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Quantum Dynamics on Potential Energy Surfaces

Simpler States and Simpler Dynamics

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Abstract

In this dissertation we analyze and simplify wave functions and observables in the context of quantum molecular dynamics. The two main topics we discuss are the structure of Hagedorn wave packets in position and phase space, and semiclassical approximations for the propagation of quantum expectations with nonnegative phase space densities. We provide algorithmic discretizations for these approximations and illustrate their validity and applicability by means of numerical experiments.

Zusammenfassung

In dieser Dissertation analysieren und vereinfachen wir Wellenfunktionen und Observablen im Kontext der molekularen Quantendynamik. Die zwei zentralen, von uns diskutierten Themen sind die Struktur der Hagedornschen Wellenpakete im Orts- und Phasenraum sowie semiklassische Approximationen für die Evolution von Erwartungswerten mit nichtnegativen Phasenraumdichten. Wir präsentieren algorithmische Diskretisierungen für diese Approximationen und illustrieren deren Anwendbarkeit anhand von numerischen Experimenten.

Contents

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Introduction

> "The underlying physical laws necessary for the mathematical theory of large parts of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complex to be solved. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."
>
> Paul A. M. Dirac in [Dir29]

As the above quotation of Dirac from 1929 shows, scientists were already very aware of the immense complexity of quantum mechanical systems well before the advent of computers and the corresponding possibility to run numerical simulations. Since those very first days of modern quantum mechanics, constructing approximations that can be used for simulating the dynamics of actual molecules is one of the prevailing aims of chemical physics, computational chemistry, and mathematical quantum dynamics.

The central equation of quantum molecular dynamics in the Born-Oppenheimer approximation is the time-dependent semiclassical Schrödinger equation

$$\mathrm{i}\varepsilon\partial_t\psi^\varepsilon(t) = \left(-\tfrac{\varepsilon^2}{2}\Delta + V\right)\psi^\varepsilon(t), \quad \psi^\varepsilon(0) = \psi_0^\varepsilon \in L^2(\mathbb{R}^d).$$

It governs the evolution of a wave function $\psi^\varepsilon(t)$ that represents the state of the molecule's nuclei on the potential energy surface $V : \mathbb{R}^d \to \mathbb{R}$. The small parameter $0 < \varepsilon \ll 1$ arises due to the fact that nuclei are heavy in comparison with electrons, and causes solutions $\psi^\varepsilon(t) : \mathbb{R}^d \to \mathbb{C}$ to be highly oscillatory in both space and time. This property, together with the high dimensionality of the nuclear configuration space $\mathbb{R}^d$, imposes severe difficulties for computations, and makes it clear that the semiclassical Schrödinger equation is in general "too complex to be solved". If one even wants to simulate realistic model systems "without too much computation", the development of powerful approximations is indispensable.

The central aim of this thesis is to pursue and interrelate two lines of simplifications for molecular quantum systems in the spirit of the agenda suggested by Dirac.

Firstly, we investigate the structure of Hagedorn wave packets in position and phase space by making a detailed analysis of their polynomial prefactors. The Hagedorn wave packets form a particularly simple yet versatile class of highly localized wave functions. They have proven to be well-suited for the semiclassical analysis of quantum systems as well as for the construction of numerical methods for the time-dependent Schrödinger equation. Our main contribution to the analysis of Hagedorn wave packets is to show that their phase space representation via Wigner functions is natural in the sense that it again yields a Hagedorn wave packet in doubled dimension. Moreover, we are able to provide an explanation for the uniform factorization of their Wigner functions in phase space, which has recently been discovered.

Secondly, we discuss various semiclassical approximations for the quantum evolution of expectation values and wave functions. Our focus lies on approximate methods for quantum expectations that simultaneously allow for both rigorous error estimates and applicable algorithmic discretizations. We present novel phase space methods for the computation of quantum expectations that utilize

smooth probability densities for the representation of the initial state. One of the main approaches we would like to promote with this thesis is the simultaneous semiclassical approximation of states and observables. An example for this beneficial combination of approximations is provided by our proof of a local Egorov theorem for long Ehrenfest times.

The two main themes of this dissertation are supported and enframed by a number of side stages. For instance, we present a rigorous proof for the Hellmann-Feynman theorem which is widely applied in chemistry in order to compute gradients of potential energy surfaces. Evaluating these gradients, in turn, is necessary for the computation of the classical trajectories utilized by semiclassical approximations.

Outline of the dissertation

The main corpus of the dissertation consists of 17 chapters that are arranged into four parts. Many of the chapters come along with their own introductory remarks that include a placement of their contents within the literature.

The first part §I is dedicated to a review and exploration of the foundations of molecular quantum dynamics and potential energy surfaces. It motivates the investigations in the subsequent parts of this dissertation. In the first two chapters we review the general ideas and concepts of quantum systems, Hamiltonian dynamics, and the Born-Oppenheimer approximation. Afterwards, in chapter §3, we discuss various properties of potential energy surfaces, like Lipschitz estimates and the diabatization problem. The topic of §4 is a proof of the Hellmann-Feynman theorem for Coulomb systems, and in the last chapter §5 we recall the basics of Weyl calculus.

Part §II contains our analysis of general Hagedorn wave packets. The preparatory chapter §6 presents ladder operators, generating functions, and tensor product expansions for a class of generalized

multidimensional Hermite polynomials. In chapter §7 and §8 these polynomials are used for the analysis of Hagedorn wave packets in position and phase space, respectively. After a short detour, in §10 we discuss anti-Wick operators and spectrograms, and derive a spectrogram expansion for Wigner transforms.

In the third part of this thesis we deal with semiclassical approximations for the propagation of quantum observables, expectation values, and wave packets. The chapters §11 and §12 present various approximative methods for the propagation of quantum expectations. Afterwards, in §13 review the semiclassical evolution of Hagedorn wave packets. The last chapters §14 and §15 of the third part are dedicated to a study of the long time evolution of wave packets on stable orbits of the classical flow. As an application we present a proof for a local Egorov theorem.

Finally, the last part §IV discusses discretizations and numerical experiments for the approximative methods for propagated quantum expectations that have been presented in the third part.

The first two parts §A and §B of the appendix contain a list of the used notation, and a short summary of symbol classes for Weyl quantized operators, respectively. In appendix §E we comment on the generation of numerical reference solutions, and the remaining parts of the appendix comprise technical details we omitted for readability.

The main results

The main new results of this dissertation are the Wigner-Hagedorn formula from Theorem 3 and the spectrogram expansion of Wigner transforms from Theorem 4, together with its application to the propagation of expectation values in Theorem 5. Other results, which might be of interest, include the rigorous Hellmann-Feynman Theorem 1 for Coulomb systems, the tensor product expansion theorem for Hagedorn wave packets from Theorem 2, the second order Egorov Theorem 6 for anti-Wick operators, and the local Egorov

approximation for long Ehrenfest time scales from Theorem 7.

Most of the results in the chapters §6, §7 and §8 have been obtained together with H. Dietert and S. Troppmann, and can be found in our preprint [DKT15]. The results in section §12.3 are taken from our joint publication with C. Lasser [KL13]. We only sketch their derivation since in a similar form they already appeared in our Master's thesis [Kel12]. The example presented in §16.4 as well as the numerical experiments illustrated in Figure 5 can also be found in our joint article [KL14] with C. Lasser. Furthermore, the first parts of Proposition 20 and Theorem 4, respectively, and the approximation with spectrogram densities from §12.2 are joint work with C. Lasser and T. Ohsawa, and can be found in the preprint [KLO15]. From there we also adopted some of the numerical experiments in §17.

The primary sources we frequently consulted during our day-to-day work on this dissertation are the paper [BR02] of A. Bouzouina and D. Robert on the Egorov theorem, the book of Ch. Lubich on molecular dynamics [Lub08], the classical monograph of T. Kato [Kat95], and M. Zworski's comprehensive introduction to semiclassical analysis [Zwo12].

Lemmata, Propositions, Theorems

Since we do not follow the usual conventions, let us shortly comment on the terminology we use in this dissertation for presenting mathematical results. For the sake of clarity we use the following classification: All the statements in this thesis that are either new, or come with a new proof, are called 'Propositions' or 'Theorems', while the latter denotation is reserved for the central results we listed above. If we employ or annotate results of other authors, we use the designation 'Lemma'. This terminology is also used for important results that deservedly are referred to as Theorems in the original reference or in the mathematical community.

I

Foundations

> " The appropriateness of the language of mathematics for the formulation of the laws of physics is a wonderful gift which we neither understand nor deserve."
>
> Eugene P. Wigner in [Wig60]

1 Quantum Systems

The theory of quantum mechanics is at the very basis of modern molecular physics and chemistry. Its origins can be traced back to Boltzmann's suggestion that the energy levels of a physical system might be discrete, and Planck's subsequent hypothesis of quantized energy emission in the the black-body radiation problem. After the concept of wave-particle duality has been extended to matter, the "old quantum theory" – with Einstein's explanation of the photoelectric effect and Bohr's model of atoms – evolved into the modern theory of quantum mechanics, first postulated in

the seminal works of Heisenberg, Schrödinger, Born and Jordan in 1925 and 1926. The theory of quantum mechnics as well as their elaboration by von Neumann, Pauli, Dirac, Weyl, Wigner and many other great scientists did not only revolutionize our understanding of matter and radiation, but also initiated and accelerated the development of various fields of mathematics.

In this chapter we recall the basic concepts of mathematical quantum dynamics, and present the fundamental model for the quantum mechanical description of nonrelativistic molecules.

1.1 States, Observables, Dynamics

In quantum mechanics, the state of a physical system is described by a vector of unit norm in a separable complex Hilbert space[1]. The elements of $\mathscr{H}$ are called *state vectors*. It is a fundamental postulate of quantum mechanics, see [Dir30], that two normalized state vectors $\psi, \phi \in \mathscr{H}$ represent the same physical state if and only if they coincide up to a global phase, that is,

$$\psi = e^{i\alpha}\phi$$

for some $\alpha \in \mathbb{R}$. In other words, the physical state associated with some $\psi \in \mathscr{H}$ can be identified with the rank one orthogonal projector $|\psi\rangle\langle\psi|$ on the span of ψ. The state vector ψ itself, however, is commonly believed not to have a direct physical interpretation. If the Hilbert space is a space of functions, state vectors are usually called wave functions.

Remark 1. *In statistical physics, projectors $|\psi\rangle\langle\psi|$ with $\psi \in \mathscr{H}$ are called* pure states. *The more general* mixed states *are defined as nonnegative trace class operators $\rho : \mathscr{H} \to \mathscr{H}$ which satisfy*

$$\mathrm{tr}_{\mathscr{H}}(\rho) = 1.$$

Mixed states appear as ensembles in quantum statistical mechanics.

[1] In this thesis we choose all inner products to be left-linear.

Quantum mechanical observables are selfadjoint linear operators on the Hilbert space $\mathscr{H}$. For an observable A and a pure state $|\psi\rangle\langle\psi|$, with some normalized $\psi \in \mathscr{H}$,

$$\langle \psi, A\psi \rangle_{\mathscr{H}} = \mathrm{tr}_{\mathscr{H}} \left(A|\psi\rangle\langle\psi| \right) =: \langle A \rangle_{\psi}$$

is called the *expectation value* of A in the state[2] $|\psi\rangle\langle\psi|$. From a physical point of view, $\langle A \rangle_{\psi}$ is the expected measurement result of the physical quantity represented by A if the system has been prepared in the state $|\psi\rangle\langle\psi|$.

According to Born's probabilistic interpretation of wave functions [Bor26], the probability for obtaining a result in $\Omega \subset \mathbb{R}$, when measuring the observable A in the state $|\psi\rangle\langle\psi|$, is given by

$$\langle \psi, P_A(\Omega)\psi \rangle_{\mathscr{H}} , \tag{1.1}$$

where P_A is the unique projection-valued measure associated with the selfadjoint operator A. Hence, $\langle A \rangle_{\psi}$ can be interpreted as an expectation value in the usual sense of probability theory.

An observable H that describes the total energy of a physical system is called the *Hamiltonian* of that system. Typically, it describes the kinetic energy as well as all relevant external and internal forces acting on the system. Starting from an initial state vector $\psi(0) = \psi_0$, the evolution $t \mapsto \psi(t)$ under a Hamiltonian H is governed by the *time-dependent Schrödinger equation*

$$\mathrm{i}\hbar\partial_t \psi(t) = H\psi(t) , \quad \psi(0) = \psi_0, \tag{1.2}$$

where $\hbar$ is the reduced Planck constant. If not stated otherwise, from now on we will only consider time independent Hamiltonians in order to facilitate a simpler presentation. We are aware of the fact that this simplification might not be adequate to many important physical situations.

[2] Expectation values are obviously invariant under a global change of phase $\psi \mapsto \mathrm{e}^{\mathrm{i}\alpha}\psi$ in the state vector.

Stone's Theorem implies that the unique solution of (1.2) is given by the strongly continuous one-parameter unitary group generated by H,

$$\psi(t) = \mathrm{e}^{-\mathrm{i}Ht/\hbar}\psi_0, \tag{1.3}$$

which gives the so-called Schrödinger picture of quantum dynamics. By the Stone-von Neumann theorem it is physically equivalent to the Heisenberg picture, which describes the "matrix mechanics" of

$$A(t) := \mathrm{e}^{\mathrm{i}Ht/\hbar}A_0\mathrm{e}^{-\mathrm{i}Ht/\hbar}.$$

for some observable A_0. If A_0 is time-independent, the evolution of $A(t)$ is governed by *Heisenberg's equation*

$$\partial_t A(t) = \tfrac{\mathrm{i}}{\hbar}[H, A(t)], \quad A(0) = A_0, \tag{1.4}$$

where $[X, Y] = XY - YX$ denotes the commutator of X and Y. We have

$$\langle A_0 \rangle_{\psi(t)} = \langle A(t) \rangle_{\psi_0},$$

and, by (1.4), the expectation values of an observable A are conserved quantities of a quantum system with Hamiltonian H if and only if A commutes with H. In particular, the norm $\|\psi(t)\|_{\mathscr{H}}$ and the expected total energy[3] $\langle H \rangle_{\psi(t)}$ are preserved for all times.

Suppose that $\phi \in \mathscr{H}$ is a normalized eigenvector of H belonging to the energy level E, that is, ϕ solves the *stationary Schrödinger equation*

$$H\phi = E\phi.$$

Then, ϕ is invariant under time evolution up to a global phase,

$$\mathrm{e}^{-\mathrm{i}Ht/\hbar}\phi = \mathrm{e}^{-\mathrm{i}Et/\hbar}\phi,$$

and, for this reason, $|\phi\rangle\langle\phi|$ is called a stable state or eigenstate of the system. Often we use the same term for the eigenvector ϕ. If $\mathscr{H}$ is finite dimensional, the spectral theorem implies the

[3] If H is time dependent, this conclusion fails.

existence of an orthonormal basis consisting of stable states only. In infinite dimensional Hilbert spaces, however, the spectrum of an Hamiltonian might contain no eigenvalues at all, in which case there are no stable states.

1.2 Particle Systems

The appropriate Hilbert space for a single nonrelativistic quantum particle moving in $\mathbb{R}^3$ is given by the function space $L^2(\mathbb{R}^3, \mathbb{C}^{2S+1})$, where S denotes the spin of the particle type. The pointwise norm squared $|\psi|^2$ of a normalized wave function $\psi \in L^2(\mathbb{R}^3, \mathbb{C}^{2S+1})$ then is a probability density on $\mathbb{R}^3$, such that, in accordance with Born's rule (1.1), the integral

$$\int_\Omega |\psi(x)|^2 dx$$

gives the probability of finding the particle within the region $\Omega \subset \mathbb{R}^3$.

If one considers a system of N indistinguishable particles, one has to guarantee that the outcome of measurements does not depend on the labeling of the particles. This requirement leads to Pauli's principle which asserts that the common wave function of the particles must be either symmetric or antisymmetric under the exchange of any two of the particles. By the spin-statistics theorem, particles with half-integer spin, so-called *fermions*, have antisymmetric wave functions while *Bosons* have symmetric wave functions and integer spin. As a consequence, the fermionic and bosonic N-particle Hilbert spaces are given by the antisymmetrization or symmetrization of the nth tensor power of the one-particle space, respectively.

The focus of this work lies on the dynamics of the nuclei in a molecule, which are heavy in comparison to electrons. Hence, nuclear wave functions are typically strongly localized around their average position and different nuclei repel each other by Coulomb's law. Consequently, apart from the high energy regime, the average

positions of any two of the nuclei in a molecular quantum system will be well-seperated from each other for all times of interest. In other words, Pauli's principle can be safely neglected since the nuclei can be distinguished by their different positions, see also [Lub08, §I.5.2]. These heuristics justify the common practice to drop any symmetry or antisymmetry conditions on nuclear wave functions. We stress that for the much less localized wave functions of the electrons it is crucial to incorporate the Pauli exclusion principle in both, theoretical considerations and simulations.

In this work we treat neither the physical effects of nonrelativistic motion and magnetic fields, nor any corrections from quantum electrodynamics. In other words, the considered model Hamiltonians will not include any type of spin-orbit coupling. Hence, for our analysis of effective molecular motion we can ignore the nuclear spin degrees of freedom.

In summary, for a molecular quantum system with N nuclei and L electrons we arrive at the model Hilbert space

$$\mathscr{H}_{\mathrm{mol}} := L^2(\mathbb{R}^{3N}, \mathscr{H}_{\mathrm{el}}) \cong L^2(\mathbb{R}^{3N}) \otimes \mathscr{H}_{\mathrm{el}}, \tag{1.5}$$

which is the tensor product of the nuclear Hilbert space $L^2(\mathbb{R}^{3N})$ and the electronic Hilbert space

$$\mathscr{H}_{\mathrm{el}} \subset \bigotimes_{j=1}^{L} L^2(\mathbb{R}^3, \mathbb{C}^2)$$

consisting of antisymmetric wave functions. Throughout this thesis we use atomic units for all physical quantities and equations. In these units the reduced Planck constant $\hbar$, the elementary charge e, and the electronic mass m_e all equal unity.

1.3 The Molecular Hamiltonian

We consider a molecule consisting of L electrons with the positions $x = (x_1, \ldots, x_L) \in \mathbb{R}^{3L}$, and N nuclei with the positions $X =$

$(X_1, \dots, X_N) \in \mathbb{R}^{3N}$. The mass and charge of the jth nucleus are denoted by m_j and $\mathcal{Z}_j > 0$, respectively, and we choose the space $\mathscr{H}_{\mathrm{mol}}$ from (1.5) as the system's Hilbert space.

If the electrostatic interactions between the particles are modeled by the Coulomb force and there are no external forces and electromagnetic fields, the nonrelativistic molecular Hamiltonian in atomic units is given by the Schrödinger operator

$$\begin{aligned} H_{\mathrm{mol}} &= \sum_{j=1}^{L} -\tfrac{1}{2}\Delta_{x_j} + \sum_{k=1}^{N} -\tfrac{1}{2m_k}\Delta_{X_k} + \sum_{j<k} |x_k - x_j|^{-1} \\ &\quad - \sum_{j=1}^{L}\sum_{k=1}^{N} \mathcal{Z}_k |x_j - X_k|^{-1} + \sum_{j<k} \mathcal{Z}_j \mathcal{Z}_k |X_k - X_j|^{-1} \\ &= T_{\mathrm{el}} + T_{\mathrm{nuc}} + V_{\mathrm{ee}}(x) + V_{\mathrm{ne}}(X, x) + V_{\mathrm{nn}}(X). \end{aligned} \tag{1.6}$$

The Laplacians T_{el} and T_{nuc} are the nonrelativistic kinectic energy operators for the electrons and the nuclei, respectively. The potentials $V_{\mathrm{ee}}, V_{\mathrm{nn}} > 0$ generate the electronic and nucleonic repulsions, and $V_{\mathrm{ne}} < 0$ gives the attraction between electrons and nuclei. By Kato's theorem [Kat51, Theorem 1], see also [RS75, Theorem X.16], H_{mol} can be realized as a selfadjoint operator on $L^2(\mathbb{R}^{3N}, \bigotimes_{j=1}^{L} L^2(\mathbb{R}^3, \mathbb{C}^2))$. The selfadjointness as an operator acting on the closed subspace $\mathscr{H}_{\mathrm{mol}}$ follows immediately. Consequently, by (1.3), the Cauchy problem

$$\mathrm{i}\partial_t \psi(t) = H_{\mathrm{mol}} \psi(t)\,, \quad \psi(0) = \psi_0 \in \mathscr{H}_{\mathrm{mol}}$$

has the unique solution

$$\psi(t) = \mathrm{e}^{-\mathrm{i}H_{\mathrm{mol}}t}\psi_0 \in \mathscr{H}_{\mathrm{mol}}.$$

The molecular Hamiltonian can also be rewritten as the sum

$$H_{\mathrm{mol}} = T_{\mathrm{nuc}} + H_{\mathrm{el}} + V_{\mathrm{nn}}, \tag{1.7}$$

where the fibered operator

$$H_{\mathrm{el}} = \int_{\mathbb{R}^{3N}}^{\oplus} H_{\mathrm{el}}(X)\, dX$$

is known as the electronic Hamiltonian. The fiber operators

$$H_{\mathrm{el}}(X) = T_{\mathrm{el}} + V_{\mathrm{ee}} + V_{\mathrm{ne}}(X, \bullet) \tag{1.8}$$

describe a system of L electrons if the nuclei have been fixed at the position $X \in \mathbb{R}^{3N}$. Therefore, $H_{\mathrm{el}}(X)$ is often called the *clamped nuclei Hamiltonian*.

Since the masses m_j of the nuclei are large compared to the electronic mass m_e, which equals one in atomic units, the effective motion of the nuclei typically happens on much larger time scales than the electronic dynamics. This observation leads to the Born-Oppenheimer approximation, see §2.4.

1.4 Bound States

It is a natural question to ask if a quantum mechanical model can explain the stability of many molecules that is observed in reality. In this context, the issue of "stability of matter" is twofold. Firstly, in stable atoms the electrons are bound to the nucleus, and a stable molecule consists of a number of stable atoms that are bound to each other for long times. Secondly, the electrons do not collide with the nuclei, despite of their mutual attraction. From a mathematical viewpoint this corresponds to showing that the system's Hamiltonian is bounded from below, and the infimum of its spectrum gives rise to a stable state.

Many quantum dynamical models — like the molecular Coulomb Hamiltonian H_{mol} from (1.6) — have the above stability properties, see also [LS10] for a compilation of various results. It is a well-known fact that the spectrum of H_{mol} is of the form

$$\sigma(H_{\mathrm{mol}}) = \{\alpha_0 \leq \alpha_1 \leq \ldots\} \dot{\cup} [\Sigma, \infty),$$

where the infimum of the essential spectrum Σ can be interpreted as the minimal energy required to break the molecule into two pieces[4].

[4] This statement paraphrases the HVZ theorem.

The eigenvalues $\alpha_0 \leq \alpha_1 \leq \ldots$ (counted with their multiplicities) below the essential spectrum of H_{mol} are called *bound state energies*, and the corresponding eigenstates are known as *bound states* since they represent stable configurations of the bound molecule.

The molecular system described by the clamped nuclei Hamiltonian (1.8) is stable as well. Its spectrum as an operator on the electronic fiber $\mathscr{H}_{\mathrm{el}}$ is of the form

$$\sigma\left(H_{\mathrm{el}}(X)\right) = \{E_0(X) \leq E_1(X) \leq \ldots\} \dot{\cup} [\Sigma(X), \infty), \tag{1.9}$$

with a finite or countable number of bound state energies $E_k(X)$ below the essential spectrum, and $\Sigma(X)$ as their only possible accumulation point. If $H_{\mathrm{el}}(X)$ has at least k bound states, $E_k(X)$ is given by the kth minimax value

$$\lambda_k(X) = \inf_{\substack{V \subset \mathscr{H}_{\mathrm{el}} \\ \dim V = k}} \sup_{\substack{\psi \in \mathscr{H}_{\mathrm{el}} \\ \|\psi\| = 1}} \left\langle \psi, H_{\mathrm{el}}(X)\psi \right\rangle_{\mathscr{H}_{\mathrm{el}}}, \tag{1.10}$$

by invoking Courant's minimax principle, and otherwise one has $\lambda_k(X) = \Sigma(X)$. In chemistry the parametrized bound state energies $X \mapsto E_k(X)$ are known as *potential energy surfaces* (PES). They appear as effective potentials for the nuclear motion in the Born-Oppenheimer approximation, see §2.4 and §3.

Evaluating PES numerically by approximately solving the electronic structure problem

$$H_{\mathrm{el}}(X)\eta_j(\bullet, X) = E_j(X)\eta_j(\bullet, X), \quad \eta_j(\bullet, X) \in \mathscr{H}_{\mathrm{el}} \setminus \{0\}, \tag{1.11}$$

is the central challenge of quantum chemistry. For the semiclassical approximations and algorithms presented in this work, however, we will always assume that the relevant PES can be evaluated with sufficient accuracy. There is also a wealth of heuristic models and formulas for the PES in different molecules.

2 Hamiltonian Dynamics

The unitary group (1.3) that solves the time-dependent Schrödinger equation is a prominent example for the flow of a Hamiltonian system. A great variety of dynamical systems allow for a Hamiltonian formulation, including, for example, nonlinear partial differential equations like the nonlinear Schrödinger and Korteweg-de Vries equations, see [HZ07] and [MR99, §3.2]. In this chapter we reformulate both Schrödinger's equation and the equations of classical mechanics in the language of Hamiltonian systems. Moreover, we introduce the Born-Oppenheimer approximation as a subspace reduction of the full quantum molecular dynamics.

2.1 Abstract Formulation

A smooth manifold M is called symplectic if there is a non-degenerate closed two-form ω on M. In this case ω is called a symplectic form. Hamiltonian systems consist of a symplectic manifold (M, ω) and a Hamiltonian vector field Ξ_H defined by

$$\omega(\bullet, \Xi_H) = dH, \tag{2.1}$$

where $H : M \to \mathbb{R}$ is a *Hamilton function* of sufficient regularity. The integral curves $t \mapsto z(t)$ of Ξ_H satisfy Hamilton's equation

$$\partial_t z(t) = \Xi_H(z(t)), \tag{2.2}$$

and constitute the Hamiltonian flow associated with H. Symplectomorphisms (or canonical transformations) are diffeomorphisms $f : M \to M$ which preserve the symplectic form ω, that is[5],

$$f^*\omega = \omega.$$

[5] $f^*\omega$ denotes the pullback of the differential form ω by means of the function f, see [MR99, §5.2].

One can prove that the flow of a vector field X on M consists of symplectomorphisms if and only if X is a Hamiltonian vector field.

Suppose that X_A and X_H are Hamiltonian vector fields on (M, ω). Then, the Poisson bracket $\{H, A\}$ of A and H is defined as

$$\{A, H\} := \omega(X_A, X_H). \tag{2.3}$$

It determines the evolution of A along the Hamiltonian flow $\{\Phi_t\}_{t\in\mathbb{R}}$ of H, since

$$\partial_t(A \circ \Phi_t) = \{H, A\} \circ \Phi_t, \tag{2.4}$$

see [MR99, Proposition 2.7.6]. Consequently, A is constant along integral curves of Ξ_H if and only if H and A are in involution, which means that $\{H, A\} = 0$. For comprehensive presentations of Hamiltonian systems, we refer to the books [AM78, MR99].

2.2 Schrödinger Evolution

Given a complex Hilbert space $\mathscr{H}$, it becomes a symplectic vector space with the symplectic form

$$\omega(\psi, \phi) = -2\hbar \mathrm{Im} \langle \psi, \phi \rangle_{\mathscr{H}},$$

see [MR99, §2.2]. Moreover, if H is a densely defined selfadjoint operator on $\mathscr{H}$, the energy expectation value

$$h(\psi) = \langle H \rangle_\psi$$

defines a Hamilton function[6] on the form domain of H. Hamilton's equation (2.2) for the energy function h then reads

$$\mathrm{i}\hbar\partial_t\psi(t) = H\psi(t),$$

[6] Even if h is not defined on all of $\mathscr{H}$, it still yields a well-defined infinite dimensional Hamiltonian system, compare [AM78, Definition 5.5.2].

which we recognize as Schrödinger's equation (1.2), and the Hamiltonian flow associated with h is given by the unitary group generated by H. In other words, the Schrödinger equation describes a Hamiltonian system. Let us consider the expectation value

$$a(\psi) = \langle A \rangle_\psi$$

of some quantum observable A. Whenever the commutator $[H, A]$ makes sense, the Poisson bracket (2.3) of h and a is given by

$$\{h, a\}(\psi) = \langle [H, A] \rangle_\psi ,$$

and, hence, (2.4) yields precisely the Heisenberg evolution (1.4) of expectation values.

Before constructing approximation methods for simulations, it is often necessary to first simplify the typically large Hilbert space $\mathscr{H}$ of the quantum system. One way of doing this is to constrain the states to a symplectic submanifold $M \subset \mathscr{H}$. This is for instance done in widely applied model reductions like the Born-Oppenheimer approximation, Gaussian wave packet dynamics, or time-dependent Hartree-Fock methods. The dynamics on the submanifold M is then governed by the constrained Hamiltonian system

$$\omega \restriction_M (\bullet, \Xi_{h\restriction_M}) = dh \restriction_M . \tag{2.5}$$

The approximative dynamics generated by (2.5) is optimal in the sense that $\Xi_{h\restriction_M}$ is the least square approximation of Ξ_h among all vector fields on M, see e.g. [Lub08, §II.1.2] or [OL13, Proposition 2.4]. The variational formulation of this symplectic reduction procedure is known as the Dirac-Frenkel variational principle. It was used for the first time in [Dir30] in order to derive the equations for the time-dependent Hartree-Fock method. For more details and instructive examples we refer to [Lub08, §II], [OL13], and [HZ07].

2.3 Classical Mechanics

Let us consider $\mathbb{R}^d$ as the configuration space of a classical mechanical system. For example, a system of N classical point particles moving in $\mathbb{R}^3$ has the position configuration space $\mathbb{R}^{3N}$. The cotangent bundle $T^*\mathbb{R}^d \cong \mathbb{R}^{2d}$ is called the momentum phase space of classical mechanics. For a phase space vector $z = (q, p) \in \mathbb{R}^{2d}$, q and p are called the position and momentum, respectively.

The phase space $\mathbb{R}^{2d}$ is a symplectic manifold with the canonical symplectic form

$$\Omega\left((x,\xi),(q,p)\right) = \xi^T q - x^T p, \tag{2.6}$$

which one can also rewrite by means of the antisymmetric bilinear form

$$\Omega(z,w) = \langle Jz, w\rangle \quad \text{with} \quad J = \begin{pmatrix} 0 & \mathrm{Id} \\ -\mathrm{Id} & 0 \end{pmatrix}. \tag{2.7}$$

The symplectic group $\mathrm{Sp}(\mathbb{R}, d)$ constists of those invertible matrices $S \in \mathbb{R}^{2d\times 2d}$, for which $z \mapsto Sz$ is a linear symplectomorphism. This is equivalent to the condition that S satisfies

$$S^T J S = J.$$

In §7.1 we recall more concepts of symplectic linear algebra.

Let $h : \mathbb{R}^{2d} \to \mathbb{R}$ be a Hamilton function. Then, Hamilton's equation for h reads

$$\partial_t z(t) = J\nabla h(z(t)), \tag{2.8}$$

and the Hamiltonian flow $\Phi^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ of (2.8) is a canonical transformation, that is,

$$\left(D\Phi^t(z)\right)^T J D\Phi^t(z) = J \tag{2.9}$$

for all $t \in \mathbb{R}$ and $z \in \mathbb{R}^{2d}$. The observables of classical mechanics are smooth functions $a : \mathbb{R}^{2d} \to \mathbb{R}$, and the Poisson bracket (2.3) of

two observables a, b is given by

$$\{a, b\}(z) = \langle J\nabla a(z), \nabla b(z)\rangle\,. \tag{2.10}$$

The evolution (2.4) of a along the Hamiltonian flow Φ^t of h hence reads

$$\partial_t(a \circ \Phi^t) = \{h, a\} \circ \Phi^t, \tag{2.11}$$

which can be seen as a classical analog of Heisenberg's equation (1.4). We come back to this viewpoint in chapter §11 for our presentation of the Egorov theorem.

2.4 Born-Oppenheimer Approximation

The approximation of Born and Oppenheimer [BO27] is the most fundamental simplification in molecular quantum dynamics. It is commonly used as the starting point for further theoretical investigations and approximations.

Motivated by the mass difference between nuclei and electrons, the idea is to implement an adiabatic decoupling of the nuclear and electronic degrees of freedom in order to derive an effective Hamiltonian acting on nuclear wave functions only. For most real life molecules this is an enourmous simplification, since the nuclear configuration space $\mathbb{R}^{3N}$ is significantly smaller than the full configuration space $\mathbb{R}^{3(N+L)}$. First mathematical studies of this approximation have been conducted by Hagedorn [Hag80, Hag87, Hag88], and Combes, Duclos, and Seiler [CDS81].

For readability, let us assume that all nuclei in the molecule have the same mass[7] $m > 0$. Then, the molecular Hamiltonian (1.6) on $L^2(\mathbb{R}^{3N}, \mathscr{H}_{\mathrm{el}})$ reads

$$H_{\mathrm{mol}} = -\tfrac{\varepsilon^2}{2}\Delta_X + H_{\mathrm{el}} + V_{\mathrm{nn}},$$

where $H_{\mathrm{el}}(X)$ has been defined in (1.8), and $\varepsilon = \sqrt{m_e/m} > 0$ is small. In order to clarify the main ideas, in this section we

[7] If the nuclei are not of the same mass, one can use rescaled coordinates.

only discuss the first order Born-Oppenheimer approximation for the electronic ground state E_0 of the molecular Coulomb system from §1.3. We furthermore ignore the electronic spin such that E_0 becomes a simple eigenvalue. Later, in §2.5, we comment on various possible generalizations.

With the notation from §1.4, let $\eta_0(\bullet, X) \in \mathscr{H}_{\mathrm{el}}$ be a normalized eigenfunction associated with the ground state energy $E_0(X)$ of $H_{\mathrm{el}}(X)$, and recall that E_0 is globally isolated from the rest of the electronic spectrum. Then, a well-known regularity result [CS78, Theorem 2] of Combes and Seiler implies that the orthogonal projector

$$P_0(X) = |\eta_0(\bullet, X)\rangle\langle\eta_0(\bullet, X)| \in \mathcal{L}(\mathscr{H}_{\mathrm{el}})$$

on the one-dimensional eigenspace associated with $E_0(X)$ is twice differentiable in $X \in \mathbb{R}^{3N}$. Consequently, the range M of the fibered projector

$$P_0 = \int_{\mathbb{R}^{3N}}^{\oplus} P_0(X) dX \in \mathcal{L}(\mathscr{H}_{\mathrm{mol}})$$

has the structure of a twice differentiable complex vector subbundle of $\mathscr{H}_{\mathrm{mol}}$, with the one-dimensional fibers $\mathrm{Range} P_0(X) \subset \mathscr{H}_{\mathrm{el}}$. Since $\mathbb{R}^{3N}$ is contractible, M is a trivial vector bundle and, hence, the normalized eigenfunction $\eta_0(\bullet, X) \in \mathscr{H}_{\mathrm{el}}$ can be chosen differentiably in $X \in \mathbb{R}^{3N}$.

The bundle M can be mapped isometrically into the less complicated nuclear Hilbert space $L^2(\mathbb{R}^{3N})$ by means of the unitary map

$$U : M \to L^2(\mathbb{R}^{3N}), \quad \int_{\mathbb{R}^{3N}}^{\oplus} \psi(X)\eta_0(\bullet, X)\, dX \mapsto \psi(X).$$

We are interested the dynamics on the simpler space $L^2(\mathbb{R}^{3N})$ induced by the restricted dynamics (2.5) on the symplectic submanifold M. The effective Hamiltonian on $L^2(\mathbb{R}^{3N})$ can be computed to be

$$U^* P_0 H_{\mathrm{mol}} P_0 U = \tfrac{1}{2}\left(-\mathrm{i}\varepsilon\nabla - \varepsilon\mathcal{A}\right)^2 + E_0 + V_{\mathrm{nn}} + \tfrac{\varepsilon^2}{2}\phi, \qquad (2.12)$$

see for example [PST07, (16)] or [Lub08, §II.2.2]. Here,

$$\mathcal{A}(X) = \mathrm{i}\,\langle \eta_0(\bullet, X), \nabla_X \eta_0(\bullet, X)\rangle_{\mathscr{H}_{\mathrm{el}}}$$

is the coefficient of the Berry connection, and

$$\phi(X) = \langle \nabla_X \eta_0(\bullet, X), (\mathrm{Id} - P_0(X))\nabla_X \eta_0(\bullet, X)\rangle_{\mathscr{H}_{\mathrm{el}}}$$

is the Born-Huang potential. Although $\mathcal{A}$ formally plays the role of an electromagnetic vector potential, the origins of the Berry connection are purely geometric, see also §3.5 for more details.

One intuitively expects the decoupling between nuclear and electronic dynamics to become stronger as ε gets small. In fact, one can prove the propagation result (2.16) with errors of size $O(\varepsilon)$ for the first order Born-Oppenheimer Hamiltonian[8]

$$H_{\mathrm{BO}}^{(1)} = \tfrac{1}{2}\,(-\mathrm{i}\varepsilon\nabla - \varepsilon\mathcal{A})^2 + E_0 + V_{\mathrm{nn}} \tag{2.13}$$

and initial data $\Psi(X, x) = \psi(X)\eta_0(x, X)$ in M of uniformly bounded total energy in ε. Moreover, Ψ must be localized away from the nuclear collision set

$$\mathcal{C} = \{X \in \mathbb{R}^{3N}, \exists i \neq j \text{ with } X_i = X_j\}. \tag{2.14}$$

That is, there is a compact set

$$K \subset\subset \mathbb{R}^{3N} \setminus \mathcal{C} \quad \text{with} \quad \|\Psi\|_{L^2(K^c, \mathscr{H}_{\mathrm{el}})} = O(\varepsilon^\infty), \tag{2.15}$$

and by the classical propagation of localization sets, see e.g. [MS09, Corollary 2.6], the propagated wave function stays localized away from $\mathcal{C}$ for all times. Bounding the energy ensures that the nuclei move on a slower time scale than the electrons, which is crucial for an adiabatic decoupling of the dynamics to make sense. Then,

[8] We omitted the Born-Huang potential since its impact on the dynamics is of size $O(\varepsilon)$ and for a proper second order Born-Oppenheimer approximation one needs to include another term in the Hamiltonian, see [PST07].

by [MS09, Theorems 12.1 and 12.2] there is a constant $C > 0$ independent of ε such that[9]

$$\|\mathrm{e}^{-\mathrm{i}H_{\mathrm{mol}}t/\varepsilon}\Psi - U^*\mathrm{e}^{-\mathrm{i}H_{\mathrm{BO}}^{(1)}t/\varepsilon}\psi\|_{\mathscr{H}_{\mathrm{mol}}} \leq C\varepsilon(1+|t|). \tag{2.16}$$

Hence, one can approximate quantum molecular dynamics by propagating nuclear wave functions $\psi \in L^2(\mathbb{R}^{3N})$ only. Afterwards, one can reconstruct a wave function for the whole system by means of the map U^*. In practice, however, the semiclassical Schrödinger equation

$$i\varepsilon\partial_t\psi(t) = H_{\mathrm{BO}}^{(1)}\psi(t), \quad \psi(0) = \psi_0 \in L^2(\mathbb{R}^{3N}), \tag{2.17}$$

is widely treated as a bona fide model for the dynamics of molecules. In particular, one often only considers nuclear observables of the form $A \otimes \mathrm{Id}_{\mathscr{H}_{\mathrm{el}}}$, and omits the reconstruction of the full wave function.

2.5 Higher Order and Multiple Surfaces

The Born-Oppenheimer approximation (2.16) is a very special case of a general adiabatic decoupling result, see e.g. [MS09, Theorem 7.1], which can be applied to a wide class of quantum mechanical Hamiltonians, notably for Schrödinger operators with electromagnetic fields and general interaction potentials, see [ST01, PST07, MS09]. In this section we briefly indicate some possible generalizations, where we stick to the molecular Hamiltonian H_{mol} for presentation purposes.

For deriving higher order Born-Oppenheimer Hamiltonians $H_{\mathrm{BO}}^{(n)}$, which satisfy the estimate (2.16) with errors of size $O(\varepsilon^n)$, one constructs a so-called super-adiabatic subspace

$$M^\varepsilon = P_0^\varepsilon \mathscr{H}_{\mathrm{mol}}, \quad P_0^\varepsilon = P_0 + O(\varepsilon), \tag{2.18}$$

[9] We use the time rescaling $t \mapsto t/\varepsilon$ in order to capture the effective time scale of nuclear motion.

which is invariant under H_{mol} up to $O(\varepsilon^\infty)$ errors. With the corresponding unitary map $U^\varepsilon : M^\varepsilon \to L^2(\mathbb{R}^{3N})$ into the nuclear Hilbert space, Thereom 2.1 from [MS09] implies

$$\mathrm{e}^{-\mathrm{i}H_{\mathrm{mol}}t/\varepsilon}\Psi = (U^\varepsilon)^* \mathrm{e}^{-\mathrm{i}H^\varepsilon t/\varepsilon} U^\varepsilon \Psi + O(\varepsilon^\infty(1+|t|)) \tag{2.19}$$

for suitable initial data $\Psi \in M^\varepsilon$. The Hamiltonian H^ε admits an asymptotic expansion in powers of ε that can be used for deriving a formula for $H_{\mathrm{BO}}^{(n)}$.

Suppose that we consider a PES E which is only locally separated[10] from the rest of the electronic spectrum within some bounded open set $\Omega \subset \mathbb{R}^{3N}$. Then, one can still define the bundle M^ε analoguously to (2.18), and (2.19) holds as long as the propagated state stays localized within Ω. This localization time can be estimated by means of the techniques discussed in part §III. However, often the PES on which the initial state is localized has crossings with other PES in the region of physical interest. For an adequate description of the dynamics one consequently has to incorporate several electronic energy levels, and allow for transitions between them.

Suppose $\Omega \subset \mathbb{R}^{3N}$ is bounded and contractible, and there are $\ell \in \mathbb{N}$ relevant PES $F_1, \dots, F_\ell$ in Ω, which may have crossings in between each other but are separated from the rest of the electronic spectrum. Then, one can again construct a bundle M^ε, and a unitary map $U^\varepsilon : M^\varepsilon \to L^2(\mathbb{R}^{3N}, \mathbb{C}^\ell)$ into the multi-band reference Hilbert space $L^2(\mathbb{R}^{3N}, \mathbb{C}^\ell)$, such that (2.19) holds as long as the solution stays localized in Ω. For multiple PES with crossings, however, this time is in practice hard to estimate due to the absense of Egorov type theorems.

Example. Suppose that the two PES $F_1(X)$ and $F_2(X)$ are spectrally isolated for all $X \in \mathbb{R}^{3N}$. If $\Gamma \subset \mathbb{C}$ is a positively oriented countour enclosing $F_1(X), F_2(X)$ but no other parts of the spectrum of H_{el},

[10] Except for the ground state E_0, one expects this to be the generic case.

the Riesz projector

$$P(X) = \frac{1}{2\pi \mathrm{i}} \oint_{\Gamma} (z - H_{\mathrm{el}})^{-1} dz \tag{2.20}$$

is the rank two orthogonal projector on the direct sum of the eigenspaces associated with $F_1(X)$ and $F_2(X)$, see [Kat95, §VI.5.4]. Then, by [PST07, (56)],

$$\begin{aligned}\left(H_{\mathrm{BO}}^{(1)}\right)_{ij} =& \tfrac{1}{2} \sum_{k=1}^{2} \left(-\delta_{ik} \mathrm{i}\varepsilon\nabla - \varepsilon \mathcal{A}_{ik}\right) \cdot \left(-\delta_{kj} \mathrm{i}\varepsilon\nabla - \varepsilon \mathcal{A}_{kj}\right) \\ &+ V_{\mathrm{nn}} \mathrm{Id}_{\mathbb{C}^2} + W,\end{aligned}$$

$i, j \in \{1, 2\}$, is a first order Born-Oppenheimer Hamiltonian. The matrix $W(X) \in \mathbb{C}^{2\times 2}$ is defined as

$$W_{ij}(X) = \left\langle \chi_i(\bullet, X), H_{\mathrm{el}}(X) \chi_j(\bullet, X) \right\rangle \tag{2.21}$$

for some basis $\{\chi_1(\bullet, X), \chi_2(\bullet, X)\}$ of $P(X)\mathscr{H}_{\mathrm{el}}$, and has the eigenvalues $\{F_1(X), F_2(X)\}$.

$$\mathcal{A}_{ij}(X) = \mathrm{i} \left\langle \chi_i(\bullet, X), \nabla_X \chi_j(\bullet, X) \right\rangle \tag{2.22}$$

are generalized Berry connection coefficients that couple the dynamics on the two energy levels F_1 and F_2. ■

Remark 2 (Smooth coefficients)**.** *With the techniques from [KMSW92] one can show that locally the electronic Hamiltonian $H_{\mathrm{el}}(X)$ is unitary equivalent to an operator that is smooth in X. As a consequence, there is a frame $\{\chi_1(\bullet, X), \chi_2(\bullet, X)\}$ of $P(X)\mathscr{H}_{\mathrm{el}}$ such that both $\mathcal{A}(X)$ and $W(X)$ are smooth functions of $X \in \Omega$, see also [MS09, Remark 12.4] and §3.5. In particular, as has already been observed by Hunziker in [Hun86], the PES E_k are real analytic functions away from eigenvalue crossings or hitting thesholds.*

Since many aspects of interesting chemical reactions can be explained by non-adiabatic transitions between different electronic energy levels, quantum dynamics on several PES is a topic of great importance in chemistry, see [DYK04] for an overview. Systems with eigenvalue crossings are also an active field of mathematical research, for further reading and examples we refer to Hagedorn's monograph [Hag94], and the research articles [CdV03, FKL03, LT05, LST07, BDLT15].

3 Potential Energy Surfaces

How do the eigenvalues of a matrix change if one perturbs the matrix? The answer to this question plays an important role in a wide range of mathematical areas, including, for example, numerical linear algebra and random matrix theory; see [Tao12, §1.3]. In molecular quantum dynamics this problem appears if one explores the dependence of potential energy surfaces $E_j(X)$ on the nuclear configuration X. Understanding the regularity properties of PES is helpful for the a priori analysis of molecular quantum systems as well as for simulations.

In the first section of this chapter we recall classical results for Hermitian matrices. Therafter, we discuss their extension to the selfadjoint family $X \mapsto H_{\mathrm{el}}(X)$ of electronic Coulomb Hamiltonians, and present Lipschitz estimates for PES.

3.1 Eigenvalues of Hermitian Matrices

For a Hermitian matrix $M \in \mathbb{C}^{d\times d}$, let $\lambda_1(M) \leq \ldots \leq \lambda_d(M)$ denote the ordered eigenvalues, which can be computed via the Courant-Fischer minimax principle (1.10). In [Wey12] Hermann Weyl derived the following remarkable stability result for the eigen-

values of Hermitian matrices. We include a short proof.

Lemma 1 (Weyl inequality)**.** *Suppose that $A, B \in \mathbb{C}^{d\times d}$ are Hermitian matrices. Then, the ordered eigenvalues of A and B satisfy the inequality*

$$\max_{1\leq j\leq d} |\lambda_j(A) - \lambda_j(B)| \leq \|A - B\|_{\mathcal{L}(\mathbb{C}^N)}. \tag{3.1}$$

Proof. We start by recalling the Courant-Fischer minimax principle

$$\lambda_k(A) = \inf_{\substack{V\subset\mathbb{C}^N \\ \dim V = k}} \sup_{\substack{x\in V \\ \|x\|=1}} \langle x, Ax\rangle .$$

Then, after writing

$$\langle x, Ax\rangle = \langle x, Bx\rangle + \langle x, (A-B)x\rangle , \tag{3.2}$$

the assertion follows from the estimate

$$\begin{aligned}\lambda_j(A) &\leq \inf_{\substack{V\subset\mathbb{C}^N \\ \dim V = j}} \sup_{\substack{x\in V \\ \|x\|=1}} \Big(\langle x, Bx\rangle + \|A-B\|_{\mathcal{L}(\mathbb{C}^N)}\Big) \\ &\leq \lambda_j(B) + \|A-B\|_{\mathcal{L}(\mathbb{C}^N)}.\end{aligned}$$

□

Lemma 1 implies that the ordered eigenvalues of Hermitian matrices are uniformly Lipschitz continuous in the matrix. In fact, for every continuous family of matrices one can choose a numbering of the eigenvalues such that they become continuous, see [Kat95, §II.5.1]. However, a Lipschitz estimate of the form (3.1) does not hold in general since the eigenvalues of non-normal matrices can be unstable, see the examples in [TE05, §3]. Perturbation theory for eigenvalues has been extensively studied since the works of Rellich in the 1930s, and a standard reference is the classic monograph of Kato [Kat95].

As a next step we turn towards differentiable matrix families. The following simple result for curves of matrices is known as

Hadamard's first variational formula. It relates derivatives of eigenvalues to derivatives of the matrix.

Lemma 2 (Hadamard). *Let $A : \mathbb{R} \to \mathbb{C}^{d\times d}$ be a differentiable curve of Hermitian matrices, and $\lambda(t)$ a continuous eigenvalue of constant multiplicity m for t in some open set $\Omega \subset \mathbb{R}$. Then, λ is differentiable in Ω and one has*

$$\partial_t \lambda(t) = \langle v(t), \partial_t A(t) v(t) \rangle ,$$

where $v(t)$ is some normalized eigenvector belonging to $\lambda(t)$.

Proof. The resolvent $z \mapsto (z - A(t))^{-1}$ is differentiable in t for z away from the eigenvalues of $A(t)$. Consequently, by Riesz' formula (2.20), the projector $P : \Omega \to \mathbb{C}^{d\times d}$ on the m-dimensional eigenspace associated with λ is differentiable as well, and the same holds true for the eigenvalue

$$\lambda(t) = \tfrac{1}{m} \mathrm{tr} \left(A(t) P(t) \right) .$$

We can choose, at least locally, a differentiable eigenvector

$$A(t)v(t) = \lambda(t)v(t), \tag{3.3}$$

which is normalized. Scalar multiplication of

$$\partial_t A(t) v(t) + A(t) \partial_t v(t) = \partial_t \lambda(t) v(t) + \lambda(t) \partial_t v(t),$$

with $v(t)^*$ gives

$$\begin{aligned} \langle v(t), \partial_t A(t) v(t) \rangle &= - \langle v(t), A(t) \partial_t v(t) \rangle + \partial_t \lambda(t) \\ &\quad + \lambda(t) \langle v(t), \partial_t v(t) \rangle \\ &= \partial_t \lambda(t), \end{aligned}$$

since A is Hermitian. □

In physics and chemistry, the generalization of Lemma 2 to parametrized electronic ground state energies is known as the Hellmann-Feynman theorem, which is the central topic of §4.

3.2 An Operator Inequality

It is our aim to generalize Lemma 1 and Lemma 2 to the bound state energies E_j of the electronic Coulomb Hamiltonian H_{el}. The main ingredient is the following Lipschitz type operator inequality from [HG80], which immediately implies the Lipschitz continuity of PES. It is also used in chapter §4 for proving the differentiability of the clamped nuclei Hamiltonian.

Lemma 3 (Hunziker-Günther)**.** *Let $H_0 = -\frac{1}{2}\Delta$. Then, for all $X, Y \in \mathbb{R}^{3N}$ we have*

$$H_{\mathrm{el}}(Y) - H_{\mathrm{el}}(X) \leq \|X - Y\|_{\mathcal{Z}} H_0 \tag{3.4}$$

in the sense of quadratic forms, with the charge rescaled norm $\|v\|_{\mathcal{Z}} = a_0^{-1} \sum_{k=1}^{N} |\mathcal{Z}_k v_k|$ on $\mathbb{R}^{3N}$.

The proof of Lemma 3 heavily relies on the no-binding criterion for electronic dipoles by Fermi and Teller [FT47], which can be phrased as follows. Consider a neutral dipole consisting of two particles with charges $\pm\mathcal{Z}$ fixed at $X, Y \in \mathbb{R}^3$, and the corresponding Coulomb Hamiltonian

$$H_{\mathrm{dip}}(X, Y, \mathcal{Z}) = -\tfrac{1}{2}\Delta + \mathcal{Z}(|x - X|^{-1} - |x - Y|^{-1}). \tag{3.5}$$

By [HG80, Theorem 1], there is a critical constant $a_0 \in (1.245, 1.288)$ such that the spectrum of $H_{\mathrm{dip}}(X, Y, \mathcal{Z})$ consist only of the interval $[0, \infty)$ if and only if

$$|\mathcal{Z}(X - Y)| \leq a_0,$$

see also [RS78, §XIII.11] and [Cra67]. One can then rewrite $H_{\mathrm{el}}(Y) - H_{\mathrm{el}}(X) - H_0$ as a sum of neutral two-point dipole operators, and apply the Fermi-Teller theorem. A complete proof is contained in [HG80].

Together with the relative boundness estimate

$$\langle \psi, H_0 \psi \rangle \leq \gamma \langle \psi, H_{\mathrm{el}}(X)\psi \rangle + \alpha \langle \psi, \psi \rangle, \tag{3.6}$$

which holds uniformly in X for some $\gamma, \alpha > 0$, Lemma 3 implies the uniform Lipschitz continuity of PES:

Lemma 4 ([HG80])**.** *For any $\alpha, \gamma > 0$ that comply with* (3.6)*, there is a constant $\Lambda \leq \alpha$ such that the Courant minimax values $\lambda_1(X) \leq \lambda_2(X) \leq \ldots$ of $H_{\mathrm{el}}(X)$ satisfy*

$$\lambda_k(X) - \lambda_k(Y) \leq \Lambda \|X - Y\|_{\mathcal{Z}}.$$

As a consequence, the electronic PES $X \mapsto E_k(X)$ are uniformly Lipschitz continuous.

We remark that Lemma 3 can also be read as a Lipschitz inequality on the operator level. This will become important in our proof of the Hellmann-Feynman theorem.

3.3 Electronic Binding Forces

Let us take a closer look at the Lipschitz constant Λ for PES from Lemma 4. As remarked in [HG80, Remark (iv)], it *"...gives an upper bound for the electronic contribution to the binding forces in a molecule..."*. Hence, from a physical viewpoint it is interesting to estimate the size of Λ. We present two different bounds for Λ. The first one in Proposition 1 is derived from a direct estimate, while the second one in §3.4 is deduced from a stability of matter inequality.

Proposition 1. *The Lipschitz constant Λ from Lemma 4 satisfies*[11]

$$\Lambda \leq LN^2 \tfrac{|\mathcal{Z}|^2}{8}.$$

Proof. We start with the crude estimate

$$H_{\mathrm{el}}(X) \geq \sum_{k=1}^{L} \sum_{j=1}^{N} \tfrac{1}{N} \left(-\tfrac{1}{2}\Delta_{x_k} - \mathcal{Z}_j N |x_k - X_j|^{-1} \right). \tag{3.7}$$

[11] Recall that L and N are the numbers of electrons and nuclei, respectively, and $\mathcal{Z}_j > 0$ is the charge of the jth nucleus.

by simply ignoring the positive electron-electron repulsion V_{ee}. The right hand side of (3.7) is a sum of hydrogen type atoms for which the ground state energy is given by

$$\inf \sigma \left(-\tfrac{1}{2}\Delta_{x_k} - \mathcal{Z}_j N |x_k - X_j|^{-1} \right) = -\tfrac{\mathcal{Z}_j^2 N^2}{32}.$$

Consequently, we have

$$H_{\mathrm{el}}(X) \geq -LN^2 \tfrac{|\mathcal{Z}|^2}{32},$$

and for any $K > 1$ one obtains the inequality

$$\begin{aligned} KH_{\mathrm{el}}(X) &\geq -\tfrac{1}{2}\Delta + (K-1) \sum_{k=1}^{L} \left(-\tfrac{1}{2}\Delta_{x_k} - \tfrac{K}{K-1} \sum_{j=1}^{N} \mathcal{Z}_j |x_k - X_j|^{-1} \right) \\ &\geq -\tfrac{1}{2}\Delta - \tfrac{K^2}{K-1} LN^2 \tfrac{|\mathcal{Z}|^2}{32}. \end{aligned}$$

The assertion follows from the relative boundedness condition (3.6) since

$$-\tfrac{1}{2}\Delta \leq 2H_{\mathrm{el}}(X) + 4LN^2 \tfrac{|\mathcal{Z}|^2}{32}. \tag{3.8}$$

for the optimal choice $K = 2$. □

Consequently, we note that all electronic PES are globally constrained to the interval

$$E_k(X) \in \left[-LN^2 \tfrac{|\mathcal{Z}|^2}{16}, 0 \right], \tag{3.9}$$

by invoking (3.8) .

3.4 Lipschitz Estimates via Stability of Matter

In view of the observed stability of molecules in nature the bound from Proposition 1 is unsatisfactory since one would expect the

electronic binding forces to be approximately linear in N and L. For proving such an physically meaningful bound on Λ one can use the sophisticated stability bounds which have been derived for clamped nuclei Hamiltonians.

For a nuclear configuration away from the collision set $\mathcal{C}$, and $\alpha > 0$, we define the Hamiltonian

$$H^\alpha(X) = -\tfrac{1}{2}\Delta + \alpha(V_{ee} + V_{ne}(\cdot, X) + V_{nn}(X)), \quad X \notin \mathcal{C},$$

which in contrast to $H_{\mathrm{el}}(X)$ includes the nuclear repulsion potential V_{nn}. The electrostatic coupling constant α is given by $e^2 \approx 1/137$ if one looks at the Schrödinger equation in natural units. Since we use atomic units, the electrostatic coupling constant is 1, and we gain one additional degree of freedom for our estimates.

One stability of matter estimate obtained via Thomas-Fermi density functional theory is the following result from [LS10, §7.3].

Lemma 5 (Stability via Thomas-Fermi Theory)**.** *For normalized wave functions $\psi \in \mathscr{H}_{\mathrm{el}}$ that are in the form domain of $H^\alpha(X)$ one has the inequality*

$$\langle \psi, H^\alpha(X)\psi \rangle \geq -0.231\alpha^2 L 2^{2/3} \left(1 + 1.77\sqrt{\frac{1}{L}\sum_{j=1}^{N} \mathcal{Z}_j^{7/3}}\right)^2,$$

which holds uniformly in X.

Lemma 5 implies the following bound.

Proposition 2. *The uniform Lipschitz constant Λ for electronic PES from Lemma 4 satisfies*

$$\Lambda \leq 1.47 \left(\sqrt{L} + 1.77\sqrt{\sum_{j=1}^{N} \mathcal{Z}_j^{7/3}}\right)^2 =: \ell(N, L, \mathcal{Z}).$$

Proof. Assume that $X \notin \mathcal{C}$, and let $K > 1$ be an arbitrary parameter. Then, by Lemma 5,

$$\begin{aligned} K \cdot H^1(X) &\geq -\tfrac{1}{2}\Delta + (K-1)H^{\frac{K}{K-1}}(X) \\ &\geq -\tfrac{1}{2}\Delta - \tfrac{K^2}{4(K-1)}\ell(N,L,\mathcal{Z}) \end{aligned}$$

on the form domain of $H^1(X)$. Choosing the optimal value of K as in the proof of Proposition 1 yields

$$\begin{aligned} -\tfrac{1}{2}\Delta &\leq 2H^1(X) + \ell(N,L,\mathcal{Z}) \\ &= 2H_{\mathrm{el}}(X) + 2V_{nn}(X) + \ell(N,L,\mathcal{Z}). \end{aligned} \tag{3.10}$$

Consequently, with the operator family

$$T(X) := -\tfrac{1}{2}\Delta - 2V_{nn}(X) - \ell(N,L,\mathcal{Z}), \quad X \notin \mathcal{C},$$

and $\gamma(X) := 2V_{nn}(X) + \ell(N,L,\mathcal{Z})$, Lemma 3 implies that the inequality

$$H_{\mathrm{el}}(X) - H_{\mathrm{el}}(Y) \leq \|X - Y\|_{\mathcal{Z}}(T(W) + \gamma(W)) \tag{3.11}$$

holds in the sense of quadratic forms for for all $X, Y \in \mathbb{R}^{3N}$ and $W \in \mathbb{R}^{3N} \setminus \mathcal{C}$. Furthermore, by (3.10) we know that[12]

$$\mathbb{1}_{(-\infty,\delta)}(H_{\mathrm{el}}(X))T(W)\mathbb{1}_{(-\infty,\delta)}(H_{\mathrm{el}}(X)) \leq 2\delta. \tag{3.12}$$

for all $W \in \mathbb{R}^{3N} \setminus \mathcal{C}$, $X \in \mathbb{R}^{3N}$, and $\delta > 0$. By (3.12), for arbitrary $X \in \mathbb{R}^{3N}$ and $W \notin \mathcal{C}$, the eigenspace associated with the PES $E_k(X)$ is contained in the set

$$S = \{\psi \in \mathscr{H}_{\mathrm{el}} : \langle \psi, T(W)\psi \rangle \leq 2\delta \|\psi\|^2\}$$

since $\Sigma(X) \leq 0$. Now, we can mimic the proof of Weyl's inequality

[12] The spectral projection $\mathbb{1}_{(-\infty,\delta)}(H_{\mathrm{el}}(X))$ is defined via Borel functional calculus.

from Lemma 1. Starting from (3.2), by using (3.11) we estimate

$$\begin{aligned}\lambda_k\left(H_{\mathrm{el}}(X)\right) &= \inf_{\substack{V\subset S\\ \dim V=k}} \sup_{\substack{\psi\in V\\ \|\psi\|=1}} \left\langle \psi, \left(H_{\mathrm{el}}(Y) + \left(H_{\mathrm{el}}(X) - H_{\mathrm{el}}(Y)\right)\right)\psi\right\rangle \\ &\leq \inf_{\substack{V\subset S\\ \dim V=k}} \sup_{\substack{\psi\in V\\ \|\psi\|=1}} \left\langle \psi, H_{\mathrm{el}}(Y)\psi\right\rangle + \sup_{\substack{\psi\in S\\ \|\psi\|=1}} \left\langle \psi, \left(H_{\mathrm{el}}(X) - H_{\mathrm{el}}(Y)\right)\psi\right\rangle \\ &\leq \lambda_k(H_{\mathrm{el}}(Y)) + \|X-Y\|_{\mathcal{Z}} \left(\sup_{\psi\in S, \|\psi\|=1} \left\langle \psi, T(W)\psi\right\rangle + \gamma(W)\right).\end{aligned}$$

Inserting the definition of S and taking the infimum over all W yields

$$\lambda_k\left(H_{\mathrm{el}}(X)\right) - \lambda_k\left(H_{\mathrm{el}}(Y)\right) \leq \|X-Y\|_{\mathcal{Z}}(2\delta + \ell(N,L,Z)), \quad (3.13)$$

and the assertion follows as $\delta \to 0$. □

The bound provided in Proposition 2 is physically more meaningful than the one from Proposition 1, since it scales approximately linear in the number of electrons L and nuclei N. Nevertheless, in general this upper bound is far from beeing optimal, and PES typically have much smaller derivatives.

