



Car–Parrinello molecular dynamics

Jürg Hutter*

The Car–Parrinello (CP) method made molecular dynamics simulation with on-the-fly computation of interaction potentials from electronic structure theory computationally feasible. The method reformulates *ab initio* molecular dynamics (AIMD) as a two-component classical dynamical system. This approach proved to be valuable far beyond the original CP molecular dynamics method. The modern formulation of Born–Oppenheimer (BO) dynamics is based on the same basic principles and can be derived from the same Lagrange function as the CP method. These time-reversible BO molecular dynamics methods allow higher accuracy and efficiency while providing similar longtime stability as the CP method. AIMD is used in many fields of computational physics and chemistry. Its applications are instrumental in fields as diverse as enzymatic catalysis and the study of the interior of planets. With its versatility and predictive power, AIMD has become a major approach in atomistic simulations. © 2011 John Wiley & Sons, Ltd.

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INTRODUCTION

The simulation method that combines classical molecular dynamics of nuclei with electronic structure theory is called *ab initio* molecular dynamics (AIMD). With the seminal contribution by Roberto Car and Michele Parrinello,¹ the field of AIMD was kick-started and since then it has become a cornerstone of modern simulation techniques in many areas of computational science. The Car–Parrinello (CP) method not only made AIMD simulations technically feasible but also changed the way fundamental problems of the field were looked at. Following the lead of Andersen^{2,3} for constant pressure simulations, the CP method firmly established the extended Lagrangian technique in computational chemistry and physics. Many of the current state-of-the-art simulation methods are directly based or inspired by the CP method.

Up to the mid-1990s, AIMD simulations were completely dominated by the CP method, so much so that CP molecular dynamics became a synonym for AIMD.⁴ These years are characterized by an exponential growth of single applications of the CP method and a rapid expansion to new application

fields. The original CP method was proposed using Kohn–Sham density functional theory within the pseudopotential plane wave framework. Due to algorithmic developments and adaptation to modern computer architectures,⁵ the original scheme is still very popular. Slight extensions to accommodate variations to the standard framework, most notably ultrasoft pseudopotentials,⁶ the projector-augmented wave method,⁷ adaptive curvilinear coordinates,⁸ or DVR basis sets,⁹ have been introduced. The combination of the CP method with atomic basis sets has its own interesting history.^{10–12} Using other electronic structure methods than Kohn–Sham density functional theory was explored^{13,14} but never gained wide popularity. The same is true for the simulation of metals¹⁵ using CP techniques. Important were adaptations of the CP method to other simulation methods than for the microcanonical ensemble on the ground-state Born–Oppenheimer (BO) surface. The combination of the CP method with simulation techniques for canonical ensembles¹⁶ opened the way to the study of structural phase transitions^{17,18} and high-pressure chemistry¹⁹ and physics from first principles. Furthermore, the use of path integral techniques^{20–22} allowed for the inclusion of quantum effects. The CP method has also found application for hot electrons,²³ in excited-state dynamics^{24,25} and in methods for nonadiabatic simulations.²⁶ There is a

*Correspondence to: hutter@pci.uzh.ch

Physical Chemistry Institute, University of Zurich, Zurich, Switzerland

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vast amount of other simulation methods inspired by CP that have been developed, for example, the fluctuating charge polarizable force field method,²⁷ just to name one. Several reviews on the CP method have been published in the past. The reviews by Remler and Madden,²⁸ Galli and Pasquarello,²⁹ and Marx and Hutter^{4,30} are noted here because of their large impact.

Over the years, standard simulation protocols for CP simulations were established and used by many groups. With the availability of ever-increasing computer power, these protocols could be tested further and limitations of the CP method could be analyzed. In recent years, new developments were able to overcome these limitations while still keeping all of the benefits of the original method. This overview aims at describing the current status of the theory of AIMD from a modern perspective. It starts with a general extended Lagrangian scheme that will then be specialized to the two main methods: the CP method and the time-reversible BO method. The Langevin dynamics extension of BO molecular dynamics will also be explained.

