On the Singular Limit of the Quantum-Classical Molecular Dynamics Model

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Abstract

In molecular dynamics applications there is a growing interest in so-called *mixed quantum-classical* models. These models describe most atoms of the molecular system by the means of classical mechanics but an important, small portion of the system by the means of quantum mechanics. A particularly extensively used model, the QCMD model, consists of a *singularly perturbed* Schrödinger equation nonlinearly coupled to a classical Newtonian equation of motion.

This paper studies the singular limit of the QCMD model for finite dimensional Hilbert spaces. The main result states that this limit is given by the time-dependent Born-Oppenheimer model of quantum theory—provided the Hamiltonian under consideration has a smooth spectral decomposition. This result is strongly related to the *quantum adiabatic theorem*. The proof uses the method of *weak convergence* by directly discussing the density matrix instead of the wave functions. This technique avoids the discussion of highly oscillatory phases.

On the other hand, the limit of the QCMD model is of a different nature if the spectral decomposition of the Hamiltonian happens not to be smooth. We will present a generic example for which the limit set is not a unique trajectory of a limit dynamical system but rather a *funnel* consisting of infinitely many trajectories.

Keywords: QCMD model, Born-Oppenheimer model, quantum adiabatic theorem, weak convergence, density matrix, funnel, Takens-chaos

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1 Introduction

Most commonly, the simulation of the dynamical behavior of molecular systems is based on the assumption that the system of interest can sufficiently well be described by models of classical mechanics. However, such classical molecular dynamics approaches cannot be valid if the very nature of the process under consideration is *quantum mechanically*: e.g., the transfer of key protons in enzymes, clusters, or matrices. In all these cases, a quantum dynamical description is unavoidable. Since a full quantum dynamics simulation of, e.g., a complete enzyme is not feasible, so-called *mixed quantum-classical* models have found growing interest in applications. These models describe most atoms by the means of classical mechanics but an important, small portion of the underlying system by the means of quantum mechanics.

In the current literature various mixed quantum-classical models have been proposed. We will restrict our attention to the so-called QCMD (quantum-classical molecular dynamics) model which has been used extensively for real life applications, cf. [4][7] and the references cited therein. Our concern is a further mathematical understanding of this model.

For the sake of simplicity we introduce the QCMD model in the case of two particles. We assume that they have spatial coordinates $x \in \mathbb{R}^d$ and $q \in \mathbb{R}^n$, with mass $m = \epsilon^2 \ll 1$, respectively $M = 1$. The interaction potential will be denoted by $V(x,q)$. The lighter particle is supposed to perform quantum motion. It thus has to be described by a quantum Hamiltonian H, which is typically of the form

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

where Δ_x denotes the Laplacian with respect to x. Hence, the Hamiltonian is parametrized by the position q of the heavier particle, the description of which remains classical. The equations of motion of the QCMD model are given by

$$\begin{aligned} \ddot{q}_\epsilon &= -\operatorname{grad}_q \langle H(q_\epsilon)\psi_\epsilon, \psi_\epsilon\rangle, \\ i\epsilon\,\dot{\psi}_\epsilon &= H(q_\epsilon)\,\psi_\epsilon. \end{aligned}$$

Here, $\langle\cdot,\cdot\rangle$ denotes the scalar product in the Hilbert space of the model.

In the present paper, we will study the singular limit $\epsilon \to 0$ which is of interest for a couple of reasons: Because the QCMD model is known to be an $O(\epsilon)$-approximation of *full* quantum dynamics [7], it is typically applied to situations with $\epsilon \ll 1$. On the other hand, the quantum part ψ_ϵ is oscillating on a time scale of order $O(\epsilon)$. Unfortunately, the computational effort of any direct numerical integration of the QCMD model is heavily dominated by the approximation of these fast oscillations. The chemically interesting information, however, appears on a time scale of order $O(1)$. In the singular limit, the fast scale $O(\epsilon)$ will be eliminated but its *averaged* influence will still be present. Thus, besides yielding analytical insight into the model, the study of the limit $\epsilon \to 0$ opens the way towards advanced numerical techniques.

We will assume that the Hilbert space of the quantum state ψ_ϵ is *finite dimensional*. Thus, H denotes an Hermitean matrix, which, for example, can be viewed as the representation of the Hamiltonian (1) according to a discretization of the Laplacian Δ_x. By employing considerable technical tools from functional analysis, the first author was recently able to extend the ideas presented below to the infinitely dimensional case, cf. [6]. However, the present short account on the finite dimensional case helps to concentrate on the basic ideas, which, in the opinion of the authors, could be of general interest for singular perturbation problems with highly oscillatory solutions.

We will obtain a limit equation that can be motivated by referring to the *quantum adiabatic theorem*, originating from work of BORN and FOCK [5]. The classical position q influences the Hamiltonian very slowly compared to the time scale of oscillations of ψ_ϵ, in fact, "infinitely slowly" in the limit $\epsilon \to 0$. Thus, in analogy to the quantum adiabatic theorem, one would expect—under certain assumptions on the eigenstates $\psi_\lambda(q)$ and eigenenergies $E_\lambda(q)$ of the Hamiltonian $H(q)$—the following *adiabatic invariance*:

$$|\langle \psi_\epsilon, \psi_\lambda(q_\epsilon)\rangle|^2 \;\to\; \theta_\lambda = \text{const}, \qquad \epsilon \to 0,$$

uniformly as functions of time. Together with a uniform convergence $q_\epsilon \to q_0$, this would imply the convergence of the "potential" energy,

$$\langle H(q_\epsilon)\psi_\epsilon, \psi_\epsilon\rangle \;\to\; U_{\mathrm{BO}}(q_0) = \textstyle\sum_\lambda \theta_\lambda\, E_\lambda(q_0).$$

Thus, we are led to expect the *limit equation* being

$$\ddot{q}_0 \;=\; -\operatorname{grad}_q U_{\mathrm{BO}}(q_0),$$

which is the well-known *time-dependent Born-Oppenheimer approximation* of quantum theory, cf. [9][12]. In §2 we will present a rigorous proof for this fact, which we call the *quantum–classical adiabatic theorem*. We employ a variant of the *weak convergence method* which we have introduced for the *homogenization* of certain singularly perturbed equations of classical mechanics, cf. [8]. This method allows to address the limit motion straightforwardly without explicit knowledge of the phase of ψ_ϵ. This phase drops out since we directly discuss the weak limit of the density matrix $\rho_\epsilon = \psi_\epsilon\psi_\epsilon^\dagger$. In contrast, all proofs of the quantum adiabatic theorem, the present authors know of, proceed by first, representing the phase of ψ_ϵ asymptotically correct, and second, approximating the amplitude.