We note that the same proof works for any stability estimate of the form given in Lemma 5, in particular for Theorem 7.1 from [LS10] which provides a bound via the Lieb-Thirring inequality and exchange energy estimates.

3.5 Berry Connection

In this section we review some properties of the Berry connection, which arises naturally in the derivation of the Born-Oppenheimer approximation, see §2.4.

Suppose that the PES E_j is separated from the rest of the electronic spectrum within some region $\Omega \subset \mathbb{R}^{3N}$, and let $P_j(X) =$

$|\eta_j(\bullet, X)\rangle\langle\eta_j(\bullet, X)|$, $X \in \Omega$, denote the projector on the eigenspace associated with $E_j(X)$. Then,

$$S = \{(X, \psi) : X \in \Omega, \psi \in P_j(X)\mathscr{H}_{\mathrm{el}}\} \tag{3.14}$$

is a complex subbundle of the trivial Hilbert space bundle $B = \Omega \times \mathscr{H}_{\mathrm{el}} \mapsto \Omega$. The Berry connection is the connection induced on S by the trivial connection on B, see also the comments before Proposition 6 in [ST13]. If Ω is simply connected, the vector bundle S is trivial and the coefficients $\mathcal{A}$ can be removed by a gauge transformation

$$\eta_j(\bullet, X) \mapsto \mathrm{e}^{\mathrm{i}\alpha(X)}\eta_j(\bullet, X).$$

If Ω is not simply connected, S might not be a trivial bundle anymore, in which case the Berry connection has a physical impact and its coefficients cannot be gauged away. The study of geometric phases and the Berry connection started with the works of Berry [Ber84] and Simon [Sim83].

In the case of multiple PES, the off-diagonal gauge potentials $\mathcal{A}_{ij}$, $i \neq j$, defined in (2.22) are responsible for non-adiabatic transitions between the different electronic energy levels. Assume that $\Omega \subset \mathbb{R}^{3N}$ is simply connected and the relevant PES

$$\{E_k\}_{k\in\mathcal{J}}, \quad |\mathcal{J}| = \ell < \infty,$$

are separated from the rest of the electronic spectrum. From [CS78] we know that the projector $P : \Omega \to \mathcal{L}(\mathscr{H}_{\mathrm{el}})$ on the trivial eigenspace bundle associated with $\{E_k : \Omega \to \mathbb{R}\}_{k\in\mathcal{J}}$ is differentiable, and hence there is a differentiable global frame

$$F : X \mapsto (\chi_1(\bullet, X), \ldots, \chi_\ell(\bullet, X)).$$

As commented in Remark 2, for such a frame F one can show that the generalized Berry coefficients $\mathcal{A}_{jk}(X)$ as well as the potential matrix $W(X)$ defined in (2.21) are smooth functions of X.

In chemistry, frames of Range$P$ are called *diabatic bases*[13] if the non-adiabatic gauge potentials $\mathcal{A}_{jk}$ are smooth. If there is a diabatic basis in which all gauge potentials $\mathcal{A}_{jk}$ are equal to zero, this frame is called a *strictly diabatic basis*, see [MT82]. A necessary condition for the existence of such a basis is that the gauge field tensors

$$\omega_{jk} = -\mathrm{i}\left(\partial_j \mathcal{A}_k - \partial_k \mathcal{A}_j\right) + [\mathcal{A}_k, \mathcal{A}_j], \quad j,k \in \{1,\ldots,3N\},$$

vanish in Ω, see [PST07]. Here, $\mathcal{A}_j$ denotes the $\ell \times \ell$ matrix of the jth entries of the gauge vector potentials. The matrix-valued maps ω_{jk} can be seen as off-diagonal generalizations of the curvature two-form for the Berry connection.

For an *adiabatic basis*, which consists of bound states associated with the PES $\{E_k(X)\}_{k\in\mathcal{J}}$, the situation is different. In an adiabatic basis the potential matrix W is diagonal with the entries $\{E_k\}_{k\in\mathcal{J}}$. However, an adiabatic frame is usually not differentiable, and $\mathcal{A}_{ij}$ and W are only smooth away from crossing points of different PES. While W is still uniformly Lipschitz continuous by Corollary (4), the gauge potentials $\mathcal{A}_{ij}$ typically exhibit singularities at points where two PES E_k, E_j, $j \neq k \in \mathcal{J}$ cross.

3.6 Diabatization

In most applications one usually only knows the approximate PES and bound states obtained from ab initio calculations. It is a formidable problem, which is in general unsolved, to find a basis which is diabatic or at least "quasidiabatic" in the sense that the gauge potentials $\mathcal{A}_{jk}$ are not too singular.

Suppose we are in the setting of §3.5, with ℓ relevant PES and some given frame $F(X) = (\chi_1(\bullet, X), \ldots, \chi_\ell(\bullet, X))$ for the corresponding eigenspace bundle. If the unitary change of basis $T : \Omega \to U(\ell)$ is differentiable almost everywhere, and $\mathcal{A}$ denotes the generalized Berry coefficients for the frame F, in the frame

[13] One can identify F also with a frame of the reference space bundle $\Omega \times \mathbb{C}^\ell \mapsto \Omega$.

$X \mapsto T(X)F(X)$ the corresponding connection coefficients $\mathcal{B}$ are given by

$$\mathcal{B}(X) = T(X)^* \mathcal{A}(X) T(X) + T^*(X) \nabla T(X), \tag{3.15}$$

where both $\mathcal{A}$, and ∇T are interpreted as $\ell \times \ell$ matrices with vector-valued entries.

In the chemical literature there exist various heuristic methods for constructing quasidiabatic bases. The strategy of [PMCK89] is to impose the incomplete Lorenz gauge

$$\nabla \cdot \mathcal{B}_{ij} = 0\,, \quad i,j \in \{1,\dots,\ell\}, \tag{3.16}$$

that is, the vector potentials are required to be divergence free. Let us sketch the mathematical heuristics underlying this choice by looking at minimizers of the functional[14]

$$\begin{aligned} \Phi &: \mathcal{C}_c^\infty(\Omega, \mathfrak{u}(\ell)) \to \mathbb{R}, \\ \Phi(S) &= \tfrac{1}{2} \int_\Omega \| \mathrm{e}^{-S(X)} \mathcal{B}(X) \mathrm{e}^{S(X)} + \nabla S(X) \|_{\mathrm{F}}^2 \, dX. \end{aligned} \tag{3.17}$$

We interpret $\mathcal{B}(X)$ and $\nabla S(X)$ as matrices in $\mathbb{C}^{3N\ell \times \ell}$, and use the Frobenius norm

$$\|\mathcal{B}(X)\|_F = \sqrt{\mathrm{tr}\,(\mathcal{B}(X)^* \mathcal{B}(X))}.$$

Φ has a stationary point at 0 if its Fréchet derivative vanishes, that is,

$$\Phi(S) = \Phi(0) + O(\|S\|^2) + O(\|\nabla S\|^2) \tag{3.18}$$

since the "Lagrangian density" of Φ depends on both S, and ∇S. A Taylor expansion and integration by parts lead to the condition that the integral

$$\int_\Omega \mathrm{tr}\big(S(x)(\nabla \cdot \mathcal{B})(x) + (\nabla \cdot \mathcal{B})(x) S(x)\big) dx$$

[14] We identify the Lie algebra $\mathfrak{u}(\ell)$ with the space of skew-Hermitian matrices.

has to vanish for all S. Hence, the Lorenz gauge $\nabla \cdot \mathcal{B} = 0$ is a necessary condition for the frame that gives the coefficients $\mathcal{B}$ to be a local L^2-minimizer in the set of all frames that can be reached by a smooth gauge transformation $T : \Omega \to U(\ell)$.

Example. Let us revisit Rellich's celebrated two-level Hamiltonian

$$H_{\text{dia}} = -\tfrac{\varepsilon^2}{2}\Delta \cdot \mathrm{Id}_2 + \begin{pmatrix} x_1 & x_2 \\ x_2 & -x_1 \end{pmatrix} \tag{3.19}$$

acting on $L^2(\mathbb{R}^2, \mathbb{C}^2)$, which has been extensively studied in [Las04]. It provides a simple model Hamiltonian for a two-level system with a conical eigenvalue crossing of codimension two. A frame of eigenfunctions that is smooth away from 0 is given by

$$\begin{aligned} \xi_+(r,\theta) &= \mathrm{e}^{\mathrm{i}\theta/2} \begin{pmatrix} \cos(\theta/2) \\ \sin(\theta/2) \end{pmatrix}, \\ \xi_-(r,\theta) &= \mathrm{e}^{\mathrm{i}\theta/2} \begin{pmatrix} -\sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix} \end{aligned} \tag{3.20}$$

in polar coordinates (r, θ). As expected, the gradient of these eigenfunctions diverges at the eigenvalue crossing, and the corresponding diagonalized Hamiltonian reads

$$H_{\text{ad}} = \tfrac{1}{2}\left(-\mathrm{i}\varepsilon\nabla \cdot \mathrm{Id}_2 + \frac{\varepsilon}{2|x|^2}\begin{pmatrix} x_2 \\ -x_1 \end{pmatrix} \cdot \begin{pmatrix} 1 & \mathrm{i} \\ -\mathrm{i} & 1 \end{pmatrix}\right)^2 + \begin{pmatrix} |x| & 0 \\ 0 & -|x| \end{pmatrix}.$$

It is striking that the singular coefficients of H_{ad} can be gauged away. In the notation of (3.15), the frame transformation T from the adiabatic basis (3.20) into the strictly diabatic basis of (3.19) is given by

$$T(r,\theta) = \mathrm{e}^{\mathrm{i}\theta/2} \begin{pmatrix} \cos(\theta/2) & -\sin(\theta/2) \\ \sin(\theta/2) & \cos(\theta/2) \end{pmatrix}, \tag{3.21}$$

which satisfies the Lorenz gauge condition. ■

4 Hellmann-Feynman Theory

In this chapter we investigate the differentiability of the electronic Coulomb Hamiltonian $H_{\mathrm{el}}(X)$ in the nuclear coodinates via Lipschitz analysis. The application of our findings yields a novel proof for the Hellmann-Feynman theorem, which is a popular and widely used formula in chemistry that can be employed for computing derivatives of PES. A passing mention of this result for diatomic systems can be found in the work of Combes and Seiler [CS78, Corollary 2], though without a detailed proof.

For later reference, we introduce the differential quotients

$$H^s_\xi(X) = \frac{H_{\mathrm{el}}(X + s\xi) - H_{\mathrm{el}}(X)}{s}, \quad \xi = (\xi_1, \dots, \xi_N) \in \mathbb{R}^{3N},$$

for $s > 0$, and denote the formal directional derivatives of $H_{\mathrm{el}}(X)$ in direction ξ by

$$dH_{\mathrm{el}}(X)[\xi] = -\sum_{j=1}^{L}\sum_{k=1}^{N} \mathcal{Z}_k \frac{\xi_k \cdot (x_j - X_k)}{|x_j - X_k|^3}.$$

For the Sobolev spaces[15] $H^m := H^m(\mathbb{R}^{3L}, \mathbb{C})$, $m \in \mathbb{R}$, we introduce the duality brackets

$$\langle \cdot, \cdot \rangle_{m,-m} : H^m \times H^{-m} \to \mathbb{C}$$

as continuous extensions of the inner product $\langle \cdot, \cdot \rangle$ on $L^2 = L^2(\mathbb{R}^{3L})$, and note that H^m is a Banach space with the norm

$$\|\psi\|_m = \|(1 - \Delta)^{m/2}\psi\|_{L^2}.$$

[15] For readability we ignore the spin degrees of freedom, but all assertions and proofs generalize readily.

4.1 Extension to the Sobolev Rigging

Since $1/|x|^2$ is not locally square integrable on $\mathbb{R}^3$, the domain of the multiplication operator $dH_{\mathrm{el}}(X)[\xi]$ cannot contain all wave functions in $\mathscr{H}_{\mathrm{el}} \cap H^2$. Moreover, though the spectral projections on bound state energies of the electronic Hamiltonian $H_{\mathrm{el}}(X)$ are locally twice differentiable in X, this does not directly imply a corresponding regularity of $H_{\mathrm{el}}(X)$ since it is an unbounded operator. In order to circumvent this problem, we make use of the Hilbert space rigging

$$\ldots \subset H^2 \subset H^1 \subset L^2 \subset H^{-1} \subset H^{-2} \subset \ldots \tag{4.1}$$

of Sobolev spaces, and extend $H_{\mathrm{el}}(X)$ to its form domain H^1, see also §2 in [Bor98, Appendix B]. The next Proposition confirms that this extension is natural for the analysis of differentiability properties.

Proposition 3. *Both $H_{\mathrm{el}}(X)$, and $dH_{\mathrm{el}}(X)[\xi]$ extend to operators in $\mathcal{L}(H^1, H^{-1})$.*

Proof. For $H_{\mathrm{el}}(X)$ this result is well-known, see [Sim71]. For $dH_{\mathrm{el}}(X)[\xi]$ we can make use of Hardy's inequality, see e.g. [Sei10],

$$\int_{\mathbb{R}^3} \frac{|\psi(x)|^2}{|x|^2} dx \leq 4 \int_{\mathbb{R}^3} |\nabla \psi(x)|^2 |dx \tag{4.2}$$

which holds for all $\psi \in H^1(\mathbb{R}^3)$. Hence, for all $\psi \in H^1(\mathbb{R}^3)$ and[16] $\phi \in \mathcal{C}^\infty_{c,\{0\}}(\mathbb{R}^3)$ we can estimate

$$\left\langle \psi, \frac{x_j}{|x|^3} \phi \right\rangle = \left\langle \psi, \frac{x_j}{|x|^3} \phi \right\rangle_{1,-1} \leq 4 \|\nabla \psi\|_{L^2} \|\nabla \phi\|_{L^2},$$

by the Cauchy-Schwarz inequality and (4.2), since $\mathcal{C}^\infty_{c,\{0\}}(\mathbb{R}^3) \subset H^1(\mathbb{R}^3)$ is an invariant core for the multiplication operator $x_j |x|^{-3}$.

[16] $\mathcal{C}^\infty_{c,\{0\}}(\mathbb{R}^3)$ contains smooth functions vanishing at the origin, see the definition in Proposition C.1.

From the density result from Proposition C.1 in the appendix hence follows

$$\sup_{\phi\in H^1(\mathbb{R}^3)}\ \sup_{\psi\in H^1(\mathbb{R}^3)}\ \frac{\left|\left\langle \phi, \frac{x_j}{|x|^3}\psi\right\rangle_{1,-1}\right|}{\|\psi\|_1\ \|\phi\|_1} \leq 4$$

and the extension to $dH_{\mathrm{el}}(X)[\xi]$ is obvious. □

In order to avoid confusion, in the following we denote the bounded operator extensions defined on the whole of H^1 by $\widehat{H}_{\mathrm{el}}(X)$, $\widehat{H^{\mathrm{s}}_{\xi}}(X)$, and $\widehat{dH}_{\mathrm{el}}(X)[\xi]$, respectively. The idea for the proof of the next result arose during our study of [HG80, KMR11].

Proposition 4. *$\widehat{H}_{\mathrm{el}} : \mathbb{R}^{3N} \to \mathcal{L}(H^1, H^{-1})$ is locally Lipschitz continuous.*

Proof. Let us start with the Lipschitz type difference estimate

$$\langle \psi, (H_{\mathrm{el}}(X) - H_{\mathrm{el}}(Y))\psi\rangle \leq \tfrac{1}{2}|X-Y|_{\mathcal{Z}}\|\nabla\psi\|^2_{L^2} \tag{4.3}$$

from Lemma 3, which holds in the sense of quadratic forms on H^1. After using the polarization identity, and rewriting evaluations of sesquilinear forms as duality products, (4.3) implies boundedness of

$$\left\{ \frac{\left\langle \phi, (\widehat{H}_{\mathrm{el}}(X) - \widehat{H}_{\mathrm{el}}(Y))\psi\right\rangle_{1,-1}}{|X-Y|_{\mathcal{Z}}} \right\}_{Y\neq X} \subset \mathbb{C} \tag{4.4}$$

for all $\phi, \psi \in H^1$. Then, by fixing an open bounded neighborhood U of X, the identification of H^1 with $(H^{-1})^*$ yields boundedness of

$$\left\{ \frac{(\widehat{H}_{\mathrm{el}}(X) - \widehat{H}_{\mathrm{el}}(Y))\psi}{|X-Y|_{\mathcal{Z}}} \right\}_{Y\in U\setminus\{X\}} \subset H^{-1}$$

for every $\psi \in H^1$, since subsets of Banach spaces are bounded if and only if all continuous linear functionals are bounded on it. Invoking the uniform boundedness principle finishes the proof. □

We refer to [BDBT14] for a thorough discussion of operators on rigged Hilbert spaces with a focus on generalized spectra and resolvents.

4.2 Differentiability

The extended electronic Hamiltonian $\widehat{H}_{\mathrm{el}}$ is not uniformly Lipschitz continuous as an operator-valued map. Nevertheless, by general results from Lipschitz analysis, the local estimate we proved in Proposition 4 is sufficient to infer existence of partial derivatives, which will exploit later to prove the Hellmann-Feynman formula.

Proposition 5. *The partial derivatives of* $\widehat{H}_{\mathrm{el}} : \mathbb{R}^{3N} \to \mathcal{L}(H^1, H^{-1})$ *exist everywhere, and are given by* $\widehat{dH}_{\mathrm{el}}(X)[e_j]$, $j = 1, \dots, 3N$, *where* e_j *denotes the jth unit vector in* $\mathbb{R}^{3N}$.

Proof. Lipschitz continuous functions $f : \mathbb{R}^n \to B$, with B a Banach space, are almost everywhere Gâteaux differentiable, see [Kir94, PZ01]. Consequently, by Proposition 4, $\widehat{H}_{\mathrm{el}}$ is Gâteaux differentiable with respect to the operator norm almost everywhere.

Now, suppose that $\widehat{H}_{\mathrm{el}}$ is differentiable at X with directional derivatives $F(X)[\xi]$, $\xi \in \mathbb{R}^{3N}$. We want to show that $F(X) = \widehat{dH}_{\mathrm{el}}(X)$, as expected. We note that the set $\mathcal{C}^\infty_{c,S}(\mathbb{R}^{3L})$ of test functions which vanish infinitely fast at the set

$$S := \bigcup_{k=1}^{N} \bigcup_{j=1}^{L} \{x \in \mathbb{R}^{3L} : x_j = X_k + s\xi_k,\ s \in [0,1]\}$$

of all occurring singularities is invariant under both $H^s_\xi(X)$, and $dH_{\mathrm{el}}(X)$. Moreover, for $\phi \in \mathcal{C}^\infty_{c,S}(\mathbb{R}^{3L})$ and $\psi \in L^2(\mathbb{R}^{3L})$ we have

$$\left\langle \widehat{H^s_\xi}(X)\phi, \psi \right\rangle_{-1,1} \to \left\langle \widehat{dH}_{\mathrm{el}}(X)[\xi]\phi, \psi \right\rangle_{-1,1}$$

as $s \searrow 0$ by the dominated convergence theorem, since

$$\widehat{H^s_\xi}(X)\phi \to \widehat{dH}_{\mathrm{el}}(X)[\xi]\phi$$

pointwise everywhere. The identification $F(X) = \widehat{dH}_{\mathrm{el}}(X)$ follows from Lemma C.2 since the set $\mathcal{C}^{\infty}_{c,S}(\mathbb{R}^{3L})$ is a fundamental subset of H^1 by Proposition C.1.

Finally, we show that if the partial derivatives of $\widehat{H}_{\mathrm{el}}$ exist at $X + Z \in \mathbb{R}^{3N}$, they also exist at X. This step removes the almost everywhere condition which is an artifact of the Lipschitz argument we employed. We fix $j \in \{1, \ldots, 3N\}$ and choose $k \in \{1, \ldots, N\}$ to be the nucleus for which $e_j \cdot Z = (Z_k)_m$ for some $m \in \{1, 2, 3\}$. Then, by applying the coordinate shift $x_j \mapsto x_j + Z_k$ for all $j = 1, \ldots, L$, with $D = (1 - \Delta)^{-1/2}$ one computes

$$
\begin{aligned}
0 &= \lim_{s \searrow 0} \| \widehat{H^s_{e_j}}(X + Z) - \widehat{dH}_{\mathrm{el}}(X + Z)[e_j] \|^2_{\mathcal{L}(H^1, H^{-1})} \\
&= \lim_{s \searrow 0} \sup_{\substack{\psi \in H^1 \\ \|\psi\|_1 = 1}} \int_{\mathbb{R}^{3L}} \left| D \left(\widehat{H^s_{e_j}}(X + Z) - \widehat{dH}_{\mathrm{el}}(X + Z)[e_j] \right) \psi(x) \right|^2 dx \\
&= \lim_{s \searrow 0} \sup_{\substack{\psi \in H^1 \\ \|\psi\|_1 = 1}} \int_{\mathbb{R}^{3L}} \left| D \left(\widehat{H^s_{e_j}}(X) - \widehat{dH}_{\mathrm{el}}(X)[e_j] \right) \psi(x + W) \right|^2 dx \\
&= \lim_{s \searrow 0} \| \widehat{H^s_{e_j}}(X) - \widehat{dH}_{\mathrm{el}}(X)[e_j] \|^2_{\mathcal{L}(H^1, H^{-1})}
\end{aligned}
$$

for $W = (Z_k, \ldots, Z_k) \in \mathbb{R}^{3L}$, due to the special form of the differential quotient and its limit, as well as the invariance of the Laplacian with respect to shifts. □

4.3 Hellmann-Feynman Formulas

Electronic potential energy surfaces appear in the Born-Oppenheimer approximation as potentials for the effective nuclear motion. Hence, the semiclassical[17] force in between the nuclei in a molecule is given by the gradient of the relevant PES and the nuclear repulsion,

[17] Here, semiclassical is meant in the sense that a quantum mechanical object, the PES, determines the classical evolution of the nuclei.

see (2.13). The observation that these molecular forces are related to the derivative of the Hamiltonian goes back to Hellmann [Hel37] and Feynman [Fey39]. It is a very popular and widely used result in chemical physics and can be seen as a generalization of Hadamard's first variational formula from Lemma 2 to the unbouded Hamiltonians $H_{\mathrm{el}}(X)$.

In fact, if one considers differentiable maps into bounded Hilbert space operators, Hellmann-Feynman type theorems follow almost immediately, see [Car10]. We present a rigorous mathmatical derivation of the Hellmann-Feynman theorem for the Coulomb Hamiltonian $H_{\mathrm{el}}(X)$ in the spirit of [IZ88], based on the operator analysis from the previous section. We stress that for our formula we do not require any further assumptions on the eigenfunctions.

Theorem 1 (Hellmann-Feynman)**.** *Let the PES E_k be of locally constant multiplicity $m < \infty$ around $X \in \mathbb{R}^{3N}$. Then, E_k is differentiable in some open neighborhood $U \ni X$ and there is a corresponding L^2-normalized eigenfunction $\psi : U \to \mathscr{H}_{\mathrm{el}}$ satisfying*

$$\partial_{X_j} E_k(X) = \left\langle \psi(X), \widehat{dH}_{\mathrm{el}}(X)[e_j]\psi(X) \right\rangle_{1,-1}, \quad j = 1, \dots, 3N, \quad (4.5)$$

where e_j denotes the jth unit vector in $\mathbb{R}^{3N}$.

Proof. Since the eigenvalue E_k is assumed to be of constant multiplicity $m < \infty$ in some simply connected open neighborhood $U \ni X$, it is analytic in U as noted in Remark 2. Let $P(Y)$ be the eigenprojector on the corresponding m-dimensional eigenspace associated with $E_k(Y)$. By invoking Lemma 1.1 in [KMSW92], the fibered eigenprojector P induces a trivial vector bundle over U, and hence we can find a parametrized eigenfunction

$$U \ni Y \mapsto \eta(Y) \in P(Y)\mathscr{H}_{\mathrm{el}} \subset H^2$$

which is both, continuous and normalized as a H^2-valued map.

The symmetry of the quadratic form associated with $H_{\mathrm{el}}(X)$ im-

plies

$$\left\langle \eta(Y), \widehat{H_{\mathrm{el}}}(Y)\eta(X) \right\rangle_{1,-1} = E_k(Y) \left\langle \eta(Y), \eta(X) \right\rangle_{L^2}$$

and

$$\left\langle \eta(Y), \widehat{H_{\mathrm{el}}}(X)\eta(X) \right\rangle_{1,-1} = E_k(X) \left\langle \eta(Y), \eta(X) \right\rangle_{L^2}.$$

Consequently,

$$\begin{aligned} &\frac{E_k(X+he_j) - E_k(X)}{h} = \\ &= \frac{\frac{1}{h}\left\langle \eta(X+he_j), \left(\widehat{H}_{\mathrm{el}}(X+he_j) - \widehat{H}_{\mathrm{el}}(X)\right)\eta(X) \right\rangle_{1,-1}}{\left\langle \eta(X+he_j), \eta(X) \right\rangle_{L^2}}, \end{aligned}$$

and we can pass to the limit $h \searrow 0$ since $Y \mapsto \eta(Y)$ is norm continuous in H^1, and the partial derivatives in the operator norm of $Y \mapsto \widehat{H_{\mathrm{el}}}(Y)$ exist by Proposition 5. We note that $\|\eta(X)\|_{L^2}^2 \neq 0$ because of the the H^2-normalization of η. Consequently, setting

$$\psi(X) = \frac{\eta(X)}{\|\eta(X)\|_{L^2}}$$

gives the L^2-normalization and completes the proof. □

We highlight that the right hand side of (4.5) can also be interpreted as evaluating the quadratic form associated with $dH_{\mathrm{el}}(X)$ on H^1, but not as an L^2-inner product. This is due to the fact that the operator derivative $\widehat{dH}_{\mathrm{el}}(X)[e_j]$ does not map H^2 into L^2. Theorem 1 clearly holds as well if we ignore spin degrees of freedom.

Remark 3. *In the case $m = 1$ of a non-degenerate PES, Theorem 1 holds for every choice of a normalized eigenfunction. This is due to the fact that the right hand side of* (4.5) *is invariant under a change of phase that depends on the nuclear coordinates only.*

The generalized Berry coefficients from §2.5 can also be expressed via the derivatives of the operator $\widehat{H_{\mathrm{el}}}$. The following result is known as the off-diagonal Hellmann-Feynman formula.

Proposition 6 (Off-diagonal Hellmann-Feynman formula)**.** *Suppose that the PES E_k, E_ℓ, $k \neq \ell \in \mathbb{N}$, satisfy $E_k(X) \neq E_\ell(X)$ at $X \in \mathbb{R}^{3N}$, and let $\psi_k(X)$, $\psi_\ell(X)$ be corresponding eigenfunctions. We assume that $Y \mapsto \psi_k(Y)$ can be chosen both H^1-continuous and H^{-1}-differentiable*[18] *in a small neighborhood of X. Then, one has*

$$\left\langle \psi_\ell(X), \partial_{X_j} \psi_k(X) \right\rangle_{1,-1} = \frac{\left\langle \psi_\ell(X), \widehat{dH_{\mathrm{el}}}(X)[e_j] \psi_k(X) \right\rangle_{1,-1}}{E_k(X) - E_\ell(X)} \quad (4.6)$$

for all $\xi \in \mathbb{R}^{3N}$.

Proof. From the eigenvalue property and the selfadjointness of H_{el} we deduce

$$\begin{aligned} &\left\langle \psi_\ell(X), \tfrac{1}{h} \left(\widehat{H}_{\mathrm{el}}(X + h\xi) - \widehat{H}_{\mathrm{el}}(X) \right) \psi_k(X + h\xi) \right\rangle_{1,-1} \\ &= (E_\ell(X) - E_k(X + h\xi)) \left\langle \psi_\ell(X), \tfrac{1}{h} \left(\psi_k(X + h\xi) - \psi_k(X) \right) \right\rangle_{1,-1}. \end{aligned}$$

Now, the claim follows in the limit $h \searrow 0$ because of the differentiablity of $\widehat{H_{\mathrm{el}}}$, the continuity of E_k, and the regularity assumptions on ψ_k. □

Proposition 6 strongly supports the intuition that in an adiabatic basis the generalized Berry connection coefficients $\mathcal{A}_{ij}$ from (2.22) generically exhibit hyperbolic singularities at conical crossings of PES, see also the example in §3.6. In chemistry, see e.g. [DYK04, Var09], this observation serves as a main motivation for the development of diabatization or quasidiabatization procedures.

Remark 4. *The multi-configuration Hartree-Fock method is a very popular method for ab initio electronic structure calculations in which one constructs approximate electronic eigenfunctions as sums of antisymmetrized tensor producs of one-particle wave functions in $L^2(\mathbb{R}^3)$. Since the derivative $dH_{\mathrm{el}}(X)$ is a sum of multiplication operators acting on*

[18] We can always find an eigenfunction ψ_k that satisfies one of the both conditions.

one-particle wave functions only, the computation of gradients of PES via Theorem 1, or generalized Berry coefficients via Proposition 6, reduces to a finite number of quadrature problems in $\mathbb{R}^3$. This favorable property is a reason for the popularity of Hellmann-Feynman type formulas in theoretical and computational chemistry.

5 Weyl Correspondence

It is a natural and important question to ask in how far classical mechanics can be treated as a limiting case of quantum mechanics. This problem of quantum-classical correspondence has been an issue of investigation since the first days of quantum theory, see [Boh20]. Very successful tools for answering this type of questions are provided by the phase space quantization techniques of semiclassical analysis, see e.g. [Zwo12, Mar02, Fol89] for comprehensive introductions. This chapter shortly reviews the basics of Weyl calculus. We apply these techniques later on to derive semiclassical approximations for the dynamics of molecular quantum systems.

From now on we take a slightly different perspective than in the chapters before. We view $L^2(\mathbb{R}^d)$ as the nuclear reference Hilbert space, and consider selfadjoint Hamiltonians H on $L^2(\mathbb{R}^d)$ that are given as the Weyl quantization of some smooth Hamilton function h on the classical phase space

$$H = \mathrm{op}_\varepsilon^{\mathrm{We}}(h), \quad h : \mathbb{R}^{2d} \to \mathbb{R}, \tag{5.1}$$

see also §5.3 for definitions. The evolution of the quantum system described by H is then governed by the time-dependent semiclassical Schrödinger equation

$$\mathrm{i}\varepsilon\partial_t\psi(t) = \mathrm{op}_\varepsilon^{\mathrm{We}}(h)\psi(t), \quad \psi(0) = \psi_0 \in L^2(\mathbb{R}^d). \tag{5.2}$$

If one requires the nuclear interaction potential V_{nn} to be smooth[19]

[19] For example, one can treat the nuclei as extended particles by introducing a

and stays away from crossings of PES, Born-Oppenheimer Hamiltonians of the form (2.13) fit into this framework. Hence, in the following we will assume that the nuclei evolve in a region where the relevant PES is well seperated from the rest of the electronic spectrum. Then, the solutions of (5.2) yield good approximations for the quantum evolution of the molecule.

5.1 Wigner Functions

There are various ways to represent a quantum state $|\psi\rangle\langle\psi|$ on the classical phase space $\mathbb{R}^{2d}$. The most popular one is the canonical Weyl representation based on Wigner functions, which goes back to [Wig32] and [Moy49].

Definition 1. *Let $\psi, \phi \in L^2(\mathbb{R}^d)$. The* cross-Wigner function *(or simply* Wigner function*) $\mathcal{W}(\psi,\phi) \in L^2(\mathbb{R}^{2d})$ of ψ and ϕ is defined as*

$$\mathcal{W}^\varepsilon(\psi,\phi)(q,p) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^d} \mathrm{e}^{\mathrm{i}p\cdot y/\varepsilon} \psi(q - \tfrac{1}{2}y)\overline{\phi}(q + \tfrac{1}{2}y)dy, \quad (5.3)$$

and $\mathcal{W}^\varepsilon(\psi) := \mathcal{W}^\varepsilon(\psi,\psi)$ is called the Wigner transform *of ψ.*

One can show that Wigner transforms $\mathcal{W}^\varepsilon(\psi)$ are real-valued continuous functions on phase space. Their marginals[20] yield the position and momentum density of the corresponding state,

$$\begin{aligned} \int_{\mathbb{R}^d} \mathcal{W}^\varepsilon(\psi)(q,p)dp &= |\psi(q)|^2 \quad \text{and} \\ \int_{\mathbb{R}^d} \mathcal{W}^\varepsilon(\psi)(q,p)dq &= |\mathcal{F}^\varepsilon\psi(p)|^2, \end{aligned} \quad (5.4)$$

where

$$\mathcal{F}^\varepsilon\psi(p) = (2\pi\varepsilon)^{-d/2} \int_{\mathbb{R}^d} \mathrm{e}^{-\mathrm{i}p\cdot y/\varepsilon} \psi(y)dy \quad (5.5)$$

smooth charge density.

[20] If ψ or $\mathcal{F}^\varepsilon\psi$ are not integrable, the respective formulas for the marginals might not absolutely convergent, but still make sense as oscillatory integrals.

is the semiclassically rescaled Fourier transform. As we shall see below in §5.3, Wigner transforms are the Weyl symbols of pure states. In particular, for two normalized wave functions $\psi, \phi \in L^2(\mathbb{R}^d)$ we have

$$\mathcal{W}^\varepsilon(\psi) = \mathcal{W}^\varepsilon(\phi) \iff |\psi\rangle\langle\psi| = |\phi\rangle\langle\phi|,$$

and, by (5.4), the Wigner transform has mass one,

$$\int_{\mathbb{R}^{2d}} \mathcal{W}^\varepsilon(\psi)(z)dz = 1. \tag{5.6}$$

These properties make $\mathcal{W}^\varepsilon(\psi)$ a natural candidate for the representation of the state $|\psi\rangle\langle\psi|$ on the classical phase space. However, Wigner transforms $\mathcal{W}^\varepsilon(\psi)$ are nonnegative if and only if ψ is a Gaussian function, as shown in [Hud74, SC83]. Hence, in spite of the normalization property (5.6), Wigner transforms are generically not probability densities, and in general not even functions in $L^1(\mathbb{R}^{2d})$. As a consequence, in spite of its formal similarity, quantum dynamics cannot directly be interpreted as some type of statistical mechanics on phase space.

Exemplary states for which the Wigner transform becomes negative are superposition states. They induce highly oscillatory quantum interferences as illustrated by the example in Figure 1. These interferences can be seen as a phase space indicator of quantum entanglement, and hence represent a manifestly non-classical effect. For an extensive discussion and further reading we refer to [Zur03] and the references given therein. We note that the lack of nonnegativity of Wigner functions can be overcome by using Husimi transforms or other spectrograms instead, see §10.

Cross-Wigner functions are always square-integrable and satisfy *Moyal's identity*

$$\langle \mathcal{W}^\varepsilon(\psi_1, \phi_1), \mathcal{W}^\varepsilon(\psi_2, \phi_2) \rangle_{L^2(\mathbb{R}^{2d})} = \frac{\langle \psi_1, \psi_2 \rangle_{L^2(\mathbb{R}^d)} \overline{\langle \phi_1, \phi_2 \rangle}_{L^2(\mathbb{R}^d)}}{(2\pi\varepsilon)^d}, \tag{5.7}$$

see, e.g., [dG11, §9.4]. Thus, we have

$$\|\mathcal{W}^\varepsilon(\psi)\|_{L^2(\mathbb{R}^{2d})} = (2\pi\varepsilon)^{-d/2}\|\psi\|_{L^2(\mathbb{R}^d)}$$

and the L^2-norm of Wigner functions is invariant under the Schrödinger evolution. For a deeper analysis of the geometry and phase space properties of Wigner functions we refer to the monograph of de Gosson [dG11].

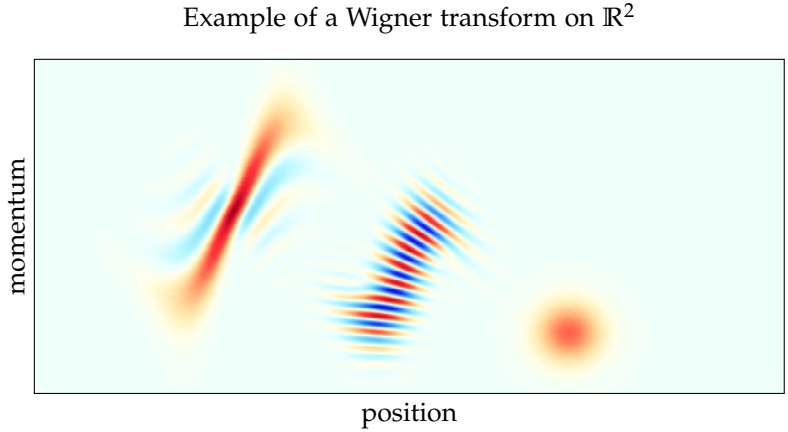

FIGURE 1: This contour plot shows the Wigner transform of a one-dimensional wave function representing a superposition of a Gaussian coherent state (right) and a Lagrangian type delocalized state (left), where the interferences in the middle are due to the entanglement between the two states. Red color indicates positive, and blue color negative values of the Wigner transform.

Remark 5. *Wigner functions can equivalently be defined via so-called Grossmann-Royer operators, see [dG11, §9.2.1], which can be seen as quantized phase space reflections.*

5.2 Heisenberg-Weyl Operators

In the article [Wey27] published in 1927, Hermann Weyl introduced a quantization procedure for associating Hilbert space operators to classical phase space functions, which is *" in many ways still the most satisfactory one"*, as Folland writes in [Fol89, p.78]. We will substantiate this assertion in the following sections.

Weyl's postulate was to associate the complex exponential

$$(x, \xi) \mapsto \mathrm{e}^{\mathrm{i}(x\cdot q+\xi\cdot p)}, \quad q, p \in \mathbb{R}^d, \tag{5.8}$$

with the so-called *Heisenberg-Weyl operator*

$$\widehat{T}_{(q,p)}\psi(x) = \mathrm{e}^{\mathrm{i}p\cdot(x-\frac{1}{2}q)/\varepsilon}\psi(x-q), \quad \psi \in L^2(\mathbb{R}^d), \tag{5.9}$$

that acts as a unitary transformation on $L^2(\mathbb{R}^d)$. This quantization approach is somehow complementary to the one of the previous section, where we looked at phase space representations of wave functions. However, as we will see below, these two complementary views are perfectly compatible.

The quantization rule from (5.9) can be motivated by constructing "quantized versions" of the phase space translations

$$T_{(q,p)} : \mathbb{R}^{2d} \to \mathbb{R}^{2d}, \quad T_{(q,p)}(z) = z + (q, p),$$

where $(q, p) \in \mathbb{R}^{2d}$, see [dG11, §8.1.1]. Let us consider the classical Hamilton function

$$h(z) = \Omega(z, (q, p)), \quad z \in \mathbb{R}^{2d},$$

where Ω is the canonical symplectic form on $\mathbb{R}^{2d}$ from (2.6). Then, $T_{(q,p)}$ can be written as the Hamiltonian flow of h at time $t = 1$. If one replaces the vector $z = (x, \xi)$ by its naive quantization $\widehat{z} = (x, -\mathrm{i}\varepsilon\nabla)$, $\widehat{T}_{(q,p)}$ analogously gives the $t = 1$ propagator for the semiclassical Schrödinger equation (5.2) with the quantized Hamiltonian $\Omega(\widehat{z}, (q, p))$,

$$\widehat{T}_z = \mathrm{e}^{-\mathrm{i}z^T J\widehat{z}/\varepsilon}. \tag{5.10}$$

The naturality of this quantization procedure becomes more clear if one revisits the Wigner functions introduced in Definition 1.

Lemma 6. *Let $\psi, \phi \in L^2(\mathbb{R}^d)$ be wave functions. Then*

$$\mathcal{W}^\varepsilon(\widehat{T}_z\psi, \widehat{T}_z\phi) = T_z\mathcal{W}^\varepsilon(\psi, \phi) \tag{5.11}$$

for all $z \in \mathbb{R}^{2d}$.

Hence, Heisenberg-Weyl operators truly act as simple phase space translations if one employs the phase space representation of states via Wigner functions. This result is a classic; we refer to [dG11, Proposition 174] for a more general formula incorporating two different Heisenberg-Weyl operators.

5.3 Quantization

By recalling the properties of the Fourier transform, one can see that the quantization rule for the exponentials (5.8) already uniquely determines the quantization $\mathrm{op}_\varepsilon^{\mathrm{We}}(a)$ of any tempered distribution $a \in \mathcal{S}'(\mathbb{R}^{2d})$. One arrives at the following quantization rule.

Definition 2 (Weyl quantization)**.** *For $\varepsilon > 0$, let $a \in \mathcal{S}'(\mathbb{R}^{2d})$ be a (possibly ε-dependent) distribution. Then, the* Weyl quantized operator $\mathrm{op}_\varepsilon^{\mathrm{We}}(a)$ *is defined as the integral operator*

$$\left(\mathrm{op}_\varepsilon^{\mathrm{We}}(a)\psi\right)(x) = (2\pi\varepsilon)^{-d}\int_{\mathbb{R}^d}\int_{\mathbb{R}^d} \mathrm{e}^{\mathrm{i}(x-y)\cdot\xi/\varepsilon} a\left(\tfrac{x+y}{2}, \xi\right)\psi(y)\, dy\, d\xi \tag{5.12}$$

for all $\psi \in \mathcal{S}(\mathbb{R}^d)$. We call a the Weyl symbol *of $\mathrm{op}_\varepsilon^{\mathrm{We}}(a)$, and write $a = \sigma^{\mathrm{We}}(\mathrm{op}_\varepsilon^{\mathrm{We}}(a))$.*

We note that for any $a \in \mathcal{S}'(\mathbb{R}^{2d})$ the integral operator $\mathrm{op}_\varepsilon^{\mathrm{We}}(a)$ has a Schwartz kernel in $\mathcal{S}'(\mathbb{R}^{2d})$, due to the properties of the Fourier transform. Consequently,

$$\mathrm{op}_\varepsilon^{\mathrm{We}}(a) : \mathcal{S}(\mathbb{R}^d) \to \mathcal{S}'(\mathbb{R}^d)$$

is continuous and (5.12) is well-defined, see also [Zwo12, Theorem 4.2]. Moreover, from Definition 2 one can infer that the adjoint operator $\mathrm{op}_\varepsilon^{\mathrm{We}}(a)^*$ is a Weyl operator with symbol $\overline{a}$. In particular, selfadjoint Weyl operators on $L^2(\mathbb{R}^d)$ have real-valued symbols, and the Weyl quantization rule (5.12) arranges the position and momentum variables symmetrically, that is,

$$a(q,p) = q \cdot p \quad \Longleftrightarrow \quad \mathrm{op}_\varepsilon^{\mathrm{We}}(a) = \tfrac{1}{2}\left(x \cdot (-\mathrm{i}\varepsilon\nabla_x) + (-\mathrm{i}\varepsilon\nabla_x) \cdot x\right).$$

Example. The Weyl quantization of the classical position and momentum (q,p) yields the canonical position and momentum observables $(x, -\mathrm{i}\varepsilon\nabla)$. Similarly, quantizing the classical kinetic and potential energies

$$E_{\mathrm{kin}}(q,p) = \tfrac{1}{2}|p|^2, \quad E_{\mathrm{pot}}(q,p) = V(q)$$

results in the quantum observables

$$\mathrm{op}_\varepsilon^{\mathrm{We}}(E_{\mathrm{kin}}) = -\tfrac{\varepsilon^2}{2}\Delta, \quad \mathrm{op}_\varepsilon^{\mathrm{We}}(E_{\mathrm{pot}}) = V$$

for the kinetic and potential energy. As a consequence, the Schrödinger operator

$$H = -\tfrac{\varepsilon^2}{2}\Delta + V$$

is the Weyl quantization of the classical Hamilton function $h(q,p) = \frac{1}{2}|p|^2 + V(q)$. ■

As already indicated by (5.6), Wigner transforms are the Weyl symbols of pure states, that is

$$\mathrm{op}_\varepsilon^{\mathrm{We}}\left(\mathcal{W}^\varepsilon(\psi)\right) = (2\pi\varepsilon)^{-d}|\psi\rangle\langle\psi| \tag{5.13}$$

for every $\psi \in L^2(\mathbb{R}^d)$ with $\|\psi\|_{L^2} = 1$. Moreover, one can use Wigner functions to express matrix elements of a Weyl operator via the phase space integral

$$\left\langle \mathrm{op}_\varepsilon^{\mathrm{We}}(a)\psi, \phi \right\rangle_{L^2} = \int_{\mathbb{R}^{2d}} a(z)\mathcal{W}^\varepsilon(\psi,\phi)(z)dz, \tag{5.14}$$

which can easily be checked, compare also (5.17) below.

There is a wealth of theory about classes of Weyl symbols yielding operators with certain regularity or boundedness properties, see e.g. the monographs [Zwo12, dG11, Ler10] for presentations with different emphases. In the following Lemma as well as in appendix B we summarize some of the most important facts. We would like to stress that symbol classes are not in the focus of this work.

Lemma 7. *Let $a \in \mathcal{S}'(\mathbb{R}^{2d})$ such that $\partial_q^\alpha \partial_p^\beta a(q,p) \in L^\infty(\mathbb{R}^{2d})$ for all $|\alpha|, |\beta| \leq \lceil d/2 \rceil + 1$. Then, $\mathrm{op}_\varepsilon^{\mathrm{We}}(a)$ defines a bounded operator on $L^2(\mathbb{R}^d)$, and there is a constant C independent of ε such that*

$$\|\mathrm{op}_\varepsilon^{\mathrm{We}}(a)\|_{\mathcal{L}(L^2)} \leq C \sup_{\substack{|\alpha|,|\beta| \leq \lceil d/2 \rceil + 1 \\ (q,p) \in \mathbb{R}^{2d}}} |\partial_q^\alpha \partial_p^\beta a(q,p)|. \tag{5.15}$$

Suppose that $b \in \mathcal{C}^\infty(\mathbb{R}^{2d})$ with $\partial^\alpha b \in L^1(\mathbb{R}^{2d})$ for all $|\alpha| \leq 2d+1$. Then, $\mathrm{op}_\varepsilon^{\mathrm{We}}(b)$ is a trace class operator on $L^2(\mathbb{R}^d)$, and

$$\mathrm{tr}(\mathrm{op}_\varepsilon^{\mathrm{We}}(b)) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} b(z) dz. \tag{5.16}$$

If $\mathrm{op}_\varepsilon^{\mathrm{We}}(a)$ and $\mathrm{op}_\varepsilon^{\mathrm{We}}(b)$ are Hilbert-Schmidt operators, one has

$$\mathrm{tr}(\mathrm{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{op}_\varepsilon^{\mathrm{We}}(b)) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} a(z)b(z) dz. \tag{5.17}$$

The first assertion (5.15) of Lemma 7 is known as the Calderón-Vaillancourt Theorem, and can be traced back to [CV72]. The form of the result we stated here is due to Boulkhemair [Bou99], and includes a minimal number of derivatives. A proof for the second assertion can be found in the book of Dimassi and Sjöstrand [DS99, §9], and one for the third formula in [dG11, Proposition 284].

The composition of two Weyl operators yields again a Weyl operator that allows for an expansion in powers of ε. The next Lemma summarizes several results from [Zwo12, §4], see also appendix B for the definition of order functions and the symbol classes $S_\delta(m)$.

Lemma 8. *Let m_1, m_2 be order functions and suppose $a \in S_\delta(m_1)$ and $b \in S_\delta(m_2)$ for some $0 \leq \delta \leq \frac{1}{2}$. Then,*

$$\mathrm{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{op}_\varepsilon^{\mathrm{We}}(b) = \mathrm{op}_\varepsilon^{\mathrm{We}}(a\sharp b), \tag{5.18}$$

where the Moyal product *of a and b is defined as*

$$(a\sharp b)(z) = \mathrm{e}^{-\mathrm{i}\varepsilon A(\nabla)}(a(z)b(w))\Big|_{w=z} \tag{5.19}$$

with $A(\nabla) = \frac{1}{2}\Omega(\nabla_z, \nabla_w)$. It holds $a\sharp b \in S_\delta(m_1 m_2)$, and for $\delta < \frac{1}{2}$ we have the asymptotic expansion

$$a\sharp b \sim \sum_{k=0}^{\infty} \frac{(-\mathrm{i}\varepsilon)^k}{2^k k!}\Omega(\nabla_z, \nabla_w)a(z)b(w)\Big|_{\mathrm{diag}}$$

in $S_\delta(m_1 m_2)$. In particular, we have

$$\begin{aligned} a\sharp b &= ab + \tfrac{\varepsilon}{2\mathrm{i}}\{a,b\} + O_{S_\delta(m_1m_2)}(\varepsilon^{1-2\delta}), \\ \sigma^{\mathrm{We}}\left([\mathrm{op}_\varepsilon^{\mathrm{We}}(a), \mathrm{op}_\varepsilon^{\mathrm{We}}(b)]\right) &= \tfrac{\varepsilon}{\mathrm{i}}\{a,b\} + O_{S_\delta(m_1m_2)}(\varepsilon^{3(1-2\delta)}), \end{aligned} \tag{5.20}$$

where $\{\bullet,\bullet\}$ is the classical Poisson bracket from (2.10)*, and $[\bullet,\bullet]$ is the commutator.*

The expansion (5.20) of the Moyal bracket is a starting point for various semiclassical approximations, and can be used for answering questions of quantum-classical correspondence. It relates the Heisenberg evolution of observables generated by the commutator and the classical evolution determined by the Poisson bracket, compare §2.2 and §2.3.

5.4 The Semiclassical Limit

The semiclassical parameter ε that appears in the definition of Weyl quantized operators and the semiclassical Schrödinger equation (5.2) can represent different physical quantities depending on

the considered model. In the context of the Born-Oppenheimer approximation, which is the main application we have in mind for the methods developed in this work, $\varepsilon = \sqrt{m_e/m}$ represents the square root of the electronic versus average nuclear mass. The semiclassical limit $\varepsilon \searrow 0$ here corresponds to large mass asymptotics, and (5.20) indicates that quantum observables evolve almost classically for molecules with heavy nuclei. A rigorous mathematical justification of this observation is provided by Egorov's theorem, see §11.

We note that, at least formally, the semiclassical parameter ε plays the role of the reduced Planck constant $\hbar$ in the Schrödinger equation (5.2). While we have $\hbar = 1$ in atomic units, one has $\hbar \approx 1.054 \cdot 10^{-34} Js$ in SI units. Hence, the limit $\hbar = \varepsilon \searrow 0$ can also be interpreted as the classical limit of quantum mechanics. This view served as a main motivation for the development of semiclassical analysis.

For time-independent Schrödinger equations on compact manifolds, the semiclassical limit usually denotes the limit of high eigenvalues, or high energies. In this context one typically explores in how far characteristic properties of the classical flow – like periodic orbits or ergodicity – are reflected in the "quantized system". Problems of quantum chaos have been an active area of research in microlocal analysis since decades, starting with Gutzwiller's derivation of the trace formula [Gut71], and the proof of the quantum ergodicity theorem, see,e.g., [Shn74, Zel87]. However, many important questions in this field are still open. We refer to [Sch01] and [Zwo12, §15] for further reading and many references.

Interlude
Simpler States and Simpler Dynamics

Even after conducting the Born-Oppenheimer approximation, the resulting effective equation for the evolution of the nuclei in a molecule is still a PDE on a typically high dimensional space. Computing reliable approximate solutions of these equations by means of direct numerical discretizations often is unfeasible, and one needs to conduct further simplifications. For instance, in the case of a single water molecule H_2O one is already confronted with the task of solving a Schrödinger equation on $\mathbb{R}^9_x \times \mathbb{R}_t$. A naive space discretization based on a tensor grid with as little as 10 points per space direction results in a system of 10^9 ODEs, see §E.

In the last years there has been a lot of research on numerical methods for Schrödinger equations that utilize sparse grids or reduced bases, see e.g. [Yse10, FGL09, Lub08], or [BG04] for a review. Although these procedures provide enormous simplifications, they are not powerful enough for entirely breaking the "curse of dimension". Moreover, since solutions of the semiclassical Schrödinger equation are highly oscillatory in space and time[21], one often requires a high spacial and temporal resolution for obtaining meaningful results, see [JMS11]. For methods that yield reliable approximations in moderately high dimensions "without too much computation" one consequently has to incorporate further model reductions.

In the remaining parts of this thesis we present two classes of simplifications for semiclassical quantum systems. In part §II we investigate the structure of Hagedorn wave packets, which form a class of simple wave functions with many nice properties. They can

[21] The frequencies are of size $O(\varepsilon^{-1})$

also be used for propagating and approximating more general wave functions. The semiclassical dynamics of a Hagedorn wave packet can be captured in a particularly simple way, since it employs only a single classical trajectory describing the center of the wave packet. In part §III we discuss various phase space methods for the semiclassical propagation of quantum observables, states, and Wigner functions. These approximations rely either on Egorov type results derived from expansions of the form (5.20), or on propagated Hagedorn wave packets. In §IV, the applicability and validity of the methods from §III are illustrated by means of various numerical experiments.

In view of the quotation of Dirac, which we stated at the beginning of the introduction, we provide rigorously derived "practical methods" for simplifying both, the Hilbert space of wave functions, and the quantum evolution of observables and states. It is our hope that in the future our investigations will lead to further simplifications, novel computational methods, and insights into molecular quantum systems.

II

Wave Packet Analysis

Hagedorn wave packets are multidimensional generalizations of Hermite functions with arbitrary phase space centers and complex width matrices. They have been introduced by George Hagedorn in [Hag81, Hag85] and are generalizations of parametrized Gaussian coherent states, see also the definition in §7. Since the pioneering works of Hepp and Heller [Hep74, Hel75], parametrized wave packets have evolved into a central tool of semiclassical analysis. They have found manifold applications, notably in the computation of the quantum dynamics of molecules, see [FGL09], or in quantum optics [Wün99]. Mathematical treatises are for instance contained in [Lub08, §5] and [Hag98, CR12].

Semiclassical Hagedorn wave packets are prototypes of states which are highly localized in position and momentum. They can be constructed as generalized multidimensional harmonic oscillator eigenstates, and consequently share many properties with usual Hermite functions, see [LT14]. In this chapter we analyze the structure of Hagedorn wave packets in configuration and phase space. Moreover, we introduce anti-Wick quantized operators together

with the associated spectrograms. This will serve as a basis for the semiclassical approximations developed in §12.

On $\mathbb{R}^d$, the Hagedorn wave packets are indexed by $k \in \mathbb{N}^d$ and can be written as

$$\varphi_k(x) = p_k(x)g(x), \tag{5.1}$$

where p_k is a multivariate polynomial of degree $|k|$, and g is a complex Gaussian function independent of k. In §6, we investigate a class of Hermite type multivariate polynomials that can be used in a natural way for analyzing the structure of the polynomials p_k. The Wigner-Hagedorn formula presented in §8 is one of the main results of our thesis. It allows to rewrite Wigner functions of Hagedorn wave packets as another Hagedorn wave packet on phase space.

At this point, we would like to highlight that the results in §6–§8.3 have been obtained in collaboration with Helge Dietert and Stephanie Troppmann, and can be found in our joint paper [DKT15]. The spectrogram analysis and approximation of Wigner transforms from §10.4 and §10.5 is based on the joint work [KLO15] with Caroline Lasser and Tomoki Ohsawa.

6 Multivariate Polynomials of Hermite Type

We investigate collections $\{q_k^M\}_{k\in\mathbb{N}^d}$ of multivariate polynomials with complex coefficients, generated from the three-term recursion relation (TTRR)

$$(q_{k+e_j}^M(x))_{j=1}^d = 2xq_k^M(x) - 2M \cdot (k_j q_{k-e_j}^M(x))_{j=1}^d, \tag{6.1}$$

where e_j denotes the jth unit vector in $\mathbb{R}^d$. We impose the conditions $q_0^M = 1$ and $q_\ell^M = 0$ for all $\ell \notin \mathbb{N}^d$, and require $M \in \mathbb{C}^{d\times d}$ to be symmetric. The latter compatibility condition guarantees that the polynomials are well-defined.

Hermite type multivariate polynomials of a closely related form and their generating functions have already been studied in [Erd39], and there [App26] is named as the original resource for the definition of the polynomials. In [Wün00] one can find some results in the two-dimensional case. Generalized Hermite functions of the above form are common tools in probability theory and statistics, see e.g. [Hol96, Wit00], although to the best of our knowledge they are not very well-known in the mathematical physics community. As we will see in §7 and §8, the polynomials appear naturally in the characterization of Hagedorn wave packets in configuration and phase space. Our presentation of the polynomials is tailored to this application.

Similarly as for many special polynomials in one variable, the polynomials q_k^M can equivalently be defined via their generating function, ladder operators, or, if M is invertible, a Rodrigues formula. We start from the TTRR (6.1) and subsequently derive formulas for the aforementioned quantities. This chapter is in large parts close to [DKT15, §2].

6.1 Growth Bound and Univariate Case

We first present our analysis for the one-dimensional setup in order to clarify the main ideas. In this case the TTRR reads

$$H_{n+1}^{\mu}(x) = 2xH_n^{\mu}(x) - 2\mu n H_{n-1}^{\mu}(x), \qquad n \in \mathbb{N}, \tag{6.2}$$

for some $\mu \in \mathbb{C}$, where $H_0^{\mu} = 1$, and $H_{-1}^{\mu} = 0$. We note that for $\mu = 1$ the resulting sequence coincides with the classical (physicist's) Hermite polynomials. In fact, we will see that many important properties of Hermite polynomials directly extend to the more general polynomials $\{H_n^{\mu}\}_{n\in\mathbb{N}}$.

Example. If $\mu \in (0, \infty)$, the polynomials are related to the classical

Hermite polynomials via the rescaling

$$H_n^\mu(x) = \mu^{\frac{n}{2}} H_n^1\left(\tfrac{x}{\sqrt{\mu}}\right). \tag{6.3}$$

In other words, H_n^μ corresponds to a Hermite polynomial with "variance" μ. In the case $\mu = 0$ the simplified recursion generates a sequence of monomials. ■

A central tool in our analysis of the polynomials is their generating function

$$g(x,\tau) = \sum_{n=0}^{\infty} \frac{\tau^n}{n!} H_n^\mu(x). \tag{6.4}$$

The power series $g(x,\tau)$ converges absolutely for all $\tau \in \mathbb{C}^d$. This can be seen by employing the following growth estimate for the general polynomials q_k^M.

Proposition 7 (Growth bound)**.** *Let $M \in \mathbb{C}^{d\times d}$ be symmetric. Then, for all $k \in \mathbb{N}^d$ we have the estimate*

$$|q_k^M(x)| \leq \theta(x)^{|k|}\sqrt{k!} \tag{6.5}$$

with the continuous function

$$\theta(x) = 1 + 2\sqrt{2d\|M\|_\infty} + 4\|x\|_\infty.$$

Proof. We prove the claim by induction over $|k| = N$. The base clause is obvious, since $\theta \geq 1$. Now, suppose that (6.5) holds for all $|\ell| \leq N$, and let $k \in \mathbb{N}^d$ with $|k| = N+1$. We can choose a direction e_j such that one has $k_j \geq k_i$ for all $i = 1,\ldots,d$. After applying the TTRR (6.1) in the jth direction, the induction hypothesis yields

$$\begin{aligned}\frac{|q_k^M(x)|}{\theta(x)^{|k|}\sqrt{k!}} &\leq \frac{2|x_j|}{\theta(x)\sqrt{k_j}} + 2\|M\|_\infty \sum_{i=1}^{d} \frac{(k-e_j)_i}{\theta(x)^2\sqrt{k_j(k-e_j)_i}} \\ &\leq \frac{2|x_j|}{\theta(x)\sqrt{k_j}} + \frac{2d\|M\|_\infty}{\theta(x)^2},\end{aligned}$$

where in the second step we utilized the fact that $k_j \geq (k - e_j)_i$. The claim follows from our choice of the function θ. □

As a next step, we derive a closed expression for the one-dimensional generating function $g(x, \tau)$. From (6.4) and the assumption $H^{\mu}_{-1} = 0$ one deduces

$$\partial_\tau g(x,\tau) = \sum_{n=0}^{\infty} \frac{\tau^n}{n!} H^{\mu}_{n+1}(x), \quad \tau g(x,\tau) = \sum_{n=0}^{\infty} \frac{\tau^n}{n!} n H^{\mu}_{n-1}(x),$$

since g can be differentiated termwise by Proposition 7. Then, applying the recursion (6.2) gives the differential equation

$$\partial_\tau g(x,\tau) = 2x g(x,\tau) - 2\tau\mu g(x,\tau), \tag{6.6}$$

which can be solved by separation of variables. Inserting the initial condition $g(x, 0) = H^{\mu}_0(x) = 1$ leads to the explicit expression

$$g(x,\tau) = \exp(2x\tau - \mu\tau^2). \tag{6.7}$$

Consequently, $g(x, \tau)$ is an entire function of both x, and τ, and one can evaluate the generalized Hermite polynomials via

$$H^{\mu}_n(x) = \partial^n_\tau \exp(2x\tau - \mu\tau^2)\big|_{\tau=0}.$$

Equivalently, by invoking Cauchy's formula, one has

$$H^{\mu}_n(x) = \frac{n!}{2\pi \mathrm{i}} \oint_\Gamma z^{-n-1} \mathrm{e}^{2xz-\mu z^2} dz$$

if the positively oriented contour $\Gamma \subset \mathbb{C}$ encircles the origin, see also [Sze75, (5.5.12)].

By recalling the differential equation (6.6), we can also use the raising operator

$$a^{\dagger}_{\mu} := 2x - \mu\partial_x, \quad \mu \in \mathbb{C}, \tag{6.8}$$

for constructing the generalized Hermite polynomials via

$$H^{\mu}_n = a^{\dagger}_{\mu} H^{\mu}_{n-1} = (a^{\dagger}_{\mu})^n 1. \tag{6.9}$$

We remark that $a_\mu^\dagger$ can be interpreted as the polynomial part of Dirac's creation operator for generalized one-dimensional harmonic oscillator eigenstates, see [Dir30, LT14]. The meaning of this comment will become more clear in §7.2.

The raising operator $a_\mu^\dagger$ is complemented by the gradient formula

$$\tfrac{1}{2n}\partial_x H_n^\mu(x) = H_{n-1}^\mu(x), \tag{6.10}$$

which is independent of μ and allows to lower the index of the polynomials. Formula (6.10) follows from combining (6.9) and (6.2). The identity

$$\partial_x \left(2^{-n} H_n^\mu(x)\right) = 2^{-(n-1)} H_{n-1}^\mu(x),$$

implies that $\{2^{-n} H_n^\mu\}_{n\in\mathbb{N}}$ is an Appel sequence, see [App80], and hence the polynomials $\{H_n^\mu\}_{n\in\mathbb{N}}$ have various favorable properties. For instance, one has the sum rule

$$H_n^\mu(x+y) = \sum_{j=0}^{n} \binom{n}{j} H_j^\mu(x)(2y)^{n-j},$$

which can easily be checked, compare also [LT14, Proposition 3].

