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# Adaptive accuracy control for Car-Parrinello simulations

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*Dedicated to Olof B. Widlund on the occasion of his 60th birthday*

**Summary.** 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 $\mu$ 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 $\mu$ 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 $\mu$: the parameter $\mu$ is repeatedly adapted during the simulation by choosing $\mu$ 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.

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## Introduction

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]. Here, one

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exploits the large mass ratio between ions and electrons by describing the ions classically and the electrons quantally. The equation governing the ionic movement is obtained by a semiclassical limit [4], i.e., becomes a classical Newtonian equation of motion. The electronic configuration is given by the ground state of the corresponding energy functional, i.e., by the state of minimal energy. Thus, a straightforward numerical simulation of the adiabatic approach requires the solution of a minimization problem for a highly dimensional functional *at each* time step of the simulation. As noted in [7], even for very small realistic time steps, state-of-the-art minimization algorithms often require an order of ten iterations to converge which prevents 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 the adiabatic motion of the electrons by another *fictitious* classical Newtonian dynamics which oscillates around the energy minimum. Therefore, an artificial, but free parameter — the fictitious "electronic mass" $\mu$ — is introduced. In [2], the present authors in detail discussed the connection of the CP approach with the quantum adiabatic approximation. In particular, it was shown that, under a crucial nondegeneracy condition, the deviation between the CP solution and the quantum adiabatic solution is of order $\mathcal{O}(\mu^{1/2})$.

In an inspiring paper [7], Pastore, Smargiassi, and Buda illustrated that $\mu$ constitutes a kind of control parameter. In this paper we pick up this idea and exploit the approximation result from [2] to construct an algorithm which *automatically* controls the value of $\mu$ with respect to a predefined accuracy requirement for the CP solution.

## 1. Theoretical background

In the quantum adiabatic model the equations of motion are given by

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

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 [6] in the context of density functional theory (cf. [2] for details). The corresponding solution will always be denoted $q^{BO}$ and the corresponding electronic ground state as $\psi^{BO}$ and, in particular, the initial state $\psi^{BO}(t = 0)$ as $\psi_0$.

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 $\psi_j$ are regarded as classical fields, $M_I$ are the ionic masses and $\mu$ is the named masslike parameter introduced by the method. The Lagrange parameters $\Lambda_{jk}$ 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

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

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

The accuracy of the Car-Parrinello solution $(q^\mu,\psi^\mu)$ for given $\mu$ in comparison with the quantum adiabatic model $(q^{BO},\psi^{BO})$ is given by:

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

with appropriate norms $|\cdot|$ and $\|\cdot\|$.

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 $\mu$ 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 $0<T\le T_*$, there is a $\mu_*>0$ and a constant $C>0$ so that*

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

*and the fake kinetic energy satisfies*

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

*for all values of the parameter $\mu$ 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.

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 $\psi^\mu$ 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, 7].

## 2. The automatic control scheme

In some cases, CP–simulations with fixed $\mu$ develop large deviations from the BO–dynamics even if initially $\mu$ is small enough: The fake energy $K_f^\mu$ and with it the error $\Delta_\mu$ accumulatively increase after some time, an effect which may lead to an explosion of $K_f^\mu$ 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. [7] and the next section, in particular Fig. 3). Here, "too small" means "too small in comparison with the $\mu$–value chosen", because, according to the theoretical statement from above, we can avoid the error increase and bound $K_f^\mu$ and $\Delta_\mu$ by choosing $\mu$ small enough. In this section a $\mu$–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 $\mu$ by limiting the maximal value of the fake energy $K_f$ in the simulation interval $I = [t_0, t_1]$, i.e., choose $\mu$ so that

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

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 $\Delta_\mu$. The construction of the scheme similar to that designed for controlling the stepsize in the numerical integration of ordinary differential equations (cf. [5]).

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 $\mu_*$ 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, $I_{\mathrm{tot}}$, 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 $\mu_0$ produces the result $K_f^{\mu_0}(I_j) > \mathrm{TOL}$, we have to reject this attempt. Then, a new $\mu$–proposal is computed using (4) and the simulation on $I_j$ is repeated. The results of the previous simulation are neglected.

*2. $\mu$-choice for the next step:* Assume that the simulation on $I_j$ using $\mu_j$ has been successful, i.e., $K_f^{\mu_j}(I_j) \leq \mathrm{TOL}$. Via (4), we could compute another $\mu$–proposal $\mu_*$ 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 $\mu_*$ as the initial $\mu$–value for the simulation on $I_{j+1}$. Because (4) leads to $\mu_* \geq \mu_j$ and a large increase in $\mu$ may be dangerous, this increase is limited, i.e., (4) is replaced by, e.g.,

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

With respect to reliability it is advisable to add an explicit minimization of $E(\psi, q)$ after each subinterval $I_j = [t_j, t_j + \Delta T]$. 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 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.