We will prove the quantum-classical adiabatic theorem in a way that the quantum adiabatic theorem is a simple corollary. We will discuss in §3 to which extend our approach weakens the assumptions known in the literature.

The proof of the quantum-classical adiabatic theorem relies strongly on the assumption of a smooth dependence of the spectral decomposition of H on the parameter vector q. Whereas this is generically true for a scalar parameter dependence, it is *not* true for a vector parameter dependence in general. In §4 we will illustrate what can happen in the case of a nonsmooth spectral decomposition: The QCMD solutions can depend extremely sensitively on the initial data for small ϵ. In the singular limit, this sensitivity leads to a *funnel* of limit solutions instead of a single unique limit. For certain singularly perturbed classical equations of motion, the appearance of such funnels as the limit set has been discovered by Takens, cf. [8][21]. With regard to his work we speak of *Takens-chaos*. However, its relevance for problems in applications has yet to be studied.

2 The Singular Limit of the QCMD Model

For simultaneously addressing the quantum adiabatic theorem, we consider a *time-dependent* version of the QCMD model given by the following set of ordinary differential equations

$$\begin{aligned} &\text{(i)} & \ddot{q}_\epsilon^j &= -\langle \partial_j H(t,q_\epsilon)\psi_\epsilon, \psi_\epsilon\rangle, \qquad j=1,\dots,n,\\ &\text{(ii)} & i\epsilon\dot{\psi}_\epsilon &= H(t,q_\epsilon)\psi_\epsilon. \end{aligned} \tag{2}$$

Here, $q = (q^1,\dots,q^n) \in \mathbb{R}^n$, $\psi \in \mathbb{C}^r$, and $\langle\cdot,\cdot\rangle$ denotes the Euclidean sesquilinear form on $\mathbb{C}^r$. The Euclidean norm on $\mathbb{R}^n$, resp. $\mathbb{C}^r$ will be denoted by $|\cdot|$. We consider *converging* initial values, namely

$$\lim_{\epsilon\to 0} q_\epsilon(t_0) = q_*, \qquad \lim_{\epsilon\to 0} \dot{q}_\epsilon(t_0) = v_*, \qquad \lim_{\epsilon\to 0} \psi_\epsilon(t_0) = \psi_*, \tag{3}$$

with the normalization $|\psi_\epsilon(t_0)| = 1$ for all ϵ. We assume that the Hamiltonian H satisfies the following conditions on a finite time interval $[t_0, t_1]$:

(H1) $H : [t_0,t_1]\times\mathbb{R}^n \to \mathbb{C}^{r\times r}$ is a smooth map, the values of which are Hermitean matrices, uniformly bounded from below

$$\langle H(t,q)\psi,\psi\rangle \ge H_* > -\infty \qquad t\in[t_0,t_1],\, q\in\mathbb{R}^n,\, |\psi| = 1.$$

(H2) The time derivative $\partial_t H(t,q)$ is uniformly bounded for $t \in [t_0, t_1]$ and $q \in \mathbb{R}^n$.

(H3) There is a smooth spectral decomposition of H,

$$H(t,q) = \sum_{\lambda=1}^{s} E_\lambda(t,q) P_\lambda(t,q) \qquad t \in [t_0,t_1],\ q \in \mathbb{R}^n,$$

where P_λ denotes the orthogonal projections onto the mutually orthogonal eigenspaces of H which span $\mathbb{C}^r$: $I = \sum_\lambda P_\lambda$.

The reader should note, that the smooth multiplicities[1] n_λ of the eigenvalues E_λ are *constants*,

$$n_\lambda = \dim \operatorname{range} P_\lambda(t,q) = \text{const}, \qquad t \in [t_0,t_1],\ q \in \mathbb{R}^n. \tag{4}$$

As we have already mentioned in the introduction, we will prove that the singular limit of the QCMD model (2) is given by the *time-dependent Born-Oppenheimer model*

$$\ddot{q}^j_{\mathrm{BO}} = -\partial_j U_{\mathrm{BO}}(t, q_{\mathrm{BO}}) \qquad j = 1,\dots,n. \tag{5}$$

The Born-Oppenheimer potential U_{BO} is defined by

$$U_{\mathrm{BO}}(t,q) = \sum_{\lambda=1}^{s} \theta_\lambda\, E_\lambda(t,q), \qquad \theta_\lambda = \langle P_\lambda(t_0,q_*)\psi_*, \psi_* \rangle,$$

and the initial values of the system are the limit ones of QCMD model, $q_{\mathrm{BO}}(t_0) = q_*$ and $\dot{q}_{\mathrm{BO}}(t_0) = v_*$.

We have to introduce a further notion concerning *resonances* of the energy levels E_λ along the Born-Oppenheimer solution q_{BO}. If for any resonance

$$E_\lambda(t_r, q_{\mathrm{BO}}(t_r)) = E_\mu(t_r, q_{\mathrm{BO}}(t_r)) \qquad \lambda \neq \mu$$

at a time $t_r \in [t_0, t_1]$ the transversality condition

$$\left.\frac{d}{dt}\left(E_\lambda(t, q_{\mathrm{BO}}(t)) - E_\mu(t, q_{\mathrm{BO}}(t))\right)\right|_{t=t_r} \neq 0$$

holds, we will call q_{BO} *at most generically resonant.*

[1] More precisely, this is the multiplicity of the parameter-dependent eigenvalue $E_\lambda(\cdot)$. At a *resonance* point q the multiplicity of the eigenvalue $E_\lambda(q)$ itself might be accidentally higher.