Remark 6. *The form of the raising operator $a_\mu^\dagger$ and* (6.10) *imply that the polynomials H_n^μ are solutions to the eigenvalue problem*

$$\left(-\mu\partial_x^2 + 2x\partial_x\right) H_n^\mu(x) = 2n H_n^\mu(x),$$

which is a type of generalized Hermite differential equation, compare [Sze75, 5.5.2].

6.2 Generating Function and Ladder Operators

Generalizing the results from the previous paragraph to the multivariate polynomials $q_k^M : \mathbb{R}^d \to \mathbb{C}$ is straightforward. In the

following we use standard multiindex notation, that is, for $k \in \mathbb{N}^d$ and $x \in \mathbb{C}^d$ we set

$$k! = k_1! \cdots k_d!, \quad x^k = x_1^{k_1} \cdots x_d^{k_d}, \quad \text{and} \quad \partial^k = \partial_1^{k_1} \cdots \partial_d^{k_d}.$$

The generating function of the multivariate polynomials is defined as the power series

$$f(x,t) = \sum_{k \in \mathbb{N}^d} \frac{t^k}{k!} q_k^M(x), \quad t \in \mathbb{C}^d, \tag{6.11}$$

which by Proposition 7 converges absolutely for all $t \in \mathbb{C}^d$. Proposition 8 provides an explicit form for f.

Proposition 8 (Generating function)**.** *Let $M \in \mathbb{C}^{d \times d}$ be symmetric. Then, the generating function of the polynomials $\{q_k^M\}_{k \in \mathbb{N}^d}$ is given by the entire function*

$$f(x,t) = \exp(2x^T t - t^T M t). \tag{6.12}$$

Proof. As a first step, we note that for the indices $k = ne_j$, with $n \in \mathbb{N}$ and $j \in \{1, .., d\}$, the TTRR (6.1) simplifies to

$$q_{(n+1)e_j}^M(x) = 2x_j q_{ne_j}^M(x) - 2nM_{j,j} q_{(n-1)e_j}^M(x). \tag{6.13}$$

By (6.2), this one-dimensional recursion generates the tensor product polynomials

$$1 \otimes \ldots \otimes H_n^{M_{jj}} \otimes \ldots \otimes 1 \in \mathbb{C}[x_1, \ldots, x_d], \quad n \in \mathbb{N}. \tag{6.14}$$

Hence, from (6.7) follows that the generating function f must satisfy the conditions

$$f(x, \tau e_j) = \exp(2x_j \tau_j - M_{jj} \tau_j^2), \quad \tau \in \mathbb{C}, \tag{6.15}$$

for all coordinate directions $j = 1, \ldots, d$. For arbitrary indices $k \in \mathbb{N}^d$ we then proceed similarly as in the one-dimensional case.

One has

$$\partial_{t_j} f(x,t) = \sum_k \frac{t^k}{k!} q^M_{k+e_j}(x) \ , \quad t_j f(t,x) = \sum_k \frac{t^k}{k!} k_j q^M_{k-e_j}(x), \qquad (6.16)$$

since f can be differentiated termwise by Proposition 7. Applying the TTRR yields the system of differential equations

$$\nabla_t f = 2xf - 2fMt, \qquad (6.17)$$

and we look for a solution that is analytic in t. Since M is symmetric, we have

$$\nabla_t (t^T M t) = (M + M^T)t = 2Mt,$$

and the claim follows from imposing the coordinate conditions (6.15). □

Remark 7. *From the formula for the generating function in Proposition 8 one can infer that if M is real, the polynomials q^M_k coincide up to a prefactor with the multivariate Hermite polynomials that are used in probability theory and statistics, see e.g. [Hol96, Wit00].*

As in the one-dimensional case, the explicit form of the generating function allows for an easy evaluation of the polynomials q^M_k. For $k \in \mathbb{N}^d$, one has

$$q^M_k(x) = \partial_t^k \exp(2x^T t - t^T M t)\big|_{t=0},$$

and one can invoke the multidimensional Cauchy formula from [Hör73, Theorem 2.2.1]

$$q^M_k(x) = \frac{k!}{(2\pi \mathrm{i})^d} \oint_{\partial D} \mathrm{e}^{2x^T z - z^T M z} \prod_{j=1}^d z_j^{-k_j - 1} dz,$$

where $D \subset \mathbb{C}^d$ is a d-dimensional polydisc[1] that contains the origin.

The raising operator representation and the gradient formula translate readily to the multivariate case.

[1] D is a tensor product of d one-dimensional complex discs.

Proposition 9 (Ladder operators). *Let $M \in \mathbb{C}^{d\times d}$ be symmetric and $k \in \mathbb{N}^d$. Then,*

$$(q^M_{k+e_j})_{j=1}^d = b^\dagger_M q^M_k \quad \text{and} \quad \nabla q^M_k = 2(k_j q^M_{k-e_j})_{j=1}^d,$$

with the vector-valued raising operator $b^\dagger_M = 2x - M\nabla_x$.

Proof. The generating function f from (6.12) satisfies $\nabla_x f = 2tf$, and $\partial_{t_j} f$ simply shifts the summation index in (6.11) by one into the jth direction. Hence, after recalling (6.17), we obtain the first assertion from

$$\nabla_t f = 2xf - M\nabla_x f = b^\dagger_M f.$$

The gradient formula follows as in the one-dimensional case. □

With the ladder operators from Proposition 9 one can mimic the computation of harmonic oscillator eigenvalues. Since

$$\tfrac{1}{2}\left((b^\dagger_M)_j 2k_j q^M_{k-e_j} + \partial_{x_j} q^M_{k+e_j}\right) = (2k_j+1) q^M_k,$$

the polynomials $\{q^M_k\}_{k\in\mathbb{N}^d}$ form a set of simultaneous eigenvectors for the operators[2]

$$T_j = \frac{(b^\dagger_M)_j \partial_{x_j} + \partial_{x_j}(b^\dagger_M)_j}{2} = (1 + 2x_j\partial_{x_j}) - \partial_{x_j}(M\nabla)_j\ ,\ j = 1,\dots,d.$$

More precisely, q^M_k is an eigenvector of T_j belonging to the eigenvalue $2k_j+1$. If there is no direct coupling between the jth and nth direction, that is, $M_{jn} = M_{nj} = 0$ for some $j \neq n$, the operators T_j and T_n commute.

Whenever M is invertible, the raising operator $b^\dagger_M$ from Proposition 9 together with the TTRR gives rise to the multidimensional Rodrigues formula

$$q^M_k(x) = \exp\left(-x^T M^{-1} x\right)(-M\nabla)^k \exp\left(x^T M^{-1} x\right). \tag{6.18}$$

[2] The operators T_j can be seen as acting on the space of polynomials on $\mathbb{R}^d$.

We note that the Rodrigues formula (6.18) is in general not sufficient for deducing orthogonality relations for the polynomials. However, if M^{-1} is real and positive definite, the polynomials q_k^M are orthogonal with respect to the inner product on the Hilbert space $L^2(\mathbb{R}^d, \exp(-x^T M^{-1} x)dx)$. The construction of suitable inner products for more general complex symmetric matrices M is possible but less straightforward, see [DKT15, Remark 5].

6.3 Factorization

The Hermite type multivariate polynomials q_k^M can exhibit very different structures, depending on the matrix M that governs the mixing between the different coordinate directions in the TTRR (6.1).

Example. If $M = \mathrm{diag}(\lambda_1, ..., \lambda_d)$ is a diagonal matrix, there is no mixing between the different coordinate directions. Hence, the polynomials $\{q_k^M\}_{k \in \mathbb{N}^d}$ are simple tensor products

$$q_k^M(x) = \prod_{j=1}^{d} H_{k_j}^{\lambda_j}(x_j) \tag{6.19}$$

of d one-dimensional generalized Hermite polynomials. ■

In fact, it is easy to see that the polynomials q_k^M can be written as a tensor product with $s \leq d$ factors for all $k \in \mathbb{N}^d$ if and only if their generating function factorizes into s lower dimensional generating functions. In particluar, the explicit form of the generating function from Proposition 8 allows to formulate a simple criterion on when the polynomials factorize, see the following Proposition 10.

Proposition 10 (Tensor product polynomials)**.** *Let $M \in \mathbb{C}^{d \times d}$ be symmetric and $\sigma : \{1, \dots, d\} \to \{1, \dots, d\}$ be a permutation with permutation matrix $P_\sigma \in \mathbb{N}^{d \times d}$. Then, the following are equivalent:*

i) $P_\sigma M P_\sigma^T$ is a block-diagonal matrix with s blocks.

ii) For the partition

$$x^T P_\sigma^T = (y_1^T, \dots, y_s^T), \quad y_j \in \mathbb{R}^{d_j}, \quad \sum_{j=1}^{s} d_j = d,$$

of the variable vector x, there are polynomials $q^{M_j}_{(P_\sigma k)_j} : \mathbb{R}^{d_j} \to \mathbb{C}$ such that for all $k \in \mathbb{N}^d$

$$q_k^M(x) = \prod_{j=1}^{s} q^{M_j}_{(P_\sigma k)_j}(y_j), \tag{6.20}$$

where $(P_\sigma k)^T = \left((P_\sigma k)_1^T, \dots (P_\sigma k)_s^T\right)$. Moreover, $q^{M_j}_{(P_\sigma k)_j}$ satisfies a TTRR of the form (6.1) in d_j dimensions, with $M_j \in \mathbb{C}^{d_j \times d_j}$ and $P_\sigma M P_\sigma^T = \operatorname{diag}(M_1, \dots, M_s)$.

Proof. Suppose that i) holds true. Then, there are m matrices $M_j \in \mathbb{C}^{d_j \times d_j}$ with

$$\sum_{j=1}^{s} d_j = d, \quad d_j \in \mathbb{N},$$

such that the generating function of $\{q_k^M\}_{k \in \mathbb{N}^d}$ factorizes as

$$f(x,t) = \exp(2x^T t - t^T M t) = \prod_{j=1}^{s} \exp\left(2y_j^T v_j - v_j^T M_j v_j\right) \tag{6.21}$$

where $y_j, v_j \in \mathbb{C}^{d_j}$ are defined by

$$P_\sigma x = y \quad \text{and} \quad P_\sigma t = v. \tag{6.22}$$

Each of the factors on the right hand side of (6.21) can be recognized as the generating function for the polynomials $\{q^{M_j}_{\ell_j}\}_{P_\sigma^T \ell \in \mathbb{N}^d}$ obtained from a TTRR of the form (6.1) in dimension d_j, $j \in \{1, \dots, s\}$. Moreover, by Proposition 7, the product of the generating functions is the generating function of the tensor product.

The other implication follows from Proposition 8 in a similarly simple way. □

The characterization of factorization from Propostion 10 will become important in §8.3, where we prove that the Wigner functions of normalized Hagedorn wave packets always factorize.

6.4 Laguerre Connection

In Proposition 10 we showed that the polynomials $q_k^M : \mathbb{R}^d \to \mathbb{C}$ are tensor products of $s \leq d$ lower dimensional Hermite type polynomials for all $k \in \mathbb{N}^d$ if and only if there is a relabeling $\sigma : \{1, \ldots, d\} \to \{1, \ldots, d\}$ of the coordinates such that $P_\sigma M P_\sigma^T$ is block-diagonal with s blocks. For diagonal M the resulting polynomials (6.19) are tensor products of d univariate polynomials. However, if M has offdiagonal entries which are different from zero, the resulting polynomials q_k^M are not anymore tensor products of univariate polynomials.

We take this as motivation to develop a procedure that allows to express polynomials q_k^M with a potentially complicated matrix M by means of polynomials q_k^N associated with a simpler matrix N. Our strategy is to describe the effect on the polynomials q_k^M when deleting offdiagonal pairs of entries from the matrix M. Surprisingly, as shown in Proposition 11, on the level of polynomials this matrix simplification can be rewritten by applying a Laguerre polynomial

$$L_n^{(\alpha)}(x) = \sum_{j=0}^{n} \left(\begin{array}{c} n+\alpha \\ n-j \end{array} \right) \frac{1}{j!} (-x)^j \ , \quad n \in \mathbb{N} \ , \quad \alpha \geq 0,$$

to raising operators associated with the reduced matrix.

The connections between the classical Hermite and Laguerre polynomials are manifold, see, e.g., [Tha93] and [Sze75, §5.6]. Proposition 11 provides a novel type of Laguerre connection for the class of generalized Hermite polynomials q_k^M.

For a symmetrix matrix $M \in \mathbb{C}^{d\times d}$, we denote by

$$(M[n,m])_{ij} = \begin{cases} 0\,, & \{i,j\} = \{n,m\}, \\ M_{ij}\,, & \text{otherwise.} \end{cases}$$

the matrix which arises from M by deleting the offdiagonal entries M_{nm} and M_{mn}.

Proposition 11 (Laguerre Reduction). *Let $M \in \mathbb{C}^{d\times d}$ be symmetric, and $M_{nm} = \mu \neq 0$ for some $n \neq m$. Suppose $k \in \mathbb{N}^d$ with $k_n \geq k_m$. Then,*

$$\begin{aligned} q_k^M(x) &= \left(b_M^\dagger\right)^k 1 \\ &= \left(c^\dagger\right)^{k-k_m(e_n+e_m)} (-2\mu)^{k_m} k_m! L_{k_m}^{(k_n-k_m)}\left(\tfrac{1}{2\mu} c_n^\dagger c_m^\dagger\right) 1, \end{aligned} \tag{6.23}$$

where $c^\dagger = b^\dagger_{M[n,m]}$ denotes the polynomial raising operator for the reduced matrix $M[n,m]$. The case $k_n < k_m$ is analogous.

Proof. We denote by f_M the generating function of the polynomials q_k^M derived in Proposition 8, and by $f_{M[n,m]}$ the generating function for the polynomials $q_k^{M[n,m]}$. With the shorthand $k[n,m] = k - e_n k_n - e_m k_m$ one obtains

$$\begin{aligned} f_M(x,t) &= f_{M[n,m]}(x,t)\exp(-2\mu t_n t_m) \\ &= \left(\sum_{k\in\mathbb{N}^d} \frac{t^k}{k!}\left(c^\dagger\right)^k\right)\left(1 - 2\mu t_n t_m + \tfrac{1}{2!}(2\mu t_n t_m)^2 - \ldots\right) \\ &= \sum_{k\in\mathbb{N}^d} \frac{t^k \left(c^\dagger\right)^{k[n,m]}}{(k[n,m])!}\left(\sum_{j=0}^{\min(k_n,k_m)} \frac{(-2\mu)^j}{j!}\cdot\frac{(c_n^\dagger)^{k_n-j}}{(k_n-j)!}\cdot\frac{(c_m^\dagger)^{k_m-j}}{(k_m-j)!}\,1\right). \end{aligned}$$

Consequently, due to the definition of the generating function, this

implies

$$q_k^M(x) = \left(c^\dagger\right)^{k[n,m]} \sum_{j=0}^{\min(k_n,k_m)} \frac{k_n! k_m! (-2\mu)^j}{j!(k_n-j)!(k_m-j)!} (c_n^\dagger)^{k_n-j} (c_m^\dagger)^{k_m-j}\, 1 \tag{6.24}$$

and we can reorder the sum by means of the index $\ell = k_m - j \geq 0$ since $k_n \geq k_m$ holds by assumption. Thus,

$$\begin{aligned} q_k^M(x) &= \left(c^\dagger\right)^{k[n,m]} (-2\mu)^{k_m} k_m! (c_n^\dagger)^{k_n-k_m} \sum_{\ell=0}^{k_m} \frac{k_n! (-\frac{1}{2\mu} c_n^\dagger c_m^\dagger)^{k_m-\ell} 1}{(k_m-\ell)!(k_n-k_m+\ell)!\ell!} \\ &= \left(c^\dagger\right)^{k[n,m]} (-2\mu)^{k_m} k_m! (c_n^\dagger)^{k_n-k_m} L_{k_m}^{(k_n-k_m)} \left(\tfrac{1}{2\mu} c_n^\dagger c_m^\dagger\right) 1, \end{aligned}$$

where we utilised that $c_n^\dagger$ and $c_m^\dagger$ commute. □

Proposition 11 provides an expansion of the polynomials q_k^M in terms of the simpler Hermite type polynomials

$$q_\ell^{M[n,m]} \quad \text{with} \quad \ell \leq k.$$

In §6.5 we will proceed in the same direction, and derive expansions of the general polynomials q_M^k in terms of simple tensor product Hermite polynomials.

Remark 8. *By inspecting* (6.23) *one can see that the deleted matrix entry M_{nm} does not enter the formula apart from a simple rescaling. Moreover, the mixing induced by the offdiagonal entry M_{nm} happens only within the sets of polynomials that have the same difference of degree in direction n and m.*

In two dimensions there is at most one pair of nonzero offdiagonal entries of the symmetric matrix M, and hence the analysis simplifies considerably. Any symmetric matrix $M \in \mathbb{C}^{2\times 2}$ is of the form

$$M = \begin{pmatrix} \lambda_1 & \lambda_2 \\ \lambda_2 & \lambda_3 \end{pmatrix} \quad \text{with } \lambda_1, \lambda_2, \lambda_3 \in \mathbb{C}.$$

Hence, applying Proposition 11 at most one time yields a diagonal matrix that gives rise to tensor product Hermite polynomials of the form (6.19). The following Corollary 1 contains the complete charaterization of the polynomials q_k^M in two dimensions.

Corollary 1 (Two-dimensional polynomials)**.** *Let $k \in \mathbb{N}^2$ with $k_1 \geq k_2$. Then,*

$$q_k^M(x) = \begin{cases} (-2\lambda_2)^{k_2} k_2! (a_{\lambda_1}^\dagger)^{k_1-k_2} L_{k_2}^{(k_1-k_2)}\left(\frac{1}{2\lambda_2} a_{\lambda_1}^\dagger a_{\lambda_3}^\dagger\right) 1, & \lambda_2 \neq 0 \\ \left(a_{\lambda_1}^\dagger\right)^{k_1} \left(a_{\lambda_3}^\dagger\right)^{k_2} 1, & \lambda_2 = 0 \end{cases} \tag{6.25}$$

and the case $k_1 \leq k_2$ is analogous.

Proof. Note that (6.19) covers the case $\lambda_2 = 0$. For $\lambda_2 \neq 0$, a single application of Proposition 11 yields the desired formula. □

Corollary 1 asserts that we can rewrite $\left(b_M^\dagger\right)^k$ via products of the one-dimensional raising operator $a_\bullet^\dagger$ from (6.8). Let us take a closer look on the form of the polynomials defined on the right hand side of (6.25). If $\lambda_2 = 0$, one directly has the factorization

$$q_k^M(x) = H_{k_1}^{\lambda_1}(x_1) H_{k_2}^{\lambda_3}(x_2).$$

Furthermore, in the case $\lambda_2 \neq 0$ one can deduce that each polynomial q_k^M is a linear combination of at most $\min\{k_1, k_2\}$ many tensor products of the form

$$\left(a_{\lambda_1}^\dagger\right)^n \left(a_{\lambda_3}^\dagger\right)^m 1 = H_n^{\lambda_1}(x_1) H_m^{\lambda_3}(x_2), \tag{6.26}$$

where $n - m = k_1 - k_2$.

A class of polynomials which is of interest with regard to Hagedorn wave packets are those polynomials generated from the anti-diagonal matrix

$$M = \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix} =: N_\lambda. \tag{6.27}$$

Since here the diagonal raising operator $a_0^\dagger$ creates monomials, we end up with the Laguerre formula

$$q_k^{N_\lambda}(x) = (-\lambda)^{k_2} k_2! 2^{k_1} x_1^{k_1-k_2} L_{k_2}^{(k_1-k_2)}\left(\tfrac{2}{\lambda} x_1 x_2\right) \tag{6.28}$$

whenever $\lambda \neq 0$ and $k_1 \geq k_2$. In fact, polynomials of the form (6.28) with $\lambda = 1$ appear in the Wigner function of a pair of Hermite functions, see [Fol89, §1.6], [LT14, Theorem 1], or §8 for the general Hagedorn-Wigner formula.

6.5 Tensor Product Representation

In more than two dimensions the mixing matrix M can have more than one offdiagonal pair of nonzero entries. Then, in order to arrive at simple Hermite tensor products generated from a diagonal mixing matrix, one eventually has to apply the Laguerre reduction from Proposition 11 several times. Hence, a simple characterization as in the bivariate case is not available anymore. The following Theorem 2 provides an expansion of the general polynomials in terms of Hermite tensor product polynomials.

Theorem 2 (Tensor product representation)**.** *Let $M \in \mathbb{C}^{d\times d}$ be symmetric, and suppose that there are precisely $0 \leq r \leq \frac{1}{2}d(d-1)$ nonzero offdiagonal pairs of entries $M_{\alpha_j\beta_j} = M_{\beta_j\alpha_j} = \lambda_j \neq 0$, where $1 \leq \alpha_j < \beta_j \leq d$ for all $j = 1, \ldots, r$. Then, for $k \in \mathbb{N}^d$,*

$$q_k^M(x) = \sum_{\substack{\ell\in\mathbb{N}^r \\ \ell_j \leq \min\{k_{\alpha_j}, k_{\beta_j}\}}} (-2\lambda)^\ell \ell! \binom{k_\alpha}{\ell} \binom{k_\beta}{\ell} \prod_{i=1}^d H_{k_i-(E\ell)_i}^{M_{ii}}(x_i)$$

where $k_\alpha \in \mathbb{N}^r$ with $(k_\alpha)_j = k_{\alpha_j}$. The index matrix $E \in \{0,1\}^{d\times r}$ is defined by

$$E_{ij} = (e_{\alpha_i} + e_{\beta_i})_j.$$

Proof. We start by recalling (6.24), which implies

$$q_k^M(x) = \sum_{m=0}^{\min\{k_{\alpha_j}, k_{\beta_j}\}} m! \binom{k_{\alpha_j}}{m} \binom{k_{\beta_j}}{m} (-2\lambda_j)^m q_{k-m(e_{\alpha_j}+e_{\beta_j})}^{M[\alpha_j,\beta_j]}(x) 1, \quad (6.29)$$

for all $j = 1, \ldots, n$. One can use the matrix E in order to write

$$k - m(e_{\alpha_j} + e_{\beta_j}) = k - (Em\widehat{e}_j)$$

where $\widehat{e}_j$ denotes the jth unit vector in $\mathbb{R}^r$. Iterating this procedure until all non-vanishing offdiagonal entries of M are deleted completes the proof. □

By Theorem 2, one can rewrite any polynomial q_k^M as a sum of finitely many tensor product Hermite polynomials

$$q_\ell^{\mathrm{diag}(M)}(x) = \prod_{j=1}^{d} H_\ell^{M_{jj}}(x_j), \quad \ell \leq k,$$

associated with the diagonal of M. The number of summands in the expansion depends on the number of nonzero offdiagonal entries $M_{ij} = M_{ji} \neq 0$ of M, and the corresponding indices k_i, and k_j. We remark that in the case $r = 1$ one regains the Laguerre formula (6.25), multiplied with a tensor Hermite polynomial associated with the remaining directions unaffected by the mixing.

Theorem 2 suggests the rule of thumb that the polynomials q_k^M typically become more complicated for matrices M that are not sparse. As examples, we consider the real coefficient polynomials

$$q_{k_1,k_2}^{M^{(j)}} \in \mathbb{R}[x_1, x_2], \quad j \in \{1, 2, 3, 4\},$$

in two dimensions, generated from the real symmetric matrices

$$M^{(1)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad M^{(2)} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$M^{(3)} = \tfrac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \quad M^{(4)} = \begin{pmatrix} \frac{73}{16} & \frac{1}{2} \\ \frac{1}{2} & \frac{73}{16} \end{pmatrix}.$$

We only consider real polynomials in order to facilitate their illustration. Note that $M^{(1)}, M^{(2)}$, and $M^{(3)}$ are orthogonal whereas $M^{(4)}$ is not.

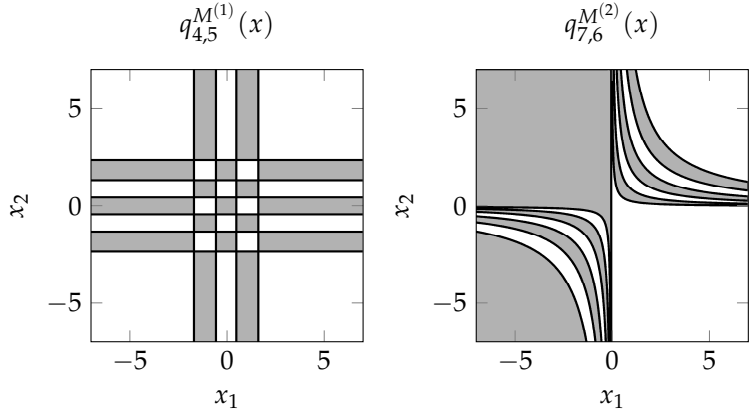

FIGURE 2: Illustration of the two examplary polynomials $q_{4,5}^{M^{(1)}}$ (left) and $q_{7,6}^{M^{(2)}}$ (right). The nodal sets of the polynomials are depicted by black lines. Grey coloring is used for the areas in which the polynomials attain negative values.

For an explicit form of the polynomials $q_{4,6}^{M^{(1)}}$, and $q_{7,6}^{M^{(2)}}$, we invoke (6.26) and (6.28). We observe that the first polynomial

$$q_{4,6}^{M^{(1)}}(x) = H_4^1(x_1)H_6^1(x_2),$$

is a simple tensor product of two classical Hermite polynomials. For the second polynomial, one obtains the formula

$$q_{7,6}^{M^{(2)}}(x) = 6!2^7 x_1 L_6^{(1)}(2x_1x_2). \tag{6.30}$$

The consequences of these simple formulas are reflected in the structure of the nodal sets[3] of the polynomials depicted in figure 2. The nodal set of the tensor Hermite polynomial $q_{4,6}^{M^{(1)}}$ has the form

[3]The nodal set of a polynomial $p : \mathbb{R}^d \to \mathbb{C}$ is the set of roots $\{x \in \mathbb{R}^d : p(x) = 0\}$.

of a rectangular grid with 6 horizontal and 4 vertical lines. In contrast, for $q_{7,6}^{M^{(2)}}$ the nodal set contains 6 disjoint hyperbolas. This is due to the fact that the Laguerre polynomial $L_6^{(1)}$ has 6 distinct positive roots.

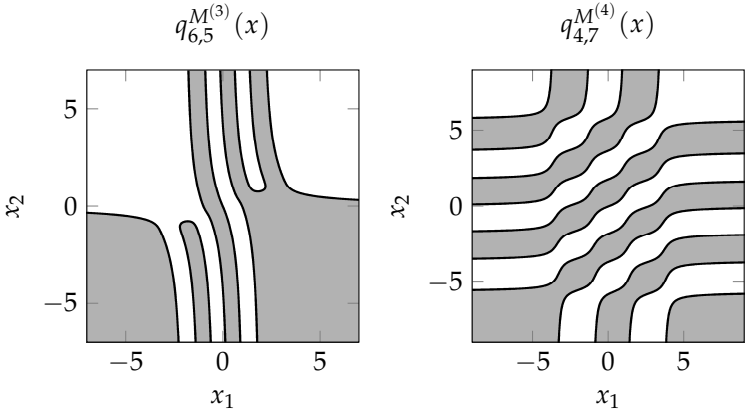

FIGURE 3: Illustration of the bivariate polynomials $q_{6,5}^{M^{(3)}}$ (left) and $q_{4,7}^{M^{(4)}}$ (right). The nodal sets of the polynomials are depicted by black lines. Grey coloring is used for the areas in which the polynomials attain negative values.

In contrast to $M^{(1)}$ and $M^{(2)}$, the matrices $M^{(3)}$ and $M^{(4)}$ have no vanishing entries. Hence, in view of Theorem 2, we expect the corresponding polynomials to exhibit more involved structures. The illustrations of the nodal sets of $q_{6,5}^{M^{(3)}}$ and $q_{4,7}^{M^{(4)}}$ from figure 3 support this intuition. It is fascinating that for real matrices[4] M, the polynomials q_k^M can develop such nontrivial structures. We find it even more surprising that, by Corollary 1, $q_{6,5}^{M^{(3)}}$ and $q_{4,7}^{M^{(4)}}$ can be written as a sum of only 5 and 4 Hermite tensor product polynomials, respectively.

[4] $M^{(3)}$ is even orthogonal.

7 Hagedorn Wave Packets

In general it is not possible to compute explicit solutions for Schrödinger equations. However, for harmonic oscillator Hamiltonians of the form

$$H_{\text{ho}} = \tfrac{1}{2}\left(-\varepsilon^2\partial_x^2 + \omega x^2\right), \quad \omega > 0, \tag{7.1}$$

both the stationary, and the evolution problem can be solved analytically. The solutions of the stationary problem

$$H_{\text{ho}}\psi = E\psi, \quad \psi \in L^2(\mathbb{R}), \tag{7.2}$$

are Hermite functions, and can be computed by means of simple ladder operators. This "algebraic method" of solving the Schrödinger equation goes back to Dirac, see [Dir30].

Hagedorn wave packets take the place of the Hermite function solutions of (7.2) if one considers multidimensional, non-isotropic generalizations of the harmonic oscillator Hamiltonian (7.1). They were first introduced in [Hag80], and are also known as generalized squeezed states in the literature, see [CR12, §3.4]. We take the general viewpoint of [GS12, LST15, DKT15] and parametrize Hagedorn wave packets via positive Lagrangian frames, see also §7.1 for the background in symplectic linear algebra. In particular, our analysis includes non-normalized wave packets that can be used for treating non-selfadjoint evolution problems, see [GS12, LST15].

The ladder operator representation of Hagedorn wave packets is the topic of §7.2. Afterwards, in §7.4 we discuss the connection to the polynomials q_k^M we investigated in §6. This chapter mainly resembles the contents of §3 in our joint paper [DKT15].

7.1 Symplectic Linear Algebra

This section contains a summary of results from symplectic linear algebra with an emphasis on complex Lagrangian subspaces, see also [Hör07, §21.6], and [GS12, LST15].

Let us recall from (2.7) that the classical phase space $\mathbb{R}^{2d}$ is a symplectic vector space, equipped with the symplectic form $\Omega(z,w) = -z^T J w$. Furthermore, the matrix J defines a complex structure on $\mathbb{R}^{2d}$, that is, $J^2 = -\mathrm{Id}_{2d}$. We consider the complexification $(\mathbb{C}^{2d}, \Omega_{\mathbb{C}})$ of phase space, where the symplectic form

$$\Omega_{\mathbb{C}}(z,w) = -z^T J w, \quad z,w \in \mathbb{C}^{2d}, \tag{7.3}$$

is the holomorphic extension of Ω, see e.g. [Zwo12, §13.2]. As in [Hö95], we are interested in Lagrangian subspaces of $(\mathbb{C}^{2d}, \Omega_{\mathbb{C}})$.

Definition 3 (Isotropic and Lagrangian subspaces)**.** *Let $L \subset \mathbb{C}^{2d}$ be a linear subspace.*

i) If $\Omega_{\mathbb{C}}(z,w) = 0$ for all $z,w \in L$, L is called an isotropic subspace *of $\mathbb{R}^{2d}$.*

ii) If L is an isotropic subspace of complex dimension d, it is called a Lagrangian subspace.

Due to the non-degeneracy of $\Omega_{\mathbb{C}}$, it is easy to see that Lagrangian subspaces are isotropic subspaces of maximal dimension. By means of the Hermitian quadratic form $i\Omega_{\mathbb{C}}(\overline{w}, z)$ on $\mathbb{C}^d$ one can further define positive and negative Lagrangian subspaces, see also [LST15, §2].

Definition 4 (Positive and negative Lagrangian subspaces)**.** *Let $L \subset \mathbb{C}^{2d}$ be a Lagrangian subspace. L is called* positive *(or* negative*) if*

$$\tfrac{1}{2\mathrm{i}}\Omega_{\mathbb{C}}(\overline{z}, z) > 0 \qquad \big(\text{or} \quad \tfrac{\mathrm{i}}{2}\Omega_{\mathbb{C}}(z, \overline{z}) < 0\big)$$

for all $z \in L$.

The more general Lagrangian submanifolds together with the associated generating functions and distributions play a prominent role in the theory of Fourier integral operators. A standard reference is [Hör09, §25]. In this dissertation we restrict ourselves to linear Lagrangian subspaces.

Definition 5 (Lagrangian frame)**.** *Let $Z \in \mathbb{C}^{2d\times d}$. Then, the matrix Z is called* isotropic *if*

$$Z^T J Z = 0, \tag{7.4}$$

and a Lagrangian frame*, if Z has full rank. We call a Lagrangian frame Z* positive *, if*

$$\tfrac{1}{2\mathrm{i}} Z^* J Z =: \Gamma_Z > 0 \tag{7.5}$$

and normalized *if $\Gamma_Z = \mathrm{Id}_d$.*

Lagrangian frames are precisely the ordered bases of Lagrangian subspaces. In other words, the image of a (positive) Lagrangian frame $Z \in \mathbb{C}^{2d\times d}$ is a (positive) Lagrangian subspace of $\mathbb{C}^{2d}$, as one can easily verify. We employ positive Lagrangian frames in §7.2 for the parametrization of Hagedorn wave packets. Similarly as for phase space points $z = (q, p)$, for Lagrangian frames $Z \in \mathbb{C}^{2d\times d}$ we will use the notation $Z = (Q; P)$ with $Q, P \in \mathbb{C}^{d\times d}$.

Remark 9. *Normalized Lagrangian frames are in one-to-one correspondence with symplectic matrices. If Z is a normalized Lagrangian frame, then $(\mathrm{Re}(Z), \mathrm{Im}(Z)) \in \mathbb{R}^{2d\times 2d}$ is a symplectic matrix. On the other hand, given a symplectic matrix $S = (A, B) \in \mathbb{R}^{2d\times 2d}$, the matrix $A + iB \in \mathbb{C}^{2d\times d}$ defines a normalized Lagrangian frame.*

By comparing (7.4) and (7.5), one can immediately see that positive Lagrangian frames cannot have real entries only. In fact, for a positive Lagrangian frame $Z = (Q; P) \in \mathbb{C}^{2d\times d}$ one can easily show that Q and P are invertible, and PQ^{-1} is complex symmetric with

$$\mathrm{Im}\left(PQ^{-1}\right) = \left(Q\Gamma_Z^{-1}Q^*\right)^{-1} > 0. \tag{7.6}$$

In other words, PQ^{-1} lies in the upper Siegel half space

$$\Sigma_d = \{C \in \mathbb{C}^{d\times d} : C \text{ is symmetric and } \mathrm{Im}C > 0\}.$$

By [GS12, Lemma 2.2] one can actually rewrite any positive Lagrangian subspace as the graph of a linear map induced by a matrix in the upper Siegel half space. This parametrization is unique for a large class of Lagrangian subspaces, see [LST15, Lemma 2.3].

A proof for the following Lemma can be found in [LST15, Proposition 2.4].

Lemma 9 (Symplectic metric and complex structure)**.** *Let $Z \in \mathbb{C}^{2d\times d}$ be a normalized Lagrangian frame. Then, one has*

$$ZZ^* = \mathrm{Re}\,(ZZ^*) - iJ, \tag{7.7}$$

and $\mathrm{Re}\,(ZZ^*)$ *is a real symmetric, positive definite, symplectic matrix. Moreover, one has*

$$(\mathrm{Re}\,(ZZ^*)\,J)^2 = -\mathrm{Id}_{2d}. \tag{7.8}$$

We remark that if two normalized Lagrangian frames Z, Y span the same Lagrangian subspace L, there is an unitary matrix $U \in U(d)$ such that $Z = YU$. In particular $ZZ^* = YY^*$ only depends on the Lagrangian subspace L. Hence, by Lemma 9 and (7.8),

$$G_Z := \mathrm{Re}\,(ZZ^*)^{-1} = J^T \mathrm{Re}\,(ZZ^*)\,J$$

defines a symplectic metric, and

$$J_Z = JG_Z, \quad J_Z^2 = -\mathrm{Id}_{2d}, \tag{7.9}$$

a complex structure on phase space, both of which only depend on the positive Lagrangian subspace $L = \mathrm{Range}Z$. Since $-JJ_Z$ is symmetric and positive definite, the complex structure J_Z is called *compatible with the symplectic structure* Ω, see [GS12] or [LST15, §2.4].

Let $\varepsilon > 0$ be a small semiclassical parameter. Then, given a phase space center $z = (q, p) \in \mathbb{R}^{2d}$ and a positive Lagrangian

frame $Z = (Q;P) \in \mathbb{C}^{2d\times d}$, we define the *Hagedorn ground state* $\varphi_0^\varepsilon[Z;z] : \mathbb{R}^d \to \mathbb{C}$ as

$$\varphi_0^\varepsilon[Z;z](x) = (\pi\varepsilon)^{-\frac{d}{4}} \det(Q)^{-\frac{1}{2}} \mathrm{e}^{\left(\frac{\mathrm{i}}{2\varepsilon}(x-q)^T PQ^{-1}(x-q)+\frac{\mathrm{i}}{\varepsilon}p\cdot(x-q)\right)}. \tag{7.10}$$

From (7.6) we know that $\varphi_0^\varepsilon[Z;z]$ decays exponentially as $|x| \to \infty$, and hence defines a Schwartz function on $\mathbb{R}^d$. We note that $\varphi_0^\varepsilon[Z;z]$ is only defined up to a global phase since one has to choose a branch for the square root of $\det(Q)$. This phase is typically fixed by imposing a continuity condition.

Remark 10 (Complex centers)**.** *In* (7.10)*, we could also allow for complex phase space centers $z \in \mathbb{C}^{2d}$. This is done in [GS12, LST15], where the authors consider non-selfadjoint evolution problems for which the underlying classical Hamiltonian flow is complex.*

However, by using the projection

$$P_Z : \mathbb{C}^{2d} \to \mathbb{R}^{2d}, \quad P_Z(z) = \mathrm{Re}z + J_Z \mathrm{Im}z,$$

it is sufficient to treat wave packets with real centers only, see also [GS12, Theorem 2.1] or [LST15, Theorem 3.12 and §4.5]. Since in this thesis we do not deal with non-selfadjoint evolution problems, in the following we only consider real phase space centers $z \in \mathbb{R}^{2d}$.

If $Z \in \mathbb{C}^{2d\times d}$ is a positive Lagrangian frame, it can be normalized by means of the matrix Γ_Z from (7.5). We denote by

$$Z_0 = Z\Gamma_Z^{-1/2},$$

the normalization of Z. The normalization of the Lagrangian frame implies the L^2-normalization of the corresponding ground state, since one has

$$\varphi_0^\varepsilon[ZC;z] = \det(C)^{-1/2}\varphi_0^\varepsilon[Z;z] \tag{7.11}$$

for any invertible $C \in \mathbb{C}^{d\times d}$, and $\|\varphi_0^\varepsilon[Z_0;z]\|_{L^2} = 1$.

7.2 Ladder Operators and Excited States

Given a positive Lagrangian frame $Z \in \mathbb{C}^{2d\times d}$ and a phase space center $z \in \mathbb{R}^{2d}$, one constructs the Hagedorn wave packets

$$\varphi_k^\varepsilon[Z;z] = \tfrac{1}{\sqrt{k!}}(A^\dagger[Z;z])^k \varphi_0^\varepsilon[Z;z], \quad k \in \mathbb{N}^d, \tag{7.12}$$

from the Hagedorn ground state (7.10) by applying the raising operator

$$A^\dagger[Z;z] = -\tfrac{\mathrm{i}}{\sqrt{2\varepsilon}} Z^* J(\mathrm{op}_\varepsilon^{\mathrm{We}}(z) - z), \tag{7.13}$$

where

$$\mathrm{op}_\varepsilon^{\mathrm{We}}(z) = \begin{pmatrix} x \\ -i\varepsilon\nabla_x \end{pmatrix}$$

denotes the Weyl quantized vector of coordinate symbols, see §5.2. We introduce the operator $A[Z;z]$ as the formal adjoint of $A^\dagger[Z;z]$,

$$A[Z;z] = \tfrac{\mathrm{i}}{\sqrt{2\varepsilon}} Z^T J(\mathrm{op}_\varepsilon^{\mathrm{We}}(z) - z). \tag{7.14}$$

If $Z = Z_0$ is normalized, $A[Z_0;z]$ acts as a lowering operator, that is,

$$A_j[Z_0;z]\varphi_k^\varepsilon[Z_0;z] = \sqrt{k_j}\,\varphi_{k-e_j}^\varepsilon[Z_0;z]. \tag{7.15}$$

This property fails to hold for non-normalized Lagrangian frames, where the appropriate lowering operator is not anymore the formal adjoint of the raising operator $A^\dagger[Z;z]$. One can prove that the so-called *Lagrangian ideal*

$$\mathcal{I}(L,z) = \{\psi \in \mathcal{S}'(\mathbb{R}^d) : A[Z;z]\psi = 0 \text{ for all } Z \text{ with } \mathrm{Range} Z = L\}$$

associated with a positive Lagrangian subspace $L \subset \mathbb{C}^{2d}$ and a phase space center $z \in \mathbb{R}^{2d}$ is given by the one-dimensional span of the ground state $\varphi_0^\varepsilon[Z_0;z]$ for some normalized Z_0 with $\mathrm{Range} Z_0 = L$, see[5] [LST15, Proposition 3.5] or [Hö95, Proposition 5.1]. This

[5] The lowering operator in [LST15] is defined differently from (7.14), but the proof works all the same.

makes sense since by (7.11) the ground states associated with two different Lagrangian frames that span the same positive Lagrangian subspace coincide up to a global prefactor. In particular, for two positive Lagrangian frames $Z, Y \in \mathbb{C}^{2d\times d}$ one has

$$A_j[Z;z]\varphi_0[Y,z] = 0, \quad \text{for all } \ j = 1,\dots,d$$

if and only if $\mathrm{Range} Z = \mathrm{Range} Y$.

The ladder operators satisfy the following commutation relations, see [LST15, Lemma 3.2]. We include a proof for the convenience of the reader.

Lemma 10 (Commutation relations)**.** *Let Z, Y be positive Lagrangian frames and $z \in \mathbb{R}^{2d}$. Then, one has*

$$\begin{aligned}
\left[\, A_i^\dagger[Z;z], A_j^\dagger[Y;z] \,\right] &= \tfrac{\mathrm{i}}{2}\left(Z^* J \overline{Y}\right)_{ij}, \\
\left[\, A_i[Z;z], A_j[Y;z] \,\right] &= -\tfrac{\mathrm{i}}{2}\left(Z^T J Y\right)_{ij}, \\
\left[\, A_i[Z;z], A_j^\dagger[Y;z] \,\right] &= \tfrac{\mathrm{i}}{2}\left(Z^T J \overline{Y}\right)_{ij}
\end{aligned}$$

for all $i, j \in \{1,\dots,d\}$.

Proof. We start by noting that both $A_i[Z;z]$ and $A_i^\dagger[Z;z]$ are Weyl quantized operators with linear symbols. Moreover, one computes

$$\nabla\sigma^{\mathrm{We}}\left(A_i[Z;z]\right) \equiv -\tfrac{i}{\sqrt{2\varepsilon}} J Z_i, \quad \nabla\sigma^{\mathrm{We}}\left(A_j^\dagger[Y;z]\right) \equiv \tfrac{i}{\sqrt{2\varepsilon}} J \overline{Y}_j,$$

with $Z = (Z_1,\dots,Z_d)$ and $Y = (Y_1,\dots,Y_d)$. Hence, from Lemma 8 we know that

$$\begin{aligned}
\left[\, A_i[Z;z], A_j[Y;z] \,\right] &= -\mathrm{i}\varepsilon \mathrm{op}_\varepsilon^{\mathrm{We}}\left(\{\sigma^{\mathrm{We}}(A_i[Z;z]), \sigma^{\mathrm{We}}(A_j[Y;z])\}\right) \\
&= \tfrac{\mathrm{i}}{2}\left(Z_i^T J^T J^T J Y_j\right) \\
&= -\tfrac{\mathrm{i}}{2}\left(Z^T J Y\right)_{ij}
\end{aligned}$$

and the other identities then follow from

$$A[Z;z] = -A^\dagger[\overline{Z};z],$$

which just makes sense as a calculative identity since $\overline{Z}$ is a negative Lagrangian frame. □

From Lemma 10 and Definition 5 follows that the components of the raising and lowering operators commute,

$$\Big[\, A_i^\dagger[Z;z], A_j^\dagger[Z;z] \,\Big] = 0, \quad \big[\, A_i[Z;z], A_j[Z;z] \,\big] = 0.$$

Moreover, one has

$$\Big[\, A_i[Z;z], A_j^\dagger[Z;z] \,\Big] = (\Gamma_Z)_{ij}$$

and hence the ladder operators associated with a normalized Lagrangian frame satisfy canonical commutation relations.

The Heisenberg-Weyl operator $\widehat{T}_z$ from (5.10) can be used for translating Hagedorn wave packets as

$$\varphi_k^\varepsilon[Z;(q,p)] = \mathrm{e}^{-\frac{\mathrm{i}}{2\varepsilon}p\cdot q}\widehat{T}_{(q,p)}\varphi_k^\varepsilon[Z;0],$$

and the corresponding ladder operators transform accordingly,

$$\widehat{T}_w \mathrm{op}_\varepsilon^{\mathrm{We}}(z)\widehat{T}_w^{-1} = \mathrm{op}_\varepsilon^{\mathrm{We}}(z) - w, \quad w \in \mathbb{R}^{2d}.$$

For this reason it is sufficient to consider wavepackets and ladder operators centered in the origin, and we write

$$\varphi_k^\varepsilon[Z;0] =: \varphi_k^\varepsilon[Z], \quad A[Z;0] =: A[Z], \quad A^\dagger[Z;0] =: A^\dagger[Z]$$

for readability. In their work on non-selfadjoint quadratic Hamiltonians, the authors of [LST15] encounter the situation that the positive Lagrangian subspace Range$Y$ associated with the ladder operator $A^\dagger[Y]$ is different from the Lagrangian subspace Range$Z$ that defines the ground state $\varphi_0^\varepsilon[Z]$. In order to take these wave

functions into account, we also allow for more general Hagedorn wave packets of the form

$$\varphi_k^\varepsilon[Z,Y] := \frac{1}{\sqrt{k!}}(A^\dagger[Y])^k \varphi_0^\varepsilon[Z], \tag{7.16}$$

which are associated with two arbitrary positive Lagrangian frames $Z, Y \in \mathbb{C}^{2d\times d}$. Without loss of generality, in the following we can assume that $Z = Z_0$ is normalized, since by (7.11) this only amounts to neglecting a prefactor.

7.3 Spectral Properties

Suppose that $Z_0 = (Q;P)$ is a normalized Lagrangian frame. Then, the commutation relations from Lemma 10 together with (7.12) and (7.15) imply

$$\langle \varphi_k^\varepsilon[Z_0;z], \varphi_\ell^\varepsilon[Z_0;z]\rangle_{L^2} = \delta_{k\ell}. \tag{7.17}$$

In particular, the Hagedorn wave packets associated with a normalized Lagrangian frame are L^2-normalized. One observes that $\varphi_k^\varepsilon[Z_0;z]$ is an eigenfunction for the eigenvalue $|k|+d$ of the quadratic number operator

$$\begin{aligned} N_{Z_0} &= A[Z_0;z]\cdot A^\dagger[Z_0;z] \\ &= \frac{1}{2\varepsilon}(\mathrm{op}_\varepsilon^{\mathrm{We}}(z)-z)^T \begin{pmatrix} PP^* & -PQ^* \\ -QP^* & QQ^* \end{pmatrix} (\mathrm{op}_\varepsilon^{\mathrm{We}}(z)-z) + \frac{d}{2}, \end{aligned}$$

that is elliptic and essentially selfadjoint on $L^2(\mathbb{R}^d)$. Hence, normalized Hagedorn wave packets can be seen as generalizations of the Hermite functions, which diagonalize the one-dimensional Harmonic oscillator (7.1). They appear as the eigenfunctions of higher dimensional harmonic oscillators of the form[6]

$$H_{\mathrm{ho}}^{Z_0} = \tfrac{1}{2}(\mathrm{op}_\varepsilon^{\mathrm{We}}(z)-z)^T G_{Z_0} (\mathrm{op}_\varepsilon^{\mathrm{We}}(z)-z). \tag{7.18}$$

[6]Since z is real, we can use the real width matrix G_{Z_0} by recalling (7.7).

where $G_{Z_0} \in \mathbb{R}^{2d \times 2d}$ is the symplectic metric associated with a positive Lagrangian frame Z. Since the normalized Hagedorn wave packets are orthogonal by (7.17) and form a complete set of eigenvectors for $H_{\text{ho}}^{Z_0}$,

$$\{\varphi_k^\varepsilon[Z_0; z]\}_{k \in \mathbb{N}^d} \tag{7.19}$$

is an orthonormal basis of $L^2(\mathbb{R}^d)$, as has been shown in [Hag98].

If Z is not normalized, the commutation relations from Lemma 10 imply that the Hagedorn wave packets $\varphi_k^\varepsilon[Z]$ are typically not orthogonal anymore. However, by expressing the ladder operators for the unnormalized Lagrangian frame in terms of its normalization one can show that Hagedorn wave packets of different total degree are still orthogonal.

Proposition 12 (Level orthogonality)**.** *Let $Z \in \mathbb{C}^{2d \times d}$ be a positive Lagrangian frame, and Z_0 its normalization. Then,*

$$A^\dagger[Z; z] = \Gamma_Z^{1/2} A^\dagger[Z_0; z] \quad , \quad A[Z; z] = \overline{\Gamma_Z^{1/2}} A[Z_0; z]$$

and $\{\varphi_k^\varepsilon[Z, z]\}_{k \in \mathbb{N}^d}$ is a basis of $L^2(\mathbb{R}^d)$. Furthermore, one has

$$\langle \varphi_k^\varepsilon[Z; z], \varphi_\ell^\varepsilon[Z; z] \rangle_{L^2} = 0 \tag{7.20}$$

whenever $|\ell| \neq |k|$.

Proof. Inspecting the definitions of the ladder operators (7.13) and (7.14) yields the formulas for the ladder operators. The basis property of the unnormalized wave packets $\{\varphi_k^\varepsilon[Z, z]\}_{k \in \mathbb{N}^d}$ then follows from the invertibility of Γ_Z, and the fact that

$$\{\varphi_k^\varepsilon[Z_0; z]\}_{k \in \mathbb{N}^d}$$

is a basis of $L^2(\mathbb{R}^d)$.

We can use the normalized raising operator in order to rewrite $\varphi_k^\varepsilon[Z; z]$ as a linear combination of normalized wave packets

$$\varphi_k^\varepsilon[Z; z](x) = \sum_{|\ell|=k} \alpha_\ell \varphi_\ell^\varepsilon[Z_0; z](x) \tag{7.21}$$

of the same total degree for some constants $\alpha_\ell \in \mathbb{C}$. Consequently $\varphi_k^\varepsilon[Z;z]$ is contained in the eigenspace of N_{Z_0} associated with the eigenvalue $|k|+d$. The assertion (7.20) then follows from the fact that eigenfunctions $\varphi_k^\varepsilon[Z;z]$ and $\varphi_\ell^\varepsilon[Z;z]$ belonging to different eigenspaces of the selfadjoint operator N_{Z_0} are orthogonal. □

From the proof of Proposition 12 follows in particular that the non-normalized Hagedorn wave packet $\varphi_k^\varepsilon[Z;z]$ is an eigenfunction of the harmonic oscillator $H_{\mathrm{ho}}^{Z_0}$ defined in (7.18), belonging to the eigenvalue $\varepsilon(|k|+\frac{d}{2})$.

7.4 Polynomial Relation

From the definition of the raising operator is it clear that

$$\varphi_k^\varepsilon[Z,Y](x) = p_k^\varepsilon[Z,Y](x)\varphi_0^\varepsilon[Z](x),$$

for some polynomial $p_k^\varepsilon[Z,Y]$ of total degree $|k|$. In this section, we interrelate these polynomials to the generalized Hermite polynomials q_k^M we analyzed in §6. This will facilitate to extend the generating function calculus developed for the polynomials q_k^M to Hagedorn wave packets. A generating function for the polynomials $p_k^\varepsilon[Z_0,Z_0]$ has also been recently derived by George Hagedorn in [Hag15], but with different techniques.

For simplicity we first state the relation for normalized Hagedorn wave packets, which can also be found in [LST15].

Lemma 11. *Let $Z = Z_0 = (Q;P) \in \mathbb{C}^{2d\times d}$ be a normalized Lagrangian frame. Then, the k-th Hagedorn wave packet, $k \in \mathbb{N}^d$, can be rewritten as*

$$\varphi_k^\varepsilon[Z](x) = \frac{1}{\sqrt{2^{|k|}k!}} q_k^M\left(\tfrac{1}{\sqrt{\varepsilon}}Q^{-1}x\right)\varphi_0^\varepsilon[Z](x), \tag{7.22}$$

where $M = Q^{-1}\overline{Q}$ is symmetric and unitary, and q_k^M is a generalized Hermite polynomial satisfying the TTRR (6.1)*.*

The formula from Lemma 11 provides a first connection between Hagedorn wave packets and the generalized Hermite polynomials from §6.

Example: Rescaled Hermite functions. From Lemma 11 one can infer that semiclassically rescaled tensor Hermite functions are a special case of Hagedorn wave packets, namely those associated with the normalized Lagrangian frame $Z_{\text{Hermite}} = (\text{Id}, \text{iId}) \in \mathbb{C}^{2d\times d}$. In this case we have $M = \text{Id}$, and Lemma 11 together with (6.19) implies

$$\varphi_k^\varepsilon[Z_{\text{Hermite}}](x) = \frac{(\pi\varepsilon)^{-d/4}}{\sqrt{2^{|k|}k!}} \prod_{j=1}^{d} H_{k_j}^1\left(\tfrac{1}{\sqrt{\varepsilon}}x_j\right) \mathrm{e}^{-\frac{|x_j|^2}{2\varepsilon}}.$$

■

From Lemma 11 we conclude that the polynomial $p_k^\varepsilon[Z_0]$ associated with the normalized Lagrangian frame $Z_0 = (Q; P)$ depends only on Q, and not on P. Furthermore, the observation

$$Q \in \mathbb{R}^{d\times d} \quad \Longleftrightarrow \quad M = Q^{-1}\overline{Q} = \text{Id},$$

by (7.22) and the above example implies that the resulting Hagedorn wave packet is a usual tensor Hermite function evaluated on the the transformed coordinates $y = Q^{-1}x$.

In general, however, the structure of Hagedorn wave packets can be much more involved. In particular, if Q is not real, M is typically not block-diagonal, and hence the polynomials $p_k^\varepsilon[Z_0, Y_0]$ do not factorize, as can be seen by invoking Proposition 10. In the following Proposition 13 we extend Lemma 11 to the generalized Hagedorn wave packets $\varphi_k^\varepsilon[Z, Y]$. In [LST15] one can also find a proof of (7.23), which uses the projector

$$\pi_L = \tfrac{\mathrm{i}}{2} Z Z^* \Omega$$

on the positive Lagrangian subspace $L = \text{Range}Z$, and the commutation relations from Lemma 10. Our approach is more direct and employs the polynomial raising operator $b_M^\dagger$ from Proposition 9.

Proposition 13. *Let $Y = (X; K) \in \mathbb{C}^{2d\times d}$ and $Z = Z_0 = (Q; P)$ be a positive and a normalized Lagrangian frame, respectively. Define $B = -\frac{\mathrm{i}}{2} Z_0^* J Y$. Then, for $k \in \mathbb{N}^d$ one has*

$$\varphi_k^\varepsilon[Z, Y](x) = \frac{1}{\sqrt{2^{|k|} k!}} q_k^M \left(\tfrac{1}{\sqrt{\varepsilon}} B^* Q^{-1} x \right) \varphi_0^\varepsilon[Z](x), \tag{7.23}$$

with the symmetric matrix

$$M = X^* Q^{-T} \overline{B} = \tfrac{1}{4} \overline{Y^T G_{Z_0} Y} + B^* Q^{-1} \overline{QB}. \tag{7.24}$$

Proof. We start by checking the symmetry of M and (7.24) which is necessary for (7.23) to make sense. We know that QQ^* is a positive definite matrix with real entries. Hence, the square root of QQ^* is real-valued as well, and we obtain the polar decomposition

$$Q = (QQ^*)^{1/2} U$$

with some unitary matrix U, and $(QQ^*)^{1/2} \in \mathbb{R}^{d\times d}$. Consequently,

$$Q^{-1}\overline{Q} = U^{-1}(QQ^*)^{-1/2}(QQ^*)^{1/2}\overline{U} = \overline{U^T U} \tag{7.25}$$

is unitary and complex symmetric, and the symmetry of M follows readily. The symmetry of $Q^{-1}\overline{Q}$ furthermore implies that

$$B^*Q^* = \tfrac{i}{2}(K^*Q - X^*P)Q^* = \tfrac{\mathrm{i}}{2}(K^*QQ - X^*\overline{P}Q^T - 2iX^*)$$

since $PQ^* = (QP^* + 2i\mathrm{Id})^T$. We conclude

$$\begin{aligned} B^*Q^*Q^{-T}\overline{B} &= \tfrac{\mathrm{i}}{2}(K^*\overline{QB} - X^*\overline{PB}) + X^*Q^{-T}\overline{B} \\ &= \tfrac{\mathrm{i}}{2} Y^*\Omega\overline{ZB} + X^*Q^{-T}\overline{B} \\ &= \tfrac{1}{4} Y^*\Omega\overline{Z}Z^T\Omega\overline{Y} + X^*Q^{-T}\overline{B} = -\tfrac{1}{4} Y^*\overline{G_{Z_0}Y} + X^*Q^{-T}\overline{B}, \end{aligned}$$

where in the last equality we used the isotropy of Y.

Let us recall the definition (7.16) of the wave packets $\varphi_k[Z, Y]$. It is clear from the ladder operator construction that $\varphi_k[Z, Y]$ is given

by a polynomial times the ground state $\varphi_0^\varepsilon[Z]$. We prove the special form of the polynomials asserted in (7.23) by induction over the total degree $|k|$.

Since $q_0^M \equiv 1$, the base clause $k = 0$ is obviously true. Now, assume that (7.23) is true for all $\ell \in \mathbb{N}^d$ with $|\ell| = N$, and let k with $|k| = N$ be arbitrary. Then, from (7.16) and the induction hypothesis follows

$$\begin{aligned}\varphi_{k+e_i}[Z,Y](x) &= \frac{A_i^\dagger[Y]}{\sqrt{k_i+1}}\varphi_k[Z,Y](x)\\ &= \frac{2^{-|k|-1}\mathrm{i}}{\sqrt{(k+e_i)!\varepsilon}}\Big(\Big[\mathrm{i}\varepsilon X^*\nabla_x - X^*PQ^{-1}x + K^*x\Big]_i q_k^M\left(\tfrac{1}{\sqrt{\varepsilon}}B^*Q^{-1}x\right)\Big)\varphi_0(x)\end{aligned}$$

for all $i = 1,\ldots,d$ and $\varphi_0 = \varphi_0[Z,Y]$. With the matrix B one can rewrite

$$\tfrac{\mathrm{i}}{\sqrt{\varepsilon}}\left[\mathrm{i}\varepsilon X^*\nabla_x - X^*PQ^{-1}x + K^*x\right]_i = \left[-\sqrt{\varepsilon}X^*\nabla_x + \tfrac{2}{\sqrt{\varepsilon}}B^*Q^{-1}x\right]_i,$$

and hence

$$q_{k+e_i}^M\left(\tfrac{1}{\sqrt{\varepsilon}}B^*Q^{-1}x\right) = [-\sqrt{\varepsilon}X^*\nabla_x + \tfrac{2}{\sqrt{\varepsilon}}B^*Q^{-1}x]_i q_k^M\left(\tfrac{1}{\sqrt{\varepsilon}}B^*Q^{-1}x\right)$$

by recalling the definition of the polynomial raising operator $b_M^\dagger$ from Proposition 9. This observation completes the proof. □

The representation of Hagedorn wave packets from Proposition 13 immediately implies a TTRR for the wave packets. For the normalized case see also [Lub08, §V.2].

Corollary 2 (General three-term recurrence relation)**.** *Let $Z = Z_0 = (Q;P), Y \in \mathbb{C}^{2d\times d}$ and M be as above. Then, the generalized Hagedorn wave packets satisfy the TTRR*

$$\begin{aligned}\left(\sqrt{k_j+1}\varphi_k^\varepsilon[Z,Y](x)\right)_{j=1}^d &= \sqrt{\tfrac{2}{\varepsilon}}Q^{-1}x\varphi_k^\varepsilon[Z,Y]\\ &\quad - M\left(\sqrt{k_j}\varphi_{k-e_j}^\varepsilon[Z,Y]\right)_{j=1}^d \qquad (7.26)\end{aligned}$$

for all $k \in \mathbb{N}^d$.

Proof. Using Proposition 13 together with the TTRR (6.1) for the polynomials q_k^M yields the assertion. □

In the next chapter §8, we apply Proposition 13 in order to identify Wigner functions as multiples of Hagedorn wave packets on phase space. Let us remark at this point that by a similar argument as in the proof of Proposition 13 one can also derive the appropriate lowering operator

$$-\frac{\mathrm{i}}{\sqrt{2\varepsilon}}\overline{B}^{-1}\left(i\varepsilon X^T\nabla_x + K^T x\right)\varphi_k^\varepsilon[Z] = \overline{B}^{-1}A[(X;K)]\varphi_k^\varepsilon[Z] \\ = (\sqrt{k_i}\varphi_{k-e_i}^\varepsilon[Z])_{i=1}^d,$$

for the generalized Hagedorn wave packets.

8 Wigner-Hagedorn Formula

In [LT14] the authors recently proved that the cross-Wigner function of two normalized Hagedorn wave packets is given by an exponential function times a tensor product of d bivariate Laguerre polynomials of the form (6.28). This observation generalizes the well-known Laguerre connection for Hermite functions, see e.g. [Fol89, §1.9] or [Tha93, §1.3]. In this chapter we provide an explanation for this phase space factorization result that remarkably holds independently from a possible factorization of the corresponding wave packets in position space. Wigner functions of general Hagedorn wave packets are of the form

$$\mathcal{W}^\varepsilon(\varphi_k^\varepsilon[Z_0,Y],\varphi_\ell^\varepsilon[Z_0,Y])](z) = (\pi\varepsilon)^{-d}\mathrm{e}^{-z^T G_{Z_0} z}\gamma_{k,\ell}(z), \quad k,\ell \in \mathbb{N}^d,$$

where G_{Z_0} is the symplectic metric from (7.8). We will use the shorthand

$$\mathcal{W}^{\varepsilon}_{k,\ell}[Z,Y] = \mathcal{W}^{\varepsilon}(\varphi^{\varepsilon}_k[Z,Y], \varphi^{\varepsilon}_\ell[Z,Y]),$$

and in the case $Z = Y$ we write $\mathcal{W}^{\varepsilon}_{k,\ell}[Z] := \mathcal{W}^{\varepsilon}_{k,\ell}[Z,Z]$. The polynomial $\gamma_{k,\ell}$ can be expressed via a generalized Hermite polynomial $q^{\mathscr{M}}_{k,\ell}$ on phase space with a lifted matrix $\mathscr{M} \in \mathbb{C}^{2d\times 2d}$. For normalized wave packets, that is, if $Z_0 = Y$, one always obtains the same sparse matrix $\mathscr{M}$. By invoking Proposition 10 this implies the uniform factorization result.

