Chapter 4

Adiabatic limits

Subsequently, we will study the *limit equations* governing the QD and QCMD solutions for the *adiabatic* limit, that is, the dynamics for $\epsilon = \sqrt{m/M} \to 0$, in which the motions in the degree of freedom x are infinitely faster than the slow processes in the classical coordinate q. Note, that the preceding justification of QCMD does not reveal the adiabatic limit of QCMD.

We restrict ourselves to finite-dimensional Hilbert spaces making H a Hermitian matrix as described in §4.[1] So, what is the limit dynamics of (2.8) and (2.9) for $\epsilon \to 0$, respectively? Before we address this question, we examine some ways to compute the adiabatic limit. A variety of analytical concepts yield the correct limit behavior, but differ in the required assumptions as well as in the possibility to compute first order correction terms. However, since the construction of numerical integrators in the Chapters 8 and 9 is strongly influenced by the analysis of the adiabatic limit, an inspection of the methods as well as the QCMD limit will be of great advantage.

§1 Three methods to compute the adiabatic limit

Before we state the convergence results for QD and QCMD in the case $\epsilon \to 0$, we will present three approaches to compute the adiabatic limit of a given system.

1. A convergence analysis in a weak* topology offers a very convenient way to compute the adiabatic limit. A short overview over the technique is given in Appendix 10.

2. So–called near–identity or averaging transformations have been evolved from the "method of averaging" by Krylov and Bogoliubov [68] and were generalized later [84]. A detailed overview over near–identity–transformations can be found in [64].

3. A transformation on rotating axes explicitly constructs a mapping onto a coordinate system moving in time. For the case of the time–dependent Schrödinger equation in Sec. §1.2, this method is presented in [77].

To illustrate the techniques, we will apply them to two examples: a highly oscillatory perturbed Hamiltonian system and the quantum adiabatic theorem, originating from work of Born and Fock [12, 62, 77]. Since both examples will be cited throughout this work, we will focus on the differences between the analytical concepts in the assumptions required and in the statements resulting.

[1] For a generalization with respect to the infinitely dimensional case of the results presented in this chapter, see [13].

§1.1 The highly oscillatory perturbed Hamiltonian test system

Consider the dynamics of a canonical system in the variables $q_\epsilon, p_\epsilon : \mathbb{R} \to \mathbb{R}^d$ perturbed by a highly oscillatory force. The Hamiltonian system under consideration is defined by the time–dependent and separable Hamiltonian function $\mathcal{H}_\epsilon = \mathcal{H}_\epsilon(q_\epsilon, p_\epsilon, t)$

$$\mathcal{H}_\epsilon(q_\epsilon, p_\epsilon, t) = \frac{\|p_\epsilon\|^2}{2} + V(q_\epsilon) + \phi(\epsilon^{-1}\, t)U(q_\epsilon). \tag{4.1}$$

with initial conditions $q_\epsilon(t_0) \in \mathbb{R}^d$, $p_\epsilon(t_0) \in \mathbb{R}^d$. The corresponding canonical equations of motion are given by

$$\begin{aligned} \frac{dq_\epsilon}{dt} &= \frac{\partial \mathcal{H}_\epsilon}{\partial p_\epsilon} = p_\epsilon \\ \frac{dp_\epsilon}{dt} &= -\frac{\partial \mathcal{H}_\epsilon}{\partial q_\epsilon}. \end{aligned} \tag{4.2}$$

Subsequently, assume that

(OSC1) the potentials V and U are differentiable: $V \in C^1(\mathbb{R}^d)$ and $U \in C^1(\mathbb{R}^d)$ and the derivatives are locally Lipschitz continuous,

(OSC2) the function $\phi \in C(\mathbb{R})$ is continuous with $\frac{d}{dt}g(t) = \phi(t)$ and $\phi(t/\epsilon)$ as well as $g(t/\epsilon)$ are uniformly bounded for all $0 < \epsilon < \epsilon_0$,

(OSC3) the energy $\mathcal{H}_\epsilon$ is uniformly bounded for finite times $t \in [t_0, T]$,

$$|\mathcal{H}_\epsilon(q_\epsilon(t), p_\epsilon(t), t)| < E_*, \qquad \forall\, 0 < \epsilon < \epsilon_0,$$

(OSC4) and that the initial values converge uniformly for $\epsilon \to 0$,

$$q_\epsilon(t_0) \to q_* \qquad p_\epsilon(t_0) \to p_*.$$

Remark. Note, that Assumption (OSC2) requires some kind of oscillatory character of the function ϕ.

Remark. Assumption (OSC3) is very restrictive. It is used to obtain uniform bounds on q_ϵ, p_ϵ and $\ddot{q}_\epsilon$. It can be omitted, if we require that $\nabla_q V$ and $\nabla_q U$ are globally Lipschitz continuous instead of only locally Lipschitz continuous (OSC1). Then, uniform bounds on q_ϵ, p_ϵ and $\ddot{q}_\epsilon$ result from a Gronwall lemma for "second order" differential inequalities (cf, [102, Lemma 4.49]).

Theorem 4.1 *Let Assumptions (OSC1) – (OSC4) apply. Then the location* q_ϵ *converges uniformly* $q_\epsilon \to q_0$ *for* $\epsilon \to 0$ *in* $C([t_0, T])$. *The limit* q_0 *is given by the solution of*

$$\ddot{q}_0 = -\nabla_q V(q_0), \qquad q_0(t_0) = q_*. \tag{4.3}$$

§1.1.1 Proof of Thm. 4.1 in a weak* topology

The proof is given in three steps. At first, we find some *a priori* uniform bounds on $q_\epsilon, \dot{q}_\epsilon$ and $\ddot{q}_\epsilon$ by making use of the bound of the energy: Since $\mathcal{H}_\epsilon$ is bounded, we obtain a bound on $\dot{q}_\epsilon$ for finite times $t \in [t_0, T]$. Through integration, we derive a bound on q_ϵ and finally via (4.2) a bound on $\ddot{q}_\epsilon$

$$q_\epsilon, \dot{q}_\epsilon, \ddot{q}_\epsilon = \mathcal{O}(1).$$

An application of the extended Arzelà-Ascoli Theorem 10.7 as well as the Banach–Alaoglu Theorem 10.5 yields for a subsequence $\{\epsilon'\}$ with $\epsilon' \to 0$

$$q_{\epsilon'} \quad \to \quad q_0 \quad \text{in} \quad C\big([t_0, T], \mathbb{R}^d\big) \tag{4.4}$$

$$\ddot{q}_{\epsilon'} \quad \overset{*}{\rightharpoonup} \quad \ddot{q}_0 \quad \text{in} \quad L^\infty\big([t_0, T], \mathbb{R}^d\big). \tag{4.5}$$

