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Abstract

The Car-Parrinello (CP) approach to ab initio molecular dynamics serves as an approximation to time-dependent Born-Oppenheimer (BO) calculations. It replaces the explicit minimization of the energy functional by a fictitious Newtonian dynamics and therefore introduces an artificial mass parameter μ which controls the electronic motion. A recent theoretical investigation shows that the CP-error, i.e., the deviation of the CP–solution from the BO-solution *decreases* like $\mu^{1/2}$ asymptotically. Since the computational effort *increases* like $\mu^{-1/2}$, the choice of μ has to find a compromise between efficiency and accuracy. The asymptotical result is used in this paper to construct an easily implemented algorithm which automatically controls μ: the parameter μ is repeatedly adapted during the simulation by choosing μ as large as possible while pushing an error measure below a user-given tolerance. The performance and reliability of the algorithm is illustrated by a typical example.

Keywords: Born-Oppenheimer approximation, Car-Parrinello method, accuracy control.

Introduction

The study of the full quantum dynamics of a molecular system including many electrons and ions is beyond computational possibilities — for now and the next decades. For this reason, computer simulations for realistic systems require some approximations which simplify the full quantum model.

The most prominent approach to approximative ab–initio molecular dynamic calculations is based on the *quantum adiabatic approximation*, also called the time-dependent *Born-Oppenheimer* approximation [1, 5]. 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 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. The electronic configuration is given by the ground state of the corresponding energy functional. The commonly used methods for such a ground state computation, i.e., the Hartree-Fock approximation and density functional theory with the Kohn-Sham scheme, replace the many-body ground state by a set of one-particle wave functions which are computed by a self-consistent eigenstate problem.

Thus, a straightforward numerical simulation of the adiabatic approach requires the solution of a self-consistent electronic structure problem *at each* time step of the simulation. As noted in [8], even for very small realistic time steps, state-of-the-art minimization algorithms often require an order of ten iterations to converge which prevents even this approach from being feasible for more complicated systems.

In 1985, Car and Parrinello [3] presented their method which largely extended the set of treatable systems. They replaced this adiabatic motion by a *fictitious* classical Newtonian dynamics which oscillates around the energy minimum. However, in most of the interesting cases that turns out to be much more feasible to compute.

The CP–approach contains an artificial, but free parameter — the fictitious “electronic mass” μ. In an interesting paper [8], Pastore, Smargiassi, and Buda illustrated that μ constitutes a kind of control parameter: the smaller μ is chosen, the smaller the deviation of the CP solution from the solution of 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 of the CP–model 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 (the deviation from the adiabatic solution).

In [2], the authors studied the influence of μ on the accuracy of the method *quantitatively.* In this paper we show, that the obtained result allows the construction of an algorithm which chooses μ *automatically.* The value of μ is repeatedly changed *during* the simulation, following the philosophy that it should always be *adapted* to the actual properties of the molecular system. The algorithm tries to adjust μ to the value which actually is *optimal*, i.e., as large as possible with respect to the accuracy required.

However, it is not the major priority of this algorithmic approach to increase the efficiency of CP–simulations. Rather, we provide the user an efficient tool for more *reliable* calculations which control the accuracy throughout.

1 Theoretical Background

The Lagrangian of the quantum adiabatic motion is given by an expression of the form

$$\mathcal{L}_{BO} = \frac{1}{2}\sum_I M_I\,\dot{q}_I^2 - U(q),$$

where $q = (q_1, \ldots, q_n)$ denotes the ionic positions and the potential U is given by minimizing the electronic energy potential E,

$$U(q) = \min_{\psi} E(\psi; q).$$

The minimum is taken over all orthonormal m-tuple $\psi = (\psi_1, \ldots, \psi_m)$. The energy functional is given for instance by the Kohn-Sham scheme [7] in the context of density functional theory. The resulting second order equation of motion reads

$$M\ddot{q}^{BO} + \left.\frac{\partial U(q)}{\partial q}\right|_{q=q^{BO}} = 0. \tag{1}$$

Its solution will always be denoted q^{BO} and the corresponding electronic ground state as ψ^{BO} and, in particular, the initial state $\psi^{BO}(t=0)$ as ψ_0. It is well known that this quantum adiabatic model serves as a good approximation for the full quantum dynamics as long as the ground state ψ^{BO} of $E(\psi, q^{BO})$ is *nondegenerate* (for details see [5]).