Theorem 1. *On the time interval $[t_0, t_1]$, there exists a smooth unique solution q_{BO} of the Born-Oppenheimer model, and, for every $\epsilon > 0$, a smooth unique solution q_ϵ of the QCMD model. Let q_{BO} be at most generically resonant.*[2] *Then, given a sequence $\epsilon \to 0$, the classical components of the QCMD model converge to those of the Born-Oppenheimer model,*

$$q_\epsilon \to q_{\text{BO}} \quad \textit{in} \quad C^1([t_0, t_1], \mathbb{R}^n),$$

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

$$\langle P_\lambda(\cdot, q_\epsilon)\psi_\epsilon, \psi_\epsilon\rangle \to \theta_\lambda \quad \textit{in} \quad C[t_0, t_1].$$

Proof. The proof will be given in several steps.

Step 1. We start with estimating the solutions on a time interval of existence. According to a well-known formula of Ehrenfest [18, Eq. (V.72)] we obtain for any time-dependent observable A (Hermitean matrix) that

$$\frac{d}{dt}\langle A\psi_\epsilon, \psi_\epsilon\rangle = \frac{i}{\epsilon}\langle [H(\cdot, q_\epsilon), A]\psi_\epsilon, \psi_\epsilon\rangle + \langle \dot{A}\psi_\epsilon, \psi_\epsilon\rangle. \tag{6}$$

Inserting $A = I$, the identity matrix, yields the conservation of the norm of the wave function

$$|\psi_\epsilon(t)| = |\psi_\epsilon(t_0)| = 1, \qquad t \geq t_0. \tag{7}$$

A key quantity to look at is the energy of the QCMD model, i.e.,

$$E_\epsilon(t) = \frac{1}{2}|\dot{q}_\epsilon|^2 + \langle H(t, q_\epsilon)\psi_\epsilon, \psi_\epsilon\rangle.$$

Inserting $A(t) = H(t, q_\epsilon)$ into the Ehrenfest formula (6) yields the time derivative of the energy

$$\dot{E}_\epsilon = \langle \partial_t H(t, q_\epsilon)\psi_\epsilon, \psi_\epsilon\rangle.$$

By assumption (H2) and the conservation of norm (7) we obtain a uniform bound on $\dot{E}_\epsilon$. Integration shows that the energy is uniformly bounded on finite time intervals of existence (since $E_\epsilon(t_0)$ is converging for $\epsilon \to 0$). Hence, assumption (H1) yields a uniform bound for $\dot{q}_\epsilon$ and, after integration, one for q_ϵ. Now, these *a priori* bounds in phase space prove the existence and uniqueness of solutions $(q_\epsilon, \psi_\epsilon)$ for the time interval $[t_0, t_1]$ under consideration. Summarizing, we have obtained the uniform bounds

$$q_\epsilon, \dot{q}_\epsilon, \ddot{q}_\epsilon = O(1) \tag{8}$$

in $C([t_0, t_1], \mathbb{R}^n)$ for $\epsilon \to 0$, where the bound for $\ddot{q}_\epsilon$ immediately follows from equation (2(i)).

[2] In particular, there are at most *finitely* many resonances, cf. Step 7 of the proof below.

Step 2. Analogously to Step 1 one can prove the existence of the Born-Oppenheimer solution $q_{\rm BO}$ on $[t_0, t_1]$. Here, one considers the energy

$$E_{\rm BO} = \frac{1}{2}|\dot{q}_{\rm BO}|^2 + U_{\rm BO}(t, q_{\rm BO})$$

with the time derivative $\dot{E}_{\rm BO} = \partial_t U_{\rm BO}(t, q_{\rm BO})$. Once more, assumption (H2) yields the boundedness of $\dot{E}_{\rm BO}$, and after integration, assumption (H1) the boundedness of $E_{\rm BO}$.

Step 3. We recall the fact, that the space $L^\infty[t_0, t_1] = (L^1[t_0, t_1])^*$ is the dual of a separable space. Thus, by the Arzelà-Ascoli theorem [20, Theorem 11.28] and the Banach-Alaoglu theorem [20, Theorem 11.29] for spaces with a separable predual, the bounds (8) imply the existence of a subsequence of ϵ—which we will denote by ϵ again—such that

$$q_\epsilon \to q_0 \quad \text{in} \quad C^1([t_0, t_1], \mathbb{R}^n), \qquad \ddot{q}_\epsilon \stackrel{*}{\rightharpoonup} \ddot{q}_0 \quad \text{in} \quad L^\infty([t_0, t_1], \mathbb{R}^n).$$

We introduce the time-dependent *density matrix* ρ_ϵ belonging to the *pure state* ψ_ϵ,

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

It turns out, that the sequence ρ_ϵ is *bounded* in $L^\infty([t_0, t_1], \mathbb{C}^{r\times r})$. For that, we use the *trace class norm* $\|\cdot\|_1$ on the space of $r \times r$-matrices,

$$\|A\|_1 = \operatorname{tr}(AA^\dagger)^{1/2}, \qquad A \in \mathbb{C}^{r\times r},$$

and observe that

$$\|\rho_\epsilon\|_1 = \operatorname{tr} \rho_\epsilon = \langle \psi_\epsilon, \psi_\epsilon \rangle = 1.$$

By a further application of the Alaoglu theorem for spaces with a separable predual, we may assume that a limit

$$\rho_\epsilon \stackrel{*}{\rightharpoonup} \rho_0 \quad \text{in} \quad L^\infty([t_0, t_1], \mathbb{C}^{r\times r})$$

exists for the above chosen subsequence. This limit matrix ρ_0 is a time-dependent density matrix as well, i.e., for each time its value is a nonnegative Hermitian matrix with

$$\operatorname{tr} \rho_0 = 1.$$

However, since quadratic functionals are *not* weakly sequentially continuous, ρ_0 does not belong to a pure state in general, but to a *mixture* of states.[3]

[3]Mathematically speaking, the limit ρ_0 might have a rank higher than one, as we will see in Eq. (14) below, despite the fact that all the ρ_ϵ are rank one matrices.

The significance of the limit ρ_0 becomes clear, if we take weak limits in the first set (2(i)) of the QCMD equation, yielding

$$\ddot{q}_0^j = -\operatorname{tr}(\rho_0\, \partial_j H(t, q_0)). \tag{9}$$

For that, we rewrite $\langle H(t, q_\epsilon)\psi_\epsilon, \psi_\epsilon\rangle = \operatorname{tr}(\rho_\epsilon \partial_j H(t, q_\epsilon))$ and observe that we may pass to the weak limit because of the uniform convergence of q_ϵ.

