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Second Order Transitions in Quantum–Classical Molecular Dynamics

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Abstract

Mixed quantum–classical models have attracted considerable interest due to the expectation that they correctly describe non–adiabatic processes of full quantum dynamics. One of these models, the so–called QCMD model, represents most degrees of freedom of the molecular system by the means of classical mechanics but an important, small portion of the system is modeled by a quantum wavefunction: the wavefunction is nonlinearly coupled to the classical motion via a singularly perturbed Schrödinger equation. In extension to the analysis given by F.A. Bornemann [*Homogenization in Time of Singularly Perturbed Mechanical Systems*, Lecture Notes in Mathematics, no. 1687, 1998, Springer, Berlin], the article presents an asymptotic expansion up to second order in the perturbation parameter. This result allows for the construction of new models and numerical integration schemes.

Keywords: quantum–classical molecular dynamics; mixed quantum–classical models; asymptotics; quantum populations
MSC classification: 81Q20, 41A60

1 Introduction

Many chemical reactions are characterized by a crucial influence of quantum processes in the molecular dynamics. Adversely, a complete quantum dynamical simulation (QD) of realistic molecular systems is by far too complex to be applicable. Thus, various kinds of mixed quantum–classical models composed of quantum degrees of freedom in a classical modeled system have been worked out. A typical example of these models, the so–called Quantum–Classical Molecular Dynamics (QCMD) model, consists of a singularly perturbed Schrödinger equation nonlinearly coupled to classical Newtonian equations, see §2.

An important insight with respect to this model is that both, the QCMD model and the full QD evolution, in fact have the same *adiabatic limit system*, the well–known time–dependent Born–Oppenheimer (BO) model, see §2. Since non–adiabatic processes account for many important situations, simulations based on the BO model lead to a wrong description of the inherent dynamics. In contrast to the BO model, the quantum–classical QCMD model includes a population dynamics in the quantum subsystem. So, one could expect that QCMD correctly describes the dynamics. Unfortunately, the splitting of wavepackets in a complete quantum representation due to a non–adiabatic change in the populations cannot be resolved by one single QCMD trajectory. Thus, specific surface hopping extensions of QCMD based on trajectory bundles have been proposed [11].

The construction of such new models as well as efficient numerical algorithms requires a detailed knowledge of the QCMD dynamics in the case of non–adiabatic changes in the populations. In [5], the limit system as well as an asymptotic expansion up to first order in the perturbation parameter is given, see §4. But it turns out that the first order correction terms of the populations are just high–frequency oscillations around the initial populations without any non–oscillatory drift. What matters even more is that in the case of only one initially occupied quantum state these first order correction terms vanish altogether.

Now, this article presents in a theorem (§3) the second order correction terms of the asymptotic expansion of the populations under the condition that only one state is initially occupied. The later assumption corresponds well to surface hopping extensions of QCMD [11].

The proof of the theorem follows closely [5] in transforming the quantum subsystem into action–angle variables, see §4 and §5. Finally, the result is numerically illustrated in application to a QCMD version of the non–adiabatic avoided crossing example (§6).

2 The QCMD model and its limit system

The Quantum–Classical Molecular Dynamics (QCMD) model describes the dynamics of quantum degrees of freedom non–linearly coupled to classically modeled degrees of freedom. The quantum degrees of freedom are represented by a wavefunction $\psi_\epsilon = \psi_\epsilon(x,t)$ at time t and location x. It obeys Schrödinger's equation with a parameterized coupling potential V which depends on the location $q_\epsilon = q_\epsilon(t)$ of the classical degrees of freedom. This location $q_\epsilon(t)$ is the solution of a classical Hamiltonian equation of motion in which the time–dependent potential arises from the expectation value of V with regard to ψ_ϵ. Thus, we obtain the following equations of motion of the *QCMD model*:[1]

$$
\begin{aligned}
i\epsilon\partial_t\psi_\epsilon &= H(q_\epsilon)\,\psi_\epsilon, \qquad & \psi_\epsilon|_{t=0} &= \psi_*, \\
\ddot{q}_\epsilon &= -\mathrm{grad}_q\langle\psi_\epsilon, V(q_\epsilon)\psi_\epsilon\rangle, \qquad & q_\epsilon(0) &= q_*,\ \dot{q}_\epsilon(0) = \dot{q}_*
\end{aligned}
\tag{1}
$$

where $H = H(q)$ is the q-parameterized Hamiltonian

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

When considering a physical system containing a *light* "quantum" particle with associated mass m and a *heavier* "classical" particle with mass M, the smallness parameter ϵ [10] corresponds to $\epsilon = \sqrt{m/M}$.

Throughout the present paper, we make use of the decomposition

$$H(q) \;=\; \textstyle\sum_\lambda E_\lambda(q)\,P_\lambda(q), \tag{2}$$

where $P_k(q)$ is the orthogonal projection onto the eigenspace associated with eigenvalue $E_k(q)$ of $H(q)$. With respect to a quantum state ψ_ϵ, the number $\vartheta_\epsilon^\lambda = \langle\psi_\epsilon, P_\lambda\psi_\epsilon\rangle$ is the *population* of the *energy level* E_λ.

In recent years, the approximation properties of the QCMD model (1) with respect to a complete quantum dynamical description were thoroughly analyzed [3]. Additionally, the adiabatic limit equation of (1) governing $\lim_{\epsilon\to 0} q_\epsilon$ was determined [4, 5]. This limit equation can be motivated by referring to the *quantum adiabatic theorem* which originates from work of Born and Fock [2, 9]: 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, the populations of the energy levels should remain *invariant* during the evolution:

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

[1] Subsequently, it will be of advantage to explicitly denote the dependence of its solution $(q_\epsilon, \dot{q}_\epsilon, \psi_\epsilon)$ on the parameter ϵ.