The fictitious Newtonian dynamics introduced by the alternative CP–approach is given by the Lagrangian

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

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 the named masslike parameter introduced by the method. The Lagrange parameters Λ_{jk} ensure the orthonormality of the wave functions. The total energy of the CP–method contains an "unphysical" part, the so called "fake" kinetic energy

$$K_f = \sum_{j=1}^{m} \frac{\mu}{2} \langle \dot{\psi}_j, \dot{\psi}_j \rangle.$$

The second order equations of motion belonging to $\mathcal{L}_{CP}$ are

$$\begin{aligned} M\ddot{q}^\mu + \left.\frac{\partial E(\psi^\mu; q)}{\partial q}\right|_{q=q^\mu} &= 0, \\ \mu\ddot{\psi}_j^\mu + \left.\frac{\delta E(\psi; q^\mu)}{\delta \psi^*}\right|_{\psi=\psi^\mu} &= \sum_{k=1}^{m} \Lambda_{jk}\psi_k^\mu, \qquad j = 1, \ldots, m, \\ \langle \psi_j^\mu, \psi_k^\mu \rangle &= \delta_{jk}, \qquad j, k = 1, \ldots, m \end{aligned}$$

where $\delta/\delta\psi^*$ denotes the functional derivative of E with respect to the state ψ and the superscript the explicit dependence on the "control parameter" μ.

To construct an *automatic* scheme for the appropriate choice of μ we must gain a more quantitative understanding of the influence of μ on the accuracy of the method. Herein, the accuracy is defined via the deviation of the Car-Parrinello solution (q^μ, ψ^μ) for given μ from that of the quantum adiabatic model (q^{BO}, ψ^{BO}):

$$\Delta_\mu = |q^\mu(t) - q^{BO}(t)| + |\psi^\mu(t) - \psi^{BO}(t)|.$$

Let T_* be the maximal time for which the ground state of $E(\psi, q^{BO})$ is still nondegenerate. Before T_* is reached, the quantitative influence of μ on the accuracy is described by the following *convergence result* which holds under the condition that the evolution starts in the initial ground state with vanishing velocity, i.e., $\psi^\mu(0) = \psi_0$ and $\dot{\psi}^\mu(0) = 0$:

For every time T with $0 < T \leq T_*$, there is a $\mu_* > 0$ and a constant $C > 0$ so that

$$\Delta_\mu \leq C\mu^{1/2} \qquad 0 \leq t \leq T$$

and the fake kinetic energy satisfies

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

for all values of the parameter μ satisfying $0 < \mu \leq \mu_*$.

For the case of the Kohn–Sham functional $E = E_{KS}$, a rigorous mathematical proof of this assertion is given in the work [2] of the authors.

According to this result, the error can be pushed below any tolerance desired via an appropriately small choice of μ. It should be remembered that we have to find a compromise between the computational cost (the number of time steps, increasing with $\mu^{-1/2}$) and the accuracy (which decreases with $\mu^{1/2}$). However, we can bound the error Δ_μ via controlling the increase in fake energy K_f. Exactly this is the basic idea on which the automatic control scheme proposed in the next section is based: Try to find the maximal μ which allows to push the fake energy under a predefined tolerance.

The reader should note, that the convergence results are only valid for times $T < T_*$, i.e., before the first degeneracy of the electronic ground state may occur. After T_* the state ψ^μ can largely deviate from the ground state for all choices of $\mu > 0$. Then, the validity of the Car–Parrinello approach and the quantum adiabatic approach itself are at least questionable [2, 8].

Moreover, the results do in general not hold if the CP–system is coupled to a heat bath for simulating canonical ensembles with defined temperature (for those temperature control methods see [9]). This significantly alters the oscillatory behaviour of the system and forces the solution to the BO–dynamics. The herein presented algorithm is designed for simulations of the original closed system without those external interactions, i.e., for *micro-canonical* calculations.

2 The Automatic Control Scheme

In some cases, CP–simulations with fixed μ develop large deviations from the BO–dynamics even if initially μ is small enough: The fake energy K_f^μ and with it the error Δ_μ accumulatively increase after some time, an effect which may lead to an explosion of K_f^μ and, thus, may destroy any reliable information. Obviously, this can happen if the ground state gets degenerate. But it can also be observed if the energy gap between the ground state and the first excited state of the electronic configuration gets too small in the course of the evolution of the system (cf. [8] and the next section, in particular Figure 5). Here, "too small" means "too small in comparison with the μ–value chosen", because, according to the theoretical statement from above, we can avoid the error increase and bound K_f^μ and Δ_μ by choosing μ small enough. In this section a μ–controlling algorithm will be explained which is designed to avoid model instabilities away from true ground state degeneracies.