Step 4. A simple calculation reveals, that the Schrödinger equation (2(ii)) is equivalent to the well-known evolution equation [18, Eq. (VIII.68)] for the density matrix,

$$i\epsilon\dot{\rho}_\epsilon = [H(t, q_\epsilon), \rho_\epsilon].$$

Taking weak limits on both sides of the equation yields[4] the commutativity relation

$$0 = [H(t, q_0), \rho_0]. \tag{10}$$

If we *exclude* resonances of the energy levels along q_0, we would get a simultaneous block-diagonalization of $H(t, q_0)$ and ρ_0. In fact, it is sufficient to exclude resonances *almost everywhere*. Therefore, until Step 7, we make the following assumption:

(Z) The resonance set

$$R = \{t \in [t_0, t_1] : E_\lambda(t, q_0(t)) = E_\mu(t, q_0(t)) \text{ for some } \lambda \neq \mu\}$$

is a set of Lebesgue measure zero.[5]

Now, multiplying the commutativity relation (10) by $P_\lambda(t, q_0)$ from the left, and by $P_\mu(t, q_0)$ from the right, gives

$$(E_\lambda(t, q_0) - E_\mu(t, q_0)) \cdot P_\lambda(t, q_0)\rho_0 P_\mu(t, q_0) = 0$$

as functions in $L^\infty([t_0, t_1], \mathbb{C}^{r\times r})$. Thus, we obtain in L^∞ that

$$P_\lambda(t, q_0)\rho_0 P_\mu(t, q_0) = 0, \qquad \lambda \neq \mu,$$

which implies the block-diagonal form of the limit density matrix ρ_0,

$$\rho_0 = \sum_\lambda P_\lambda(t, q_0)\rho_0 P_\lambda(t, q_0). \tag{11}$$

[4] For bounded sequences in L^∞, the weak*-convergence is equivalent to the convergence in the sense of distributions. In the sense of distributions, the limit of the left hand side is given by $i \cdot 0 \cdot \dot{\rho}_0 = 0$.

[5] Since the resonance set R is a *closed* subset of the real line $\mathbb{R}$, it has measure zero if and only if it is *countable*. This follows immediately from the fact [15, Theorem 6.59] that every open subset of $\mathbb{R}$ is the countable disjoint union of open *intervals*.

Step 5. Using the abbreviation $P_\lambda^\epsilon = P_\lambda(t, q_\epsilon)$, we define the *energy level populations* of the state ψ_ϵ as

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

Using the commutativity relation $[H(t, q_\epsilon), P_\lambda^\epsilon] = 0$, the Ehrenfest formula (6) yields the time derivative

$$\dot\theta_\lambda^\epsilon = \langle \dot P_\lambda^\epsilon \psi_\epsilon, \psi_\epsilon \rangle = \operatorname{tr}(\rho_\epsilon \dot P_\lambda^\epsilon).$$

Hence, the time derivatives form a *bounded* sequence in $L^\infty[t_0, t_1]$, showing by the Arzelà-Ascoli theorem that

$$\theta_\lambda^\epsilon \to \theta_\lambda^0 = \operatorname{tr}(\rho_0 P_\lambda^0) \quad \text{in} \quad C[t_0, t_1], \qquad \dot\theta_\lambda^\epsilon \overset{*}{\rightharpoonup} \dot\theta_\lambda^0 = \operatorname{tr}(\rho_0 \dot P_\lambda^0) \quad \text{in} \quad L^\infty[t_0, t_1].$$

Here, we have used the uniform convergence $\dot P_\lambda^\epsilon \to \dot P_\lambda^0$ in $C([t_0, t_1], \mathbb{C}^{r\times r})$ which follows from $\dot q_\epsilon \to \dot q_0$ in $C([t_0, t_1], \mathbb{R}^n)$. However, the block diagonal form (11) of ρ_0 yields

$$\dot\theta_\lambda^0 = \operatorname{tr}(\rho_0 \dot P_\lambda^0) = \sum_\mu \operatorname{tr}(P_\mu^0 \rho_0 P_\mu^0 \dot P_\lambda^0) = \sum_\mu \operatorname{tr}(\rho_0 P_\mu^0 \dot P_\lambda^0 P_\mu^0) = 0, \tag{12}$$

since $P_\mu^0 \dot P_\lambda^0 P_\mu^0 = 0$ for all λ and μ.[6] Thus, the limit populations θ_λ^0 are *constants* and their values are given by

$$\theta_\lambda^0(t) = \theta_\lambda^0(t_0) = \lim_{\epsilon\to 0} \theta_\lambda^\epsilon(t_0) = \theta_\lambda. \tag{13}$$

Step 6. Inserting the spectral decomposition of H into the force term of the abstract limit equation (9) yields

$$\operatorname{tr}(\rho_0\, \partial_j H) = \sum_\lambda \partial_j E_\lambda \cdot \operatorname{tr}(\rho_0 P_\lambda) + \sum_j E_\lambda \cdot \operatorname{tr}(\rho_0\, \partial_j P_\lambda).$$

The same argument as in Step 5, Eq. (12), shows that

$$\operatorname{tr}(\rho_0\, \partial_j P_\lambda(t, q_0)) = 0.$$

This and the fact that the limit population is constant, $\operatorname{tr}(\rho_0\, P_\lambda(t, q_0)) = \theta_\lambda$,

[6] For $\lambda \neq \mu$ we have $P_\lambda^0 P_\mu^0 = 0$ and therefore $\dot P_\lambda^0 P_\mu^0 + P_\lambda^0 \dot P_\mu^0 = 0$. Multiplying P_μ^0 from the left yields the asserted result for $\lambda \neq \mu$. From $P_\lambda^0 P_\lambda^0 = P_\lambda^0$ we obtain $\dot P_\lambda^0 = \dot P_\lambda^0 P_\lambda^0 + P_\lambda^0 \dot P_\lambda^0$. Multiplying by P_λ^0 from the left and cancelling equal terms yields the desired result for $\lambda = \mu$.

reveals that the force term belongs to the Born-Oppenheimer potential,

$$\mathrm{tr}(\rho_0\, \partial_j H(t,q_0)) = \sum_\lambda \theta_\lambda \cdot \partial_j E_\lambda(t,q_0) = \partial_j U_{\mathrm{BO}}(t,q_0).$$

Thus, q_0 is the solution of the Born-Oppenheimer equation (5). Since the initial values coincide, we obtain the equality $q_0 = q_{\mathrm{BO}}$—*provided* the resonance condition of Step 4, Assumption (Z), is satisfied for q_0.

