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Abstract

The Car-Parrinello method for ab-initio molecular dynamics avoids the explicit minimization of energy functionals given by functional density theory in the context of the quantum adiabatic approximation (time-dependent Born-Oppenheimer approximation). Instead, it introduces a fictitious classical dynamics for the electronic orbitals. For many realistic systems this concept allowed first-principle computer simulations for the first time. In this paper we study the *quantitative* influence of the involved parameter μ, the fictitious electronic mass of the method. In particular, we prove by use of a carefully chosen two-time-scale asymptotics that the deviation of the Car-Parrinello method from the adiabatic model is of order $\mathcal{O}(\mu^{1/2})$ — provided one starts in the ground state of the electronic system and the electronic excitation spectrum satisfies a certain non-degeneracy condition. Analyzing a two-level model problem we prove that our result cannot be improved in general. Finally, we show how to use the gained quantitative insight for an automatic control of the unphysical "fake" kinetic energy of the method.

Keywords: Born-Oppenheimer approximation, density functional theory, Car-Parrinello method, oscillatory Hamiltonian systems, adiabatic invariant, two-time-scale asymptotics, Kohn-Sham scheme

AMS classification: 34C15,34C40,70F20,81Q15,81V55

Introduction

A typical molecular system consists of two essentially different parts: the *electronic* configuration and the remaining *ionic* configuration. The study of the full quantum dynamics of an polyatomic system is beyond computational possibilities — for now and the next decades. For this reason, computer simulations for realistic systems require some simplifications of the model, mathematically speaking a kind of approximation within a certain range of applicability.

Until recently the most commonly used simplifications modeled the ionic dynamics by classical dynamics using *empirical potentials* for the ionic interaction. Unfortunately, this is bound to special systems and inappropriate in many interesting situations. Moreover, the lack of systematic techniques for deriving such potentials has caused continuous research in the direction of a true "first-principles" approach.

Such an approach can be based on the *quantum adiabatic approximation*, also called the time-dependent *Born-Oppenheimer* approximation. Here, one exploits the large mass ratio between ions and electrons. The approximation is valid if the time scales of the fast electronic and slow ionic movement are always well separated. Adiabaticity now means, that averaging the electronic movement with respect to the slow ionic time scale relaxes the electrons to their energetic ground state. The equation governing the ionic movement is obtained by a semiclassical limit, i.e., becomes a classical Newtonian equation of motion. This approach can rigorously be justified on mathematical grounds [6, 12] provided the electronic excitation spectrum fulfills certain non-resonance conditions. The adiabatic approach formally ends up with an effective Hamiltonian function for the (now classically modeled) ionic positions q and momenta p:

$$H_I = H_I^0(q,p) + U(q) = T_I^0(p) + U_I^0(q) + U(q).$$

Here, H_I^0 contains the ionic kinetic energy T_I^0 and the bare ion-ion interaction potential U_I^0 whereas $U(q)$ denotes the ground state energy of the electronic configuration in the presence of the ions fixed at positions q. However, an *evaluation* of $U(q)$ requires a many-body ground state computation.

The most prominent methods for quantum many-body ground state computations, i.e., the Hartree-Fock approximation and the density functional theory (DFT) of Hohenberg and Kohn [7], approximate the many-body ground state by a set of one-particle wave functions. Because of its flexibility we concentrate on the density functional theory approach here. A detailed account can be found in [5].

In essence, the Hohenberg-Kohn theorem [5, 7] states that the ground state energy can be obtained *exactly* by minimizing the energy expressed as a functional of the *number density*. However, in general such a density functional expression of the energy is not known and one has to rely on various approximations. Using the Kohn-Sham scheme [5, 10] for the electronic density functional one ends up with a total energy functional $E_{KS}(\psi_1, \dots, \psi_m; q)$, where the ψ_j describe one-particle wave functions belonging to the different occupied electronic orbitals. They build an L^2-orthonormal system. As an important feature the one-particle wave functions ψ_j enter the potential energy part of E_{KS} only via their density

$$n(x) = \sum_{j=1}^{m} f_j |\psi_j(x)|^2.$$

Here, $f_j > 0$ denotes the *occupation number* of the jth orbital. Now, one replaces the ground state energy $U(q)$ of the electronic configuration by the potential

$$U_{KS}(q) = \min_{\psi} E_{KS}(\psi; q), \tag{1}$$

where the minimum is taken over all orthonormal m-tuple $\psi = (\psi_1, \dots, \psi_m)$. One observes that the functional derivative of the energy functional with respect to ψ can be expressed in the form

$$\frac{\delta E_{KS}(\psi; q)}{\delta \psi_j^*} = f_j \cdot H_{KS}(\psi; q)\psi_j, \qquad j = 1, \dots, m \tag{2}$$

which defines for *fixed* electronic states ψ and ionic positions q the *Kohn-Sham Hamiltonian* operator $H_{KS}(\psi; q)$, i.e., a linear selfadjoint operator operating on one-particle wave functions. The time-dependent wave functions ψ_j which realize the energy minimization of (1) along the ionic motion q are in fact *eigenstates* of the Kohn-Sham Hamiltonian,

$$H_{KS}(\psi(t); q(t))\, \psi_j(t) = \epsilon_j(t)\psi_j(t), \qquad j = 1, \dots, m. \tag{3}$$

Since the operator H_{KS} depends on these eigenstates itself, one speaks of a *self-consistent* solution of the (nonlinear) eigenvalue problem.

Summarizing, the density functional approach replaced the linear eigenvalue problem for the m-particle ground state by a nonlinear eigenvalue problem involving a set of m corresponding one-particle states. This provides a dramatic reduction of the dimensional complexity of the problem.[1]

[1] Application of the Hartree-Fock approximation instead of density functional theory results in the same *formal* situation as given in equations (1) and (3).