The algorithm is based on the following idea: Compute an appropriate choice μ by limiting the maximal value of the fake energy K_f in the simulation interval $I = [t_0, t_1]$, i.e., choose μ so that

$$K_f^\mu(I) = \max_{t \in I} \frac{1}{2}\mu|\dot{\psi}(t)|^2 \ \le \ \mathrm{TOL}, \tag{3}$$

where the tolerance TOL is predefined by the user. The fake energy can easily be computed during the simulation and can be used as a monitor for the error Δ_μ. The construction of a scheme which automatically realizes (3) exploits the theoretical result (2). It is similar to the schemes designed for controlling the stepsize in the numerical integration of ordinary differential equations (cf. [4, 6]).

Let the initial electronic state for a CP–simulation on the time interval I be the initial ground state and let its velocity be zero. Moreover, we assume for a moment that we still have computed $K_f^{\mu_0}(I)$ for a $\mu_0 < \mu_*$ with μ_* from the statement above. Then, according to (2),

$$\mu \ = \ \frac{\mathrm{TOL}}{K_f^{\mu_0}(I)}\,\mu_0 \tag{4}$$

will be near the optimal choice for realizing (3) on I. Now, let the total time interval of interest, I_{tot}, be decomposed in several subintervals $I_1, \ldots, I_N$ without overlap. The algorithm works successively on all subintervals I_j by exploiting (4) in two different situations:

1. Step rejection: If a CP–simulation on I_j using μ_0 has the result $K_f^{\mu_0}(I_j) > \mathrm{TOL}$, we have to reject this attempt. Then, a new μ–proposal is computed using (4) and the simulation on I_j is repeated. The results of the previous simulation are neglected.

2. μ-choice for the next step: Assume that the simulation on I_j using μ_j has been successful, i.e., $K_f^{\mu_j}(I_j) \le \mathrm{TOL}$. Via (4), we could compute another μ–proposal μ_* which then is expected to be optimal on I_j. Instead of repeating the successful calculation on I_j, we switch to the next step, hope that the situation does not change too much, and use μ_* as the initial μ–value for the simulation on I_{j+1}. Because (4) leads to $\mu_* \ge \mu_j$ and a large increase in μ may be dangerous, this increase is limited, i.e., (4) is replaced by, e.g.,

$$\mu = \min\left(2,\ \frac{\mathrm{TOL}}{K_f^{\mu_j}(I_j)}\right) \cdot \mu_j.$$

The algorithm resulting from these ideas is collected in Figure 1.

Note, that it contains an explicit minimization of $E(\psi, q)$ after each subinterval $I_j = [t_j, t_j + \Delta T]$ (step $(*)$ in Figure 1). Theoretically this is necessary, because the construction of the algorithm depends on the assumption that the initial electronic state for the simulation on I_{j+1} is the momentary ground state. But if the tolerance TOL is small enough, the

Predefined:

Initial values: $\quad q_0,\ \dot{q}_0,\ \ \psi_0 \leftarrow \min\limits_{\psi} E(\psi, q_0)$

User: $\quad T,\ \mathrm{TOL},\ \Delta T,\ \mu_0$

Initialization:

$k = 0, \ \ t_0 = 0, \ \ \mu = \mu_0$

Loop:

while $t_k < T$

    repeat

        $(q, \psi, \dot{q}, \dot{\psi}) \ = \ \mathrm{CP}_\mu \, (t_k, t_k + \Delta t,\ q_k, \psi_k, \dot{q}_k, 0)$

        $K_f = \max\limits_{t_k < t < t_k + \Delta T} \frac{1}{2}\mu |\dot{\psi}(t)|^2$

        if $K_f > \mathrm{TOL}$ {step rejection}

            then $\mu := 0.9 \cdot \frac{\mathrm{TOL}}{K_f}\, \mu$ { μ–reduction }

    until $K_f \leq \mathrm{TOL}$

    $q_{k+1} = q, \quad \dot{q}_{k+1} = \dot{q}$

(∗) $\psi_{k+1} \leftarrow \min\limits_{\psi} E(\psi, q_{k+1})$ { compute ground state}