In §8.1 introduce a lift of Lagrangian frames to the phase space. Afterwards, in §8.2 we use this lift in order to identify the Wigner functions $\mathcal{W}^{\varepsilon}_{k,\ell}[Z,Y]$ as generalized Hagedorn wave packets on phase space. This Wigner-Hagedorn formula from Theorem 3 is one of the main results of this dissertation. The first three parts of this chapter are similar to [DKT15, §4], while §8.4 contains a novel result for expressing cross-Wigner functions in terms of Wigner transforms.

8.1 Phase Space Lift

We first investigate the Wigner transforms of normalized ground states $\mathcal{W}^{\varepsilon}_{0,0}[Z_0]$. By solving a Gaussian integral and employing the normalization of Z_0, these Wigner transforms can be explicitely computed as

$$\mathcal{W}^{\varepsilon}_{0,0}[Z](z) = (\pi\varepsilon)^{-d}\mathrm{e}^{-\frac{1}{\varepsilon}z^T G_{Z_0} z}, \tag{8.1}$$

see [LT14] for the details. For identifying (8.1) with a Hagedorn ground state on phase space, in view of (7.10) the phase space lift $\mathscr{Z}_0 = (\mathscr{Q}, \mathscr{P}) \in \mathbb{C}^{4d\times 2d}$ of the Lagrangian frame Z_0 has to satisfy

$$2\mathrm{i}G_{Z_0} = \mathscr{P}\mathscr{Q}^{-1}. \tag{8.2}$$

Moreover, for the phase space lift $\mathscr{Y} \in \mathbb{C}^{4d\times 2d}$ of some positive Lagrangian frame $Y \in \mathbb{C}^{2d\times d}$ we demand that the lifted raising operator $\mathcal{A}^{\dagger}[\mathscr{Y}]$, which is defined similarly as in (7.13), is compatible

with the Weyl correspondence. That is,

$$\begin{aligned}\mathcal{A}_j^\dagger[\mathscr{Y}]\mathcal{W}^\varepsilon(\phi,\psi) &= \mathcal{W}^\varepsilon(A_j^\dagger[Y]\phi,\psi), \quad j=1,...,d, \\ \mathcal{A}_{j+d}^\dagger[\mathscr{Y}]\mathcal{W}^\varepsilon(\phi,\psi) &= \mathcal{W}^\varepsilon(\phi,A_j^\dagger[Y]\psi), \quad j=1,...,d,\end{aligned} \tag{8.3}$$

for all Schwartz functions $\phi,\psi\in\mathcal{S}(\mathbb{R}^d)$. This condition determines the phase space lift $Y\mapsto\mathscr{Y}$ uniquely, as can be seen from the following calculation that can also be found in [LST15, §5].

For some test function $a\in\mathcal{S}(\mathbb{R}^{2d})$ and a positive Lagrangian frame $Y=(Y_1\dots Y_d)\in\mathbb{C}^{2d\times d}$ one computes

$$\begin{aligned}\int_{\mathbb{R}^{2d}}\mathcal{W}^\varepsilon(\phi,A_j^\dagger[Y]\psi)(z)a(z)dz &= \left\langle A_j[Y]\mathrm{op}_\varepsilon^{\mathrm{We}}(a)\phi,\psi\right\rangle \\ &= \int_{\mathbb{R}^{2d}}\mathcal{W}^\varepsilon(\phi,\psi)(z)\ (\sigma^{\mathrm{We}}(A_j[Y])\sharp a)(z)dz\end{aligned}$$

by (5.14) and Lemma 8. Since $\sigma^{\mathrm{We}}(A_j[Y])$ is a polynomial of degree one, we get

$$\begin{aligned}(\sigma^{\mathrm{We}}(A_j[Y])\sharp a)(z) &= \tfrac{\mathrm{i}}{\sqrt{2\varepsilon}}Y_j\cdot Jz\ a(z)+\tfrac{\varepsilon}{2\mathrm{i}}\nabla(\tfrac{\mathrm{i}}{\sqrt{2\varepsilon}}Y_j\cdot Jz)\cdot J^T\nabla a(z) \\ &= \tfrac{\mathrm{i}}{\sqrt{2\varepsilon}}Y_j\cdot\left(Jz+\tfrac{1}{2}(-\mathrm{i}\varepsilon\nabla)\right)a(z).\end{aligned}$$

Using integration by parts results in the condition

$$\mathcal{A}_{j+d}^\dagger[\mathscr{Y}]=\tfrac{\mathrm{i}}{\sqrt{2\varepsilon}}Y_j\cdot\left(Jz-\tfrac{1}{2}(-\mathrm{i}\varepsilon\nabla)\right),\quad j=1,\dots,d, \tag{8.4}$$

and the computation for $\mathcal{A}_j^\dagger[\mathscr{Y}]$ analoguously gives

$$\mathcal{A}_j^\dagger[\mathscr{Y}]=\tfrac{\mathrm{i}}{\sqrt{2\varepsilon}}\overline{Y}_j\cdot\left(-Jz-\tfrac{1}{2}(-\mathrm{i}\varepsilon\nabla)\right),\quad j=1,\dots,d. \tag{8.5}$$

Recalling the form of the raising operator (7.13) then leads to the following Definition 6 of the lifted Lagrangian frame.

Definition 6 (Phase space lift)**.** *Let $Z\in\mathbb{C}^{2d\times d}$ be a positive Lagrangian frame. Then we define the* phase space lift $\mathscr{Z}\in\mathbb{C}^{4d\times 2d}$ *of Z as*

$$\mathscr{Z}=\begin{pmatrix}\frac{1}{2}\left(\overline{Z}Z\right)\\ J(Z\overline{Z})J\end{pmatrix}.$$

One can easily verify that the phase space lift $Y \mapsto \mathscr{Y}$ indeed satisfies the conditions (8.3) and (8.2). The contents of the following Lemma can also be found in [LST15, §5].

Lemma 12. *Let $Z = (Q; P) \in \mathbb{C}^{2d\times d}$ be a positive Lagrangian frame. Then, the lifted matrix $\mathscr{Z} = (\mathscr{Q}; \mathscr{P}) \in \mathbb{C}^{4d\times 2d}$ has the following properties.*

i) $\mathscr{Z}$ is a positive Lagrangian frame, and normalized if and only if Z is.

ii) $\mathcal{A}^\dagger[\mathscr{Z}]$ satisfies (8.3).

iii) If $\mathscr{Z} = \mathscr{Z}_0$ is normalized, the symplectic metric fulfills $2iG_{Z_0} = \mathscr{P}\mathscr{Q}^{-1}$ and $\mathscr{Q}\mathscr{Q}^* = \mathrm{Im}(2iG_{Z_0})^{-1}$.

Proof. The first property follows from checking the isotropy and positivity conditions from Definition 5, namely

$$\mathscr{Q}^T\mathscr{P} - \mathscr{P}^T\mathscr{Q} = \begin{pmatrix} -\overline{Z^TJZ} & 0 \\ 0 & Z^TJZ \end{pmatrix} = 0$$
$$\tfrac{1}{2i}\left(\mathscr{Q}^*\mathscr{P} - \mathscr{P}^*\mathscr{Q}\right) = \tfrac{1}{2i}\begin{pmatrix} -\overline{Z^*JZ} & 0 \\ 0 & Z^*JZ \end{pmatrix} = \begin{pmatrix} \overline{\Gamma_Z} & 0 \\ 0 & \Gamma_Z \end{pmatrix}.$$

Therefore, $\mathscr{Z}$ is normalized if and only if Z is. The second property follows directly from the construction, see (8.4) and (8.5).

Now, let us assume that $\mathscr{Z} = (\mathscr{Q}; \mathscr{P})$ is normalized. Then, for the third part we first note that $\mathscr{Q}^{-1} = i\mathscr{P}^*$, which can easily be checked. The assertion follows from

$$\mathscr{Q}\mathscr{Q}^* = \tfrac{1}{4}\begin{pmatrix}\overline{Z} & Z\end{pmatrix}\begin{pmatrix} Z^T \\ Z^*\end{pmatrix} = \tfrac{1}{2}\mathrm{Re}(ZZ^*) = \mathrm{Im}(2iG_{Z_0})^{-1}.$$

□

Given a lifted Lagrangian frame $\mathscr{Z} \in \mathbb{C}^{4d\times 2d}$, as a next step we want to charaterize the phase space lift of the matrices B and M from the polynomial formula in Proposition 13.

Proposition 14. *Let $Z = (Q; P) = Z_0 \in \mathbb{C}^{2d\times d}$ be a normalized, and $Y \in \mathbb{C}^{2d\times d}$ a positive Lagrangian frame. We set $B = -\frac{\mathrm{i}}{2} Z_0^* J Y$, and consider the lifted Lagrangian frames $\mathscr{Z} = (\mathscr{Q}; \mathscr{P}) = \mathscr{Z}_0 \in \mathbb{C}^{4d\times 2d}$ and $\mathscr{Y} \in \mathbb{C}^{4d\times 2d}$.*

i) One has

$$\mathscr{B} := -\tfrac{i}{2} \mathscr{Z}_0^* J_{4d} \mathscr{Y} = \begin{pmatrix} \overline{B} & 0 \\ 0 & B \end{pmatrix}$$

with the canonical complex structure[7] $J_{4d} = J \otimes \mathrm{Id}_2$ on $\mathbb{R}^{4d}$.

ii) The lifted recursion matrix is given by

$$\begin{aligned} \mathscr{M} &:= \tfrac{1}{4} \overline{\mathscr{Y}^T G_{\mathscr{Z}_0} \mathscr{Y}} + \mathscr{B}^* \mathscr{Q}^{-1} \overline{\mathscr{Q}\mathscr{B}} \\ &= \tfrac{1}{4} \begin{pmatrix} Y^T G_{Z_0} Y & 0 \\ 0 & \overline{Y^T G_{Z_0} Y} \end{pmatrix} + \mathscr{B}^* \mathscr{Q}^{-1} \overline{\mathscr{Q}\mathscr{B}} \end{aligned}$$

and has the block form

$$\mathscr{M} = \begin{pmatrix} R & F \\ F^T & \overline{R} \end{pmatrix}$$

where $R \in \mathbb{C}^{d\times d}$ is symmetric, and $F \in \mathbb{C}^{d\times d}$ is positive definite with $F \geq \frac{1}{2}\Gamma_Z > 0$.

iii) In the special case $Y = Y_0 = Z_0$ we have $\mathscr{B} = \mathrm{Id}$ and

$$\mathscr{M} = \mathscr{Q}^{-1}\overline{\mathscr{Q}} = \begin{pmatrix} 0 & \mathrm{Id} \\ \mathrm{Id} & 0 \end{pmatrix}. \tag{8.6}$$

Proof. From Lemma 12 we know that $\mathscr{Z}, \mathscr{Y}$ are positive Lagrangian frames, and $\mathscr{Z}$ is normalized. We note that the matrices $\mathscr{B}, \mathscr{M} \in \mathbb{C}^{2d\times 2d}$ are defined just as $B, M \in \mathbb{C}^{d\times d}$ in Proposition 13.

[7] Here, the tensor product $\otimes$ is the Kronecker product of matrices.

The formula for $\mathscr{B}$ is a direct calculation. For $\mathscr{M}$ one begins by computing

$$\begin{aligned} B^*B &= \frac{1}{4} Y^* \Omega^T Z_0 Z_0^* \Omega Y \\ &= \frac{1}{4} Y^* (G_{Z_0} + i\Omega) Y = \frac{1}{4} (Y^* G_{Z_0} Y + 2\Gamma_Y), \end{aligned}$$

and consequently we can rewrite

$$\mathscr{M} = \tfrac{1}{4} \begin{pmatrix} Y^T G_{Z_0} Y & Y^T G_{Z_0} \overline{Y} + 2\Gamma_Y^T \\ Y^* G_{Z_0} Y + 2\Gamma_Y & \overline{Y^T G_{Z_0} Y} \end{pmatrix}. \tag{8.7}$$

The block structure of $\mathscr{M}$ follows immediately.

Showing the special form of $\mathscr{M}$ for the situation considered in the third part is an easy calculation based on the isotropy and normalization conditions. □

Lemma 12 and Proposition 14 provide all the necessary prelimilaries for proving the Wigner-Hagedorn formula Theorem 3. In [LT14] it has recently been discovered that, for a normalized Lagrangian frame Z, the Wigner functions $\{\mathcal{W}^{\varepsilon}_{k,\ell}[Z]\}_{k,\ell \in \mathbb{N}^d}$ can be written as a phase space Gaussian times a tensor product of Laguerre polynomials. By means of part iii) of Proposition 14 we can explain this factorization with the special form of the lifted matrix $\mathscr{M}$, see §8.3.

8.2 The Wigner-Hagedorn Formula

Suppose that $Z \in \mathbb{C}^{2d \times d}$ is a positive Lagrangian frame. Then, by Lemma 12, the lifted Lagrangian frame $\mathscr{Z} \in \mathbb{C}^{4d \times 2d}$ is positive as well. Consequently we can lift all our previous results to the phase space and consequentially find a family of Hagedorn wave packets in doubled dimensions, see Theorem 3.

In [Hag15], Hagedorn recently derived the generating function for the polynomials p_k that define the normalized wave packets

$\varphi_k^\varepsilon[Z]$. By combining the polynomial formula Proposition 13 and the generating function from Proposition 8, we obtain

$$\sum_{k\in\mathbb{N}^d} \frac{t^k}{\sqrt{k!}} \sqrt{2^{|k|}} \varphi_k^\varepsilon[Z,Y](x) = \mathrm{e}^{\frac{2}{\sqrt{\varepsilon}} t^T B^* Q^{-1} x - t^T M t} \varphi_0^\varepsilon[Z,Y](x) \quad (8.8)$$

which generalizes the formula for the generating function from [Hag15, Theorem 1.1] to the wave packets $\varphi_k^\varepsilon[Z,Y]$.

If one formally interchanges the integral in the definition of the Wigner transform with the sum in the generating function, for the Wigner functions of Hagedorn wave packets one gets

$$\begin{aligned} h_{Z,Y}(z,v) &:= \sum_{k,\ell\in\mathbb{N}^d} \frac{t^k s^\ell}{\sqrt{k!\ell!}} \sqrt{2^{|k|+|\ell|}} \mathcal{W}_{k,\ell}[Z,Y](z) \\ &= (\pi\varepsilon)^{-d} \mathrm{e}^{-z^T G_{Z_0} z/\varepsilon} \mathrm{e}^{\frac{2}{\sqrt{\varepsilon}} v^T \mathscr{B}^* \mathscr{Q}^{-1} z + v^T \mathscr{M} v}, \end{aligned}$$

with $z = (x,\xi)$, $v = (t,s)$, and the matrices $\mathscr{B}, \mathscr{M}$ from Proposition 14. Hence, $h_{Z,Y}$ is of the same form as the generating function of the Hagedorn wave packets. We note that this formal calculation can be made rigorous in the case of normalized wave packets. Motivated by this instructive calculation, we state the Wigner-Hagedorn formula. In order to avoid confusion, we denote Hagedorn wave packets on phase space by upper case letters $\Phi_{k,\ell}^\varepsilon[\mathscr{Z},\mathscr{Y}]$.

Theorem 3 (Wigner-Hagedorn Formula). *Let $Z = Z_0 = (Q;P) \in \mathbb{C}^{2d\times d}$ and $Y \in \mathbb{C}^{2d\times d}$ be a normalized and a positive Lagrangian frame, respectively, and $k,\ell \in \mathbb{N}^d$. Then, the Wigner function $\mathcal{W}_{k,\ell}[Z,Y]$ is a generalized Hagedorn wave packet on phase space,*

$$\mathcal{W}_{k,\ell}^\varepsilon[Z,Y] = (2\pi\varepsilon)^{-d/2} \Phi_{(k,\ell)}^\varepsilon[\mathscr{Z},\mathscr{Y}],$$

where $\mathscr{Z} = (\mathscr{Q},\mathscr{P}), \mathscr{Y} \in \mathbb{C}^{4d\times 2d}$ are the lifted Lagrangian frames. Consequently, we have the polynomial formula

$$\mathcal{W}_{k,\ell}^\varepsilon[Z,Y](z) = \frac{(2\pi\varepsilon)^{-d/2}}{\sqrt{2^{|k|+|\ell|}k!\ell!}} q_{(k,\ell)}^{\mathscr{M}} \left(\tfrac{1}{\sqrt{\varepsilon}} \mathscr{B}^* \mathscr{Q}^{-1} z\right) \Phi_0^\varepsilon[\mathscr{Z}](z),$$

for $z \in \mathbb{R}^{2d}$, where the matrices $\mathscr{B}, \mathscr{M} \in \mathbb{C}^{2d\times 2d}$ have been defined in Proposition 14.

Proof. Let us first consider the ground state $\Phi_0^\varepsilon[\mathscr{Z}]$. From part iii) of Lemma 12 we know that $\mathscr{P}\mathscr{Q}^{-1} = 2iG_{Z_0}$ as well as $(\mathscr{Q}\mathscr{Q}^*)^{-1} = \mathrm{Im}(2iG_{Z_0})$. Consequently,

$$\det(\mathscr{Q})^{-\frac{1}{2}} = \det(\mathscr{Q}\mathscr{Q}^*)^{-\frac{1}{4}} = \det(2G_{Z_0})^{\frac{1}{4}} = 2^{\frac{d}{2}}, \tag{8.9}$$

and by using (8.1) we get

$$\mathcal{W}_{0,0}^\varepsilon[Z](z) = (\pi\varepsilon)^{-d}\mathrm{e}^{-\frac{1}{\varepsilon}z^T G_{Z_0} z} = (2\pi\varepsilon)^{-d/2}\Phi_0^\varepsilon[\mathscr{Z}].$$

For the excited states the major part of the work has already been done in Lemma 12. By part ii) of Lemma 12 we can apply the phase space raising operator $\mathcal{A}^\dagger[\mathscr{Y}]$. This gives

$$\begin{aligned}\mathcal{W}_{k,\ell}[Z,Y] &= \frac{(2\pi\varepsilon)^{-d/2}}{\sqrt{k!\ell!}}(\mathcal{A}^\dagger[\mathscr{Y}])^{(k,\ell)}\Phi_0^\varepsilon[\mathscr{Z}] \\ &= (2\pi\varepsilon)^{-d/2}\Phi_{(k,\ell)}^\varepsilon[\mathscr{Z},\mathscr{Y}].\end{aligned}$$

The polynomial formula follows from Proposition 13, since the matrices $\mathscr{B}$ and $\mathscr{M}$ from Proposition 14 are defined via the Lagrangian frames $\mathscr{Z}$ and $\mathscr{Y}$ in the same way as on position space. □

By using the Heisenberg-Weyl operators $\widehat{T}_z$ from §5.2 and the symplectic covariance of the Wigner function from Lemma 6, Theorem 3 directly extends to Hagedorn wave packets with different phase space centers.

Example. A possible application of Therem 3 is to construct approximations for the Wigner transforms of more general states. For instance, suppose that the state $\psi \in L^2(\mathbb{R}^d)$ can be written as a

linear combination of N Hagedorn wave packets[8]

$$\psi(x) = \sum_{j=1}^{N} c_j \varphi^{\varepsilon}_{k_j}[Z,Y](x), \quad k_1,\dots,k_N \in \mathbb{N}^d,$$

for some $c_1,\dots,c_N \in \mathbb{C}$, where $Z,Y \in \mathbb{C}^{2d\times d}$ are positive Lagrangian frames. Then, Theorem 3 implies that the Wigner transform has a similar form, namely

$$\begin{aligned}\mathcal{W}^{\varepsilon}(\psi) &= (2\pi\varepsilon)^{-d/2} \sum_{i,j=1}^{N} c_i\bar{c}_j \Phi^{\varepsilon}_{(k_i,k_j)}[\mathscr{Z},\mathscr{Y}] \\ &= (2\pi\varepsilon)^{-d/2}\Phi^{\varepsilon}_0[\mathscr{Z},\mathscr{Y}] \left(\sum_{i,j=1}^{N} \frac{c_i\bar{c}_j 2^{-|k_i|+|k_j|}}{\sqrt{k!\ell!}} q_{(k_i,k_j)}^{\mathscr{M}} \left(\tfrac{1}{\sqrt{\varepsilon}} \mathscr{B}^* \mathscr{Q}^{-1} z \right) \right)\end{aligned}$$

by the sesquilinearity of the Wigner transform. ■

The computation or approximation of the Wigner transforms is one of the central bottlenecks in most phase space propagation methods for the time-dependent semiclassical Schrödinger equation (5.2), see §16.2. If one directly uses the Definition 1, for every evaluation of a Wigner transform one would need to solve a highly oscillatory quadrature problem on $\mathbb{R}^d$. This is not feasible already in moderately high dimensions. The Wigner-Hagedorn formula provides a method for explicitly computing the Wigner transform, whenever one can expand the considered state in some finite set of Hagedorn wave packets, see for instance the above example.

8.3 Factorization of Wigner Functions

The Wigner-Hagedorn formula from Theorem 3 shows that the Wigner function of two Hagedorn wave packets is a Hagedorn

[8] This finite expansion could for instance be a L^2-approximation of the state of interest.

wave packet on phase space. Moreover, we can express the Wigner function $\mathcal{W}^{\varepsilon}_{k,\ell}$ via the generalized Hermite polynomial $q^{\mathscr{M}}_{k,\ell}$. This facilitates to use the results and explicit formulas for the polynomials we derived in §6. In particular, we can use the factorization condition for the polynomials from Proposition 10 to analyze the Wigner functions. For normalized Hagedorn wave packets, part iii) of Proposition 14 ensures that $\mathscr{M}$ is always a simple permutation matrix. This implies the uniform factorization of Hagedorn wave packets in phase space. Moreover, by employing the explicit expression for the two-dimensional polynomials, in Corollary 3 we regain the Laguerre connection from [LT14, Theorem 1].

Corollary 3 (Hagedorn-Laguerre Connection)**.** *Suppose $Z = Z_0 = (Q; P) \in \mathbb{C}^{2d\times d}$ is a normalized Lagrangian frame, and $k, \ell \in \mathbb{N}^d$. Then, for $y = \frac{1}{\sqrt{\varepsilon}}\mathscr{Q}^{-1}z$,*

$$\begin{aligned}\mathcal{W}^{\varepsilon}_{k,\ell}[Z](z) &= \frac{(\pi\varepsilon)^{-d/2}}{\sqrt{2^{|k|+|\ell|}k!\ell!}}\mathrm{e}^{-\frac{1}{\varepsilon}z^T G_Z z}\prod_{j=1}^{d} q^{N_1}_{(k_j,\ell_j)}\left(y_j, y_{d+j}\right) \qquad (8.10)\\ &= \frac{(\pi\varepsilon)^{-d/2}}{\sqrt{2^{|k|+|\ell|}k!\ell!}}\mathrm{e}^{-\frac{1}{\varepsilon}z^T G_Z z}\prod_{j=1}^{d} \mathcal{L}_{k_j\ell_j}\left(\tfrac{\mathrm{i}}{\sqrt{\varepsilon}}(Q^T\xi - P^T x)_j\right)\end{aligned}$$

with the anti-diagonal matrix $N_1 \in \mathbb{R}^{2\times 2}$ from (6.27)*, and*

$$\mathcal{L}_{nm}(y) = \begin{cases}(-1)^m 2^n m! y^{n-m} L_m^{(n-m)}(2|y|^2), & n \geq m\\ (-1)^n 2^m n!\,(-\overline{y})^{m-n}\, L_n^{(m-n)}(2|y|^2), & m \geq n\end{cases}. \qquad (8.11)$$

Proof. From Theorem 3 we obtain the expression for $\mathcal{W}^{\varepsilon}_{k,\ell}[Z]$ in terms of the phase space polynomial $q^{\mathscr{M}}_{k,\ell}$, and Proposition 14 implies that the mixing matrix $\mathscr{M} \in \mathbb{C}^{2d\times 2d}$ takes the simple form

$$\mathscr{M} = \begin{pmatrix} 0 & \mathrm{Id}_d \\ \mathrm{Id}_d & 0\end{pmatrix}.$$

By a relabeling of the standard basis, the matrix $\mathscr{M}$ can be transformed into a block-diagonal matrix with d blocks of size 2×2,

and hence Proposition 10 yields the factorized representation. The Laguerre connection then follows from inserting the explicit form of the polynomials $q^{N_1}_{(i,j)}$ from (6.28). □

Remark 11. *Laguerre connections in the form of Corollary 3 appear frequently in the quantization of finite and infinite systems. A closely related result for the Wick quantization of the bosonic Fock space can be found in [AN08, Proposition 3.5].*

We highlight that the Laguerre type polynomials $q^{N_1}_k$ from (6.28) associated with the anti-diagonal matrix N_1 precisely define the polynomial part in the Wigner function $\mathcal{W}^1_{m,n}[(1,\mathrm{i})]$ of two one-dimensional Hermite functions. In the harmonic analysis literature the Wigner functions of tensorized one-dimensional Hermite functions

$$\mathcal{W}^1_{k,\ell}[(\mathrm{Id},\mathrm{iId})](x,\xi) = \prod_{j=1}^{d} \mathcal{W}^1_{k_j,\ell_j}[(1,\mathrm{i})](x_j,\xi_j)$$

are also known as *special Hermite functions*, see e.g. [Tha93, §1.3].

Remark 12 (Optimality)**.** *The factorization result from Corollary 3 is optimal in the sense that the polynomials $\{q^{\mathscr{M}}_{(k,\ell)}\}_{k,\ell\in\mathbb{N}^d}$ characterizing the Wigner functions $\{\mathcal{W}^{\varepsilon}_{k\ell}[Z,Y]\}_{k,\ell\in\mathbb{N}^d}$ of generalized Hagedorn wave packets can never factorize into more than d polynomials for all $k,\ell\in\mathbb{N}^d$. This follows from part ii) of Proposition 14, where we proved that the offdiagonal blocks F, F^T of $\mathscr{M}$ satisfy $F \geq \frac{1}{2}\Gamma_Z > 0$. This inequality can be interpreted as an expression of the non-commutativity of the quantum position and momentum operators. In other words, there is a lower bound on the mixing between position and momentum variables in the polynomials that appear in Wigner functions.*

If Y is not a normalized Lagrangian frame, the Wigner functions $\mathcal{W}^{\varepsilon}_{k,\ell}[Z,Y]$ only factorize under strong additional assumptions.

Corollary 4. *Let $Y\in\mathbb{C}^{2d\times d}$ be a positive Lagrangian frame. Suppose*

that there is a normalised Lagrangian frame $Z = Z_0 = (Q; P) \in \mathbb{C}^{2d\times d}$ and a permutation matrix $P_\sigma \in \mathbb{N}^{d\times d}$ such that Y is isotropic with respect to G_{Z_0}, that is, $Y^T G_{Z_0} Y = 0$, and

$$P_\sigma^T \left(\tfrac{1}{2} Y^* G_{Z_0} Y + \Gamma_Y\right) P_\sigma \in \mathbb{C}^{d\times d}$$

is block-diagonal with $n \leq d$ blocks. Then, $\mathcal{W}^\varepsilon_{k,\ell}[Z, Y]$ is a tensor product of n wave packets for all $k, \ell \in \mathbb{N}^d$.

Proof. By part ii) of Proposition 14, the additional assumption $Y^T G_{Z_0} Y = 0$ implies that the lifted matrix $\mathscr{M}$ is of the form

$$\mathscr{M} = \begin{pmatrix} 0 & P_\sigma^{-T} \mathrm{diag}(M_1, \dots, M_n) P_\sigma^{-1} \\ P_\sigma^{-1} \mathrm{diag}(A_1^T, \dots, A_n^T) P_\sigma^{-T} & 0 \end{pmatrix}$$

with some square matrices $A_1, \cdots, A_n$. Hence, there is a phase space permutation matrix $\mathscr{P}_\pi \in \mathbb{R}^{2d\times 2d}$ such that $\mathscr{P}_\pi \mathscr{M} \mathscr{P}_\pi^T$ is blockdiagonal with n blocks. Now, the claim follows from Theorem 3 and Proposition 10. □

8.4 Rewriting cross-Wigner Functions

It is well-known that for some orthonormal basis $\{\phi_\alpha\}_{\alpha\in\mathcal{J}}$ of $L^2(\mathbb{R}^d)$ with a countable index set $\mathcal{J}$,

$$\{(2\pi\varepsilon)^{d/2} \mathcal{W}^\varepsilon(\phi_\alpha, \phi_\beta)\}_{\alpha,\beta\in\mathcal{J}}$$

is an orthonormal basis of $L^2(\mathbb{R}^{2d})$. This follows directly from Moyal's identity (5.7), see also [dG11, Proposition 188]. In particular, for $Z = Z_0 \in \mathbb{C}^{2d\times d}$ a normalized Lagrangian frame, the set of cross-Wigner functions

$$\{(2\pi\varepsilon)^{d/2} \mathcal{W}^\varepsilon_{k,\ell}[Z_0]\}_{k,\ell\in\mathbb{N}^d} = \{\Phi^\varepsilon_{(k,\ell)}[\mathscr{Z}_0]\}_{k,\ell\in\mathbb{N}^d}$$

is an orthonormal basis of $L^2(\mathbb{R}^{2d})$ consisting of normalized Hagedorn wave packets, see also (7.19). As a consequence, one cannot ex-

press a cross-Wigner function $\mathcal{W}^{\varepsilon}_{k,\ell}[Z_0]$ merely as a linear combination of some Wigner transforms $\mathcal{W}^{\varepsilon}_{m_i,m_i}[Z_0]$, $m_1, m_2, \ldots \in \mathbb{N}^d$. However, as we shall prove below, the cross-Wigner function $\mathcal{W}^{\varepsilon}_{k,\ell}[Z_0]$ can be written as a finite linear combination of the diagonal Wigner transforms

$$\mathcal{W}^{\varepsilon}_{m,m}[Z_0], \quad \in \mathbb{N}^d \text{ with } \min(k_j, \ell_j) \leq m_j \leq \max(k_j, \ell_j),$$

and inverse powers of the ladder operator symbols as additional prefactors.

Let us first note the special structure of the three-term recurrence relation satisfied by Wigner functions of normalized Hagedorn wave packets. For a different derivation of the following result we refer to Corollary 4 in [LT14].

Proposition 15 (Wigner TTRR). *Let $Z = Z_0 \in \mathbb{C}^{2d\times d}$ be a normalized Lagrangian frame. Then, the Wigner functions satisfy the three-term recurrence relations*

$$\begin{aligned}\left(\sqrt{k_j+1}\mathcal{W}^{\varepsilon}_{k+e_j,\ell}[Z_0](z)\right)_{j=1}^{d} &= \sqrt{\tfrac{2}{\varepsilon}}(\mathrm{i}Z_0^T J z)\mathcal{W}^{\varepsilon}_{k,\ell}[Z_0](z) \\ &\quad + \left(\sqrt{\ell_j}\mathcal{W}^{\varepsilon}_{k,\ell-e_j}[Z_0](z)\right)_{j=1}^{d} \qquad (8.12)\\ \left(\sqrt{\ell_j+1}\mathcal{W}^{\varepsilon}_{k,\ell+e_j}[Z_0](z)\right)_{j=1}^{d} &= \sqrt{\tfrac{2}{\varepsilon}}(-\mathrm{i}Z_0^* J z)\mathcal{W}^{\varepsilon}_{k,\ell}[Z_0](z) \\ &\quad + \left(\sqrt{k_j}\mathcal{W}^{\varepsilon}_{k-e_j,\ell}[Z_0](z)\right)_{j=1}^{d} \qquad (8.13)\end{aligned}$$

for all $k, \ell \in \mathbb{N}^d$.

Proof. The Wigner-Hagedorn formula from Theorem 3 implies that

$$\mathcal{W}^{\varepsilon}_{k,\ell}[Z_0] = (2\pi\varepsilon)^{-d/2}\Phi^{\varepsilon}_{(k,\ell)}[\mathscr{Z}_0]$$

with the normalized Lagrangian frame $\mathscr{Z}_0 = (\mathscr{Q}; \mathscr{P}) \in \mathbb{C}^{4d\times 2d}$.

Then, since one has $\mathscr{Q}^{-1} = i\mathscr{P}$, we obtain

$$\mathscr{Q}^{-1} z = \begin{pmatrix} \mathrm{i} Z_0^T J z \\ -\mathrm{i} Z^* J z \end{pmatrix}.$$

Consequently, invoking the TTRR for Hagedorn wave packets from Corollary 2, and the special form of $\mathscr{M}$ from part iii) of Proposition 14 completes the proof. □

By means of the TTRR from Proposition 15 one can rewrite the cross-Wigner function of two Hagedorn wave packets via Wigner transforms.

Proposition 16. *Let $Z = Z_0 \in \mathbb{C}^{2d\times d}$ be a normalized Lagrangian frame, and $k, \ell \in N^d$. We set $\alpha = (\max(k_j, \ell_j))_{j=1}^d \in \mathbb{N}^d$ and $\beta = (\min(k_j, \ell_j))_{j=1}^d \in \mathbb{N}^d$. Then,*

$$\begin{aligned} \mathcal{W}^{\varepsilon}_{k,\ell}[Z](z) = & \begin{pmatrix} -2a[Z](z) \\ -2a^{\dagger}[Z](z) \end{pmatrix}^{\binom{\beta-\ell}{\beta-k}} \sqrt{\tfrac{\alpha!}{\beta!}} \\ & \times \sum_{\substack{m\in\mathbb{N}^d \\ m\leq\alpha-\beta}} \binom{\alpha-\beta}{m} (-1)^m \mathcal{W}^{\varepsilon}_{\beta+m,\beta+m}[Z](z) \end{aligned} \tag{8.14}$$

for all $z \in \mathbb{R}^{2d}$ with standard multiindex notation, where

$$a^{\dagger}[Z] = \sigma^{\mathrm{We}}\left(A^{\dagger}[Z]\right), \quad a[Z] = \sigma^{\mathrm{We}}\left(A[Z]\right), \tag{8.15}$$

denote the Weyl symbols of the Hagedorn ladder operators.

Proof. We first note that

$$a^{\dagger}[Z](z) = -\tfrac{\mathrm{i}}{\sqrt{2\varepsilon}} Z^* J z, \quad a[Z](z) = \tfrac{\mathrm{i}}{\sqrt{2\varepsilon}} Z^T J z, \tag{8.16}$$

by the linearity of the Weyl quantization. Moreover, since (8.14) is

of product form, it suffices to show that

$$\mathcal{W}^{\varepsilon}_{k,\ell}[Z](z) = \begin{pmatrix} -2a_j[Z](z) \\ -2a_j^{\dagger}[Z](z) \end{pmatrix}^{\binom{\beta_j-\ell_j}{\beta_j-k_j}} \sqrt{\tfrac{\alpha_j!}{\beta_j!}} \times \sum_{i=0}^{\alpha_j-\beta_j} \binom{\alpha_j-\beta_j}{i} (-1)^i \mathcal{W}^{\varepsilon}_{k[j]+ie_j,\ell[j]+ie_j}[Z](z) \tag{8.17}$$

holds for all $j = 1, \dots, d$, where

$$k[j] := k + e_j(\beta_j - k_j) \quad \text{and} \quad \ell[j] := \ell + e_j(\beta_j - \ell_j).$$

We prove (8.17) by induction over $\alpha_j - \beta_j$. The base clause $k_j = \ell_j$ is obviously true. Now, suppose that the assertion holds for all $r, s \in \mathbb{N}^d$ with $\max(r_j, s_j) - \min(r_j, s_j) = n$, and let $k_j + n + 1 = \ell_j$. By (8.12) one has

$$\sqrt{k_j+1}\mathcal{W}^{\varepsilon}_{k+e_j,\ell}[Z](z) = 2a_j[Z](z)\mathcal{W}^{\varepsilon}_{k,\ell}[Z](z) + \sqrt{\ell_j}\mathcal{W}^{\varepsilon}_{k,\ell-e_j}[Z](z)$$

and hence, for all $z \neq 0$,

$$-2a_j[Z](z)\mathcal{W}^{\varepsilon}_{k,\ell}[Z](z) = \sqrt{\ell_j}\mathcal{W}^{\varepsilon}_{k,\ell-e_j}[Z](z) - \sqrt{k_j+1}\mathcal{W}^{\varepsilon}_{k+e_j,\ell}[Z](z). \tag{8.18}$$

From now on, we omit the dependence on z and Z for readability. Since $k_j < \ell_j$, we can apply the induction hypothesis to both summands on the right hand side of (8.18). This yields

$$\mathcal{W}^{\varepsilon}_{k,\ell} = (-2a_j)^{-n-1}\sqrt{\tfrac{\alpha_j!}{\beta_j!}} \times \sum_{i=0}^{n} \binom{n}{i} (-1)^i \left(\mathcal{W}^{\varepsilon}_{k+e_j i,\ell[j]+e_j i} - \mathcal{W}^{\varepsilon}_{k+e_j(i+1),\ell[j]+e_j(i+1)} \right)$$

with $\ell[j]$ as above. By the addition theorem for binomial coefficients we calculate

$$\begin{aligned}
&\sum_{i=0}^{n}\binom{n}{i}(-1)^i\left(\mathcal{W}^{\varepsilon}_{k+e_ji,\ell[j]+e_ji}-\mathcal{W}^{\varepsilon}_{k+e_j(i+1),\ell[j]+e_j(i+1)}\right)\\
&=\sum_{i=0}^{n}\binom{n}{i}(-1)^i\mathcal{W}^{\varepsilon}_{k+e_ji,\ell[j]+e_ji}+\sum_{i=1}^{n+1}\binom{n}{i-1}(-1)^i\mathcal{W}^{\varepsilon}_{k+e_ji,\ell[j]+e_ji)}\\
&=\sum_{i=0}^{n+1}\binom{n}{i}(-1)^i\mathcal{W}^{\varepsilon}_{k+e_ji,\ell[j]+e_ji}.
\end{aligned}$$

For the case $k_j+n+1=\ell_j$ the proof works similarly by using the second TTRR for Wigner functions (8.13), and, hence, (8.17) follows. Applying this procedure iteratively for all directions $j=1,\dots,d$, and noting that the singularity at $z=0$ is smoothly removable complete the proof. □

We can rewrite Proposition 16 as

$$\mathcal{W}^{\varepsilon}_{k,\ell}[Z]=\begin{pmatrix}-2a[Z]\\-2a^{\dagger}[Z]\end{pmatrix}^{\begin{pmatrix}\beta-\ell\\\beta-k\end{pmatrix}}\sqrt{\tfrac{\alpha!}{\beta!}}\left(\left(1-\mathcal{A}^{\dagger}_j[\mathscr{Z}]\mathcal{A}^{\dagger}_{j+d}[\mathscr{Z}]\right)_{j=1}^{d}\right)^{\alpha-\beta}\mathcal{W}^{\varepsilon}_{\beta,\beta}[Z] \tag{8.19}$$

which shows that our expansion employs a mixing on the ladder operators on position and phase space.

Furthermore, from Proposition 16 one can see that the imaginary part of a cross-Wigner function $\mathcal{W}^{\varepsilon}_{k,\ell}[Z]$ is only generated by the powers of the linear symbols $a[Z], a^{\dagger}[Z]$, since the diagonal Wigner transforms $\mathcal{W}^{\varepsilon}_{k,k}[Z]$, are real-valued.

9 Excursus
The Hagedorn Semigroup

For a normalized Lagrangian frame $Z_0 \in \mathbb{C}^{2d\times d}$, the elliptic harmonic oscillator Hamiltonian

$$H_{\mathrm{ho}}(Z_0) = \tfrac{1}{2}\mathrm{op}_\varepsilon^{\mathrm{We}}(z)^T G_{Z_0}\mathrm{op}_\varepsilon^{\mathrm{We}}(z), \tag{9.1}$$

from (7.18) gives rise to the strongly continuous contraction semigroup

$$\{\mathrm{e}^{-tH_{\mathrm{ho}}(Z_0)}\}_{t>0} \subset \mathcal{L}\left(L^2(\mathbb{R}^d)\right), \quad \|\mathrm{e}^{-tH_{\mathrm{ho}}(Z_0)}\|_{\mathcal{L}(L^2)} \leq 1, \tag{9.2}$$

see [Kat95, §9.1]. We call (9.2) the *Hagedorn semigroup* associated with Z_0. It is a special case of a general harmonic oscillator semigroup since G_{Z_0} is not only positive definite, but also symplectic.

The motivation for this short excursus is the analysis of Hermite and Laguerre semigroups conducted in [RT09]. With the results presented in this chapter we would like to highlight an aspect which might prove useful for investigations of harmonic oscillator semigroups in the spirit of [RT09]. We show that every Hagedorn semigroup consists of Weyl quantized operators with particularly simple symbols, in contrast to the complicated structure of the semigroup's Mehler kernel. Moreover, the choice of the symplectic metric G_{Z_0} does not influence the structure of the symbols. These properties strongly suggest to explore generalized Hermite and Laguerre semigroups with tools of semiclassical analysis. This could be benefial because of the simple structure of the symbols.

In §7.3 we remarked that the normalized Hagedorn wave packets $\{\varphi_k^\varepsilon[Z_0]\}_{k\in\mathbb{N}^d}$ define an orthonormal basis of $L^2(\mathbb{R}^d)$, namely the eigenbasis of the harmonic oscillator Hamiltonian (9.1). In other words, given a function $\psi \in L^2(\mathbb{R}^d)$, we have the L^2-convergent

expansion

$$\psi = \sum_{n=0}^{\infty} P_n[Z_0]\psi,$$

where $P_n[Z_0]$ denotes the orthogonal projector on the set

$$E_n[Z_0] = \mathrm{Span}\left(\varphi_k^\varepsilon[Z_0] : |k| = n\right)$$

spanned by all Hagedorn wavepackets of total degree n. $E_n[Z_0]$ is an eigenspace associated with the eigenvalue $\varepsilon(n + \frac{d}{2})$ of $H_{\mathrm{ho}}(Z_0)$, and has the degeneracy

$$\dim E_n[Z_0] = \binom{n+d-1}{d-1}. \tag{9.3}$$

Hence, we could equivalently define the Hagedorn semigroup via

$$\mathrm{e}^{-tH_{\mathrm{ho}}(Z_0)}\psi = \sum_{n=0}^{\infty} \mathrm{e}^{-\varepsilon\left(n+\frac{d}{2}\right)t} P_n[Z_0]\psi,$$

for all $\psi \in L^2(\mathbb{R}^d)$.

Since G_{Z_0} is symmetric, an easy application of Lemma 8 shows that $H_{\mathrm{ho}}(Z_0)$ is a Weyl quantized operator with symbol

$$\sigma^{\mathrm{We}}\left(H_{\mathrm{ho}}(Z_0)\right)(z) = \tfrac{1}{2} z^T G_{Z_0} z. \tag{9.4}$$

Moreover, the general classification of exponentials of quadratic forms by Hörmander shows that $\mathrm{e}^{-tH_{\mathrm{ho}}(Z_0)}$ is a trace class Weyl operator for all $t > 0$. From [Hö95, Theorem 4.2] we obtain the following result.

Proposition 17. *Let Z be a normalized Lagrangian frame and $t > 0$. Then, $\mathrm{e}^{-tH_{\mathrm{ho}}(Z_0)}$ is a Weyl quantized trace class operator with symbol*

$$\sigma^{\mathrm{We}}\left(\mathrm{e}^{-tH_{\mathrm{ho}}(Z)}\right)(z) = \cosh(\varepsilon t)^{-d} \exp\left(\frac{\tanh(-\varepsilon t)}{\varepsilon} \tfrac{1}{2} z^T G_{Z_0} z\right) \tag{9.5}$$

in the Schwartz class $\mathcal{S}(\mathbb{R}^{2d})$.

Sketch of proof. The statements in [Hö95] are formulated for the case $\varepsilon = 1$, but the semiclassical formula follows along the same line of argumentation. One can use the semiclassical expansions from Lemma 8 and then retrace the proofs in Section 4 of [Hö95]. A key identity is given by

$$J_Z^3 = -J_Z,$$

which holds since J_Z is a complex structure by (7.9). Consequently,

$$\tan(-t\varepsilon J_Z) = J_Z \tanh(-t\varepsilon), \quad \cos(-\varepsilon t J_Z) = J_Z \cosh(\varepsilon t),$$

and we observe that the symbol of the Hagedorn semigroup is a function of the classical Hamiltonian (9.4), see also [Der93]. From Lemma 7 we know that the Weyl symbol gives rise to a trace class operator, since it is of Schwarz class. □

Let us comment that since $\sigma^{\mathrm{We}}\left(\mathrm{e}^{-tH_{\mathrm{ho}}(Z)}\right) \in \mathcal{S}(\mathbb{R}^{2d})$, the Hagedorn semigroup defines a continuous map on the tempered distributions,

$$\mathrm{e}^{-tH_{\mathrm{ho}}(Z)} : \mathcal{S}'(\mathbb{R}^{2d}) \to \mathcal{S}(\mathbb{R}^{2d}),$$

and consequently is a smoothing operator.

Remark 13 (Gibbs ensemble)**.** *In view of Remark 1, the normalized, positive trace class operator*

$$\mathrm{e}^{-tH_{\mathrm{ho}}(Z)} / \mathrm{tr}\left(\mathrm{e}^{-tH_{\mathrm{ho}}(Z)}\right) \tag{9.6}$$

defines a mixed quantum state. If we write $t = (k_B T)^{-1}$, where T denotes the temperature and k_B is the Boltzmann constant, (9.6) *defines the* thermal equilibrium state *or* Gibbs ensemble *at temperature T of a statistical ensemble of particles in $\mathbb{R}^d$ with Hamiltonian $H_{\mathrm{ho}}(Z)$.*

From the Definition 2 of Weyl quantized operators and Lemma 17 one can also compute the Schwartz kernel of the Hagedorn semigroup. One has

$$\mathrm{e}^{-tH_{\mathrm{ho}}(Z)}\psi(x) = \int_{\mathbb{R}^d} K_t^{\varepsilon}(x,y)\psi(y)dy,$$

with the generalized Mehler kernel

$$K_t^\varepsilon(x,y) = \frac{(2\pi\varepsilon)^{-d}}{\cosh(\varepsilon t)^d} \times \int_{\mathbb{R}^d} \mathrm{e}^{\mathrm{i}(x-y)\cdot\xi/\varepsilon} \exp\left(\tfrac{\tanh(-\varepsilon t)}{2\varepsilon}(\tfrac{x+y}{2},\xi)\cdot G_{Z_0}(\tfrac{x+y}{2},\xi)\right) d\xi.$$

We recall the standard Gaussian integral formula

$$(2\pi)^{-d/2}\int_{\mathbb{R}^d} \mathrm{e}^{-\frac{1}{2}x^TAx+x^Tb}dx = \det(A)^{-1/2}\mathrm{e}^{\frac{1}{2}b^TA^{-1}b}$$

for $A \in \mathbb{R}^{d\times d}$ symmetric positive definite, and $b \in \mathbb{C}^d$. Then,

$$\begin{aligned}
K_t^\varepsilon(x,y) &= \tfrac{(2\pi\varepsilon)^{-d/2}\det(Q)^{-1/4}}{\sinh(2\varepsilon t)^{d/2}} \\
&\times \mathrm{e}^{-\frac{\tanh(\varepsilon t)}{4\varepsilon}\left((x+y)PP^*(x+y)-(x+y)(-PQ^*+\mathrm{i}\mathrm{Id})(QQ^*)^{-1}(-QP^*-\mathrm{i}\mathrm{Id})(x+y)\right)} \\
&\times \mathrm{e}^{-(x-y)\frac{(QQ^*)^{-1}}{\varepsilon\tanh(\varepsilon t)}(x-y)-\frac{\mathrm{i}}{\varepsilon}(x-y)^T(-PQ^*+\mathrm{i}\mathrm{Id})(QQ^*)^{-1}(x+y)} \\
&= \tfrac{(2\pi\varepsilon)^{-d/2}\det(Q)^{-1/4}}{\sinh(2\varepsilon t)^{d/2}}\mathrm{e}^{-\frac{\tanh(\varepsilon t)}{4\varepsilon}\left(2\mathrm{i}(x+y)PQ^{-1}(x+y)-(x+y)(QQ^*)^{-1}(x+y)\right)} \\
&\times \mathrm{e}^{-(x-y)\frac{(QQ^*)^{-1}}{\varepsilon\tanh(\varepsilon t)}(x-y)+\frac{1}{\varepsilon}(x-y)^T(QQ^*)^{-1}(x+y)+\frac{\mathrm{i}}{\varepsilon}(x-y)^TPQ^{-1}(x+y)} \\
&= \tfrac{(2\pi\varepsilon)^{-d/2}\det(Q)^{-1/4}}{\sinh(2\varepsilon t)^{d/2}}\mathrm{e}^{-\frac{\mathrm{i}\tanh(\varepsilon t)}{2\varepsilon}(x+y)PQ^{-1}(x+y)+\frac{\mathrm{i}}{\varepsilon}(x-y)^TPQ^{-1}(x+y)} \\
&\times \mathrm{e}^{-\left(\frac{\sqrt{\tanh(\varepsilon t)}(x+y)}{2}+\frac{x-y}{\sqrt{\tanh(\varepsilon t)}}\right)^T(\varepsilon QQ^*)^{-1}\left(\frac{\sqrt{\tanh(\varepsilon t)}(x+y)}{2}+\frac{x-y}{\sqrt{\tanh(\varepsilon t)}}\right)},
\end{aligned}$$

and we observe that the Mehler kernel has a much more complicated structure than the Weyl symbol (9.5).

10 Anti-Wick Operators and Spectrograms

Pseudodifferential operators provide a way to associate linear operators with functions on phase space. The most popular and important pseudodifferential calculus is given by the Weyl quantization procedure we presented in §5.3. The immense popularity of Weyl operators can be explained by both, compliance with intuitive quantization rules for quantum mechanical observables, and the wealth of favorable properties such as the symplectic covariance, see e.g. Lemma 6 and [dG11, Theorem 215]. However, there are also drawbacks. Firstly, the major part of the theory of Weyl operators relies on classes of smooth symbols, and every extension to a more singular setting is a demanding task. We mention the twisted pseudifferential calculus of Martinez and Sordoni [MS09] for a method that works for Coulomb potentials. Secondly, some important properties of symbols, like positivity, are not necessarily reflected in their Weyl quantization. The sharpest available inequality for Weyl operators is the *Fefferman-Phong inequality*

$$\mathrm{op}_\varepsilon^{\mathrm{We}}(a) + C\varepsilon^2 \geq 0, \quad C > 0,$$

which holds for nonnegative symbols $a \geq 0$ that are regular enough[9]. We refer to [Ler10, §2.5.3] for a discussion and proofs.

A promising way to overcome the two shortcomings of Weyl operators mentioned above is to switch to the anti-Wick quantization procedure, which can be used for quantizing very irregular distributions. In this section we discuss anti-Wick quantized operators and their relation to the canonical Weyl correspondence. Our approach is based on the wave packets from §7 and tailored for the semiclassical propagation with probability densities considered in §12. For

[9] It is for example sufficient if $\partial^4 a$ belongs to the Sjöstrand algebra, see [Ler10, Theorem 2.5.10].

details and further reading we refer to [dG11, §11.4],[Ler10, §2.4] and [Sch01, §4.1]. A closely related concept in analytic microlocal analysis is that of a Toeplitz operator, see Remark 14 or [Zwo12, §13.4] for an introduction.

The Wick and anti-Wick quantization procedures were originally invented to reflect Wick or anti-Wick ordering of creation and annihilation operators, see [Ber71], and hence appear naturally in the analysis of many-particle systems. We refer to [AN08] for results on the quantization of infinite dimensional systems in the context of bosonic quantum field theories. For a recent application of Wick quantization to Bose-Einstein condensation see [LNR15].

In our analysis of quantum molecular dynamics we stick to the quantization of the finite-dimensional phase space $\mathbb{R}^{2d}$. Particular versions of the results in section §10.4 can be found in our joint publication [KLO15].

10.1 Generalized F.B.I. Transforms

For many problems in PDEs and mathematical physics it is often necessary to analyze a distribution in position and momentum space simultaneously. A central tool for this *microlocalization* is provided by the *Fourier-Bros-Iagolnitzer (F.B.I.) transform*[10]

$$(\mathcal{T}^\varepsilon \psi)(z) = (2\pi\varepsilon)^{-d/2} \langle \psi, \varphi_0^\varepsilon[z] \rangle_{\mathcal{S}',\mathcal{S}} \tag{10.1}$$

of a tempered distribution $\psi \in \mathcal{S}'(\mathbb{R}^d)$. In the definition (10.1), $\varphi_0^\varepsilon[z] := \varphi_0^\varepsilon[(\mathrm{Id}, \mathrm{iId}); z]$ denotes the isotropic Hagedorn ground state with phase space center $z \in \mathbb{R}^{2d}$. This definition is accordance with the one in [Mar02, Chapter 3]. In the context of analytic microlocal analysis one often defines the F.B.I. transform of ψ as the holomorphic function

$$(\mathcal{B}\psi)(q - \mathrm{i}p) = (\pi\varepsilon)^{-3d/4} 2^{-d/2} \int_{\mathbb{R}^d} \mathrm{e}^{-\frac{1}{2\varepsilon}(q-\mathrm{i}p-x)^2} \psi(x) dx. \tag{10.2}$$

[10] Here, $\langle \bullet, \bullet \rangle_{\mathcal{S}',\mathcal{S}}$ denotes the extension of the left-linear inner product $\langle \bullet, \bullet \rangle_{L^2}$.

We refer to [Del92, §I.2] or [Zwo12, §13] for more general holomorphic phase functions and the relation to complex Lagrangian submanifolds of $\mathbb{C}^{2d}$. The transformation (10.2) is also known as the Bargmann or Segal-Bargmann transform. F.B.I. and Bargmann transforms can for instance be used for exploring the microlocal or semiclassical regularity of solutions of PDEs, see e.g. [Sjö82] for the concept of an analytic wavefront set. (10.1) is the most suitable choice for the analysis of anti-Wick operators.

We also consider generalized F.B.I. transforms defined via the linear maps

$$(\mathcal{T}^{\varepsilon}_{k,Z}\psi)(z) = (2\pi\varepsilon)^{-d/2}\,\langle \psi, \varphi^{\varepsilon}_{k}[Z;z]\rangle_{\mathcal{S}',\mathcal{S}} \tag{10.3}$$

where $\varphi^{\varepsilon}_{k}[Z;z]$, $k \in \mathbb{N}^d$, is the semiclassical Hagedorn wave packet associated with the normalized Lagrangian frame $Z = Z_0 \in \mathbb{C}^{2d\times d}$. We recall some basic properties of the F.B.I. transform in the following Lemma 13, which is straightforward to prove.

Lemma 13. *Let $Z \in \mathbb{C}^{2d\times d}$ be a normalized Lagrangian frame, and $k \in \mathbb{N}^d$.*

i) $\mathcal{T}^{\varepsilon}_{k,Z} : L^2(\mathbb{R}^d) \to L^2(\mathbb{R}^{2d})$ is an isometry.

ii) The adjoint operator $\left(\mathcal{T}^{\varepsilon}_{k,Z}\right)^* : L^2(\mathbb{R}^{2d}) \to L^2(\mathbb{R}^d)$ is given by[11]

$$\left(\mathcal{T}^{\varepsilon}_{k,Z}\right)^* u(x) = (2\pi\varepsilon)^{-d/2}\int_{\mathbb{R}^{2d}} u(z)\varphi^{\varepsilon}_{k}[Z,z](x)dz$$

for $u \in L^2(\mathbb{R}^{2d})$.

iii) $\mathcal{T}^{\varepsilon}_{k,Z} : \mathcal{S}(\mathbb{R}^d) \to \mathcal{S}(\mathbb{R}^{2d})$ and $\left(\mathcal{T}^{\varepsilon}_{k,Z}\right)^* : \mathcal{S}(\mathbb{R}^{2d}) \to \mathcal{S}(\mathbb{R}^d)$ are continuous, and the same is true for tempered distributions.

iv) One has $\left(\mathcal{T}^{\varepsilon}_{k,Z}\right)^* \mathcal{T}^{\varepsilon}_{k,Z} = \mathrm{Id}_{L^2(\mathbb{R}^d)}$.

[11] The integral has to interpreted as a highly oscillatory integral in the momentum variable.

From (10.2) it is easy to see that the image $\mathcal{T}^\varepsilon(L^2(\mathbb{R}^d))$ of the standard F.B.I. transform is given by

$$\left\{u \in L^2(\mathbb{R}^{2d}) : \mathrm{e}^{\frac{|p|^2}{2\varepsilon}} u(q,p) \text{ holomorphic in } \ q - \mathrm{i}p \in \mathbb{C}^d\right\} \quad (10.4)$$

compare also [Mar02, Remark 3.1.3]. In other words, $\mathcal{B}$ maps $L^2(\mathbb{R}^d)$ into a semiclassical Segal-Bargmann space of square-integrable holomorphic functions. For a generalized F.B.I. transform $\mathcal{T}^\varepsilon_{k,Z}$ with $k \neq 0$ there is no immediate generalization of the analyticity property (10.4), since the polynomial prefactor of the wave packet $\varphi^\varepsilon_k[Z,(q,p)]$ depends on q but not on p.

The generalized F.B.I. transforms are closely related to the wave packet and Gabor transforms in time-frequency analysis, see [dG11, §9.3.2] and [Pos92]. In fact,

$$\mathcal{T}^\varepsilon_{k,Z}\psi(q,p) = \mathrm{e}^{\mathrm{i}pq/\varepsilon} V^\varepsilon_{\varphi^\varepsilon_k[Z]}\psi(q,p) \quad (10.5)$$

where $V_{\varphi^\varepsilon_k[Z]}$ denotes the semiclassically rescaled Gabor transform (or short-time Fourier transform)

$$V^\varepsilon_{\varphi^\varepsilon_k[Z]}\psi(q,p) = (2\pi\varepsilon)^{-d/2} \int_{\mathbb{R}^d} \mathrm{e}^{-\mathrm{i}py/\varepsilon} \psi(y) \overline{\varphi^\varepsilon_k[Z](y-q)} dy \quad (10.6)$$

with window $\varphi^\varepsilon_k[Z]$, see [dG11, Definition 177].

Remark 14 (Toeplitz Quantization)**.** *The orthogonal projector $\mathcal{B}\mathcal{B}^*$ on the holomorphic Segal-Bargmann space is called the* Bergman projector. *It can be used to define the* Toeplitz quantization *$\mathcal{B}\mathcal{B}^* a \mathcal{B}\mathcal{B}^*$ of a symbol $a \in L^\infty(\mathbb{R}^{2d})$ acting on phase space wave functions, see [Zwo12, §13.4].*

10.2 Quantization

Similarly as Toeplitz operators are defined by multiplication with the symbol in a Segal-Bargmann space, see Remark 14, we can use the F.B.I. transform to define operators via multiplication with the symbol in phase space.

Definition 7 (Anti-Wick Quantization)**.** *Let $Z \in \mathbb{C}^{2d\times d}$ be a normalized Lagrangian frame and $k \in \mathbb{N}^d$. For a symbol $a \in \mathcal{S}'(\mathbb{R}^{2d})$ we define the* anti-Wick quantized *operator* $\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a) : \mathcal{S}(\mathbb{R}^d) \to \mathcal{S}'(\mathbb{R}^d)$ *as*

$$\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a) = \left(\mathcal{T}^{\varepsilon}_{k,Z}\right)^* a \mathcal{T}^{\varepsilon}_{k,Z}, \tag{10.7}$$

and abbreviate $\mathrm{op}^{\mathrm{AW}}_{\varepsilon}(a) = \mathrm{op}^{\mathrm{AW}}_{\varepsilon,(\mathrm{Id},\mathrm{iId}),0}(a)$.

We note that since a defines a continuous multiplication operator $\mathcal{S}(\mathbb{R}^{2d}) \to \mathcal{S}'(\mathbb{R}^{2d})$, by part iii) of Lemma 13 $\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)$ is a well-defined continuous operator.

Since $\varphi^{\varepsilon}_k[Z,z]$ and $\widehat{T}_z\varphi^{\varepsilon}_k[Z]$ only differ by a constant phase, one can equivalently define the anti-Wick quantization of a function $a \in \mathcal{S}'(\mathbb{R}^{2d})$ as the Bochner integral[12]

$$\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} a(z) |\widehat{T}_z\varphi^{\varepsilon}_k[Z]\rangle\langle\widehat{T}_z\varphi^{\varepsilon}_k[Z]| dz, \tag{10.8}$$

see e.g. [dG11, Definition 255], where we recall that $|\varphi^{\varepsilon}_k[Z]\rangle\langle\varphi^{\varepsilon}_k[Z]|$ denotes the rank one orthogonal projector on the span of $\varphi^{\varepsilon}_k[Z] \in L^2(\mathbb{R}^d)$. For general anti-Wick quantization procedures from a time-frequency perspective see also [BCG04].

Part iv) of Lemma 13 implies that $\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(1) = \mathrm{Id}$. This can also be deduced from the following Lemma which states that one can decompose the identity on $L^2(\mathbb{R}^{2d})$ by simply shifting a single wave function, the "window", in phase space.

Lemma 14 (Completeness)**.** *Let $\psi \in \mathcal{S}(\mathbb{R}^d)$ be L^2-normalized. Then one has*

$$(2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} |\widehat{T}_z\psi\rangle\langle\widehat{T}_z\psi| dz = \mathrm{Id}_{L^2(\mathbb{R}^d)}, \tag{10.9}$$

where the integral on the left hand side is a Bochner integral.

[12] If a is not a function, one can still rewrite matrix elements of the integral via duality brackets.

Proof. By (5.13), the Weyl symbol of $(2\pi\varepsilon)^{-d}|\widehat{T}_z\psi\rangle\langle\widehat{T}_z\psi|$ is given by the Wigner transform $\mathcal{W}^\varepsilon(\widehat{T}_z\psi)$. Hence, the covariance property for Wigner functions from Lemma 6 implies

$$\sigma^{\mathrm{We}}\left((2\pi\varepsilon)^{-d}\int_{\mathbb{R}^{2d}}|\widehat{T}_z\psi\rangle\langle\widehat{T}_z\psi|dz\right)=\int_{\mathbb{R}^{2d}}\mathcal{W}^\varepsilon(\psi)(z)dz=1.$$

Note that ψ is of Schwartz class, such that $\mathcal{W}^\varepsilon(\psi)$ is integrable and we can exchange the phase space integral with the one appearing in the Weyl quantization. The claim follows since $\mathrm{op}_\varepsilon^{\mathrm{We}}(1)=\mathrm{Id}_{L^2(\mathbb{R}^d)}$. □

Lemma 15 summarizes some important properties of anti-Wick quantized operators. We would particularly like to stress that in contrast to the Weyl quantization the positivity and boundedness properties of the symbol directly translate to the anti-Wick operator.

