Multiple Time Scale Hartree–Fock
Molecular Dynamics

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Abstract

This is the first application of a rigorous, established multiple time-step method to ab initio molecular dynamics. The resulting algorithm is conceptually simple and easy to implement, but very effective. It simulates the large time scales present in ab initio molecular dynamics into substantial savings in computer time while retaining high accuracy. This renders ab initio molecular dynamics from a desirable but prohibitively expensive possibility into a viable method, at least for short-time phenomena in small systems or for otherwise inaccessible complicated potential energy surfaces. © 1993 John Wiley & Sons, Inc.

1. introduction

For the purpose of this paper, we define ab initio molecular dynamics (AIMD) as classical molecular dynamics of atomic nuclei governed by first-principles forces derived from a molecular quantum mechanical wave function for the electrons, which, in turn, is made to follow the movements of the nuclei. This method is computationally very demanding, but also extremely attractive since the potential energy surface for the nuclear motion is calculated only at the points actually visited by the trajectory. In recent years, several approaches have been developed, differing mostly in the way the electronic wave function is treated. For example, Landman and co-workers [1] propagate the wave function quantum mechanically using density functional theory (DFT); Michl and co-workers [2] employ time-dependent Hartree–Fock (TDHF) theory; and there are even attempts to join nuclear and electronic motion without invoking the Born–Oppenheimer approximation [3]. In this paper, however, our focus is on the group of algorithms often termed Car–Parrinello propagations [4–6]. Their main idea is to treat the time evolution of the wave function within the framework of the Born–Oppenheimer separation by a classical mechanical propagation of wave-function parameters on the same footing as the nuclear propagation [7–9]. These algorithms have seen many applications within DFT [10], semiempirical methods [11], tight-binding models [12], and Hartree–Fock (HF) theory, both without [13] and with nuclear dynamics [14,15] for geometry optimization. We have recently introduced implementations of AIMD for free dynamics and geometry optimization, both on the HF [16] and generalized valence bond (GVB) [17] levels of theory.

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In spite of these promising developments, amdm computations are still very time-consuming. But there is one feature of the method that allows for straightforward improvement of performance: To propagate the wave-function parameters, fictitious masses have to be assigned to them. These masses are typically orders of magnitude smaller than the masses of the nuclei. The fast movement of the ultralight wave-function parameters [9] makes a very small time step necessary, while the movement of the nuclei could well be described using a much larger time step. We present here a multiple time-step algorithm that exploits the fact that nuclear motion is so much slower than electronic motion, leading to considerable CPU time savings. Some workers have utilized different time steps for these different systems in related theoretical approaches (e.g., Landman and co-workers [1] and Michal and co-workers [2]), but to our knowledge, this idea has not yet been systematically used in amdm methods of the Car-Rehren type.

Previous tests of our aamd implementation have shown [16,17] that while retaining a very small time step dictated by the fictitious masses one can get away with recomputing basis function integrals and forces on the nuclei only every 5-10th step. This gains a factor of 7 overall performance, but it is a compromise between making the computations faster and decreasing their accuracy; furthermore, it is a purely empirical approach without further theoretical foundation.

Yet, the problem of disparate time scales has already been solved in the domain of traditional molecular dynamics by several multiple time-step methods: Some authors [18–20] divide many-particle systems into “primary” and “secondary” neighbor regions and calculate forces arising from the secondary region less frequently than those from the primary region. These methods are able to gain a factor of 3–10 in speedup depending on the system and technical details about the neighbor list. Obviously, such a method is not advantageous for a system of a few atoms (most of them will be “primary” anyway) and a lot of wave-function parameters (which have no clear-cut definition of “neighborhood”). Another group of methods [21–23] focuses directly on the issue of disparate masses. These are directly applicable to the present problem, even for small systems. Of these latter methods, we chose the RESPA (reference system propagator algorithm) procedure of Berne et al. [23], since it includes an inherent self-correction. Not only are the systems of heavy masses (here, the nuclei) and light masses (here, the wave-function coefficients) propagated quasi-separately, but also is the difference between them. This difference is then used to improve upon the quasi-separate propagation, without incurring significant additional computational cost. The method of Swendsrud and Halé [22] is also more accurate than that of Telemann and Joosse [21], but it needs higher-order spatial derivatives of the potential. This has to be avoided, since most of the time is already spent calculating first derivatives.