    $\mu := \min\left(2,\ \frac{\mathrm{TOL}}{K_f}\right) \cdot \mu$ { μ–choice for next step }

    $t_{k+1} = t_k + \Delta T$

    $k := k + 1$

end   { of while }

Figure 1: Scheme of the μ–controlling algorithm. $\mathrm{CP}_\mu(t, t+\Delta t,\ q, \psi, \dot{q}, \dot{\psi})$ denotes the subroutine which numerically solves the CP–equations in the interval $[t, t+\Delta t]$ using the initial values $(q, \psi, \dot{q}, \dot{\psi})$ and fixing the free parameter μ and which returns the solution at time $t + \Delta T$. It should use appropriate numerical techniques like those proposed in [9]. The minimization step (∗) may be skipped if the tolerance TOL is small enough, cf. p. 6.

deviation of the final state $\psi(t_j + \Delta T)$ at the end of the simulation on I_j from the corresponding ground state is also small and the minimization may be omitted.

After each subinterval the accumulated fake energy is skipped by starting at the next subinterval with the velocity $\dot{\psi} = 0$. This leads to a small loss of total energy, which is of no importance as long as TOL is small enough and there are not too many subintervals. If this is not the case, the skipped fake energy can be added to the kinetic energy of the ions by slightly increasing their momenta.

In some sense the algorithm replaces the choice of the model parameter μ by the choice of a control parameter TOL. But the interpretation of TOL as an upper bound for the fake energy gives much more physical insight and serves as a reliable monitor for the error Δ_μ.

The performance of this algorithm will be illustrated in the next section using a simple but appropriate example. Therein, it will be demonstrated that neither step rejections and nor minimization steps destroy the efficiency of this μ–control.

3 Illustrative Examples

In [8], Pastore, Smargiassi, and Buda constructed a simple linear two-level model which *cum grano salis* contains all important features of the Car-Parrinello method. In this model, ψ is a simple two-dimensional one-electron state, i.e., it is $m = 1$, and the electronic energy functional is quadratic:

$$E(\psi, q) = \langle \psi, A(q)\psi \rangle,$$

with a 2×2-matrix A. The time-dependence of the two eigenvalues $\lambda_0 = \lambda_0(q)$ and $\lambda_1 = \lambda_1(q)$ of A along the solution $q = q(t)$ is essential for the evolution: As long as $\lambda_0 < \lambda_1$ the ground state $\psi^0(q)$ of $E(\psi, q)$ is *nondegenerate.* Thus, quantum adiabatic and CP-simulations do only make sense as long as the *energy gap* $\Delta\lambda = \lambda_1 - \lambda_0$ remains *positive.*

In this simple case the Car-Parrinello equations of motion can explicitly be transformed into a system without constraints (cf. [8] p. 6344 and be aware of some typos):

$$\begin{aligned} \mu\ddot{\theta} &= -G_0\, g\, \sin(\theta - \theta_0) \\ M_0\ddot{\theta}_0 &= G_0\, g\, \sin(\theta - \theta_0) - \omega_2^2 M_0 \theta_0 \\ M_g \ddot{g} &= G_0 \cos(\theta - \theta_0) - \omega_1^2 M_g G_0^2\, (g - 1), \end{aligned}$$

where the angle θ represents the state ψ via the parametrization $\psi = (\cos\theta/2, \sin\theta/2)^T$, and g and θ_0 mimic the ionic motions. While g directly gives us the gap via

$$\Delta\lambda(t) = \frac{g(t)}{g(0)}\, \Delta\lambda(0),$$

the angle θ_0 represents the ground state $\psi^0 = (\cos\theta_0/2, \sin\theta_0/2)^T$ of E. Thus, the difference $\theta - \theta_0$ measures the deviation of ψ from the ground state ψ^0.