Lemma 15. *Anti-Wick quantized operators have the following properties:*

i) Let $a\in L^p(\mathbb{R}^{2d})$ for some $1\leq p\leq\infty$. Then, $\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)$ is bounded on $L^2(\mathbb{R}^d)$, with

$$\|\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)\|_{L^2\to L^2}\leq C_{Z,k,p}(2\pi\varepsilon)^{-p/d}\|a\|_{L^p}$$

where $C_{Z,k,p}$ is independent of a. If $p\leq 2$, $\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)$ is compact.

ii) For real-valued symbols a the operator $\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)$ is symmetric, and one has

$$\inf a\leq\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)\leq\sup|a|$$

in the sense of quadratic forms. In particular,

$$\|\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)\|_{L^2\to L^2}\leq\sup|a|.$$

Proof. A proof for the assertions in the case $k=0$ can be found in §4.1 of [Sch01], see in particular Proposition 4.1.5 for the first part. Another reference is [BC02]. The generalization to $k\in\mathbb{N}^d$ works along the same line of argumentation. □

The anti-Wick correspondence is particularly well-suited for the quantization of measures and characteristic functions. For instance, the quantization of a delta distribution δ_z, $z \in \mathbb{R}^{2d}$, in phase space yields the corresponding Hagedorn state

$$\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(\delta_z) = (2\pi\varepsilon)^{-d} |\varphi^\varepsilon_k[Z,z]\rangle\langle\varphi^\varepsilon_k[Z,z]|.$$

Moreover, the quantization of characteristic functions results in approximate semiclassical projection operators, which are useful for phase space localization estimates. See [Sch01, §4.3 and §4.4] for details and applications to quantum ergodicity.

10.3 Relation to Weyl Operators

From the Definition 7 of Anti-Wick operators it is not immediately clear that there is a close relation between Weyl and anti-Wick operators. In fact, one can easily show that anti-Wick operators are Weyl operators, while the other implication is not true in general. The Weyl symbol of an anti-Wick operator can be expressed explicitely via a convolution with a Wigner transform, see also [dG11, Proposition 258].

Proposition 18. *Let $a \in \mathcal{S}'(\mathbb{R}^{2d})$. Then $\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)$ is a Weyl operator with smooth symbol*

$$\sigma^{\mathrm{We}}\left(\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)\right) = a * \mathcal{W}^\varepsilon_{k,k}[Z],$$

where $\mathcal{W}^\varepsilon_{k,k}[Z]$ is the Wigner transform of $\varphi^\varepsilon_k[Z]$. The situation $k = 0$ is typically of the greatest interest.

Proof. Let us first recall that

$$\begin{aligned}(2\pi\varepsilon)^{-d}\sigma^{\mathrm{We}}\left(|\widehat{T}_z\varphi^\varepsilon_k[Z]\rangle\langle\widehat{T}_z\varphi^\varepsilon_k[Z]|\right)(w) &= \mathcal{W}^\varepsilon(\widehat{T}_z\varphi^\varepsilon_k[Z])(w)\\ &= \mathcal{W}^\varepsilon_{k,k}[Z](w-z)\end{aligned}$$

is a Schwartz function in w for all z and vice versa.

It suffices to show the asserted operator identity for all matrix elements. The Wigner function of any pair $\psi, \phi \in \mathcal{S}(\mathbb{R}^d)$ is of Schwartz class. Hence, by (10.8), (10.10), and Fubini's theorem we obtain

$$\begin{aligned}
&\left\langle \mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)\psi, \phi \right\rangle_{\mathcal{S}'(\mathbb{R}^d),\mathcal{S}(\mathbb{R}^d)} \qquad (10.10)\\
&= (2\pi\varepsilon)^{-d} \left\langle a, \langle\psi|\widehat{T}_\bullet \varphi^\varepsilon_k[Z]\rangle\langle \widehat{T}_\bullet \varphi^\varepsilon_k[Z]|\phi\rangle \right\rangle_{\mathcal{S}'(\mathbb{R}^{2d}),\mathcal{S}(\mathbb{R}^{2d})}\\
&= \left\langle a, \left(\int_{\mathbb{R}^{2d}} \mathcal{W}^\varepsilon_{k,k}[Z](w-\bullet)\mathcal{W}^\varepsilon(\psi,\phi)(w)dw \right) \right\rangle_{\mathcal{S}'(\mathbb{R}^{2d}),\mathcal{S}(\mathbb{R}^{2d})}\\
&= \int_{\mathbb{R}^{2d}} (a * \mathcal{W}^\varepsilon_{k,k}[Z])(z)\mathcal{W}^\varepsilon(\psi,\phi)(z)dz \qquad (10.11)
\end{aligned}$$

and the assertion follows from recalling the matrix element formula (5.14) for Weyl quantized operators. The fact that $a * \mathcal{W}^\varepsilon_k[Z]$ is a smooth function follows from basic distribution theory. □

Suppose that A is both a Weyl operator and an anti-Wick operator. Then, on the one hand, from Proposition 18 we know that the regularity of the Weyl symbol of A is typically much higher than the regularity of the anti-Wick symbol. On the other hand, (10.11) implies that matrix elements of anti-Wick operators can be evaluated as

$$\left\langle \mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)\psi, \phi \right\rangle = \int_{\mathbb{R}^{2d}} a(z)(\mathcal{W}^\varepsilon(\psi,\phi) * \mathcal{W}^\varepsilon_{k,k}[Z])(z)dz \qquad (10.12)$$

and hence the representation of pure states $|\psi\rangle\langle\psi|$ in matrix elements is more regular than via Wigner functions in the Weyl correspondence. We show in the next section §10.4 that in the anti-Wick correspondence states are represented by smooth probability densities on phase space.

Remark 15. *Proposition 18 immediately implies a semiclassical expansion of the Weyl symbol of an anti-Wick operator. In particular, the*

principal symbols coincide,

$$\mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a) = \mathrm{op}^{\mathrm{We}}_{\varepsilon}(a + O(\varepsilon))$$

for suitable a.

For deriving higher order semiclassical expansions of the Weyl symbol and composition formulas one can proceed similarly as in [Kel12, KL13], see, e.g., §12.1. for second order conversion formulas. We remark that suitable symbol classes for anti-Wick calculus are given by Gelfand-Shilov type spaces of ultradifferentiable functions, see [AMP09, Sol13].

10.4 Spectrograms

Since we are interested in discretizing approximations for propagated expectation values, it is desirable to work in a phase space representation of quantum mechanics for which states $|\psi\rangle\langle\psi|$ are represented by smooth probability densities on phase space. For the anti-Wick correspondence introduced in §10.2 this is indeed the case. Before proving this important property, we first recall the concept of a spectrogram from time-frequency analysis.

Definition 8 (Spectrogram)**.** *Let $\psi, \phi \in L^2(\mathbb{R}^d)$ be normalized and recall the Gabor transform V^ϵ from* (10.6)*. The non-negative function*

$$S_\phi(\psi)(z) := |V^\varepsilon_\phi \psi(z)|^2$$

is called the Spectrogram *of ψ with window ϕ.*

Spectrograms can be used for the simultaneous representation of wave functions in position and momentum space. As the following Proposition shows, spectrograms are probability densities on phase space that are obtained by convolving two Wigner transforms, or taking the modulus squared of a generalized F.B.I. type transform.

Proposition 19. *Let $\psi, \phi \in L^2(\mathbb{R}^d)$ and define $\phi_- = \phi(-\bullet)$. Then, the spectrogram $S_\phi(\psi)$ satisfies*

$$S_\phi(\psi)(z) = (2\pi\varepsilon)^{-d} \left| \left\langle \psi, \widehat{T}_z \phi \right\rangle_{L^2} \right|^2 = (\mathcal{W}^\varepsilon(\psi) * \mathcal{W}^\varepsilon(\phi_-))(z) \tag{10.13}$$

for all $z \in \mathbb{R}^{2d}$, and

$$\int_{\mathbb{R}^{2d}} S_\phi(\psi)(z) dz = \|\psi\|^2 \|\phi\|^2.$$

Furthermore, as for Wigner transforms, we have the Weyl-Heisenberg covariance property

$$S_\phi(\widehat{T}_z \psi)(z) = S_\phi(\psi)(z)(\bullet - z). \tag{10.14}$$

Proof. We start by noting that by definition the Gabor transform $V_\phi^\varepsilon \psi$ and $(2\pi\varepsilon)^{-d/2} \left\langle \psi, \widehat{T}_z \phi \right\rangle_{L^2}$ only differ by a phase, which yields the first equality in (10.13). For $z = (q, p)$ we have

$$\begin{aligned}
\mathcal{W}^\varepsilon(\phi)(-z) &= (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^d} \overline{\phi}(-q + \tfrac{y}{2}) \phi(-q - \tfrac{y}{2}) \mathrm{e}^{-\mathrm{i}y\cdot p/\varepsilon} dy \\
&= (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^d} \overline{\phi}(-q - \tfrac{y}{2}) \phi(-q + \tfrac{y}{2}) \mathrm{e}^{\mathrm{i}y\cdot p/\varepsilon} dy \\
&= (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^d} \overline{\phi}_-(q + \tfrac{y}{2}) \phi_-(q - \tfrac{y}{2}) \mathrm{e}^{\mathrm{i}y\cdot p/\varepsilon} dy = \mathcal{W}^\varepsilon(\phi_-)(z).
\end{aligned}$$

Consequently, Moyal's identity (5.7) gives

$$\begin{aligned}
(\mathcal{W}^\varepsilon(\psi) * \mathcal{W}^\varepsilon(\phi_-))(z) &= \int_{\mathbb{R}^{2d}} \mathcal{W}^\varepsilon(\psi)(w) \mathcal{W}^\varepsilon(\phi)(w - z) dw \\
&= \int_{\mathbb{R}^{2d}} \mathcal{W}^\varepsilon(\psi)(w) \mathcal{W}^\varepsilon(\widehat{T}_z \phi)(w) dw \\
&= (2\pi\varepsilon)^{-d} \left| \left\langle \psi, \widehat{T}_z \phi_- \right\rangle \right|^2 \geq 0.
\end{aligned}$$

For the integral one computes

$$\begin{aligned}\int_{\mathbb{R}^{2d}} S_\phi(\psi)(z)dz &= \int_{\mathbb{R}^{2d}} (\mathcal{W}^\varepsilon(\psi) * \mathcal{W}^\varepsilon(\phi_-))(z)dz \\ &= \int_{\mathbb{R}^{2d}}\int_{\mathbb{R}^{2d}} \mathcal{W}^\varepsilon(\psi)(w)\mathcal{W}^\varepsilon(\widehat{T}_w\phi_-)(z)dwdz \\ &= \|\psi\|^2\|\phi\|^2,\end{aligned}$$

since for all $w \in \mathbb{R}^{2d}$,

$$\int_{\mathbb{R}^{2d}} \mathcal{W}^\varepsilon(\widehat{T}_w\phi_-)(z)\partial z = \|\widehat{T}_w\phi_-\|^2 = \|\phi\|^2. \tag{10.15}$$

Finally, for all $w \in \mathbb{R}^{2d}$ we find

$$\begin{aligned}(\mathcal{W}^\varepsilon(\widehat{T}_z\psi) * \mathcal{W}^\varepsilon(\phi_-))(w) &= \int_{\mathbb{R}^{2d}} \mathcal{W}^\varepsilon(\psi)(y-z)\mathcal{W}^\varepsilon(\phi_-)(w-y)dy \\ &= \int_{\mathbb{R}^{2d}} \mathcal{W}^\varepsilon(\psi)(y)\mathcal{W}^\varepsilon(\phi_-)(w-y-z)dy \\ &= (\mathcal{W}^\varepsilon(\psi) * \mathcal{W}^\varepsilon(\phi_-))(w-z)\end{aligned}$$

by using the covariance property of the Wigner transform. □

Proposition 19 implies that a convolution of two Wigner transforms is always a nonnegative probability density on phase space. In view of the fact that Wigner transforms generically attain negative values, this might be surprising at first sight. However, if one encounters the relation between spectrograms and anti-Wick operators, it can be explained by the positivity property of anti-Wick operators from part ii) of Proposition 15. By Proposition 19 and (10.19), we can rewrite expectation values of anti-Wick operators as

$$\left\langle \mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)\psi, \psi \right\rangle = \int_{\mathbb{R}^{2d}} a(z) S_{\varphi^\varepsilon_k[Z]}(\psi)(z)dz, \tag{10.16}$$

which is the the expectation value of a with respect to the probability measure $S_{\varphi^\varepsilon_k[Z]}(\psi)(z)dz$ on phase space. Generalizing the concept of a spectrogram to offdiagonal matrix elements leads to Husimi functions, which go back to [Hus40].

Definition 9. *For $\phi, \psi \in L^2(\mathbb{R}^d)$, $k \in \mathbb{N}^d$, and a normalized Lagrangian frame $Z \in \mathbb{C}^{2d\times d}$ we define the* Husimi function *of ψ and ϕ as*

$$\mathcal{H}^\varepsilon_{k,Z}(\psi,\phi) = \mathcal{W}^\varepsilon(\psi,\phi) * \mathcal{W}^\varepsilon_{k,k}[Z] \tag{10.17}$$

and write $\mathcal{H}^\varepsilon_k(\psi,\phi) := \mathcal{H}^\varepsilon_{k,(\mathrm{Id};i\mathrm{Id})}(\psi,\phi)$. If $\psi = \phi$, we call the smooth spectrogram

$$\mathcal{H}^\varepsilon_{k,Z}(\psi) = \mathcal{H}^\varepsilon_{k,Z}(\psi,\psi) = S_{\varphi^\varepsilon_k[Z]}(\psi) \tag{10.18}$$

the Husimi transform *of ψ.*

Remark 16. *Note that $\mathcal{H}^\varepsilon_{k,Z}(\psi) = S_{\varphi^\varepsilon_k[Z]}(\psi)$ is compatible with the Wigner convolution formula in* (10.13)*, since by Corollary 3 the Wigner transform of normalized Hagedorn wavepackets is symmetric, $\mathcal{W}^\varepsilon_k[Z](z) = \mathcal{W}^\varepsilon_k[Z](-z)$.*

With the Husimi functions we can then rewrite matrix elements of anti-Wick operators as

$$\left\langle \mathrm{op}^{\mathrm{AW}}_{\varepsilon,Z,k}(a)\psi,\phi \right\rangle = \int_{\mathbb{R}^{2d}} a(z)\mathcal{H}^\varepsilon_{k,Z}(\psi,\phi)dz, \tag{10.19}$$

which is the equivalent of the Wigner function formula (5.14) for Weyl operators.

In applications one typically only uses the Gaussian version of the Husimi transform with $k = 0$, see [AMP09, §4.1] and [AP11]. In particular, the isotropic Gaussian convolution

$$\mathcal{H}^\varepsilon_0(\psi)(z) = (\pi\varepsilon)^{-d}\int_{\mathbb{R}^{2d}} \mathcal{W}^\varepsilon(\psi)(w)\mathrm{e}^{-|z-w|^2/\varepsilon}\,dw, \tag{10.20}$$

is considered as the standard definition of Husimi transforms, compare also [Ler10, §2.4.1]. More general Husimi transforms appear naturally in our semiclassical spectrogram expansion of Wigner transforms discussed in §10.5.

In contrast to Wigner transforms, Husimi transforms are smooth probability densities on phase space. Hence, they are better amenable for numerical sampling purposes, which is the main motivation for

introducing and applying the semiclassical propagation methods from §12.

10.5 Spectrogram Expansion of Wigner Transforms

By Remark 15, the difference between the operators obtained by Weyl and anti-Wick quantization of the same symbol is of size $O(\varepsilon)$. In other words, for suitable a one has

$$a * \mathcal{W}^{\varepsilon}_{k,k}[Z] = a + O(\varepsilon)$$

which can be seen from a simple Taylor expansion. It is a goal of this section to introduce a quantization procedure that is both closer to the Weyl correspondence and, at the same time, allows for a representation of states in terms of spectrograms. This is possible by formally inverting the convolution in the symbols up to some error of size $O(\varepsilon^k)$ with $k > 1$. For simplicity we stick to the isotropic case $Z = (\mathrm{Id}, \mathrm{iId})$, but the same analysis works also for the more general case. Combining anti-Wick quantizations associated with different energies, that is, different indices k, makes is possible to approximate Wigner functions more accurately than just with the ground state quantization $\mathrm{op}^{\mathrm{AW}}_{\varepsilon}$. We first rephrase the Laplacian of ground state Wigner transforms in terms of higher order Wigner transforms.

Proposition 20. *Let $\varepsilon > 0$ and $\mathcal{W}^{\varepsilon}_{k} = \mathcal{W}^{\varepsilon}_{k,k}[(\mathrm{Id}; \mathrm{iId})]$. Then,*

$$(1 - \tfrac{\varepsilon}{4}\Delta)\mathcal{W}^{\varepsilon}_{0} = (1 + \tfrac{d}{2})\,\mathcal{W}^{\varepsilon}_{0} - \tfrac{1}{2}\sum_{|k|=1} \mathcal{W}^{\varepsilon}_{k}$$

as well as the higher order formula

$$\begin{aligned}(1 - \tfrac{\varepsilon}{4}\Delta + \tfrac{\varepsilon^2}{32}\Delta^2)\mathcal{W}^{\varepsilon}_{0} = (1 + \tfrac{1}{2}d + \tfrac{d(d+1)}{8})\,\mathcal{W}^{\varepsilon}_{0} \\ - (\tfrac{1}{2} + \tfrac{d+1}{4})\sum_{|k|=1} \mathcal{W}^{\varepsilon}_{k} + \tfrac{1}{4}\sum_{|\ell|=2} \mathcal{W}^{\varepsilon}_{\ell}.\end{aligned}$$

Proof. Let $z = (q, p) \in \mathbb{R}^{2d}$ and set $z_j = q_j + \mathrm{i}p_j \in \mathbb{C}^d$. We compute

$$\begin{aligned}\Delta \mathcal{W}_0^\varepsilon(z) &= (\pi\varepsilon)^{-d} \Delta \mathrm{e}^{-|z|^2/\varepsilon} = (\pi\varepsilon)^{-d} \nabla \cdot \left(-\tfrac{2}{\varepsilon} z \, \mathrm{e}^{-|z|^2/\varepsilon}\right) \\ &= (\pi\varepsilon)^{-d} \left(-\tfrac{4d}{\varepsilon} + \tfrac{4}{\varepsilon^2}|z|^2\right) \mathrm{e}^{-|z|^2/\varepsilon}.\end{aligned}$$

By Corollary 3 or [LT14, Theorem 1],

$$\mathcal{W}_{e_j}^\varepsilon(z) = -(\pi\varepsilon)^{-d} \left(1 - \tfrac{2}{\varepsilon}|z_j|^2\right) \mathrm{e}^{-|z|^2/\varepsilon}, \tag{10.21}$$

such that we have

$$\begin{aligned}\sum_{j=1}^d \mathcal{W}_{e_j}^\varepsilon(z) &= -(\pi\varepsilon)^{-d} \left(2d - d - \tfrac{2}{\varepsilon}|z|^2\right) \mathrm{e}^{-|z|^2/\varepsilon} \\ &= -(\pi\varepsilon)^{-d} \left(2d - \tfrac{2}{\varepsilon}|z|^2\right) \mathrm{e}^{-|z|^2/\varepsilon} + d \cdot \mathcal{W}_0^\varepsilon(z)\end{aligned}$$

and

$$\begin{aligned}\Delta \mathcal{W}_0^\varepsilon(z) &= -\tfrac{2}{\varepsilon}(\pi\varepsilon)^{-d} \left(2d - \tfrac{2}{\varepsilon}|z|^2\right) \mathrm{e}^{-|z|^2/\varepsilon} \\ &= \tfrac{2}{\varepsilon} \sum_{j=1}^d \mathcal{W}_{e_j}^\varepsilon(z) - \tfrac{2d}{\varepsilon} \mathcal{W}_0^\varepsilon(z).\end{aligned}$$

This gives the first assertion. For the second expansion we start similarly, and observe

$$\begin{aligned}\Delta^2 \mathcal{W}_0^\varepsilon &= \Delta \left(-\tfrac{4d}{\varepsilon} \mathcal{W}_0^\varepsilon + \tfrac{4}{\varepsilon^2}|z|^2 \mathcal{W}_0^\varepsilon\right) \\ &= -\tfrac{4d}{\varepsilon} \left(-\tfrac{4d}{\varepsilon} + \tfrac{4}{\varepsilon^2}|z|^2\right) \mathcal{W}_0^\varepsilon \\ &\quad + \tfrac{4}{\varepsilon^2} \left(|z|^2 \left(-\tfrac{4d}{\varepsilon} + \tfrac{4}{\varepsilon^2}|z|^2\right) - \tfrac{8}{\varepsilon}|z|^2 + 4d\right) \mathcal{W}_0^\varepsilon \\ &= \mathcal{W}_0^\varepsilon \left(\tfrac{16d^2+16d}{\varepsilon^2} - \tfrac{32d+32}{\varepsilon^3}|z|^2 + \tfrac{16}{\varepsilon^4}|z|^4\right).\end{aligned} \tag{10.22}$$

Furthermore, by Corollary 3, one computes

$$\begin{aligned}\sum_{i\neq j}\mathcal{W}^{\varepsilon}_{e_i+e_j}(z) &= \sum_{i\neq j}\mathcal{W}^{\varepsilon}_0(z)L_1(\tfrac{2}{\varepsilon}|z_i|^2)L_1(\tfrac{2}{\varepsilon}|z_j|^2)\\ &= \sum_{i\neq j}\left(1-\tfrac{2}{\varepsilon}|z_i|^2-\tfrac{2}{\varepsilon}|z_j|^2+\tfrac{4}{\varepsilon^2}|z_i|^2|z_j|^2\right)\mathcal{W}^{\varepsilon}_0(z)\\ &= \left((d^2-d)-\tfrac{4d-4}{\varepsilon}|z|^2+\tfrac{4}{\varepsilon^2}\left(|z|^4-\sum_{j=1}^{d}|z_j|^4\right)\right)\mathcal{W}^{\varepsilon}_0(z)\end{aligned}$$

as well as

$$\begin{aligned}\sum_{j=1}^{d}\mathcal{W}^{\varepsilon}_{2e_j}(z) &= \sum_{j=1}^{d}\mathcal{W}^{\varepsilon}_0(z)L_2(\tfrac{2}{\varepsilon}|z_j|^2)\\ &= \sum_{j=1}^{d}\left(1-\tfrac{4}{\varepsilon}|z_j|^2+\tfrac{2}{\varepsilon^2}|z_j|^4\right)\mathcal{W}^{\varepsilon}_0(z)\\ &= \left(d-\tfrac{4}{\varepsilon}|z|^2+\tfrac{2}{\varepsilon^2}\sum_{j=1}^{d}|z_j|^4\right)\mathcal{W}^{\varepsilon}_0(z).\end{aligned}$$

Consequently, we have

$$\begin{aligned}\sum_{i\neq j}\mathcal{W}^{\varepsilon}_{e_i+e_j}(z)+2\sum_{j=1}^{d}\mathcal{W}^{\varepsilon}_{2e_j}(z) &= \left((d^2+d)+\tfrac{-4d-4}{\varepsilon}|z|^2+\tfrac{4}{\varepsilon^2}|z|^4\right)\mathcal{W}_0(z)\\ &= 8\left(\tfrac{d^2+d}{8}-\tfrac{d+1}{2\varepsilon}|z|^2+\tfrac{1}{2\varepsilon^2}|z|^4\right)\mathcal{W}^{\varepsilon}_0(z)\\ &= 8\left(\left(-\tfrac{3(d^2+d)}{8}+\tfrac{d+1}{2\varepsilon}|z|^2\right)+\left(\tfrac{d^2+d}{2}-\tfrac{d+1}{\varepsilon}|z|^2+\tfrac{1}{2\varepsilon^2}|z|^4\right)\right)\mathcal{W}^{\varepsilon}_0(z)\\ &= 8\left(\left(-\tfrac{3(d^2+d)}{8}+\tfrac{d+1}{2\varepsilon}|z|^2\right)+\tfrac{\varepsilon^2}{32}\Delta^2\right)\mathcal{W}^{\varepsilon}_0(z)\end{aligned}$$

since by (10.22) we have

$$\tfrac{\varepsilon^2}{32}\Delta^2\mathcal{W}^{\varepsilon}_0(z)=\left(\tfrac{d^2+d}{2}-\tfrac{d+1}{\varepsilon}|z|^2+\tfrac{1}{2\varepsilon^2}|z|^4\right)\mathcal{W}^{\varepsilon}_0(z).$$

Finally, we obtain

$$\begin{aligned}\left(\tfrac{3(d^2+d)}{8} - \tfrac{d+1}{2\varepsilon}|z|^2\right)\mathcal{W}_0^\varepsilon(z) &= \left(\tfrac{d^2+d}{2} - \tfrac{d+1}{2\varepsilon}|z|^2 - \tfrac{d^2+d}{8}\right)\mathcal{W}_0^\varepsilon(z)\\ &= -\tfrac{d+1}{2}\tfrac{\varepsilon}{4}\Delta\mathcal{W}_0(z) - \left(\tfrac{d^2+d}{8}\right)\mathcal{W}_0^\varepsilon(z)\\ &= \tfrac{d+d^2}{8}\mathcal{W}_0^\varepsilon(z) - \tfrac{d+1}{4}\sum_{j=1}^{d}\mathcal{W}_{e_j}^\varepsilon(z)\end{aligned}$$

and since

$$\sum_{i\neq j}\mathcal{W}_{e_i+e_j}^\varepsilon + 2\sum_{j=1}^{d}\mathcal{W}_{2e_j}^\varepsilon = 2\sum_{|\ell|=2}\mathcal{W}_\ell^\varepsilon.$$

we arrive at

$$\begin{aligned}(1 - \tfrac{\varepsilon}{4}\Delta + \tfrac{\varepsilon^2}{32}\Delta^2)\mathcal{W}_0^\varepsilon =& (1 + \tfrac{1}{2}d + \tfrac{d(d+1)}{8})\,\mathcal{W}_0^\varepsilon - (\tfrac{1}{2} + \tfrac{d+1}{4})\sum_{|k|=1}\mathcal{W}_k^\varepsilon\\ &+ \tfrac{1}{4}\sum_{|\ell|=2}\mathcal{W}_\ell^\varepsilon,\end{aligned}$$

which completes the proof. □

The expansions from Proposition 20 represent the first two respectively three terms in the series of formal deconvolution for the Husimi transform. They can be applied to approximate Wigner functions and Weyl symbols of anti-Wick operators up to second or third oder errors in ε. Since we are interested in the propagation of expectation values, we state only state the spectrogram expansion for Wigner transforms. With the same arguments as used in the proof below one can derive a similar expansion for cross-Wigner functions and Weyl symbols of anti-Wick operators.

Theorem 4 (Spectrogram Expansion). *Let $\psi \in L^2(\mathbb{R}^d)$ and $\varepsilon > 0$. Then,*

$$\mathcal{W}^\varepsilon(\psi) = \underbrace{(1 + \tfrac{d}{2})\,\mathcal{H}_0^\varepsilon(\psi) - \tfrac{1}{2}\sum_{|k|=1}\mathcal{H}_k^\varepsilon(\psi)}_{=:\mu_2(\psi)} + O(\varepsilon^2) \tag{10.23}$$

as well as the third order formula

$$\begin{aligned}\mathcal{W}^\varepsilon(\psi) &= \left(1 + \tfrac{1}{2}d + \tfrac{d(d+1)}{8}\right)\mathcal{H}_0^\varepsilon(\psi) - (\tfrac{1}{2} + \tfrac{d+1}{4})\sum_{|k|=1}\mathcal{H}_k^\varepsilon(\psi) \\ &\quad + \tfrac{1}{4}\sum_{|\ell|=2}\mathcal{H}_\ell^\varepsilon(\psi) + O(\varepsilon^3) \\ &=: \mu_3(\psi) + O(\varepsilon^3)\end{aligned}$$

in the weak sense. The error terms depend on bounds for the fourth or sixth order derivatives of the applied test function, respectively.

Proof. Let $a \in \mathcal{S}(\mathbb{R}^{2d})$ be a test function. We only prove the formula for $\mu_3(\psi)$, since the proof for $\mu_2(\psi)$ works in the same way. A Taylor expansion of the Gaussian convolution implies

$$\begin{aligned}\mathcal{W}_0^\varepsilon * (a - \tfrac{\varepsilon}{4}\Delta a + \tfrac{\varepsilon^2}{32}\Delta^2 a) &= (a - \tfrac{\varepsilon}{4}\Delta a + \tfrac{\varepsilon^2}{32}\Delta^2 a) + \tfrac{\varepsilon}{4}\Delta(a - \tfrac{\varepsilon}{4}\Delta a) \\ &\quad + \tfrac{\varepsilon^2}{32}\Delta^2 a + O(\varepsilon^3) \\ &= a + O(\varepsilon^3),\end{aligned}$$

where the error term contains derivatives of a of order six. Integration by parts yields

$$\begin{aligned}\int_{\mathbb{R}^{2d}} a(z)\mathcal{W}^\varepsilon(\psi)(z)dz &= \int_{\mathbb{R}^{2d}} \mathcal{W}_0^\varepsilon * (a - \tfrac{\varepsilon}{4}\Delta a + \tfrac{\varepsilon^2}{32}\Delta^2 a)(z)\mathcal{W}^\varepsilon(\psi)(z)dz \\ &\quad + O(\varepsilon^3) \\ &= \int_{\mathbb{R}^{2d}} (a - \tfrac{\varepsilon}{4}\Delta a + \tfrac{\varepsilon^2}{32}\Delta^2 a)(z)\mathcal{H}_0^\varepsilon(\psi)(z)dz + O(\varepsilon^3) \\ &= \int_{\mathbb{R}^{2d}} a(z)(1 - \tfrac{\varepsilon}{4}\Delta + \tfrac{\varepsilon^2}{32}\Delta^2)\mathcal{H}_0^\varepsilon(\psi)(z)dz + O(\varepsilon^3)\end{aligned}$$

and consequently we observe

$$(1 - \tfrac{\varepsilon}{4}\Delta + \tfrac{\varepsilon^2}{32}\Delta^2)\mathcal{H}_0^\varepsilon(\psi) = \mathcal{W}^\varepsilon(\psi) * \left((1 - \tfrac{\varepsilon}{4}\Delta + \tfrac{\varepsilon^2}{32}\Delta^2)\mathcal{W}_0^\varepsilon\right).$$

Applying Proposition 20 completes the proof. □

Remark 17 (Normalized weight)**.** *For a normalized wave function $\psi \in L^2(\mathbb{R}^d)$, the two densities $\mu_2(\psi)$ and $\mu_3(\psi)$ are of mass one,*

$$\int_{\mathbb{R}^{2d}} \mu_2(\psi)(z)dz = \int_{\mathbb{R}^{2d}} \mu_3(\psi)(z)dz = 1,$$

as one can easily verify. Moreover, $\mu_2(\psi)$ and $\mu_3(\psi)$ are integrable for all $\psi \in L^2(\mathbb{R}^d)$, which is in general not true for the Wigner transform.

The form of the expansions in Theorem 4 suggests an inductive proof of higher order spectrogram expansions of Wigner transforms. We suppose the following closed form of a spectrogram expansion of Wigner transforms.

Conjecture 1. *Let $\psi \in L^2(\mathbb{R}^d)$ and $\varepsilon > 0$. Then, for all $N \in \mathbb{N}$ one has*

$$\mathcal{W}^\varepsilon(\psi) = \sum_{j=0}^{N} (-1)^j \sum_{m=j}^{N} 2^{-m} \binom{d-1+m}{d-1+j} \sum_{|k|=j} \mathcal{H}_k^\varepsilon(\psi) + O(\varepsilon^{N+1})$$

in the weak sense.

In figure 4 one can see the Wigner transform, the Husimi transform, and the phase space density $\mu_2(\psi)$ from Theorem 4 for the superposition $\psi \in L^2(\mathbb{R})$ of a Gaussian wave packet and a Lagrangian or WKB type state. While the Wigner transform exhibits strong oscillations due to the entanglement of the Gaussian wave packet and the WKB state, see also figure 1, the Husimi transform does not show any of the oscillations. The new density $\mu_2(\psi)$ displays some of the characteristic features of the oscillations in the Wigner function. We find this observation remarkable, since the fast oscillations vanish in the limit $\varepsilon \searrow 0$, and the spectrogram expansion from Theorem 4 only holds in the weak sense.

In our preprint [KLO15] one can find explicit expressions for the density $\mu_2(\psi)$ for the cases that ψ is a Gaussian wave packet, a Gaussian superposition, or a Hermite function.

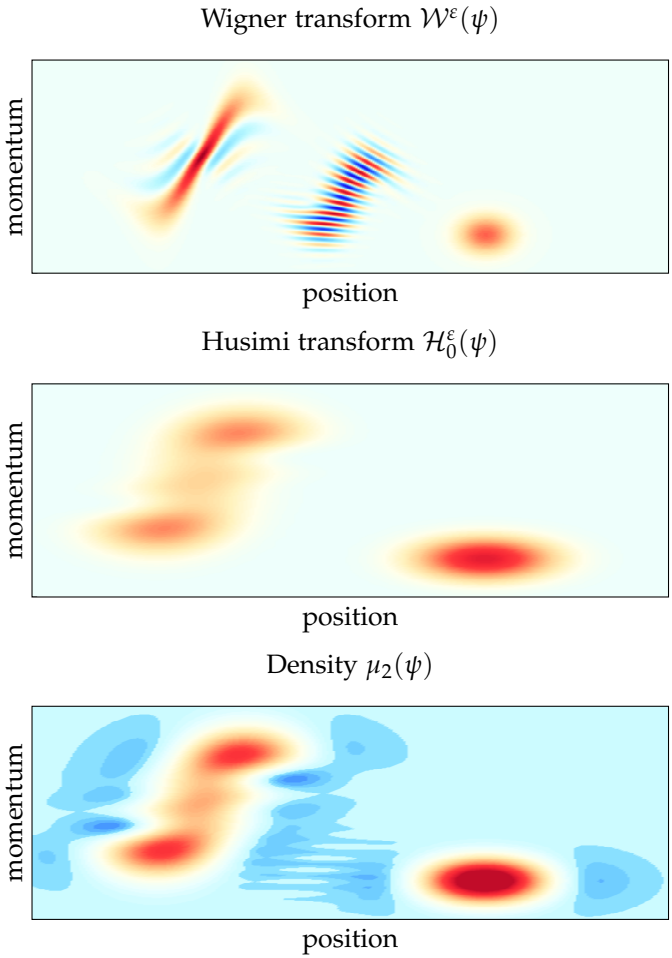

FIGURE 4: Phase space densities for a superposition $\psi \in L^2(\mathbb{R})$ of a Gaussian wave packet (right) and a Lagrangian state (left). Negative values are indicated by blue color. The Husimi transform does not include any of the interferences that arise in the Wigner transform. However, the corrected density $\mu_2(\psi)$ already shows some qualitative features of the oscillations. The momentum axis is compressed for illustration purposes.

III

Semiclassical Propagation

In the previous part §II we analyzed the structure and properties of Hagedorn wave packets, and derived spectrogram approximations of Wigner transforms. Both, the wave packet analysis, and the spectrogram approximation can be seen as simplifications of the typically highly complicated structure of general quantum states in position and phase space. The basis property of Hagedorn wave packets together with the formulas for Wigner transforms and spectrograms allow for a simplified and explicit representation of a large variety of quantum states.

After the simplifications of the Hilbert space of wave functions in §II, we now turn towards approximations for the time evolution of quantum systems. Part §III is devoted to various semiclassical propagation results for observables, states, and Wigner functions. All these approximations are constructed by employing the classical flow and its linearization. More precisely, they are either based on Egorov type results derived from pseudifferential commutator

expansions of the form (5.20), or they employ propagated Hagedorn wave packets.

In §11 we make a short review of the Egorov theorem. Thereafter, in §12 we discuss semiclassical approximations for quantum expectation that are well-amenable for numerical purposes, by employing the phase space representations of states via spectrograms we explored in §10.5.

In §13 we recall basic results on the propagation of semiclassical wave packets, and give a short overview over different lines of research that are present in the literature. The analysis in §14 and §15 is motivated by the unexpectedly good long-time behaviour of semiclassical approximations which is observed in many numerical experiments.

Annother popular approach to approximate the semiclassical time evolution of wave functions, which we do not discuss in this dissertation, are Gaussian beam methods or the Herman-Kluk propagator. Both methods are closely related to the semiclassical Hagedorn wave packet dynamics from §13. The equations of motion governing the evolution of Gaussian beams are essentially equivalent to the ones for evolved Hagedorn wave packets, except for an additional profile part for the Gaussian beams, see [JMS11, §8.1] and [Lub08, §II.4 and §V.1]. However, the motivation for Gaussian beam methods is to avoid the problems occuring at caustics in the time-dependent WKB approximation. In particular, the focus is on WKB type initial data, and one is required to sum $O(\varepsilon^{-1/2})$ many Gaussian beams in order to obtain a decent approximation of WKB type states. We refer to [JMS11, LRT13] and the references given therein for an overview over Gaussian beam methods. The Herman-Kluk propagator or the frozen Gaussian method build on the phase space representation of states via the F.B.I. transform, see §10.1. Here, the dynamics simplifies an evolution of the phase prefactors and classical motion of the Gaussian centers in the superposition integral. The frozen Gaussian methods go back to the Herman-Kluk

approximation [HK84], which is one of the most popular initial value representation in chemistry. For mathematical analysis of the Herman-Kluk propagator see [Rob10, SR09], and [LY12a, LY12b] for general frozen Gaussian approximations.

11 Egorov's Theorem

In this chapter we recall Egorov's celebrated theorem for the semiclassical evolution of quantum observables, which provides one of the most fundamental yet simple connections between classical and quantum dynamics. For a suitable Weyl quantized Hamiltonian $H = \mathrm{op}_\varepsilon^{\mathrm{We}}(h)$ and an observable $\mathrm{op}_\varepsilon^{\mathrm{We}}(a)$ it reads

$$\mathrm{e}^{\mathrm{i}Ht/\varepsilon}\mathrm{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon} = \mathrm{op}_\varepsilon^{\mathrm{We}}(a \circ \Phi^t) + O(\varepsilon^2) \tag{11.1}$$

where Φ^t is the Hamiltonian flow of h. Consequently, it relates the solution of Heisenberg's equation (1.4) for the evolution of quantum observables with the transport (2.11) of a classical observable along the Hamiltonian flow. We will give a more precise formulation of the Egorov theorem in section §11.1.

The result goes back to a short note [Ego69] by Yuri Egorov, and was later translated to the semiclassical context, see e.g. Robert's book [Rob87]. The most general version of the theorem is due to Bouzouina and Robert in [BR02] and in our presentation we will keep close to their work. Since the focus of this work lies on second order semiclassical asymptotics for the evolution with Schrödinger type Hamiltonians, in order to avoid distracting technicalities we only consider ε-independent Hamilton functions h.

11.1 Approximate Evolution with ODEs

We use the following common definition of subquadratic and sublinear symbols.

Definition 10 (Subquadratic and sublinear symbols)**.** *A smooth symbol $a : \mathbb{R}^{2d} \to \mathbb{C}$ is called* subquadratic *if for all $\alpha \in \mathbb{N}^{2d}$ with $|\alpha| \geq 2$ there is some $C_\alpha > 0$ such that*

$$|\partial^\alpha a(z)| \leq C_\alpha$$

holds for all $z \in \mathbb{R}^{2d}$. It is called sublinear *if the above inequality holds for all $\alpha \in \mathbb{N}^{2d} \setminus \{0\}$.*

For subquadratic Hamilton functions $h : \mathbb{R}^{2d} \to \mathbb{R}$ the classical flow Φ^t is globally defined and smooth. Moreover, the resulting Hamiltonian $\mathrm{op}_\varepsilon^{\mathrm{We}}(h)$ is essentially selfadjoint on the Schwartz space, see e.g. Exercise IV.12 in [Rob87] or [Swa08, Proposition 1.7], and, hence, the quantum evolution (1.3) is well-defined and unique. For symbols that are not subquadratic one typically requires further assumptions, such as semi-boundedness, in order to ensure that the resulting Hamiltonian is not only symmetric, but essentially selfadjoint.

We adopt the convenient notation from [GL14] by introducing the generalized Poisson bracket

$$\{a, b\}_k(x, \xi) = \sum_{\substack{\alpha,\beta \in \mathbb{N}^d \\ |\alpha+\beta|=k}} \frac{(-1)^\beta}{\alpha!\beta!} \partial_{(x,\xi)}^{(\beta,\alpha)} a(x, \xi)\, \partial_{(x,\xi)}^{(\alpha,\beta)} b(x, \xi), \quad k \in \mathbb{N},$$

for two functions $a, b \in \mathcal{C}^\infty(\mathbb{R}^{2d})$. The Egorov theorem from [BR02, Theorem 1.2] for bounded time intervals then reads as follows.

Lemma 16 (Egorov's theorem)**.** *Suppose $h : \mathbb{R}^{2d} \to \mathbb{R}$ is subquadratic, $a : \mathbb{R}^{2d} \to \mathbb{R}$ is sublinear, and let Φ^t denote the Hamiltonian flow of h. Then,*

$$\mathrm{e}^{\mathrm{i}Ht/\varepsilon} \mathrm{op}_\varepsilon^{\mathrm{We}}(a) \mathrm{e}^{-\mathrm{i}Ht/\varepsilon} = \mathrm{op}_\varepsilon^{\mathrm{We}}(a(t)) \tag{11.2}$$

is a Weyl quantized operator with sublinear symbol $a(t) : \mathbb{R}^{2d} \to \mathbb{R}$, where $H = \mathrm{op}_\varepsilon^{\mathrm{We}}(h)$. Moreover, $a(t) - a \circ \Phi^t \in S$ has an asymptotic

expansion in S

$$a(t) - a \circ \Phi^t \asymp \sum_{n=1}^{\infty} \varepsilon^{2n} a_{2n}(t),$$

in even powers of ε, uniformly on bounded time intervals. With $a_0(t,z) = a(\Phi^t(z))$ one can recursively compute

$$a_{2n}(t) = \sum_{m \le n-1} (-\tfrac{1}{4})^{n-m} \int_0^t \{h, a_{2m}(\tau)\}_{2(n-m)+1} \circ \Phi^{t-\tau}\, d\tau \quad (11.3)$$

for $n \ge 1$.

Sketch of proof. Let us give short sketch of the proof in the spirit of [GL14, §2] without caring about boundedness, domains and so on. We abbreviate $b_{2n}(t) = \sum_{k=0}^{n} \varepsilon^{2k} a_{2k}(t)$. One starts by writing the operator difference as the integral

$$\begin{aligned}
&\mathrm{e}^{\mathrm{i}Ht/\varepsilon} \mathrm{op}_\varepsilon^{\mathrm{We}}(a) \mathrm{e}^{-\mathrm{i}Ht/\varepsilon} - \mathrm{op}_\varepsilon^{\mathrm{We}}(b_{2n}(t)) \\
&= \int_0^t \frac{d}{ds} \left(\mathrm{e}^{\mathrm{i}Hs/\varepsilon} \mathrm{op}_\varepsilon^{\mathrm{We}}(b_{2n}(t-s)) \mathrm{e}^{-\mathrm{i}Hs/\varepsilon} \right) ds \\
&= \int_0^t \mathrm{e}^{\mathrm{i}Hs/\varepsilon} \left(\tfrac{\mathrm{i}}{\varepsilon} [\mathrm{op}_\varepsilon^{\mathrm{We}}(h), \mathrm{op}_\varepsilon^{\mathrm{We}}(b_{2n}(t-s))] - \frac{d}{dt} \mathrm{op}_\varepsilon^{\mathrm{We}}(b_{2n}(t-s)) \right) \mathrm{e}^{-\mathrm{i}Hs/\varepsilon} ds,
\end{aligned}$$

where we used that $b_{2n}(0) = a$. Now, with the asymptotic expansion of the Weyl commutator from Lemma 8 we obtain

$$\frac{\mathrm{i}}{\varepsilon} [\mathrm{op}_\varepsilon^{\mathrm{We}}(h), \mathrm{op}_\varepsilon^{\mathrm{We}}(b_{2n}(t-s))] \asymp \sum_{j \in \mathbb{N}} (-\tfrac{\varepsilon^2}{4})^j \mathrm{op}_\varepsilon^{\mathrm{We}} \left(\{h, b_{2n}(t-s)\}_{2j+1} \right), \quad (11.4)$$

and the construction of $b_{2n}(t)$ implies that the first n terms in the asymptotic expansion (11.4) precisely coincide with $\frac{d}{dt} \mathrm{op}_\varepsilon^{\mathrm{We}}(b_{2n}(t-s))$. □

There are several remarkable facts about the Egorov propagation theorem presented in Lemma 16. Firstly, despite the fact that the propagator $\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}$ is in general not a pseudodifferential operator,

the evolved observable (11.2) is a Weyl quantized operator again. Secondly, the symbols $a_{2n}(t)$ in the expansion only depend on derivatives of h and a and the classical flow Φ^t. In other words, the expression for $a_{2n}(t)$ on the right hand side of (11.3) is completely local and, hence, $a_{2n}(t)$ can be recursively computed by merely solving a set of ODEs that involve the symbols $a_{2m}(s)$ with $m < n$. This generalization of the "method of characteristics" has been described and successfully applied in [GL14]. There, one can also find the explicit ODEs for the first correction $a_2(t)$ together with a numerical integrator.

In [BR02], the authors allow for more general smooth semiclassical Hamiltonians $h \asymp \sum_{k=0}^{\infty} \varepsilon^k h_k$ with subquadratic principal symbol h_0, sublinear subprincipal symbol h_1 and bounded higher order symbols. In this case the odd symbols a_{2n+1} do not vanish and formula (11.3) becomes more involved.

For discretizations of the leading order semiclassical dynamics determined by the classical flow we refer to §16. In the following, we mean the second order approximation (11.1) when referring to the Egorov theorem. Discretized versions of the Egorov theorem are widely used in physical chemistry since the 1970es, see e.g. [Mil74, TW04].

11.2 Longer Times

Lemma 16 is formulated for the propagation on bounded time intervals. However, in order to investigate how the errors in semiclassical approximations depend on time, it is helpful to consider a joint limit of small parameters ε and large times t. The ε-dependent time scale t_ε up to which a semiclassical approximations is valid is known as the *Ehrenfest time*. It is a widely spread physical intuition that semiclassical approximations generically break down after Ehrenfest times of the size $t_\varepsilon \sim \log(1/\varepsilon)$. This is inferred from the observation that the derivatives of Φ^t in the worst case grow

exponentially in time. Ehrenfest times for the Egorov theorem have been extensively analyzed in [BR02], but there are also various results on Ehrenfest times for other semiclassical approximations. See for instance [Fau07] for a long-time analysis of the Gutzwiller trace formula, or [CFK11] for propagated coherent states in the context of the nonlinear Schrödinger equation. Below we summarize the results from [BR02] on Ehrenfest times for two very different classes of systems. The proof for logarithmic Ehrenfest times can also be found in [Zwo12, Theorem 11.12].

From [BR02] we recall the following Egorov theorem for logarithmic Ehrenfest times, whose proof uses

$$\Gamma = \sup_{z\in\mathbb{R}^{2d}} \|JD^2h(z)\|$$

to estimate the stability exponents of the system. Note that Γ is finite since h is subquadratic.

Lemma 17 (Ehrenfest time for general Egorov)**.** *Under the same assumptions as in Lemma 16, for any $N \geq 1$ there is $C_N > 0$ such that for every $0 < \mu$ and $|t| \leq (2-\mu)/(3\Gamma)\log(\varepsilon^{-1})$ we have*

$$\|\mathrm{op}_\varepsilon^{\mathrm{We}}(a(t)) - \sum_{k=0}^{N} \varepsilon^k \mathrm{op}_\varepsilon^{\mathrm{We}}(a_k(t))\|_{\mathcal{L}(L^2)} \leq C_N \varepsilon^{(\mu/2)N+1} \varepsilon^{(\mu-2)/3\cdot(5d+3)}.$$

As a consequence, the Egorov approximation is applicable for times of the size $t_\varepsilon \sim \log(\varepsilon^{-1})$, although one should note that the accuracy in ε detoriates more and more as one approaches this barrier. Note that Lemma 17 gives an estimate on Ehrenfest time scales on the operator level, that is, the estimate holds uniformly for all wave functions. While this is satisfying from an analytical point of view, it might not be very helpful in praxis. For applications one would be rather interested in the time scales for particular choices of initial states. We will come back to this point later in §15.3 where we present a local Egorov theorem that holds for longer times.

We introduce analyticity **(A)**, Gevrey **(G)**, and integrability **(I)** conditions for the classical system and the observable a.

(A) Suppose $\mathrm{op}_\varepsilon^{\mathrm{We}}(h)$ is selfadjoint, and h admits an analytic continuation to the strip $S(\delta) = \{z \in \mathbb{C}^{2d}, \|\mathrm{Im}(z)\| < \delta\}$ with $|h(z)| \leq C \langle z \rangle^m$ in $S(\delta)$ for some $C, m > 0$.

(G) Let $\Omega \subset \mathbb{R}^{2d}$ be bounded, open, and invariant under Φ^t. Suppose $\mathrm{supp}(a) \subset \Omega$ and a is of Gevrey class[1] G^s with $s > 1$.

(I) Suppose there is a symplectomorphism[2] $\kappa = (I, \phi) : \Omega \to Z \times \mathbb{T}^d$ with $Z \subset \mathbb{R}^d$ open, such that

$$\kappa(\Phi^t(z)) = (I(z), \phi(z) + t\omega(I(z))) \quad \forall z \in \Omega, t \in \mathbb{R}.$$

Furthermore, assume that κ is analytic in some open complex neighborhood of Ω with image in some open complex neighborhood of $Z \times \mathbb{T}^d$.

The regularity assumptions **(A)** and **(G)** and the Liouville integrability assumption **(I)** on the classical flow allow to derive polynomial Ehrenfest timescales, see [BR02, Theorem 1.13].

Lemma 18 (Integrability Ehrenfest timescale)**.** *Suppose (A), (G) and (I) hold true. Then, for bounded times one has*

$$\|\mathrm{op}_\varepsilon^{\mathrm{We}}(a)(t) - \sum_{k=0}^{N} \varepsilon^k \mathrm{op}_\varepsilon^{\mathrm{We}}(a_k(t))\| \leq C_N \varepsilon^{N+1} |t| (1 + |t|)^{2N+\delta_d}$$

and hence, for all[3] $|t| \lesssim \varepsilon^{-1/2+\mu}$ *with* $\mu > 0$ *one has*

$$\|\mathrm{op}_\varepsilon^{\mathrm{We}}(a)(t) - \sum_{k=0}^{N} \varepsilon^k \mathrm{op}_\varepsilon^{\mathrm{We}}(a_k(t))\| \leq C\varepsilon^{1/2+\mu(1+2N+\delta_d)-\delta_d/2}$$

[1] Here, this means that there is $C > 0$ such that $|\partial^\gamma a(z)| \leq C^\gamma (|\gamma|!)^s$ for $z \in \Omega$. If $s = 1$, a is analytic.

[2] $\mathbb{T}^d$ denotes the d-dimensional torus.

[3] The symbol $\lesssim$ means the same as the Landau big $O(\bullet)$ notation: $|t| \leq D\varepsilon^{-1/2+\mu}$ for some $D > 0$.

for some $C > 0$, where $\delta_d \leq 5d + 3$ is a universal constant .

For highly regular systems one hence expects to observe Ehrenfest time scales that are algebraic in ε^{-1}. We remark that one can obtain also expentially small errors by choosing N sufficiently big in dependence on ε. A similar result as Lemma 18 holds for general subquadratic Hamilton functions h and smooth symbols a if the flow Φ^t is periodic with smoothly varying period in a region that contains the support of a, see [BR02, Proposition 2.8]. In one space dimension these prerequisites are not as restrictive as they seem: Whenever

$$h(q,p) = \tfrac{1}{2}|p|^2 + V(q)$$

and the potential V has a well which is non-degenerate[4], then all trajectories in the well from above the bottom to a possible bifurcation point (or infinity) are periodic.

12 Propagation with Nonnegative Densities

By Egorov's theorem, see Lemma 16, the evolution of expectation values can be approximated as as the weighted phase space integral

$$\left\langle \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi, \mathrm{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi \right\rangle = \int_{\mathbb{R}^{2d}} (a\circ\Phi^t)(z)\mathcal{W}^\varepsilon(\psi)(z)dz + O(\varepsilon^2). \tag{12.1}$$

If ψ is a normalized Gaussian state, $\mathcal{W}^\varepsilon(\psi)$ is the density of a multivariate normal distribution on phase space [SC83]. In this case (12.1) can be well-approximated by a Monte-Carlo quadrature: one samples initial phase space points with respect to this normal distribution, propagates them up to time t along the classical flow, and then averages a over these values, see also [LR10] and §16.2.

[4]That is, there are no critical points of the Hamiltonian except for the bottom of the well.

However, for more general states the Wigner function is not a probability density anymore. In this case, following a similar procedure — for example with importance sampling — can be much more involved or even computationally unfeasible.

We suggest a different approach based on an approximation of the Wigner transform by probability densities. In this chapter we present two different methods to approximate propagated expectation values by a weighted phase space integral , where the weight is a probability density that represents the initial state. Moreover, both approximations have the same asymptotic accuracy $O(\varepsilon^2)$ as the Egorov theorem (12.1).

We first present some asymptotic formulas to express Weyl operators as anti-Wick operators with $O(\varepsilon^2)$ errors and vice versa in §12.1. Then, in §12.2 we prove a second order approximation that employs the spectrogram density $\mu_2(\psi)$ from Theorem 4 for the representation of the initial state. This result can be found in our joint publication [KLO15] with C. Lasser and T. Ohsawa. Section §12.3 is devoted to an approximation[5] that uses the initial state's Husimi transform. A comparison of the approximations illustrates that using a single spectrogram, namely the Husimi transform, requires to introduce corrections to the dynamics in order to retain errors of size $O(\varepsilon^2)$. In contrast, for the linear combination $\mu_2(\psi)$ of two probability densities built from the Husimi transform and first order Hermite spectrograms, one can use the classical flow Φ^t without deteriorating the asymptotic accuracy.

12.1 Symbol Conversion

From Proposition 18 we know that the Weyl symbol of an anti-Wick operator $\mathrm{op}_\varepsilon^{\mathrm{AW}}(a)$ is given by the convolution of a with a phase space Gaussian. If one wants to express Weyl operators as anti-Wick operators up to some error that is small in ε, one hence has to

[5] We already discussed this approximation in [Kel12, KL13].

expand the convolution. The following Lemma contains conversion formulas for Weyl and anti-Wick operators with errors of size $O(\varepsilon^2)$. This order of accuracy is sufficient for the second order propagation theorems presented in this chapter. We note that with the same arguments one can obtain approximations with errors of size $O(\varepsilon^n)$ for any $n \in \mathbb{N}$, see also [Kel12, Lemma 3 and Lemma 4]. The following version is taken from [KLO15], except that we allow for slightly more general symbols.

Lemma 19. *Let $a : \mathbb{R}^{2d} \to \mathbb{R}$ be a symbol of class[6] S, and $\varepsilon > 0$. Then, there are two families $r_j^\varepsilon : \mathbb{R}^{2d} \to \mathbb{R}$ of functions in S with $\sup_{\varepsilon>0} \|\mathrm{op}(r_j^\varepsilon)\|_{\mathcal{L}(L^2)} < \infty$ for $j = 1, 2$, such that*

$$\begin{aligned} \mathrm{op}_\varepsilon^{\mathrm{AW}}(a) &= \mathrm{op}_\varepsilon^{\mathrm{We}}(a + \tfrac{\varepsilon}{4}\Delta a) + \varepsilon^2 \mathrm{op}_\varepsilon^{\mathrm{We}}(r_1^\varepsilon), \\ \mathrm{op}_\varepsilon^{\mathrm{AW}}(a - \tfrac{\varepsilon}{4}\Delta a) &= \mathrm{op}_\varepsilon^{\mathrm{We}}(a) + \varepsilon^2 \mathrm{op}_\varepsilon^{\mathrm{We}}(r_2^\varepsilon). \end{aligned}$$

Sketch of proof. This lemma is essentially identical to [Ler10, Proposition 2.4.3] or [KL13, Lemma 1], and hence we only sketch the proof for the second of the two equivalent identities. We write out the definition

$$\mathrm{op}_\varepsilon^{\mathrm{AW}}(a - \tfrac{\varepsilon}{4}\Delta a) = \mathrm{op}_\varepsilon^{\mathrm{We}}\left(\mathcal{W}_0^\varepsilon * (a - \tfrac{\varepsilon}{4}\Delta a)\right)$$

and Taylor expand $a - \frac{\varepsilon}{4}\Delta a$ around z in the integral

$$\mathcal{W}_0^\varepsilon * (a - \tfrac{\varepsilon}{4}\Delta a) = (\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} (a - \tfrac{\varepsilon}{4}\Delta a)(\zeta) \mathrm{e}^{-|z-\zeta|^2/\varepsilon} \partial\zeta.$$

Due to the symmetry of the Gaussian, all Taylor expansion terms with odd derivatives of $(a - \frac{\varepsilon}{4}\Delta a)$ vanish. The computation

$$\sum_{|\alpha|=1} \int_{\mathbb{R}^{2d}} \frac{(\pi\varepsilon)^{-d}}{(2\alpha)!} (\partial^{2\alpha}(a - \tfrac{\varepsilon}{4}\Delta a))(\zeta - z)^{2\alpha} \mathrm{e}^{-|z-\zeta|^2/\varepsilon} \partial\zeta = \tfrac{\varepsilon}{4}\Delta(a - \tfrac{\varepsilon}{4}\Delta a)$$

[6] That is, a is bounded together with all derivatives, see §B. In this case $\mathrm{op}_\varepsilon^{\mathrm{We}}(a) : L^2 \to L^2$ is bounded.

then implies that we have the second order approximation

$$\begin{aligned}\mathcal{W}_0^\varepsilon * (a - \tfrac{\varepsilon}{4}\Delta a) &= (a - \tfrac{\varepsilon}{4}\Delta a) + \tfrac{\varepsilon}{4}\Delta(a - \tfrac{\varepsilon}{4}\Delta a) + O(\varepsilon^2) \\ &= a + O(\varepsilon^2).\end{aligned}$$

The function in the $O(\varepsilon^2)$ term is again of class S, and hence bounded together with all its derivatives. Applying the Calderón–Vaillancourt Theorem, see e.g. [Fol89, §2.5], completes the proof. □

12.2 Propagation with Spectrogram Densities

Let us recall from Theorem 4 that

$$\mu_2(\psi) = \mathcal{W}^\varepsilon(\psi) + O(\varepsilon^2)$$

in the weak sense, where

$$\mu_2(\psi) = (1 + \tfrac{d}{2})\,\mathcal{H}_0^\varepsilon(\psi) - \tfrac{1}{2}\sum_{|k|=1}\mathcal{H}_k^\varepsilon(\psi)$$

is a linear combination of the Husimi transform $\mathcal{H}_0^\varepsilon(\psi)$ and the first order Hermite spectrograms $\mathcal{H}_{e_j}^\varepsilon = \mathcal{W}^\varepsilon(\psi) * \mathcal{W}^\varepsilon(\varphi_{e_j})$. Using $\mu_2(\psi)$ for the representation of the initial state then leads to Theorem 5, which is one of the main results of this dissertation. For simplicity we restrict ourselves to bounded observables with symbols in S.

Theorem 5 (Propagation with $\mu_2(\psi)$)**.** *Suppose $h : \mathbb{R}^{2d} \to \mathbb{R}$ is subquadratic, $H = \mathrm{op}_\varepsilon^{\mathrm{We}}(h)$, and $\psi \in L^2(\mathbb{R}^d)$ with $\|\psi\|_{L^2} = 1$. Then, for all $a \in S$, and $t \in \mathbb{R}$, there exists a constant $C = C(a, h, t) > 0$ such that*

$$\left|\left\langle \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi, \mathrm{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi\right\rangle - \int_{\mathbb{R}^{2d}}(a\circ\Phi^t)(z)\mu_2(\psi)(z)dz\right| \leq C\varepsilon^2,$$

where $\Phi^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ is the Hamiltonian flow associated with h.

Proof. By Lemma 16 there is a family of symbols $r^\varepsilon \in S$ giving rise to a uniformly bounded family of Weyl quantized operators[7] $\sup_{\varepsilon>0} \|\mathrm{op}_\varepsilon^{\mathrm{We}}(r^\varepsilon)\|_{\mathcal{L}(L^2)} < \infty$ such that

$$\mathrm{e}^{\mathrm{i}Ht/\varepsilon}\mathrm{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon} = \mathrm{op}_\varepsilon^{\mathrm{We}}(a\circ\Phi^t) + \varepsilon^2\mathrm{op}_\varepsilon^{\mathrm{We}}(r^\varepsilon).$$

Note that r^ε depends on h, a, and t. Then, by the construction of $\mu_2(\psi)$, we have

$$\begin{aligned}\int_{\mathbb{R}^{2d}}(a\circ\Phi^t)(z)\mu_2(\psi)(z)dz &= \int_{\mathbb{R}^{2d}}(1-\tfrac{\varepsilon}{4}\Delta)(a\circ\Phi^t)(z)\mathcal{H}_0^\varepsilon(\psi)(z)dz\\ &= \left\langle\psi, \mathrm{op}_\varepsilon^{\mathrm{AW}}((1-\tfrac{\varepsilon}{4}\Delta)(a\circ\Phi^t))\psi\right\rangle\\ &= \left\langle\psi, \mathrm{op}_\varepsilon^{\mathrm{We}}(a\circ\Phi^t)\psi\right\rangle + \varepsilon^2\left\langle\psi, \mathrm{op}_\varepsilon^{\mathrm{We}}(r_2^\varepsilon)\psi\right\rangle\end{aligned}$$

where $r_2^\varepsilon : \mathbb{R}^{2d}\to\mathbb{R}$ depends of fourth and higher order derivatives of $a\circ\Phi^t$. Evaluating the expectation value for the state ψ hence yields

$$\begin{aligned}&\Big|\left\langle \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi, \mathrm{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi\right\rangle - \int_{\mathbb{R}^{2d}}(a\circ\Phi^t)(z)\mu_2(\psi)(z)dz\Big|\\ &\le \Big|\left\langle \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi, \mathrm{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi\right\rangle - \int_{\mathbb{R}^{2d}}(a\circ\Phi^t)(z)\mathcal{W}^\varepsilon(\psi)(z)dz\Big|\\ &\quad + \varepsilon^2\|r_2^\varepsilon\|_{\mathcal{L}(L^2)}\\ &\le C\varepsilon^2\end{aligned}$$

by Lemma 19 for some $C > 0$ independent of ε. □

Theorem 5 suggests an $O(\varepsilon^2)$ approximation to the dynamics of the expectation values of observables based on the classical flow Φ^t and initial sampling from the two probability densities

$$\mathcal{H}_0(\psi) = \mathcal{W}(\psi) * \mathcal{W}_0^\varepsilon \quad\text{and}\quad \tfrac{1}{d}\sum_{j=1}^d \mathcal{W}(\psi) * \mathcal{W}^\varepsilon(\varphi_{e_j}).$$

[7] Note that $\mathrm{op}_\varepsilon^{\mathrm{We}}(b)$ is bounded if $b \in S$.