RESPA was originally formulated based on the velocity Verlet algorithm [23], but later modified and extended to a wider class of propagation methods [24]. Since our aamd implementation is based on the simple Verlet procedure, we decided to adapt the original RESPA formulation to our needs. The next section describes this modification for fbd-aamd; the extension to ovr-aamd is obvious and straightforward. In Sections 3 and 4, we present our first test calculations and conclusions.

Technical details of our approach are given in [16,17]. The method uses two sets of parameters, one for the molecule or cluster and one for the traditional atom-fixed Gaussian wave function. The dynamical

where \( M_i \) are the atomic masses assigned to the nuclei of the molecule or cluster and \( \tau(t) \) is the trajectory of the nuclei.

These equations of motion describe the time evolution of the nuclei with the following RESPA variant:

First, we calculate the force coefficients \( \mathbf{f}_i(t) \) at times \( t \) and \( t + \Delta t \) and with the nuclei fixed in the configuration of the reference system at time \( t \):

\[
\mathbf{c}_i(t + \Delta t) = \mathbf{c}_i(t) + \mathbf{f}_i(t) \Delta t
\]

Finally, we correct the motions of the nuclei of the molecule or cluster with the reference system at time \( t + \Delta t \):

\[
\mathbf{c}_i(t + \Delta t) = \mathbf{c}_i(t + \Delta t) - \mathbf{f}_i(t + \Delta t) \Delta t / m_i
\]

The corrections \( D(t + \Delta t) \) are given by:

\[
D(t + \Delta t) = \frac{1}{m_i} \mathbf{f}(t + \Delta t)
\]

where \( \mathbf{F}(t), \mathbf{r}(t), \mathbf{R}(t - \Delta t) \) are fixed at \( t = t \) and with the nuclei fixed at \( t + \Delta t \).
computations are still very hard. This method allows for straight- 
through the wave-function parameter. 
These masses are typically nuclei. The fast movement of 
very small time step need not be described using a much 
more complicated algorithm that exploits the con- 
strained different time steps for each (e.g., Landau and co- 
where this idea has 
been shown [16, 17] that while re- 
sources masses one can get away 
the nuclei only every S- 
ance, but it is a compromise in 
their accuracy; further- 
searcher theoretical foundation.

A similar problem has already been solved in the do- 
multiparticle time-step methods: 
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direct procedure, we decided to 
see section describes this 
seems obvious and straightforward 
and conclusions.

\[ M \dot{R}_i = -\frac{\partial E}{\partial R_i} \]  
\[ m_{\nu} \dot{c}_\nu = -\frac{\partial E}{\partial c_\nu} \]  

where \( M \) are the atomic masses, \( E \) the total potential energy, and \( m_{\nu} \), the ficti-

uous mass assigned to the \( c_\nu \) coefficients.

These equations of motion can then be propagated numerically with a long 
time step \( \Delta t \) for the nuclei and a short time step \( \Delta \delta \) for the \( c_\nu \) coefficients, using 
the following Verlet variant based upon the simple Verlet algorithm:

First, we calculate the forces \( F_i[c(t), R(t)] \) and \( F_\nu[c(t - \Delta \delta), R(t)] \) on the \( c_\nu \) 
coefficients \( c_\nu \) at times \( t \) and \( t - \Delta \delta \), and the force \( F_\nu[c(t), R(t)] \) on the nuclei at 
group at \( R(t) \). Then, we propagate the nuclei for one large time step \( \Delta t \):

\[ R(t + \Delta t) = 2R(t) - R(t - \Delta t) + \frac{\Delta t^2}{M} F_\nu[c(t), R(t)] \]  
followed by propagation of the reference system \( c_\nu \) for \( n \) small time steps \( \Delta \delta \) 
(subject to the initial conditions \( c_\nu(t) = c_\nu(t - \Delta \delta) \) and \( c_\nu(t) = \dot{c}_\nu(t) \)) and with the nuclei fixed at \( R(t) \):

\[ c_\nu(t + \Delta \delta) = 2c_\nu(t) - c_\nu(t - \Delta \delta) + \frac{\Delta \delta^2}{m_{\nu}} \bar{F}_\nu[c_\nu(t), R(t)] \]  

Finally, we correct the movement of the reference system by the difference be-
tween the reference system and the full system, to obtain the true movement of 
the \( c_\nu \) with moving nuclei:

\[ c_\nu(t + \Delta t) = c_\nu(t + \Delta \delta) + D(t + \Delta \delta) \]  
\[ c_\nu(t + \Delta t - \Delta \delta) = c_\nu(t + \Delta t - \Delta \delta) + D(t + \Delta t - \Delta \delta) \]  

The corrections \( D \) are given by

\[ D(t + \Delta t) = \frac{\Delta \delta^2}{m_{\nu}} [F_\nu[c(t, R(t))] - \bar{F}_\nu[c(t), R(t - \Delta t)]] \]  
\[ D(t + \Delta t - \Delta \delta) = \frac{\Delta \delta^2}{m_{\nu}} [F_\nu[c(t - \Delta \delta, R(t))] - \bar{F}_\nu[c(t - \Delta \delta, R(t - \Delta t))] \]

where \( \bar{F}_\nu[c(t), R(t - \Delta t)] \) is the force on the reference system with the nuclei held 
fixed at \( R(t - \Delta t) \) and with \( c_\nu(t) \) referring to the coefficients of the reference sy-
tem propagated from \( t - \Delta t \) to \( t \) and where the approximation \( R(t) - R(t) = \Delta R \) is assumed to be valid. This approximation enables us to calculate the integrals over basis functions, which enter the forces \( F_k \) on the wave functions via the Fock matrix, only for those nuclear geometries obtained through propagation of Eq. (3), i.e., only once per large time step \( \Delta t \). Also, obviously, the expensive calculation of the forces \( F_k \) on the nuclei has to be done only once per large time step \( \Delta t \). Therefore, we can expect considerable saving in computer time. Because of the correction \( D \), there is no loss in accuracy other than from the finite time differences and the above-mentioned approximation.

We have tested this version of a simple Verlet respa algorithm to the propagation of a cluster of four sodium atoms in a singlet electronic state with Heitler-London forces at the 6-31G level of theory. The basis set and effective potential used here are the same as in [16, 17]. The initial geometry for all cases is a planar rectangle with side lengths of 4.82 and 2.89 Å, with slight random distortion to avoid a symmetric situation. The initial nuclear kinetic energy is 0.025 hartrees, with all velocities pointed inward with equal magnitudes. All runs attempted have been set up to run for the same length of time, approximately 36 fs.

We set the fictitious mass of the \( k \) coefficients to 3000 atomic units (au). A non-respa control run with a time step of 5 au (0.12 fs) and respa trajectories with the short time step held fixed at 5 au and long time steps of 25 au (henceforth referred to as 5:1) and 50 au (10:1) were then computed. Plots of the results of these three runs appear in the figures.

From Figure 1, we can see clearly the effect of the different times \( \Delta t \) which the first time step is composed, as the potential energy does not change until that first long-time step is finished. In this plot, as in most of the rest, the deviation from the control trajectory is two to three times as large for the 10:1 curve as for the 5:1 curve, with overall deviations of less than 0.005 hartrees.