In a next step, consider this subsequence $\{\epsilon'\}$ and denote

$$u_{\epsilon'}(t) = \phi({\epsilon'}^{-1} t), \qquad u_{\epsilon'} : [t_0, T] \to \mathbb{R}.$$

By construction (assumption (OSC2)), $u_{\epsilon'} = \mathcal{O}(1)$ and $\int_{t_a}^{t_b} u_{\epsilon'}(s) ds \to 0$ for $\epsilon' \to 0$ for all $t_a, t_b \in [t_0, T]$. This yields via Thm. 10.2 the existence of a subsequence $\{\epsilon''\}$ of $\{\epsilon'\}$ with

$$u_{\epsilon''} \overset{*}{\rightharpoonup} 0 \quad \text{in} \quad L^\infty\big([t_0, T]\big).$$

Thus, Thm. 10.4 together with (4.4) and the continuity of $\nabla_q U$ yields

$$\phi({\epsilon''}^{-1} t) \cdot \nabla_q U(q_{\epsilon''}) \overset{*}{\rightharpoonup} 0 \quad \text{in} \quad L^\infty\big([t_0, T]\big). \tag{4.6}$$

In the following step, we consider the equation of motion

$$\ddot{q}_\epsilon = -\nabla_q V(q_\epsilon) - \phi(\epsilon^{-1} t) \cdot \nabla_q U(q_\epsilon).$$

Taking the weak* limit on both sides results in

$$\ddot{q}_0 = -\nabla_q V(q_0) \tag{4.7}$$

where we have made use of (4.5) and (4.6). The limit does not depend on the subsequence $\{\epsilon''\}$ we took. Furthermore, one can show, that there exists a unique solution q_0 to system (4.7). Thus the solution q_0 is not based on a particular subsequence $\{\epsilon''\}$. We can therefore apply Thm. 10.8 and obtain the convergence

$$q_\epsilon \to q_0 \quad \text{in} \quad C\big([t_0, T]\big)$$

for the original sequence $\{\epsilon\}$.

Concluding, let us resume the main steps in analyzing this application via the weak* topology. We found that

1. uniform bounds on q_ϵ, p_ϵ and $\ddot{q}_\epsilon$ are given *a priori* via an energy bound (Assumption (OSC3)),

2. Assumption (OSC2) ensures the weak* convergence of the force term.

3. the subsequence independent limit system allows for a uniform convergence of q_ϵ for the given sequence $\{\epsilon\}$.

§1.1.2 Proof of Thm. 4.1 via averaging transformations

To proof the theorem via an averaging transformation we additionally require $U \in C^2(\mathbb{R})$. The first step of the proof is identical to the proof given above: uniform bounds on q_ϵ, p_ϵ and $\ddot{q}_\epsilon$ are given *a priori* via an energy bound (Assumption (OSC3)). Let us now introduce a canonical transformation of (4.2) defined by the time–dependent generating function

$$S_1(q_\epsilon, y_\epsilon, t) = y_\epsilon^T q_\epsilon - \epsilon g(\epsilon^{-1}\, t) U(q_\epsilon). \tag{4.8}$$

Using the rules of canonical transformations [1, 97]

$$\begin{aligned} p_\epsilon &= \tfrac{\partial S_1}{\partial q_\epsilon} = y_\epsilon - \epsilon g(\epsilon^{-1}\, t) \nabla_{q_\epsilon} U(q_\epsilon) \\ x_\epsilon &= \tfrac{\partial S_1}{\partial y_\epsilon} = q_\epsilon \end{aligned} \tag{4.9}$$

one obtains the defining equations of the new location x_ϵ and momentum y_ϵ. Obviously, we have

$$x_\epsilon = q_\epsilon; \qquad y_\epsilon = p_\epsilon + \mathcal{O}(\epsilon).$$

Moreover, we can calculate the canonical equations of motions in the transformed variables

$$\begin{aligned} \dot{x}_\epsilon &= y_\epsilon - \epsilon g(\epsilon^{-1}\, t) \nabla_{x_\epsilon} U(x_\epsilon) \\ \dot{y}_\epsilon &= -\nabla_{x_\epsilon} V(x_\epsilon) + \epsilon g(\epsilon^{-1}\, t) \nabla^2_{x_\epsilon} U(x_\epsilon) \end{aligned} \tag{4.10}$$

Thus, the transformation (4.9) separates the highly oscillatory parts of the dynamics from the limit dynamics by averaging over the fast time scale. Now, time integration of (4.10) yields the asserted result for finite times due to the uniform bounds on $\phi(\epsilon^{-1}\, t)$ and $g(\epsilon^{-1}\, t)$ (Assumption (OSC2)).

Remark. Note that this approach requires additionally a second derivative of U. But, conversely to the method of weak* convergences one might obtain higher order correction terms in ϵ.

§1.2 The quantum adiabatic theorem

The second example is a singularly perturbed quantum system with time–dependent potential. The state of the finite dimensional[2] system is described by a wave function $\psi : \mathbb{R} \to \mathbb{C}^N$. It obeys the singularly perturbed time–dependent Schrödinger equation

$$i\, \frac{d}{dt} \psi_\epsilon(t) \;=\; \epsilon^{-1}\, H(t) \psi_\epsilon(t) \tag{4.11}$$

with family of Hermitian matrices $H = H(t)$. The initial condition of the quantum state is given by $\psi_\epsilon(t_0) = \psi_*$ with $|\psi_*| = 1$.

Subsequently, we will assume that

(H1) $H : [t_0, T] \to \mathbb{C}^{r \times r}$ is a smooth map.

[2] The infinite dimensional case of the quantum adiabatic theorem was widely studied. See, for example, [13] and the bibliographic remarks therein (Chap. IV.§1.6).

(H2) H has a smooth spectral decomposition for every $t \in [t_0, T]$

$$H(t) = \sum_{\lambda=1}^{s} E_\lambda(t) P_\lambda(t)$$

where the P_λ are orthogonal projections onto mutually orthogonal eigenspaces of H which span $\mathbb{C}^r$.

(E1) the resonance set R

$$R = \big\{ t \in [t_0, T] : E_\lambda(t) = E_\mu(t) \quad \text{for some} \quad \lambda \neq \mu \big\}$$

be at most countable.