Alternatively, one can split the integral with the second density into a sum of d integrals and sample according to the probability densities $\mathcal{W}(\psi) * \mathcal{W}^{\varepsilon}(\varphi_{e_j})$, $j = 1 \dots d$. We discuss an algorithmic discretization of Theorem 5 in more detail in §16. Let us remark that since the Hamiltonian h is constant along Φ^t, the total energy error in Theorem 5 is independent of time. This is in contrast to the second order Egorov type theorem with Husimi functions we present in §12.3. There, the initial energy error is not preserved in time.

In contrast to the Egorov theorem with Husimi transforms presented in §12.3, the spectrogram approximation from Theorem 5 not requires to evaluate higher order derivatives of the potential or the observable. This is an enourmous advantage for applications, since higher derivatives of PES are typically expensive to evaluate, if at all accessible.

The main botteleneck of the presented method is that a discretization requires to sample from the Husimi transform and the first order Hermite spectrograms of the initial state. A promising way to approach this problem could be to use the F.B.I. type representation of spectrograms from Proposition 19. We stress, however, that spectrograms have the advantage of beeing probability densities in contrast to Wigner transforms, which simplifies the sampling problem considerably.

All in all, Theorem 5 provides the basis for novel semiclassical approximation methods with simplified densities at almost no additional cost in comparison to the Egorov theorem.

12.3 Corrected Symbols and Husimi Dynamics

Let us present a second order Egorov type propagation result in which the initial state is represented by its Husimi transform. For this setup one has to include correction terms since Husimi

functions are only ε-close to Wigner functions in contrast to the spectrogram density $\mu_2(\psi)$. We summarize the results and refer to [Kel12, KL13] for more details.

The main idea is to prove a second order propagation theorem for anti-Wick quantized observables $\mathrm{op}_\varepsilon^{\mathrm{AW}}(a)$, where the dynamics is governed by a Weyl quantized Hamiltonian $H = \mathrm{op}_\varepsilon^{\mathrm{We}}(h)$. By recalling the proof of the Egorov theorem, see the sketch of proof for Lemma 16, we have to expand the commutator of the Hamiltonian and the observable in powers of ε. We have the following second order formula, see [KL13, Lemma 4]. The extension to more general classes of observables is straightforward.

Lemma 20. *Let $\varepsilon > 0$, and suppose $h, a : \mathbb{R}^{2d} \to \mathbb{R}$ are a smooth function of subquadratic growth and a Schwartz function, respectively. Then, $\frac{\mathrm{i}}{\varepsilon}\left[\mathrm{op}_\varepsilon^{\mathrm{We}}(h), \mathrm{op}_\varepsilon^{\mathrm{AW}}(a)\right]$ is essentially self-adjoint in $L^2(\mathbb{R}^d)$ with core $\mathcal{S}(\mathbb{R}^d)$, and there exists a family of Schwartz functions $\kappa^\varepsilon(h,a) : \mathbb{R}^{2d} \to \mathbb{R}$ with $\sup_{\varepsilon>0} \|\mathrm{op}_\varepsilon^{\mathrm{We}}(\kappa^\varepsilon(h,a))\|_{\mathcal{L}(L^2)} < \infty$ such that*

$$\begin{aligned}\tfrac{\mathrm{i}}{\varepsilon}\left[\mathrm{op}_\varepsilon^{\mathrm{We}}(b), \mathrm{op}_\varepsilon^{\mathrm{AW}}(c)\right] =& \mathrm{op}_\varepsilon^{\mathrm{AW}}\left(\{b - \tfrac{\varepsilon}{4}\Delta b, c\} - \tfrac{\varepsilon}{2}\,\mathrm{tr}(J\,D^2 b\,D^2 c)\right) \\ &+ \varepsilon^2 \mathrm{op}_\varepsilon^{\mathrm{We}}(\kappa^\varepsilon(h,a)). \end{aligned} \tag{12.2}$$

The proof of Lemma 20 relies on the semiclassical conversion formulas from Lemma 19, and the subsequent expansion of Weyl commutators from Lemma 8. Mimicking the same proof as for the usual Egorov theorem, we hence arrive at the following second order Egorov type result for anti-Wick observables, see[KL13, Theorem 2].

Lemma 21. *Let $h : \mathbb{R}^{2d} \to \mathbb{R}$ be a smooth function of subquadratic growth, $H = \mathrm{op}_\varepsilon^{\mathrm{We}}(h)$, and $a : \mathbb{R}^{2d} \to \mathbb{R}$ be a Schwartz function. Then, for all $t \in \mathbb{R}$ there exists a constant $C = C(a,h,t) > 0$ such that all $\varepsilon > 0$*

$$\left\| \mathrm{e}^{\mathrm{i}Ht/\varepsilon} \mathrm{op}_\varepsilon^{\mathrm{AW}}(a) \mathrm{e}^{-\mathrm{i}Ht/\varepsilon} - \mathrm{op}_\varepsilon^{\mathrm{AW}}(a \circ \Phi_\varepsilon^t - \tfrac{\varepsilon}{2}\,\Xi_\varepsilon^t(a)) \right\|_{\mathcal{L}(L^2)} \leq C\varepsilon^2$$

where

$$\Xi_\varepsilon^t(a) = \int_0^t \operatorname{tr}\left(J\,D^2h\,D^2(a\circ\Phi_\varepsilon^\tau)\right)\circ\Phi_\varepsilon^{t-\tau}\,d\tau \tag{12.3}$$

and $\Phi_\varepsilon^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ *the Hamiltonian flow associated with* $h_\varepsilon = h - \frac{\varepsilon}{4}\Delta h$.

The integral (12.3) in the correction term can be interpreted as a solution operator to a set of ODEs applied to the gradient and Hessian of the anti-Wick symbol a. Hence, for applications and discretizations a reformulation via differential equations, which can be integrated simultaneously with the Hamiltonian flow, is desirable. We arrive at the following Egorov type propagation theorem with correction ODEs, see also [KL13].

Theorem 6. *Let* $a : \mathbb{R}^{2d} \to \mathbb{R}$ *be a Schwartz function,* $h : \mathbb{R}^{2d} \to \mathbb{R}$ *a smooth function of subquadratic growth, and* $H = \operatorname{op}_\varepsilon^{\mathrm{We}}(h)$. *Then, for all* $t \in \mathbb{R}$ *there exists a constant* $C = C(a,h,t) > 0$ *such that for all* $\varepsilon > 0$

$$\left\| e^{iHt/\varepsilon}\operatorname{op}_\varepsilon^{\mathrm{AW}}(a)e^{-iHt/\varepsilon} - \operatorname{op}_\varepsilon^{\mathrm{AW}}(\Psi_\varepsilon^t(a))\right\|_{\mathcal{L}(L^2)} \le C\varepsilon^2$$

with

$$\Psi_\varepsilon^t(a) = a\circ\Phi_\varepsilon^t - \tfrac{\varepsilon}{2}\left(\operatorname{tr}(\Lambda_\varepsilon^t\,(D^2a\circ\Phi_\varepsilon^t)) + \Gamma_\varepsilon^t\cdot(\nabla a\circ\Phi_\varepsilon^t)\right), \tag{12.4}$$

where $\Phi_\varepsilon^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ *is the Hamiltonian flow of* $h_\varepsilon = h - \frac{\varepsilon}{4}\Delta h$,

$$\partial_t\Phi_\varepsilon^t = J\,\nabla h_\varepsilon\circ\Phi_\varepsilon^t, \tag{12.5}$$

and the flows $\Lambda_\varepsilon^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d\times 2d}$, $\Gamma_\varepsilon^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ *solve*

$$\partial_t\Lambda_\varepsilon^t = M_\varepsilon(t) + M_\varepsilon(t)\,\Lambda_\varepsilon^t + \Lambda_\varepsilon^t\,M_\varepsilon(t)^{\mathrm{T}}, \qquad \Lambda_\varepsilon^0 = 0 \tag{12.6}$$

$$\partial_t\Gamma_\varepsilon^t = M_\varepsilon(t)\,\Gamma_\varepsilon^t + \operatorname{tr}(C_i(t)^{\mathrm{T}}\,\Lambda_\varepsilon^t)_{i=1}^{2d}, \qquad \Gamma_\varepsilon^0 = 0 \tag{12.7}$$

with

$$M_\varepsilon(t) : \mathbb{R}^{2d} \to \mathbb{R}^{2d\times 2d}, \qquad M_\varepsilon(t) = J\,D^2h\circ\Phi_\varepsilon^t,$$
$$C_i(t) : \mathbb{R}^{2d} \to \mathbb{R}^{2d\times 2d}, \qquad (C_i(t))_{jk} = \partial_k(J\,D^2h)_{ij}\circ\Phi_\varepsilon^t.$$

We observe that the corrections required for propagating anti-Wick observables with $O(\varepsilon^2)$ errors are twofold. Firstly, one has to deform the classical trajectories by using the Hamiltonian trajectories associated with $h_\varepsilon = h - \frac{\varepsilon}{4}\Delta h$. Moreover, the derivatives of a enter the first order corrections in (12.4). Intuitively, the correction flows Λ_ε^t and Γ_ε^t can be seen as taking care of the curvature of the phase space metric introduced by the deformed trajectories.

Observables of physical interest are often given in a natural way by the Weyl quantization of their classical counterparts. For this reason we would like to apply Theorem 6 for propagating Weyl quantized observables while retaining the advantage of representing states via Husimi functions, as for anti-Wick operators. This can be accomplished by revisiting the conversion formulas from Lemma 19.

Corollary 5. *Under the assumptions of Theorem 6, there exists a constant $C = C(a, h, t) > 0$ such that*

$$\left| \langle \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0, \mathrm{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0\rangle_{L^2} - \int_{\mathbb{R}^{2d}} F_\varepsilon^t(a)(z)\, \mathcal{H}_0^\varepsilon(\psi_0)(z)\, dz \right| \leq C\varepsilon^2 \tag{12.8}$$

for all $\psi_0 \in L^2(\mathbb{R}^d)$ with $\|\psi_0\|_{L^2} = 1$, where $a_\varepsilon = a - \frac{\varepsilon}{4}\Delta a$ and

$$F_\varepsilon^t(a) = a_\varepsilon \circ \Phi_\varepsilon^t - \tfrac{\varepsilon}{2}\left(\mathrm{tr}(\Lambda_\varepsilon^t (D^2 a \circ \Phi_\varepsilon^t)) + \Gamma_\varepsilon^t \cdot (\nabla a \circ \Phi_\varepsilon^t)\right).$$

$\mathcal{H}_0^\varepsilon(\psi_0)$ is the Husimi transform of ψ.

Proof. With $\psi_t := \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0$, from Theorem 6 and Lemma 19 we obtain

$$\begin{aligned}
\langle \psi_t, \mathrm{op}_\varepsilon^{\mathrm{We}}(a)\psi_t\rangle_{L^2} &= \langle \psi_t, \mathrm{op}_\varepsilon^{\mathrm{AW}}(a_\varepsilon)\psi_t\rangle_{L^2} + O(\varepsilon^2) \\
&= \langle \psi_0, \mathrm{op}_\varepsilon^{\mathrm{AW}}(\Psi_\varepsilon^t(a_\varepsilon))\psi_0\rangle_{L^2} + O(\varepsilon^2) \\
&= \int_{\mathbb{R}^{2d}} \Psi_\varepsilon^t(a_\varepsilon)(z)\, \mathcal{H}^\varepsilon(\psi_0)(z)\, dz + O(\varepsilon^2),
\end{aligned}$$

and the assertion follows since $\Psi_\varepsilon^t(a_\varepsilon) = F_\varepsilon^t(a) + O(\varepsilon^2)$. □

In §16 we present a direcretized version of Corollary 5 . There we illustrate that the approximation is useful and applicable for computing evolved expectation values in moderately high dimensions. Note, that the effort for using the Husimi approximation scales quadratically in the dimension since $\Lambda_\varepsilon^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d \times 2d}$. This is a drawback when compared to the Egorov theorem or the spectrogram approximation from Theorem 5.

13 Wave Packet Dynamics

One of the most important properties of the parametrized semiclassical wave packets $\varphi_k^\varepsilon[Z; z]$ introduced in §7.2 is that they provide exact solutions of the time-dependent semiclassical Schrödinger equation with quadratic potential V if z and Z satisfy underlying classical equations of motion. This exactness result turns them into favorable set of ansatz and basis functions for approximations and numerical discretizations. In particular, they have successfully been used for the design of Galerkin methods for the approximation of quantum evolution, see the works of Faou, Gradinaru and Lubich in [FL06, FG09, FGL09] and the recent paper by Gradinaru and Hagedorn [GH14]. A comprehensive presentation can be found in the book of Lubich [Lub08].

Time-evolved parametrized Gaussian wave packet were first introduced in the pioneering works of Hepp and Heller [Hep74, Hel75] in the 1970es. Since then, they have turned into a central tool for simulating and analyzing semiclassical quantum dynamics and exploring problems of chemical physics, see e.g. the works of Heller [Hel76, Hel81] or the book of Tannor [Tan07].

The mathematical analysis of semiclassical wave packets started with the works of Hagedorn [Hag80, Hag81, Hag98] and Littejohn [Lit86]. Since then, evolved semiclassical wave packets have been applied to a variety of different setups. We would like to highlight the work of Hagedorn and Joye on semiclassical quan-

tum dynamics with exponentially small errors up to Ehrenfest time [HJ99, HJ00], and the application to non-selfadjoint evolution problems discussed in [GS12, LST15]. Parametrized semiclassical coherent states have also been used for treating non-linear evolution problems, see [CFK11, HZ08, Har13] for analysis in the context of nonlinear Schrödinger equations. For a geometric perspective on semiclassical wave packet dynamics we refer to [OL13, Ohs15].

In this chapter we rephrase the dynamics of Hagedorn wave packet in the spirit of [Lub08, chapter 5] and [HJ00] for the Lagrangian frame parametrization $\varphi_k^\varepsilon[Z;z]$ introduced in §7.2. We only consider normalized Hagedorn wave packets, and hence from now on tacitely assume that $Z \in \mathbb{C}^{2d\times d}$ is a normalized Lagrangian frame.

13.1 Evolution Equations

As remarked before, evolved Hagedorn wave packets are exact solutions for the time-dependent Schrödinger equation with quadratic potential, see [Hag98, Theorem 3.4] or Theorem 2.5 in [Lub08, chapter 5]. More precisely, for quadratic potentials the phase space center z_0 of a normalized Hagedorn wave packet $\varphi_k^\varepsilon[z_0;Z_0]$ moves along a trajectory of the underlying classical Hamiltonian system, and the Lagrangian frame Z_0 evolves acording to the linearization of the trajectory. That is, for a Weyl quantized Hamiltonian $\mathrm{op}_\varepsilon^{\mathrm{We}}(h)$ the phase space center and Lagrangian frame satisfy the equations of motion[8]

$$\dot{z}_t = J\nabla h(z_t), \qquad z_t|_{t=0} = z_0 \in \mathbb{R}^{2d}, \tag{13.1}$$

$$\dot{Z}_t = JD^2h(z_t)Z_t, \qquad Z_t|_{t=0} = Z_0 \in \mathbb{C}^{2d\times d}. \tag{13.2}$$

[8] As in [LST15], we use the suggestive notation z_t instead of $z(t)$ to enhance readability.

The first equation is simply Hamilton's equation for the classical energy function h. It gives rise to the Hamiltonian flow

$$\Phi^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}, \quad \Phi^t(z_0) = z_t.$$

The so-called first variational equation (13.2) describes the linearization of the classical flow Φ^t along the trajectory $t \mapsto z_t$. In fact, one can easily see that the solution of (13.2) is given by

$$Z_t = D\Phi^t(z_0)Z_0, \tag{13.3}$$

and, as a consequence, the symplecticity of the Hamiltonian flow Φ^t implies that $Z(t)$ stays a normalized Lagrangian frame for all times.

The proof for the following exactness Lemma then follows from a straightforward calculation, see [Hag80].

Lemma 22. *Let V be a quadratic potential, $z_0 \in \mathbb{R}^{2d}$ and $Z_0 \in \mathbb{C}^{2d\times d}$ a positive Lagrangian frame. Then,*

$$\exp\left(-\mathrm{i}(-\tfrac{\varepsilon^2}{2}\Delta + V)t/\varepsilon\right)\varphi_k^\varepsilon[z_0; Z_0] = \mathrm{e}^{\mathrm{i}S(t)/\varepsilon}\varphi_k^\varepsilon[z_t; Z_t],$$

where z_t and Z_t are solutions of (13.1) *and* (13.2)*, respectively. $S(t)$ is the classical action*[9] *associated with the path $t \mapsto z_t$.*

Lemma (22) extends immediately to Schrödinger operators with time-dependent quadratic potentials. Hence, for treating more general potentials one can use locally quadratic expansions around the classical trajectory. This leads to the following result that can be found in [Hag98, Theorem 3.5].

Lemma 23. *Suppose $V \in \mathcal{C}^3(\mathbb{R}^{2d})$ satisfies $-C_1 \leq V(x) \leq C_2\mathrm{e}^{Ax^2}$ for some $A, C_1, C_2 > 0$. Then, for $k \in \mathbb{N}^d$, $z_0 \in \mathbb{R}^{2d}$, and $Z_0 \in \mathbb{C}^{2d\times d}$ a*

[9] The classical action associated with a path $t \mapsto (q_t, p_t)$ is defined as $S(t) = \int_0^t \frac{1}{2}|p_s|^2 - V(q_s)ds$.

positive Lagrangian frame we have

$$\| \exp\Big(-\mathrm{i}(-\tfrac{\varepsilon^2}{2}\Delta + V)t/\varepsilon\Big)\varphi_k^\varepsilon[z_0; Z_0] - \mathrm{e}^{\mathrm{i}S(t)/\varepsilon}\varphi_k^\varepsilon[z_t; Z_t]\|_{L^2} \leq C(k,t)\varepsilon^{1/2}$$

for some $C(k,t) > 0$. Here, z_t and Z_t denote the solutions of (13.1) *and* (13.2)*, respectively.*

The conditions on the potential guarantee that both the quantum evolution and the classical equations of motion are well-defined for all times. Moreover, by linearity, both Lemma 22 and Lemma 23 extend to initial conditions that are given by a linear combination of Hagedorn wave packets. The growth of the constant $C(k,t)$ in time depends on the stability of the classical Hamiltonian flow Φ^t.

Since $Y_t = (\mathrm{Re}Z_t, \mathrm{Im}Z_t)$ is a symplectic matrix for all t, one can restate (13.1) and (13.2) as a dynamical system on $\mathbb{R}^{2d} \times \mathrm{Sp}(2d, \mathbb{R})$, see [Ohs15]. Note, however, that for odd dimensions d the product space $\mathbb{R}^{2d} \times \mathrm{Sp}(2d, \mathbb{R})$ is again of odd dimension and hence cannot be a symplectic manifold . Nevertheless, by using the identification of the Siegel upper half-space Σ_d with the quotient space $\mathrm{Sp}(2d, \mathbb{R})/U(d)$, and the fact that the width matrix in Hagedorn's parametrization of wave packets can be written as $P_t Q_t^{-1} \in \Sigma_d$ for the solution $Z_t = (Q_t; P_t)$ of (13.2), one can interpret the dynamics of Z_t as a lift of the dynamics of $P_t Q_t^{-1}$ in the Siegel upper half space to an evolution of Z_t in the symplectic group, see [Ohs15, Remark 4.1].

13.2 Phase Space Dynamics

Let us take a look at the evolution of Hagedorn wave packets in phase space. By the Laguerre connection from Corollary 3 we know that the Wigner function of the two normalized Hagedorn wave

packets $\varphi_k^\varepsilon[Z_0; z_0]$ and $\varphi_\ell^\varepsilon[Z_0; z_0]$, $k, \ell \in \mathbb{N}^d$, is given by

$$\mathcal{W}_{k,\ell}^\varepsilon[Z_0, z_0](x,\xi) = \frac{(\pi\varepsilon)^{-d/2}}{\sqrt{2^{|k|+|\ell|}k!\ell!}} \mathrm{e}^{-\frac{1}{\varepsilon}(x-q_0,\xi-p_0)^T G_{Z_0}(x-q_0,\xi-p_0)} \times \prod_{j=1}^d \mathcal{L}_{k_j\ell_j}\left(\tfrac{\mathrm{i}}{\sqrt{\varepsilon}}(Q_0^T(\xi-p_0) - P_0^T(x-q_0))_j\right),$$

where $z_0 = (q_0, p_0)$ and $Z_0 = (Q_0; P_t)$. Here, $G_{Z_0} = \mathrm{Re}\,(Z_0 Z_0^*)^{-1}$ is the symplectic metric associated with Z_0, and

$$\mathcal{L}_{nm}(y) = \begin{cases} (-1)^m 2^n m! y^{n-m} L_m^{(n-m)}(2|y|^2), & n \geq m \\ (-1)^n 2^m n!\,(-\overline{y})^{m-n}\, L_n^{(m-n)}(2|y|^2), & m \geq n \end{cases}. \quad (13.4)$$

With the phase space lift from §8.1, the semiclassical time evolution for the wave packets $\varphi_k^\varepsilon[Z_0; z_0]$ and $\varphi_\ell^\varepsilon[Z_0; z_0]$ from the previous section §13.1 determines the evolution of the Wigner function $\mathcal{W}_{k,\ell}^\varepsilon[Z_0, z_0]$ in phase space: One simply replaces z_0 and Z_0 in (**??**) by the propagated center z_t and the Lagrangian frame Z_t. In particular, the symplectic metric evolves according to

$$G_{Z_t} = (D\Phi^{-t}(z_0))^* G_{Z_0} D\Phi^{-t}(z_0), \quad (13.5)$$

such that the stability of the classical flow determines the spreading of the Wigner function in phase space. We will come back to this viewpoint in §15, when we consider the long-time semiclassical evolution of Wigner functions.

There are two different matrix product representations of $G_{Z(t)}$ with symplectic factors that are useful for analyzing the behaviour of propagated wave packets in phase space.

Proposition 21 (Two symplectic factorizations)**.** *The symplectic metric G_{Z_t} from* (13.5) *can be rewritten as*

$$G_{Z_t} = F_{Z_t}^T F_{Z_t} = S_{Z_t}^T S_{Z_t}$$

for the real symplectic matrices

$$F_{Z_t} = J^T(\mathrm{Re}Z_t\ \mathrm{Im}Z_t)J \quad \textit{and} \quad S_{Z_t} = \begin{pmatrix} |Q_t|^{-1} & 0 \\ -|Q_t|\mathrm{Re}(P_tQ_t^{-1}) & |Q_t| \end{pmatrix}$$

where $Z_t = (Q_t; P_t)$ *and* $|Q_t| = \sqrt{Q_tQ_t^*}$.

Proof. The identity with F_{Z_t} follows directly from the definition of G_{Z_t}. For the second factorization one observes that QQ^* is a real matrix, and the symplectic metric can be rewritten as

$$G_{Z_t} = \begin{pmatrix} \mathrm{Im}(C_t) + \mathrm{Re}(C_t)Q_tQ_t^*\mathrm{Re}(C_t) & -\mathrm{Re}(C_t)Q_tQ_t^* \\ -Q_tQ_t^*\mathrm{Re}(C_t) & Q_tQ_t^* \end{pmatrix}$$

where $C_t = P_TQ_T^{-1}$, see also [dG11, Proposition 242] for a related formula. For the upper left block matrix this can be proved by employing

$$\begin{aligned} P_tP_t^* &= C_tQ_tQ_t^*C_t^* \\ &= (\mathrm{Re}(C_t) + \mathrm{i}Q_t^{-*}Q_t^{-1})Q_tQ_t^*(\mathrm{Re}(C_t) - \mathrm{i}Q_t^{-*}Q_t^{-1}) \\ &= \mathrm{Re}(C_t)Q_tQ_t^*\mathrm{Re}(C_t) + \mathrm{Im}(C_t) \end{aligned}$$

which holds due to the fact that $\mathrm{Im}C_t = (Q_tQ_t^*)^{-1}$. Similar identities can be used for the other entries of G_{Z_t}. The symplecticity of F_{Z_t} is a consequence of the fact that Z_t is a normalized Lagrangian frame, and the symplecticity of S_{Z_t} follows from a direct computation. □

13.3 Exponentially Small Errors

By adding higher order Hagedorn wave packets one can construct approximations in the spirit of Lemma 23 with errors of size $O(\varepsilon^{N/2})$ for any $N \in \mathbb{N}$, see [Hag98, Theorem 3.6]. If one allows an ε-dependent number of wave packets, one can even guarantee exponentially small errors up to Ehrenfest time. We sketch

the proof of the result [HJ00, Theorem 3.1] of Hagedorn and Joye on exponentially small errors over finite times. We include the crucial estimates that are the basis of the final result and will be used later on.

Lemma 24. *Suppose V is an analytic potential in a neighborhood of $S_\delta = \{z \in \mathbb{C} | \mathrm{Im}(z_j) \leq \delta\}$ with $\delta > 0$, bounded from below, and satisfies the growth condition $|V(z)| \leq M \exp(\tau |z|^2)$ for all $z \in S_\delta$ and some $M, \tau > 0$. Fix T, a classical trajectory $z_t = (q_t, p_t)$, and an initial state*

$$\psi_0^\varepsilon(x) = \sum_{|j| \leq J} c_j^\varepsilon(0) \varphi_j^\varepsilon[z_0; Z_0](x).$$

with some $c_j^\varepsilon(0) \in \mathbb{C}$. Then, there is $G > 0$ such that for all $g \in (0, G)$ there is a constant $\gamma_g > 0$ for which the L^2-error between the exact solution

$$\psi_t^\varepsilon(x) = \exp\left(-\mathrm{i}(-\tfrac{\varepsilon^2}{2}\Delta + V)t/\varepsilon\right) \psi_0^\varepsilon \tag{13.6}$$

of the time-dependent Schrödinger equation and the approximation

$$u^\varepsilon_{\lceil g/\varepsilon \rceil}(t,x) = \mathrm{e}^{\mathrm{i}S(t)/\varepsilon} \sum_{|j| \leq J + 3\lceil g/\varepsilon \rceil - 3} c_j^\varepsilon(t) \varphi_j^\varepsilon[z_t; Z_t](x)$$

is bounded by a constant times $\exp(-\gamma_g/\varepsilon)$. The form of the complex coefficients $c_j^\varepsilon(t)$ can be determined explicitely.

Sketch of proof. The error term

$$r^\varepsilon_{\lceil g/\varepsilon \rceil}(t,x) = \mathrm{i}\varepsilon \frac{d}{dt} u^\varepsilon_{\lceil g/\varepsilon \rceil}(t,x) + \frac{\varepsilon^2}{2} \Delta u^\varepsilon_{\lceil g/\varepsilon \rceil}(t,x) - V(x) u^\varepsilon_{\lceil g/\varepsilon \rceil}(t,x)$$

can be expanded as

$$\begin{aligned} r^\varepsilon_{\lceil g/\varepsilon \rceil}(t,x) &= \mathrm{e}^{\mathrm{i}S(t)/\varepsilon} \\ &\times \sum_{k=0}^{\lceil g/\varepsilon \rceil - 1} \varepsilon^{k/2} W^{(\lceil g/\varepsilon \rceil + 1 - k)}_{q(t)}(x) \sum_{|j| \leq J + 3\lceil g/\varepsilon \rceil - 3} c_{k,j}(t) \varphi_j^\varepsilon[z_t; Z_t](x) \end{aligned}$$

with the Taylor rest term

$$W^{(n)}_{q(t)}(x) = V(x) - \sum_{|m|\leq n} \frac{\partial^m V(q_t)}{m!}(x-q_t)^m,$$

and $c_{k,j}(t)$ beeing the j^{th} component of the k^{th} term in the semiclassical expansion

$$c^\varepsilon(t) = c_0(t) + \varepsilon c_1(t) + \varepsilon^2 c_2(t) + \dots \tag{13.7}$$

of the coefficient vector. The approximation error

$$E^\varepsilon(t) = \|u^\varepsilon_{\lceil g/\varepsilon \rceil}(t,\cdot) - \psi^\varepsilon_t\|_{L^2}$$

can then be estimated as

$$E^\varepsilon(t) \leq \frac{1}{\varepsilon}\int_0^t \|r^\varepsilon_{\lceil g/\varepsilon \rceil}(s,\cdot)\|_{L^2} ds. \tag{13.8}$$

At this point one chooses $b > 0$ and introduces the cutoff functions $\chi_1(t,x) = \mathbb{1}_{|x-q_t|\leq b}$ and $\chi_2(t,x) = 1 - \chi_1(t,x)$ on position space. Then, one estimates the L^2-norm of $r^\varepsilon_{\lceil g/\varepsilon \rceil}(t,\cdot)$ on the supports of χ_1 and χ_2 seperately.

In order too control the time evolution, Hagedorn and Joye introduce the numbers

$$D_1(T) = \max\left\{1, \sup_{0\leq|n|,0\leq t\leq T} \delta^{|n|}\frac{(\partial^n V)(q_t)}{n!}\right\}$$

and

$$D_2(T) = \max\left\{1, \sup_{0\leq t\leq T} \delta^{-1}\sqrt{2}d\|Q_t\|\right\}$$

which are finite, since V is analytic in S_δ. Moreover, they define

$$D_3 = \binom{d+2}{d-1}$$

as well as

$$\begin{aligned} D_4(T) &= \sup_{n\in\mathbb{N}^d, 0\le t\le T, |x-q_t|\le b} \delta^{|n|}\frac{(\partial^n V)(x)}{n!}, \\ D_5(T) &= 1 + D_1(T)D_2(T)^2 T, \\ D_6(T,\ell) &= \sum_{k=0}^{\ell-1} \delta^k (2\|Q_t\|^2)^{-k/2} \\ D_7(T) &= D_2(T)D_3D_5(T) \end{aligned}$$

which are all finite quantities. In the following we omit the dependence on T for readability. One can show that the coefficients satisfy

$$\|c_k(t)\| \le \left(\frac{(J+3k)!}{J!}\right)^{1/2} \frac{(D_2D_3D_5)^k}{k!}, \tag{13.9}$$

and $c_{k,j}(t) = 0$ whenever $|j| > J + 3k$, see Corollary 5.3 in [HJ00]. A long and technical calculation leads to the estimates

$$\frac{1}{\varepsilon}\int_0^t \|\chi_1(s,\cdot) r_\ell^\varepsilon(s,\cdot)\|_{L^2} ds \le D_4 \varepsilon^{\ell/2} \left(\frac{(J+3\ell)!}{J!}\right)^{1/2} \frac{D_2^{\ell+2} D_3^\ell}{(\ell-1)!} \frac{D_5^{\ell+1}}{D_5 - 1} \tag{13.10}$$

and

$$\|\chi_2(s,\cdot) r_\ell^\varepsilon(s,\cdot)\|_{L^2} \le C \mathrm{e}^{-b^2/(12\|Q_t\|^2\varepsilon)} D_6 D_7^{\ell-1} (C'\varepsilon\ell\|Q_t\|^2)^{1+\ell/2} \tag{13.11}$$

for some ℓ-independent constants $C, C' > 0$, if ε is small enough. The claim follows from combining the two estimates for $\ell = \lceil g/\varepsilon \rceil$ with g small enough. □

Let us remark that whenever the trajectory z_t is bounded, for instance if the corresponding connected component of the energy shell is compact, D_1 and D_4 can be chosen uniformly for all T. In the rest of this thesis, we will take the estimates (13.10) and (13.11) for granted.

14 Ehrenfest Time Scales

In section §11.2 we discussed the semiclassical propagation of expectation values up to the Ehrenfest time, which is determined by the stability properties of the classical flow. For the dynamics of wave packets, Hagedorn and Joye in [HJ00] derived propagation results similar to Lemma 24 for the typical Ehrenfest time scales of the size $t_\varepsilon \sim \log(\varepsilon^{-1})$. It is the aim of this chapter to use the analysis of Hagedorn and Joye summarized in §13.3 for proving a wave packet propagation theorem for the Ehrenfest time associated with a stable orbit of the classical flow.

14.1 Stable Orbits

The spreading of Wigner functions in phase space is determined by the stability of the classical flow. That is, by (13.5), the singular values of $D\Phi^t$ determine the amount by which the Wigner function is stretched in phase space. For the wave packet propagation error (13.10), however, also the time evolution of $D_2(t)$, that is $\|Q_t\|$, comes into play. From (13.3) we know that

$$Q_t = \partial_{q_0}(\Phi^t(q_0,p_0)_q)Q_0 + \partial_{p_0}(\Phi^t(q_0,p_0)_q)P_0$$

and hence Q_t contains the two upper blocks of $D\Phi^t(z_0)$. It is easy to see that given the stability of the flow Φ^t, the matrix Q_t is "stable" as well.

Proposition 22. *Let $z_0 \in \mathbb{R}^{2d}$ and $Z_t = (Q_t; P_t)$ solve the variational equation* (13.1)*. Suppose there are $C, \gamma > 0$ such that $\|D\Phi^t(z_0)\| \leq C(1+|t|)^\gamma$ for all t. Then,*

$$\|Q_t\|, \|P_t\| \leq C(1+|t|)^\gamma \|Z_0\|$$

for all t, and the eigenvalues $0 < \lambda_1(G_{Z_t}) \leq \ldots \leq \lambda_{2d}(G_{Z_t})$ of G_{Z_t}

satisfy

$$D(1+|t|)^{2\gamma} \geq \lambda_{2d}(G_{Z_t}) \geq \ldots \geq \lambda_1(G_{Z_t}) \geq D^{-1}(1+|t|)^{-2\gamma}$$

for some $D > 0$.

Proof. The first claim follows from the simple estimate

$$\|Q_t\| = \sup_{x\in\mathbb{R}^d} \frac{\|Q_t x\|}{\|x\|} \tag{14.1}$$

$$\leq \sup_{x\in\mathbb{R}^d} \frac{\|Z_t x\|}{\|x\|} \leq \|D\Phi^t\|\|Z_0\|, \tag{14.2}$$

and analogously for P_t. By (13.5), for the second inequality we have

$$\|G_{Z_t}\| = \|D\Phi^{-t}(z_0)^T G_{Z_0} D\Phi^{-t}(z_0)\| \leq \|G_{Z_0}\|\|D\Phi^{-t}(z_0)\|^2 \tag{14.3}$$

and since G_{Z_t} is symplectic and positive definite, all of its eigenvalues appear in pairs $\lambda, \lambda^{-1} > 0$. Hence,

$$|\lambda_1(G_{Z_t})^{-1}| = \|G_{Z_t}\|^{-1} \geq \|G_{Z_0}\|^{-1} C^{-2}(1+|t|)^{-2\gamma} \tag{14.4}$$

and the claim follows. □

Definition 11 (Stable orbit)**.** *Let* $z_t = \Phi^t(z_0)$ *be a classical orbit. We call* z_t stable with expansion rate $\gamma > 0$ *if there is* $C > 0$ *with* $\|D\Phi^t(z_0)\| \leq C(1+|t|)^\gamma$ *for all* $t \in \mathbb{R}$.

In one space dimension – away from hyperbolic fixed points of the flow – periodic orbits are stable in the sense that $\|D\Phi^t(z_0)\| \leq \sqrt{2+T'(E)^2t^2}$, see [dG06, §2.3.4]. In higher dimensions it is in general a complicated task to determine the stability properties of an orbit. In the case of periodic orbits one can use Floquet theory, but for more general trajectories this approach is not applicable.

Consider a stable orbit z_t with stability exponent $\gamma > 0$, and a potential V that has an analytic continuation into the strip S_δ

with $|V(z)| \leq M \langle z \rangle^m$ for all $z \in S_\delta$. Then, one obtains the growth bounds

$$\begin{aligned} D_1(t) &\leq C_1 \cdot (1+|t|)^m, & D_2(t) &\leq C_2 \cdot (1+|t|)^\gamma, \\ D_4(t) &\leq C_4 \cdot (1+|t|)^m, & D_5(t) &\leq C_5 \cdot (1+|t|)^{m+2\gamma+1}, \\ D_6(t,\ell) &\leq C_6^\ell, & D_7(t) &\leq C_7 \cdot (1+|t|)^{m+3\gamma+1}, \end{aligned}$$

for some constants $C_1, \ldots, C_7$ independent of ε and t, where $C_3 = D_3$. For D_1 one employs the analiticity, whereas the inequality for D_2 follows from Proposition 22. The other estimates follow similarly.

14.2 Long Time Accurate Dynamics on Stable Orbits

We can use the results from the previous section §14.1 in order to derive long Ehrenfest times for wave packet propagation on stable orbits. While the authors of [HJ00] wanted to obtain results for general systems, we use their results in order to prove exponentially good accury for stable orbits over longer time intervals that grow algebraically and not logarithmically in ε^{-1}.

Proposition 23 (Exponential accuracy up to long times)**.** *Suppose V is an analytic potential in a neighborhood of $S_\delta = \{z \in \mathbb{C}^d | \mathrm{Im}(z_j) \leq \delta\}$ with $\delta > 0$, bounded from below, and for some $m \geq 0$ satisfies the growth condition $|V(z)| \leq D \langle z \rangle^m$ for all $z \in S_\delta$. Assume that z_t is a stable classical orbit with expansion rate $\gamma > 0$, and fix the initial state*

$$\psi_0^\varepsilon(x) = \sum_{|j| \leq J} c_j^\varepsilon(0) \varphi_j^\varepsilon[z_0; Z_0](x). \tag{14.5}$$

Then, for every $\sigma' \in (0,1)$ small enough there is $\sigma \in (0,1)$ and $\alpha > 0$ such that the L^2-error between the exact solution (13.6) *of the Schrödinger*

equation and the approximation

$$u^{\varepsilon}_{\lceil \varepsilon^{-\sigma'} \rceil}(t,x) = \mathrm{e}^{\mathrm{i}S(t)/\varepsilon} \sum_{|j| \leq J+3/\varepsilon^{\sigma'}-3} c_j^{\varepsilon}(t) \varphi_j^{\varepsilon}[z_t; Z_t](x)$$

is bounded by $\exp(-\alpha/\varepsilon^{\sigma})$ *as* $\varepsilon \searrow 0$ *whenever* $|t| \lesssim \varepsilon^{-1/(6\gamma+2m+2+\delta)}$ *with some* $\delta > 0$.

Proof. If ℓ is large enough, from (13.10) and the estimates for the quantities D_j from above we can deduce

$$\begin{aligned} \frac{1}{\varepsilon} \int_0^t \|\chi_1(s,\cdot) r_{\ell}^{\varepsilon}(s,\cdot)\|_{L^2} ds \leq & A_1 B_1^{\ell} (\ell\varepsilon)^{\ell/2} (1+|t|)^{4\gamma+m+1} \\ & \times \left((1+|t|)^{3\gamma+m+1} \right)^{\ell} \end{aligned} \tag{14.6}$$

for some $A_1, B_1 > 0$ after applying Stirling's formula. Furthermore, for the second remainder (13.11) one can similarly prove the estimate

$$\frac{1}{\varepsilon} \int_0^t \|\chi_2(s,\cdot) r_{\ell}^{\varepsilon}(s,\cdot)\|_{L^2} ds \leq A_2 B_2^{\ell} (\ell\varepsilon)^{\ell/2} \mathrm{e}^{-C_2/((1+|t|)^{2\gamma}\varepsilon)} \tag{14.7}$$

$$\times \left((1+|t|)^{4\gamma+m+1} \right)^{\ell} \tag{14.8}$$

for some $A_2, B_2, C_2 > 0$, whenever ℓ is large enough. The main ingredient for the second estimate is the inequality for fixed $p \in \mathbb{N}^d$ and $\tau \geq 0$

$$\begin{aligned} \|\chi_2(t,x)(x-q_t)^p \mathrm{e}^{\tau(x-q_t)^2} \varphi_k^{\varepsilon}[z_t; Z_t](x)\|^2 \leq \\ \leq C \mathrm{e}^{-b^2/(6\|Q_t\|^2\varepsilon)} (2\varepsilon \|Q_t\|^2)^p \mathrm{e}^{\beta_d |k|} \frac{\Gamma(|k| + \frac{d}{2} + p)}{|k|!} \end{aligned} \tag{14.9}$$

which holds for some $C, \beta_d > 0$ whenever ε is small enough, $|k| < \varepsilon^{-2/3}$ and $t \lesssim \varepsilon^{-1/(6\gamma+2m+2+\delta)}$. This estimate can be proved by retracing the derivation of the inequality (6.23) in [HJ00].

We want to obtain exponentially small errors for $\varepsilon \searrow 0$ and hence set $\ell = g(t_\varepsilon)/\varepsilon$ for the Ehrenfest time t_ε and some function g. We consequently demand that

$$\begin{aligned} g(t)^{1/2}(1+|t|)^{3\gamma+m+1} &\to 0 \qquad \text{as } t \to \infty \text{ and} \\ g(t_\varepsilon)/\varepsilon &\to \infty \qquad \text{as } \varepsilon \to 0. \end{aligned}$$

These conditions are satisfied with $g(t) = |t|^{-6\gamma-2m-2-\delta'}$ and the Ehrenfest time $t_\varepsilon \lesssim \varepsilon^{-1/(6\gamma+2m+2+\delta)}$, and both (14.6) and (14.8) become exponentially small if $\delta > \delta' > 0$. □

Example. Suppose that the orbit z_t moves in a region where h gives rise to an analytic integrable Hamiltonian system in the sense of condition **(I)** from above, and contains no hyperbolic fixed points of the flow Φ^t. Then, the flow satisfies $\|D\Phi^t(z_0)\| \leq C(1+|t|)$, and hence $\gamma = 1$. If furthermore the trajectory z_t is trapped, we can set $m = 0$ and arrive at the Ehrenfest time $t_\varepsilon \lesssim \varepsilon^{-1/(8+\delta)}$ for the approximation from Proposition 23. ■

Proposition 23 can be used to derive exponential localization estimates for propagated wave functions. In the following we proceed similarly as for the proof of Theorem 3.4 in [HJ00].

Proposition 24 (Localization). *Let ψ_t^ε denote the solution of the Schrödinger equation* (13.6) *with initial condition* (14.5). *Then, under the same assumptions as in Proposition 23, for all $b > 0$ there are $C, \alpha > 0$ such that*

$$\left(\int_{|x-q_t|>b} |\psi_t^\varepsilon(x)|^2 dx \right)^{1/2} \leq C \exp(-\alpha/\varepsilon^\sigma) \tag{14.10}$$

and

$$\left(\int_{|\xi-p_t|>b} |(\mathcal{F}^\varepsilon \psi_t^\varepsilon)(\xi)|^2 d\xi \right)^{1/2} \leq C \exp(-\alpha/\varepsilon^\sigma)$$

with $\sigma \in (0,1)$, whenever $|t| \lesssim \varepsilon^{-1/(6\gamma+2m+2+\delta)}$ and ε is small enough.

Proof. We will first prove the localization estimates for the wave packet approximation $u^\varepsilon_{\lceil\varepsilon^{-\sigma'}\rceil}(t,\bullet)$ and then apply Proposition 23. We show that

$$\left(\int_{|x-q_t|>b} |u^\varepsilon_{\lceil\varepsilon^{-\sigma'}\rceil}(t,x)|^2 dx\right)^{1/2} \leq C\exp(-\alpha/\varepsilon^\sigma) \tag{14.11}$$

and

$$\left(\int_{|\xi-p_t)|>b} |(\mathcal{F}^\varepsilon u^\varepsilon_{\lceil\varepsilon^{-\sigma'}\rceil})(t,\xi)|^2 d\xi\right)^{1/2} \leq C\exp(-\alpha/\varepsilon^\sigma) \tag{14.12}$$

with $\sigma = 1 - \frac{2\gamma}{6\gamma+2m+2+\delta} > 2/3$, as long as $|t| \lesssim \varepsilon^{-1/(6\gamma+2m+2+\delta)}$.

The first assertion (14.11) is equivalent to an estimate for the L^2-norm of $\chi_2(\cdot,t)u^\varepsilon_{\lceil\varepsilon^{-\sigma'}\rceil}$, and we can use similar techniques as for the estimation of the remainder r^ε_ℓ. We begin by writing down the semiclassical expansion

$$\begin{aligned}
&\|\chi_2(\cdot,t)u^\varepsilon_{\lceil\varepsilon^{-\sigma'}\rceil}(t,\cdot)\| \leq \\
&\leq \sum_{j=0}^{\lceil\varepsilon^{-\sigma'}\rceil-1} \varepsilon^{j/2}\left(\sum_{|k|\leq J+3j} |c_{j,k}(t)|^2 \|\chi_2(\cdot,t)\varphi^\varepsilon_k[z_t;Z_t](\cdot)\|^2\right)^{1/2} \\
&\leq \sum_{j=0}^{\lceil\varepsilon^{-\sigma'}\rceil-1} \varepsilon^{j/2}\|c_j(t)\|\left(\sum_{|k|\leq J+3j} \|\chi_2(\cdot,t)\varphi^\varepsilon_k[z_t;Z_t](\cdot)\|^2\right)^{1/2}.
\end{aligned}$$

From (13.9) and (14.9) then follows the existence of a constant $\theta > 0$ such that

$$\|\chi_2(\cdot,t)u^\varepsilon_{\lceil\varepsilon^{-\sigma'}\rceil}(t,\cdot)\| \leq \mathrm{e}^{-b^2/(12\|Q_t\|^2\varepsilon)} \sum_{j=0}^{\lceil\varepsilon^{-\sigma'}\rceil-1} \left((1+|t|)^{2m+6\gamma+2}\theta\varepsilon\right)^{j/2}$$

holds for ε small. Since $|t| \lesssim \varepsilon^{-1/(6\gamma+2m+2+\delta)}$, there is a constant $D < 1$ such that for ε small enough one has

$$(1+|t|)^{2m+6\gamma+2}\theta\varepsilon \leq D.$$

and the observation

$$\exp(-b^2/(12\|Q_t\|^2\varepsilon)) \leq \exp(-\alpha/\varepsilon^{1-\frac{2\gamma}{6\gamma+2m+2+\delta}}) \tag{14.13}$$

for some $\alpha > 0$ concludes the proof of (14.11). After using the Fourier formula

$$\mathcal{F}^\varepsilon \varphi_k^\varepsilon[z;Z] = (-\mathrm{i})^{|k|} \mathrm{e}^{-\mathrm{i}p\cdot q/\varepsilon} \varphi_k^\varepsilon[Jz;JZ]$$

and repeating the same proof we obtain the second estimate (14.12). The assertion for the localization of the wave function ψ_t^ε then follows by applying the approximation from Proposition 23. □

Note that the same result holds for more general initial conditions given by a superposition of Hagedorn wave packets with phase space centers on different stable orbits of the classical flow.

15 Localization of Wigner Functions

In the previous chapter §14 we discussed the long-time evolution of states that are initially localized on stable orbits of the classical flow. As a final consequence, in Proposition 24, we derived an exponential localization estimate for the wave function and its Fourier transform around the classical trajectory for algebraically long times. However, this does not immediately imply a L^1-localization estimate for the corresponding Wigner transforms.

The goal of this section is to prove a L^1-localization estimate for the cross-Wigner functions of semiclassically evolved Hagedorn wave packets. Moreover, as an application, we combine the L^1-localization estimate with the long-time wave packet approximations from §14.2 in order to obtain a local Egorov theorem that holds for Ehrenfest times that are algebraic in ε^{-1}.

We start by giving a short overview on results for the evolution equation for Wigner transforms in §15.1. Afterwards, in §15.2 we prove the L^1-estimate for cross-Wigner functions. Finally, §15.3 is devoted to the proof of a local Egorov theorem.

15.1 Wigner Function Evolution

The quantum evolution of wave functions $t \mapsto \psi(t)$ governed by a selfadjoint Hamiltonian $H = -\frac{\varepsilon^2}{2}\Delta + V$ is physically equivalent to the evolution of the corresponding density operators $\rho(t) = |\psi(t)\rangle\langle\psi(t)|$ which is described by the von Neumann equation

$$\mathrm{i}\varepsilon\partial_t\rho(t) = [H, \rho(t)], \quad \rho(0) = |\psi(0)\rangle\langle\psi(0)|.$$

Recalling from (5.13) that the Weyl symbol of the density operator is given by the Wigner transform, on the phase space one at formally obtains the evolution equation

$$\begin{aligned}\partial_t \mathcal{W}_t^\varepsilon(q,p) &= -\tfrac{\mathrm{i}}{\varepsilon}\left(h\sharp\mathcal{W}_t^\varepsilon - \mathcal{W}_t^\varepsilon\sharp h\right)(q,p)\\ &= -p\cdot\nabla_q\mathcal{W}_t^\varepsilon(q,p) + P_\varepsilon\mathcal{W}_t^\varepsilon(q,p). \qquad (15.1)\end{aligned}$$

for the Wigner functions $\mathcal{W}_t^\varepsilon := \mathcal{W}^\varepsilon(\psi(t))$. Here, $h(q,p) = \frac{1}{2}|p|^2 + V(q)$ is the Weyl symbol of H, and $P_\varepsilon = P(x, \varepsilon\nabla_\xi)$ is a pseudodifferential operator built from the potential V. Equation (15.1) is known as the semiclassical *Quantum Liouville Equation* (QLE), which is well-posed on $L^2(\mathbb{R}^{2d})$ and mass-preserving,

$$\|\mathcal{W}_t^\varepsilon\|_{L^2} = \|\mathcal{W}_0^\varepsilon\|_{L^2} \quad \text{for all } t \in \mathbb{R},$$

if H is selfadjoint, see [Mar89]. The evolution of Wigner transforms and their weak limits as $\varepsilon \to 0$, the so-called *Wigner measures*, has drawn considerable interest in the last years, see, e.g., [GMMP97, Pul06, AP11, ER13, FKGL13].

If one aims to analyze the evolution of expectations values it would however be much more interesting develop a $L^1(\mathbb{R}^{2d})$ theory

for the (QLE). This is a hard problem since solutions of the (QLE) are highly oscillatory and can exhibit negative values. This is in contrast to the evolution of Wigner measures in the semiclassical limit $\varepsilon \to 0$ that is governed by the Liouville equation

$$\partial_t \mathcal{W}_t^0 = \{h, \mathcal{W}_t^0\} \tag{15.2}$$

see e.g. [AP11]. The solutions of (15.2) are determined by the characteristics associated with the Hamilton function h, and hence preserve the mass of the Wigner measures. If h is a polynomial of degree two, the (QLE) reduces to the Liouville equation (15.2). This is another way of stating that Egorov's theorem is exact for quadratic Hamiltonians.

The only rigorous L^1 result for solutions of the (QLE) with $\varepsilon > 0$ we are aware of is the analysis for smooth scattering type potentials $V \in H^s(\mathbb{R}^d)$, $s > \frac{1}{2}d$, from [ER05, ER13]. For a Schrödinger representation of quantum mechanics in phase space and the corresponding quantization procedures in doubled dimension we refer to [DdGLP12].

15.2 Exponential L^1-Localization in Phase Space

In this section we extend the localization estimates from (14.11) and (14.12) for semiclassically propagated wave packets and their Fourier transform to an L^1-esimate for semiclassically propagated cross-Wigner functions of Hagedorn wave packets.

Since cross-Wigner functions are complex-valued and highly oscillatory, it is difficult to analyze them directly. Therefore, we apply the expansion of cross-Wigner functions in terms of real-valued Wigner transforms from Proposition 16. This might lead to results that are far from beeing optimal, but allows for relatively simple proof techniques. Our assumtions on the potential are as follows:

Pot$_{a,m,\delta,z_t}$ Let $V : \mathbb{R}^d \to \mathbb{R}$ be a potential that gives rise to a selfadjoint Hamiltonian, and $z_t = (q_t, p_t)$ be an orbit of $h(q,p) = \frac{1}{2}|p|^2 + V(q)$. For $a > 0, \delta > 0$ set

$$B_{a,\delta} = \{x \in \mathbb{R}^d : \exists t \in \mathbb{R} \text{ with } |x - q_t| \leq a + \delta\}$$

and suppose V extends to an analytic potential in a neighborhood of

$$A_{a,\delta} = \{z \in \mathbb{C}^d : \mathrm{Re} z \in B_{a,\delta}, |\mathrm{Im} z_j| \leq \delta\},$$

and for some $m \geq 0$ satisfies the growth condition $|V(z)| \lesssim \langle z \rangle^m$ for all $z \in A_{a,\delta}$.

Note that we can choose $m = 0$ in **Pot**$_{a,m,\delta,z_t}$ if the orbit z_t is bounded. In this case, the condition **Pot**$_{a,m,\delta,z_t}$ reduces to the relatively mild assumption that V should give rise to a selfadjoint Hamiltonian and extend to an analytic function in a complex neighborhood of the orbit.

Under the above assumptions on the potential V we can prove a localization estimate for cross-Wigner functions up to Ehrenfest time. In order to avoid beeing too technical, a lengthy part of the proof is contained in the Proposition D.1 of the appendix §D.

Proposition 25 (Exponential L^1-localization of Wigner functions)**.** *Let z_t be a stable orbit with expansion rate $\gamma \geq 0$ and suppose V is a potential that satisfies the conditions* **Pot**$_{a,m,\delta,z_t}$ *with some $a, \delta > 0$ and $m \geq 0$. Let $\varepsilon > 0$ be small, and $k, \ell \in \mathbb{N}^d$ with $k_j, \ell_j \leq C\varepsilon^{-\sigma}$ for some $C > 0$ and $\sigma \in (0, 2\kappa + \frac{2}{3})$, where*

$$\kappa := \frac{1}{6} \frac{2m + 2 + \delta}{6\gamma + 2m + 2 + \delta} \in (0, \tfrac{1}{6}).$$

Then, if the positive Lagrangian frames Z_t are a solution of (13.2) *and ε is small enough,*

$$\int_{|z - z_t| > a} |\mathcal{W}^{\varepsilon}_{k,\ell}[z_t; Z_t](z)| dz \leq D\mathrm{e}^{-\Gamma \varepsilon^{-2/3 - 2\kappa}}$$

for some $D, \Gamma > 0$, whenever $|t| \lesssim \varepsilon^{-1/(6\gamma+2m+2+\delta)}$.

Proof. The symplectic matrix F_{Z_t} from Proposition 21 can be used to rewrite the variables $w = w(z) = \mathrm{i}Z_t J(z - z_t)$ in the Wigner-Hagedorn formula as

$$\begin{pmatrix} \mathrm{Re}(w) \\ \mathrm{Im}(w) \end{pmatrix} = \begin{pmatrix} \mathrm{Im}(P_t)^T & -\mathrm{Im}(Q_t)^T \\ -\mathrm{Re}(P_t)^T & \mathrm{Re}(Q_t)^T \end{pmatrix} \begin{pmatrix} x - q \\ \xi - p \end{pmatrix} = F_{Z_t}(z - z_t),$$

where $Z_t = (Q_t; P_t)$, see [LT14, §5.2]. We can use this transformation and a shift to the phase space origin to control the spreading of the Wigner function $\mathcal{W}^{\varepsilon}_{k,\ell}[z_t; Z_t]$ in phase space. Since the smallest singular value of F_{Z_t} is the square root of the smallest eigenvalue of G_{Z_t}, Propositions 21 and 22 together with Corollary 3 yield

$$\begin{aligned} \int_{|z-z_t|>a} |\mathcal{W}^{\varepsilon}_{k,\ell}[z_t; Z_t](z)| dz &= \int_{|F_{Z_t}^{-1} z|>a} |\mathcal{W}^{\varepsilon}_{k,\ell}[0; (\mathrm{Id}; \mathrm{iId})](z)| dz \\ &\leq \int_{|z|>aC_1(1+|t|)^{-\gamma}} |\mathcal{W}^{\varepsilon}_{k,\ell}[0; (\mathrm{Id}; \mathrm{iId})](z)| dz \\ &\leq \int_{|(x,\xi)|>dC_2\varepsilon^{1/6-\kappa}} \prod_{j=1}^{d} |\mathcal{W}^{\varepsilon}_{k_j,\ell_j}[0; (1; \mathrm{i})](x_j, \xi_j)| dx \, d\xi, \end{aligned}$$

for some $C_1, C_2 > 0$ whenever $|t| \lesssim \varepsilon^{-1/(6\gamma+2m+2+\delta)}$. We note that $\mathcal{W}^{\varepsilon}_{k_j,\ell_j}[0; (1; \mathrm{i})]$ are the cross-Wigner functions of one-dimensional Hermite functions. Employing the inclusion

$$\{(x, \xi) \in \mathbb{R}^{2d} : |(x, \xi)| > dC_2\varepsilon^{1/6-\kappa}\} \subset \bigcup_{j=1}^{d} \{(x, \xi) : |(x_j, \xi_j)| > C_2\varepsilon^{1/6-\kappa}\}$$

together with the L^1-norm estimate of Proposition D.1 from ap-

pendix §D gives

$$\begin{aligned}
&\int_{|z-z_t|>a} |\mathcal{W}^\varepsilon_{k,\ell}[z_t; Z_t](z)|dz = \\
&= \sum_{j=1}^{d} \int_{|(x_j,\xi_j)|>C_2\varepsilon^{1/6-\kappa}} \prod_{r=1}^{d} |\mathcal{W}^\varepsilon_{k_r,\ell_r}[0;(1;\mathrm{i})](x_r,\xi_r)|dx\, d\xi \\
&\leq \alpha\varepsilon^{-(d-1)(\sigma+\delta)} \sum_{j=1}^{d} \int_{\mathbb{R}^2} \chi_{|(x_j,\xi_j)|>C_2\varepsilon^{1/6-\kappa}} |\mathcal{W}^\varepsilon_{k_j,\ell_j}[0;(1;\mathrm{i})](x_j,\xi_j)|dx_j d\xi_j
\end{aligned}$$

for some $\alpha > 0$ and all $\delta > 0$. Since we assumed that $\sigma < \frac{2}{3} + \kappa$, the localization estimate from Proposition D.1 implies

$$\int_{\mathbb{R}^2} \chi_{|(x_j,\xi_j)|>C_2\varepsilon^{1/6-\kappa}} |\mathcal{W}^\varepsilon_{k_j,\ell_j}[0;(1;\mathrm{i})](x_j,\xi_j)|dx_j d\xi_j \leq \mathrm{e}^{-\Gamma\varepsilon^{-2\kappa-2/3}}$$

for ε small enough. The proof is complete. □

With more restrictive upper bounds for σ in Proposition 25 we could also prove exponential localization of the Wigner functions for longer times. However, since we want to combine the result with the wave packet approximations on Ehrenfest time scales from Proposition 23, we restricted ourselves to the same Ehrenfest times.

15.3 Application: A Local Egorov Theorem

In §11.2 we discussed some results from [BR02] on algebraically long Ehrenfest time scales for the Egorov theorem. The required conditions **(A)**, **(G)**, and **(I)** on the Hamiltonian and the observable, however, are very strong. This is mainly due to the fact that the authors of [BR02] wanted to obtain error estimates that are uniform in the initial wave function. For most applications, however, uniform estimates for short Ehrenfest times are not very helpful.

The times up to which discretizations of the Egorov theorem yield good results in numerical experiments often exceed the theoretically predicted Ehrenfest times by many orders of magnitude, see e.g. our experiments in [KL14]. The goal of this section is to make a first attempt to close this gap between the "theoretical and experimental Ehrenfest times". We are nevertheless aware of the fact that semiclassical approximations break down at the latest after times of size $O(\varepsilon^{-1/2})$. In all likelihood, semiclassical analysis does not provide the appropriate tools to break this barrier, see also [SVT12] and the introduction of [Fau07]. We consider initial data of the following form[10]:

(Ini)$_{z_0,N}$ Suppose that the wave function $\psi_0^\varepsilon \in L^2$, $\|\psi_0^\varepsilon\|_{L^2} = 1$, is of the form

$$\psi_0^\varepsilon(x) = \sum_{|j|\leq J} c_j^\varepsilon(0)\varphi_j^\varepsilon[z_0; Z_0](x) + O_{L^2}(\varepsilon^{N+1})$$

for some positive Lagrangian frame Z_0, $z_0 \in \mathbb{R}^{2d}$, and $J \in \mathbb{N}$.

However, we can relax the condition on the observable by allowing for general Gevrey functions in the symbol class S.

(G)$_{\text{global}}$ Suppose $a \in S$ and a is of Gevrey class G^s with some[11] $s \geq 0$.

Now, we can combine the results on the long-time wave packet approximations from §14.2 and the cross-Wigner localization estimates from §15.2 in order to derive a local Egorov theorem on stable orbits of the classical flow up to Ehrenfest times that are algebraic in ε^{-1}.

Theorem 7 (Local Egorov Theorem)**.** *Let $\varepsilon > 0$, $N \in \mathbb{N}$, and suppose $h(q,p) = \frac{1}{2}|p|^2 + V(q)$ satisfies condition* **(A)** *such that $H = \mathrm{op}_\varepsilon^{\mathrm{We}}(h)$*

[10] The generalization to initial data with several localization centers is obvious.

[11] In particular, all real-analytic symbols in S are admissable.

is selfadjoint. Assume that $a : \mathbb{R}^{2d} \to \mathbb{R}$ *fulfills* $\mathbf{(G)}_{\text{global}}$, $\psi_0^\varepsilon \in L^2$ *is of the form* $\mathbf{(Ini)}_{z_0,N}$, *and the Hamiltonian trajectory* $\Gamma = \{\Phi^t(z_0) : t \in \mathbb{R}\}$ *is bounded.*

Then, if there is an open bounded neighborhood $N(\Gamma)$ *of* Γ *invariant under* Φ^t *such that* $\operatorname{dist}(\partial N(\Gamma), \Gamma) > \theta > 0$ *and* h *satisfies the integrability condition* **(I)** *on* $N(\Gamma)$, *we have*

$$\left\langle \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0^\varepsilon \operatorname{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0^\varepsilon \right\rangle = \sum_{k=0}^{N} \varepsilon^k \left\langle \psi_0^\varepsilon \operatorname{op}_\varepsilon^{\mathrm{We}}(a_k(t))\psi_0^\varepsilon \right\rangle + O(\varepsilon^{7/8+3N/4-\delta_d/8})$$

for ε *small as long as* $|t| \lesssim \varepsilon^{-1/8+\mu}$ *with* $\mu > 0$.

Proof. The integrability condition **(I)** implies that the Hamiltonian flow Φ^t of h satisfies

$$\|\partial^\alpha \Phi^t(z)\| \leq C_\alpha (1 + |t|)^\alpha \tag{15.3}$$

for all $\alpha \in \mathbb{N}^{2d}$ and $z \in N(\Gamma)$ with some uniform constants $C_\alpha > 0$, see also [BR02, Lemma 4.2]. Because of the uniform distance assumption on $N(\Gamma)$, we can find an open set $\Gamma \subset M(\Gamma) \subset N(\Gamma)$ with

$$\operatorname{dist}(\partial M(\Gamma)\,,\,\Gamma)\,,\,\operatorname{dist}(\partial M(\Gamma)\,,\,\partial N(\Gamma)) > \tfrac{1}{4}\theta > 0. \tag{15.4}$$

There is a smooth function $\eta : \mathbb{R}^{2d} \to [0,1]$ that satisfies

$$\eta(z) = \begin{cases} 1 & z \in M(\Gamma) \\ 0 & z \in \mathbb{R}^{2d} \setminus N(\Gamma) \end{cases} \tag{15.5}$$

and which is of some Gevrey class $G^{s'}$ with $s' > 1$, see [Rod93, §I.1.4]. Now, we can analyze the expectation value close to the classical trajectory by using the ultra-differentiable partition of unity $1 = \eta + (1 - \eta)$.