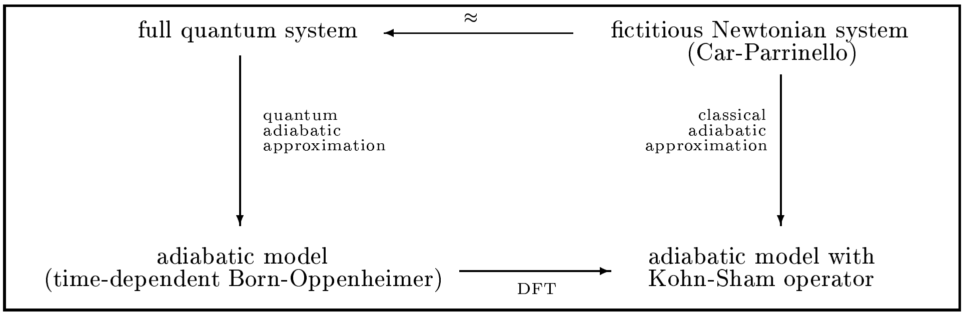

Figure 1: Logic of the Car-Parrinello method

However, a straightforward numerical simulation of the adiabatic approach using the potential U_{KS} would require the solution of a self-consistent electronic structure problem *at each* of the typical 10^4 - 10^5 time steps. As noted in [14], even for very small realistic time steps, state-of-the-art minimization algorithms require an order of ten iterations to converge which prevents even this approach from being feasible for more complicated polyatomic systems.

In 1985, Car and Parrinello [3] presented a method which largely extended the set of treatable systems. Their main idea was to circumvent the explicit minimization by partly undoing the adiabatic approach. Remember that the quantum adiabatic approach replaced the fast quantum-dynamically oscillatory behavior of the electronic wave functions (extremely difficult to compute) by the average of their motion around the minimum of the potential energy surface (still expensive to compute). Now, Car and Parrinello replaced this adiabatic motion by a *fictitious* classical Newtonian dynamics which oscillates around the energy minimum again. However, in most of the interesting cases that turns out to be much more feasible to compute. The logic of the idea can be visualized by the diagram given in Fig. 1. In detail, the fictitious Newtonian dynamics is given by the Lagrangian

$$\mathcal{L}_{CP} = \frac{\mu}{2} \sum_{j=1}^{m} \langle \dot{\psi}_j, \dot{\psi}_j \rangle + \frac{1}{2} \sum_{I} M_I \, \dot{q}_I^2 - E_{KS}(\psi, q) + \sum_{j,k=1}^{m} \Lambda_{jk} \left(\langle \psi_j, \psi_k \rangle - \delta_{jk} \right),$$

where $\langle \cdot, \cdot \rangle$ denotes the integral scalar product, the wave functions ψ_j are regarded as classical fields, M_I are the ionic masses and μ is a masslike parameter introduced by the method. The Lagrange parameters Λ_{jk} ensure the orthonormality of the wave functions.

Compared to the widespread computational use[2] of this method little attention has been paid to developing the underlying theory. According to the extremely well written paper [14] by Pastore, Smargiassi, and Buda there have even "been some misunderstandings about the justification of the method." After a particular clear presentation of the method, they analyze the method in the framework of classical mechanics and argue that the method works due to *classical* adiabatic effects. Moreover, they indicate that this classical adiabaticity is given essentially under the same condition on the electronic excitation spectrum which allows to use the quantum adiabatic approximation; *condition A* for short. This coincidence of the underlying conditions shows how well a chosen model the Car-Parrinello method is. It is, however, definitely not obvious since that would essentially mean to take for granted an intrinsic link between the quantum mechanical nature of the real system and the purely classical nature of the fictitious Newtonian system — which provides one instance of the mentioned misunderstandings. Pastore, Smargiassi, and Buda support their analysis by a number of carefully chosen numerical experiments for the Car-Parrinello method. In particular, they compare the behavior for physical meaningful systems, where one has some understanding of the underlying *quantum* mechanics, with the behavior of some model problems, where one has some understanding of the underlying *classical* mechanics.

Their study shows that the fictitious "electronic mass" μ constitutes a kind of control parameter: the smaller μ is chosen, the smaller the deviation of the Car-Parrinello method from the adiabatic model will be. On the other hand μ introduces a time scale of order $\mu^{1/2}$ thus forcing the discrete time steps in numerical simulations to be proportional to $\mu^{1/2}$. The user has to find a compromise between the computational cost (the number of time steps) and accuracy. In order to do that one should gain a more quantitative understanding of the influence of μ on the accuracy of the method. This paper is essentially devoted to that question.

Moreover, we intend to put the analysis of Pastore, Smargiassi, and Buda on a rigorous mathematical base. As they realize already, their use of dynamical system theory is rather informal and with a "more empirical attitude." Essentially their argument relies on the existence of adiabatic invariants for multifrequency systems (cf. the beginning of [14, p. 6335] and [14, formula (28)]). From the mathematical point of view this is a quite

[2] For recent results on computational issues consult the articles [8, 16, 17] and the literature cited therein. For a review of applications look at [15] or at the web address [11] and the vast pointers to the recent literature given there.

dangerous assumption. We best cite from the same book of Arnol'd which serves as a reference to the mathematical literature for them ([2, p. 173], emphasis ours): "For nonlinear systems with several degrees of freedom, the adiabatic invariance of the action variables does not hold, in spite of assertions in the physical literature: they are *only almost* adiabatic invariants, i.e., change little for the *majority of initial conditions*." One might argue that realistic initial values do us the favor of belonging to that majority — but putting that wish on a firm base seems to be at least extremely difficult.

As we will show a great deal less than adiabatic invariance will do the job. A careful two-time-scale kind of perturbation analysis will prove our main result that condition A implies that the deviation Δ_μ of the Car-Parrinello method from the adiabatic model with the Kohn-Sham operator can be estimated by

$$\Delta_\mu \leq C\mu^{1/2},$$

for some constant $C > 0$. Since the computational cost grows linearly with $\mu^{1/2}$ one can regard the Car-Parrinello method as a kind of first order method.

The paper is organized as follows. In Sec. 1 we extract the mathematical structure of the Car-Parrinello method and of condition A. We give a precise statement of the main theorem. The proof of this theorem will be given in Sec. 2. In Sec. 3 we apply the theorem to a model problem which was investigated numerically in [14]. We show that our result cannot be improved in general. Particular attention is paid to the case where condition A is not satisfied.

