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Extended Lagrangian Born-Oppenheimer molecular dynamics with dissipation.

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Abstract

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Extended Lagrangian Born–Oppenheimer molecular dynamics with dissipation

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Stability and dissipation in the propagation of the electronic degrees of freedom in time-reversible extended Lagrangian Born–Oppenheimer molecular dynamics [Niklasson *et al.*, Phys. Rev. Lett. **97**, 123001 (2006); Phys. Rev. Lett. **100**, 123004 (2008)] are analyzed. Because of the time-reversible propagation the dynamics of the extended electronic degrees of freedom is lossless with no dissipation of numerical errors. For long simulation times under “noisy” conditions, numerical errors may therefore accumulate to large fluctuations. We solve this problem by including a dissipative external electronic force that removes noise while keeping the energy stable. The approach corresponds to a Langevin-like dynamics for the electronic degrees of freedom with internal numerical error fluctuations and external, approximately energy conserving, dissipative forces. By tuning the dissipation to balance the numerical fluctuations the external perturbation can be kept to a minimum. © 2009 American Institute of Physics. [DOI: 10.1063/1.3148075]

I. INTRODUCTION

The extended Lagrangian framework of time-reversible Born–Oppenheimer molecular dynamics (TR-BOMD),^{1,2} where both the nuclear and the electronic degrees of freedom are propagated through a time-reversible integration, provides an efficient and accurate approach to *ab initio* molecular dynamics simulations. Thanks to time reversibility the dynamics is stabilized with respect to a long-term energy drift and often only a few (1–3) self-consistency cycles are necessary in each time step. However, because of time reversibility the propagation of the electronic degrees of freedom is also lossless. Small numerical errors or inaccurate initial boundary conditions will never disappear but propagate throughout the simulation. Exact time reversibility is therefore a potential problem for long-time simulations under “noisy” conditions since numerical errors can accumulate to large fluctuations. Exact time reversibility in the propagation of the electronic degrees of freedom may then lead to a substantial loss of accuracy, and in the worst case, to divergence.

In this paper we show how the problem with fluctuations due to numerical noise in TR-BOMD can be avoided. The error accumulation is removed by introducing an external dissipative force term acting on the electronic degrees of freedom. The external force is designed to conserve time reversibility and total energy to a high degree of accuracy

while at the same time optimize the dissipation of numerical noise. By tuning the dissipation to balance the numerical error fluctuations, the external force term can be kept to a minimum without causing any significant drift in the total energy or modification of the microcanonical nuclear trajectories. The technique can be viewed as a Langevin dynamics for the electronic degrees of freedom with internal numerical error fluctuations and external, approximately energy conserving, friction forces that provide dissipation of the numerical noise.

In this article, we first review extended Lagrangian Born–Oppenheimer molecular dynamics (XL-BOMD),² which can be viewed as generalization of the original TR-BOMD approach.¹ In comparison to the original scheme XL-BOMD has a more rigorous and flexible theoretical framework. The Lagrangian formulation also allows for higher-order geometric integration schemes beyond the conventional Verlet algorithm,² though higher-order symplectic schemes will not be applied in the present study. Next we show how numerical perturbations give rise to errors that do not disappear in a perfectly lossless time-reversible propagation. Thereafter, we show how a coupling to a fictitious external “dissipative reservoir” can be used to remove the numerical error fluctuations without introducing any significant energy drift or modification of the nuclear forces. An alternative approach based on a generalized Verlet integration, which has the same dissipation features as the Langevin-like dynamics, is also discussed.

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II. AB INITIO MOLECULAR DYNAMICS

A. Born–Oppenheimer molecular dynamics

Conventional Born–Oppenheimer molecular dynamics (BOMD) is described by the Lagrangian

$$\mathcal{L}^{\text{BO}}(\mathbf{R}, \dot{\mathbf{R}}) = \frac{1}{2} \sum_k M_k \dot{R}_k^2 - U[\mathbf{R}; D], \quad (1)$$

where the potential $U[\mathbf{R}; D]$ is defined at the self-consistent field (SCF) ground state, D , of the electronic degrees of freedom for a given nuclear configuration $\mathbf{R} = \{R_i\}$. We can assume that $U[\mathbf{R}; D]$ is the total electronic energy (including ion-ion repulsions) in self-consistent density functional theory, Hartree–Fock theory, or any of their many extensions, such as configuration interaction, coupled cluster and perturbation methods^{3–7} that are based on an underlying SCF description. The dynamics is described by the Euler–Lagrange equations of motion,