The expectation value of the projector to an eigenspace with respect to the wave function is called the population of that eigenspace:

$$\theta_\lambda^\epsilon(t) = \langle P_\lambda(t)\psi_\epsilon(t), \psi_\epsilon(t)\rangle.$$

Let us now present the *quantum adiabatic theorem* which states that the *populations are adiabatic invariants.*

Theorem 4.2 (Thm. 3 in [16]) *Let Assumptions (H1), (H2) and (E1) apply. Then, given a sequence $\epsilon \to 0$, the energy level populations of the wave functions converge to the constant values of the initial populations,*

$$\theta_\lambda^\epsilon = \langle P_\lambda \psi_\epsilon, \psi_\epsilon\rangle \to \theta_\lambda^* = \langle P_\lambda(t_0)\psi_*, \psi_*\rangle \quad \textit{in} \quad C([t_0, T]).$$

§1.2.1 Proof of Thm. 4.2 in a weak* topology

The proof is presented in three steps: first, a weak* limit for the density matrix is derived. Excluding larger than countable resonance sets leads to a certain block–diagonal structure of the limit density matrix . Next a bound for the populations is found and Arzelà–Ascoli's theorem applied. Finally, the statement of the theorem is shown by utilization of the particular structure of the limit density matrix.

We begin with the Ehrenfest theorem [77, Eq. (V.72)] for any time–dependent Hermitian matrix A

$$\frac{d}{dt}\langle A\psi_\epsilon, \psi_\epsilon\rangle = \frac{i}{\epsilon}\langle [H, A]\psi_\epsilon, \psi_\epsilon\rangle + \langle \dot{A}\psi_\epsilon, \psi_\epsilon\rangle.$$

Computing the expectation value with respect to the identity matrix yields the conservation of the norm of the wave function

$$|\psi_\epsilon(t)| = |\psi_*| = 1. \tag{4.12}$$

Introducing the density matrix ρ_ϵ for a *pure* quantum state

$$\rho_\epsilon = \psi_\epsilon \psi_\epsilon^\dagger$$

as well as the trace class norm $\|\cdot\|_1$ on the space of $r \times r$–matrices

$$\|A\|_1 = \mathrm{Tr}\big(AA^\dagger\big)^{\frac{1}{2}}, \qquad A \in \mathbb{C}^{r\times r},$$

one can easily show that

$$\|\rho_\epsilon\|_1 = \mathrm{Tr}(\rho_\epsilon) = 1. \tag{4.13}$$

This uniform bound on the density matrix (4.13) in $L^\infty([t_0,T],\mathbb{C}^{r\times r})$ allows for an application of the Alaoglu Theorem 10.5. For a subsequence $\{\epsilon'\}$ one obtains

$$\rho_{\epsilon'} \overset{*}{\rightharpoonup} \rho_0 \quad \text{in} \quad L^\infty([t_0,T],\mathbb{C}^{r\times r})$$

with a time–dependent and Hermitian limit density matrix ρ_0 with

$$\mathrm{Tr}(\rho_0) = 1.$$

Those properties of ρ_0 can be proved via Lemma B.5 and Lemma B.6 of [13]. However, using the upper bound of Thm. 10.6 for a weakly* converging sequence $\rho_{\epsilon'} \overset{*}{\rightharpoonup} \rho_0$ in $L^\infty([t_0,T],\mathbb{C}^{r\times r})$ we obtain

$$\mathrm{Tr}(\rho_0^2) \le 1.$$

Thus, the limit density matrix does not have to correspond to a pure quantum state but to a statistical mixture of states.[3]

Considering the equation of motion for the density matrix, as derived from (4.11)),

$$i\epsilon\dot{\rho}_\epsilon = [H,\rho_\epsilon],$$

allows for taking the weak* limit $\epsilon' \to 0$ on both sides. The limit on the left hand side can be derived by analyzing the sequence $\epsilon'\rho_{\epsilon'}$. Since $\rho_{\epsilon'}$ is bounded, the sequence $\epsilon'\rho_{\epsilon'}$ converges strongly in time to zero. Since moreover $\epsilon'\dot{\rho}_{\epsilon'} = -i[H,\rho_{\epsilon'}]$ is uniformly bounded in time, $\epsilon'\dot{\rho}_{\epsilon'}$ converges in a weak* sense to zero. Due to the linearity of the RHS with respect to $\rho_{\epsilon'}$, on obtains

$$[H,\rho_{\epsilon'}] \overset{*}{\rightharpoonup} [H,\rho_0] \quad \text{in} \quad L^\infty([t_0,T],\mathbb{C}^{r\times r})$$

and, thus,

$$0 = [H,\rho_0] \quad \text{in} \quad L^\infty([t_0,T],\mathbb{C}^{r\times r}).$$

Inserting the spectral decomposition of H gives

$$\big(E_\lambda(t) - E_\mu(t)\big)\cdot P_\lambda(t)\rho_0 P_\mu(t) = 0,$$

and for an at most countable resonance set R (Assumption (E1)) one obtains

$$P_\lambda(t)\rho_0 P_\mu(t) = 0 \quad \text{for} \quad \lambda \ne \mu.$$

Thus, the limit density matrix ρ_0 has a block–diagonal form

$$\rho_0 = \sum_\lambda P_\lambda(t)\rho_0 P_\lambda(t).$$

[3]Note, that the *pure* quantum state has the property $\rho_\epsilon^2 = \rho_\epsilon$, $\mathrm{Tr}(\rho^2) = 1$ whereas a *statistical mixture* of quantum states obeys $\rho_\epsilon^2 \ne \rho_\epsilon$, $\mathrm{Tr}(\rho^2) \le 1$.