1 The Underlying Mathematical Structure

To reveal the mathematical structure of the Car-Parrinello method we use a Hamiltonian description instead of a Lagrangian one. To simplify notation we introduce the constraint manifold

$$\mathcal{M} = \{\psi = (\psi_1, \ldots, \psi_m) : \langle \psi_j, \psi_k \rangle = \delta_{jk}\}$$

which describes the orthonormalization of the electronic one-particle wavefunctions. The Hamiltonian H_I of the quantum adiabatic model with Kohn-Sham operator is given by the expression

$$H_I = \frac{1}{2} p^T M^{-1} p + \underbrace{\min_{\psi \in \mathcal{M}} E_{KS}(\psi; q)}_{=U_{KS}(q)},$$

where we have incorporated the bare ion-ion interaction potential $U_I^0(q)$ into the energy E_{KS} and M denotes the diagonal matrix of ionic masses. The corresponding second order equation of motion reads

$$M\ddot{q}^0 + \left.\frac{\partial U_{KS}(q)}{\partial q}\right|_{q=q^0} = 0.$$

Its solution will always be denoted with the superscript 0.

The Hamiltonian of the Car-Parrinello method is given by

$$H_{CP} = \frac{1}{2}p^T M^{-1} p + \frac{1}{2\mu}\langle \pi, \pi\rangle + E_{KS}(\psi, q)$$

with the *holonomic constraints* $\psi \in \mathcal{M}$. Here, $\pi_j = \mu\dot{\psi}_j$ denotes the canonical momentum associated with ψ_j. The "unphysical" part of the energy function, the so called "fake" kinetic energy

$$K_f = \frac{1}{2\mu}\langle \pi, \pi\rangle = \sum_{j=1}^{m} \frac{\langle \pi_j, \pi_j\rangle}{2\mu}$$

is a kind of measure for the deviation between the motions belonging to H_{CP} and H_I. The second order equations of motion belonging to H_{CP} are

$$\begin{aligned} \mu\ddot{\psi}^\mu + \left.\frac{\delta E_{KS}(\psi; q^\mu)}{\delta \psi^*}\right|_{\psi=\psi^\mu} &\perp T\mathcal{M}, \qquad \psi^\mu \in \mathcal{M}, \\ M\ddot{q}^\mu + \left.\frac{\partial E_{KS}(\psi^\mu; q)}{\partial q}\right|_{q=q^\mu} &= 0, \end{aligned}$$

where the superscript denotes the explicit dependence on the parameter μ. The functional derivative $\delta E_{KS}/\delta\psi^*$ is connected to the Kohn-Sham operator as expressed in formula (2).

Condition A, which was mentioned in the Introduction, will give a more detailed description on how the minimum $\min_{\psi\in\mathcal{M}} E_{KS}(\psi; q^0)$ is attained along the solution of the adiabatic model. If

$$U_{KS}(q^0(t)) = E_{KS}(\psi^0(t); q^0(t)), \qquad \psi^0(t) \in \mathcal{M},$$

realizes at least a *local* minimum, we necessarily have that the eigenvalues ω_{jk}^2 of the second functional derivative of E_{KS} with respect to the constraints $\psi \in \mathcal{M}$ are *nonnegative*. Note that ω_{jk} constitutes a normal mode frequency of the linearized system with frozen coefficients. According to Pastore, Smargiassi, and Buda [14] these normal modes are given by

$$\omega_{jk}^2 = \begin{cases} f_j(\epsilon_k^* - \epsilon_j), & k = m+1, \ldots, \\ (f_j - f_k)(\epsilon_k - \epsilon_j)/2, & k = 1, \ldots, m, \end{cases}$$

for $j = 1, \ldots, m$. Here, we denote by ϵ_k^* the eigenvalue of the kth unoccupied level and by ϵ_j the jth occupied one of the Kohn-Sham Hamiltonian $H_{KS}(\psi^0; q^0)$. Thus, the necessary nonnegativity condition is fulfilled if the occupied states correspond to the lowest m one-particle eigenvalues and, in the case of unequal occupation numbers $f_j \neq f_k$ of two occupied states j and k, if the state with higher energy has lower occupation.

Some of the frequencies ω_{jk} are identically zero in time, for instance

$$\omega_{jj} \equiv 0, \qquad j = 1, \ldots, m,$$

and

$$\omega_{jk} \equiv 0, \qquad \text{if} \quad f_j = f_k.$$

As shown in [14] there is a one-to-one correspondence of these nonoscillating modes, which are first integrals of the adiabatic model by the way, to *first integrals* of the Car-Parrinello model H_{CP}. To be specific, phase invariance of the Hamiltonian H_{CP} and the constraint manifold $\mathcal{M}$ yields the first integral

$$I_{jj} = \langle \pi_j, \psi_j \rangle - \langle \psi_j, \pi_j \rangle,$$

whereas invariance of the Kohn-Sham operator with respect to unitary transformations of the occupied states with the *same* occupation number yields the first integral

$$I_{jk} = \langle \pi_j, \psi_k \rangle - \langle \psi_j, \pi_k \rangle,$$

provided that $f_j = f_k$.

We now give the precise statement of *condition A*: All the other modes are uniformly oscillating, i.e., there is a *gap* $\omega_{\min} > 0$ such that

$$\omega_{jk}(t) \geq \omega_{\min}, \qquad j \neq k, \ f_j \neq f_k,$$

for all times t under consideration. In particular, condition A excludes any energy level crossings of occupied states and crossings of occupied with unoccupied states.

If we eliminate[3] the degrees of freedom corresponding to the nonoscillating modes in the adiabatic model and to the first integrals in the Car-Parrinello model, we can apply the following theorem, which reveals the assertion of the Introduction. For the sake of simplicity we state and prove this theorem only for finite-dimensional (real) Hilbert spaces as arising after Ritz-Galerkin approximation of the Kohn-Sham Hamiltonian.