The *constant* ϑ_*^λ is the initial population of level E_λ and thus computable from the initial data. According to [4, 5], the limit solution $q_{\rm BO} = \lim_{\epsilon\to 0} q_\epsilon$ is given by:

$$\ddot{q}_{\rm BO} \;=\; -\mathrm{grad}_q \sum_\lambda \vartheta_*^\lambda \, E_\lambda(q_{\rm BO}), \qquad q_{\rm BO}(0) = q_*,\, \dot{q}_{\rm BO}(0) = \dot{q}_*. \tag{3}$$

whenever the following assumption on the eigenspaces and eigenenergies of $H(q)$ is satisfied:

Assumption A The spectral decomposition (2) of H depends smoothly on q and the transversality condition $\frac{d}{dt}(E_\lambda(q_{\rm BO}) - E_\eta(q_{\rm BO})) \neq 0$, $\lambda \neq \eta$.

We refer to equation (3) as to the *time-dependent Born-Oppenheimer* (BO) model of adiabatic motion. Notice that Assumption A does *not* exclude *energy level crossings* (i.e., positions q_c at which $E_\lambda(q_c) = E_\eta(q_c)$ for some $\lambda \neq \eta$).

The analysis leading to this result was done twofold: An elaborate approach [4, 5] uses a density matrix formulation of QCMD and the technique of weak convergence. Under the assumption A stated above, this allows to proof a strong convergence of the classical coordinates $q_\epsilon \to q_{\rm BO}$ and $\dot{q}_\epsilon \to \dot{q}_{\rm BO}$ as well as a weak* convergence of the wavefunction $\psi_\epsilon \stackrel{*}{\rightharpoonup} 0$.

A different approach (Appendix C in [5]) utilizes some stronger conditions — that is, an exclusion of energy level crossings. This way yields not only a strong convergence of the populations ϑ_ϵ and the corresponding phases but also higher order correction terms of the asymptotic expansion in ϵ which cannot be obtained on the first way. Thus, we will follow the later in our construction of higher order terms.

3 Theorem on second order transitions

In the following, we restrict ourselves to finite–dimensional Hilbert spaces, making H a Hermitian matrix. The reader may think of a finite dimensional subspace of the original state space. This subspace may, e.g., correspond to a suitable discretization in space.

Assumption B We assume all eigenspaces of $H(q_\epsilon)$ and $H(q_{\rm BO})$ to be simple and the corresponding orthonormal eigenfunctions e_λ real valued

$$H(q)\, e_\lambda(q) \;=\; E_\lambda(q)\, e_\lambda(q), \qquad \langle e_\lambda(q), e_\eta(q)\rangle = \delta_{\lambda\eta}$$

where $\delta_{\lambda\eta}$ denotes the Kronecker delta.

Remark 1 Assumption B can always be satisfied for finite dimensional Hamiltonians H. Complex valued eigenfunctions would additionally require the calculation of Berry phases along the solution.

Instead of Assumption A we exclude cases with symmetric resonances of order four:

Assumption C No symmetric resonances of order four along q_ϵ and q_{BO}:

$$E_{\lambda_1}(q) + E_{\lambda_2}(q) \quad \neq \quad E_{\eta_1}(q) + E_{\eta_2}(q)$$

for $\lambda_1 \neq \eta_1$, $\lambda_1 \neq \eta_2$, $\lambda_2 \neq \eta_1$ and $\lambda_2 \neq \eta_2$.

Remark 2 This condition includes the exemption of energy level crossings (i.e., resonances of order two).

An expansion of the quantum wavefunction ψ_ϵ in the (adiabatic) eigenfunctions $e_\lambda(q_\epsilon)$ yields

$$\psi_\epsilon \quad = \quad \sum_\lambda \sqrt{\vartheta_\epsilon^\lambda} \exp(-i\epsilon^{-1}\, \varphi_\epsilon^\lambda)\, e_\lambda(q_\epsilon) \tag{4}$$

with initial values

$$\psi_* \quad = \quad \sum_\lambda \sqrt{\vartheta_*^\lambda} \exp(-i\epsilon^{-1}\, \varphi_*^\lambda)\, e_\lambda(q_*)$$

where we have used the previously defined populations $\vartheta_\epsilon^\lambda$ and some corresponding phases φ_ϵ^λ. We will limit the analysis to cases where just one eigenstate — here and in the following labeled μ — is initially occupied, i.e,

Assumption D $\quad \vartheta_\epsilon^\lambda(0) \;=\; \vartheta_*^\lambda = \delta_{\lambda\mu}.$

Under these conditions, we might proof the following theorem on the second order correction term of the populations.

Theorem 1 *Let assumptions B, C and D apply and consider an initially unoccupied state $\eta \neq \mu$. For $t < t_{\max}$ the population of state η is up to the second order in ϵ:*

$$\begin{aligned}\vartheta_\epsilon^\eta(t) \;&= \epsilon^2 \left(\frac{B_{\mathrm{BO}}^{\eta\mu}(t)}{\Delta E_{\mathrm{BO}}^{\eta\mu}(t)}\right)^2 + \epsilon^2 \left(\frac{B_{\mathrm{BO}}^{\eta\mu}(0)}{\Delta E_{\mathrm{BO}}^{\eta\mu}(0)}\right)^2 \\ &\quad - 2\epsilon^2 \frac{B_{\mathrm{BO}}^{\eta\mu}(t)}{\Delta E_{\mathrm{BO}}^{\eta\mu}(t)} \frac{B_{\mathrm{BO}}^{\eta\mu}(0)}{\Delta E_{\mathrm{BO}}^{\eta\mu}(0)} \cos\left(\epsilon^{-1} \int_0^t \Delta E_{\mathrm{BO}}^{\eta\mu}(s)ds\right) \\ &\quad + \mathcal{O}(\epsilon^3)\end{aligned} \tag{5}$$