As a rule of thumb one can state that, if the error Δ_μ should remain small, the parameter μ must decrease with the minimal gap size. For studying the effects of a changing gap, Pastore, Smargiassi, and Buda constructed two illustrative examples: one with a slowly decreasing gap leading to a level crossing ("crossing example"), and another with an periodically closing, but

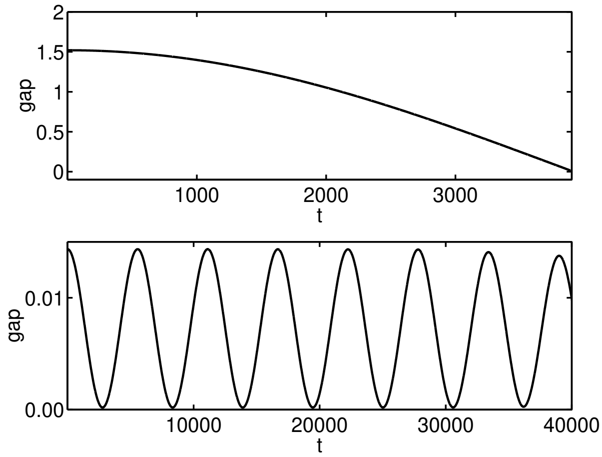

Figure 2: Time-dependence of the gap $\Delta\lambda$ in the two test cases. On top: Decreasing gap with a level crossing near t=4000. Bottom: Oscillating gap with a minimal gap size near 0.

always positive gap ("oscillating gap example"), cf. Figure 2. The parameters of these cases are given in Table 1. In both examples all initial velocities are zero and $\theta(0) = \theta_0(0) = 1$. All magnitudes are given in atomic units (cf. [8]). For both examples, Pastore, Smargiassi, and Buda proposed $\mu = 300$

Table 1: Parameters and initial values for the two test examples

example	M_0	M_g	ω_1	ω_2	G_0	$g(0)$
crossing	$6 \cdot 10^4$	$1.5 \cdot 10^8$	$4.095 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$	$8 \cdot 10^{-3}$	190
osc. gap	$6 \cdot 10^4$	$1.5 \cdot 10^8$	$1.13 \cdot 10^{-3}$	$4.2 \cdot 10^{-4}$	$2.05 \cdot 10^{-3}$	7

for the test simulations and observed that Δ_μ and the corresponding fake energy strongly increase in both examples. This problem is automatically avoided by using the proposed control algorithm:

The collision example: With $\mu = 300$ fixed, Δ_μ and K_f slowly increase with decreasing gap (cf. Figure 3, subfigure on top). In contrast to this, the fake energy remains bounded below the chosen tolerance TOL $= 1 \cdot 10^{-5}$ if the control algorithm of the preceding section is used. The μ-value is slowly decreased in accordance with the closing gap. This requires some step rejections in order to readjust μ, which consumes about 25 percent of the computational effort. If the level crossing is reached (at $t \approx 4000$) the algorithm automatically reports that no appropriate μ-choice is possible.

This performance does not change significantly if the minimization step $(*)$ (cf. Figure 1) is omitted: only the decrease in μ is stronger.

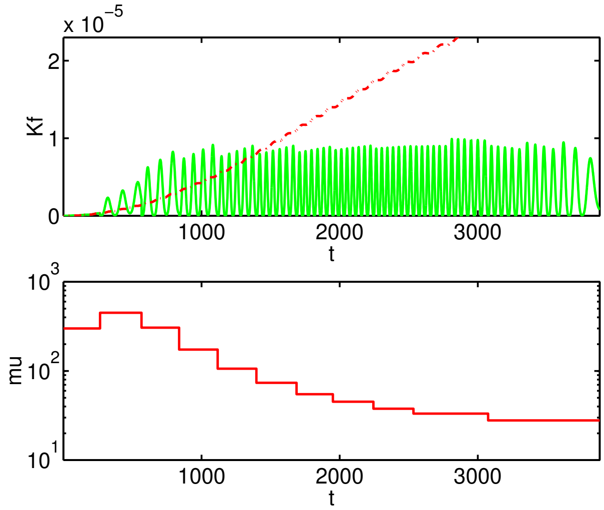

Figure 3: Crossing example. On top: Fake energies of a computation using $\mu = 300$ (dashed line) and of the controlled simulation with $\mathrm{TOL} = 10^{-5}$ (solid line) versus time. Below: The different values of μ chosen by the algorithm.