Figure 2 displays the component in the \( z \) direction of the acceleration of a selected atom in the system. Whereas the 5:1 curve is quite close to the non-respa control curve, we see that the curve for the 10:1 case deviates considerably more in places. The small peaks in the control curve and the 5:1 curve at 12 and \(<24 \) fs are due to the reconvergence of the wave function. The 10:1 case was also reconverged at these times, but the peaks due to this reconvergence are not visible against the background of the larger deviations. Note, however, that the respa force appears to oscillate nicely about the control force values.

In Figure 3, we have plotted the internuclear distance for a pair of nearest neighbors throughout the simulations. Although the trajectories are close, they are not exactly identical, and we can see that the trajectories do not exactly overlap for the 10:1 case. The curve for the 10:1 case is what is called a "smooth" curve, which, in turn, results in the potential energy control case, as observed.
to the propagation of a close
e to Heilmann-Feynman
potential energy function used here are
The results in all cases is a planar rectangle
uniform distortion to avoid
energy is 0.02 Hartrees, with
All runs attempted have
approximately 38 fs.

A 3000 atomic units (au). A
and RSPA trajectories
by the nuclei at each instant of the propagation for each of these runs. The
behavior of the trajectories at the beginning of the run is an artifact of the setup process.
In each case, the curve labeled "Control" is the non-rigid control run,
and the curves labeled "rms: 5:1" and "rms: 10:1" are the same tests run with the
same short time step as the control run and a long time step that is, respectively, 5 or
10 times larger than the control run.

are not exactly identical, with maximum deviations of \( \pm 0.01 \) Å. Note, however,
that while the trajectories are diverging slightly near the beginning of the run the
difference between the trajectories remains approximately constant for the sec-
ond half of the run.

In Figure 4, we see that the deviations in the kinetic energy of the nuclei are
most apparent in the late part of the propagation, reaching a maximum devia-
tion of \( \pm 0.0006 \) Hartrees. Close inspection of the local minima of these three
curves reveals that the 10:1 curve reaches its minimum slightly later than the 5:1
curve, which, in turn, reaches its minimum later than the control curve. This is
because the potential energy starts changing 45 as later in the 10:1 case than in
the control case, as observed in Figure 1.
Figure 2. Component in the z direction of the acceleration of a selected atom in the single Na$_2$ propargation. This plot shows the temporal behavior of the z component of the acceleration of a selected atom in each simulation, illustrating how the forces felt by the atoms differ among the test cases. The unusual behavior at the beginning of the run is because this value is found by finite difference and thus cannot be compared until two long time steps have been completed.

Figure 3. Distance between two nuclei in the z direction. This plot shows the distance between two nuclei in each simulation, illustrating the unusual in the control curve, Figure 2.

Although we have observed these forces, they appear to have little effect on the molecular structure, as the trajectories in the non-respa case exhibit a more uniform behavior than the respa case. Finally, the energies of the different cases remain relatively consistent after a short induction period, with the respa cases maintaining a lower energy than the control case.
Helmann-Feynman forces, showed quite poorly. Note that the deviation in the first step of the total energy does not change the energy of the core coefficient, as the real energies, which are most obvious in the control curve, are again due to wave-function reconvergence, as in Figure 2.

Although we have observed some deviations from the non-REPA trajectory, they appear to have little effect on the overall dynamics. For example, while the forces on the nuclei (as observed in Fig. 2) are not quite the same in the REPA trajectories as in the non-REPA trajectory, they oscillate around the forces in the non-REPA trajectory. This divergence ceases and the nuclear positions in the REPA cases maintain a fairly constant distance from those positions in the non-REPA case. Finally, although there is an observable difference in the total energy of the different cases, this manifests itself almost entirely in the first step, after which the difference in the total energy remains nearly constant.
This indicates that once the RESPA algorithm has completed a full step, it conserves energy about as well as the single time-step Verlet integrator does. We expect that further testing with the exact forces on the nuclei (which conserve energy and enable us to look at the independent criterion of total energy conservation, unlike Hellmann-Feynman forces) will further verify the accuracy of our implementation of the RESPA algorithm.