with

$$B_{\mathrm{BO}}^{\eta\mu}(t) = -\sum_j \langle e_\eta(q_{\mathrm{BO}}(t)), \partial_j\, e_\mu(q_{\mathrm{BO}}(t))\rangle \cdot \dot{q}_{\mathrm{BO}}^j(t)$$

and

$$\Delta E_{\mathrm{BO}}^{\eta\mu}(t) = E_\eta(q_{\mathrm{BO}}(t)) - E_\mu(q_{\mathrm{BO}}(t)).$$

The proof of Theorem 1 is presented in the subsequent two sections. At first, action–angle variables are introduced allowing for an asymptotic expansion of the QCMD equations of motion (1). Next, we calculate the second order perturbation of the population.

4 Asymptotic expansion of QCMD equations

In this section, we will closely follow F.A. Bornemann (Appendix C of [5]) in the introduction of an action–angle formalism for the quantum part of the QCMD equations.[2] Therefore, we split the quantum wavefunction into a scaled real– and imaginary part:

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

Introducing new locations $(q_\epsilon, z_\epsilon)^T$ and momenta $(\dot{q}_\epsilon, \zeta_\epsilon)^T$ yields a canonical system with Hamiltonian function $\mathcal{H}$

$$\mathcal{H}(q_\epsilon, \dot{q}_\epsilon, z_\epsilon, \zeta_\epsilon) = \tfrac{1}{2}|\dot{q}_\epsilon|^2 + \tfrac{1}{2}\langle\zeta_\epsilon, H(q_\epsilon)\zeta_\epsilon\rangle + \tfrac{1}{2}\epsilon^{-2}\langle z_\epsilon, H(q_\epsilon)z_\epsilon\rangle. \tag{6}$$

Using the well–known technique of action–angle variables [1] in the fast degrees of freedom —that is, the quantum variables— we obtain actions $\vartheta_\epsilon^\lambda$ and the corresponding angles φ_ϵ^λ via:

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

with initial values $\vartheta_\epsilon^\lambda(0) = \vartheta_*^\lambda$ and $\varphi_\epsilon^\lambda(0) = \varphi_*^\lambda$. The action variable $\vartheta_\epsilon^\lambda$ is, in fact, the population of energy level E_λ as already defined in § 2. A Hamiltonian system in the action–angle variables is obtained by applying a canonical transformation [1] $(q_\epsilon, \dot{q}_\epsilon, z_\epsilon, \zeta_\epsilon) \to (q_\epsilon, p_\epsilon, \vartheta_\epsilon, \varphi_\epsilon)$ to the original system with Hamiltonian function (6). This symplectic transformation — which has to act on the *whole* phase space $(q_\epsilon, \dot{q}_\epsilon, z_\epsilon, \zeta_\epsilon)$— might be constructed employing the generating function [1]

$$S(q, p, z_\epsilon, \varphi_\epsilon) = p_\epsilon^T q_\epsilon - \frac{\epsilon^{-1}}{2}\sum_\lambda \langle z_\epsilon, e_\lambda(q_e)\rangle^2 \, \tan(\epsilon^{-1}\varphi_\epsilon^\lambda)$$

via $\zeta_\epsilon = \partial S/\partial z_\epsilon$, $\vartheta_\epsilon = -\partial S/\partial \varphi_\epsilon$ and $\dot{q}_\epsilon = \partial S/\partial q_\epsilon$. Obviously, the transformation to action–angle variables influences the classical variables as well. We obtain a modified momentum

$$p_\epsilon^j = \dot{q}_\epsilon^j - \epsilon \sum_{\lambda,\eta} \sqrt{\vartheta_\epsilon^\lambda \vartheta_\epsilon^\eta}\sin(\epsilon^{-1}(\varphi_\epsilon^\lambda - \varphi_\epsilon^\eta))\, d_{\lambda\eta}^j(q_\epsilon) \tag{7}$$

[2] The reader may study [5] for a more comprehensive and detailed presentation.

with $d^j_{\lambda\eta}(q) = \langle e_\lambda(q), \partial_j\, e_\eta(q)\rangle$ and a transformed Hamiltonian function $\tilde{\mathcal{H}} = \tilde{\mathcal{H}}(q_\epsilon, p_\epsilon, \vartheta_\epsilon, \varphi_\epsilon)$

$$\begin{aligned}\tilde{\mathcal{H}} =& \tfrac{1}{2}|p_\epsilon|^2 + \sum_\lambda \vartheta^\lambda_\epsilon E_\lambda(q_\epsilon)\\ &+ \epsilon \sum_{\lambda,\eta,j} p^j_\epsilon \sqrt{\vartheta^\lambda_\epsilon \vartheta^\eta_\epsilon}\, \sin(\epsilon^{-1}\,(\varphi^\lambda_\epsilon - \varphi^\eta_\epsilon))\, d^j_{\lambda\eta}(q_\epsilon)\\ &+ \tfrac{1}{2}\epsilon^2 \sum_j \left(\sum_{\lambda,\eta} \sqrt{\vartheta^\lambda_\epsilon \vartheta^\eta_\epsilon}\, \sin(\epsilon^{-1}\,(\varphi^\lambda_\epsilon - \varphi^\eta_\epsilon))\, d^j_{\lambda\eta}(q_\epsilon) \right)^2 .\end{aligned}$$