$$M_k \ddot{R}_k = - \frac{\partial U[\mathbf{R}; D]}{\partial R_k}, \quad (2)$$

where the dots denote the number of time derivatives. The evolution of the nuclear degrees of freedom is given by the integration of Eq. (2), performed with, for example, the time-reversible Verlet scheme,⁸ where the nuclear forces are calculated at the SCF optimized ground state D for each new configuration. Due to the nonlinear nature of the SCF equations that determine the electronic ground state, the iterative SCF process dominates the computational effort. The cost can be substantially reduced by using an accurate initial guess for the electronic degrees of freedom in the SCF optimization.^{9–14} An efficient guess is provided by an extrapolation from previous time steps,

$$D(t + \delta t) = \text{SCF} \left[\sum_{n=0}^m a_n D(t - n \delta t) \right]. \quad (3)$$

The process, i.e., an extrapolation followed by the SCF optimization, corresponds to an adiabatic propagation of the electronic degrees of freedom on the self-consistent ground state potential energy surface. With an exact SCF optimization the self-consistent solution D is independent of the initial guess and there is no “propagation” of the electronic degrees of freedom. However, in practice the SCF optimization is always incomplete and the electronic degrees of freedom are therefore propagated with a “memory” from previous time steps. This leads to a fundamental problem in BOMD. Since the SCF optimization is a nonlinear irreversible process, the time-reversal symmetry in the propagation of the electronic degrees of freedom is broken in Eq. (3).¹² Because of the broken time-reversal symmetry the nuclear forces in Eq. (2) are not calculated with the correct underlying symmetry of the electronic degrees of freedom. This gives an unphysical behavior of the nuclear trajectories with a systematic drift in the total energy and phase space.^{12,14} With TR-BOMD this problem can be avoided.¹

B. Extended Lagrangian formulation of time-reversible Born–Oppenheimer molecular dynamics

TR-BOMD was originally given in terms of a lossless dual filter integration scheme,¹ but it can be described more generally by an extension of the BO Lagrangian in Eq. (1) with auxiliary electronic degrees of freedom P and its time derivative \dot{P} evolving in a harmonic potential centered around the SCF ground state solution D .² Both the extended auxiliary dynamical variable P and the self-consistent ground state D are assumed to be orthogonal density matrix representations of the electronic degrees of freedom. Other representations of the electronic degrees of freedom besides the density matrix, such as the single-particle potential, the electron density, or wave functions, can be used alternatively. The extended Born–Oppenheimer (XBO) Lagrangian is given by

$$\mathcal{L}^{\text{XBO}}(\mathbf{R}, \dot{\mathbf{R}}, P, \dot{P}) = \mathcal{L}^{\text{BO}} + \frac{\mu}{2} \text{Tr}[\dot{P}^2] - \frac{\mu\omega^2}{2} \text{Tr}[(D - P)^2]. \quad (4)$$

Here μ and ω are fictitious electronic mass and frequency parameters. The last two terms on the right hand side are the fictitious electronic kinetic and potential energy terms. Notice, no constraints, such as idempotency, corresponding to wave function orthogonality, are used, and the BO Lagrangian \mathcal{L}^{BO} is still defined at the self-consistent ground state D . This is in contrast to the popular Car–Parrinello molecular dynamics approach, which is also based on an extended Lagrangian formulation.^{15–18}

The time evolution of the system is described by the Euler–Lagrange equations of motion,

$$M_k \ddot{R}_k = - \frac{\partial U[\mathbf{R}; D]}{\partial R_k} + \mu \text{Tr}[(D - P) \partial D / \partial R_k], \quad (5)$$

$$\mu \ddot{P} = \mu\omega^2(D - P), \quad (6)$$

which in the limit $\mu \rightarrow 0$, i.e., when $\mathcal{L}^{\text{XBO}} \rightarrow \mathcal{L}^{\text{BO}}$, are given by

$$M_k \ddot{R}_k = - \frac{\partial U[\mathbf{R}; D]}{\partial R_k}, \quad (7)$$

$$\ddot{P} = \omega^2(D - P). \quad (8)$$

The dynamics of the nuclear degrees of freedom, Eq. (7), is determined by the same equations of motion as in regular BOMD, Eq. (2), and the BO total energy is a constant of motion. In this sense the extended variables P and \dot{P} are only auxiliary quantities that do not affect the BO nuclear trajectories. This also differs from the Car–Parrinello molecular dynamics approach, where the nuclear forces are determined by the extended electronic degrees of freedom and where the constant of motion is different from BOMD. It is also different from the Ehrenfest molecular dynamics approach,¹⁹ which recently has seen some very interesting developments.^{20,21}