The oscillating gap example: With $\mu = 300$ fixed, Δ_μ and K_f explode after some oscillations of the gap (cf. Figures 4 and 5, subfigures on top, respectively). These figures also present the performance of the control algorithm with tolerance $\mathrm{TOL} = 2 \cdot 10^{-5}$. The fake energy remains bounded below TOL and the error $\theta - \theta_0$ does not show any accumulative increase, too. The μ-value is slowly pushed to a low value which then remains nearly constant and which fits to the minimal gap size. The same well-behavior is observed in long term simulations which proves the stability of the control scheme. Only about 8 percent of the computational effort are used for step rejections. If the explicit minimization step $(*)$ is included the algorithm needs about 10 percent of the minimization steps which would be necessary in a full quantum adiabatic simulation. If $(*)$ is totally avoided a simulation using $\mathrm{TOL} = 2 \cdot 10^{-5}$ produces about 50 percent smaller μ's but the fake energy and $\theta - \theta_0$ behave similar to those shown in Figures 5 and 4. If the tolerance is reduced the μ-choices with and without $(*)$ tend to become identical.

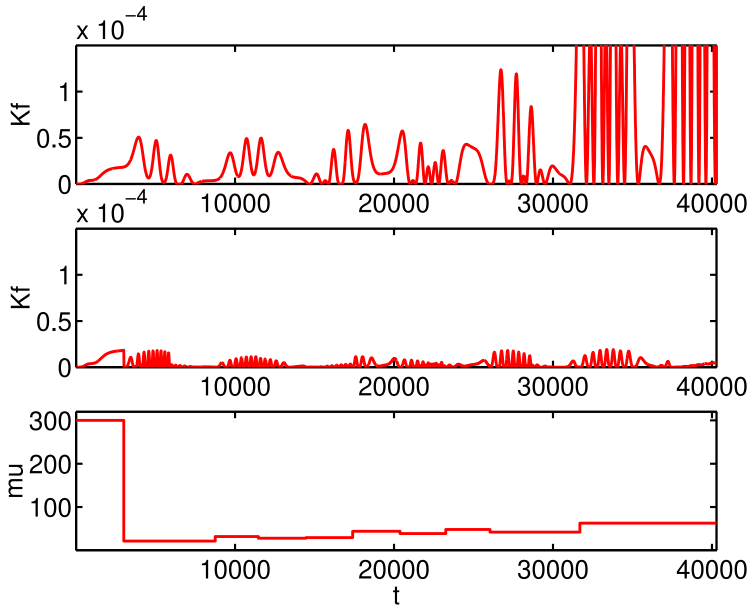

Figure 4: Oscillating gap example. On top: Fake energy versus time for a computation using $\mu = 300$ (exploding after $t = 30000$). Below: Fake energy of the controlled simulation with tol=2e-5. Bottom: The different values of μ chosen by the algorithm.

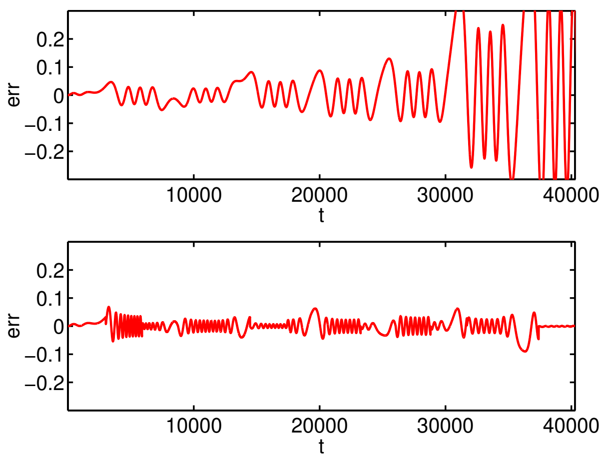

Figure 5: Oscillating gap example. On top: Increasing error $\theta - \theta_0$ of the computation using $\mu = 300$ versus time. Below: The error of the controlled simulation remains bounded.

Conclusion

- The examples demonstrate that the application of a μ-control is appropriate in order to avoid some fundamental difficulties of the CP-approach with μ fixed. The proposed algorithm reliably adjusts μ to the momentary gap size, avoids the error increase effected by nearly closing gaps, and automatically detects the presence of level crossings.
- The μ-controlling algorithm needs much less explicit ground state computations than a quantum adiabatic simulation with comparable accuracy and they can totally be omitted if the tolerance is small enough.
- The computational effort of the necessary step rejections is far from dominating the total effort produced by the simulations.
- All this is done via monitoring of the fake energy, i.e., by exploiting information which is easily accessible in the simulation.

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