At last, consider now the populations θ_λ^ϵ. They are given by

$$\theta_\lambda^\epsilon = \langle P_\lambda \psi_\epsilon, \psi_\epsilon \rangle = \mathrm{Tr}(\rho_\epsilon P_\lambda).$$

Since they are bounded in $L^\infty([t_0,T],\mathbb{C})$, we can apply the Alaoglu theorem 10.5 and obtain for a subsequence $\{\epsilon'\}$ a weak* convergence $\theta_\lambda^{\epsilon'} \overset{*}{\rightharpoonup} \theta_\lambda^0$ in $L^\infty([t_0,T],\mathbb{C})$. However, due to our assumption of a smoothly diagonizable Hamiltonian also the time derivative of θ_λ^ϵ is bounded in $L^\infty([t_0,T],\mathbb{C})$

$$\dot\theta_\lambda^\epsilon = \mathrm{Tr}(\rho_\epsilon \dot P_\lambda). \tag{4.14}$$

We apply the Arzelà-Ascoli theorem 10.7 and get for a subsequence $\{\epsilon'\}$ a strong convergence $\theta_\lambda^{\epsilon'} \to \theta_\lambda^0$ in $C([t_0,T],\mathbb{C})$ as well as $\dot\theta_\lambda^{\epsilon'} \overset{*}{\rightharpoonup} \dot\theta_\lambda^0$ in $L^\infty([t_0,T],\mathbb{C})$ for $\epsilon \to 0$. It remains to compute the strong limit θ_λ^0. We therefore take the weak* limit of (4.14) and obtain

$$\begin{aligned} \dot\theta_\lambda^0 &= \mathrm{Tr}(\rho_0 \dot P_\lambda) \\ &= \sum_\mu \mathrm{Tr}(P_\mu \rho_0 P_\mu \dot P_\lambda) \\ &= \sum_\mu \mathrm{Tr}(\rho_0 P_\mu \dot P_\lambda P_\mu). \end{aligned}$$

It is easy to show that $P_\mu \dot P_\lambda P_\mu = 0$. This yields $\dot\theta_\lambda^0 = 0$ and proves via time integration for finite times the adiabatic invariance of the populations[4]

$$\theta_\lambda^0(t) = \theta_\lambda^0(t_0) = \theta_\lambda^*.$$

§1.2.2 Proof of Thm. 4.2 via averaging transformations

For this approach, we have to make our assumptions stricter: we explicitly have to exclude energy level crossings:

(E1') Exclude energy level crossings

$$E_\lambda(t) = E_\mu(t) \quad \text{for} \quad \lambda \neq \mu.$$

Furthermore, we require

[4] Adapting Corollary 2 of [16] to the purely quantum dynamical case, it can be shown that if the initial populations θ_λ^* are nonzero only for simple eigenvalues, then the density matrices ρ_ϵ converge as

$$\rho_\epsilon \overset{*}{\rightharpoonup} \rho_0 = \sum_\lambda \theta_\lambda^* P_\lambda(\cdot) \quad \text{in} \quad L^\infty([t_0,T],\mathbb{C}^r).$$

For each $\theta_\lambda^* \neq 0$, the projection P_λ is the density matrix belonging to a corresponding normalized eigenvector e_λ,

$$P_\lambda = e_\lambda e_\lambda^\dagger, \qquad H e_\lambda = E_\lambda e_\lambda, \qquad |e_\lambda| = 1.$$

The expectation values of a time–dependent observable A converge as

$$\langle A\psi_\epsilon, \psi_\epsilon \rangle \overset{*}{\rightharpoonup} \sum_\lambda \theta_\lambda^* \langle A e_\lambda, e_\lambda \rangle \quad \text{in} \quad L^\infty([t_0,T]).$$

If the commutation relation $[H,A]=0$ holds, the convergence is strong in $C([t_0,T])$.

(E2) all eigenvalues to be simple denoting by $e_\lambda(t)$ the eigenvector to eigenvalue $E_\lambda(t)$ of $H(t)$:

$$H(t)e_\lambda(t) = E_\lambda(t)e_\lambda(t)$$

We split the quantum wave function into a scaled real– and imaginary part:

$$\psi_\epsilon = \frac{\epsilon^{-1} z_\epsilon + i\zeta_\epsilon}{\sqrt{2}}. \tag{4.15}$$

Remark. Scaled decompositions like (4.15) are commonly used in the literature to give the Schrödinger equation a canonical Hamiltonian structure. A more intrinsic way of this argument in the setting of infinite Hamiltonian systems can be found in [19][74].

Introducing conjugated locations z_ϵ and momenta ζ_ϵ yields a canonical system with Hamiltonian function $\mathcal{H}_{\text{QD}}$

$$\mathcal{H}_{\text{QD}}(z_\epsilon, \zeta_\epsilon, t) = \tfrac{1}{2}\langle \zeta_\epsilon, H(t)\zeta_\epsilon\rangle + \tfrac{1}{2}\epsilon^{-2}\langle z_\epsilon, H(t)z_\epsilon\rangle \tag{4.16}$$

and equations of motion

$$\begin{aligned} \dot{\zeta}_\epsilon &= -\frac{1}{\epsilon^2}H(t)z_\epsilon \\ \dot{z}_\epsilon &= H(t)\zeta_\epsilon. \end{aligned}$$

Using the well–known technique of action–angle variables [1] we obtain actions θ_ϵ^λ and the corresponding angles φ_ϵ^λ via:

$$\begin{aligned} z_\epsilon &= \epsilon \sum_\lambda \sqrt{2\theta_\epsilon^\lambda}\cos(\epsilon^{-1}\varphi_\epsilon^\lambda)e_\lambda(t) \\ \zeta_\epsilon &= -\sum_\lambda \sqrt{2\theta_\epsilon^\lambda}\sin(\epsilon^{-1}\varphi_\epsilon^\lambda)e_\lambda(t) \end{aligned}$$

with initial values $\theta_\epsilon^\lambda(t_0) = \theta_*^\lambda$ and $\varphi_\epsilon^\lambda(t_0) = \varphi_*^\lambda$. An expansion of the quantum wave function ψ_ϵ in the (so–called adiabatic) eigenfunctions $e_\lambda(t)$ yields

$$\psi_\epsilon = \sum_\lambda \sqrt{\theta_\epsilon^\lambda}\exp(-i\epsilon^{-1}\varphi_\epsilon^\lambda)\, e_\lambda(t) \tag{4.17}$$

with initial values

$$\psi_* = \sum_\lambda \sqrt{\theta_*^\lambda}\exp(-i\epsilon^{-1}\varphi_*^\lambda)\, e_\lambda(t_0).$$