Theorem 1 *Let $\mathcal{M}$ be a compact finite dimensional manifold and $E(\psi, q)$ be a smooth energy function on $\mathcal{M} \times \mathbb{R}^N$, i.e., uniformly bounded from below.*

i (Establish Condition A.) *Let $\psi_0 \in \mathcal{M}$ be a strict local minimizer of $E(\psi, q_0)$ for a given $q_0 \in \mathbb{R}^N$. Then there exists a neighborhood V of q_0, a unique smooth function $\psi^0 : V \to \mathcal{M}$, and a constant $\omega_{\min} > 0$ such that $\psi^0(q)$ is a strict local minimizer of $E(\psi, q)$ and the eigenvalues of the Hessian $D^2_\psi E(\psi, q)|_{\psi=\psi^0(q)}$ restricted to $T\mathcal{M}$ are bounded below by $\omega^2_{\min}$ for $q \in V$.*

ii (The Adiabatic Model.) *We define on V the adiabatic potential*

$$U(q) = E(\psi^0(q), q) \qquad \forall q \in V.$$

Given an initial momentum $p_0 \in \mathbb{R}^N$ there exists a time $T > 0$, such that the adiabatic model

$$M\ddot{q}^0 + \left.\frac{\partial U(q)}{\partial q}\right|_{q=q^0} = 0, \qquad q^0(0) = q_0,\ M\dot{q}^0(0) = p_0,$$

has a unique solution $q^0 \in C^\infty([0, T], V)$. Along this solution condition A is fulfilled.

iii (The Car-Parrinello Model.) *For each time T with the properties of step (ii) the Car-Parrinello model*

$$\begin{aligned} \mu\ddot{\psi}^\mu + \left.\frac{\partial E(\psi, q^\mu)}{\partial \psi}\right|_{\psi=\psi^\mu} \quad &\perp \quad T\mathcal{M}, \qquad \psi^\mu \in \mathcal{M}, \\ M\ddot{q}^\mu + \left.\frac{\partial E(\psi^\mu, q)}{\partial q}\right|_{q=q^\mu} \quad &= \quad 0, \end{aligned}$$

with initial data

$$q^\mu(0) = q_0,\ M\dot{q}^\mu(0) = p_0, \qquad \psi^\mu(0) = \psi_0,\ \dot{\psi}^\mu(0) = 0,$$

has a unique solution q^μ, ψ^μ for $\mu > 0$ and $0 \le t \le T$.

[3] For the *dimensional reduction* of Hamiltonian systems due to conservation laws we refer to [13, Theorem 6.35]. The original system is related to the reduced one by quadratures.

iv (The Error.) *There are constants* $C > 0$ *and* $\mu_0 > 0$ *such that*

$$\Delta_\mu = |q^\mu(t) - q^0(t)| + |\psi^\mu(t) - \psi^0(q^0(t))| \le C\mu^{1/2} \qquad 0 \le t \le T$$

and the fake kinetic energy satisfies

$$K_f = \frac{\mu}{2}|\dot\psi^\mu(t)|^2 \le C\mu \qquad 0 \le t \le T$$

for all values of the parameter μ *satisfying* $0 < \mu \le \mu_0$.

2 The Proof

Part i of Theorem 1 can directly be shown by a straightforward application of the implicit function theorem and continuity arguments. Parts ii and iii follow by well known results for the existence and uniqueness of solutions of ordinary differential equations. The final time T is reached since conservation of energy does not allow the solution to leave a sufficiently large compact subset of the phase space. The remaining part iv is considerably more difficult.

Since the total energy

$$H_{CP}^\mu = \frac{1}{2}\, p^T M^{-1} p + \frac{1}{2\mu}\langle \pi, \pi\rangle + E(\psi, q)$$

is a constant of motion and the initial data fix

$$H_{CP}^\mu = \frac{1}{2}\, p_0^T M^{-1} p_0 + E(\psi_0, q_0)$$

to be in fact *independent* of μ, we conclude that

$$p^\mu = \mathcal{O}(1), \quad \pi^\mu = \mathcal{O}(\mu^{1/2}), \qquad \text{i.e.,} \qquad \dot q^\mu = \mathcal{O}(1), \quad \dot\psi^\mu = \mathcal{O}(\mu^{-1/2}),$$

using that the energy function E is bounded from below. Since we work on a compact time interval $[0, T]$ this implies $q^\mu = \mathcal{O}(1)$. By compactness of $\mathcal{M}$ and $\psi^\mu \in \mathcal{M}$ we also have $\psi^\mu = \mathcal{O}(1)$. Below we will show that the following estimates hold in fact:

$$\psi^\mu - \psi^0(q^\mu) = \mathcal{O}(\mu^{1/2}) \qquad \text{and} \qquad \dot\psi^\mu = \mathcal{O}(1). \tag{4}$$

Now, we can readily prove the error estimates of part iv. Because ψ^0 is defined as a local minimizer we have $\partial_\psi E(\psi^0(q), q) = 0$ and get the identity

$$\begin{aligned} \frac{\partial U}{\partial q}(q) &= \frac{\partial E}{\partial \psi}(\psi^0(q), q)\frac{\partial \psi^0}{\partial q}(q) + \frac{\partial E}{\partial q}(\psi^0(q), q) \\ &= \frac{\partial E}{\partial q}(\psi^0(q), q), \end{aligned}$$

where U denotes the adiabatic potential introduced in step ii of Theorem 1. Thus, estimate (4) implies that q^μ satisfies the equation

$$0 = M\ddot{q}^\mu + \frac{\partial E}{\partial q}(\psi^\mu, q^\mu) = M\ddot{q}^\mu + \frac{\partial U}{\partial q}(q^\mu) + \mathcal{O}(\mu^{1/2}),$$

which is a *perturbation* of the adiabatic model of part ii. By stability we get the error estimate

$$q^\mu - q^0 = \mathcal{O}(\mu^{1/2}),$$

which implies

$$|\psi^\mu - \psi^0(q^0)| \le |\psi^\mu - \psi^0(q^\mu)| + |\psi^0(q^\mu) - \psi^0(q^0)| = \mathcal{O}(\mu^{1/2}).$$

The proof of Theorem 1 is finished.