Step 7. In this final step we will show by means of a continuation argument: the accessible resonance assumption of the theorem, which has been imposed on the Born-Oppenheimer solution q_{BO}, implies the validity of the somewhat inaccessible Assumption (Z), which is concerned with the limit q_0 instead.

There are only *finitely* many resonances along q_{BO} in the *compact* time interval $[t_0,t_1]$. Otherwise we would get a converging sequence $t_j \to t_*$ of crossing times for one and the same resonance surface. As a consequence, at time t_* there would be a *non transversal* crossing of q_{BO} with that resonance surface. This would contradict the assumption of transversality.

For proving the validity of Assumption (Z), and simultaneously the equality $q_0 = q_{\mathrm{BO}}$, we consider the maximal time of equality,

$$t_* = \max\left\{t \in [t_0,t_1] \;:\; q_0|[t_0,t] = q_{\mathrm{BO}}|[t_0,t]\right\}.$$

Because of $q_0(t_0) = q_{\mathrm{BO}}(t_0)$, this is a well defined quantity. Suppose we have $t_* < t_1$. Then, there are only finitely many resonances of q_0 during the time interval $[t_0,t_*]$. Since q_0 and q_{BO} are C^1-functions of time, we get

$$\dot q_0(t_*) = \dot q_{\mathrm{BO}}(t_*),$$

just using the initial values if $t_* = t_0$. Hence, if q_0 crosses a resonance surface at time t_* it does so *transversally.* As a consequence, there is a small $\delta > 0$ such that there are no further resonances of q_0 during the time interval $]t_*, t_* + \delta]$. Thus, the resonance set of q_0 restricted to the time interval $[t_0, t_* + \delta]$ has measure zero, i.e., Assumption (Z) is satisfied for this time interval. Employing the results of the previous steps to this time interval proves that

$$q_0|[t_0,t_*+\delta] = q_{\mathrm{BO}}|[t_0,t_*+\delta],$$

contradicting the maximality of t_*. We therefore obtain $t_* = t_1$, which is equivalent to $q_0 = q_{\mathrm{BO}}$.

We have shown that the limits of *any* converging subsequence of q_ϵ and θ_λ^ϵ are *uniquely* given by q_{BO} and θ_λ. Thus, we can finally discard the extraction of subsequences. □

Despite the fact that we have made use of the density matrix $\rho_\epsilon = \psi_\epsilon \psi_\epsilon^\dagger$ during the proof of Theorem 1, we could not state a convergence result involving it. This is because the limit relations (11) and (13) do *not* identify the limit density matrix ρ_0 *uniquely* in general. However, there is a special case, where ρ_0 can be identified unambiguously. This allows to recover information about the quantal part other than energy level populations.

Corollary 2. *Let the limit populations θ_λ be nonzero only for simple eigenvalues.*[7] *Then, the density matrix converges as*

$$\rho_\epsilon \stackrel{*}{\rightharpoonup} \rho_0 = \sum_\lambda \theta_\lambda P_\lambda(\cdot, q_0) \quad \textit{in} \quad L^\infty([t_0, t_1], \mathbb{C}^r).$$

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

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

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

$$\langle A\psi_\epsilon, \psi_\epsilon \rangle \stackrel{*}{\rightharpoonup} \sum_\lambda \theta_\lambda \langle A\psi_\lambda, \psi_\lambda \rangle \quad \textit{in} \quad L^\infty[t_0, t_1].$$

If the commutation relation $[H(\cdot, q_0), A] = 0$ holds, the convergence is strong in $C[t_0, t_1]$.

Proof. We go back to Steps 4 and 5 of the proof of Theorem 1. The diagonal blocks $P_\lambda(\cdot, q_0)\rho_0 P_\lambda(\cdot, q_0)$ of ρ_0 are nonnegative Hermitean matrices. Therefore, their trace class norm is given by

$$\|P_\lambda(\cdot, q_0)\rho_0 P_\lambda(\cdot, q_0)\|_1 = \mathrm{tr}(P_\lambda(\cdot, q_0)\rho_0 P_\lambda(\cdot, q_0)) = \mathrm{tr}(\rho_0 P_\lambda(\cdot, q_0)) = \theta_\lambda.$$

By assumption, all nonzero populations θ_λ belong to one-dimensional block-diagonal entries of the matrix ρ_0, which yields

$$P_\lambda(\cdot, q_0)\rho_0 P_\lambda(\cdot, q_0) = \theta_\lambda P_\lambda(\cdot, q_0)$$

for *all* λ. Thus, ρ_0 is *uniquely* given by the asserted expression. As in the final step of the proof of Theorem 1, we may discard any extraction of subsequences. The convergence of the expectation values follows directly from

$$\langle A\psi_\epsilon, \psi_\epsilon \rangle = \mathrm{tr}(\rho_\epsilon A) \stackrel{*}{\rightharpoonup} \mathrm{tr}(\rho_0 A) = \sum_\lambda \theta_\lambda \langle A\psi_\lambda, \psi_\lambda \rangle.$$

[7] This means, the smooth multiplicity n_λ as defined in Eq. (4) is one, $n_\lambda = 1$. Resonances are still allowed.

If $[H(\cdot,q_0),A]=0$, the Ehrenfest formula (6) shows that the time derivative of the expectation value remains bounded. Thus, a further application of the Arzelà-Ascoli theorem proves the uniform convergence in time. □

In the setting of this corollary we obtain that the limit density matrix ρ_0 is a *convex combination* of density matrices belonging to pure states, namely the simple eigenstates of H. In particular, the rank of ρ_0 is given by

$$\operatorname{rank}\rho_0 = \#\{\lambda : \theta_\lambda \neq 0\}. \tag{14}$$

3 The Adiabatic Theorem of Quantum Mechanics

The case $n=0$ of Theorem 1, i.e., the absence of a "classical" particle, corresponds to the so-called *quantum adiabatic theorem.* This theorem is of considerable interest in itself and we have actually proven more for that case than stated in Theorem 1. For thus, we will discuss it in detail here.