The action variable θ_ϵ^λ is, in fact, the population of energy level E_λ as already defined in §1.2.1. A Hamiltonian system in the action–angle variables is obtained by applying a canonical transformation [1] $(z_\epsilon, \zeta_\epsilon) \to (\theta_\epsilon, \varphi_\epsilon)$ to the original system with Hamiltonian function (4.16). This symplectic transformation might be constructed employing the generating function [1]

$$S(z_\epsilon, \varphi_\epsilon, t) = -\frac{\epsilon^{-1}}{2}\sum_\lambda \langle z_\epsilon, e_\lambda(t)\rangle^2 \tan(\epsilon^{-1}\varphi_\epsilon^\lambda)$$

via $\zeta_\epsilon = \partial S/\partial z_\epsilon$, $\theta_\epsilon = -\partial S/\partial \varphi_\epsilon$. We obtain a transformed Hamiltonian function $\tilde{\mathcal{H}}_{\mathrm{QD}} = \tilde{\mathcal{H}}_{\mathrm{QD}}(\theta_\epsilon, \varphi_\epsilon, t)$

$$\tilde{\mathcal{H}}_{\mathrm{QD}} = \sum_\lambda \theta_\epsilon^\lambda E_\lambda(t) + \epsilon \sum_{\substack{\lambda,\eta \\ \lambda\neq\eta}} \sqrt{\theta_\epsilon^\lambda \theta_\epsilon^\eta}\, \sin\left(\epsilon^{-1}\left(\varphi_\epsilon^\lambda - \varphi_\epsilon^\eta\right)\right) \big\langle e_\lambda(t), \dot{e}_\eta(t)\big\rangle.$$

The canonical equations

$$\dot{\varphi}_\epsilon^\lambda = \frac{\partial \tilde{\mathcal{H}}_{\mathrm{QD}}}{\partial \theta_\epsilon^\lambda}, \quad \dot{\theta}_\epsilon^\lambda = -\frac{\partial \tilde{\mathcal{H}}_{\mathrm{QD}}}{\partial \varphi_\epsilon^\lambda}$$

finally lead to the equations of motions in action–angle variables

$$\begin{aligned}
\dot{\varphi}_\epsilon^\lambda &= E_\lambda(t) + \epsilon \sum_{\substack{\eta \\ \eta\neq\lambda}} \sqrt{\frac{\theta_\epsilon^\eta}{\theta_\epsilon^\lambda}}\, \sin(\epsilon^{-1}\left(\varphi_\epsilon^\lambda - \varphi_\epsilon^\eta\right)) \big\langle e_\lambda(t), \dot{e}_\eta(t)\big\rangle \\
\dot{\theta}_\epsilon^\lambda &= -2 \sum_{\substack{\eta \\ \eta\neq\lambda}} \sqrt{\theta_\epsilon^\lambda \theta_\epsilon^\eta}\, \cos(\epsilon^{-1}\left(\varphi_\epsilon^\lambda - \varphi_\epsilon^\eta\right)) \big\langle e_\lambda(t), \dot{e}_\eta(t)\big\rangle
\end{aligned}$$

Excluding symmetric energy level crossings (Assumption (E1')) and making use of the near–identity averaging transformation

$$\Theta_\epsilon^\lambda = \theta_\epsilon^\lambda - 2\epsilon \sum_{\substack{\eta \\ \eta\neq\lambda}} \frac{\sqrt{\theta_\epsilon^\lambda \theta_\epsilon^\eta}}{E_\lambda - E_\eta}\, \sin(\epsilon^{-1}\left(\varphi_\epsilon^\lambda - \varphi_\epsilon^\eta\right)) \big\langle e_\lambda(t), \dot{e}_\eta(t)\big\rangle \tag{4.18}$$

leads to the following equations of motion for the new variables $\phi_\epsilon^\lambda, \Theta_\epsilon^\lambda$

$$\dot{\phi}_\epsilon^\lambda = E_\lambda(t) + \mathcal{O}(\epsilon) \qquad \dot{\Theta}_\epsilon^\lambda = \mathcal{O}(\epsilon)$$

and with integration over finite time spans

$$\phi_\epsilon^\lambda(t) = \phi_*^\lambda + \int_{t_0}^t E_\lambda(s)\, ds + \mathcal{O}(\epsilon) \qquad \Theta_\epsilon^\lambda(t) = \Theta_\epsilon^\lambda(t_0) + \mathcal{O}(\epsilon) = \theta_*^\lambda + \mathcal{O}(\epsilon)$$

where we have transformed $\Theta_\epsilon^\lambda(t_0)$ back using (4.18). Obviously, the populations θ_ϵ^λ are adiabatic invariants as stated in Thm. 4.2.

Let us concludingly point out, that the proof in the context of weak* convergence requires much weaker assumptions: instead of excluding energy level crossings altogether, one might there allow a countable resonance set R. However, the method of weak* convergence does not allow to compute higher order terms in ϵ.

§1.2.3 Proof of Thm. 4.2 using rotating axes

Again, we have to exclude energy level crossings (Assumption (E1')). Furthermore, assume that

(H2') the time derivatives of the orthogonal projections $\frac{d}{dt} P_\lambda$ and $\frac{d^2}{dt^2} P_\lambda$ exist and are piecewise continuous.

Denote the unitary time propagator to (4.11) with $U_\epsilon(t)$:

$$\psi_\epsilon(t) = U_\epsilon(t)\psi_\epsilon(t_0).$$

Obviously, it obeys the following Schrödinger equation:

$$i\,\frac{d}{dt}U_\epsilon(t) \quad = \quad \epsilon^{-1}\,H(t)U_\epsilon(t), \qquad U_\epsilon(t_0) = \mathbb{I}. \tag{4.19}$$

Subsequently, we will transform (4.11) into a system with rotating axes. Beginning with the construction of the *adiabatic transformation* (4.20), we will introduce a kind of interaction picture which allows us to distinguish between the motion due to the rotating axes and the "non–adiabatic" dynamics.

Adiabatic transformation

Definition 4.3 *The unitary transformation $A_\epsilon(t)$, mapping the projector $P_\lambda(t_0)$ corresponding to the eigenspace associated with $E_\lambda(t_0)$ onto the projector $P_\lambda(t)$*

$$P_\lambda(t) = A_\epsilon(t)P_\lambda(t_0)A_\epsilon^+(t); \qquad A_\epsilon(t_0) = \mathbb{I}. \tag{4.20}$$

is called adiabatic transformation*.*

The adiabatic transformation obeys the following differential equation

$$i\,\frac{d}{dt}A_\epsilon(t) = N_\epsilon(t)A_\epsilon(t), \qquad A_\epsilon(t_0) = \mathbb{I} \tag{4.21}$$

with a suitable Hermitian operator $N_\epsilon(t)$. The relation (4.20) is only satisfied under condition

$$i\,\frac{d}{dt}P_\lambda(t) = [N_\epsilon(t), P_\lambda(t)]. \tag{4.22}$$

Since $N_\epsilon(t)$ is not uniquely defined — one could add any operator of the form $\sum_\lambda P_\lambda(t)f_\lambda(t)P_\lambda(t)$ with an arbitrary smooth operator f_λ— we require in addition that

$$P_\lambda(t)N_\epsilon(t)P_\lambda(t) = 0. \tag{4.23}$$

Directly follows the next lemma:

Lemma 4.4 *Under the conditions given above and with respect to (4.23) one obtains*

$$N_\epsilon(t) = i\sum_\lambda \frac{dP_\lambda(t)}{dt}P_\lambda(t). \tag{4.24}$$

Remark. In the case of simple eigenspaces (Assumption (E2)) the Hermitian operator N_ϵ in application to a wave function ψ equals

$$N_\epsilon(t)\psi = i\sum_\lambda \Big(\frac{d}{dt}e_\lambda(t)\Big)\langle e_\lambda(t), \psi\rangle.$$

Likewise, the application of $A_\epsilon(t)$ onto eigenvector $e_\lambda(t_0)$ gives

$$e_\lambda(t) = A_\epsilon(t)e_\lambda(t_0).$$

Here, the interpretation of A_ϵ as adiabatic transformation becomes evident.