The canonical equations

$$q^j_\epsilon = \frac{\partial\tilde{\mathcal{H}}}{\partial p^j_\epsilon}, \quad p^j_\epsilon = -\frac{\partial\tilde{\mathcal{H}}}{\partial q^j_\epsilon}, \quad \varphi^\lambda_\epsilon = \frac{\partial\tilde{\mathcal{H}}}{\partial \vartheta^\lambda_\epsilon}, \quad \vartheta^\lambda_\epsilon = -\frac{\partial\tilde{\mathcal{H}}}{\partial \varphi^\lambda_\epsilon}$$

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

$$\dot\varphi^\lambda_\epsilon = E_\lambda(q_\epsilon) + \epsilon \sum_{\substack{j,\eta\\ \eta\neq\lambda}} p^j_\epsilon \sqrt{\frac{\vartheta^\eta_\epsilon}{\vartheta^\lambda_\epsilon}}\, \sin(\epsilon^{-1}\,(\varphi^\lambda_\epsilon - \varphi^\eta_\epsilon))\, d^j_{\lambda\eta}(q_\epsilon) + \mathcal{O}\big(\epsilon^2\big) \tag{8}$$

$$\begin{aligned}\dot\vartheta^\lambda_\epsilon =& -2 \sum_{\substack{j,\eta\\ \eta\neq\lambda}} p^j_\epsilon \sqrt{\vartheta^\lambda_\epsilon \vartheta^\eta_\epsilon}\, \cos(\epsilon^{-1}\,(\varphi^\lambda_\epsilon - \varphi^\eta_\epsilon))\, d^j_{\lambda\eta}(q_\epsilon)\\ &+ 2\epsilon \sum_{\substack{j,\nu,\xi\\ \nu\neq\lambda,\xi\neq\lambda\\ \nu\neq\xi}} p^j_\epsilon \vartheta^\xi_\epsilon \sqrt{\vartheta^\lambda_\epsilon \vartheta^\nu_\epsilon}\, \sin(\epsilon^{-1}\,(\varphi^\lambda_\epsilon - \varphi^\nu_\epsilon))\, d^j_{\nu\xi}(q_\epsilon)\, d^j_{\lambda\xi}(q_\epsilon)\\ &- 2\epsilon \sum_{\substack{j,\eta,\nu,\xi,\\ \nu\neq\lambda,\xi\neq\lambda,\\ \eta\neq\nu,\eta\neq\xi}} p^j_\epsilon \sqrt{\vartheta^\eta_\epsilon \vartheta^\nu_\epsilon \vartheta^\lambda_\epsilon \vartheta^\xi_\epsilon}\, \sin(\epsilon^{-1}\,(\varphi^\lambda_\epsilon + \varphi^\eta_\epsilon - \varphi^\nu_\epsilon - \varphi^\xi_\epsilon))\, d^j_{\eta\nu}(q_\epsilon)\, d^j_{\lambda\xi}(q_\epsilon)\end{aligned}$$

$$\dot q^j_\epsilon = p^j_\epsilon + \epsilon \sum_{\eta,\lambda} \sqrt{\vartheta^\lambda_\epsilon \vartheta^\eta_\epsilon}\, \sin(\epsilon^{-1}\,(\varphi^\lambda_\epsilon - \varphi^\eta_\epsilon))\, d^j_{\lambda\eta}(q_\epsilon) \tag{9}$$

$$\begin{aligned}\dot p^j_\epsilon =& -\sum_\lambda \vartheta^\lambda_\epsilon \cdot \partial_j E_\lambda(q_\epsilon)\\ &- \epsilon \sum_{r,\lambda,\eta} p^r_\epsilon \sqrt{\vartheta^\lambda_\epsilon \vartheta^\eta_\epsilon}\, \sin(\epsilon^{-1}\,(\varphi^\lambda_\epsilon - \varphi^\eta_\epsilon))\, \partial_{q^j}\, d^r_{\lambda\eta}(q_\epsilon) + \mathcal{O}\big(\epsilon^2\big)\,.\end{aligned} \tag{10}$$

Excluding symmetric energy level crossings of order four (assumption C) and making use of near–identity averaging transformations [8], one does not only obtain the above stated strong convergence of the QCMD model versus the Born-Oppenheimer model but also the first order correction terms [5]

$$
\begin{aligned}
\varphi_\epsilon &= \varphi_{\mathrm{BO}} + \mathcal{O}(\epsilon^2) \\
\vartheta_\epsilon^\lambda &= \vartheta_*^\lambda + 2\epsilon \sum_{\eta\neq\lambda,j} \frac{\dot q_*^j \sqrt{\vartheta_*^\eta \vartheta_*^\lambda}}{E_\lambda(q_*) - E_\eta(q_*)} \sin\Big(\epsilon^{-1}(\varphi_*^\lambda - \varphi_*^\eta)\Big)\, d_{\lambda\eta}^j(q_*) \\
&\quad -2\epsilon \sum_{\eta\neq\lambda,j} \frac{\dot q_{\mathrm{BO}}^j \sqrt{\vartheta_*^\eta \vartheta_*^\lambda}}{E_\lambda(q_{\mathrm{BO}}) - E_\eta(q_{\mathrm{BO}})} \sin\Big(\epsilon^{-1}(\varphi_{\mathrm{BO}}^\lambda - \varphi_{\mathrm{BO}}^\eta)\Big)\, d_{\lambda\eta}^j(q_{\mathrm{BO}}) \\
&\quad +\mathcal{O}(\epsilon^2) \\
q_\epsilon &= q_{\mathrm{BO}} + \mathcal{O}(\epsilon^2) \\
\dot q_\epsilon^j &= \dot q_{\mathrm{BO}}^j + \epsilon \sum_\eta \sqrt{\vartheta_*^\eta \vartheta_*^\lambda} \sin\Big(\epsilon^{-1}(\varphi_{\mathrm{BO}}^\lambda - \varphi_{\mathrm{BO}}^\eta)\Big)\, d_{\lambda\eta}^j(q_\epsilon) + \mathcal{O}(\epsilon^2)
\end{aligned}
$$