We consider a time-dependent Schrödinger equation in a finite dimensional state space,

$$i\epsilon\dot{\psi}_\epsilon = H(t)\psi_\epsilon, \qquad \psi(t_0)=\psi_*, \;\; |\psi_*|=1. \tag{15}$$

We assume that the Hamiltonian H satisfies the following conditions on a finite time interval $[t_0,t_1]$:

(A1) $H:[t_0,t_1]\to\mathbb{C}^{r\times r}$ is a smooth map, the values of which are Hermitean matrices.

(A2) There is a smooth spectral decomposition of H,

$$H(t)=\sum_{\lambda=1}^{s} E_\lambda(t)P_\lambda(t) \qquad t\in[t_0,t_1],$$

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

Notice, that the assumptions (A1) and (A2) imply those of the previous section, i.e., (H1)–(H3). Asymptotically in the limit $\epsilon\to 0$, the quantum adiabatic theorem now states the following: An initial value which belongs to the λ-eigenspace of $H(t_0)$ leads to a solution at time t_1 which likewise belongs to the λ-eigenspace of $H(t_1)$.

Theorem 3. (Quantum Adiabatic Theorem). *Let the resonance set*

$$R = \{t \in [t_0, t_1] : E_\lambda(t) = E_\mu(t) \text{ for some } \lambda \neq \mu\}$$

be at most countable.[8] *Then, given a sequence $\epsilon \to 0$, the energy level populations of the wave functions converge to the constant values of the initial populations,*

$$\langle P_\lambda \psi_\epsilon, \psi_\epsilon \rangle \;\to\; \langle P_\lambda(t_0)\psi_*, \psi_* \rangle \quad \text{in} \quad C[t_0, t_1].$$

If the initial populations θ_λ are nonzero only for simple eigenvalues, $n_\lambda = 1$, the assertions of Corollary 2 hold likewise.

Proof. The proof is given *literally* by the Steps 1–6 of the proof of Theorem 1. Since there is no q-variable, we do not have to distinguish between q_0 and q_{BO}. Thus, Step 7 is not needed, explaining the considerably weaker resonance condition of Theorem 3, which is just Assumption (Z) of Step 4. □

Under stronger assumptions, the first mathematical proof of the quantum adiabatic theorem for finite dimensional state spaces was given by Born and Fock [5]. They considered *simple* eigenvalues with at most finitely many resonances. Further, they assumed that there exists a $\kappa \in \mathbb{N}_0$ such that for each resonance $E_\lambda(t_*) = E_\mu(t_*)$ a higher order nondegeneracy condition holds,

$$\left.\frac{d^\kappa}{dt^\kappa}(E_\lambda - E_\mu)\right|_{t=t_*} \neq 0,$$

just putting $\kappa = 0$ if there are no resonances at all. By estimating oscillatory integrals as arising in geometrical optics, they were able to prove the asymptotic result [5, Eq. (60)]

$$\langle P_\lambda \psi_\epsilon, \psi_\epsilon \rangle = \langle P_\lambda(t_0)\psi_*, \psi_* \rangle + O\left(\epsilon^{\frac{1}{\kappa+1}}\right).$$

This shows in particular, that the rate of convergence in Theorem 3 can be arbitrary slow as a power of the singular perturbation parameter ϵ.

Remark 4. The proof of Born and Fock for the case $\kappa = 0$ can also be found in the textbook of Messiah [18, Ch. XVII, §12]. The proof involves the so-called "rotating axis representation" and needs a careful tracking of the phases of the wave function. The proof presented here avoids the discussion of phases by directly discussing the density matrix. The work of Born and Fock was later extended to the infinite dimensional setting by Kato [16] and Friedrichs [10][11]. The most complete account of this method of proof can be found in recent work of Avron, Seiler, and Yaffe [2][3].

[8] By Footnote 5 on p. 7 this is *equivalent* to saying that R has Lebesgue measure zero.

4 Takens-Chaos

According to Theorem 1, the limit dynamics as given by the Born-Oppenheimer equations does *only* depend on the *limit* initial values q_*, v_*, and ψ_*. Thus, the details of the limiting process leading to these values do not matter at all—which is a far-reaching *stability property* of the limit model.

In this section, we will show that a completely different situation may appear if the assumption (H3) of a smooth spectral decomposition of the Hamiltonian H is hurt. The perturbation theory of linear operators, [17, Chap. 2, §6], teaches that property (H3) can only be hurt if there are eigenvalues of multiplicity greater than one for some parameter values. Now, the set of Hermitean matrices, having at least one eigenvalue with multiplicity greater than one, has *real* codimension two in the set of all Hermitean matrices.[9] Thus, for hurting property (H3) *generically* we need at least a two parameter dependence of H, acting itself on a two-dimensional space. We will construct an example with a time-independent Hamiltonian having $n = r = 2$.

We consider the "classical" positions $q = (q^1, q^2)$ and take as Hamiltonian the real symmetric matrix

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

This is the famous example of Rellich [19, §2][17, Chap. 2, Example 5.12] for a smooth symmetric matrix which is not smoothly diagonizable. This matrix also occurs in the work of Hagedorn [13][14] on the relation of the time-dependent Born-Oppenheimer model to the full Schrödinger equation. There, it appears as the *normal form* of so-called "energy level crossings of codimension two." The latter fact makes the matrix H particularly interesting for our study.

The eigenvalues of H are $E_1(q) = -|q|$ and $E_2(q) = |q|$. Excluding the origin $q = 0$ and using polar coordinates,

$$q^1 = r\cos\varphi, \qquad q^2 = r\sin\varphi,$$

[9] The "loss" of two real dimensions can be explained as follows. Representing an Hermitean matrix H by its diagonalization $H = S^\dagger DS$ shows that one real dimension is lost due to the eigenvalue resonance in the real diagonal matrix D. Another real dimension is lost, however, in the unitary matrix S since the corresponding eigenspace of dimension greater than one can be freely rotated without changing the resulting matrix H. See also [1].

yields the corresponding eigenvectors in the form

$$\psi_1 = \begin{pmatrix} -\sin(\varphi/2) \\ \cos(\varphi/2) \end{pmatrix}, \qquad \psi_2 = \begin{pmatrix} \cos(\varphi/2) \\ \sin(\varphi/2) \end{pmatrix}.$$

The occurrence of the argument $\varphi/2$ shows that these eigenvectors are defined up to a sign only. For a unique representation we have to cut the plane along a half-axis, e.g., along $\varphi = 3\pi/2$. Hence, we restrict the angular variable to the open interval

$$\varphi \in \left]-\frac{\pi}{2}, \frac{3\pi}{2}\right[.$$

By this, ψ_1 and ψ_2 become smooth vector fields uniquely defined on the cut plane

$$\mathbb{R}^2_c = \mathbb{R}^2 \setminus \{q : q^1 = 0, q^2 \leq 0\}.$$

They cannot, however, be continued over the cut, but change their roles there instead.