The major advantage with the XL-BOMD, which will be explained below, is the efficient and accurate SCF optimiza-

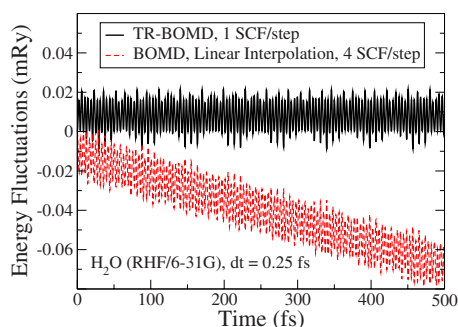


FIG. 1. (Color online) The fluctuations in total Born–Oppenheimer energy ($E^{\text{BO}}(t) - E_0$) for conventional BOMD with a linear interpolation of the electronic degrees of freedom and for a TR-BOMD.

tion and integration of the equations of motion. This is enabled by the coupling between P and D given in Eq. (8), which is the key equation in our XL-BOMD.

C. Time-reversible integration

If we apply the time-reversible Verlet scheme⁸ to the integration of the electronic degrees of freedom in Eq. (8) we get

$$P(t + \delta t) = 2P(t) - P(t - \delta t) + \delta t^2 \omega^2 (D(t) - P(t)). \quad (9)$$

In the first initial steps we set $P(t) \equiv D(t)$. The stability of the integration will be determined by the size of the dimensionless factor $\kappa = \delta t^2 \omega^2$. If we choose κ as large as possible, consistent with stability under incomplete SCF convergence,² the curvature of the extended harmonic potential in Eq. (4), which is determined by ω , is maximized and P will evolve close to the self-consistent ground state solution D . It can be shown that the optimal value in the Verlet scheme above is for $\kappa=2$. This value gives the largest possible value of ω that is allowed under incomplete SCF convergence for a given time step δt . A more detailed stability analysis for an approximate SCF optimization is given in Sec. III. Besides the Verlet integration scheme above, higher-order geometric integration algorithms can be applied.² The properties of higher-order symplectic integration schemes in our XL-BOMD will be analyzed in a separate article.²²

Since $P(t)$ evolves in a harmonic potential centered around the ground state $D(t)$, the extended electronic degrees of freedom $P(t)$ will always be close to the self-consistent solution $D(t)$. It is therefore natural to use $P(t)$ as an initial guess to the SCF optimization procedure,

$$D(t) = \text{SCF}[P(t)]. \quad (10)$$

This choice of initial guess leads to the same reduction of the computational cost as the extrapolation schemes used in regular BOMD, Eq. (3). However, because $P(t)$ is a dynamical variable that can be integrated with a time-reversible scheme, the SCF optimization in Eq. (10) keeps the time-reversal symmetry in the underlying electronic propagation. The unphysical behavior, associated with the broken time-reversal symmetry of regular BOMD, is therefore avoided. Figure 1 shows the typical behavior of the total energy fluctuations for regular BOMD using a linear interpolation from two previous time steps, Eq. (3), in comparison to a

TR-BOMD based on Eqs. (9) and (10). TR-BOMD provides a significant qualitative improvement. The small systematic drift seen in regular BOMD is avoided in TR-BOMD, even under incomplete SCF convergence with only one single iteration cycle per time step. The accuracy in the simulation of the two methods can be estimated from the amplitude of the energy fluctuations. Despite using only a single SCF cycle in the time-reversible propagation the accuracy is essentially unaffected. TR-BOMD therefore provides a substantial reduction in the computational cost. Moreover, by extending TR-BOMD to higher-order symplectic integration schemes, it is often possible to significantly improve the accuracy without any additional computational effort.^{2,22}

III. STABILITY AND DISSIPATION

There is a fundamental problem with a time-reversible propagation—there is no loss of information. Any perturbation or error will propagate without ever disappearing. This is particularly serious for long simulation times under numerically noisy conditions, for example, occurring from an approximate sparse matrix algebra in reduced complexity algorithms since numerical errors then may accumulate to large fluctuations or even divergence. A similar effect occurs in classical molecular dynamics, but the errors are much smaller and of minor significance. The main problem in TR-BOMD is the distance between $P(t)$ and $D(t)$, i.e., the extended potential energy, which may slowly increase due to an accumulation of numerical errors.