## 3. Illustrative examples

In [7], a simple linear two-level model is constucted which *cum grano salis* contains all important features of the Car-Parrinello method. In this model, $\psi$ is a simple two-dimensional one-electron state, i.e., it is $m = 1$, and the electronic energy functional is quadratic:

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

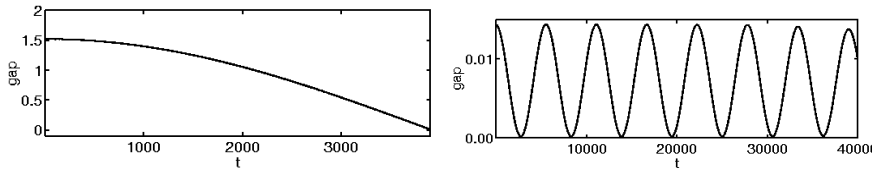


**Fig. 1.** Time-dependence of the gap $\Delta\lambda$ in the two test cases. Left: Decreasing gap with a level crossing near $t$=4000. Right: Oscillating gap with minimal gap size near 0

with a $2 \times 2$-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. [7] 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 $\theta$ represents the state $\psi$ via $\psi = (\cos\theta/2, \sin\theta/2)^{\mathrm{T}}$, and $g$ and $\theta_0$ 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 $\theta_0$ represents the ground state $\psi^0 = (\cos\theta_0/2, \sin\theta_0/2)^{\mathrm{T}}$ of $E$. Thus, the difference $\theta - \theta_0$ measures the deviation of $\psi$ from the ground state $\psi^0$.

As a rule of thumb one can state that, if the error $\Delta_\mu$ should remain small, the parameter $\mu$ must decrease with the minimal gap size. For studying the effects of a changing gap, we consider two illustrative examples: one with a slowly decreasing gap leading to a level crossing ("crossing example"), and another with a periodically closing, but always positive gap ("oscillating gap example"), cf. Fig. 1. 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. [7]). For both examples have also been consider in [7] for a constant $\mu = 300$. Therein, it has been observed that $\Delta_\mu$ 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, $\Delta_\mu$ and $K_f$ slowly increase with decreasing gap (cf. Fig. 2, subfigure on top). In contrast to this, the

**Table 1.** Parameters and initial values for the two test examples

| example | $M_0$ | $M_g$ | $\omega_1$ | $\omega_2$ | $G_0$ | $g(0)$ |
|---|---|---|---|---|---|---|
| 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 |

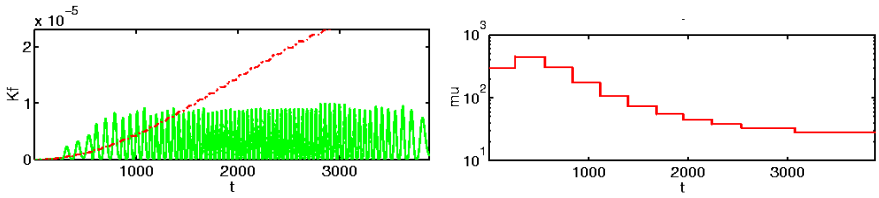


**Fig. 2.** Crossing example. On top: Fake energies for $\mu = 300$ constant (dashed line) and with $\mu$-control for $\mathrm{TOL} = 10^{-5}$ (solid line) versus time. Below: $\mu$-values chosen by the algorithm

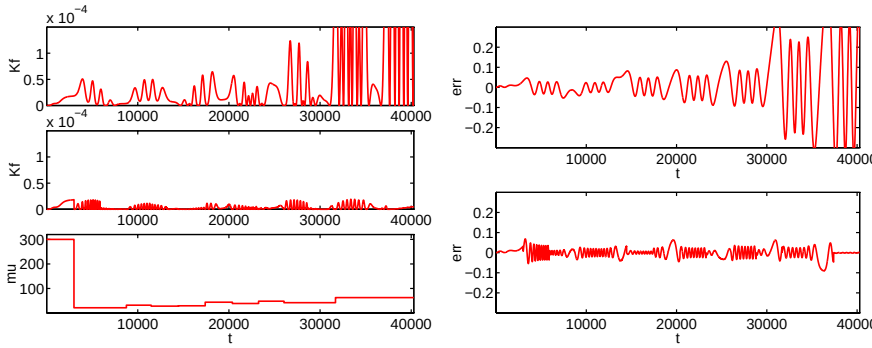


**Fig. 3.** Oscillating gap example. On the left: Fake energy versus time for $\mu = 300$ constant (on top) and for a simulation with $\mu$-control and tol=2e-5 (fake energy and $\mu$-values chosen). On the right: Increasing error $\theta - \theta_0$ for $\mu = 300$ (on top) and bounded error with $\mu$-control

fake energy remains bounded below the chosen tolerance $\mathrm{TOL} = 1 \cdot 10^{-5}$ if the control algorithm of the preceding section is used. The $\mu$-value is slowly decreased in accordance with the closing gap. This requires some step rejections in order to readjust $\mu$, which consumes about 25 percent of the computational effort. When arriving at the level crossing ($t \approx 4000$) the algorithm automatically reports that no appropriate $\mu$-choice is possible.

*The oscillating gap example.* With $\mu = 300$ fixed, $\Delta_\mu$ and $K_f$ explode after some oscillations of the gap, compare Fig. 3. The figure also presents 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 $\mu$-value is slowly pushed to a low value which then remains nearly constant and which fits to the minimal gap size. Only about 8 percent of the computational effort are used for step rejections.

The results reported have been produced without any additional minimization step. In all cases, including a minimization after each subinterval causes only minor changes in the performance of the algorithm.

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