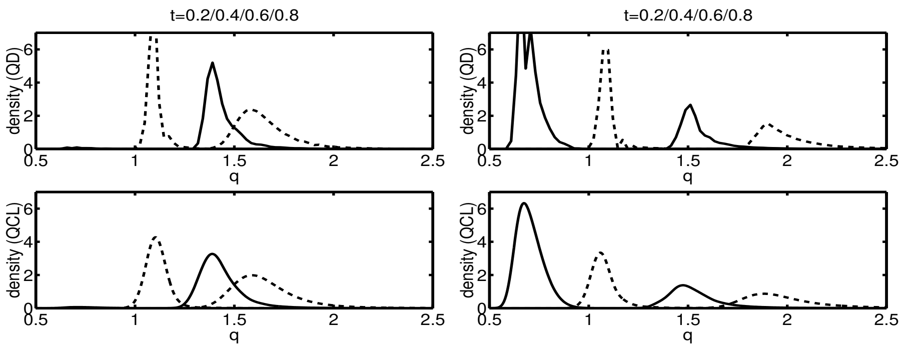

Figure 5: Comparison between QD and QCL position densities at times $t = 0.2/0.4/0.6/0.8$ for $\epsilon = 0.01$. On top: QD ($|\Psi_1(\cdot,t)|^2$ and $|\Psi_2(\cdot,t)|^2$); bottom: QCL ($Q_{11}^{\mathrm{ad}}(\cdot,t)$ and $Q_{22}^{\mathrm{ad}}(\cdot,t)$).

Last but not least, we will inspect the behavior of the *off-diagonal entry* of the QCL solution. Fig. 6 shows the snapshot of the solution at $t_0 = 0.5$, i.e., as it moves through the transition zone; we observe that the off-diagonal entry is oscillatory and takes significantly large values.

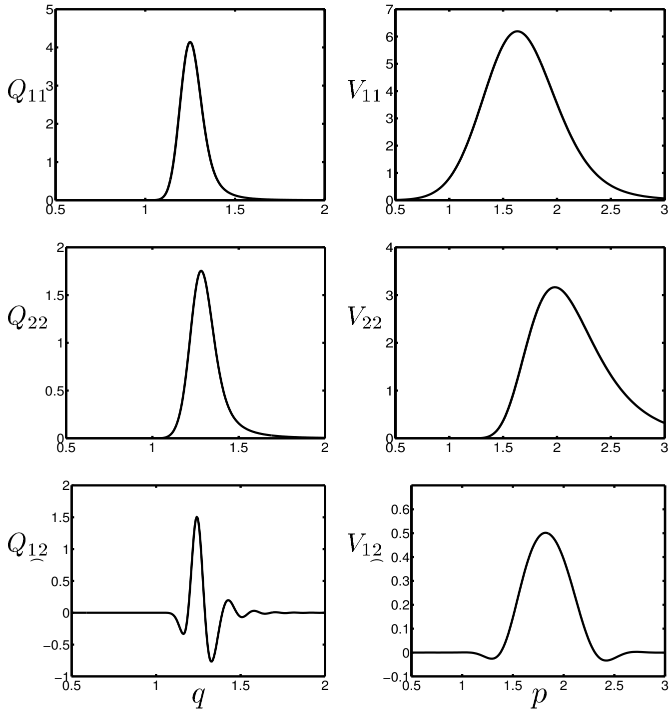

Figure 6: Snapshot of the solution of the adiabatic QCL for $t_0 = 0.5$. The three left hand side figures show the associated position distributions $Q_{11}^{\mathrm{ad}}, Q_{22}^{\mathrm{ad}}, Q_{\underset{\frown}{12}}^{\mathrm{ad}}$ (versus q) ; the three right hand side figures the corresponding momentum distributions $V_{11}^{\mathrm{ad}}, V_{22}^{\mathrm{ad}}, V_{\underset{\frown}{12}}^{\mathrm{ad}}$, $V_{jk}^{\mathrm{ad}} = \int \rho_{jk}^{\mathrm{ad}}(q,p,t_0)dq$, versus p.

Appendix A: Product Weyl Operators and Associated Symbols

Suppose that A and B are matrix-valued symbols with $A \in \mathcal{S}$ and B satisfying Assumption 3.3. Let A^W and B^W be the associated Weyl operators. Then, also the product operator $A^W B^W$ is a Weyl operator. Its symbol is denoted $A \odot B$, i.e., we write $A^W B^W = (A \odot B)^W$. Due to [20] (Appendix A) or [31], Sec. 18.5, this symbol also satisfies the Assumption 3.3 and is given by

$$(A \odot B)(q,p) \;=\; A(q,p)\,B(q,p) \;+\; \frac{\epsilon}{2i}\,\{A,B\}\,(q,p) \;+\; \epsilon^2 R_\epsilon(q,p), \tag{45}$$

where R_ϵ is bounded in $\mathcal{S}$.

In some simple cases, the representation of $A \odot B$ can be determined directly. As an example, let us consider the case required in Sec. 4:

PROPOSITION 6.1 *Let be C be some smooth tensor-valued symbol. The symbol associated with $A^W = C(q)\cdot\epsilon D_q$ is given by $A(q,p) = ip\cdot C(q) - \frac{\epsilon}{2}\,(D_q \cdot C(q))$, where $D_q \cdot C(q)$ is matrix-valued with entries $(D_q \cdot C)_{kl} = \sum_j D_{q_j} C^j_{kl}$.*

This can be seen by direct evaluation:

$$\begin{aligned}
&\tfrac{1}{(2\pi)^d}\int_{\mathbb{R}^d}\int_{\mathbb{R}^d} A\left(\tfrac{q+y}{2},\epsilon\xi\right)\,u(\xi)\,\exp(i(q-y)\xi)\,d\xi\,dy \\
&\qquad = \tfrac{\epsilon}{(2\pi)^d}\int_{\mathbb{R}^d}\int_{\mathbb{R}^d}\left[D_q e^{i(q-y)\xi}\right]\cdot C\left(\tfrac{q+y}{2}\right)\,u(\xi)\,d\xi\,dy \\
&\qquad\quad -\; \tfrac{\epsilon}{2}\,(D_q \cdot C(q))\,u(q) \\
&\qquad = \tfrac{\epsilon}{(2\pi)^d} D_q \cdot \left[\int_{\mathbb{R}^d}\int_{\mathbb{R}^d} C\left(\tfrac{q+y}{2}\right)\,u(\xi)\,e^{i(q-y)\xi}\,d\xi\,dy\right] \\
&\qquad\quad -\; \tfrac{\epsilon}{(2\pi)^d}\int_{\mathbb{R}^d}\int_{\mathbb{R}^d}\tfrac{1}{2}\,(D_q\cdot C)\left(\tfrac{q+y}{2}\right)\,u(\xi)\,e^{i(q-y)\xi}\,d\xi\,dy \\
&\qquad\quad -\; \tfrac{\epsilon}{2}\,(D_q \cdot C(q))\,u(q) \\
&\qquad = \epsilon\left(D_q\cdot[C(q)u(q)] - \tfrac{1}{2}\,(D_q\cdot C(q))\,u(q)\right) - \tfrac{\epsilon}{2}\,(D_q\cdot C(q))\,u(q) \\
&\qquad = C(q)\cdot\epsilon D_q u(q)
\end{aligned}$$

Thus, we find $R_\epsilon \equiv 0$ in (45) with $A(q,p) = C(q)$ and $B(q,p) = ip$.

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