Proof of the estimates (4). We embed the manifold $\mathcal{M}$ to some Euclidean space and introduce in the neighborhood of $\psi_0 \in \mathcal{M}$ an orthonormal parametrization $x \mapsto \psi(x) \in \mathcal{M}$, i.e.,

$$\langle \partial_i \psi, \partial_j \psi \rangle = \delta_{ij}, \qquad \partial_i \psi \in T\mathcal{M}, \tag{5}$$

where $\partial_i = \partial/\partial x_i$ and $\langle \cdot, \cdot \rangle$ denotes the inner product of the embedding space. In the following we always assume that T and μ are small enough that we live in this coordinate patch around ψ_0. The global result can be easily obtained by continuation exploiting compactness.

Using summation convention we obtain

$$\dot{\psi} = \partial_i \psi \cdot \dot{x}_i, \qquad \ddot{\psi} = \partial_j \partial_i \psi \cdot \dot{x}_i \dot{x}_j \; + \; \partial_i \psi \cdot \ddot{x}_i.$$

Inserting that into the equation

$$\mu \ddot{\psi}^\mu + \left. \frac{\partial E(\psi, q^\mu)}{\partial \psi} \right|_{\psi = \psi^\mu} \perp T\mathcal{M}$$

which uses the same embedding of $\mathcal{M}$ by the way, and taking the inner product with $\partial_k \psi$ yields

$$\mu \ddot{x}_k^\mu + \frac{\partial E}{\partial x_k}(x^\mu, q^\mu) + \mu \sigma_{kij}(x^\mu) \dot{x}_i^\mu \dot{x}_j^\mu = 0 \qquad \forall k. \tag{6}$$

Here, we introduced the preimage x^μ by $\psi^\mu = \psi(x^\mu)$, the tensor

$$\sigma_{kij} = \langle \partial_k \psi, \partial_i \partial_j \psi \rangle,$$

and by "abus de langage"

$$E(x,q) = E(\psi(x),q).$$

The tensor σ_{kij} obeys the symmetries

$$\sigma_{kij} = -\sigma_{ijk}, \qquad \sigma_{kij} = \sigma_{kji}, \tag{7}$$

where the first one can be obtained by differentiating the orthogonality relation (5) and the second one is obvious. With $\Sigma = (\sigma_{kij})_{kij}$ we write the second order equation (6) in the short form

$$\mu\ddot{x}^\mu + \frac{\partial E}{\partial x}(x^\mu, q^\mu) + \mu\,\Sigma(x^\mu) : \dot{x}^\mu \otimes \dot{x}^\mu = 0. \tag{8}$$

The corresponding initial values are given by

$$x^\mu(0) = x_0 \quad \text{with} \quad \psi_0 = \psi(x_0), \qquad \text{and} \quad \dot{x}^\mu(0) = 0.$$

Along the same lines we introduce $x^0(t,\mu)$ as the preimage of $\psi^0(q^\mu(t))$,

$$\psi^0(q^\mu(t)) = \psi(x^0(t,\mu)).$$

This allows us to conclude from condition A the properties

$$\frac{\partial E}{\partial x}(x^0(t,\mu), q^\mu(t)) = 0$$

and

$$\frac{\partial^2 E}{\partial x^2}(x^0(t,\mu), q^\mu(t)) : \eta \otimes \eta \;\geq\; \omega_{\min}^2 |\eta|^2 \qquad \forall \eta.$$

Now, the crucial methodical idea is to make the *two-time-scale ansatz*

$$x^\mu(t) = x^0(t,\mu) + \epsilon\rho^\mu(t/\epsilon),$$

where we have introduced $\epsilon = \mu^{1/2}$ for short. By $\psi^\mu = \mathcal{O}(1)$ and $q^\mu = \mathcal{O}(1)$ we surely get $x^\mu = \mathcal{O}(1)$ and $x^0(\cdot,\mu) = \mathcal{O}(1)$, but this implies only

$$\epsilon\rho^\mu(\cdot/\epsilon) = \mathcal{O}(1). \tag{9}$$

The asserted estimate (4) requires but a far sharper estimate of ρ^μ. To this aim we seriously simplify notation in the following. We suppress all superscripts μ and set

$$\tau = t/\epsilon.$$

The derivative with respect to τ will be denoted by a prime throughout. We are done, if we can show that there is a constant $M > 0$, such that

$$\max\big(|\rho(\tau)|, |\rho'(\tau)|\big) \le M \qquad 0 \le \tau \le T/\epsilon, \tag{10}$$

since this immediately implies the asserted estimate (4). Inserting the two-time-scale ansatz into (8) and using a Taylor expansion of the force term $\partial E/\partial x$ we finally get after division by ϵ:

$$\begin{aligned} 0 \;=\; & \rho''(\tau) \;+\; \frac{\partial^2 E}{\partial x^2}(x^0(\epsilon\tau,\epsilon^2), q(\epsilon\tau)) \cdot \rho(\tau) \\ & + \epsilon \int_0^1 (1-s) \frac{\partial^3 E}{\partial x^3}\big(x^0(\epsilon\tau,\epsilon^2) + s\epsilon\rho(\tau), q(\epsilon\tau)\big) : \rho(\tau)\otimes\rho(\tau)\; ds \\ & + \epsilon\,\Sigma(x(\epsilon\tau)) : \dot{x}^0(\epsilon\tau,\epsilon^2)\otimes\dot{x}^0(\epsilon\tau,\epsilon^2) \\ & + 2\epsilon\,\Sigma(x(\epsilon\tau)) : \rho'(\tau)\otimes\dot{x}^0(\epsilon\tau,\epsilon^2) \\ & + \epsilon\,\Sigma(x(\epsilon\tau)) : \rho'(\tau)\otimes\rho'(\tau) \;+\; \epsilon\,\ddot{x}^0(\epsilon\tau,\epsilon^2). \end{aligned} \tag{11}$$

We observe the following properties:

A The symmetries (7) of Σ yield

$$\langle \Sigma : \rho'\otimes\rho', \rho'\rangle = \langle \Sigma : \rho'\otimes\dot{x}^0, \rho'\rangle = 0.$$

B The integral can be written as a force term,

$$\int_0^1 (1-s)\frac{\partial^3 E}{\partial x^3}\big(x^0(\epsilon\tau,\epsilon^2) + s\epsilon\rho, q(\epsilon\tau)\big) : \rho\otimes\rho\; ds = \frac{\partial W}{\partial\rho}(\epsilon\tau,\rho,\epsilon),$$

where the potential W satisfies by virtue of estimate (9)

$$\max(|W(t,\rho,\epsilon)|, |W_t(t,\rho,\epsilon)|) \le c_0(1+|\rho|^3)$$

for $0 \le t \le T$ and $0 < \epsilon \le \epsilon_0$. Here we have to restrict x to a simply connected coordinate patch.