Since $a\eta$ is of Gevrey class and supported in $N(\Gamma)$, we can apply the long time Egorov theorem from Lemma 18 which gives

$$\left\langle \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0^\varepsilon \operatorname{op}_\varepsilon^{\mathrm{We}}(a\eta)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0^\varepsilon \right\rangle = \sum_{k=0}^{N} \varepsilon^k \left\langle \psi_0^\varepsilon \operatorname{op}_\varepsilon^{\mathrm{We}}((a\eta)_k(t))\psi_0^\varepsilon \right\rangle + O(\varepsilon^{7/8+3N/4-\delta_d/8})$$

for the considered times. Hence, it remains to estimate the part of the expectation value away from $N(\Gamma)$, and to show that we can replace $(a\eta)_k(t)$ in the above formula by $a_k(t)$.

We partition the phase space into a ball around the phase space center z_0 and its complement,

$$\left\langle \psi_0^\varepsilon \operatorname{op}_\varepsilon^{\mathrm{We}}((a\eta)_k(t))\psi_0^\varepsilon \right\rangle = \int_{B_{\varepsilon^{1/4}}(z_0)} \mathcal{W}^\varepsilon(\psi_0^\varepsilon)(z)(a\eta)_k(t)(z)dz \tag{15.6}$$

$$+ \int_{\mathbb{R}^{2d}\setminus B_{\varepsilon^{1/4}}(z_0)} \mathcal{W}^\varepsilon(\psi_0^\varepsilon)(z)(a\eta)_k(t)(z)dz, \tag{15.7}$$

and treat the integrals (15.6) and (15.7) seperately. For (15.6) we observe that due to the stability of the flow in $N(\Gamma)$ one has $\Phi^t(B_{\varepsilon^{1/4}}(z_0)) \subset M(\Gamma)$ if $|t| \lesssim \varepsilon^{-1/8+\mu}$ and ε is small enough. Hence,

$$(a\eta)_k(t)(z) = a_k(t)(z) \tag{15.8}$$

for all $z \in B_{\varepsilon^{1/2+\delta}}(z_0)$ and $|t| \lesssim \varepsilon^{-1/8+\mu}$ by the construction of $(a\eta)_k(t)$, see Lemma 16. The value of the integral (15.7) is exponentially small in ε by Proposition D.1.

Finally, we have to estimate the value of

$$\left\langle \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0^\varepsilon \operatorname{op}_\varepsilon^{\mathrm{We}}(a(1-\eta))\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0^\varepsilon \right\rangle. \tag{15.9}$$

Since $t \mapsto \Phi^t(z_0)$ is a bounded trajectory that is stable with expansion rate 1, see (15.3), Proposition 23 implies that for every small

$\sigma' > 0$ it follows

$$\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0^\varepsilon(x) = \mathrm{e}^{\mathrm{i}S(t)/\varepsilon} \sum_{|j|\leq J+3/\varepsilon^{\sigma'}-3} c_j^\varepsilon(t)\varphi_j^\varepsilon[z_t;Z_t](x) + O_{L^2}(\varepsilon^{N+1}) \tag{15.10}$$

as long as $|t| \lesssim \varepsilon^{-1/8+\mu}$ and ε is small. The $O_{L^2}(\varepsilon^N)$ error contains the error from the initial condition and the exponentially small error from the semiclassical time propagation. Moreover, since the wave packets $\varphi_j^\varepsilon[z_t;Z_t]$, $j \in \mathbb{N}^d$, are pairwise orthogonal and φ_0^ε is L^2-normalized, from (15.10) we can infer $|c_j^\varepsilon(t)| \leq 2$ for all[12] j if ε is small enough. We estimate

$$\begin{aligned}
&\Big| \sum_{|k|,|\ell|\leq J+3/\varepsilon^{\sigma'}-3} c_k^\varepsilon(t)\overline{c_\ell^\varepsilon(t)} \left\langle \varphi_k^\varepsilon[z_t;Z_t], \mathrm{op}_\varepsilon^{\mathrm{We}}(a(1-\eta))\varphi_\ell^\varepsilon[z_t;Z_t]\right\rangle \Big| \\
&\leq 4 \sum_{|k|,|\ell|\leq J+3/\varepsilon^{\sigma'}-3} \int_{\mathbb{R}^{2d}} \big|\mathcal{W}_{k,\ell}^\varepsilon[Z_t;z_t](w)a(w)(1-\eta)(w)\big|dw \\
&\leq 4\|a\|_{L^\infty} \sum_{|k|,|\ell|\leq J+3/\varepsilon^{\sigma'}-3} \int_{\mathbb{R}^{2d}\setminus M(\Gamma)} \big|\mathcal{W}_{k,\ell}^\varepsilon[Z_t;z_t](w)\big|dw.
\end{aligned}$$

We have $z_t \in M(\Gamma)$ by construction, and $\mathrm{dist}(z_t, M(\Gamma)) \geq \frac{1}{4}\theta > 0$. Consequently, applying Proposition 25 leads to the estimate

$$\int_{\mathbb{R}^{2d}\setminus M(\Gamma)} \big|\mathcal{W}_{k,\ell}^\varepsilon[Z_t;z_t](w)\big|dw \leq C\mathrm{e}^{-D\varepsilon^{-2/3}}$$

for some $C, D > 0$ independent of $k, \ell \in \{\alpha \in \mathbb{N}^d : |\alpha| \leq J + 3\varepsilon^{-\sigma'} - 3\}$ if ε is small. Combining this with (15.10) yields an $O(\varepsilon^{N+1})$ bound for (15.9) since $a(1-\eta)$ is bounded. This completes the proof. □

Theorem 7 implies that the Egorov theorem holds for long Ehrenfest times that are algebraic in ε^{-1} if one considers initial wave functions that are localized in a phase space region where the

[12] Every number larger than 1 serves as an upper bound for $|c_j^\varepsilon(t)|$ if ε is small.

Hamiltonian dynamics is integrable. Intuitively it is clear that the behaviour of the Hamiltonian flow and the observable away from the classical trajectory should not play a role for the error. We rigorously verified this anticipation by using the long time wave packet approximation from Proposition 23 and the localization estimate for Wigner functions from Proposition 25. Hence, in comparison with the results in [BR02], we gain more freedom for the regularity of the dynamics and the localization of the observable at the price of loosing some power of ε in the Ehrenfest time. This loss is probably only due to our proof, since it originates in the involved estimates for the long-time wave packet approximation from [HJ00] or Proposition 23. We note that our local Theorem implies the algebraic Ehrenfest time scales of size $\varepsilon^{1/8}$ for more general situations than captured by the conditions **(A)**, **(G)**, and **(I)** from [BR02].

IV

Algorithms and Applications

The reliable simulation of the dynamics of molecular quantum systems is one of the central challenges of physical chemistry. In the Born-Oppenheimer approximation, the evolution of the molecule's nuclei in atomic units is governed by a semiclassical Schrödinger equation of the form

$$\mathrm{i}\varepsilon\partial_t\psi(t) = \mathrm{op}_\varepsilon^{\mathrm{We}}(h)\psi(t), \qquad \psi(0) = \psi_0 \in L^2(\mathbb{R}^d), \tag{15.1}$$

compare (5.2) and section §2.4. There are two key features of the solutions of equation (15.1) which make a direct numerical discretization expensive or — for many real-world systems — even unfeasible. Firstly, the configuration space is typically high dimensional, $d \gg 1$, which makes the use of tensor grids impossible due to the "curse of dimension", see e.g. [Lub08, §III.1.2]. Secondly, solutions of the semiclassical Schrödinger equation are typically highly oscillatory in space and time, with frequencies of size $O(\varepsilon^{-1})$.

The smallness of ε induces severe constraints on the discretization parameters, since one has to resolve the oscillations.

By direct numerical discretization we typically mean a (pseudo-)spectral discretization, e.g. Fourier collocation or a Galerkin method, in space, and a splitting in time, see also appendix E. For details, discussions, and comparisons of various discretizations we refer to [Lub08, §III] and [JMS11] and the references given therein.

In this chapter we discuss discretizations for the evolution of expectation values that build on the semiclassical Egorov type approximations presented in chapter III. While these phase space methods inherit a structural ε-dependent error arising from the semiclassical approximation, they do not need to resolve high oscillations, and the required computational efforts scale polynomially (in fact, mostly linear) in the dimension. In §16 we discuss algorithmic discretizations of the Egorov theorem from §11, and the Husimi and spectrogram approximations from §12. The last chapter §17 is devoted to numerical experiments in various setups and dimensions.[1]

16 Discretization

In this chapter we provide discretizations for the semiclassical approximations of quantum expectations discussed in §III. We describe and compare four different methods for approximating the time evolution of the expectation value

$$t \mapsto \left\langle \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi, \mathrm{op}_\varepsilon^{\mathrm{We}}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi \right\rangle =: \left\langle \widehat{a(t)} \right\rangle_\psi ,$$

where the observable $\mathrm{op}_\varepsilon^{\mathrm{We}}(a)$ and the Hamiltonian $H = \mathrm{op}_\varepsilon^{\mathrm{We}}(h)$ are Weyl quantized operators. Throughout this chapter, by Φ^t we

[1] All simulations have been performed with MATLAB 8.3 on a 3.33GHz Intel Xeon X5680 processor.

denote the Hamiltonian flow of h, and by Φ_ε^t the Hamiltonian flow of $h - \frac{\varepsilon}{4}\Delta h$. The initial wave function $\psi \in L^2(\mathbb{R}^d)$ is assumed to be L^2-normalized, $\|\psi\|_{L^2} = 1$.

We consider the following four phase space approximations as starting points for the development of numerical methods for the computation of expectation values.

A Wigner method: Applying the Egorov theorem from §11 yields

$$\left\langle \widehat{a(t)} \right\rangle_\psi = \int_{\mathbb{R}^{2d}} (a \circ \Phi^t)(z) \mathcal{W}^\varepsilon(\psi)(z) dz + O(\varepsilon^2) \tag{16.1}$$

for suitable a, where $\mathcal{W}^\varepsilon(\psi) : \mathbb{R}^{2d} \to \mathbb{R}$ is the Wigner transform of ψ.

B Spectrogram method: By Theorem 5, one has the approximation

$$\begin{aligned} \left\langle \widehat{a(t)} \right\rangle_\psi &= \int_{\mathbb{R}^{2d}} (a \circ \Phi^t)(z) \mu_2(\psi)(z) dz + O(\varepsilon^2) \qquad (16.2) \\ &= (1 + \tfrac{d}{2}) \int_{\mathbb{R}^{2d}} (a \circ \Phi^t)(z)\, \mathcal{H}_0^\varepsilon(\psi) dz \\ &\quad - \tfrac{d}{2} \int_{\mathbb{R}^{2d}} (a \circ \Phi^t)(z) \tfrac{1}{d} \sum_{|k|=1} \mathcal{H}_k^\varepsilon(\psi) dz + O(\varepsilon^2) \end{aligned}$$

with the spectrogram phase space density $\mu_2(\psi)$. Note, that $\mathcal{H}_0^\varepsilon(\psi)$ and $\frac{1}{d}\sum_{|k|=1} \mathcal{H}_k^\varepsilon(\psi)$ are smooth probability densities.

C Husimi method: Corollary 5 makes is possible to compute expectation values via Husimi functions,

$$\left\langle \widehat{a(t)} \right\rangle_\psi = \int_{\mathbb{R}^{2d}} F_\varepsilon^t(a)(z)\, \mathcal{H}_0^\varepsilon(\psi)(z)\, dz + O(\varepsilon^2) \tag{16.3}$$

$$= -\tfrac{\varepsilon}{2} \int_{\mathbb{R}^{2d}} \left(\mathrm{tr}(\Lambda_\varepsilon^t\, (D^2 a \circ \Phi_\varepsilon^t)) + \Gamma_\varepsilon^t \cdot (\nabla a \circ \Phi_\varepsilon^t) \right)(z) \mathcal{H}_0^\varepsilon(\psi)(z)\, dz \tag{16.4}$$

$$+ \int_{\mathbb{R}^{2d}} (a_\varepsilon \circ \Phi_\varepsilon^t)(z) \mathcal{H}_0^\varepsilon(\psi)(z)\, dz + O(\varepsilon^2)$$

where $\mathcal{H}_0^\varepsilon(\psi)$ is the Husimi transform of ψ, and F_ε^t contains the vector flows $\Phi_\varepsilon^t, \Gamma_\varepsilon^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ as well as the matrix flow $\Lambda_\varepsilon^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d\times 2d}$.

D naive Husimi method: We simply replace the Wigner transform in the Wigner method (16.1) by the Husimi transform. The resulting approximation

$$\left\langle \widehat{a(t)} \right\rangle_\psi = \int_{\mathbb{R}^{2d}} (a \circ \Phi^t)(z)\, \mathcal{H}_0^\varepsilon(\psi)(z)\, dz + O(\varepsilon), \tag{16.5}$$

is of first order in ε, only.

We present algorithmic discretizations of the four methods A–D from above, based on a sampling from the initial density and integration of the respective ODEs. Discretizations of the Wigner method have first been discussed in [LR10], see also our work with Caroline Lasser in [KL14]. For the discretization of the Husimi method we refer to our joint publication [KL13] with Caroline Lasser, and for the spectrogram method to the joint preprint [KLO15] with Caroline Lasser and Tomoki Ohsawa. In [GL14] one can find a scheme for discretizing a higher order Egorov approximation with $O(\varepsilon^4)$ errors, which in some sense is similar to our discretization of the Husimi method.

The first section §16.1 contains an algorithmic description of the phase spce methods derived from approximations A–D. Thereafter, in §16.2 and §16.3, we discuss the sampling and time propagation parts of the algorithms in greater detail.

16.1 Phase Space Algorithms

The formulas for the spectrogram and Husimi method both decompose into a linear combination of two phase space integrals with a probability density as weight. Since the two integrals can be treated independently, we are left with the task of discretizing phase space

integrals of the form[2]

$$\int_{\mathbb{R}^{2d}} \Theta^t(z) \cdot (b \circ \Phi^t)(z) p(z) dz =: \mathbb{E}_p[\Theta^t \cdot (b \circ \Phi^t)] \tag{16.6}$$

where p is a probability density, $b : \mathbb{R}^{2d} \to \mathbb{R}^k$ with $k \geq 1$, $\Phi^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ is the Hamiltonian flow associated with some energy function h, and $\Theta^t : \mathbb{R}^{2d} \to \mathbb{R}^k$ is the vector-valued flow of some ODE

$$\partial_t \Theta^t = A(h, \Theta^t, \Phi^t), \quad \Theta^0(z) = C \in \mathbb{R}^k \ \ \forall z \in \mathbb{R}^{2d}, \tag{16.7}$$

with smooth right hand side. One can see that all integrals appearing in the approximations A–D from above are of this form, except that the Wigner transform $\mathcal{W}^\varepsilon(\psi)$ is only a probability density for Gaussian states ψ, see [SC83]. We ignore this restriction for the moment. Note that one has $k = 1$ and $\Theta^t \equiv 1$ for all the phase space integrals except for the first order correction (16.4) in the Husimi method. To see that this correction is in fact of the form (16.6) one can vectorize the matrices Λ_ε^t and $D^2 a$ and write down a joint ODE in $\mathbb{R}^{4d^2+2d}$ for Λ_ε^t and Γ_ε^t, whoose right hand side only depends on h and Φ_ε^t, see [KL13, §4.2] for the details.

The algorithmic discretization of (16.6) consists of two steps, namely sampling from the density p, and integrating the ODEs for Θ^t and Φ^t. In other words, we use the quadrature

$$\mathbb{E}_p[\Theta^t \cdot (b \circ \Phi^t)] \approx \frac{1}{N} \sum_{j=1}^N \Theta^t(z_j) \cdot b(\Phi^t(z_j)) =: \mathbb{Q}_p^N[\Theta^t \cdot (b \circ \Phi^t)] \tag{16.8}$$

$$\approx \mathbb{Q}_p^N[T_\tau^t \cdot (b \circ f_\tau^t)] \tag{16.9}$$

where $z_1, \ldots, z_N$ are distributed according to the probability measure $p(x)dx$. T_τ^t and f_τ^t are numerical discretizations of Θ^t and Φ^t

[2]The notation $\mathbb{E}_p[\bullet]$ highlights that if p is a probability density, the integral is an expectation value in the sense of probability theory.

with stepsize $\tau > 0$, respectively. The first quadrature formula (16.8) corresponds to a space discretization, and (16.9) to an additional time discretization of the expectation value. The full discretization of the expectation value then can be implemented in the spirit of the following MATLAB type pseudocode `quadrature()`.

```
function [out] = quadrature(t,h,b,A,p,N,τ)
% INPUT:    t     time for evaluation
%           h     the Hamilton function for Φ^t
%           b     phase space function
%           A     right hand side of ODE for Θ^t
%           p     probability density
%           N     number of sampling points
%           τ     time stepping for integrator
% OUTPUT:   out   approximate value of the
%                 phase space integral

% Sample N points from p(x)dx
[z_1,...,z_N] = sample(p,N);
% set up initial values for the flow  Φ^t
z = [z_1,...,z_N];
% set up initial values for Θ^t
T = C*ones(1,N);
% apply a numerical solver  to integrate the
% joint ODE for [Φ^t;Θ^t]  up to time t with time
% stepping τ and initial conditions z and T
[z,T] = integrator(z,T,h,A,τ,t)
% Compute inner products for all evolved points
temp = [T(:,1)'*b(z(:,1)),...,T(:,N)'*b(z(:,N))]
% Take the average
out = (1/N) * sum(temp)
end
```

We are going to explain the sampling and numerical quadrature substeps `sample()` and `integrator()` in more detail in the sections §16.2 and §16.3 below. The schematic formulation from above illustrates that the symbol b enters only in the final averaging step, which is not expensive. Consequently, the main part of the algorithm is independent of b, and the outcome of the sampling and propagation steps can be used to approximate the integral (16.8) for all functions (observables) $b : \mathbb{R}^{2d} \to \mathbb{R}^k$ of interest.

16.2 Sampling

The sampling step `sample()` in the phase space algorithm described in §16.1 should create points $z_1, \dots, z_N$ that are distributed according to a phase space density representing the initial state ψ, that is, $\mathcal{W}^\varepsilon(\psi)$, $\mathcal{H}^\varepsilon_0(\psi)$ or $\frac{1}{d}\sum_{|k|=1}\mathcal{H}^\varepsilon_k(\psi)$. For the Wigner method this is however a hard or even unsolvable task since Wigner transforms are typically not probability densities. Although there are techniques to circumvent this sampling problem for certain classes of states, like stratified or importance sampling, or generalized Metropolis algorithms, see [KLW09, LR10], it is a source of severe difficulties. It was our leading motivation for the development of the Husimi and spectrogram methods to obtain approximations that build on phase space densities that are well-amenable for numerical sampling purposes for all types of initial states.

We focus on two different sampling techniques for probability distributions that are suitable for the moderately high dimensional setups we are aiming for, namely *Monte Carlo* and *Quasi-Monte Carlo* or low star-discrepancy sampling schemes.

Monte Carlo quadrature

For Monte Carlo sampling one either generates random variables $z_1, \dots, z_N$ that are independently and identically distributed with respect to the probability density p, or, as for Markov chain Monte

Carlo methods, create a uniformly ergodic Markov chain $z_1, z_2, \ldots$ with stationary distribution p. Then, by central limit theorems, for all $\alpha > 0$ one has the convergence

$$\mathbb{P}\left(\left|\mathbb{E}_p[a] - \mathbb{Q}_p^N[a]\right| \leq \frac{\alpha\gamma(a)}{\sqrt{N}}\right) = \frac{1}{\sqrt{2\pi}}\int_{-\alpha}^{\alpha} \mathrm{e}^{-x^2/2}dx$$

where the constant $\gamma(a)$ in the quadrature error depends on the variance of the integrand a, but not on the dimension. As noted in [KL14, §4.1], for our applications $\gamma(a)$ typically decreases for small ε, and the observed accuracy of Monte Carlo quadrature becomes better in the semiclassical setup.

In [KLO15, §5 and Appendix A] we computed the Husimi functions and first oder Hermite spectrograms for translated Hermite functions. They give rise to linear combinations of products of two-dimensional probability distributions that factorize into an uniform distribution for the angular part and a Gamma distribution for the radial part. Hence, one can use the routines `rand()` and `gaminv()` in MATLAB in order to generate a uniform random sampling on $[0, 1]$ and transform it back to the radial distribution by means of the inverse distribution function.

Quasi-Monte Carlo quadrature

In contrast to Monte Carlo methods, Quasi-Monte Carlo quadrature is totally deterministic. It builds on sequences $z_1, z_2, \ldots \in \mathbb{R}^{2d}$ that minimize the star-discrepancy with respect to the measure $p(z)dz$. That is, the star-discrepancy

$$\mathcal{D}^*(z_1, \ldots, z_N) = \sup_{w\in\mathbb{R}^{2d}} \Big|\frac{1}{N}\sharp\{z_j : z_j \in (-\infty, w)\} - \int_{(-\infty,w)} p(z)dz\Big|$$

satisfies $\mathcal{D}^*(z_1, \ldots, z_N) = O(\log(N)^{2d}N^{-1})$ as $N \to \infty$, where we used the convention $(-\infty, w) := (-\infty, w_1) \times \ldots \times (-\infty, w_{2d})$. Then, for suitable integrands a, by the Koksma-Hlawka inequality it holds

$$\left|\mathbb{E}_p[a] - \mathbb{Q}_p^N[a]\right| \leq \frac{\gamma(a)(\log N)^{c_d}}{N}$$

for some constants $\gamma(a)$ and $c_d \geq 2d$, see the proof of [HKT04, Theorem 3.4] or [LR10, §3.2]. Again, numerical experiments suggest that $\gamma(a)$ becomes smaller for $\varepsilon \to 0$, and in practice one observes convergence rates of $O(N^{-1})$ for moderately high dimensions.

There are various well-known low-discrepancy sequences for the uniform distribution on the torus $[0,1]^d$, for instance the Halton and Sobol sequences[3]. If the probability density $p : \mathbb{R}^{2d} \to [0,\infty)$ factorizes into a product of $2d$ probability densities $p_1, \ldots, p_{2d}$ for which one can evaluate the inverse distribution function, one can map such a low star-discrepancy sequence on the torus to a low star-discrepancy sequence for the measure $p(z)dz$. This is for example the case for the Husimi transform of isotropic Gaussians, where one uses the inverse error function. However, for most states the density p neither factorizes, nor can one access any inverse distribution function. Hence, one would like to directly generate low-discrepancy sequences for non-uniform measures on more general domains. This is a hard problem which to the best of our knowledge is still more or less unsolved; see [BB09]. Even the existence of low-discrepancy sequences for non-uniform measures on the torus has been investigated only recently in [AD14].

For translated Hermite functions we use a heuristic sampling approach by mimicking the procedure used for Monte-Carlo samplings. We simply replace the uniform random numbers on $[0,1]^d$ by Halton or Sobol sequences and then transform them to the radial Gamma distribution by means of the inverse distribution function. If this procedure, combined with pseudorandom numbers for the angular part, in fact yields a low star-discrepancy series is an open question not adressed by the current literature. However, in numerical experiments these heuristical sequences perform very well, see also the experiments in chapter §17.

[3] In MATLAB they are accessible via the commands `haltonset()` and `sobolset()`.

16.3 Integration of ODEs

The discretization of the phase space approximations described in §16.1 contains as the substep `integration()` a numerical solver for the Hamiltonian flow Φ^t associated with a Hamilton function[4] $h : \mathbb{R}^{2d} \to \mathbb{R}$ with initial conditions generated by the initial sampling step `sample` discussed in §16.2. For the Husimi method one additionally has to integrate the flows Λ_ε^t and Γ_ε^t for the correction.

For the numerical integration of the Hamiltonian flow Φ^t it is crucial to use a symplectic integrator in order to obtain physically meaningful and accurate solutions, especially over long time intervals.

Definition 12. *A numerical one-step integrator for a Hamiltonian system* $(\mathbb{R}^{2d}, \Omega, h)$ *is called* symplectic *if the one-step map* $z_{n+1} = F_\tau(z_n) \in \mathbb{R}^{2d}$ *is symplectic for all step sizes* $\tau > 0$.

For the abstract and practical properties of symplectic integrators we refer to the book of Hairer, Lubich, and Wanner [HLW10, §VI]. In particular, symplectic integrators preserve all first integrals of the system, like the total energy, and phase space volumes, see e.g. the illustrations for the pendulum in [HLW10, Figure 3.1 in §VI]. The importance of using a symplectic integrator for the discretized Egorov theorem (and the other methods) is also illustrated in [LR10, Figure 4.2], where the non-symplectic `ode45` solver from MATLAB is shown to give rise to a drift in energy.

If the Hamilton function has the common form

$$h(q, p) = \tfrac{1}{2}|p|^2 + V(q), \tag{16.10}$$

[4]For the Husimi method one has to use the corrected energy function h_ε, but this does not alter the discretization procedure. Therefore, we suppress this possibility in the rest of the section.

for computing Φ^t one has to solve the Hamiltonian system

$$\begin{cases} \dot{q}_t = p_t, & q_0 \in \mathbb{R}^d \\ \dot{p}_t = -\nabla V(q_t), & p_0 \in \mathbb{R}^d \end{cases}. \tag{16.11}$$

The structure of (16.11) suggests to approximate Φ^t by suitable compositions of the linear flows Φ_a^t and Φ_b^t of the simpler differential equations

$$\begin{cases} \dot{q}_t^a = 0 \\ \dot{p}_t^a = -\nabla V(q_t^a) \end{cases} \quad \text{and} \quad \begin{cases} \dot{q}_t^b = p_t^b \\ \dot{p}_t^b = 0 \end{cases} \tag{16.12}$$

obtained from splitting the Hamiltonian vector field in (16.11) into two parts. The most commonly used symplectic splitting method is the Störmer-Verlet scheme

$$F_\tau = \Phi_a^{\tau/2}\Phi_b^\tau\Phi_a^{\tau/2} \quad \left(\text{or} \quad \widetilde{F}_\tau = \Phi_b^{\tau/2}\Phi_a^\tau\Phi_b^{\tau/2}\right)$$

which yields a second order method. Compositions of $\Phi_a^{\alpha_j}$ and $\Phi_b^{\beta_j}$ with suitable step sizes α_j and β_j can also be used to construct higher order symplectic splitting methods, see for example the schemes in [Yos90].

If h is of the form (16.10), the Hessian D^2h is independent of the momentum p, and hence the vector field in the ODE for Λ_ε^t and Γ_ε^t does not depend on the momentum p either, compare Theorem 6. Consequently, in this case one can integrate the ODE for the full system by using the splitting (16.12) and propagating Λ_ε^t and Γ_ε^t together with the momentum Φ_a^t, see also [KL14, §4.2].

For the semiclassical approximations A–D one can solve the relevent ODEs parallelly for all initial data, which allows for a tremendous speed up. Below one can find a MATLAB type pseudocode `stoermer-verlet()` for the popular Störmer-Verlet method F_τ^t applied for the integration of (16.11) with initial data $z_1, \dots, z_N \in \mathbb{R}^{2d}$. It can be used as integrator in the `quadrature()` routine

whenever one only has to solve Hamilton's equation(16.11) and no additional ODEs. This is the case for all phase space integrals in the approximations A–D except for the Husimi correction (16.4), for which one also has to approximate $\Lambda_\varepsilon^t(z_j)$ and $\Gamma_\varepsilon^t(z_j)$, $j = 1, \ldots, N$.

```
function [out] = stoermer-verlet(z,V,τ,t)
% INPUT:    z     initial conditions [z_1,...,z_N]
%           V     the potential
%           τ     time stepping for integrator
%           t     time for evaluation
% OUTPUT:   out    [F_τ^t(z_1),...,F_τ^t(z_N)]
q = z(1:d,:);      % initial positions
p = z(d+1:2d,:);   % initial momenta

p = p - (τ/2)*∇V(q); % first half step with Φ_a^{τ/2}
% apply F_τ as often as it is required to reach
% the time  t-τ
for j=1:((t/τ)-2);
    q = q + τ*p;
    p = p - τ*∇V(q);
end
% do the last step with the integrator
q = q + τ*p;
p = p - (τ/2)*∇V(q)
out = [q,p];
end
```

In order to avoid unnecessary computational efforts, in the above algorithm we replaced two subsequent steps with $\Phi_a^{\tau/2}$ by a full step Φ_a^τ.

16.4 The Error

If one combines the structural ε-dependent errors of the semiclassical approximations B–D from above with the discretization errors

from §16.2 and §16.3, we arrive at the following formulas for the overall error of the discretized Spectrogram, Husimi, and naive Husimi methods. In Proposition 26 we do not treat the Wigner method for which the sampling step is not feasible in general. As soon as one has a sampling strategy for $\mathcal{W}^\varepsilon(\psi)$, similar error estimates apply.

Proposition 26. *Let $\varepsilon > 0$, $t > 0$, $a \in \mathcal{S}(\mathbb{R}^{2d})$, $N, M \in \mathbb{N}$ and $\psi \in L^2(\mathbb{R}^d)$. Suppose that f_τ^t, g_τ^t are order κ symplectic integrators for $\Phi^t, \Phi_\varepsilon^t$ with stepsize τ, and L_σ^t, G_σ^t are order κ approximations for $\Lambda_\varepsilon^t, \Gamma_\varepsilon^t$ with stepsize σ. Then, if we apply Monte-Carlo sampling, one has*

$$\begin{aligned}
\left\langle \widehat{a(t)} \right\rangle_\psi &= (1+\tfrac{d}{2})\mathbb{Q}_{p_0}^N[a \circ f_\tau^t] - \tfrac{d}{2}\mathbb{Q}_{p_1}^N[a \circ f_\tau^t] + O(\varepsilon^2 + N^{-1/2} + \tau^\kappa) \\
\left\langle \widehat{a(t)} \right\rangle_\psi &= \mathbb{Q}_{p_0}^N[a_\varepsilon \circ g_\tau^t] - \tfrac{\varepsilon}{2}\mathbb{Q}_{p_0}^M[\mathrm{tr}(L_\sigma^t(D^2 a \circ g_\sigma^t)) + G_\sigma^t \cdot (\nabla a \cdot g_\sigma^\varepsilon)] \\
&\qquad + O(\varepsilon^2 + N^{-1/2} + \tau^\kappa + \varepsilon(M^{-1/2} + \sigma^\kappa)) \\
\left\langle \widehat{a(t)} \right\rangle_\psi &= \mathbb{Q}_{p_0}^N[a \circ f_\tau^t] + O(\varepsilon + N^{-1/2} + \tau^\kappa)
\end{aligned}$$

for the spectrogram (upper) the Husimi (middle), and the naive Husimi (lower) methods, where $p_0 = \mathcal{H}_0^\varepsilon(\psi)$ and $p_1 = \frac{1}{d}\sum_{|k|=1} \mathcal{H}_k^\varepsilon(\psi)$.

The error estimates in the case of Quasi-Monte Carlo quadrature just differ by the convergence rate in N and M, see §16.2.

Proof. The ε- dependent part in the error is due to the semiclassical approximation, see (16.2), (16.3), and (16.5), while the parts dependent on N and M stem from the Monte-Carlo quadrature (16.8). The other errors are due to the approximation of the time evolution in (16.9). □

Let us highlight that for the Husimi method one requires less sampling points for the quadrature of the correction integral since it comes with an additional prefactor ε, see also the comments in [GL14, §3.4]. In order to obtain overall errors of size $O(\varepsilon^2)$ or

$O(\varepsilon)$, one consequently has to choose the appropriate ε-dependent number of sampling points, and ε-dependent time stepping for the numerical integrators.

Example. We apply the Wigner method to a one-dimensional model for the dynamics of a diatomic iodine molecule I_2 on the lowest PES, see also [KL14]. The degree of freedom is the internuclear distance r, and the electronic ground state is modelled by a Morse potential fitted to data, see [BY73],

$$V_{I_2}(r) = D_e \left(1 - \mathrm{e}^{-\alpha(r-r_e)}\right)^2 . \tag{16.13}$$

One has $D_e = 0.0572$ hartree, $\alpha = 0.983 a_0^{-1}$, and $r_e = 5.03855 a_0$, where the Bohr radius a_0 is unity in atomic units. After an energy rescaling, see [KL14, §V.A], one arrives at the semiclassical Schrödinger operator

$$H = -\tfrac{\varepsilon^2}{2}\partial_r^2 + (1 - \mathrm{e}^{-\alpha(r-r_e)})^2 \tag{16.14}$$

with $\varepsilon = \sqrt{1/(mD_e)} = 0.0122$, where $m = 1.165 \cdot 10^5$ a.u is the reduced mass. This model has been used for the exploration of methods in the chemistry literature before, see [FM96, WTS$^+$01, TW04].

As in [KL14, WTS$^+$01], we consider the Gaussian initial data $\varphi_0^\varepsilon[(4.53, 0); (1.38, \mathrm{i})]$, which implies that the Wigner transform is a two-dimensional Gaussian function. Hence, the sampling step poses no difficulties. We use Sobol quasirandom numbers for the sampling, and choose the Störmer-Verlet scheme for time propagation.

In figure 5 we depict the error of the Wigner method with respect to highly accurate reference solutions[5] for four observables, and different values numbers of Sobol points N and time steppings τ.

[5]The reference solutions are generated by the Fourier split-step method, see also appendix §E, with $2 \cdot 10^4$ Fourier modes on the interval $[3, 11]$, and $2 \cdot 10^6$ time steps.

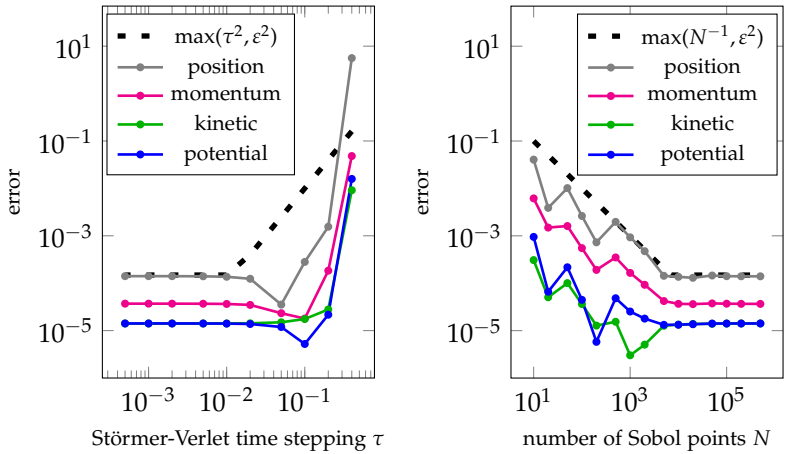

FIGURE 5: Average errors of the Wigner method applied to four observables on the time interval $[0, 166\text{fs}]$ for the one-dimensional Hamiltonian (16.14) with initial data $\varphi_0^\varepsilon[(4.53, 0); (1.38, \mathrm{i})]$. We compare different numbers N of Sobol points for the quadrature, and time steppings τ for the Störmer-Verlet integrator. For the left plot we use 10^5 Sobol points, and for the right plot a time stepping of $\tau = 10^{-3}$.

As expected, the overall error of the approximation converges to the structural error of size $O(\varepsilon^2)$ of the Egorov theorem whenever the time steppings become small[6], $\tau \approx \varepsilon$, or the number of Quasi-Monte Carlo quadrature points becomes large, $N^{-1} \approx \varepsilon^2$, compare also Proposition 26. ■

17 Numerical Experiments

17.1 Accuracy

Let us first present numerical experiments with varying parameter ε in order to validate the second order accuracy in ε of the Husimi

[6]Recall that the Störmer-Verlet method is of second order.

and Spectrogram method, and the first order accuracy of the naive Husimi method. For this purpose, as in [FGL09, LR10, KL13, GL14, KLO15] we consider the two-dimensional torsional potential

$$V(q_1, q_2) = 2 - \cos(q_1) - \cos(q_2), \qquad q \in \mathbb{R}^2,$$

and different values $10^{-3} \leq \varepsilon \leq 10^{-1}$ of the semiclassical parameter. As initial data we take the Gaussian wave packet $\varphi_0^\varepsilon[z, (\mathrm{Id}, \mathrm{iId})]$ with phase space center $z = (1, 0, 0, 0)$. Then, we apply the Husimi and the spectrogram method to compute the expectation values for the following classical observables $a : \mathbb{R}^4 \to \mathbb{R}$:

i) Position: $a(q, p) = q_1$ and $a(q, p) = q_2$,

ii) Momentum: $a(q, p) = p_1$ and $a(q, p) = p_2$,

iii) Kinetic energy: $a(q, p) = \frac{1}{2}|p|^2$,

iv) Potential energy: $a(q, p) = V(q)$,

v) Total energy: $a(q, p) = \frac{1}{2}|p|^2 + V(q)$.

We compare the outcome of the Husimi and spectrogram method with highly accurate grid based reference solutions generated by the split-step Fourier method, see appendix §E and table 3 for details. The error for the position and momentum expectations is measured via the euclidean distance on $\mathbb{R}^2$. A variety of experiments for the Wigner method can be found in [LR10] and our joint paper with Caroline Lasser [KL14].

In all experiments we used the eighth order symplectic splitting integrator from [Yos90, Table 2.D] with time stepping 10^{-1} for the time propagation. For the Husimi and naive Husimi methods we employed Sobol sequences for the quadrature, see also table 1. The two panels in figure 6 confirm that the Husimi and naive Husimi methods are indeed of second respectively first order in ε, as predicted by Proposition 26.

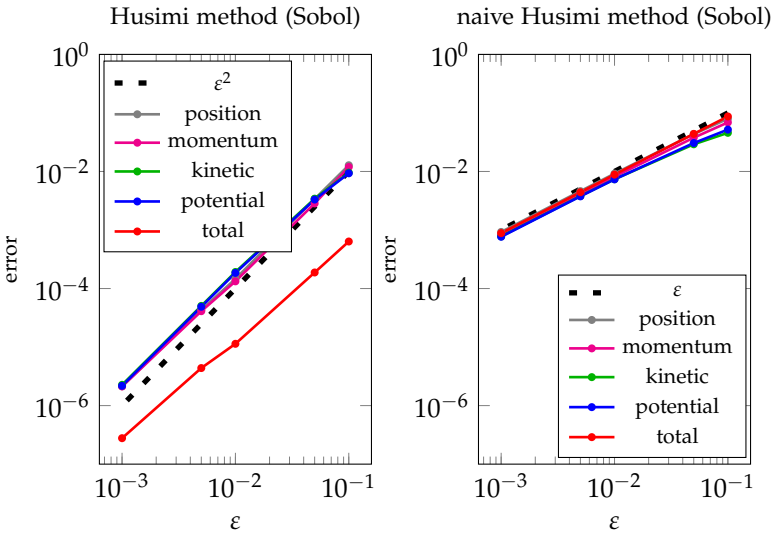

FIGURE 6: Average errors over the time interval $[0, 20]$ for the position, momentum, and energy expectations computed by the the Husimi (left) and naive Husimi (right) methods with Sobol sampling. As setup we used the two-dimensional torsional potential and Gaussian initial data $\varphi_0^\varepsilon[z_0, (\mathrm{Id}, \mathrm{iId})]$ centered in $z_0 = (1, 0, 0, 0)$.

Moreover, figure 7 illustrates that the spectrogram method is of second order in ε. Both, Monte Carlo quadrature and the heuristic Halton sampling method described in §16.2, yield good results for the spectrogram method, compare also [KLO15, Figure 6.1 and Appendix A.3]. The used number of sampling points and required computation times for the spectrogram method with Halton respectively Monte-Carlo sampling can be found in table 2. As expected, the computational efforts scale linearly with respect to the number of initial sampling points.

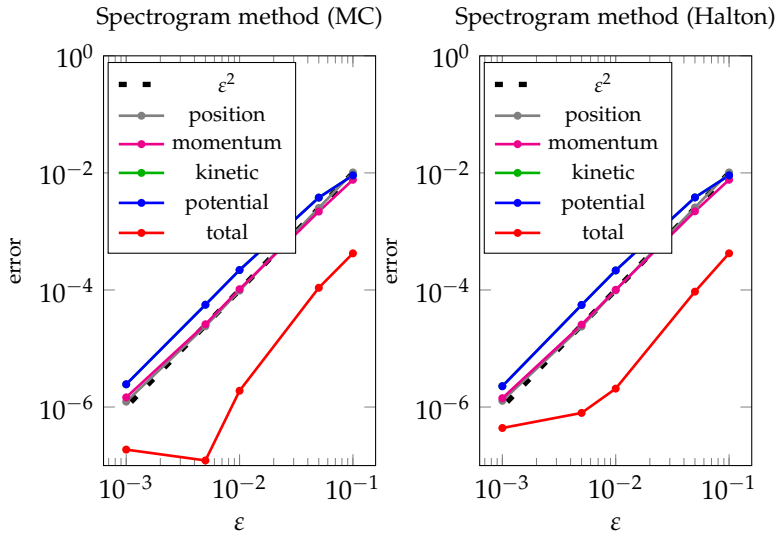

FIGURE 7: Average errors over the time interval $[0, 20]$ for different observables computed by the the Spectrogram method with Monte Carlo (left) and the heuristic Halton (right) sampling for the two-dimensional torsional potential and Gaussian initial data $\varphi_0^\varepsilon[z_0, (\mathrm{Id}, \mathrm{iId})]$ centered in $z_0 = (1, 0, 0, 0)$.

ε	flow nodes N_1	correction nodes N_2
10^{-1}	10^4	10^3
$5 \cdot 10^{-2}$	$3 \cdot 10^4$	$3 \cdot 10^3$
10^{-2}	10^5	10^4
$5 \cdot 10^{-3}$	$3 \cdot 10^5$	$2 \cdot 10^4$
10^{-3}	10^6	$5 \cdot 10^4$

TABLE 1: Number of Sobol points N_1 for the naive Husimi method and the leading term in the Husimi method, and number of Sobol points N_2 for the first order correction integral (16.4) in the Husimi method. The results for the Husimi and naive Husimi algorithm are depicted in Figure 6.

Experiments for the Husimi method applied to the same two-dimensional torsional potential with Gaussian superpositions as initial data can be found in [KL13].

ε	MC points	comp. time	Halton points	comp. time
10^{-1}	$5 \cdot 10^4$	23s	$5 \cdot 10^4$	16s
$5 \cdot 10^{-2}$	$3 \cdot 10^5$	1m59s	10^5	33s
10^{-2}	$6 \cdot 10^5$	7m16s	$2 \cdot 10^5$	1m59s
$5 \cdot 10^{-3}$	$1.5 \cdot 10^6$	14m15s	$8 \cdot 10^5$	6m50s
10^{-3}	$10 \cdot 10^6$	68m30s	$2 \cdot 10^6$	18m31s

TABLE 2: Computational data for the execution of the spectrogram algorithm for the two dimensional torsional potential and Gaussian initial data centered in $z_0 = (1, 0, 0, 0)$ on the time interval $[0, 20]$. The computation times are for one run only.

ε	#timesteps	comp. domain	space grid
10^{-1}	$5 \cdot 10^3$	$[-3, 3] \times [-3, 3]$	1536×1536
$5 \cdot 10^{-2}$	$5 \cdot 10^3$	$[-3, 3] \times [-3, 3]$	1536×1536
10^{-2}	$7.5 \cdot 10^3$	$[-2, 2] \times [-2, 2]$	2048×2048
$5 \cdot 10^{-3}$	10^4	$[-2, 2] \times [-2, 2]$	2048×2048
10^{-3}	10^4	$[-2, 2] \times [-2, 2]$	2048×2048

TABLE 3: The parameters for the numerically converged, grid-based reference solutions of the two-dimensional torsional potential. The discretization has been performed by Fourier collocation in space and Strang splitting in time.

17.2 Quantum Effects: Escape from a Potential Well

It is important to investigate in how far the semiclassical algorithms are capable of describing important quantum effects, like the escape

of a quantum particle from a cubic potential well [7].

For this purpose we consider the Schrödinger operator $H = -\frac{\varepsilon^2}{2}\Delta + V$ with the large semiclassical parameter $\varepsilon = 0.4642$ and the one-dimensional barrier potential

$$V(q) = 2.328 \cdot q^2 + q^3 + 0.025q^4, \qquad q \in \mathbb{R},$$

see also figure 8. Starting from the Schrödinger operator

$$-\tfrac{1}{2}\hbar^2\Delta + \tfrac{1}{2}x^2 + 0.1x^3$$

with $\hbar = 1$ from [OL13, PP00], one arrives at the Hamiltonian H by conducting the space rescaling $x \mapsto \sqrt[3]{0.1}x$. We add a small quartic confinement term $0.025 \cdot q^4$ that prevents trajectories from finite time blow up, and guarantees that H is essentially self-adjoint on $\mathcal{C}_c^\infty(\mathbb{R}^d)$, see [RS75, Theorem X.28]. The global potential energy minimum $V(x_{\text{glob}}) \approx -4765$ is attained at $x_{\text{glob}} \approx -28.4$, and the confinement term is negligible in the region of interest close to the origin.

As initial data we use translated Hermite functions $\varphi_k^\varepsilon[z_0, (1, \mathrm{i})]$ localized $z_0 = (0.4642, -1)$, which corresponds to the phase space center used in [OL13]. Since the associated classical energy $h(z_0) \approx 1.1$ lies below the barrier energy $V_b \approx 2.03$, which is attained at $x_{\max} \approx -1.62$, the classical particle is trapped in the well for all times. Hence, it moves on a periodic orbit since the configuration space is one-dimensional. The energy of the Gaussian state $\varphi_0^\varepsilon[z_0, (i, \mathrm{i})]$ and the excited states $\varphi_k^\varepsilon[z_0, (1, \mathrm{i})]$, $k \in \mathbb{N}$, however, is larger than the potential barrier. Consequently, the expected phase space center of the quantum particle will escape from the potential after short times. We investigate in how far the spectrogram algorithm is capable of desribing the qualitative dynamics of this escape process, even when the semiclassical parameter is large.

[7] This section in large parts corresponds to section §6.2 in our joint work [KLO15] with Caroline Lasser and Tomoki Ohsawa.

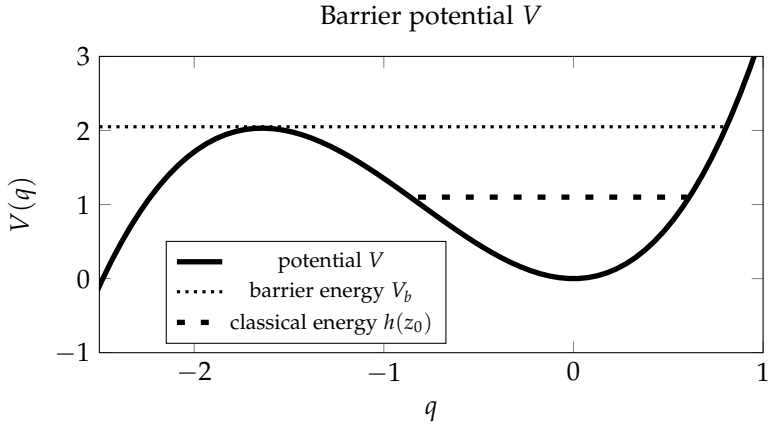

FIGURE 8: The cubic barrier potential V with the barrier energy V_b. The energy $h(z_0)$ of the classical particle is smaller than V_b and, hence, the classical particle is trapped.

In order to obtain numerically converged results, for the spectrogram algorithm we used 2^{14} Halton points and the same eighth-order symplectic integrator as for the experiments presented in §17.1 with time stepping 10^{-2}. This choice results in overall computation times of 2 seconds. The highly accurate quantum references are generated by means of a Strang splitting with 2^{15} Fourier modes on the interval $[-40, 4]$.

As initial data we use the translated Hermite functions $\varphi_k^\varepsilon[z_0, (1, \mathrm{i})]$ with $k \in \{0, 1, 3, 6\}$, and we compare the evolution of the expected position and momentum obtained by the spectrogram method with the quantum references. Figure 10 confirms that the spectrogram method is capable of giving a decent qualitative description of the escape process, despite the fact that the semiclassical parameter is large.

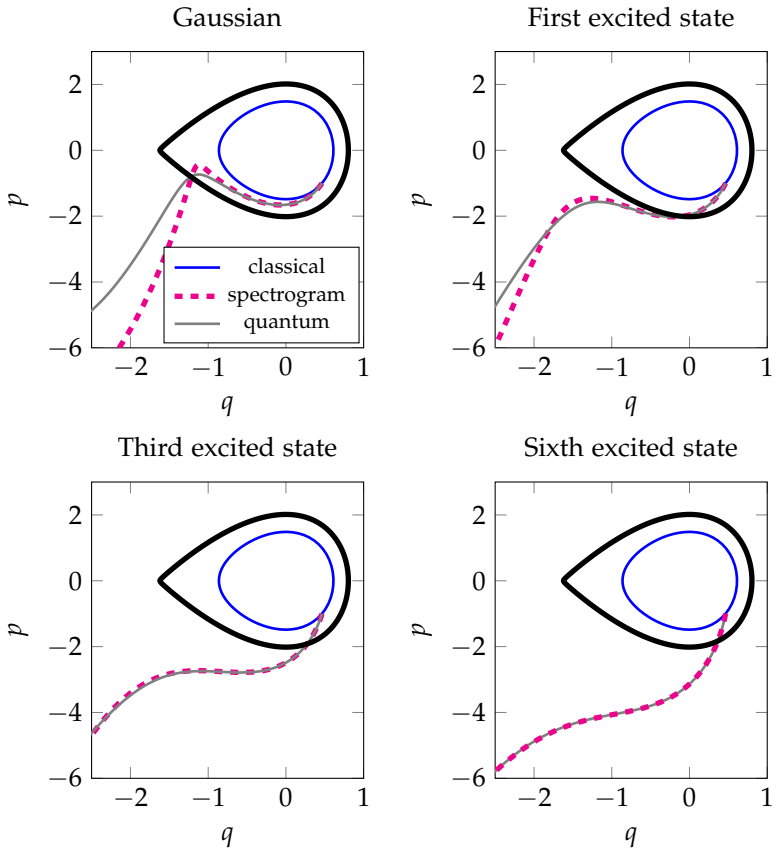

FIGURE 9: The phase space trajectories of the classical particle, and the trajectories of the expected phase space centers for the quantum solution, and the spectrogram approximation for the barrier potential V and the four initial states $\varphi_k^\varepsilon[z_0, (1, \mathrm{i})]$ with $k \in \{0, 1, 3, 6\}$. The border of the classical trapping region is illustrated by the thick black line.

We furthermore note that the errors become smaller for higher energy initial data. This can be explained by the shorter times after

which the trajectories leave the classical trapping region, compare figure 10, and by the fact that fewer of the classical trajectories used by the spectrogram method come close to the hyperbolic fixed point $(x_{\max}, 0)$ of the flow. At such local maxima of the potential the errors in Egorov's theorem are known to grow exponentially in time, see [BR02, Example 6.2].

The spectrogram algorithm can also be used to explore the evolution of the probability that the particle escaped from the potential well and can be found within the region $(-\infty, x_{\max}]$. We approximate this escape probability by

$$\langle \psi_t, \mathrm{op}(r)\psi_t \rangle \approx \|\psi_t \chi_{(-\infty, x_{\max}]}\|_{L^2}^2 =: P_{\mathrm{esc}}(t), \tag{17.1}$$

with the smooth symbol $r(q,p) = \exp(-0.01/(q - x_{\max})^2)\mathbb{1}_{(-\infty, x_{\max}]}(q)$. Then, $P_{\mathrm{esc}}(t)$ can be approximated by the spectrogram algorithm.

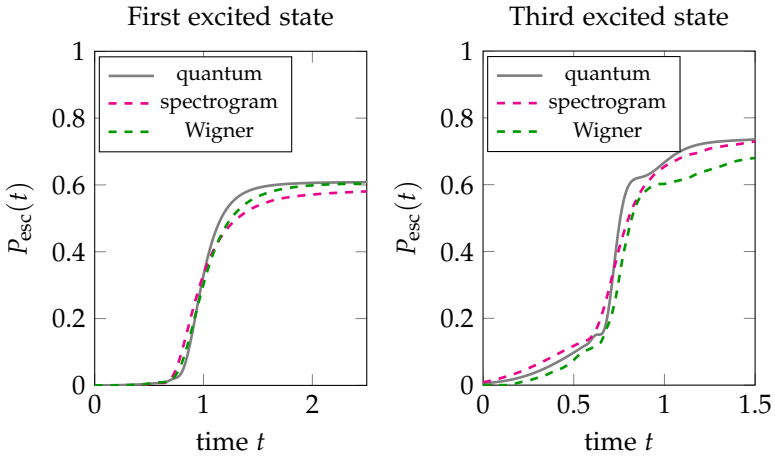

FIGURE 10: Approximate escape probabilities $P_{\mathrm{esc}}(t)$ for a highly accurate quantum reference, and the results of the spectrogram and Wigner methods for the initial states $\varphi_k^\epsilon[z_0, (1, \mathrm{i})]$ with $k \in \{1, 3\}$.

Figure 10 shows by means of the two different initial states $\varphi_k^\varepsilon[z_0, (1, \mathrm{i})]$ with $k \in \{1, 3\}$ that the spectrogram algorithm yields a good qualitative picture of the evolution of escape probabilities. Moreover, it illustrates that the results are comparable to the outcome of the Wigner method.

17.3 High Dimensions

In a final experimental setup we demostrate the applicability of the spectrogram method in moderately high dimensions. For our experiments, which can also be found in [KLO15, §6.3], we consider the 32-dimensional Hénon–Heiles tyle potential[8]

$$V_{32}(q) = \tfrac{1}{2}|q|^2 + 1.8436 \sum_{j=1}^{31} (q_j^2 q_{j+1} - \tfrac{1}{3} q_{j+1}^3) + 0.4 \sum_{j=1}^{31} (q_j^2 + q_{j+1}^2)^2, \tag{17.2}$$

and the semiclassical parameter $\varepsilon = 0.0029$.

In [NM02], Hénon–Heiles potentials in different dimensions have been used for benchmark calculations with the multiconfiguration time-dependent Hartree method (MCTDH) method. There, they are taken as a model for exploring the dynamics of a hydrogen atom on a high-dimensional potential energy surface that exhibits regions of instable motion. As in [RM00], or for the potential well in §17.2, we add a small quartic confinement in order to obtain a self-adjoint Hamiltonian, and classical trajectories of finite speed.

We investigate the performance of the Wigner, spectrogram, and naive Husimi methods for the evolution of potential energies. As in [NM02, KL14, KLO15], the initial state is a Gaussian wave packet $\psi_0 = \varphi_0^\varepsilon[z, (\mathrm{Id}, \mathrm{iId})]$ centered at $z = (q, p)$ with $p = 0$ and $q_j = 0.1215$ for all $j = 1, \ldots, 32$. There is no possibility to generate reliable references for the the 32-dimensional Henon–Heiles system.

[8] The two-dimensional version of this potential can be traced back to the work [HH64] of Hénon and Heiles on celestial mechanics.

However, since the initial data is Gaussian, there is no difficulty in the sampling when applying the Wigner method and we can compare the outcome of the Wigner, the spectrogram, and the naive Husimi method. We do not include the Husimi method in this experiment since approximating the flows $\Lambda_\varepsilon^t : \mathbb{R}^{64} \to \mathbb{R}^{64\times 64}$ and $\Gamma_\varepsilon^t : \mathbb{R}^{64} \to \mathbb{R}^{64}$ for the correction is extremely costy with the MATLAB implementation we used. For all three methods we used 2^{17} Sobol points for the quadrature, and the same eighth order symplectic integrator as for the calculations in §17.1 and §17.1 with time stepping $2 \cdot 10^{-2}$.

Potential energies for the 32-dimensional Hénon–Heiles system

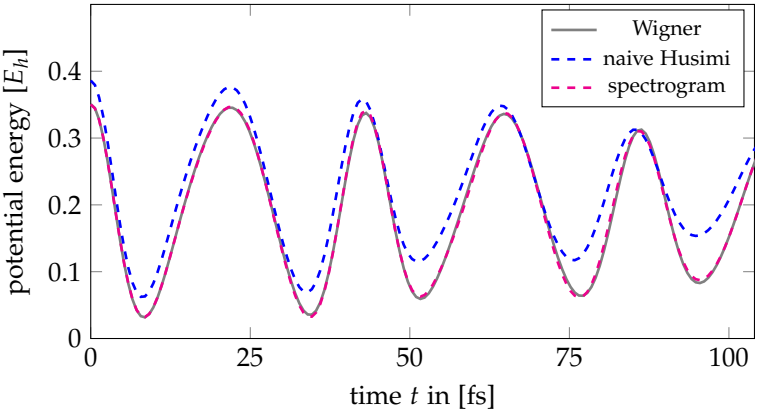

FIGURE 11: Approximate dynamics of the expected potential energies measured in hartree (E_h) for the 32-dimensional Hénon–Heiles system computed by the Wigner, spectrogram, and naive Husimi methods up to 104 femtoseconds.

Figure 11 illustrates by means of the potential energies that the outcomes of the Wigner and the spectrogram method are virtually indistinguishable, while the results of the naive Husimi method differ substantially.

Remark 18. *For parallel GPU implementations of semiclassical algorithms like the Wigner method, and experiments for Hénon–Heiles systems in up to* 512 *dimensions see the recent work of David Sattlegger and Manfred Liebmann [LS15].*

Summary and Outlook

In this dissertation we investigated various simplifications for the states and the dynamics of molecular quantum systems. We started with a discussion of the Born-Oppenheimer approximation and potential energy surfaces in the first part §I. Afterwards, in §II , we investigated the structure of the highly localized Hagedorn wave packets in configuration and phase space. In part §III we explored semiclassical approximations for the quantum evolution of expectation values and states. In part §IV we finally provided algorithmic discretizations for the expectation value approximations discussed before, and illustrated their applicability in numerical experiments.

For the applications in chemistry we have in mind, solving the corresponding time-dependent Schrödinger equation with direct numerical methods is computationally unfeasible and the use of approximations is indespensable. The central goal of our investigations is the development of approximations for molecular quantum dynamics that allow for both, applicable algorithmic discretizations, and rigorous error estimates. In this second demand our approach differs from many popular approximations that are successfully applied in chemistry, like the MCTDH method, since for many of them there are no rigorous convergence results or error estimates.

A strategy which we would like to advertise with this dissertation is the concerted use of approximations for quantum states and observables. This combination of wave packet techniques and semiclassical operator analysis can be useful for the enhancement or development of semiclassical approximations. One example is the local Egorov theorem in §15.3, whose proof requires both, the semiclassical Moyal expansion to approximate the Heisenberg evolution of quantum observables, and propagated Hagedorn wave packets to control the errors away from the classical path. Another example is provided by our Egorov type approximation with spectrogram

densities, for which we used wave packets to derive the structure and the explicit form of the new density $\mu_2(\psi)$.

The results and discussions in this thesis immediately suggest several generalizations and applications that would be interesting to address in future research. One could for instance include the following topics (of varying inticracy):

It would be desirable to exploit the fine properties of Hagedorn wave packets we derived in §II in numerical schemes for selfadjoint and non-selfadjoint evolution problems. For instance, the phase space factorization of the Wigner functions of Hagedorn wave packets could alleviate the quadrature for the matrix elements in Galerkin type spacial discretizations of the Schrödinger equation with wave packet bases, see e.g. [FGL09, GH14].

The Wigner-Hagedorn formula from §8 ensures that the Wigner functions of Hagedorn wave packets are again Hagedorn wave packets in phase space. Hence, one could directly develop semi-classical approximations and numerical methods for the evolution of Wigner functions in phase space, that is, for solutions of the Quantum Liouville equation. One could use the same techniques as for the evolution in configuration space and benefit from the additional knowledge about the special form of the wave packets.

Another line of investigation would be to generalize the second order Egorov type propagation result with spectrogram densities from §12.2 to higher order errors. This can presumably be achieved without too much effort by proving a higher order spectrogram expansion in the spirit of Conjecture 1 , and combining it with higher order versions of the Egorov theorem, see §11. One could then derive algorithmic discretizations by using similar methods as in [GL14]. A deeper analysis of the properties of spectrogram expansions could also be very fruitful for understanding the structure of quantum states in phase space.

The size of the Ehrenfest time scales for the local Egorov theorem in §15.3 is determined by the lower bound for the delocalization

time of the involved wave packets. Nevertheless, we strongly believe that this bound is due to our proof technique, and the result holds for the longer Ehrenfest time scales from [BR02]. However, with standard semiclassical techniques it impossible to prove anything beyond Ehrenfest time, although numerical experiments suggest that the approximations are valid for much longer time intervals. This could serve as a motivation to develop new tools for analyzing the evolution of quantum systems beyond the Ehrenfest time. A promising first approach could be to use explicit quantum dispersion operators as introduced in [GS12]. Similarly as the advent of quantum mechanics inspired and stimulated the development of many fields of mathematics, novel mathematical insights into the long-time behaviour of quantum systems could in turn deepen our understanding of the foundations of molecular dynamics and chemistry.

Appendix

A Notation

For the sake of completeness, let us summarize some definitions and denotations for important mathematical objects we use. For the most part they can be considered as basic knowledge. Note that in this dissertation we assume the set of natural numbers $\mathbb{N}$ to include zero.

For any two vectors $x, y \in \mathbb{C}^d$ the inner product is defined as

$$\langle x, y \rangle = \sum_{j=1}^{d} x_j \overline{y_j}.$$

The norm of x is given by $|x| = \sum_{j=1}^{d} |x_j|^2$, and the 'Japanese brackets' are defined as

$$\langle x \rangle := (1 + |x|^2)^{1/2}, \quad x \in \mathbb{R}^d.$$

Let $d \in \mathbb{N}$ and $X \in \{\mathbb{R}^m, \mathbb{C}^m\}$ with $m \in \mathbb{N}$. We use the spaces of smooth functions

$$\mathcal{C}^n(\mathbb{R}^d, X) := \{f : \mathbb{R}^d \to X \text{ is } n \in \mathbb{N} \cup \{\infty\} \text{ times cont. differentiable}\}$$
$$\mathcal{C}_c^n(\mathbb{R}^d, X) := \{f \in \mathcal{C}^n(\mathbb{R}^d, X) \text{ and } f \text{ has compact support}\}$$
$$\mathcal{S}(\mathbb{R}^d, X) := \{f \in \mathcal{C}^\infty(\mathbb{R}^d, X) : \sup_{x \in \mathbb{R}^d} |x^\alpha \partial^\beta f(x)| < \infty \ \forall \alpha, \beta \in \mathbb{N}^d\}$$

where the third one is called the Schwartz space. The dual space $\mathcal{S}'(\mathbb{R}^d, X)$ of the Schwartz space is the space of tempered distributions. We employ the following infinite-dimensional Banach spaces (L^2 and the Sobolev spaces H^s are actually Hilbert spaces)

$$L^p(\mathbb{R}^d, X) := \Big\{ f : \mathbb{R}^d \to X \text{ measurable} : \big(\int_{\mathbb{R}^d} |f(x)|^p dx \big)^{1/p} < \infty \Big\}$$
$$H^s(\mathbb{R}^d, \mathbb{C}^m) := \big\{ f \in \mathcal{S}'(\mathbb{R}^d, \mathbb{C}^m) : \langle \xi \rangle^s \, (\mathcal{F}\psi)(\xi) \in L^2(\mathbb{R}^d, \mathbb{C}^m) \big\}$$

for $p \geq 1$ and $s \in \mathbb{R}$. For the definition of the Sobolev spaces we used the Fourier transform

$$(\mathcal{F}\psi)(\xi) = (2\pi)^{-d/2} \int_{\mathbb{R}^d} \mathrm{e}^{-\mathrm{i}\xi \cdot x} \psi(x) dx, \quad \xi \in \mathbb{R}^d,$$

which defines a unitary map in $L^2(\mathbb{R}^d, \mathbb{C}^m)$, and maps both the Schwartz space $\mathcal{S}(\mathbb{R}^d, \mathbb{C}^m)$ and $\mathcal{S}'(\mathbb{R}^d, \mathbb{C}^m)$ into itself. Whenever the image space coincides with $\mathbb{C}$ we omit the second argument in the notation. Hence, $\mathcal{C}^n(\mathbb{R}^d, \mathbb{C}) = \mathcal{C}^n(\mathbb{R}^d)$, $L^p(\mathbb{R}^d, \mathbb{C}) = L^p(\mathbb{R}^d)$ and so on.