where φ_{BO} denotes the Born-Oppenheimer phase, i.e., the solution to

$$\dot\varphi_{\mathrm{BO}}^\lambda(t) = E_\lambda(q_{\mathrm{BO}}(t)), \qquad \varphi_{\mathrm{BO}}^\lambda(0) = \varphi_*^\lambda.$$

Obviously, the highly oscillatory first order correction terms vanish in the case of only one initially occupied state (assumption D).

5 Proof of Theorem 1

Instead of applying again near–identity averaging transformations, we try to simplify the argumentation by focusing just on the population dynamics. Considering the results of §4, let us introduce $\mathcal{O}(1)$ second order correction terms $\delta\varphi_\epsilon^\lambda, \delta\vartheta_\epsilon^\lambda$ and δq_ϵ^j

$$
\begin{aligned}
\varphi_\epsilon^\lambda &= \varphi_{\mathrm{BO}}^\lambda + \epsilon^2\, \delta\varphi_\epsilon^\lambda + \mathcal{O}(\epsilon^3) \\
\vartheta_\epsilon^\lambda &= \vartheta_\epsilon^\lambda(0) + \epsilon^2\, \delta\vartheta_\epsilon^\lambda + \mathcal{O}(\epsilon^3) = \delta_{\lambda\mu} + \epsilon^2\, \delta\vartheta_\epsilon^\lambda + \mathcal{O}(\epsilon^3) \\
q_\epsilon^j &= q_{\mathrm{BO}}^j + \epsilon^2\, \delta q_\epsilon^j + \mathcal{O}(\epsilon^3)\,.
\end{aligned} \tag{11}
$$

The reader might have noticed that we already have applied condition D — initially, only state μ is occupied. Immediately, we conclude that

$$
\sqrt{\vartheta_\epsilon^\lambda} = \begin{cases} 1+\mathcal{O}(\epsilon^2) & \text{for } \lambda=\mu, \\ \epsilon\sqrt{\delta\vartheta_\epsilon^\lambda} + \mathcal{O}(\epsilon^2) & \text{for } \lambda\neq\mu \end{cases}
$$

$$
\sqrt{\vartheta_\epsilon^\lambda \vartheta_\epsilon^\eta} = \begin{cases} 1+\mathcal{O}(\epsilon^2) & \text{for } \lambda=\eta=\mu, \\ \epsilon\sqrt{\delta\vartheta_\epsilon^\eta} + \mathcal{O}(\epsilon^2) & \text{for } \lambda=\mu \text{ and } \eta\neq\mu \\ \epsilon\sqrt{\delta\vartheta_\epsilon^\lambda} + \mathcal{O}(\epsilon^2) & \text{for } \lambda\neq\mu \text{ and } \eta=\mu \\ \mathcal{O}(\epsilon^2) & \text{for } \lambda\neq\mu \text{ and } \eta\neq\mu \end{cases} \tag{12}
$$

which helps us a lot in the subsequent analysis.

At first, let us have a closer look onto $\delta\varphi_\epsilon^\lambda$ and δq_ϵ^j before we determine $\delta\vartheta_\epsilon^\lambda$. Under condition B, C and D we obtain in a straightforward calculation based on inserting (7), (11) and (12) into (8) the second order correction $\delta\varphi_\epsilon^\mu$ to the phase of the initially occupied state μ

$$\begin{aligned}\delta\varphi_\epsilon^\mu(t) =& \sum_j \int_0^t \partial_j E_\mu(q_{\mathrm{BO}})\,\delta q_\epsilon^j\,ds \\ &- \sum_{\lambda,\lambda\neq\mu}\int_0^t B_{\mathrm{BO}}^{\mu\lambda}\,\sin(\epsilon^{-1}\,(\varphi_{\mathrm{BO}}^\mu-\varphi_{\mathrm{BO}}^\lambda))\sqrt{\delta\vartheta_\epsilon^\lambda}+\mathcal{O}(\epsilon)\end{aligned} \tag{13}$$

Next, we compute via (10) an $\mathcal{O}(\epsilon^3)$–approximation of p_ϵ analogously to the previous calculation of $\delta\varphi_\epsilon^\mu$

$$\begin{aligned}p_\epsilon^j(t) \;=& \;\dot q_{\mathrm{BO}}^j(t) - \epsilon^2\int_0^t ds\,\sum_\lambda \delta\vartheta_\epsilon^\lambda \partial_j E_\lambda(q_{\mathrm{BO}}) \\ &- \epsilon^2\sum_k\int_0^t ds\,\partial_k\partial_j E_\mu(q_{\mathrm{BO}})\delta q_\epsilon^k \\ &+ 2\epsilon^2\sum_{\lambda,\lambda\neq\mu}\int_0^t ds\,\sqrt{\delta\vartheta_\epsilon^\lambda}\,\sin(\epsilon^{-1}\,(\varphi_{\mathrm{BO}}^\lambda-\varphi_{\mathrm{BO}}^\mu))\,\partial_j B_{\mathrm{BO}}^{\lambda\mu} \\ &+ \mathcal{O}(\epsilon^3)\,.\end{aligned}$$