Interaction picture Let us now introduce some transformed operators H^A, N_ϵ^A and U_ϵ^A:

$$\begin{aligned} H_\epsilon^A(t) &= A_\epsilon^+(t)\,H(t)\,A_\epsilon(t) \\ N_\epsilon^A(t) &= A_\epsilon^+(t)\,N_\epsilon(t)\,A_\epsilon(t) \\ U_\epsilon^A(t) &= A_\epsilon^+(t)\,U_\epsilon(t). \end{aligned}$$

The new operator H_ϵ^A represents the Hamiltonian operator in the rotating frame. The resulting differential equation for the transformed propagator $U_\epsilon^A(t)$ has two parts on the right hand side: the part corresponding to the transformed H_ϵ^A as well as a part, which includes the deviation from this rotating frame:

$$i\,\frac{d}{dt}U_\epsilon^A = (\epsilon^{-1}\,H_\epsilon^A - N_\epsilon^A)U_\epsilon^A, \qquad U_\epsilon^A(t_0) = \mathbb{I}. \tag{4.25}$$

Now, let us concentrate on the so–called *adiabatic system*

$$i\,\frac{d}{dt}\sigma_\epsilon = \epsilon^{-1}\,H_\epsilon^A\sigma_\epsilon, \qquad \sigma_\epsilon(t_0) = \mathbb{I}. \tag{4.26}$$

It's solution is given by

$$\sigma_\epsilon(t) = \sum_\lambda \exp\left(-i\epsilon^{-1}\int_0^t E_\lambda(q_\epsilon(s))ds\right)P_\lambda(t_0). \tag{4.27}$$

Thus, the propagator corresponding to the adiabatic system just adds a Born–Oppenheimer phase but does not induce population changes. Considering the following lemma, the name of the adiabatic system becomes clear and Thm. 4.2 is proved.

Lemma 4.5 *Under Assumptions (E1')(no eigenvalue crossings) and (H2') one obtains*

$$U_\epsilon^A(t) = \sigma_\epsilon(t) + \mathcal{O}(\epsilon). \tag{4.28}$$

PROOF. To proof this lemma, let us separate the adiabatic motion from the non–adiabatic parts of the dynamics. Therefore we define a modified propagator

$$W_\epsilon(t) = \sigma_\epsilon^+(t)U_\epsilon^A(t) = \sigma_\epsilon^+(t)A_\epsilon^+(t)U_\epsilon(t) \tag{4.29}$$

with initial value $W_\epsilon(t_0) = \mathbb{I}$. Obviously, W_ϵ represents just the remaining non–adiabatic dynamics after stripping off the adiabatic motion. It satisfies the differential equation

$$\frac{d}{dt}W_\epsilon(t) = i\bar{N}_\epsilon(t)W_\epsilon(t) \quad \text{with} \quad \bar{N}_\epsilon(t) = \sigma_\epsilon^+(t)N_\epsilon^A(t)\sigma_\epsilon(t) \tag{4.30}$$

or, respectively, the integral equation

$$\begin{aligned} W_\epsilon(t) &= \mathbb{I} + i\int_0^t \bar{N}_\epsilon(s)W_\epsilon(s)ds \qquad (4.31) \\ &= \mathbb{I} + i\int_0^t \sigma_\epsilon^+(s)N_\epsilon^A(s)U_\epsilon^A(s)ds \end{aligned}$$

To show that (4.26) is the limit system of (4.25), one expands the integral kernel of (4.31) into the eigenspaces of H and applies a partial integration [63, 77]. The highly oscillatory character of the integral kernel yields an $\mathcal{O}(\epsilon)$ approximation under the exclusion of eigenvalue crossings. Thus, we get:

$$W_\epsilon(t) = \mathbb{I} + \mathcal{O}(\epsilon). \tag{4.32}$$

and therefore the above stated result. □

§2 Adiabatic limit of QD

What is the limit equation of the full quantum dynamics (2.8) governing $\epsilon \to 0$? Exactly this question has been addressed in different mathematical approaches, [21], [40], and [76]. We will follow Hagedorn [40] whose results are based on the product state assumption (IP) on page 8. Furthermore, assume that

(IP2') the the initial state ϕ_* is given by an approximate δ-function, e.g.,

$$\phi_*(q) \;=\; \tfrac{1}{A_\epsilon}\, \exp\left(-\tfrac{1}{4\epsilon}(q-q_*)^2\right) \exp\left(\tfrac{i}{\epsilon}\dot{q}_* q\right). \tag{4.33}$$

Analogously to our investigation of the quantum adiabatic theorem in Sec. §1.2, we have to require

(A1) the q–parameterized Hamiltonian $H(q) = -\frac{1}{2}\Delta_x + V(x,q)$ to have a spectral decomposition

$$H(q) \;=\; \textstyle\sum_k E_k(q)\, P_k(q), \tag{4.34}$$

where $P_k(q)$ is the orthogonal projection onto the eigenspace associated with $E_k(q)$. With respect to a quantum state ψ, the number $\theta_k = \langle\psi, P_k\psi\rangle$ is the *population* of the *energy level* E_k.