Stability under incomplete SCF convergence and dissipation of numerical noise can be analyzed from the roots of the characteristic equation of the homogeneous (steady state) part of the integration scheme.^{2,10} Assume a linearization of an approximate SCF optimization, Eq. (10), around the hypothetical exact solution D^* , where

$$D = \text{SCF}[P] \approx D^* + \Gamma_{\text{SCF}}(P - D^*). \quad (11)$$

Let γ be the largest eigenvalue of the SCF response kernel Γ_{SCF} . If $\gamma=0$ the SCF optimization is exact. In general, we can expect $\gamma \in [-1, 1]$. Inserting Eq. (11) in the Verlet scheme, Eq. (9), with Γ_{SCF} replaced by γ , for the homogeneous steady state solution for which $D^* \equiv 0$, gives

$$P_{n+1} = 2P_n - P_{n-1} + \kappa(\gamma - 1)P_n. \quad (12)$$

Here $P_n = P(t_0 + n\delta t)$ and $\kappa = \delta t^2 \omega^2$. The characteristic roots of this equation are exponentially increasing or decaying solutions of the form λ^n given by

$$\lambda^{n+1} = 2\lambda^n - \lambda^{n-1} + \kappa(\gamma - 1)\lambda^n. \quad (13)$$

If the magnitude of the largest root $|\lambda|_{\text{max}} > 1$ we have exponentially increasing solutions, which will cause numerical instability. If the largest root $|\lambda|_{\text{max}} < 1$ we have dissipation with exponentially decaying solutions. In an exact time-reversible dynamics the roots are on the unit circle and $|\lambda|_{\text{max}} = 1$. Figure 2 shows the magnitude of $|\lambda|_{\text{max}}$ as a function of the degree of SCF convergence, as measured by γ , for the Verlet integration, Eqs. (9) and (13), with $\kappa=2$. In comparison we show a conventional linear interpolation scheme, based on Eq. (3) for $m=1$,

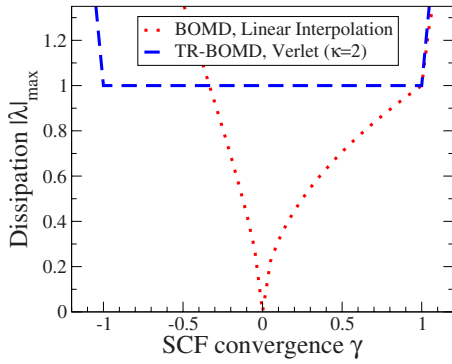


FIG. 2. (Color online) The largest roots of the characteristic equation, $|\lambda|_{\max}$, as a function of the degree of SCF convergence measured by $\gamma \in [-1, 1]$. If the value of κ would be increased above 2, the largest root $|\lambda|_{\max}$ would be larger than 1 for some intervals of $\gamma \in [-1, 1]$ and XL-BOMD would no longer be stable under incomplete SCF convergence.

$$P_{n+1} = 2D_n - D_{n-1}, \quad (14)$$

with the characteristic equation

$$\lambda^{n+1} = 2\gamma\lambda^n - \gamma\lambda^{n-1}. \quad (15)$$

As can be seen in the figure, the time-reversible XL-BOMD is stable under incomplete SCF convergence in the full interval of $\gamma \in [-1, 1]$, whereas the conventional linear interpolation scheme in regular BOMD is stable only for $\gamma \in [-1/3, 1]$. On the other hand, the linear interpolation has a substantial dissipation, with roots $|\gamma|_{\max} < 1$, which is not the case for the time-reversible scheme that has all roots on the unit circle. Time-reversible XL-BOMD therefore has no natural dissipation that can suppress an accumulation of numerical noise.

IV. DISSIPATIVE FORCES IN EXTENDED LAGRANGIAN BORN–OPPENHEIMER MOLECULAR DYNAMICS

In this paper we will propose dissipation mechanisms that can remove the accumulation of numerical errors in time-reversible XL-BOMD. Thanks to the underlying exactly time-reversible dynamics, this is fairly straightforward to achieve in a number of different ways.