This allows us to calculate from (9) the following integral equation for δq_ϵ^j

$$\begin{aligned}\delta q_\epsilon^j(t) \;=&\; -\sum_\lambda\int_0^t d\tau\int_0^\tau ds\,\delta\vartheta_\epsilon^\lambda\,\partial_j E_\lambda(q_{\mathrm{BO}}) \\ &- \sum_k\int_0^t d\tau\int_0^\tau ds\,\partial_k\partial_j E_\mu(q_{\mathrm{BO}})\delta q_\epsilon^k \\ &+ 2\sum_{\lambda,\lambda\neq\mu}\int_0^t d\tau\int_0^\tau ds\,\partial_j B_{\mathrm{BO}}^{\lambda\mu}\sqrt{\delta\vartheta_\epsilon^\lambda}\,\sin(\epsilon^{-1}\,(\varphi_{\mathrm{BO}}^\lambda-\varphi_{\mathrm{BO}}^\mu)) \\ &+ 2\sum_{\lambda,\lambda\neq\mu}\int_0^t d\tau\,\sqrt{\delta\vartheta_\epsilon^\lambda}\,\sin(\epsilon^{-1}\,(\varphi_{\mathrm{BO}}^\lambda-\varphi_{\mathrm{BO}}^\mu))\,\langle e_\lambda(q_{\mathrm{BO}}),\partial_j e_\mu(q_{\mathrm{BO}})\rangle \\ &+ \mathcal{O}(\epsilon)\end{aligned} \tag{14}$$

Now, we come back to the population dynamics, that is, we analyze $\delta\vartheta_\epsilon$.

LEMMA 2 *Consider an initially unoccupied state η, i.e. $\eta \neq \mu$, and let assumptions B, C and D apply, then $\sqrt{\delta\vartheta_\epsilon^\eta}$ obeys the integral equation*

$$
\begin{aligned}
\sqrt{\delta\vartheta_\epsilon^\eta(t)} &= \frac{1}{\epsilon}\int_0^t B_{\mathrm{BO}}^{\eta\mu} \exp\left(i\epsilon^{-1}\left(\varphi_{\mathrm{BO}}^\eta - \varphi_{\mathrm{BO}}^\mu\right)\right) d\tau \\
&\quad + \sum_{\lambda,\lambda\neq\mu,\lambda\neq\eta} \int_0^t B_{\mathrm{BO}}^{\eta\lambda} \exp\left(i\epsilon^{-1}\left(\varphi_{\mathrm{BO}}^\eta - \varphi_{\mathrm{BO}}^\lambda\right)\right) \sqrt{\delta\vartheta_\epsilon^\lambda}\, d\tau \\
&\quad + i\int_0^t B_{\mathrm{BO}}^{\eta\mu} \exp\left(i\epsilon^{-1}\left(\varphi_{\mathrm{BO}}^\eta - \varphi_{\mathrm{BO}}^\mu\right)\right) \cdot \\
&\qquad \cdot \left(\sum_j \int_0^\tau \Big(\partial_j E_\eta(q_{\mathrm{BO}}(s)) - \partial_j E_\mu(q_{\mathrm{BO}}(s))\Big)\delta q_\epsilon^j(s)ds\right) d\tau \\
&\quad + i\int_0^t B_{\mathrm{BO}}^{\eta\mu} \exp\left(i\epsilon^{-1}\left(\varphi_{\mathrm{BO}}^\eta - \varphi_{\mathrm{BO}}^\mu\right)\right) \cdot \\
&\qquad \cdot \left(\sum_{\lambda,\lambda\neq\mu} \int_0^\tau B_{\mathrm{BO}}^{\mu\lambda} \sin(\epsilon^{-1}\left(\varphi_{\mathrm{BO}}^\mu - \varphi_{\mathrm{BO}}^\lambda\right))\sqrt{\delta\vartheta_\epsilon^\lambda} ds\right) d\tau \\
&\quad + \mathcal{O}(\epsilon)\,.
\end{aligned}
\tag{15}
$$

PROOF. Let us consider an expansion of the wavefunction ψ_ϵ in the eigenfunctions of $H(q_\epsilon)$

$$\psi_\epsilon = \sum_\lambda c_\epsilon^\lambda\, e_\lambda(q_\epsilon). \tag{16}$$

For the resulting ordinary differential equation for c_ϵ

$$i\,\epsilon\,\dot{c}_\epsilon^\eta = E_\eta(q_\epsilon)c_\epsilon^\eta - i\epsilon\sum_{\lambda,j} c_\epsilon^\lambda \langle e_\eta(q_\epsilon), \partial_j e_\lambda(q_\epsilon)\rangle\, \dot{q}_\epsilon^j$$

we make the following ansatz (with $|\gamma_\epsilon^\eta|^2 = \vartheta_\epsilon^\eta$)

$$c_\epsilon^\eta(t) = \gamma_\epsilon^\eta(t)\exp\left(-i\epsilon^{-1}\left(\varphi_*^\eta + \int_0^t E_\eta(q_\epsilon(s))ds\right)\right). \tag{17}$$

We obtain a differential equation for γ_ϵ

$$\dot{\gamma}_\epsilon^\eta(t) = \sum_{\lambda,\lambda\neq\eta} B_\epsilon^{\eta\lambda}\exp\left(i\epsilon^{-1}\left(\varphi_*^\eta - \varphi_*^\lambda + \int_0^t \Delta E_\epsilon^{\eta\lambda}(s))ds\right)\right)\gamma_\epsilon^\lambda(t) \tag{18}$$

with $B_\epsilon^{\eta\lambda} := -\sum_j \langle e_\eta(q_\epsilon), \partial_j e_\lambda(q_\epsilon)\rangle\, \dot{q}_\epsilon^j$ and $\Delta E_\epsilon^{\lambda\eta}(s) := E_\lambda(q_\epsilon(s)) - E_\eta(q_\epsilon(s))$. Notice that $B_\epsilon^{\lambda\lambda}$ vanishes due to the antisymmetric character of $\langle e_\eta(q_\epsilon), \partial_j e_\lambda(q_\epsilon)\rangle$.