Definition 4.6 *The* Born–Oppenheimer dynamics *(BO) is defined by*

$$\begin{aligned} \ddot{q}_{\mathrm{BO}} &= -grad_q \sum_\lambda \theta_*^\lambda\, E_\lambda(q_{\mathrm{BO}}), \\ q_{\mathrm{BO}}(t_0) &= q_*, \qquad \dot{q}_{\mathrm{BO}}(t_0) = \dot{q}_* \end{aligned} \tag{4.35}$$

with the initial values q_* and $\dot{q}_*$ corresponding to (4.33). The constant *θ_*^λ is the initial population of level E_λ and thus computable from the initial data: $\theta_*^\lambda = \langle\psi_*, P_\lambda(q_*)\psi_*\rangle$.*

Corresponding to assumption (E1'), exclude now all energy level crossings along the BO solution:

(E1") Along the BO solution q_{BO}, crossings between initially occupied energy levels are excluded, i.e., for all pairs (E_λ, E_μ) of energy levels with $\lambda \neq \mu$ and $\theta_*^\lambda + \theta_*^\mu > 0$, we have $E_\lambda(q_{\mathrm{BO}}(t)) \neq E_\mu(q_{\mathrm{BO}}(t))$ for all $t \in [t_0, T]$.

Using these conditions and the BO solution q_{BO}, a wave function Ψ_{BO} is constructed which comes out to be the limit of the sequence of QD solution Ψ_ϵ for $\epsilon \to 0$, [40]. In particular, for the position expectation

$$\langle q \rangle_\epsilon^{\text{QD}} = \langle \Psi_\epsilon, q\Psi_\epsilon \rangle(t),$$

the statement of Hagedorn is:

Theorem 4.7 (Thm. 2.1 in [40]) *Assume $q_{\text{BO}} = q_{\text{BO}}(t)$ to be the solution of the BO equation, Eq. (4.35), in a finite time interval $[0, T]$ and let Assumptions (IP2'), (A1) and (E1") be satisfied. Furthermore assume that only one energy level is initially occupied. Then, we have*

$$\lim_{\epsilon \to 0} \langle q \rangle_\epsilon^{\text{QD}} = q_{\text{BO}} \qquad \textit{in } [0, T].$$

That is, in the limit $\epsilon \to 0$, the center of the QD wave packet Ψ_ϵ moves along the BO-solution.

§3 Adiabatic limit of QCMD

The limit equation of (2.9) governing $\epsilon \to 0$ can be motivated by referring to the *quantum adiabatic theorem* (Thm. 4.2): The classical position q_ϵ influences the Hamiltonian very slowly compared to the time scale of oscillations of ψ_ϵ, in fact, "infinitely slowly" with respect to the unscaled time in the limit $\epsilon \to 0$. Thus, in analogy to the quantum adiabatic theorem, one would expect that the populations of the energy levels with respect to $H(q_\epsilon)$ remain *invariant* during the evolution:

$$\lim_{\epsilon \to 0} \theta_\lambda^\epsilon(t) = \lim_{\epsilon \to 0} \langle \psi_\epsilon, P_\lambda(q_\epsilon)\psi_\epsilon \rangle = \theta_*^\lambda = \langle \psi_*, P_\lambda(q_*)\psi_* \rangle.$$

All this turns out to be true: According to [16], the BO dynamics is the limit solution, whenever the following assumption on the eigenspaces and eigenenergies of $H(q)$ is satisfied:

(E3) The spectral decomposition Eq. (4.34) of H depends smoothly on q and the transversality condition

$$\frac{d}{dt}\big(E_\lambda(q_{\text{BO}}) - E_\mu(q_{\text{BO}})\big) \neq 0 \tag{4.36}$$

holds.

Remark. Note, that Assumption [(E3)] does *not* exclude *energy level crossings.*

Theorem 4.8 (Theorem in [16]) *On the time interval $[t_0, T]$, there exists a smooth unique solution q_{BO} of the Born–Oppenheimer model (4.35), and, for every $\epsilon > 0$, a smooth unique solution q_ϵ of the QCMD model (2.9). Let assumption (E3) apply. Then, given a sequence $\epsilon \to 0$, the classical components of the QCMD model converge to those of the Born–Oppenheimer model (4.35),*

$$q_\epsilon \to q_{\text{BO}} \qquad \textit{in} \qquad C^1\big([t_0, T], \mathbb{R}^n\big),$$

and the energy level populations of the wave functions converge to the constants given by their initial values,

$$\langle \psi_\epsilon, P_\lambda(q_\epsilon)\psi_\epsilon \rangle \to \theta_*^\lambda \qquad in \qquad C^1[t_0, T].$$

The proof of this theorem is quite similar to the proofs given in §1.1.1 and §1.2.1. At first, the existence and uniform boundedness of the QCMD solution is shown using energy estimates. Then the existence of a limit solution is proven. In a next step, a density matrix is introduced and its weak* limit derived. An application onto the equations of motion lead to the adiabatic invariance of the populations. Finally, the limit force of the classical equation is computed.

Remark. The reader might note that the transversality condition in assumption (E3) just ensures a countable resonance set R as in §1.2.

Summarizing, QD and QCMD have the same adiabatic limit solution which is given by the BO model if the initial conditions are appropriate and if we exclude energy level crossings and discontinuities of the spectral decomposition. Consequently, QCMD is justified as an approximation of QD if only ϵ is small enough and these conditions are satisfied (see Fig. 4.1). These are important

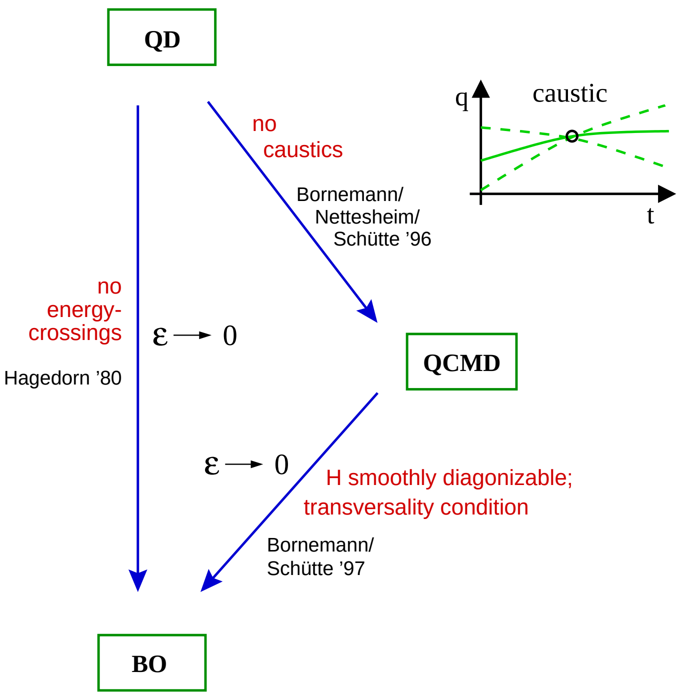

FIGURE 4.1. Abstract representation of full quantum dynamics (QD), quantum–classical molecular dynamics (QCMD) and the Born–Oppenheimer dynamics (BO). The justification of QCMD from QD fails at the presence of caustics, whereas the BO model requires assumptions on the energy levels of $H(q)$.

results. However, the following questions remain: What happens, if $H(q)$ has no smooth spectral decomposition? Can QCMD describe anything beyond the correct adiabatic limit of QD? Can it describe *non–adiabatic effects*, i.e., deviations of the QD solution from its adiabatic limit for realistically small $\epsilon > 0$? The following chapters try to give answers to these questions.