We consider the following family of initial values:

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

depending on a parameter $\mu \geq 0$. For the discussion of the singular limit $\epsilon \to 0$ we have to distinguish *two cases.*

The Case $\mu = 0$. In this case, the solutions of the QCMD model can be calculated explicitly. The QCMD equations are given by

$$\ddot{q}^1_\epsilon = -\left(|\psi^1_\epsilon|^2 - |\psi^2_\epsilon|^2\right), \qquad \ddot{q}^2_\epsilon = -2\,\Re\left(\overline{\psi^1_\epsilon}\psi^2_\epsilon\right),$$

and

$$i\epsilon\dot{\psi}^1_\epsilon = q^1_\epsilon\psi^1_\epsilon + q^2_\epsilon\psi^2_\epsilon, \qquad i\epsilon\dot{\psi}^2_\epsilon = q^2_\epsilon\psi^1_\epsilon - q^1_\epsilon\psi^2_\epsilon.$$

A short calculation reveals that the unique solution is given by

$$q^1_\epsilon(t) = 1 - \frac{1}{2}t^2, \quad q^2_\epsilon \equiv 0, \quad \psi^1_\epsilon(t) = \exp\left(-\frac{i}{\epsilon}\int_0^t q^1_\epsilon(\tau)\,d\tau\right), \quad \psi^2_\epsilon \equiv 0.$$

Surprisingly, the q-components are *independent* of the singular perturbation parameter ϵ. Therefore, the limit $\epsilon \to 0$ of q_ϵ is trivially given by

$$q_0^{\mu=0} = \left(1 - \frac{1}{2}t^2, 0\right).$$

As a particularity, this limit solution crosses the singularity $q = 0$ of the spectral decomposition at time $t = \sqrt{2}$.

The Case $\mu > 0$. We will see that, in this case, the adiabatic Theorem 1 is applicable on the time interval $[0, 2\sqrt{2}]$, at least for small $\mu > 0$ and $\epsilon > 0$. For then, the limit would be given by the Born-Oppenheimer initial value problem

$$\ddot{q}_0 = -\frac{q_0}{|q_0|}, \qquad q_0(0) = (1,0), \quad \dot{q}_0(0) = (0,\mu). \tag{16}$$

At the end of this section we will prove the following lemma.

Lemma 5. *Let $\mu > 0$ be small enough. Then, for all $t \in [0, 2\sqrt{2}]$, the Born-Oppenheimer solution q_0 takes values in the cut plane $\mathbb{R}^2_c$.*

Hence, for $\mu > 0$ and $\epsilon > 0$ small enough, the hypothesis (H3) of §2 is fulfilled and Theorem 1 indeed applicable, showing that

$$q_\epsilon \to q_0 \quad \text{in} \quad C^1[0, 2\sqrt{2}].$$

Now, we take the limit $\mu \downarrow 0$ of the Born-Oppenheimer solution q_0, which will be denoted by $q_0^{\mu\downarrow 0}$. A direct calculation reveals that

$$q_0^{\mu\downarrow 0}(t) = \begin{cases} \left(1 - \frac{1}{2}t^2, 0\right), & t \in [0, \sqrt{2}], \\ \left(\frac{1}{2}t^2 - 2\sqrt{2}t + 3, 0\right), & t \in [\sqrt{2}, 2\sqrt{2}]. \end{cases}$$

Notice, that $q_0^{\mu\downarrow 0} \in C^1[0, 2\sqrt{2}]$.

Discussion. These two cases show that the limits $\epsilon \to 0$ and $\mu \downarrow 0$ are *not* interchangeable: In fact, after passing the singularity $q = 0$ at $t = \sqrt{2}$, the two limit functions separate,

$$\lim_{\epsilon \to 0} \lim_{\mu \downarrow 0} q_\epsilon(t) = q_0^{\mu=0}(t) \neq q_0^{\mu\downarrow 0}(t) = \lim_{\mu\downarrow 0} \lim_{\epsilon \to 0} q_\epsilon(t), \qquad t > \sqrt{2}.$$

Thus, if we consider the simultaneous limit by taking an ϵ-dependent sequence $\mu(\epsilon) \downarrow 0$, the resulting limit solution q_0 would depend on *how* the limit initial velocity

$$\lim_{\epsilon \to 0} \dot{q}_\epsilon(0) = \lim_{\epsilon \to 0}(0, \mu(\epsilon)) = (0,0)$$

is obtained. This is in sharp contrast to the assertion of Theorem 1, showing the *necessity* of hypothesis (H3)—even for the principal structure of the result. The situation here is even worse: By continuity we may obtain as the limit value of $q_\epsilon(t)$ at time $t > \sqrt{2}$ *any* value $\tilde{q}$ with

$$q_0^{\mu=0}(t) \le \tilde{q} \le q_0^{\mu\downarrow 0}(t).$$

One only has to choose the sequence $\mu(\epsilon)$ accordingly. In a way, the limit dynamics is thus described by the *funnel* between the two extreme cases $q_0^{\mu=0}$ and $q_0^{\mu\downarrow 0}$. Figure 1 illustrates the situation.

The appearance of such funnels as the limit set of certain singularly perturbed problems has been discovered by TAKENS in his work [21] on Hamiltonian systems with a strong constraining potential. With regard to this work we speak of *Takens-chaos*, cf. [8].