Taking the inner product of the second order equation (11) with ρ' we are led to (while suppressing several arguments)

$$\langle \rho'', \rho'\rangle + \langle \partial_x^2 E\cdot\rho, \rho'\rangle + \epsilon\,\partial_\rho W\cdot\rho' + \epsilon\,\langle\phi(\epsilon\tau,\epsilon), \rho'\rangle = 0. \tag{12}$$

Here, we collected all "nice" terms into the function

$$\phi(t,\epsilon) = \Sigma(x(t)) : \dot{x}^0(t,\epsilon^2) \otimes \dot{x}^0(t,\epsilon^2) \;+\; \ddot{x}^0(t,\epsilon^2),$$

which can easily be estimated by

$$|\phi(t,\epsilon)| \le c_1 \qquad 0 \le t \le T, \quad 0 < \epsilon \le \epsilon_0.$$

We rewrite the equation (12) in the following energy-type form:

$$\frac{d}{d\tau}\left(\frac{1}{2}|\rho'|^2 + \frac{1}{2}\langle \partial_x^2 E\cdot\rho,\rho\rangle + \epsilon\, W\right) \;=\; \frac{\epsilon}{2}\langle \partial_x^2\partial_t E\cdot\rho,\rho\rangle + \epsilon^2\, W_t - \epsilon\,\langle \phi(\epsilon\tau,\epsilon),\rho'\rangle.$$

Using (9) and observation B we can estimate the right hand side of this equation by

$$\text{RHS} \quad \le \;\epsilon\, c_2(1+|\rho|^2+|\rho'|^2) \le \epsilon\, c_3\left(1+\frac{\omega_{\min}^2}{2}|\rho|^2+\frac{1}{2}|\rho'|^2\right) \tag{13}$$

for $0<\epsilon\le\epsilon_0$ and $0\le t\le T$. After setting

$$K = \gamma\exp(c_3 T/2),$$

where γ is a constant which we will fix later on, we modify W for $|\rho| > 2K$ to a potential W_* in such a way that the estimates of observation B are not touched but additionally

$$|W_*| \le c_4 \qquad 0\le t\le T, \quad 0<\epsilon\le\epsilon_0,$$

holds for all ρ. This leads to $\epsilon\,|W_*|\le 1$ for all $0<\epsilon\le\epsilon_*$ if we choose $\epsilon_*\le\epsilon_0$ but small enough. Replacing the integral in equation (11) by the term $\partial_\rho W_*$ we get an equation which determines a certain function ρ_* instead of ρ subject to the same initial conditions. However, by construction estimate (13) holds for ρ_* instead of ρ with the *same* constant c_4. Surely we have to replace W by W_* on the left hand side. Thus, introducing

$$\Theta_* = \frac{1}{2}|\rho_*'|^2 + \frac{1}{2}\langle \partial_x^2 E\cdot\rho_*,\rho_*\rangle + \epsilon\, W_* \ge \frac{1}{2}|\rho_*'|^2 + \frac{\omega_{\min}^2}{2}|\rho_*|^2 - 1,$$

where we have to restrict $\epsilon \le \epsilon_*$, estimate (13) gives us the *differential inequality*

$$\frac{d}{d\tau}\Theta_* \le \epsilon\, c_3(\Theta_*+2). \tag{14}$$

Note that this is the place where we finally made use of condition A. The initial value of Θ_* is given by

$$\Theta_*(0) = \frac{1}{2}|\rho_*'(0)|^2 + \epsilon W_*(0,0,\epsilon) = \frac{1}{2}|\rho'(0)|^2 + \epsilon W(0,0,\epsilon)$$

and can be estimated by $|\Theta_*(0)| \le c_5$ for all $\epsilon \le \epsilon_*$. Obviously, the constant c_5 does *not* depend on the modified potential W_*.

Observing $\Theta_* + 2 > 0$ an application of Gronwall's lemma to the differential inequality (14) leads to the estimate

$$\frac{1}{2}|\rho_*'|^2 + \frac{\omega_{\min}^2}{2}|\rho_*|^2 \le \Theta_* + 2 \ \le \ (\Theta_*(0) + 2)\exp(c_3 T) \tag{15}$$

for $\tau \le T/\epsilon$ and $\epsilon \le \epsilon_*$. We immediately see that the choice (which could have been made *prior* to the modification step!)

$$\gamma^2 = \frac{2(c_5+2)}{\omega_{\min}^2}$$

yields $|\rho_*| \le K$ for the times t and parameter ϵ under consideration. But this means, that ρ_* does not "see" the modification of W into W_* and therefore ρ_* is a solution of the original equation (11). By uniqueness we thus get

$$\rho_* = \rho.$$

Hence, the estimate (15) already implies the desired estimate (10) of ρ and ρ'. The proof of Theorem 1 is finished.

Remark. Exactly the same line of arguments which led to the proof of the central estimate (4) can be used to prove the following time-dependent version of Theorem 1.