GENERAL EXTENDED LAGRANGIAN METHOD

The key to an efficient and accurate AIMD method is the combined treatment of nuclear and electronic degrees of freedom. This property is at the heart of the CP method but it took some time to realize its general importance. In a series of papers, Niklasson^{31–33} developed a theoretical framework that we will here use in a slightly generalized form. In the spirit of Car and Parrinello, we base AIMD on a Lagrangian function of nuclear and electronic coordinates, \mathbf{q} and \mathbf{x} , respectively. Possible constraints on these coordinates are, for the sake of simplicity, neglected but can easily be introduced. The generalized Lagrangian of AIMD is

$$\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, \mathbf{x}, \dot{\mathbf{x}}) = \frac{1}{2} M \dot{\mathbf{q}}^2 + \frac{1}{2} \mu \dot{\mathbf{x}}^2 - E(\mathbf{q}, \mathbf{y}) + k\mu G(\|\mathbf{x} - \mathbf{y}\|), \quad (1)$$

where the further electronic variables \mathbf{y} are calculated from the vector-valued function $\mathbf{y} = \mathbf{F}(\mathbf{q}, \mathbf{x})$ and the function $G(\|\mathbf{x} - \mathbf{y}\|)$ is positive everywhere and zero for $\|\mathbf{x} - \mathbf{y}\| = 0$. In this Lagrangian, we have introduced two parameters, μ and k , along with the functions \mathbf{F} and G . The parameter μ takes the role of the mass of the electronic degrees of freedom, whereas k has the role of a force constant regulating the distance between the vectors \mathbf{x} and \mathbf{y} . The equations of motion based on this Lagrangian can be easily derived from

the Euler–Lagrange equation

$$M\ddot{\mathbf{q}} = -\frac{\partial E}{\partial \mathbf{q}} - \frac{\partial E}{\partial \mathbf{y}} \frac{\partial \mathbf{F}}{\partial \mathbf{q}} + k\mu \frac{\partial G}{\partial \mathbf{y}} \frac{\partial \mathbf{F}}{\partial \mathbf{q}}, \quad (2)$$

$$\mu\ddot{\mathbf{x}} = -\frac{\partial E}{\partial \mathbf{y}} \frac{\partial \mathbf{F}}{\partial \mathbf{x}} + k\mu \left[\frac{\partial G}{\partial \mathbf{x}} + \frac{\partial G}{\partial \mathbf{y}} \frac{\partial \mathbf{F}}{\partial \mathbf{x}} \right]. \quad (3)$$

The salient feature of the Lagrangian $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, \mathbf{x}, \dot{\mathbf{x}})$ is that it defines a parameterized set of methods with well-defined properties that can be exploited in efficient numerical algorithms. At the same time, however, it is necessary to choose the parameters in a range that is compatible with the physical system that we want to simulate. For example, with the special choice $\mathbf{y} = \mathbf{x}$ and therefore $G(\|\mathbf{x} - \mathbf{y}\|) = 0$ the Lagrangian in Eq. (1) simplifies to the standard Car–Parrinello Lagrangian with the sole parameter μ , the so called fictitious electron mass. Another choice of the function \mathbf{F} , namely, $\mathbf{y} = \arg \min_{\mathbf{z}} E(\mathbf{q}, \mathbf{z})$, together with the limit $\mu \rightarrow 0$, leads to the two Lagrangians

$$\mathcal{L}_{\text{BO}}(\mathbf{q}, \dot{\mathbf{q}}) = \frac{1}{2} M \dot{\mathbf{q}}^2 - E(\mathbf{q}, \mathbf{y}), \quad (4)$$

$$\mathcal{L}_{\text{x}}(\mathbf{x}, \dot{\mathbf{x}}) = \frac{1}{2} \dot{\mathbf{x}}^2 + kG(\|\mathbf{x} - \mathbf{y}\|). \quad (5)$$

Equations (4) and (5) describe a dynamical system (see Figure 1) where the Lagrangian \mathcal{L}_{BO} is independent of \mathbf{x} and \mathcal{L}_{x} depends on the coordinates \mathbf{q} through the functions \mathbf{y} . These Lagrangians describe BO molecular dynamics (\mathcal{L}_{BO}) and a dynamics for wavefunction initial guesses (\mathcal{L}_{x}). They build the basis for the modern implementations discussed in a later section.