A. Langevin-like approach

In the case of some unknown internal numerical noise, $\eta(t)$, the electronic equations of motion in XL-BOMD, Eq. (8), is modified to

$$\ddot{P}(t) = \omega^2(D(t) - P(t)) + \eta(t). \quad (16)$$

The noise accumulation can be balanced by coupling the electronic degrees of freedom to a fictitious external system through a dissipative force term, F^{diss} . This modifies the electronic equations of motion to a Langevin-like equation for the auxiliary electronic degrees of freedom,

$$\ddot{P}(t) = \omega^2(D(t) - P(t)) + \eta(t) + \alpha\mu^{-1}F^{\text{diss}}(t), \quad (17)$$

where α is some small coupling constant and the inverse mass parameter μ^{-1} is included to give the correct dimensionality. There are numerous ways to choose $F^{\text{diss}}(t)$ and

they will all break time-reversal symmetry to some degree. In a more conventional Langevin approach we would probably choose $F^{\text{diss}}(t) \sim \dot{P}(t)$. However, this choice would give rise to a fairly strong perturbation with large deviations from a time-reversible microcanonical dynamics. The goal here is to find an efficient dissipation term with no significant effect on the energy conservation and the dynamics of the nuclear degrees of freedom. The dissipative force should thus in principle correspond to a weak coupling of the auxiliary electronic degrees of freedom to a hypothetical external ensemble that removes noise without any significant perturbation of the microcanonical nuclear trajectories.

B. Dissipative force term

Here we will choose $F^{\text{diss}}(t)$ such that the time-reversal symmetry is broken only to a very small degree in the propagation of the auxiliary variable P . Our construction of F^{diss} is very similar to a standard derivation of the classical Verlet scheme by extrapolation [see Eqs. (25) and (26) below]. Let P_{n-k} be expanded in a Taylor series around P_n , i.e.,

$$P_{n-k} = \sum_{m=0}^M \frac{(-k\delta t)^m}{m!} P_n^{(m)} + \mathcal{O}(\delta t^{M+1}), \quad k = 0, 1, \dots, K, \quad (18)$$

where $P_n^{(m)} = d^m P(t) / dt^m$ at $t = t_0 + n\delta t$. By choosing some linear combination of this set of $K+1$ equations it is possible to remove all δt^m terms that are odd up to some order in δt^{2m+1} as well as the zeroth order term. As a comparison, in the derivation of the classical Verlet scheme we remove *all* odd orders in δt using $k = \pm 1$. A similar idea of removing odd-order terms in δt was recently used by Kolafa in the construction of a set of predictor-corrector schemes in the always stable predictor-corrector method.²³ From the linear combination of the Taylor expansions of P_{n-k} in Eq. (18) we can express the second order time derivative of P as

$$\delta t^2 \ddot{P}_n = \frac{1}{d_K} \sum_{k=0}^K c_k P_{n-k} + \mathcal{O}_{\text{even}}(\delta t^4) + \mathcal{O}_{\text{odd}}(\delta t^{(2K-3)}). \quad (19)$$

Here $\mathcal{O}_{\text{even}}(\delta t^4)$ and $\mathcal{O}_{\text{odd}}(\delta t^{(2K-3)})$ are the leading even and odd order of the error in the expansion, respectively. Only the leading odd-order term is of interest since it determines the order of the broken time-reversal symmetry. The constant d_K and the expansion coefficients c_k are given from the extrapolation, i.e., the particular linear combination of the Taylor expanded P_{n-k} in Eq. (18) that removes the odd-order terms of δt . We now define our dissipative force term as

$$F_n^{\text{diss}} = \mu \ddot{P}_n^{\text{diss}} = \frac{\mu}{d_K \delta t^2} \sum_{k=0}^K c_k P_{n-k}. \quad (20)$$

This force term is time reversible up to some higher order in δt and should thus only have a minor effect on the energy conservation for sufficiently small values of δt . In comparison, the more conventional velocity-dependent friction term in Langevin dynamics, $F_n^{\text{diss}} \sim \dot{P}_n$, breaks the time-reversal symmetry already in the first order of δt .

TABLE I. The optimized α and κ values and the c_k coefficient for the dissipative electronic force term in Eq. (22).