Theorem 2 *Let $\mathcal{M}$ be a compact finite dimensional manifold and $E(\psi, t, \mu)$ be a smooth energy function on $\mathcal{M} \times \mathbb{R}^2$, i.e., uniformly bounded from below.*

- i *Let $\psi_0 \in \mathcal{M}$ be a strict local minimizer of $E(\psi, 0, 0)$. Then there exists a time $T > 0$, a parameter $\mu_0 > 0$, a unique smooth function $\psi^0 : [0,T] \times [0,\mu_0] \to \mathcal{M}$, and a constant $\omega_{\min} > 0$ such that $\psi^0(t,\mu)$ is a strict local minimizer of $E(\psi,t,\mu)$ and the eigenvalues of the Hessian $D_\psi^2 E(\psi,t,\mu)|_{\psi=\psi^0(t,\mu)}$ restricted to $T\mathcal{M}$ are bounded below by $\omega_{\min}^2$ for $0 \le t \le T$ and $0 \le \mu \le \mu_0$.*
- ii *For each time T with the properties of step (i) there is a $\mu_* > 0$ with $\mu_* \le \mu_0$, such that the second order problem*

$$\mu\ddot{\psi}^\mu + \frac{\partial E}{\partial \psi}(\psi^\mu, t, \mu) \perp T\mathcal{M}, \qquad \psi^\mu \in \mathcal{M}, \quad \psi^\mu(0) = \psi_0,\ \dot{\psi}^\mu(0) = 0,$$

has a unique smooth solution ψ^μ for $0 < \mu \le \mu_*$ and $0 \le t \le T$. There is a constant $C > 0$ such that

$$|\psi^\mu(t) - \psi^0(t,\mu)| \le C\mu^{1/2} \quad \textit{and} \quad |\dot{\psi}^\mu(t)| \le C \quad \textit{for} \quad 0 \le t \le T, \quad 0 < \mu \le \mu_*.$$

3 An Example

To exemplify our theorems and the relevance of condition A we pick up a linear two-level model which was already discussed to some extend by Pastore, Smargiassi, and Buda [14, Sec. IV.B] using numerical experiments. These experiments show that *cum grano salis* the example contains all important features of the Car-Parrinello method.

Let $A(t)$ be a smooth time-dependent family of symmetric two-by-two matrices and consider the energy

$$E(\psi, t) = \frac{1}{2} \langle A(t)\psi, \psi \rangle$$

on the constraint manifold

$$\mathcal{M} = \{\psi \in \mathbb{R}^2 : \langle \psi, \psi \rangle = 1\}.$$

The corresponding second order equation is given by

$$\mu \ddot{\psi}^\mu + A(t)\psi^\mu = \lambda^\mu \psi^\mu, \qquad \psi^\mu \in \mathcal{M}, \tag{16}$$

with initial values $\psi^\mu(0) = \psi_0 \in \mathcal{M}$ and $\dot{\psi}^\mu(0) = 0$. For ψ_0 satisfying the assumptions of Theorem 2 it has to be a strict local minimizer of $E(\psi, 0)$. This is the case *if and only if* there are two *different* eigenvalues $\lambda^0(0) < \lambda^1(0)$ of $A(0)$ with corresponding eigenstates $\psi^0(0)$ and $\psi^1(0)$ where ψ_0 is given by the *lower state* $\psi_0 = \psi^0(0)$. Clearly we can continue these values as smooth functions of t up to every time $T > 0$ prior to any point of level crossing:

$$A(t)\psi^\kappa(t) = \lambda^\kappa(t)\psi^\kappa(t), \qquad \kappa = 0, 1, \quad 0 \le t \le T,$$

where $\lambda^0(t) < \lambda^1(t)$. The gap $\omega_{\min} > 0$ is defined by

$$\omega^2(t) = \lambda^1(t) - \lambda^0(t) \ge \omega^2_{\min}, \qquad 0 \le t \le T.$$

Theorem 2 states, that there is a constant $C > 0$ such that the deviation from the time-dependent ground state ψ^0 is given by

$$|\psi^\mu(t) - \psi^0(t)| \le C\mu^{1/2}$$

for $0 \le t \le T$ and sufficiently small parameter μ.

We will go further and show *two more facts*. First, the convergence estimate $\mathcal{O}(\mu^{1/2})$ cannot be improved in general. Second, if we start in the higher state, $\psi_0 = \psi^1(0)$, the Car-Parrinello solution ψ^μ keeps on oscillating for $\mu \to 0$ and not even time averages converge to any of the eigenstates.

To this end we introduce Lagrangian coordinates on the manifold $\mathcal{M}$. Each $\psi \in \mathcal{M}$ can be written as

$$\psi = \psi(\theta) = \Big(\cos(\theta/2), \sin(\theta/2)\Big)^T.$$

Introducing $\psi^\mu = \psi(\theta^\mu)$, $\psi^\kappa = \psi(\theta^\kappa)$, $\kappa = 0, 1$, and $\psi_0 = \psi(\theta_0)$ a straightforward calculation shows that (16) is equivalent to the equation

$$\mu\ddot{\theta}^\mu + \omega^2 \sin(\theta^\mu - \theta^0) = 0, \tag{17}$$

of a *nonlinear pendulum* with initial data $\theta^\mu(0) = \theta_0$ and $\dot{\theta}^\mu = 0$.

The Case $\boldsymbol{\theta_0 = \theta^0(0)}$. As in the proof of Theorem 1 we use a two-time-scale ansatz

$$\theta^\mu(t) = \theta^0(t) + \epsilon\rho(t/\epsilon), \qquad \epsilon = \mu^{1/2}.$$

With $\tau = t/\epsilon$ and $d/d\tau$ denoted by a prime, we get the initial values

$$\rho(0) = 0, \qquad \rho'(0) = -\dot{\theta}^0(0).$$

Insertion of the two-time-scale ansatz into (17) yields after division by ϵ

$$\rho''(\tau) + \omega^2(\epsilon\tau)\frac{\sin(\epsilon\rho(\tau))}{\epsilon} + \epsilon\,\ddot{\theta}^0(\epsilon\tau) = 0.$$

This is a *single frequency* problem and the theorem of the adiabatic invariance of the action variable [2, p. 169] is applicable. It states that there is a constant c_0, such that

$$|I(\tau) - I(0)| \le c_0\epsilon \qquad \text{for} \quad 0 \le \tau \le T/\epsilon,$$

where the action is given by

$$I(\tau) = \frac{1}{2}\frac{|\rho'(\tau)|^2 + \omega^2(\epsilon\tau)|\rho(\tau)|^2}{\omega(\epsilon\tau)}.$$

By a little calculation we obtain the estimate

$$|\theta^\mu(t) - \theta^0(t)| \;\le\; \frac{|\dot{\theta}^0(0)|}{\sqrt{\omega(0)\omega(t)}}\,\mu^{1/2} \,+\, c_1\,\mu \;\le\; \frac{|\dot{\theta}^0(0)|}{\omega_{\min}}\,\mu^{1/2} \,+\, c_1\,\mu \tag{18}$$

for $0 \le t \le T$ and some constant c_1. Thus, the existence of an adiabatic invariant provides a proof of Theorem 2 indeed, but only in a very special case.