CAR–PARRINELLO MOLECULAR DYNAMICS

The CP method for independent particle models, for example, Kohn–Sham density functional theory or Hartree–Fock method, is based on the Lagrangian

$$\mathcal{L}_{\text{CP}} = \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 + \frac{\mu}{2} \sum_i \langle \dot{\Phi}_i | \dot{\Phi}_i \rangle - E(\mathbf{R}, \{\Phi\}) + \sum_{ij} \lambda_{ij} (\langle \Phi_i | \Phi_j \rangle - \delta_{ij}), \quad (6)$$

where the sums extend over all nuclei with mass M_I and all orbitals Φ_i . The function \mathcal{L}_{CP} also includes the orthogonality constraint for the orbitals. The corresponding equations of motion are

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial E(\mathbf{R}, \{\Phi\})}{\partial \mathbf{R}_I} + \sum_{ij} \lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle \Phi_i | \Phi_j \rangle, \quad (7)$$

$$\mu \ddot{\Phi}_i = -\mathcal{H}(\mathbf{R}, \{\Phi\}) \Phi_i + \sum_j \lambda_{ij} \Phi_j, \quad (8)$$

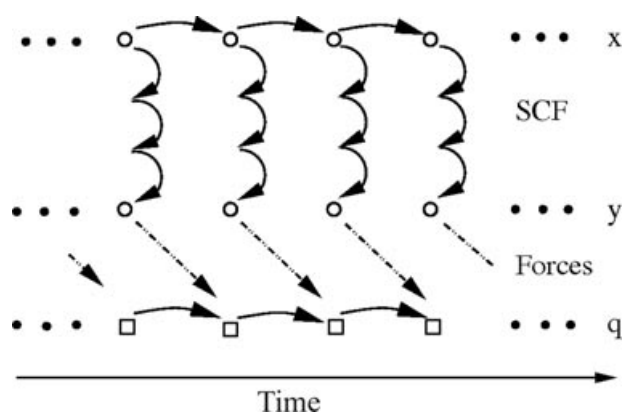


FIGURE 1 | Schematic view of a Born–Oppenheimer-type dynamical system with slow variables \mathbf{q} , propagated initial guess fast variables \mathbf{x} , and optimized fast variables \mathbf{y} .

where $\mathcal{H}(\mathbf{R}, \{\Phi\})$ is the one-particle Hamiltonian. All the forces in Eqs. (7) and (8) can be calculated easily. The nuclear forces are not the BO forces but the sum of Hellmann–Feynman forces and Pulay-type forces for nuclei dependent basis sets, at the current electron density. The constant of motion for this dynamical system is

$$E_{\text{const}} = \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 + \frac{\mu}{2} \sum_i \langle \dot{\Phi}_i | \dot{\Phi}_i \rangle + E(\mathbf{R}, \{\Phi\}), \quad (9)$$

$$= E_{\text{phys}} + \frac{\mu}{2} \sum_i \langle \dot{\Phi}_i | \dot{\Phi}_i \rangle = E_{\text{phys}} + T_e. \quad (10)$$

As the kinetic energy T_e of the electronic degrees of freedom will vary with time, so will E_{phys} , the total energy of the relevant BO system. For a physically meaningful simulation, it is therefore necessary that T_e only performs bound oscillations around a constant small value. The interpretation of this state of the system is that the total CP dynamical system consists of two adiabatically decoupled subsystems, the cold electronic degrees of freedom and the nuclear degrees of freedom at the relevant physical temperature. The adiabatic separation will never be complete and it will be necessary to choose the mass parameter μ in a way that the two systems stay decoupled over the full range of the simulation.^{34,35} However, the choice of μ also directly affects the efficiency of the simulation, as the maximal time step of the numerical integration is proportional to $\sqrt{\mu}$. The choice of an optimal value of the free parameter μ in a CP simulation needs care and has been discussed at length in a series of reviews.^{4,29,30,36}

Car and Parrinello proposed their scheme for Kohn–Sham density functional theory and within a plane wave pseudopotential framework.¹ The CP method was adapted to other electronic structure methods and other basis sets, still the original setup is most popular. There is a good reason for this as basis sets that do not depend on nuclear coordinates lead to equations of motion, Eqs (7) and (8), that can easily be integrated. Another reason is that the CP method requires a frequent calculation of nuclear forces, which can for plane waves, in contrast to atomic basis sets, be done with minimal overhead.³⁰

The original CP method has been further developed in order to increase efficiency and applicability. Multiple time step methods^{37,38} and generalizations that can handle metallic and small band gap systems¹⁵ have been proposed, but their impact has been limited. Another direction of development targeted the orthogonality constraint of the molecular orbitals. It was proposed to either propagate auxiliary function³⁹ that guarantee orthogonality, in the spirit of orbital rotations in wavefunction electronic structure methods, or to propagate nonorthogonal orbitals⁴⁰ and move the orthogonalization step into the energy functional. Although these methods did not have a large impact in applications, they influenced other method development in optimization and linear scaling algorithms.