Equation (18) is identical to the integral equation

$$\begin{aligned}\gamma_\epsilon^\eta(t) =& \gamma_\epsilon^\eta(0) \\ &+ \int_0^t \sum_{\lambda,\lambda\neq\eta} B_\epsilon^{\eta\lambda} \exp\left(i\epsilon^{-1}\left(\varphi_*^\eta - \varphi_*^\lambda + \int_0^\tau \Delta E_\epsilon^{\eta\lambda}(s))ds\right)\right)\gamma_\epsilon^\lambda \, d\tau.\end{aligned} \tag{19}$$

A simple comparison of (16), (17) with (4) returns

$$\gamma_\epsilon^\lambda(t) \;=\; \sqrt{\vartheta_\epsilon^\lambda}\exp(-i\epsilon^{-1}\varphi_\epsilon^\lambda)\exp\left(+i\epsilon^{-1}\left(\varphi_*^\lambda + \int_0^t E_\lambda(q_\epsilon(s))ds\right)\right).$$

Applying again (11) and (12) yields

$$\gamma_\epsilon^\lambda(t) \;=\; \begin{cases} 1 - i\epsilon\,\delta\varphi_\epsilon^\mu + i\epsilon\sum_j \int_0^t \partial_j E_\mu(q_{\mathrm{BO}})\,\delta q_\epsilon^j\,ds + \mathcal{O}(\epsilon^2) & for\ \lambda = \mu \\ \epsilon\sqrt{\delta\vartheta_\epsilon^\lambda} + \mathcal{O}(\epsilon^2) & for\ \lambda \neq \mu. \end{cases}$$

The contribution of (13) eases the case $\lambda = \mu$ even further

$$\gamma_\epsilon^\mu(t) \;=\; 1 + i\epsilon\sum_{\lambda,\lambda\neq\mu}\int_0^t B_{\mathrm{BO}}^{\mu\lambda}\sin(\epsilon^{-1}(\varphi_{\mathrm{BO}}^\mu - \varphi_{\mathrm{BO}}^\lambda))\sqrt{\delta\vartheta_\epsilon^\lambda} + \mathcal{O}(\epsilon^2).$$

The completion of the proof is obtained by inserting these results into (19).
□

Obviously, we have to compute the zeroth order of the solution of the integral equation (15) to prove Theorem 1. Unfortunately, (15) depends on δq_ϵ, itself as well a solution of integral equation (14). Thus we have to deal with two coupled integral equations. A simple transformation shows that this system is identical to an inhomogeneous, nonlinear Volterra integral equation of second kind. Existence and uniqueness of its solution for finite times $t < t_{\max}$ can be proven [6] via the smoothness of its kernel and via a Lipschitz condition. A Picard–iteration of the system of integral equations yields an $\mathcal{O}(\epsilon)$-approximation of its solution for the initially unoccupied state $\eta \neq \mu$

$$\begin{aligned}\sqrt{\delta\vartheta_\epsilon^\eta(t)} \;=\; & -i\,\frac{B_{\mathrm{BO}}^{\eta\mu}(t)}{\Delta E_{\mathrm{BO}}^{\eta\mu}(t)}\exp\left(i\epsilon^{-1}(\varphi_{\mathrm{BO}}^\eta(t) - \varphi_{\mathrm{BO}}^\mu(t))\right) \\ & + i\,\frac{B_{\mathrm{BO}}^{\eta\mu}(0)}{\Delta E_{\mathrm{BO}}^{\eta\mu}(0)}\exp\left(i\epsilon^{-1}(\varphi_*^\eta - \varphi_*^\mu)\right) \\ & + \mathcal{O}(\epsilon)\end{aligned}$$

Immediately, we obtain now the result of Theorem 1. □

6 Numerical example

In the subsequent, let us consider the particularly simple test case where the quantum subsystem can be described as a two state system and the classical subsystem is one-dimensional. This example is the quantum–classical analogue of a purely quantum dynamical avoided crossing example [11]. Thus, $q \in \mathbb{R}^1$ and the Schödinger equation has the form:

$$i\epsilon \dot{\psi} = H(q)\,\psi, \qquad \psi \in \mathbb{C}^2$$

with $H = H(q)$ denoting a 2×2 Hermitian matrix:

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

Herein, we choose the potentials to be $V_1(q) = q^2$ and $V_2(q) = 1/q$. The interpretation is the following: V_1 describes a harmonic bond, V_2 a repulsive potential, and c a weak coupling between these two (electronic) configurations. We choose $\epsilon = 0.01$ which is a suitable scaling for electrons. Furthermore, we set $c = 0.1$. We are interested in the following initial conditions: Let $\psi(t = 0)$ be the eigenvector to E_1 of $H(q_0)$, $q_0 = 0.4$ and $p_0 = 0.5$.