One other interesting result has been observed in testing the RESPA algorithm for AIMD. It turns out that when RESPA is applied to AIMD, $\Delta t/\Delta t_c$ is not the only factor that affects the performance of the RESPA algorithm relative to the simple Verlet algorithm. Comparing trajectories with a short time step of 5 a.u., we find that, for this particular system, time-step ratios of 5:1 and 10:1 work for a fictitious mass of 3000 a.u., but if the fictitious mass is reduced to 300 a.u., the RESPA algorithm fails completely for time-step ratios of even 4:1 and 5:1. With a fictitious mass of 3000 a.u., a time-step ratio of 20:1 (long time step = 100 a.u.) also fails completely. This can be understood by noting that $(\Delta t)^2/m_0$ is larger than in the previous case (4:1 or 5:1) and the accuracy of the orbitals breaks down. The correction term $D$ in the Hamiltonian function $\Psi\tilde{H}\Psi_c = \Psi_c^2$ is not sufficient to account for changes in the wavefunction due to the fictitious mass. Therefore, the choice of fictitious mass should be optimized for the specific system and time-step ratio.
completed a full step, it conserves the total energy of the system of total energy conservation does not verify the accuracy of our integrator. When testing the RESPA algorithm for AM1, we find that a time step of 5 au, we find that 10:10:10 work for a fictitious mass of 300 au, the RESPA also fails completely. This can be traced back to the observation that when the factor \( \Delta T/m_0 \), is larger than approximately unity (our test runs have been sufficient only to bound this number by 0.83 below and 1.33 above for this particular system), the corrections \( D \) grow until they are of the same order of magnitude as the \( \sigma \) coefficients \( c_i \), which point the algorithm used to enforce the orthonormality of the orbitals breaks down and the simulation fails. Note that this factor is the prefactor in Eqs. (7) and (8), which bear some similarity to the differential equations that describe exponential growth, when we consider that the forces are obtained by multiplying a Fock matrix by the \( \sigma \) coefficient vector and that the correction vector \( D \) is the difference between the two coefficient vectors that appear in those equations. Thus, the choice of time-step ratio is constrained by the choice of fictitious mass(es), which, in turn, is bounded from above by the desire to minimize the fictitious kinetic energy contribution to the total energy. How-
Figure 6. Fictitious kinetic energy of the 

 ever, this does not seriously impair the computer time savings that can be expected for other systems. For example, a mixed system containing lighter atoms forces a choice of a smaller fictitious mass, but the lighter atoms will also be moving faster; this necessitates the choice of shorter time steps $\Delta t$ (to accommodate the faster changing wave function) and $\Delta v$, and a shorter $\Delta t$, may, in turn, reduce the critical factor $(\Delta t)^2/m_v$, back to an acceptable value.

4. Conclusions

We have presented a simple Verlet $\textit{MD}$ $\textit{tr}	ext{m}$ algorithm. Our test calculations have suggested that for this system time-step ratios of up to $10:1$ can be safely used and lead to a savings in computer time of up to a factor of 7. Other systems with different parameters may necessitate a reassessment of this limit, particu-

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time savings that can be obtained when replacing the innermost loop with an outer loop. For example, the code in the innermost loop can be replaced with a call to a subroutine that performs the same operation for all values of i.

Our test calculations of the effects of replacing the outermost loop with an outer loop show that the speedup is significant. For example, the code in the outermost loop can be replaced with a call to a subroutine that performs the same operation for all values of j.

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Bibliography


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Variational Principle

The Frenkel's variational principle for the single particle approach to the problem on the optimal wave function can be used in atomic and molecular systems. A variational principle for the wave function is considered, a solution of the Hamiltonian:

\[ \delta \int \langle \phi | H - \epsilon | \phi \rangle d\mathbf{r} \]

where \( H = H(r_1, \ldots, r_n) \)

Since a complete basis set is considered, a solution to the Hamiltonian:

\[ \frac{\partial}{\partial \epsilon} \int \langle \phi | H | \phi \rangle d\mathbf{r} \]

with a fixed initial condition is possible.