The most notable development was the introduction of more flexible free parameters μ_i , where we now have a different parameter for each electronic degree of freedom. This was first introduced^{38,41} in combination with plane wave basis sets and later also adapted for Gaussians.⁴² The fictitious mass is made an explicit function of the momentum of the plane wave basis

$$\mu(G) = \begin{cases} \mu_0 & G^2 \leq \alpha, \\ (\mu/\alpha)G^2 & G^2 \geq \alpha. \end{cases} \quad (11)$$

This selective mass scaling reduces the frequency of the high-lying electronic modes without increasing the overlap of the spectra of nuclear and electronic degrees of freedom. It therefore allows for larger time steps in integration without sacrificing the adiabatic decoupling of the two dynamical systems. However, a side effect of this mass rescaling is an increased dependency of the actual dynamics of the nuclei on the fictitious masses μ_i . We will discuss this point in more detail below.

Major progress has been achieved in the combination of the CP method with local basis set methods. There have been early attempts,¹⁰ with varying success, but only more recent developments resulted in efficient schemes. The use of the electronic one-particle

density matrix¹¹ as dynamical degrees of freedom allows the combination with linear scaling algorithms. The idea of circumventing the constraint condition by introducing curvilinear coordinates¹² has also been successfully explored in connection with Gaussian basis sets.

To what extent the two-component CP system reproduces the dynamics and static properties of the physical system defined by the BO potential has been a matter of investigation early on. Theoretical examinations of model systems^{34,35} showed that basic properties such as adiabaticity and the limit to the physical system can be correctly reached. The role of the mass parameter μ on physical quantities has first been discussed by Blöchl and Parrinello⁴³ and later studied extensively by Tangney and Scandolo.^{44,45} Using the frozen orbital approximation, where it is assumed that orbitals follow atoms rigidly, they showed that the CP system is equivalent to

$$(M_I + \Delta M_I) \ddot{\mathbf{R}}_I = F_I^{\text{CP}} \quad (12)$$

with ΔM_I a mass correction that is proportional to μ . The proportionality factor of the mass correction can be calculated in this approximation and is related to the quantum mechanical kinetic energy of the orbital. It is now further assumed that $F_I^{\text{CP}} \approx F_I^{\text{BO}}$, meaning that the CP system moves on average in a potential that is shifted from the BO potential by a constant amount. Under these assumptions results from CP simulations are expected to provide correct static, statistical mechanics, properties,⁴⁶ but will need mass rescaling for dynamical properties. Vibrational frequencies are probably the most investigated dynamical properties and corrections, for the electron mass dependence are good practice in applications of CP simulations. With the availability of more computer resources, it became possible in recent years to converge CP simulations better and therefore to highlight shortcomings of the above interpretation. It was mainly the first peak height of the oxygen–oxygen radial distribution function of liquid water that attracted attention. From the large series of published data, a clear correlation between the mass μ and the height could be inferred. However, the analysis of this effect shows that it is due to the temperature dependence of the radial distribution function. The temperature reported for the microcanonical simulations are statistical averages of the kinetic energy of the atoms. This energy is calculated assuming the physical masses, instead of the rescaled atomic masses as suggested by Eq. (12). If the results of the simulations are corrected for the temperature, almost all reported O–O radial distribution function (RDF) agree within acceptable statistical errors.⁴

If a correct simulation protocol is followed, CP simulations provide static system properties in excellent agreement with corresponding simulations using the BO potential surface directly.⁴⁶ For most systems the errors introduced by the CP method will be far smaller than statistical uncertainties and other errors introduced, for example, by the limited system size or the choice of electronic structure method and basis set. All dynamical quantities need careful rescaling due to the mass effect introduced by μ . This effect exists in all CP simulations independent of the basis sets used.¹² However, the size and structure of the effect will strongly depend on the basis set type.