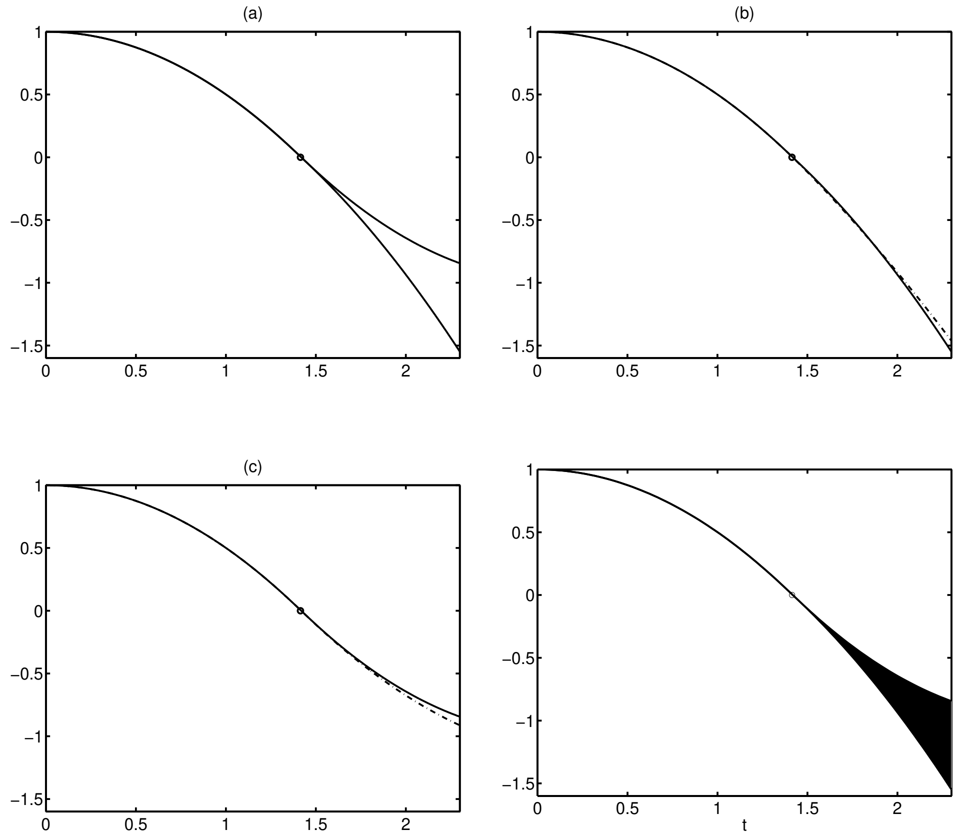

Figure 1: Illustration (q^1 vs. t) of the sensitivity on μ and ϵ, indicating Takens-chaos: (a) the two different limit solutions $q_0^{\mu=0}$ and $q^{\mu\downarrow 0}$, (b) the limit solution $q_0^{\mu=0}$ (solid line) and the QCMD–solution for $\epsilon = 0.05$ and $\mu = 0.1$ (dashed line), (c) the limit solution for $\epsilon \to 0$ with $\mu = 0.1$ (solid line) and the QCMD–solution for $\epsilon = 0.005$ and $\mu = 0.1$ (dashed line), (d) the funnel of possible limits for $\epsilon \to 0$, $\mu \to 0$.

Proof of Lemma 5. The Born-Oppenheimer equation (16) belongs to the Lagrangian

$$\mathcal{L} \;=\; \frac{1}{2}|\dot q|^2 - |q| \;=\; \frac{1}{2}\dot r^2 + \frac{1}{2}r^2\dot\varphi^2 - r.$$

Thus, Eq. (16) transforms into polar coordinates as the set of Euler-Lagrange equations

$$\ddot r = r\dot\varphi^2 - 1, \qquad \frac{d}{dt}(r^2\dot\varphi) = 0.$$

The corresponding initial values are given by $r(0) = 1$, $\varphi(0) = 0$, $\dot r(0) = 0$, and $\dot\varphi(0) = \mu$. Along the solution there is conservation of energy,

$$E = \frac{1}{2}\dot r^2 + \frac{1}{2}r^2\dot\varphi^2 + r = \alpha^2 + 1, \qquad \alpha = \frac{\mu}{\sqrt{2}}.$$

Using this and eliminating the cyclic variable φ yields

$$\dot r^2 = -\frac{2}{r^2}\left(r^3 - (1+\alpha^2)r^2 + \alpha^2\right) = \frac{2}{r^2}(1-r)(r-r_+)(r-r_-), \tag{17}$$

with

$$r_\pm \;=\; \frac{\alpha^2}{2} \pm \sqrt{\frac{\alpha^4}{4} + \alpha^2}.$$

Because of $r^2\dot\varphi \equiv \mu > 0$ we always have $r > 0$ and $\dot\varphi > 0$. Thus, the local extrema of $r(t)$, given at $\dot r = 0$, are $r_{\min} = r_+$ and $r_{\max} = 1$. In particular, we obtain

$$0 < \alpha < r_+ \le r(t) \le 1.$$

It remains to show that $0 \le \varphi(t) < 3\pi/2$ for $0 \le t \le 2\sqrt{2}$. Since the motion is *periodic* and φ is monotonely increasing, it suffices to compute the period T of the motion and the angular difference $\Delta\varphi = \varphi(T) - \varphi(0)$ during that period. Using Eq. (17), we obtain

$$T = 2\int_{r_+}^{1} \frac{dr}{\dot r} = \sqrt{2}\int_{r_+}^{1} \frac{r\,dr}{\sqrt{(1-r)(r-r_+)(r-r_-)}}.$$

Correspondingly, we obtain

$$\begin{aligned}
\Delta\varphi = 2\int_{r_+}^{1} \frac{\dot\varphi\,dr}{\dot r} \;&=\; 2\int_{r_+}^{1} \frac{\alpha\,dr}{r\sqrt{(1-r)(r-r_+)(r-r_-)}} \\
&=\; 2\int_{r_+}^{1} \frac{\alpha\sqrt{z}\,dz}{r_+\sqrt{(1-z)(1-zr_-/r_+)(z-r_+)}}.
\end{aligned}$$

In the limit $\alpha \to 0$, these elliptic integrals can be evaluated explicitly:

$$T \;\to\; \sqrt{2}\int_0^1 \frac{dr}{\sqrt{1-r}} = 2\sqrt{2}, \qquad \Delta\varphi \;\to\; 2\int_0^1 \frac{dz}{\sqrt{1-z^2}} = \pi.$$

By continuity, these results readily imply the assertion for $\mu = \sqrt{2}\alpha$ being small enough. □

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