K	κ	$\alpha \times 10^{-3}$	c_0	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9
3	1.69	150	-2	3	0	-1						
4	1.75	57	-3	6	-2	-2	1					
5	1.82	18	-6	14	-8	-3	4	-1				
6	1.84	5.5	-14	36	-27	-2	12	-6	1			
7	1.86	1.6	-36	99	-88	11	32	-25	8	-1		
8	1.88	0.44	-99	286	-286	78	78	-90	42	-10	1	
9	1.89	0.12	-286	858	-936	364	168	-300	184	-63	12	-1

A simple and fairly efficient alternative dissipative force term is given by the electronic force from the previous time step,

$$F_n^{\text{diss}} = \mu \ddot{P}_{n-1} = \mu \omega^2 (D_{n-1} - P_{n-1}). \quad (21)$$

Because of the time shift in the force term, the time-reversal symmetry is broken. The amount of dissipation and energy drift depends on the choice of the coupling constant α in Eq. (17). Generalizations of Eq. (21) to higher-order polynomial extrapolations of previous force terms are also possible.

C. Integration

The Verlet integration for the electronic degrees of freedom in Eq. (17), with the dissipative force in Eq. (20) and with the noise term $\eta(t)$ included implicitly by assumed numerical errors, has the following form:

$$P_{n+1} = 2P_n - P_{n-1} + \kappa(D_n - P_n) + \alpha \sum_{k=0}^K c_k P_{n-k}. \quad (22)$$

We have rescaled the coupling parameter, $\alpha/d_K \rightarrow \alpha$, for simplicity. In the initial steps we set $P_n \equiv D_n$. The problem is now to choose K and M in Eq. (18) and find a set of expansion coefficients c_k in Eq. (19), and thereafter to choose α and κ for which the dissipation is as large as possible under the condition of stability for incomplete SCF convergence. Of many possible choices we have found the set of coefficients in Table I to be particularly efficient for the Verlet scheme in Eq. (22). The c -coefficients have been calculated from an overdetermined extrapolation in Eq. (18). The α and κ values have thereafter been “optimized” with respect to damping under the condition of stability under incomplete

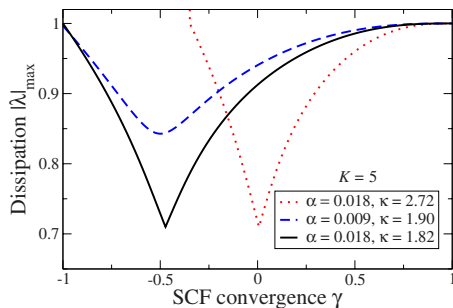


FIG. 3. (Color online) The largest roots of the characteristic equation, $|\lambda|_{\text{max}}$, in Eq. (23), as a function of the degree of SCF convergence measured by $\gamma \in [-1, 1]$ for various values of α and κ . For the optimal values of α and κ the damping is optimized under the condition of stability for $\gamma \in [-1, 1]$.

SCF convergence. The “optimization” is a somewhat subjective procedure. Figure 3 illustrates our approach. The first graph is not stable under incomplete SCF convergence for $\gamma \in [-1, 1]$. The second graph is stable, but has a damping that can be further improved to what we decide to be the “optimal” since it has the largest damping at $\gamma=0$ (one of many possible choices), which is given by the last curve.

Figure 4 illustrates the dissipation of the damped Verlet integration in Eq. (22) as a function of SCF convergence for $K=4, 5$, and 6 as measured by the largest root $|\lambda|_{\text{max}}$ to the characteristic equation,

$$\lambda^{n+1} = 2\lambda^n - \lambda^{n-1} + \kappa(\gamma - 1)\lambda^n + \alpha \sum_{k=0}^K c_k \lambda^{n-k}. \quad (23)$$

If we break time-reversal symmetry at a lower order the dissipation is increased and if the coupling constant α is reduced to 0 the dissipation vanishes and the integration is exactly time reversible. This gives us the flexibility to balance the numerical noise with a minimum of dissipation. In this way it is possible to keep the time-reversal symmetry and the total energy to the highest possible degree of accuracy without any significant modifications of the nuclear trajectories.

If we use the alternative force term in Eq. (21) in the Verlet integration scheme with optimized values of κ we get

$$P_{n+1} = 2P_n - P_{n-1} + (2 - \alpha)(D_n - P_n) - \alpha(D_{n-1} - P_{n-1}), \quad (24)$$

which is stable for all coupling constants $\alpha \in [0, 1]$. In the limit $\alpha \rightarrow 0$ the dissipation disappears and the integration is exactly time reversible.