BORN–OPPENHEIMER MOLECULAR DYNAMICS

The BO scheme derived as a limit of the generalized Lagrangian [Eq. (1)] for a Kohn–Sham density functional scheme is defined by

$$\mathcal{L}_{\text{BO}}(\mathbf{R}, \dot{\mathbf{R}}) = \frac{1}{2} M \dot{\mathbf{R}}^2 - E(\mathbf{R}), \quad (13)$$

$$E(\mathbf{R}) = \min_{\{\Phi\}} \left[E_{\text{KS}}(\mathbf{R}, \{\Phi\}) - \sum_{ij} \lambda_{ij} (\langle \Phi_i | \Phi_j \rangle - \delta_{ij}) \right], \quad (14)$$

$$\mathcal{L}_{\psi}(\psi, \dot{\psi}) = \frac{1}{2} \sum_i \dot{\psi}_i^2 + kG(\{\psi\}, \{\Phi\}). \quad (15)$$

This set of Lagrangians suggests a simple scheme where the nuclei are propagated on the BO surface according to the forces calculated from the derivatives of the optimized Kohn–Sham energy functional, and an independent dynamical system that can be used to propagate an initial guess for the wavefunction. Accuracy and stability of the propagation of nuclei are seemingly independent from the details, initial guess, and optimization method of the electronic structure calculation. Obviously, accuracy of the nuclear forces will be an important factor in the stability of the dynamics. The variational nature of the energy functional guarantees a quadratic dependence of the error in energy on the residual error in wavefunction. However, the derivative with respect to nuclear coordinates will show a linear dependence on the error in wavefunction. A rather tight convergence of wavefunction will be needed and this will require a rather large number of SCF cycles. It is therefore natural to try to reduce the number of self-consistent field (SCF) cycles by using a

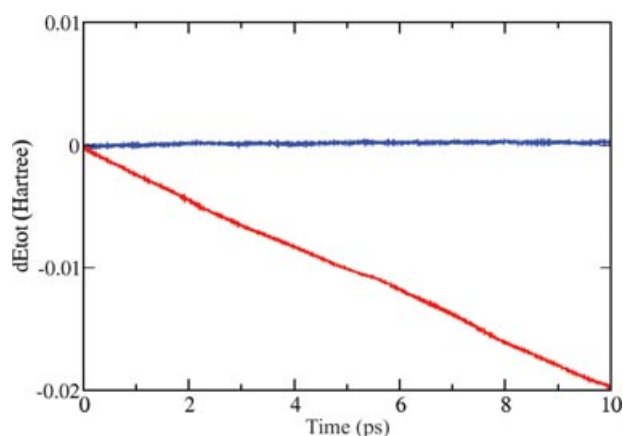


FIGURE 2 | Constant of motion along a 10 ps trajectory calculated using Born–Oppenheimer molecular dynamics. The system is 32 water molecules at 300K and experimental density. The blue line shows the result from a simulation using the always stable predictor–corrector (ASPC) integrator with $K = 3$. The red line is the result from a simulation using a linear extrapolation of density matrix. The convergence criteria was in both cases $\epsilon = 10^{-5}$ (root mean square of orbital transformation gradient⁴⁸). The average number of iterations was 3 for ASPC and 4 for the linear density matrix extrapolation.

cleverly chosen initial wavefunction. A first simple choice would be to use the last optimized wavefunction along the trajectory. However, simulations using this approach have been shown to have large drifts in total energy⁴⁷ (see also Figure 2), even for tight SCF convergence criteria. What is going wrong? This problem has been analyzed by Niklasson and coworkers^{31–33} in a series of papers. They realized that the incomplete SCF convergence leads to errors in the energy and forces of the BO system. Because the forces are calculated under the assumption of complete optimization, i.e., the wavefunction derivatives are neglected,

$$\sum_i \frac{\partial \left(E_{KS} - \sum_{ij} \lambda_{ij} \langle \Phi_i | \Phi_j \rangle \right)}{\partial \Phi_i} \frac{\partial \Phi_i}{\partial \mathbf{R}_I} \approx 0, \quad (16)$$

energy and forces are also no longer fully consistent. This would be, for energies sufficiently close to the BO energy, no real problem if these errors would not depend on the optimization method and initial guess wavefunction. Initial wavefunctions chosen in a non-time-reversible way, for example, by taking the last optimized wavefunction, will transfer this property with the force error to the nuclear dynamics. The nuclear dynamics is therefore no longer time reversible, despite a seemingly time-reversible integration algorithm, and very poor stability of integration results. To cure this problem, a time-reversible propagation of the initial wavefunction has to be chosen.