For the choices made, Fig. 1 **(a)** shows the potentials as well as the energy eigenvalues $E_1 = E_1(q)$ and $E_2 = E_2(q) < E_1(q)$ of $H(q)$. Notice that

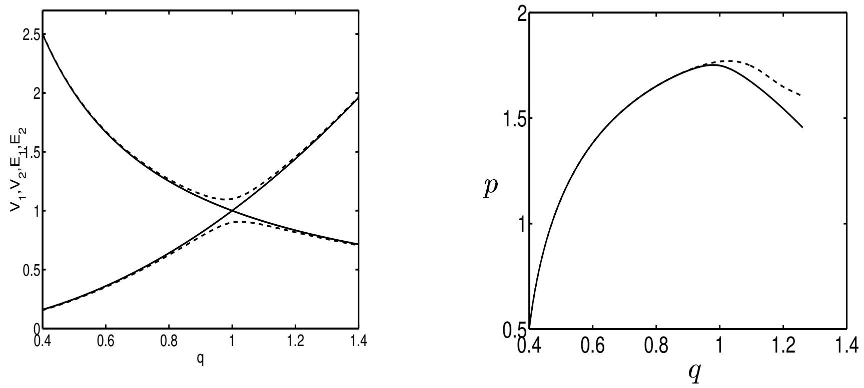

Figure 1: **(a)** Potentials V_1 and V_2 (*solid lines*) and energy levels E_1 and E_2 (*dashed lines*) versus q. **(b)** Phase space trajectories of Born-Oppenheimer simulation (*solid line*) and of the classical subsystem of the QCMD calculation (*dashed line*)

there is some "transition zone" around $q = 1$ where the gap between the two energy levels is minimal and the coupling matrix entry significantly large. In this "transition zone" (at around $t \approx 0.4$), the difference in the dynamics between Born-Oppenheimer and QCMD motion becomes apparent (see Fig. 1 **(b)**).

For this avoided crossing example, we have computed the QCMD as well as the Born–Oppenheimer dynamics. Based on the BO motion, we have calculated the second order correction terms (5) of the population of the initially unoccupied state ϑ_ϵ^2. A comparison between this analytically obtained excitation dynamics and the QCMD population ϑ_ϵ^2 of the simulation is given in Fig. 2 **(a)** and **(b)** for different time spans.

Obviously, the approximation is just valid in a region, where the QCMD motion is close to the corresponding BO motion. Thus, the second order

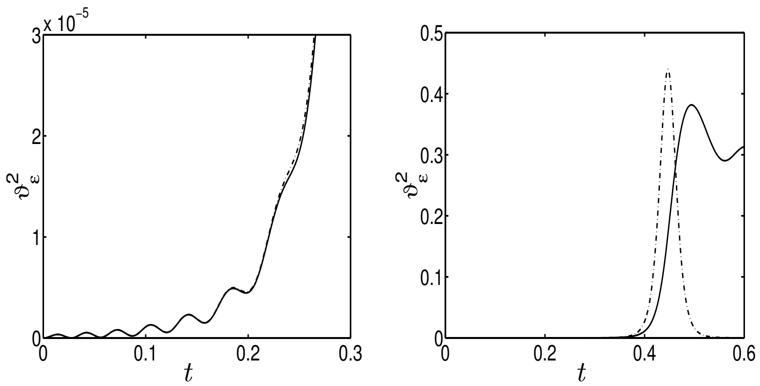

Figure 2: Population of initially unoccupied state ϑ_ϵ^2 versus time t for different time spans. Population ϑ_ϵ^2 computed in a QCMD simulation (*solid lines*) and via the second order approximation presented in Theorem 1 (*dashed dotted lines*)

approximation based on the expansion around the Born-Oppenheimer solution fails in the transition zone. Nonetheless, the initial excitation of the second level is correctly represented. This might help as an indicator of a beginning excitation of a previously unoccupied energy level as, for example, in a QCMD surface hopping algorithm [11].

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References

[1] V.I. Arnold. *Mathematical Methods of Classical Mechanics.* Springer Verlag, Berlin, Heidelberg, New York, Tokyo, 1978.

[2] M. Born and V. Fock. Beweis des Adiabatensatzes. *Z. Phys.*, 51:165–180, 1928.

[3] F. A. Bornemann, P. Nettesheim, and Ch. Schütte. Quantum-classical molecular dynamics as an approximation to full quantum dynamics. *J. Chem. Phys.*, 105:1074–1083, 1996.

[4] F. A. Bornemann and C. Schütte. On the singular limit of the quantum-classical molecular dynamics model. *To appear in SIAM J. Appl. Math.*, 1998.

[5] F.A. Bornemann. *Homogenization in Time of Singularly Perturbed Mechanical Systems*, volume 1687 of *Lecture Notes in Mathematics, no. 1687.* Springer, Berlin, Heidelberg, New York, 1998.

[6] C. Corduneanu. *Integral equations and applications.* Cambridge University Press, Cambridge, 1991.

[7] P. Deuflhard, J. Hermans, B. Leimkuhler, A. Mark, B. Skeel, and S. Reich, editors. *Computational Molecular Dynamics: Challenges, Methods, Ideas. Proceedings of the 2nd International Symposium "Algorithms for Macromolecular Modelling"*, Lecture Notes in Computational Science and Engineering, No. 4. Springer-Verlag, 1998.

[8] J. Kevorkian and J.D. Cole. *Multiple scale and singular perturbation methods*, volume 114 of *Appl.Math.Series.* Springer, New York, 1996.

[9] A. Messiah. *Quantum Mechanics. Vol. I & II.* North-Holland Publ. Co., Amsterdam, New York, 1962.

[10] Ch. Schütte and F. Bornemann. Approximation properties and limits of the quantum-classical molecular dynamics model. pages 380–395. 1998. Published in collection [7].

[11] Ch. Schütte and P. Nettesheim. Non–adiabatic effects in quantum–classical molecular dynamics. *Preprint SC 98–38, Konrad–Zuse–Center, Berlin*, 1998.