Intuitively, having a look on the estimate (18) one expects that the order of approximation cannot be better than $\mathcal{O}(\mu^{1/2})$, whenever the ground state is moving initially, i.e., $\dot\theta^0(0) \neq 0$. In fact, for the special choice

$$\omega(t) \equiv 1, \qquad \theta^0(t) = t, \tag{19}$$

equation (17) can be solved explicitly in terms of elliptic functions, cf., [9, eq. C 6·17]:

$$\theta^\mu = t - 2\arcsin\left(\frac{\epsilon}{2}\,\mathrm{sn}\left(\frac{t}{\epsilon}\,\middle|\,\frac{\epsilon}{2}\right)\right) = t - \epsilon\sin(t/\epsilon) + \mathcal{O}(\epsilon^2), \qquad \epsilon = \mu^{1/2},$$

where the asymptotics is in accordance with the estimate (18). The asymptotic result for Jacobi's sine amplitude function $\mathrm{sn}(\cdot|\cdot)$ which we have used can be found in [1, eq. 16.13.1].

The Case $\boldsymbol{\theta_0 = \theta^1(0)}$. Now, the assumptions of Theorem 2 are violated at time $t = 0$. We will show, that this constitutes a kind of catastrophe for the Car-Parrinello method which does not converge to any state in any reasonable way then.

Again, we consider the special choice (19) which implies by orthogonality of the eigenstates

$$\theta^1(t) = \theta^0(t) + \pi = t + \pi,$$

if we fix the phase initially as $\theta^1(0) = \pi$. Thus we can write the second order problem (17) in the form

$$\mu\ddot\phi^\mu - \sin(\phi^\mu) = 0, \qquad \phi^\mu(0) = 0, \quad \dot\phi^\mu(0) = 1, \tag{20}$$

where

$$\phi^\mu = \theta^1(t) - \theta^\mu(t) = t + \pi - \theta^\mu(t).$$

Lemma 3 *The functions $\cos(\phi^\mu/2)$ and $\sin(\phi^\mu/2)$ are periodically oscillating between -1 and 1 with a period*

$$T_\mu = \mathcal{O}(\epsilon\log\epsilon^{-1}), \qquad \epsilon = \mu^{1/2}.$$

Their means are converging for $\mu \to 0$ as

$$\cos(\phi^\mu/2) \overset{*}{\rightharpoonup} 0 \qquad \text{and} \qquad \sin(\phi^\mu/2) \overset{*}{\rightharpoonup} 0,$$

where the weak convergence is meant to hold in the space $L^\infty[0,T]$.*

We postpone the proof and study the consequence for the solution ψ^μ of the model equation (16). It is rapidly oscillating while covering the whole of manifold $\mathcal{M}$ on an exceedingly small time scale and converges weakly to zero,

$$\psi^\mu = \begin{pmatrix} \cos(\theta^\mu/2) \\ \sin(\theta^\mu/2) \end{pmatrix} = \begin{pmatrix} \cos(\theta^1/2)\cos(\phi^\mu/2) + \sin(\theta^1/2)\sin(\phi^\mu/2) \\ \sin(\theta^1/2)\cos(\phi^\mu/2) - \cos(\theta^1/2)\sin(\phi^\mu/2) \end{pmatrix}$$

$$\stackrel{*}{\rightharpoonup} 0.$$

Thus, in the limit average the Car-Parrinello solution ψ^μ does not give preference to any particular state ψ of the two-level state space under consideration at any time.

Remark. The start of the Car-Parrinello method at the wrong energy level resembles the situation of the method shortly after an energy level crossing, cf., [14]. Our example suggests that averaging the rapid oscillations would probably not cure the method from breakdown after level crossings.

Proof of Lemma 3. The second order equation for ϕ^μ has Hamiltonian structure. Hence, we have conservation of "energy"

$$\frac{\epsilon^2}{2}|\dot\phi^\mu|^2 + \cos\phi^\mu = \frac{\epsilon^2}{2} + 1, \tag{21}$$

which immediately yields $|\dot\phi^\mu| \geq 1$. Even more, by $\dot\phi^\mu(0) = 1$ we conclude that $\dot\phi^\mu \geq 1$. Thus, the function ϕ^μ increases strictly monotone. In particular, it reaches the value 2π after a certain time T^*_μ, which can be calculated by separation of variables,

$$T^*_\mu = \epsilon \int_0^{2\pi} \frac{d\phi}{\sqrt{\epsilon^2 + 2(1-\cos\phi)}} = \mathcal{O}(\epsilon \log \epsilon^{-1}).$$

By the energy relation (21) we have

$$\phi^\mu(T^*_\mu) = 2\pi \qquad \text{and} \qquad \dot\phi^\mu(T^*_\mu) = 1$$

which implies by the 2π-periodicity of the sine function and uniqueness of the solutions of problem (20) that

$$\phi^\mu(t + T^*_\mu) - 2\pi = \phi^\mu(t) \qquad t \geq 0. \tag{22}$$

Consequently, the function $\cos(\phi^\mu/2)$ is periodic with period $T_\mu = 2T_\mu^*$ and of the form

$$\cos(\phi^\mu(t)/2) = \chi(t/T_\mu, \mu)$$

for some smooth function χ which is 1-periodic in the first argument. A well known generalization of the Riemann-Lebesgue lemma, which can be found in [4, p. 8], yields the weak convergence

$$\cos(\phi^\mu/2) \stackrel{*}{\rightharpoonup} \gamma = \int_0^1 \chi(\tau, 0)\, d\tau.$$

Using (22) again, one can establish the anti-symmetry

$$\cos(\phi^\mu(t + T_\mu^*)/2) = -\cos(\phi^\mu(t)/2),$$

which directly implies $\gamma = 0$. The assertions concerning $\sin(\phi^\mu/2)$ are proved in a completely analogous fashion.

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