Let $(X, \| \bullet \|_X)$ and $(Y, \| \bullet \|_Y)$ be Banach spaces. We denote by $\mathcal{L}(X, Y)$ the space of bounded operators from X to Y, and abbreviate $\mathcal{L}(X, X) = \mathcal{L}(X)$. Suppose that $A : X \to Y$ is bounded. Then the operator norm of A is defined as

$$\|A\|_{\mathcal{L}(X,Y)} := \sup\{ \|Ax\|_Y : \ x \in X \text{ with } \|x\|_X \leq 1 \}.$$

The adjoint operator of A is defined by

$$A^\dagger : Y^* \to X^*, \quad \langle Ax, y \rangle_{Y,Y^*} = \Big\langle x, A^\dagger y \Big\rangle_{X,X^*}$$

for all $(x, y) \in X \times Y$. Here, X^* and Y^* denote the dual spaces of X and Y, respectively, and $\langle \bullet, \bullet \rangle_{X,X^*}$ is the duality bracket. The same definition extends to closed operators A with dense domain $D(A) \subset X$.

If X is a Hilbert space, one can identify X and X^* by Riesz' representation theorem. Then, a densely defined and closed Hilbert

space operator $H : D(H) \subset X \to X$ is called *selfadjoint* if the adjoint operator coincides with H and has the same dense domain,

$$H^\dagger = H, \quad D(H) = D(H^\dagger) \subset X.$$

For the derivatives of a function $f : \mathbb{R}^d \to \mathbb{C}$ we use the conventions

$$\begin{aligned}
\partial_j f(x) &:= \frac{d}{dx_j} f(x) \\
\partial^\alpha f &:= \partial_1^{\alpha_1} \cdots \partial_d^{\alpha_d} f \qquad \text{for } \alpha \in \mathbb{N}^d \\
\nabla f &:= (\partial_1 f, \ldots, \partial_d f)^T && \text{(gradient)} \\
D^2 f &:= (\partial_i \partial_j f)_{i,j=1}^d && \text{(Hessian)} \\
\Delta f &:= \mathrm{tr} D^2 f && \text{(Laplacian)}
\end{aligned}$$

and if $g : \mathbb{R}^d \to \mathbb{R}^m$, we write

$$Dg := (\partial_1 g, \ldots, \partial_d g) : \mathbb{R}^d \to \mathbb{R}^{m \times d} \qquad \text{(Jacobian)}.$$

B Symbol Classes

Any calculus of pseudodifferential operators usually cames along with appropriate classes of symbols whose quantization results in linear operators with certain properties. The most well-known symbol classes are probably the Hörmander classes

$$\begin{aligned}
S^m_{\rho,\delta} = \{ a \in \mathcal{C}^\infty(\mathbb{R}^{2d}) : &\text{for all } \alpha, \beta \in \mathbb{N}_0^d \exists C_{\alpha\beta} > 0 \text{ with} \\
&|\partial_\xi^\alpha \partial_x^\beta a(x,\xi)| \leq C_{\alpha\beta} \langle \xi \rangle^{m - \rho|\alpha| + \delta|\beta|} \}
\end{aligned}$$

with $0 \leq \delta \leq \rho \leq 1$, $\delta < 1$. However, the classes $S^m_{\rho,\delta}$ are in a certain way unbalanced in their treatment of position and momentum, as symbols are not allowed to be unbounded in the position variables.

We therefore use the definition of symbol classes from [Zwo12, §4.4]: A measurable function $m : \mathbb{R}^{2d} \to (0, \infty)$ is called an *order function*, if there are C, N such that

$$m(w) \leq C \langle z - w \rangle^N m(z)$$

for all $z, w \in \mathbb{R}^{2d}$. For example, $m(z) = \langle z \rangle$ or $m(q, p) = \langle x \rangle^\alpha \langle \xi \rangle^\beta$ are order functions. For an order function m we then define the symbol classes

$$\begin{aligned} S(m) = \{a \in \mathcal{C}^\infty(\mathbb{R}^{2d}) : &\text{ for all } \alpha \in \mathbb{N}^{2d} \text{ there is } C_\alpha > 0 \text{ with} \\ &|\partial^\alpha a(z)| \leq C_\alpha m(z)\} \end{aligned}$$

as well as

$$\begin{aligned} S_\delta(m) = \{a \in \mathcal{C}^\infty(\mathbb{R}^{2d}) : &\text{ for all } \alpha \in \mathbb{N}^{2d} \text{ there is } C_\alpha > 0 \text{ with} \\ &|\partial^\alpha a(z)| \leq \varepsilon^{-\delta|\alpha|} C_\alpha m(z)\}. \end{aligned}$$

For the case $m \equiv 1$ we use the shorthands $S(1) = S$ and $S_\delta(1) = S_\delta$. Note that one often has to assume $\delta < \frac{1}{2}$ in order to obtain meaningful semiclassical expansions. For the quantization of operator-valued symbols, as used in the context of adiabatic perturbation theory, we refer to [ST13]. The quantization of molecular Hamiltonians with singular interactions, like Coulomb potentials, is adressed in [MS09].

For a definition and discussion of very general symbol classes associated with metrics on the phase space we refer to the monograph of N. Lerner [Ler10].

C Fundamental Subsets

Weakly dense subsets can be used for identifying Banach space operators on some convenient subspace of the domain. We use this

technique in §4.2 in order to show that the formal derivative of the electronic Hamiltonian coincides with the derivative taken in $\mathcal{L}(H^1, H^{-1})$.

Let X be a Banach space and $V \subset X$. V is called *weakly dense in* X if for all $x \in X$ there is a sequence $\{x_n\} \subset V$ such that

$$\langle x_n, f \rangle_{X,X^*} \to \langle x, f \rangle_{X,X^*} \tag{C.1}$$

for all $f \in X^*$. The following Lemma C.1 follows directly from a classical diagonal argument.

Lemma C.1. *let X be a Banach space, let $A \subset X$ be a dense subset, $V \subset A$, and for all $x \in A$ there is a sequence $\{x_n\}_n \subset V$ such that*

$$\langle x_n, f \rangle_{X,X^*} \to \langle x, f \rangle_{X,X^*}$$

for all $f \in X^*$. Then V is weakly dense in X.

Let us take a look at the density properties of collections of smooth functions that vanish at a subset of the configuration space, e.g., at the singularities of a family of multiplication operators. For any bounded real interval $[a, b]$, $a \leq b$, and $n \in \mathbb{N}$, we can define a family of smooth, real-valued cutoff functions

$$\kappa_n^{[a,b]} \in \mathcal{C}^\infty(\mathbb{R}), \quad \kappa_n^{[a,b]} : (x) = \begin{cases} 1 & , \ x \leq a - \frac{1}{n} \\ \kappa_n^{[a,b]}(x) \in (0,1) & , \ x \in (a - \frac{1}{n}, a) \\ 0 & , \ x \in [a, b] \\ \kappa_n^{[a,b]}(x) \in (0,1) & , \ x \in (b, b + \frac{1}{n}) \\ 1 & , \ x \geq b + \frac{1}{n} \end{cases} \tag{C.2}$$

that satisfies

$$\frac{d^j}{dx^j} \kappa_n^{[a,b]}(x) \leq C_j \cdot n^j, \quad \operatorname{supp}\left(\frac{d^j}{dx^j} \kappa_n^{[a,b]} \right) \subset [a - \tfrac{1}{n}, a] \cup [b, b + \tfrac{1}{n}]$$

for all x and some constant $C_j > 0$. We write

$$\kappa_n^{[a,a]} = \kappa_n^a,$$

and define higher dimensional cutoff functions by taking tensor products. Let

$$L = [a_1, b_1] \times \ldots \times [a_k, b_k] \times \{0\} \times \ldots \{0\} \subset \mathbb{R}^n$$

denote an embedding of a k dimensional cuboid into $\mathbb{R}^n$, where $0 \leq k \leq n$. Then, we define the functions $K_n^L : \mathbb{R}^n \to \mathbb{R}$ analoguously to $\kappa_n^{[a,b]}$ via

$$K_n^L(x) = 1 - \prod_{j=1}^{n} (1 - \kappa_n^{[a_j,b_j]}(x_j)) \,, \tag{C.3}$$

where $a_j = b_j = 0$ for all $j > k$. K_n^L is smooth and vanishes to infinite order when approaching the boundary of L from any direction. Moreover, it holds

$$\frac{d^\alpha}{dx^\alpha} K_n^L(x) \leq D_\alpha n^{|\alpha|} \tag{C.4}$$

for $\alpha \in \mathbb{N}^n$ and some $D_\alpha > 0$ independent of L. Given any k-dimensional cuboid $C \subset \mathbb{R}^n$, there is an cartesian embedded k-dimensional cuboid L as above with the same side lengths as C, and an affine transformation $T(x) = Ax + b$ with some orthogonal matrix A, such that $T(C) = L$. We then define

$$K_n^C(x) := K_n^L(T(x))$$

and note that (C.4) still holds for K_n^C with the same constants as for K_n^L.

Spaces of smooth functions vanishing at hypercubes are not necessarily dense in Sobolev spaces. However, as the following result shows, they are weakly dense whenever the order of the Sobolev space is small enough.

Proposition C.1. *Let $A = \bigcup_{j=1}^{S} A_k \subset \mathbb{R}^m$ be a finite union of compact hypercubes A_k in $\mathbb{R}^d$, where[9] $d_k := \operatorname{codim}(A_k) \geq 1$. Then, the set of*

[9] The codimension of a set $A \subset \mathbb{R}^d$ here is defined as $\operatorname{codim}(A) = d - \dim A$.

smooth functions vanishing at A

$$\mathcal{C}^\infty_{c,A}(\mathbb{R}^d) = \{\psi \in \mathcal{C}^\infty_c(\mathbb{R}^d) : \lim_{x\to x_0} \frac{\psi(x)}{|x-x_0|^\alpha} = 0 \text{ for all } x_0 \in A, \alpha \in \mathbb{N}^d\}$$

is dense in $L^2(\mathbb{R}^d)$ and $H^p(\mathbb{R}^d)$ for all $p < \frac{1}{2}\min_k d_k$, and weakly dense in $H^{\frac{1}{2}\min_k d_k}(\mathbb{R}^d)$.

Proof. We only show the weak density approximation property for functions in $\mathcal{C}^\infty_c(\mathbb{R}^d)$. This is enough by the density of $\mathcal{C}^\infty_c(\mathbb{R}^d)$ in $L^2(\mathbb{R}^d)$ and the Sobolev spaces, see Lemma C.1. Let us define the family of functions

$$K^A_n(x) = \prod_{j=1}^S K^{A_k}_j(x)$$

which vanish to infinite order when approaching A and satisfy $0 \le K^A_n \le 1$. Let $T_{1/n}(A) = \operatorname{supp}(1-K^A_n)$ denote a cuboid type neighborhood of width $\frac{1}{n}$ in $\mathbb{R}^d$ around A, and fix $\psi \in \mathcal{C}^\infty_c(\mathbb{R}^d)$. Then, it holds $\psi K^A_n \in \mathcal{C}^\infty_{c,A}(\mathbb{R}^d)$ for all $n \in \mathbb{N}$, and

$$\begin{aligned}\|\psi - \psi K^A_n\|^2_{L^2} &= \|\psi(1-K^A_n)\|^2_{L^2} \\ &= \int_{\mathbb{R}^m} |\psi(x)|^2 (1-K^A_n(x))^2\, dx \le \int_{T_{1/n}(A)} |\psi(x)|^2\, dx \\ &\le \sup_{x\in\mathbb{R}^m} |\psi(x)|^2 \cdot \lambda^d\left(T_{1/n}(A)\right) \to 0\end{aligned}$$

since the volume of $T_{1/n}(A)$ is of size $O(n^{-\min_k d_k})$.

The proof for Sobolev spaces is similar. By definition

$$\|\psi - \psi K^A_n\|^2_{H^p} = \|\psi - \psi K^A_n\|^2_{L^2} + \sum_{|\alpha|\le p} \|\partial^\alpha(\psi - \psi K^A_n)\|^2_{L^2},$$

and for any $\alpha \in \mathbb{N}^d$ it holds

$$\|\partial^\alpha(\psi - \psi K^A_n)\|^2_{L^2} \le \left(\sum_{\beta+\gamma=\alpha} \binom{\alpha}{\beta} \left\|\partial^\beta\psi\partial^\gamma(1-K^A_n)\right\|_{L^2}\right)^2$$

where $\partial^\gamma(1-K_n^A)$ has support in $T_{1/n}(A)$. We can estimate

$$\begin{aligned}
&\left\|\partial^\beta\psi\partial^\gamma(1-K_n^A)\right\|_{L^2}^2 = \int_{\mathbb{R}^d}|\partial^\beta\psi(x)|^2|\partial^\gamma(1-K_n^A)(x)|^2\,dx\\
&\leq \sup_{x\in\mathbb{R}^d}|\partial^\beta\psi(x)|^2\ \lambda^d\left(T_{1/n}(A)\right)\sup_{x\in T_{1/n}(A)}|\partial^\gamma(1-K_n^A)(x)|^2\\
&\leq Cn^{-\min_k d_k}D_\gamma\cdot n^{2|\gamma|}
\end{aligned}$$

for some $C>0$. Moreover, for all $\phi\in\mathcal{C}_c^\infty(\mathbb{R}^d)$ one computes

$$\begin{aligned}
\left\langle\partial_x^\alpha(\psi-\psi K_n^A),\phi\right\rangle &= (-1)^{|\alpha|}\left\langle\psi-\psi K_n^A,\partial_x^\alpha\phi\right\rangle\\
&\to 0
\end{aligned}$$

as $n\to\infty$. The assertion follows from [Kat95, §III, Lemma 1.31]. □

We can exploit the (weak) density of $\mathcal{C}_{c,A}^\infty(\mathbb{R}^d)$ in some Sobolev spaces from Proposition C.1 for identifying the operator derivative of $\widehat{H_{\mathrm{el}}}$ on the Sobolev space H^1, see §4.2. The identification result we use is the following.

Lemma C.2 (Weak fundamental subsets)**.** *Let X, Y be reflexive Banach spaces, $A,B\in\mathcal{L}(X,Y)$ and suppose $\langle\psi,A\phi\rangle_{Y^*,Y}=\langle\psi,B\phi\rangle_{Y^*,Y}$ for all $\psi\in Y^*$ and $\phi\in V\subset X$ where V is weakly dense in X. Then, it holds*

$$\langle\psi,A\phi\rangle_{Y^*,Y}=\langle\psi,B\phi\rangle_{Y^*,Y}$$

for all $\psi\in Y^*$, $\phi\in X$.

Proof. First recall, that the adjoint operators $A^\dagger$, $B^\dagger$ are well-defined operators in $\mathcal{L}(Y^*,X^*)$, see [Kat95, §III.3.3]. It holds

$$\langle\psi,A\phi\rangle_{Y^*,Y}=\left\langle A^\dagger\psi,\phi\right\rangle_{X^*,X}$$

for all $\phi\in X$, $\psi\in Y^*$. Now let $\phi\in X$ be arbitrary. Then, by assumption there is a sequence $\{\phi_n\}\subset V$ which fulfills $\phi_n\overset{w}{\to}\phi$ in

the weak topology of X. Hence, for any $\psi \in Y^*$ we compute

$$\begin{aligned}\langle \psi, A\phi\rangle_{Y^*,Y} &= \left\langle A^\dagger\psi, \phi\right\rangle_{X^*,X} = \lim_{n\to\infty}\left\langle A^\dagger\psi, \phi_n\right\rangle_{X^*,X}\\ &= \lim_{n\to\infty}\left\langle B^\dagger\psi, \phi_n\right\rangle_{X^*,X} = \left\langle B^\dagger\psi, \phi\right\rangle_{X^*,X}\\ &= \langle \psi, B\phi\rangle_{Y^*,Y}\end{aligned}$$

since $A^\dagger\psi$ and $B^\dagger\psi$ are fixed elements in X^*. □

D L^1 Estimates for Hermite cross-Wigner Functions

We prove an estimate for the L^1-norm of the cross-Wigner functions of two semiclassically rescaled, L^2-normalized Hermite functions

$$h_n = \varphi_n^\varepsilon[0,0,1,i].$$

where the order n of the Hermite functions is allowed to grow as $\varepsilon \to 0$. It is a well-known fact that all roots x_k of the Laguerre polynomial $L_n^{(\alpha)}$ satisfy $x_k \leq 4n + 2\alpha + 2$. In the semiclassical setting we can hence infer that the roots y_k of $y \mapsto L_n^{(\alpha)}\left(\frac{2}{\varepsilon}y^2\right)$ lie in the interval

$$y_k \in (0, \sqrt{2\varepsilon n + \varepsilon\alpha + \varepsilon}], \quad k = 1, \ldots, n. \tag{D.1}$$

As usual, we denote the ball of radius r in $\mathbb{R}^2$ by

$$B_r = \{z \in \mathbb{R}^2 : |z| \leq r\}. \tag{D.2}$$

Our localization result is the following.

Proposition D.1 (Phase space L^1-estimates). *Let $\sigma \in (0,1)$ and $n, m \in \mathbb{N}$ with $0 \leq n, m \leq C\varepsilon^{-\sigma}$ for some $C > 0$. Then, for all $\delta > 0$ and $r(\varepsilon) = \alpha\sqrt{\varepsilon^{1-\sigma-\delta}}$ with some constant $\alpha > 0$ one has*

$$\int_{\mathbb{R}^2 \setminus B_{r(\varepsilon)}} |\mathcal{W}^\varepsilon(h_m, h_n)(z)| dz \leq \mathrm{e}^{-\Gamma\varepsilon^{-\sigma-\delta}} \tag{D.3}$$

for some $\Gamma > 0$ independent of n and m if $\varepsilon > 0$ is small enough. Consequently, for all $\delta > 0$

$$\|\mathcal{W}^\varepsilon(h_m, h_n)\|_{L^1} = O(\varepsilon^{-\sigma-\delta})$$

as $\varepsilon \to 0$.

Proof. Without loss of generality, assume $m \leq n$ and abbreviate $\mathcal{W}^\varepsilon(h_n, h_m) = \mathcal{W}^\varepsilon_{n,m}$. Then, by the Wigner-Hagedorn formula from Corollary 3

$$\begin{aligned}\mathcal{W}^\varepsilon_{n,m}(x,\xi) =& \frac{(-1)^m 2^n m! \varepsilon^{-(n-m+2)/2}}{\pi\sqrt{2^{m+n} m! n!}} \\ &\times \mathrm{e}^{-(x^2+\xi^2)/\varepsilon}(x + \mathrm{i}\xi)^{n-m} L_m^{(n-m)}(\tfrac{2}{\varepsilon}(x^2+\xi^2))\end{aligned}$$

and we recall that by the Cauchy-Schwartz inequality

$$\|\mathcal{W}^\varepsilon_{n,m}\|_{L^\infty} \leq (\pi\varepsilon)^{-1}, \tag{D.4}$$

see also [dG11, Proposition 183]. By (D.1) and the definition of $r(\varepsilon)$ we know that

$$(-1)^n L_n^{(n-m)}(\tfrac{2}{\varepsilon}|z|^2) = |L_n^{(n-m)}(\tfrac{2}{\varepsilon}|z|^2)| \tag{D.5}$$

whenever

$$z \notin B_{r(\varepsilon)} = \{z \in \mathbb{R}^2 : |z| \leq r(\varepsilon)\},$$

and ε is small enough. Now, we will cut the phase space into two pieces, namely a ball around the origin and its complement. By

(D.4) we have

$$\int_{\mathbb{R}^2}|\mathcal{W}^{\varepsilon}_{n,m}(z)|dz = \int_{\mathbb{R}^2\setminus B_{\sqrt{2}r(\varepsilon)}}|\mathcal{W}^{\varepsilon}_{n,m}(z)|dz + \int_{B_{\sqrt{2}r(\varepsilon)}}|\mathcal{W}^{\varepsilon}_{n,m}(z)|dz$$
$$\leq \int_{\mathbb{R}^2\setminus B_{\sqrt{2}r(\varepsilon)}}|\mathcal{W}^{\varepsilon}_{n,m}(z)|dz + (\pi\varepsilon)^{-1}|B_{\sqrt{2}r(\varepsilon)}|$$

and $(\pi\varepsilon)^{-1}|B_{\sqrt{2}r(\varepsilon)}|$ yields the leading order asymptotics $\varepsilon^{-\sigma-\delta}$ of the L^1-norm. We treat the integral over $\mathbb{R}^2\setminus B_{\sqrt{2}r(\varepsilon)}$ seperately for the first decay estimate (D.3). In order to get rid of the phases, we apply the cross-Wigner expansion from Proposition 16 which yields

$$\mathcal{W}^{\varepsilon}_{n,m}(x,\xi) = \left(\mathrm{i}\sqrt{\tfrac{2}{\varepsilon}}(\xi+\mathrm{i}x)\right)^{m-n}\sqrt{\tfrac{n!}{m!}}$$
$$\times\sum_{j=0}^{n-m}\binom{n-m}{j}(-1)^j\mathcal{W}^{\varepsilon}_{m+j,m+j}(x,\xi),$$

and hence

$$|\mathcal{W}^{\varepsilon}_{n,m}(x,\xi)| \leq \sqrt{\frac{n!\varepsilon^{n-m}}{m!2^{n-m}}}\frac{1}{|x+\mathrm{i}\xi|^{n-m}}\sum_{j=0}^{n-m}\binom{n-m}{j}|\mathcal{W}^{\varepsilon}_{m+j,m+j}(x,\xi)|$$
$$\leq \frac{(n-m)!\sqrt{n!}}{\left(\lfloor\frac{n-m}{2}-1\rfloor!\right)^2}\left(\frac{\sqrt{\frac{\varepsilon}{2}}}{|x+\mathrm{i}\xi|}\right)^{n-m}\sum_{j=0}^{n-m}|\mathcal{W}^{\varepsilon}_{m+j,m+j}(x,\xi)|. \tag{D.6}$$

By Stirling's approximation one has

$$(n-m)!\sqrt{n!} \leq (C\varepsilon^{-\sigma})!^{3/2} \leq \mathrm{e}^{D\varepsilon^{-\sigma}\log(\varepsilon^{-1})} \tag{D.7}$$

for some $D>0$ if $\varepsilon>0$ is small. Moreover, if $z\in\mathbb{R}^2\setminus B_{\sqrt{2}r(\varepsilon)}$, it holds

$$\left(\frac{\sqrt{\frac{\varepsilon}{2}}}{|x+\mathrm{i}\xi|}\right)^{n-m} \leq (2\alpha\sqrt{\varepsilon^{-\sigma-\delta}})^{-(n-m)/2} \leq 1.$$

for ε small enough. We note that for any $a > 0$ one can prove

$$\|\chi_{\{|x|>a\}} h_n\|_{L^2} \leq C' \mathrm{e}^{-a^2/(12\varepsilon)} \mathrm{e}^{\beta_d |n|} \tag{D.8}$$

for some constants C', β_d independent of ε and n, see also [HJ00, (6.23) and (7.2)]. The same localization estimate holds for the semiclassical Fourier transform $\mathcal{F}^\varepsilon h_n$. Since by (D.5) the Wigner transform $\mathcal{W}^\varepsilon(h_{m+j})$ is positive outside of $B_{r(\varepsilon)}$, we consequently obtain for all j

$$\begin{aligned}
\int_{\mathbb{R}^2 \setminus B_{\sqrt{2}r(\varepsilon)}} |\mathcal{W}^\varepsilon_{m+j,m+j}(z)| dz &\leq \int_{|x|>r(\varepsilon)} \mathcal{W}^\varepsilon_{m+j,m+j}(x,\xi) dx\, d\xi \\
&\quad + \int_{|\xi|>r(\varepsilon)} \mathcal{W}^\varepsilon_{m+j,m+j}(x,\xi) dx\, d\xi \\
&= \|\chi_{\{|x|>r(\varepsilon)\}} h_{m+j}(x)\|^2_{L^2_x} + \|\chi_{\{|\xi|>r(\varepsilon)\}} \mathcal{F}^\varepsilon h_{m+j}(\xi)\|^2_{L^2_\xi} \\
&\leq E \mathrm{e}^{-\alpha\varepsilon^{-\sigma-\delta}/6 + 2\beta_d C\varepsilon^{-\sigma}}
\end{aligned}$$

with some $E > 0$ by invoking (D.8). Since $\delta > 0$, combining the last estimate with (D.6) and (D.7) yields

$$\begin{aligned}
\int_{\mathbb{R}^2 \setminus B_{\sqrt{2}r(\varepsilon)}} |\mathcal{W}^\varepsilon_{n,m}(z)| dz &\leq \alpha \mathrm{e}^{-C\varepsilon^{-\sigma-\delta}/4 + \beta_d C\varepsilon^{-\sigma}} (C\varepsilon^{-\sigma}) \mathrm{e}^{D\varepsilon^{-\sigma}\log(\varepsilon^{-1})} \\
&\leq \mathrm{e}^{-\Gamma\varepsilon^{-\sigma-\delta}}
\end{aligned}$$

for some $\Gamma > 0$ if ε is small. □

E Reference Solutions

There are many different ways to compute numerical solutions for the time-dependent Schrödinger equation in low dimensions. For an overview over some of the most popular methods we refer to chapter III. in [Lub08], and also [BJM02, JMS11] for the semiclassical setting.

The grid-based numerical reference solutions we use in this dissertation are generated by a time-splitting spectral method that uses Fourier collocation for the space discretization and a Strang splitting in time. This scheme is also known as the 'split-step Fourier method'. For the convenience of the reader we give a short sketch of the split-step Fourier method based on the presentation in [Lub08, §III.1.3 and §III.3.1].

We consider the time-dependent semiclassical Schrödinger equation for a Hamiltonian

$$H = -\tfrac{\varepsilon^2}{2}\Delta + V$$

of Schrödinger type. Moreover, suppose that the solution $\psi^\varepsilon(t)$ with initial condition $\psi^\varepsilon(0) = \psi_0^\varepsilon \in L^2(\mathbb{R}^d)$ stays well-localized in position space within a cuboid $[a_1, b_1] \times \dots [a_d, b_d]$ for all times of interest. This is for example the case if the potential V is confining. Without loss of generality we assume

$$[a_1, b_1] \times \dots [a_d, b_d] = [-\pi, \pi]^d,$$

since otherwise one can simply shift and rescale. We then can safely truncate the solutions outside of $[-\pi, \pi]^d$ and instead of the Schrödinger equation on $\mathbb{R}^d$ solve the corresponding equation on the torus $\pi\mathbb{T}^d = [-\pi, \pi]^d$ with periodic boundary conditions.

For the space discretization we impose the collocation condition that the approximate solution $u(x,t) \approx \psi^\varepsilon(x,t)$ shall satisfy the Schrödinger equation for all points $x \in G_N$ in the tensor grid

$$\begin{aligned} G_N &= \{\tfrac{1}{N}(2\pi k_1, \dots, 2\pi k_d) : k_1, \dots, k_d \in \{-N/2, \dots, N/2-1\}\} \\ &\subset [-\pi, \pi]^d, \end{aligned}$$

which is generated from N equidistant grid points per space direction. One then ends up with the linear equation

$$\mathrm{i}\varepsilon\dot{u} = \left(\mathcal{F}^\varepsilon_{G_N}\right)^{-1} T_N \mathcal{F}^\varepsilon_{G_N} u + V_N u \tag{E.1}$$

where $u = (u(x,t))_{x\in G_N}$ is a vector that contains the values of the approximation on the grid, and $\mathcal{F}^{\varepsilon}_{G_N} : \mathbb{C}^{G_N} \to \mathbb{C}^{G_N}$ is the discrete semiclassical Fourier transform on G_N. Now, one can exploit that the potential operator is diagonal in position space, $V_N = \mathrm{diag}(\{V(x)\}_{x\in G_N})$, and the discrete Laplacian is diagonal in momentum space, $T_N = \mathrm{diag}(\{\frac{1}{2}|\xi|^2\}_{\xi\in G_N})$.

Remark 19. *The fact that the grids in position and momentum space coincide is due to our special choise fo the tensor grid and the domain of periodicity. In general this is not the case. For instance, if one uses a Smolyak type sparse grid in position space, the discrete Fourier transform maps to momenta in a hyperbolic cross, see [Lub08, §III.1.4].*

The split-step Fourier method is obtained by using a Strang splitting numerical integrator for (E.1) that splits the vector field into the (discrete) kinetic and potential parts, see [Lub08, Algorithm 3.1]. The update formula for a time-step of size h then reads

$$u(t+h) \approx \mathrm{e}^{-\mathrm{i}V_N h/2\varepsilon} \left(\mathcal{F}^{\varepsilon}_{G_N}\right)^{-1} \mathrm{e}^{-\mathrm{i}T_N h/\varepsilon} \mathcal{F}^{\varepsilon}_{G_N} \mathrm{e}^{-\mathrm{i}V_N h/2\varepsilon} u(t), \quad \text{(E.2)}$$

where the matrix exponentials of the diagonal matrices V_N, T_N are easily evaluated. For the implementation of $\mathcal{F}^{\varepsilon}_{G_N}$ one uses the fast Fourier transform. If the value of ε is fixed, the symmetric splitting scheme (E.2) yields a second order method for (E.1). We refer to the book of Lubich and [JMS11] for further details like, e.g., step size restrictions on h and N in the semiclassical regime.

Bibliography

[AD14] Christoph Aistleitner and Josef Dick. Low-discrepancy point sets for non-uniform measures. *Acta Arith.*, 163(4):345–369, 2014.

[AM78] Ralph Abraham and Jerrold E. Marsden. *Foundations of mechanics*. Advanced book program. Benjamin/Cummings Pub. Co., 1978.

[AMP09] Agissilaos G. Athanassoulis, Norbert J. Mauser, and Thierry Paul. Coarse-scale representations and smoothed Wigner transforms. *J. Math. Pures Appl. (9)*, 91(3):296–338, 2009.

[AN08] Zied Ammari and Francis Nier. Mean field limit for bosons and infinite dimensional phase-space analysis. *Ann. Henri Poincaré*, 9(8):1503–1574, 2008.

[AP11] Agissilaos G. Athanassoulis and Thierry Paul. Strong phase-space semiclassical asymptotics. *SIAM J. Math. Anal.*, 43(5):2116–2149, 2011.

[App80] Paul Appell. Sur une classe de polynômes. *Ann. Sci. École Norm. Sup. (2)*, 9:119–144, 1880.

[App26] Paul Appell. *Fonctions hypergéométriques et hypersphériques : polynomes d'Hermite*. Gauthier-Villars, Paris, 1926.

[BB09] Eiichi Bannai and Etsuko Bannai. A survey on spherical designs and algebraic combinatorics on spheres. *European Journal of Combinatorics*, 30(6):1392 – 1425, 2009. Association Schemes: Ideas and Perspectives.

[BC02] Paolo Boggiatto and Elena Cordero. Anti-Wick quantization with symbols in L^p spaces. *Proc. Amer. Math. Soc.*, 130(9):2679–2685 (electronic), 2002.

[BCG04] Paolo Boggiatto, Elena Cordero, and Karlheinz Gröchenig. Generalized anti-Wick operators with symbols in distributional Sobolev spaces. *Integral Equations Operator Theory*, 48(4):427–442, 2004.

[BDBT14] Giorgia Bellomonte, Salvatore Di Bella, and Camillo Trapani. Operators in rigged Hilbert spaces: some spectral properties. *J. Math. Anal. Appl.*, 411(2):931–946, 2014.

[BDLT15] Andrey K. Belyaev, Wolfgang Domcke, Caroline Lasser, and Giulio Trigila. Nonadiabatic nuclear dynamics of the ammonia cation studied by surface hopping classical trajectory calculations. *The Journal of Chemical Physics*, 142(10):–, 2015.

[Ber71] Feliks A. Berezin. Wick and anti-Wick symbols of operators. *Mat. Sb. (N.S.)*, 86(128):578–610, 1971.

[Ber84] Michael V. Berry. Quantal phase factors accompanying adiabatic changes. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, 392(1802):45–57, 1984.

[BG04] Hans-Joachim Bungartz and Michael Griebel. Sparse grids. *Acta Numer.*, 13:147–269, 2004.

[BJM02] Weizhu Bao, Shi Jin, and Peter A. Markowich. On time-splitting spectral approximations for the schrödinger equation in the semiclassical regime. *Journal of Computational Physics*, 175(2):487–524, 2002.

[BO27] Max Born and J. Robert Oppenheimer. Zur Quantentheorie der Molekeln. *Annalen der Physik*, 389(20):457–484, 1927.

[Boh20] Niels Bohr. Über die Serienspektra der Elemente. *Zeitschrift für Physik*, 2(5):423–469, 1920.

[Bor26] Max Born. Zur Quantenmechanik der Stoßvorgänge. *Zeitschrift für Physik*, 38(11-12):803–827, 1926.

[Bor98] Folkmar Bornemann. *Homogenization in time of singularly perturbed mechanical systems*, volume 1687 of *Lecture Notes in Mathematics*. Springer-Verlag, Berlin, 1998.

[Bou99] Abdesslam Boulkhemair. L^2 Estimates for Weyl Quantization. *Journal of Functional Analysis*, 165(1):173 – 204, 1999.

[BR02] Abdelkader Bouzouina and Didier Robert. Uniform semiclassical estimates for the propagation of quantum observables. *Duke Math. J.*, 111(2):223–252, 2002.

[BY73] Richard F. Barrow and Kim K. Yee. $B^3\ \Pi_{0_u^+} - X^1\Sigma_g^+$ system of $^{127}I_2$: rotational analysis and long-range potential in the $B_3\Pi_{0_u^+}$ state. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*, 69:684–700, 1973.

[Car10] David Carfì. The pointwise Hellmann-Feynman theorem. *AAPP | Physical, Mathematical, and Natural Sciences*, 88(1), 2010.

[CDS81] Jean-Michel Combes, Pierre Duclos, and Rudolf Seiler. The Born-Oppenheimer Approximation. In G. Velo and A.S. Wightman, editors, *Rigorous Atomic and Molecular Physics*, volume 74 of *NATO Advanced Study Institutes Series*. Springer US, 1981.

[CdV03] Yves Colin de Verdière. The level crossing problem in semiclassical analysis. I. The symmetric case. In *Proceedings of the International Conference in Honor of Frédéric Pham (Nice, 2002)*, volume 53, pages 1023–1054, 2003.

[CFK11] Rémi Carles and Clotilde Fermanian Kammerer. Nonlinear Coherent States and Ehrenfest Time for Schrödinger Equation. *Communications in Mathematical Physics*, 301(2):443–472, 2011.

[CR12] Monique Combescure and Didier Robert. *Coherent states and applications in mathematical physics*. Theoretical and Mathematical Physics. Springer, Dordrecht, 2012.

[Cra67] Oakley H. Crawford. Bound states of a charged particle in a dipole field. *Proc. Phys. Soc.*, 91:279–284, 1967.

[CS78] Jean-Michel Combes and Rudolf Seiler. Regularity and asymptotic properties of the discrete spectrum of electronic hamiltonians. *International Journal of Quantum Chemistry*, 14(2):213–229, 1978.

[CV72] Alberto-P. Calderón and Rémi Vaillancourt. A class of bounded pseudo-differential operators. *Proc. Nat. Acad. Sci. U.S.A.*, 69:1185–1187, 1972.

[DdGLP12] Nuno Costa Dias, Maurice A. de Gosson, Franz Luef, and João Nuno Prata. Quantum mechanics in phase space: the Schrödinger and the Moyal representations. *Journal of Pseudo-Differential Operators and Applications*, 3(4):367–398, 2012.

[Del92] Jean-Marc Delort. *F.B.I. transformation*, volume 1522 of *Lecture Notes in Mathematics*. Springer-Verlag, Berlin, 1992. Second microlocalization and semilinear caustics.

[Der93] Jan Derezinski. Some remarks on Weyl pseudodifferential operators. *Journées équations aux dérivées partielles*, pages 1–14, 1993.

[dG06] Maurice A. de Gosson. *Symplectic geometry and quantum mechanics*, volume 166 of *Operator Theory: Advances and Applications*. Birkhäuser Verlag, Basel, 2006. Advances in Partial Differential Equations (Basel).

[dG11] Maurice A. de Gosson. *Symplectic methods in harmonic analysis and in mathematical physics*, volume 7 of *Pseudo-Differential Operators. Theory and Applications*. Birkhäuser/Springer Basel AG, Basel, 2011.

[Dir29] Paul A. M. Dirac. Quantum mechanics of many-electron systems. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 123(792):714–733, 1929.

[Dir30] Paul A. M. Dirac. *Die Prinzipien der Quantenmechanik*. S. Hirzel, 1930.

[DKT15] Helge G.W. Dietert, Johannes Keller, and Stephanie Troppmann. An invariant class of Hermite type multivariate polynomials for the Wigner transform, 2015. Preprint at `http://arxiv.org/abs/1505.06192`.

[DS99] Mouez Dimassi and Johannes Sjöstrand. *Spectral asymptotics in the semi-classical limit*, volume 268 of *London Mathematical Society Lecture Note Series*. Cambridge University Press, Cambridge, 1999.

[DYK04] Wolfgang Domcke, David Yarkony, and Horst Köppel. *Conical Intersections: Electronic Structure, Dynamics & Spectroscopy*. Advanced series in physical chemistry. World Scientific, 2004.

[Ego69] Yuri V. Egorov. The canonical transformations of pseudodifferential operators. *Uspehi Mat. Nauk*, 24(5 (149)):235–236, 1969.

[ER05] Hassan Emamirad and Philippe Rogeon. Scattering theory for the Wigner equation. *Math. Methods Appl. Sci.*, 28(8):947–960, 2005.

[ER13] Hassan Emamirad and Philippe Rogeon. Semiclassical limit of Husimi function. *Discrete Contin. Dyn. Syst. Ser. S*, 6(3):669–676, 2013.

[Erd39] Artur Erdélyi. Über eine erzeugende Funktion von Produkten Hermitescher Polynome. *Mathematische Zeitschrift*, 44(1):201–211, 1939.

[Fau07] Frédéric Faure. Semi-classical formula beyond the Ehrenfest time in quantum chaos. I. Trace formula. *Ann. Inst. Fourier (Grenoble)*, 57(7):2525–2599, 2007. Festival Yves Colin de Verdière.

[Fey39] Richard P. Feynman. Forces in molecules. *Phys. Rev.*, 56:340–343, Aug 1939.

[FG09] Erwan Faou and Vasile Gradinaru. Gauss-Hermite wave packet dynamics: convergence of the spectral and pseudo-spectral approximation. *IMA J. Numer. Anal.*, 29(4):1023–1045, 2009.

[FGL09] Erwan Faou, Vasile Gradinaru, and Christian Lubich. Computing semiclassical quantum dynamics with Hagedorn wavepackets. *SIAM J. Sci. Comput.*, 31(4):3027–3041, 2009.

[FKGL13] Clotilde Fermanian Kammerer, Patrick Gérard, and Caroline Lasser. Wigner measure propagation and conical singularity for general initial data. *Archive for Rational Mechanics and Analysis*, 209(1):209–236, 2013.

[FKL03] Clotilde Fermanian Kammerer and Caroline Lasser. Wigner measures and codimension two crossings. *Journal of Mathematical Physics*, 44(2), 2003.

[FL06] Erwan Faou and Christian Lubich. A Poisson integrator for Gaussian wavepacket dynamics. *Comput. Vis. Sci.*, 9(2):45–55, 2006.

[FM96] Jian-Yun Fang and Craig C. Martens. One-atom cage effect in collinear I_2(B)–Ar complexes: A time-dependent wave packet study. *The Journal of Chemical Physics*, 105(20):9072–9082, 1996.

[Fol89] Gerald B. Folland. *Harmonic analysis in phase space*, volume 122 of *Annals of Mathematics Studies*. Princeton University Press, Princeton, NJ, 1989.

[FT47] Enrico Fermi and Edward Teller. The capture of negative mesotrons in matter. *Phys. Rev.*, 72:399–408, Sep 1947.

[GH14] Vasile Gradinaru and George A. Hagedorn. Convergence of a semiclassical wavepacket based time-splitting for the Schrödinger equation. *Numerische Mathematik*, 126(1):53–73, 2014.

[GL14] Wolfgang Gaim and Caroline Lasser. Corrections to Wigner type phase space methods. *Nonlinearity*, 27:2951–2974, 2014.

[GMMP97] Patrick Gérard, Peter A. Markowich, Norbert J. Mauser, and Frédéric Poupaud. Homogenization limits and Wigner transforms. *Comm. Pure Appl. Math.*, 50(4):323–379, 1997.

[GS12] Eva-Maria Graefe and Roman Schubert. Complexified coherent states and quantum evolution with non-hermitian hamiltonians. *Journal of Physics A: Mathematical and Theoretical*, 45(24):244033, 2012.

[Gut71] Martin C. Gutzwiller. Periodic Orbits and Classical Quantization Conditions. *Journal of Mathematical Physics*, 12(3), 1971.

[Hag80] George A. Hagedorn. A time dependent Born-Oppenheimer approximation. *Comm. Math. Phys.*, 77(1):1–19, 1980.

[Hag81] George A. Hagedorn. Semiclassical quantum mechanics. iii. the large order asymptotics and more general states. *Annals of Physics*, 135(1):58 – 70, 1981.

[Hag85] George A. Hagedorn. Semiclassical quantum mechanics, iv : large order asymptotics and more general states in more than one dimension. *Annales de l'institut Henri Poincaré (A) Physique théorique*, 42(4):363–374, 1985.

[Hag87] George A. Hagedorn. High order corrections to the time-independent Born-Oppenheimer approximation. I. Smooth potentials. *Ann. Inst. H. Poincaré Phys. Théor.*, 47(1):1–16, 1987.

[Hag88] George A. Hagedorn. High order corrections to the time-dependent Born-Oppenheimer approximation. II. Coulomb systems. *Comm. Math. Phys.*, 117(3):387–403, 1988.

[Hag94] George A. Hagedorn. Molecular propagation through electron energy level crossings. *Mem. Amer. Math. Soc.*, 111(536):vi+130, 1994.

[Hag98] George A Hagedorn. Raising and lowering operators for semiclassical wave packets. *Annals of Physics*, 269(1):77 – 104, 1998.

[Hag15] George A. Hagedorn. Generating functions for the polynomials in d-dimensional semiclassical wave packets, 2015. Preprint at `http://www.math.vt.edu/people/hagedorn/GenFunPaper.pdf`.

[Har13] Lysianne Hari. Coherent States for Systems of L^2-Supercritical Nonlinear Schrödinger Equations. *Communications in Partial Differential Equations*, 38(3):529–573, 2013.

[Hel37] Hans Hellmann. *Einführung in die Quantenchemie*. Franz Deuticke, 1937.

[Hel75] Eric J. Heller. Time-dependent approach to semiclassical dynamics. *The Journal of Chemical Physics*, 62(4):1544–1555, 1975.

[Hel76] Eric J. Heller. Classical S-matrix limit of wave packet dynamics. *The Journal of Chemical Physics*, 65(11), 1976.

[Hel81] Eric J. Heller. Frozen Gaussians: A very simple semiclassical approximation. *The Journal of Chemical Physics*, 75(6), 1981.

[Hep74] Klaus Hepp. The classical limit for quantum mechanical correlation functions. *Communications in Mathematical Physics*, 35(4):265–277, 1974.

[HG80] Walter Hunziker and Christoph-Georg Günther. Bound states in dipole fields and continuity properties of electronic spectra. *Helv. Phys. Acta*, 53(2):201–208, 1980.

[HH64] Michel Hénon and Carl Heiles. The applicability of the third integral of motion: Some numerical experiments. *Astronomical Journal*, 69:73, February 1964.

[HJ99] George A. Hagedorn and Alain Joye. Semiclassical dynamics with exponentially small error estimates. *Comm. Math. Phys.*, 207(2):439–465, 1999.

[HJ00] George A. Hagedorn and Alain Joye. Exponentially accurate semiclassical dynamics: propagation, localization, Ehrenfest times, scattering, and more general states. *Ann. Henri Poincaré*, 1(5):837–883, 2000.

[HK84] Michael F. Herman and Edward Kluk. A semiclassical justification for the use of non-spreading wavepackets in dynamics calculations. *Chemical Physics*, 91(1):27 – 34, 1984.

[HKT04] Jürgen Hartinger, Reinhold F. Kainhofer, and Robert F. Tichy. Quasi-monte carlo algorithms for unbounded, weighted integration problems. *Journal of Complexity*, 20(5):654 – 668, 2004. Dagstuhl 2002 - Festschrift for the 70th Birthday of Joseph F. Traub.

[HLW10] Ernst Hairer, Christian Lubich, and Gerhard Wanner. *Geometric numerical integration*, volume 31 of *Springer Series in Computational Mathematics*. Springer, Heidelberg, 2010. Structure-preserving algorithms for ordinary differential equations, Reprint of the second (2006) edition.

[Hol96] Björn Holmquist. The d-variate vector hermite polynomial of order k. *Linear Algebra and its Applications*, 237–238(0):155 – 190, 1996. Linear Algebra and Statistics: In Celebration of C. R. Rao's 75th Birthday (September 10, 1995).

[Hör73] Lars Hörmander. *An introduction to complex analysis in several variables*. North-Holland Publishing Co., Amsterdam-London; American Elsevier Publishing Co., Inc., New York, revised edition, 1973. North-Holland Mathematical Library, Vol. 7.

[Hör07] Lars Hörmander. *The analysis of linear partial differential operators. III*. Classics in Mathematics. Springer, Berlin, 2007. Pseudo-differential operators, Reprint of the 1994 edition.

[Hör09] Lars Hörmander. *The analysis of linear partial differential operators. IV*. Classics in Mathematics. Springer-Verlag, Berlin, 2009. Fourier integral operators, Reprint of the 1994 edition.

[Hud74] Robin L. Hudson. When is the Wigner quasi-probability density non-negative? *Rep. Mathematical Phys.*, 6(2):249–252, 1974.

[Hun86] Walter Hunziker. Distortion analyticity and molecular resonance curves. *Ann. Inst. H. Poincaré Phys. Théor.*, 45(4):339–358, 1986.

[Hus40] Kodi Husimi. Some formal properties of the density matrix. *Proceedings of the Physico-Mathematical Society of Japan. 3rd Series*, 22(4):264–314, 1940.

[HZ07] Justin Holmer and Maciej Zworski. Slow soliton interaction with delta impurities. *Journal of Modern Dynamics*, 1(4):689–718, 2007.

[HZ08] Justin Holmer and Maciej Zworski. Soliton interaction with slowly varying potentials. *Int. Math. Res. Not. IMRN*, (10):Art. ID rnn026, 36, 2008.

[Hö95] Lars Hörmander. Symplectic classification of quadratic forms, and general Mehler formulas. *Mathematische Zeitschrift*, 219(1):413–449, 1995.

[IZ88] Mourad E. H. Ismail and Ruiming Zhang. On the Hellmann-Feynman theorem and the variation of zeros of certain special functions. *Adv. in Appl. Math.*, 9(4):439–446, 1988.

[JMS11] Shi Jin, Peter Markowich, and Christof Sparber. Mathematical and computational methods for semiclassical Schrödinger equations. *Acta Numer.*, 20:121–209, 2011.

[Kat51] Tosio Kato. Fundamental properties of Hamiltonian operators of Schrödinger type. *Trans. Amer. Math. Soc.*, 70:195–211, 1951.

[Kat95] Tosio Kato. *Perturbation theory for linear operators*. Classics in Mathematics. Springer-Verlag, Berlin, 1995. Reprint of the 1980 edition.

[Kel12] Johannes Keller. Computing Semiclassical Quantum Expectations by Husimi Functions. Master's thesis, 2012.

[Kir94] Bernd Kirchheim. Rectifiable metric spaces: local structure and regularity of the Hausdorff measure. *Proc. Amer. Math. Soc.*, 121(1):113–123, 1994.

[KL13] Johannes Keller and Caroline Lasser. Propagation of quantum expectations with Husimi functions. *SIAM J. Appl. Math.*, 73(4):1557–1581, 2013.

[KL14] Johannes Keller and Caroline Lasser. Quasi-classical description of molecular dynamics based on Egorov's theorem. *The Journal of Chemical Physics*, 141(5):054104, 2014.

[KLO15] Johannes Keller, Caroline Lasser, and Tomoki Ohsawa. A new phase space density for quantum expectations., 2015. Preprint at `http://arxiv.org/abs/1506.08880`.

[KLW09] Susanna Kube, Caroline Lasser, and Marcus Weber. Monte Carlo sampling of Wigner functions and surface hopping quantum dynamics. *J. Comput. Phys.*, 228(6):1947–1962, 2009.

[KMR11] Andreas Kriegl, Peter W. Michor, and Armin Rainer. Denjoy-Carleman differentiable perturbation of polynomials and unbounded operators. *Integral Equations Operator Theory*, 71(3):407–416, 2011.

[KMSW92] Markus Klein, André Martinez, Rudolf Seiler, and Xue P. Wang. On the Born-Oppenheimer expansion for polyatomic molecules. *Comm. Math. Phys.*, 143(3):607–639, 1992.

[Las04] Caroline Lasser. *Conical energy level crossings in molecular dynamics*. Dissertation, Technische Universität München, München, 2004.

[Ler10] Nicolas Lerner. *Metrics on the phase space and non-selfadjoint pseudo-differential operators*, volume 3 of *Pseudo-Differential Operators. Theory and Applications*. Birkhäuser Verlag, Basel, 2010.

[Lit86] Robert G. Littlejohn. The semiclassical evolution of wave packets. *Physics Reports*, 138(4–5):193 – 291, 1986.

[LNR15] Mathieu Lewin, Phan Thành Nam, and Nicolas Rougerie. Remarks on the Quantum de Finetti Theorem for Bosonic Systems. *Appl. Math. Res. Express. AMRX*, (1):48–63, 2015.

[LR10] Caroline Lasser and Susanna Röblitz. Computing expectation values for molecular quantum dynamics. *SIAM J. Sci. Comput.*, 32(3):1465–1483, 2010.

[LRT13] Hailiang Liu, Olof Runborg, and Nicolay M. Tanushev. Error estimates for Gaussian beam superpositions. *Math. Comp.*, 82(282):919–952, 2013.

[LS10] Elliott H. Lieb and Robert Seiringer. *The stability of matter in quantum mechanics*. Cambridge University Press, Cambridge, 2010.

[LS15] Manfred Liebmann and David Sattlegger. Parallel algorithms for semiclassical quantum dynamics, 2015. Preprint at `https://www.ma.tum.de/foswiki/pub/IGDK1754/Preprints/LiebmannSattlegger_2015.pdf`.

[LST07] Caroline Lasser, Torben Swart, and Stefan Teufel. Construction and validation of a rigorous surface hopping algorithm for conical crossings. *Commun. Math. Sci.*, 5(4):789–814, 2007.

[LST15] Caroline Lasser, Roman Schubert, and Stephanie Troppmann. Non-Hermitian propagation of Hagedorn wavepackets, 2015.

[LT05] Caroline Lasser and Stefan Teufel. Propagation through conical crossings: an asymptotic semigroup. *Comm. Pure Appl. Math.*, 58(9):1188–1230, 2005.

[LT14] Caroline Lasser and Stephanie Troppmann. Hagedorn wavepackets in time-frequency and phase space. *Journal of Fourier Analysis and Applications*, pages 1–36, 2014.

[Lub08] Christian Lubich. *From quantum to classical molecular dynamics: reduced models and numerical analysis*. Zurich Lectures in Advanced Mathematics. European Mathematical Society (EMS), Zürich, 2008.

[LY12a] Jianfeng Lu and Xu Yang. Convergence of frozen Gaussian approximation for high-frequency wave propagation. *Comm. Pure Appl. Math.*, 65(6):759–789, 2012.

[LY12b] Jianfeng Lu and Xu Yang. Frozen gaussian approximation for general linear strictly hyperbolic systems: Formulation and eulerian methods. *Multiscale Modeling & Simulation*, 10(2):451–472, 2012.

[Mar89] Peter A. Markowich. On the equivalence of the Schrödinger and the quantum Liouville equations. *Math. Methods Appl. Sci.*, 11(4):459–469, 1989.

[Mar02] André Martinez. *An introduction to semiclassical and microlocal analysis*. Universitext. Springer-Verlag, New York, 2002.

[Mil74] William H. Miller. Quantum mechanical transition state theory and a new semiclassical model for reaction rate constants. *J. Chem. Phys.*, 61:1823, 1974.

[Moy49] José E. Moyal. Quantum mechanics as a statistical theory. *Proc. Cambridge Philos. Soc.*, 45:99–124, 1949.

[MR99] Jerrold E. Marsden and Tudor S. Ratiu. *Introduction to Mechanics and Symmetry: A Basic Exposition of Classical Mechanical Systems*. Texts in Applied Mathematics. Springer, 1999.

[MS09] André Martinez and Vania Sordoni. Twisted pseudodifferential calculus and application to the quantum evolution of molecules. *Mem. Amer. Math. Soc.*, 200(936):vi+82, 2009.

[MT82] C. Alden Mead and Donald G. Truhlar. Conditions for the definition of a strictly diabatic electronic basis for molecular systems. *The Journal of Chemical Physics*, 77(12), 1982.

[NM02] Mathias Nest and Hans-Dieter Meyer. Benchmark calculations on high-dimensional Henon–Heiles potentials with the multiconfiguration time dependent Hartree (MCTDH) method. *The Journal of Chemical Physics*, 117(23):10499–10505, 2002.

[Ohs15] Tomoki Ohsawa. Symmetry and conservation laws in semiclassical wave packet dynamics. *Journal of Mathematical Physics*, 56(3):–, 2015.

[OL13] Tomoki Ohsawa and Melvin Leok. Symplectic semiclassical wave packet dynamics. *Journal of Physics A: Mathematical and Theoretical*, 46(40):405201, 2013.

[PMCK89] Tibor Pacher, C. Alden Mead, Lorenz S. Cederbaum, and Horst Köppel. Gauge theory and quasidiabatic states in molecular physics. *The Journal of Chemical Physics*, 91(11), 1989.

[Pos92] Theodore E. Posch. The wave packet transform (WPT) as applied to signal processing. In *Signals, Systems and Computers, 1992. 1992 Conference Record of The Twenty-Sixth Asilomar Conference on*, pages 484–487 vol.1, Oct 1992.

[PP00] Oleg V. Prezhdo and Yu. V. Pereverzev. Quantized Hamilton dynamics. *The Journal of Chemical Physics*, 113(16), 2000.

[PST07] Gianluca Panati, Herbert Spohn, and Stefan Teufel. The time-dependent Born-Oppenheimer approximation. *M2AN Math. Model. Numer. Anal.*, 41(2):297–314, 2007.

[Pul06] Mario Pulvirenti. Semiclassical expansion of Wigner functions. *J. Math. Phys.*, 47(5):052103, 12, 2006.

[PZ01] David Preiss and Luděk Zajiček. Directional derivatives of Lipschitz functions. *Israel J. Math.*, 125:1–27, 2001.

[RM00] A. Raab and Hans-Dieter Meyer. A numerical study on the performance of the multiconfiguration time-dependent hartree method for density operators. *J. Chem. Phys.*, 112(24):10718–10729, 2000.

[Rob87] Didier Robert. *Autour de l'approximation semi-classique*. Number 68. Birkhauser, 1987.

[Rob10] Didier Robert. On the Herman-Kluk semiclassical approximation. *Rev. Math. Phys.*, 22(10):1123–1145, 2010.

[Rod93] Luigi Rodino. *Linear Partial Differential Operators in Gevrey Spaces*. World Scientific, 1993.

[RS75] Michael Reed and Barry Simon. *Methods of modern mathematical physics. II. Fourier analysis, self-adjointness*. Academic Press [Harcourt Brace Jovanovich Publishers], New York, 1975.

[RS78] Michael Reed and Barry Simon. *Methods of modern mathematical physics. IV. Analysis of operators*. Academic Press [Harcourt Brace Jovanovich Publishers], New York, 1978.

[RT09] Ramakrishnan Radha and Sundaram Thangavelu. Holomorphic Sobolev spaces, Hermite and special Hermite semigroups and a Paley-Wiener theorem for the windowed Fourier transform. *J. Math. Anal. Appl.*, 354(2):564–574, 2009.

[SC83] Francisco Soto and Pierre Claverie. When is the Wigner function of multidimensional systems nonnegative? *Journal of Mathematical Physics*, 24(1), 1983.

[Sch01] Roman Schubert. *Semiclassical localization in phase space*. Dissertation, Universität Ulm, 2001.

[Sei10] Robert Seiringer. Inequalities for Schrödinger Operators and Applications to the Stability of Matter Problem. *Entropy and the Quantum*, 529:53–72 202, 2010.

[Shn74] Alexander I. Shnirelman. Ergodic properties of eigenfunctions. *Uspehi Mat. Nauk*, 29(6(180)):181–182, 1974.

[Sim71] Barry Simon. *Quantum Mechanics for Hamiltonians Defined As Quadratic Forms*. Princeton Series in Physics. Princeton University Press, 1971.

[Sim83] Barry Simon. Holonomy, the quantum adiabatic theorem, and Berry's phase. *Phys. Rev. Lett.*, 51(24):2167–2170, 1983.

[Sjö82] Johannes Sjöstrand. Singularités analytiques microlocales. In *Astérisque, 95*, volume 95 of *Astérisque*, pages 1–166. Soc. Math. France, Paris, 1982.

[Sol13] Michael A. Soloviev. Algebras with convergent star products and their representations in Hilbert spaces. *J. Math. Phys.*, 54(7):073517, 16, 2013.

[SR09] Torben Swart and Vidian Rousse. A mathematical justification for the Herman-Kluk propagator. *Comm. Math. Phys.*, 286(2):725–750, 2009.

[ST01] Herbert Spohn and Stefan Teufel. Adiabatic decoupling and time-dependent Born-Oppenheimer theory. *Comm. Math. Phys.*, 224(1):113–132, 2001. Dedicated to Joel L. Lebowitz.

[ST13] Hans-Michael Stiepan and Stefan Teufel. Semiclassical Approximations for Hamiltonians with Operator-Valued Symbols. *Comm. Math. Phys.*, 320(3):821–849, 2013.

[SVT12] Roman Schubert, Raúl O. Vallejos, and Fabricio Toscano. How do wave packets spread? Time evolution on Ehrenfest time scales. *J. Phys. A*, 45(21):215307, 28, 2012.

[Swa08] Torben Swart. *Initial Value Representations*. Dissertation, Freie Universität Berlin, 2008.

[Sze75] Gábor Szegö. *Orthogonal polynomials*. American Mathematical Society, Providence, R.I., fourth edition, 1975. American Mathematical Society, Colloquium Publications, Vol. XXIII.

[Tan07] David J. Tannor. *Introduction to Quantum Mechanics: A Time-dependent Perspective*. University Science Books, 2007.

[Tao12] Terence Tao. *Topics in random matrix theory*, volume 132 of *Graduate Studies in Mathematics*. American Mathematical Society, Providence, RI, 2012.

[TE05] Lloyd N. Trefethen and Mark Embree. *Spectra and pseudospectra*. Princeton University Press, Princeton, NJ, 2005. The behavior of nonnormal matrices and operators.

[Tha93] Sundaram Thangavelu. *Lectures on Hermite and Laguerre Expansions*. Mathematical Notes - Princeton University Press. Princeton University Press, 1993.

[TW04] Michael Thoss and Haobin Wang. Semiclassical description of molecular dynamics based on initial-value representation methods. *Annual Review of Physical Chemistry*, 55(1):299–332, 2004. PMID: 15117255.

[Var09] António J.C. Varandas. A simple, yet reliable, direct diabatization scheme. The $^1\Sigma_g^+$ states of C_2. *Chemical Physics Letters*, 471(4–6):315 – 321, 2009.

[Wey12] Hermann Weyl. Das asymptotische Verteilungsgesetz der Eigenwerte linearer partieller Differentialgleichungen (mit einer Anwendung auf die Theorie der Hohlraumstrahlung). *Mathematische Annalen*, 71:441–479, 1912.

[Wey27] Hermann Weyl. Quantenmechanik und Gruppentheorie. *Zeitschrift für Physik*, 46(1-2):1–46, 1927.

[Wig32] Eugene P. Wigner. On the quantum correction for thermodynamic equilibrium. *Phys. Rev.*, 40:749–759, Jun 1932.

[Wig60] Eugene P. Wigner. The unreasonable effectiveness of mathematics in the natural sciences. richard courant lecture in mathematical sciences delivered at new york university, may 11, 1959. *Communications on Pure and Applied Mathematics*, 13(1):1–14, 1960.

[Wit00] Christopher S. Withers. A simple expression for the multivariate Hermite polynomials. *Statistics & Probability Letters*, 47(2):165 – 169, 2000.

[WTS+01] Haobin Wang, Michael Thoss, Kathy L. Sorge, Ricard Gelabert, Xavier Gimenez, and William H. Miller. Semiclassical description of quantum coherence effects and their quenching: A forward–backward initial value representation study. *The Journal of Chemical Physics*, 114(6):2562–2571, 2001.

[Wün99] Alfred Wünsche. Transformations of Laguerre 2D polynomials with applications to quasiprobabilities. *Journal of Physics A: Mathematical and General*, 32(17):3179, 1999.

[Wün00] Alfred Wünsche. General Hermite and Laguerre two-dimensional polynomials. *Journal of Physics A: Mathematical and General*, 33(8):1603, 2000.

[Yos90] Haruo Yoshida. Construction of higher order symplectic integrators. *Phys. Lett. A*, 150(5-7):262–268, 1990.

[Yse10] Harry Yserentant. *Regularity and Approximability of Electronic Wave Functions*. Number 2000 in Lecture Notes in Mathematics. Springer, 2010.

[Zel87] Steven Zelditch. Uniform distribution of eigenfunctions on compact hyperbolic surfaces. *Duke Math. J.*, 55(4):919–941, 1987.

[Zur03] Wojciech Hubert Zurek. Decoherence, einselection, and the quantum origins of the classical. *Rev. Mod. Phys.*, 75:715–775, May 2003.

[Zwo12] Maciej Zworski. *Semiclassical analysis*, volume 138 of *Graduate Studies in Mathematics*. American Mathematical Society, Providence, RI, 2012.