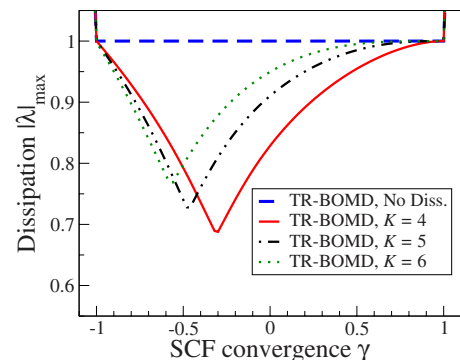


FIG. 4. (Color online) The dissipation measured by the largest roots of the characteristic equation, $|\lambda|_{\text{max}}$, as a function of the degree of SCF convergence measured by $\gamma \in [-1, 1]$ for three different dissipation schemes, Eq. (22) with coefficients in Table I.

D. Generalized Verlet integration

As an equivalent alternative to the dissipative force term introduced in the Langevin-like dynamics above, it is possible to integrate the equation of motion, Eq. (16), with a generalized Verlet algorithm. By performing the extrapolation in Eq. (18) for $k=-1, 1, 2, 3, \dots, K$ and remove odd-order terms in δt^m up to some order δt^{2m+1} , it is possible to construct an efficient dissipative Verlet-like schemes. For $k=\pm 1$ we can remove all odd orders, as in the standard derivation of the Verlet algorithm, i.e.,

$$P_{n+1} = P_n + \delta t \dot{P} + \frac{1}{2} \delta t^2 \ddot{P}_n + \frac{1}{3!} \delta t^3 P_n^{(3)} + \dots, \quad (25)$$

$$P_{n-1} = P_n - \delta t \dot{P} + \frac{1}{2} \delta t^2 \ddot{P}_n - \frac{1}{3!} \delta t^3 P_n^{(3)} + \dots,$$

which after addition gives

$$\begin{aligned} P_{n+1} + P_{n-1} &= 2P_n + \delta t^2 \ddot{P}_n + \mathcal{O}(\delta t^4), \\ P_{n+1} - P_{n-1} &= 2\delta t \dot{P} + \delta t^3 P_n^{(3)} + \mathcal{O}(\delta t^5), \\ P_{n+1} - P_{n-1} &= 2\delta t \dot{P} + \delta t^2 \omega^2 (D_n - P_n) + \mathcal{O}(\delta t^4). \end{aligned} \quad (26)$$

We can find additional extrapolations of, for example,

$$\begin{aligned} P_{n+1} &= P_n + \delta t \dot{P} + \frac{1}{2} \delta t^2 \ddot{P}_n + \frac{1}{3!} \delta t^3 P_n^{(3)} + \dots, \\ P_{n-1} &= P_n - \delta t \dot{P} + \frac{1}{2} \delta t^2 \ddot{P}_n - \frac{1}{3!} \delta t^3 P_n^{(3)} + \dots, \\ P_{n-2} &= P_n - 2\delta t \dot{P} + \frac{2^2}{2} \delta t^2 \ddot{P}_n - \frac{2^3}{3!} \delta t^3 P_n^{(3)} + \dots, \\ P_{n-3} &= P_n - 3\delta t \dot{P} + \frac{3^2}{2} \delta t^2 \ddot{P}_n - \frac{3^3}{3!} \delta t^3 P_n^{(3)} + \dots, \\ P_{n-4} &= P_n - 4\delta t \dot{P} + \frac{4^2}{2} \delta t^2 \ddot{P}_n - \frac{4^3}{3!} \delta t^3 P_n^{(3)} + \dots \end{aligned} \quad (27)$$

that remove only the δt and δt^3 terms. The integration scheme is then given by inserting the Euler-Lagrange equation for \ddot{P} in XL-BOMD, Eq. (8). The value of $\kappa = \delta t^2 \omega^2$ is thereafter optimized to guarantee stability under incomplete SCF convergence, which is given by the roots of the characteristic equation. For example

$$P_{n+1} = (1/0.3016)[0.5513P_n - 0.1984P_{n-1} - 0.033P_{n-2} - 0.036P_{n-3} + 0.0177P_{n-4}] + 1.75(D_n - P_n), \quad (28)$$

is one possible generalized dissipative Verlet integration of TR-BOMD, which is approximately time-reversible and stable under incomplete SCF convergence. This approach, which avoids the Langevin-like formulation, provides the same performance and (similar) coefficients to the Langevin approach in Eq. (22). However, the generalized Verlet scheme is physically less transparent, the damping is not