§4 Multivalued adiabatic limit: Takens chaos

What happens, if one of the assumptions leading to the adiabatic limit of QCMD is not valid? In this section, we will follow [16] in focusing on the case, that the spectral decomposition (Assumption (E3)) is discontinuous at one point of q. The smallest generical example having a smooth symmetric matrix which is not smoothly diagonizable was given by Rellich [94, §2]. Consider the classical positions $q = (q^1, q^2)$ and take as Hamiltonian the real symmetric matrix

$$H(q) = \begin{pmatrix} q^1 & q^2 \\ q^2 & -q^1 \end{pmatrix}. \tag{4.37}$$

The eigenvalues of $H(q)$ are given by $E_1(q) = -|q|$ and $E_2(q) = |q|$ (Fig. 4.2). Using polar coordinates $q^1 = r\cos\varphi$ and $q^2 = r\sin\varphi$ and excluding $q = 0$, the

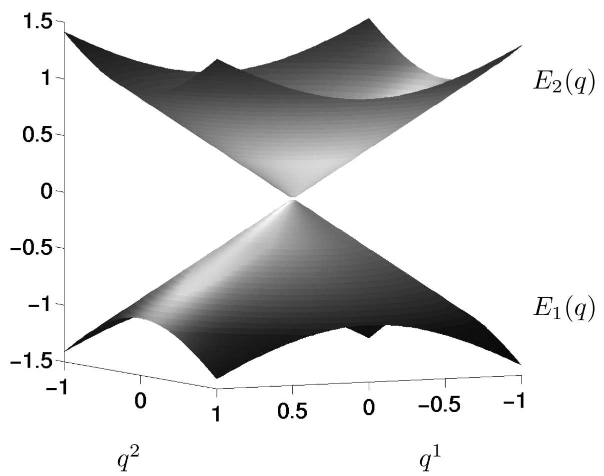

Figure 4.2. Eigenvalues of Hamiltonian (4.37).

eigenvectors to E_1 and E_2 are

$$e_1 = \begin{pmatrix} -\sin(\varphi/2) \\ \cos(\varphi/2) \end{pmatrix}, \qquad e_2 = \begin{pmatrix} \cos(\varphi/2) \\ \sin(\varphi/2) \end{pmatrix}.$$

Obviously, we have to cut the plane along a half–axis to obtain a unique representation, because these eigenvectors are defined up to a sign only. But note, a discontinuity of the eigenvectors remain a the cut: there they change their role. Consider now the following initial values

$$q_\epsilon(0) = (1, 0), \qquad \dot{q}_\epsilon(0) = (0, \mu), \qquad \psi_\epsilon(0) = (1, 0),$$

depending on a parameter $\mu \geq 0$. The case $\mu = 0$ leads to a unique limit trajectory through the singularity $q = 0$: $q_{\text{BO}}^{\mu=0}(t)$. Much more interesting is the case of a given limit sequence $\mu \downarrow 0$ with $\mu > 0$. One obtains a limit solution $q_{\text{BO}}^{\mu\downarrow 0}(t)$. Now, a thorough analysis in [16] reveals that after the singularity is passed, i.e., for times $t > \sqrt{2}$, the limits $\epsilon \to 0$ and $\mu \to 0$ are not interchangeable

$$\lim_{\epsilon \to 0} \lim_{\mu \downarrow 0} q_\epsilon(t) = q_{\text{BO}}^{\mu=0}(t) \neq q_{\text{BO}}^{\mu\downarrow 0}(t) = \lim_{\mu \downarrow 0} \lim_{\epsilon \to 0} q_\epsilon(t), \qquad t > \sqrt{2}.$$

But not only this, at time $t > \sqrt{2}$ any value

$$q_{\text{BO}}^{\mu=0}(t) \leq \tilde{q} \leq q_{\text{BO}}^{\mu\downarrow 0}(t).$$

can be obtained by a suitable simultaneous limit sequence $\mu(\epsilon) \downarrow 0$. Thus, after the singularity, a funnel of trajectories between the two extreme cases $q_{\text{BO}}^{\mu=0}(t)$ and $q_{\text{BO}}^{\mu\downarrow 0}(t)$ is obtained. Since the appearance of such funnels as the limit set of certain singularly perturbed problems has been discovered by TAKENS [110] we speak of *Takens-chaos*, cf. [16].

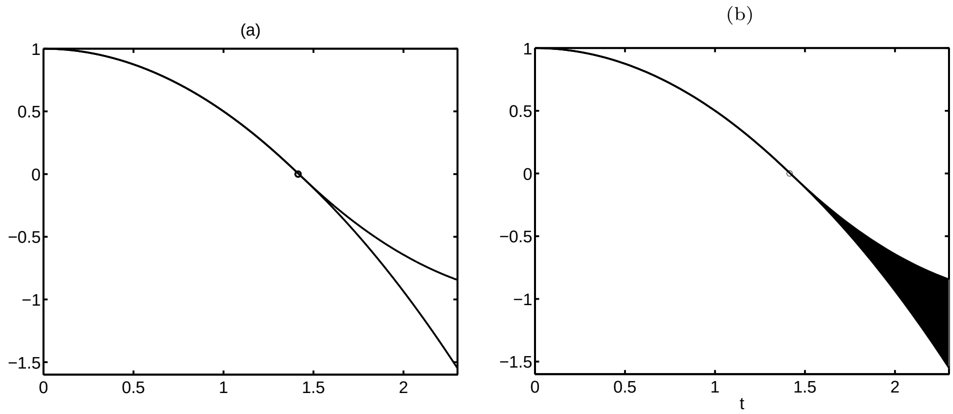

FIGURE 4.3. Illustration (q^1 vs. t) of Takens-chaos from [16]: (a) the two different limit solutions $q_{\text{BO}}^{\mu=0}$ and $q_{\text{BO}}^{\mu\downarrow 0}$, (b) the funnel of possible limits for $\epsilon \to 0$, $\mu \to 0$.