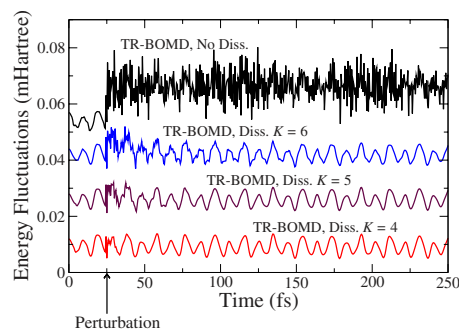


FIG. 5. (Color online) The response in the total energy in XL-BOMD to a perturbation at $t=25$ fs, with and without dissipation (diss), for a water molecule (HF/6-31G) with $\delta t=0.5$ fs and 1 SCF/step. The integration in Eq. (22) with coefficients from Table 1 was used.

naturally tuned by a coupling constant, and it is not straightforward to extend to higher-order symplectic integration schemes^{2,24} or to alternative ensembles. Nevertheless, the generalized Verlet technique presented above illustrates the possibility for a large number of integration schemes with dissipation that can be derived thanks to the underlying exactly time-reversible dynamics, which is provided by the extended Lagrangian formulation of BOMD.

E. Examples

Figure 5 illustrates the behavior of XL-BOMD, with and without dissipation, for a perturbation at $t=25$ fs. The perturbation was performed by switching places of two successive auxiliary density matrices in a simulation of a water molecule using the FreeON suite of *ab initio* linear scaling electronic structure programs.²⁵ Without damping the numerical noise does not disappear although the simulation remains stable without any growth of the error. The dissipative force terms, Eq. (20), in the Verlet integration, Eq. (22), removes the effect of the perturbation without causing any significant drift in the energy. The lower-order dissipation force terms give a faster decay of the perturbation in agreement with the behavior of the characteristic roots shown in Fig. 4. Often we have found that we achieve a more efficient dissipation at a given energy drift using a higher-order extrapolation expression for the dissipation force than by reducing the coupling constant α for a lower-order expansion, with the corresponding reoptimization of κ .

V. DISCUSSION AND SUMMARY

BOMD is the gold standard for a majority of atomistic simulations of dynamical, structural, chemical, and thermodynamics properties of materials. BOMD based on a self-consistent optimization of the electronic structure for each new configuration at each time step has been used in quantum chemistry and materials science for over 30 years.^{9,19,26-30} The direct or indirect applications of BOMD range from the problem of high-temperature stabilization of basic elements to the folding structures of protein molecules in human cells. BOMD, based on self-consistent density functional theory, Hartree-Fock theory, or their extensions, is thus one of the most important theoretical frameworks of computational materials science, chemistry and biology. De-

spite its status, regular BOMD has two serious shortcomings that have been given very little attention: (a) the computational cost is very high because of the required SCF optimization, and (b) the time-reversal symmetry in the underlying evolution of the electronic degrees of freedom is broken, which leads to an unphysical behavior of the dynamics. These two fundamental and interconnected problems are addressed by TR-BOMD,¹ whose extended Lagrangian generalization² provides an efficient theoretical framework for high-performance *ab initio* molecular dynamics simulations.

In this paper we have used a (time-reversible) BOMD given through the extended Lagrangian in Eq. (4), its Euler-Lagrange equations of motion, Eqs. (7) and (8), and the SCF initialization, Eq. (10), in a Langevin-like framework, Eq. (17), with various possible forms of the integration of the electronic degrees of freedom, e.g., Eq. (22). The focus in this paper has been on this integration and its sensitivity to numerical noise. A strictly TR-BOMD is perfectly lossless with no natural dissipation of numerical errors. For long simulation times under noisy conditions, numerical errors may therefore accumulate to large fluctuations. We solved this problem by including a dissipative external force that removes noise while keeping the energy stable. The external force is constructed to keep the time-reversal symmetry almost exact. By choosing the dissipation to balance the numerical fluctuations the external force can be kept to a minimum. The approach corresponds to a Langevin-like dynamics for the electronic degrees of freedom with internal numerical error fluctuations and external, approximately energy conserving, dissipative forces.

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