A time-reversible BO molecular dynamics scheme based on the propagation of one-particle density matrices has been proposed by Niklasson.³³ The equation of motion for the density matrix is

$$\ddot{P} = \omega^2 (D - P). \quad (17)$$

Here, D is the self-consistent, optimized density matrix and the equation of motion corresponds to the choice

$$G(\|D - P\|) = (D - P)^2 \quad (18)$$

in the generalized Lagrangian in Eq. (1). Using a time-reversible Verlet scheme we get an explicit integration of the form

$$P(t + \delta t) = 2P(t) - P(t - \delta t) + \delta t^2 \omega^2 [D(t) - P(t)]. \quad (19)$$

Taking $\kappa = \delta t^2 \omega^2 = 2$ is the original form proposed. Using stability analysis,³³ the largest possible value of κ can be determined. A larger value of κ is desirable, as for a given time step δt , a larger κ corresponds to a stiffer harmonic potential keeping the propagated density matrix P closer to the optimized density matrix D . The largest value of κ that is consistent with stability is the one that guarantees that the distance $D(t) - P(t)$ does not diverge. For the Verlet family of integrators, this optimal value is in fact $\kappa = 2$. Higher-order integrators allow for larger values of κ .

The propagation of wavefunctions expanded in atom-centered basis functions needs special care. It is best to use an extrapolated contra-covariant density matrix PS as a projector on to the occupied subspace⁴⁹:

$$C^P(t + \delta t) = \sum_{m=0}^{K-1} B_m C(t - m\delta t) C^T(t - m\delta t) \times S(t - m\delta t) C(t - \delta t), \quad (20)$$

where $S(t)$ is the overlap matrix, $C(t)$ are the orbital expansion coefficients at time t , and K is the order of extrapolation. An approximate time-reversible predictor–corrector method proposed by Kolafa,⁵⁰ always stable predictor–corrector (ASPC), originally for classical polarizable force fields, can be used. The extrapolation coefficients for this method are

$$B_k = (-1)^m (m+1) \frac{\binom{2K+2}{K-m}}{\binom{2K}{K}}. \quad (21)$$

The coefficients B_k ensure time reversibility to $\mathcal{O}(\delta t^{K+3})$. The corrector associated with this method is

$$C(t) = \omega \arg \min_C E_{KS}(\mathbf{R}, C) + (1 - \omega) C^P(t), \quad (22)$$

with $\omega = (K + 1)/(2K + 1)$. Variations of the above two methods are possible and have been discussed together with, for example, a noise dissipation algorithm^{51–53} for additional stability.

LANGEVIN DYNAMICS

Using a time-reversible BO scheme, as discussed in the last section, allows for efficient and stable dynamics. However, a sufficient accuracy of the nuclear forces is still needed. In systems with slow convergence, this will require many self-consistency cycles and therefore slow down the simulation. For such systems, an algorithm that would allow to relax the accuracy requirements on the forces could bring considerable gains in efficiency.

Based on previous work by Krajewski and Parrinello⁵⁴ on molecular dynamics using noisy forces, Kühne et al.⁵⁵ demonstrated a novel AIMD method that combines Langevin dynamics for the nuclei with time-reversible dynamics for the electronic degrees of freedom and incomplete SCF convergence. The method is based on the observations⁵⁶ that the error of the nuclear forces has a Gaussian distribution, that the autocorrelation function of the force errors decays rapidly, and that the force errors show a

random distribution with respect to the velocities. From these observations (see Figure 3 for an actual example), it was deduced that the canonical distribution can be sampled using a Langevin-type equation:

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_{\text{inc}} - \gamma \dot{\mathbf{R}}_I + [\Xi_I + \Xi_I^{\text{inc}}], \quad (23)$$

where γ is a Langevin friction coefficient and Ξ_I a random noise term, and $\mathbf{F}_{\text{BO}} = \mathbf{F}_{\text{inc}} + \Xi_I^{\text{inc}}$. The force from the incomplete SCF optimization is here denoted by \mathbf{F}_{inc} and the corresponding fully converged force \mathbf{F}_{BO} . Sampling of the Boltzmann distribution requires that the fluctuation dissipation theorem is obeyed

$$\langle \Xi_I(0) \Xi_I(t) \rangle = 6\gamma M_I k_B T \delta(t). \quad (24)$$

In applications, the friction term is split into two contributions $\gamma = \gamma_D + \gamma_L$, where γ_L is taken to be an arbitrary constant and γ_D is determined by requiring that the correct temperature $T = \frac{1}{3k_B} \langle M_I \dot{\mathbf{R}}_I^2 \rangle$ is generated.

If the parameter γ_D can be kept small the Langevin method not only generates the correct canonical distribution but also dynamical properties are accurately described.⁵⁷ In order to achieve this goal, the error of the forces can be consistently reduced by noting that the last self-consistent cycle can be interpreted as a Harris functional.⁵⁸ The missing

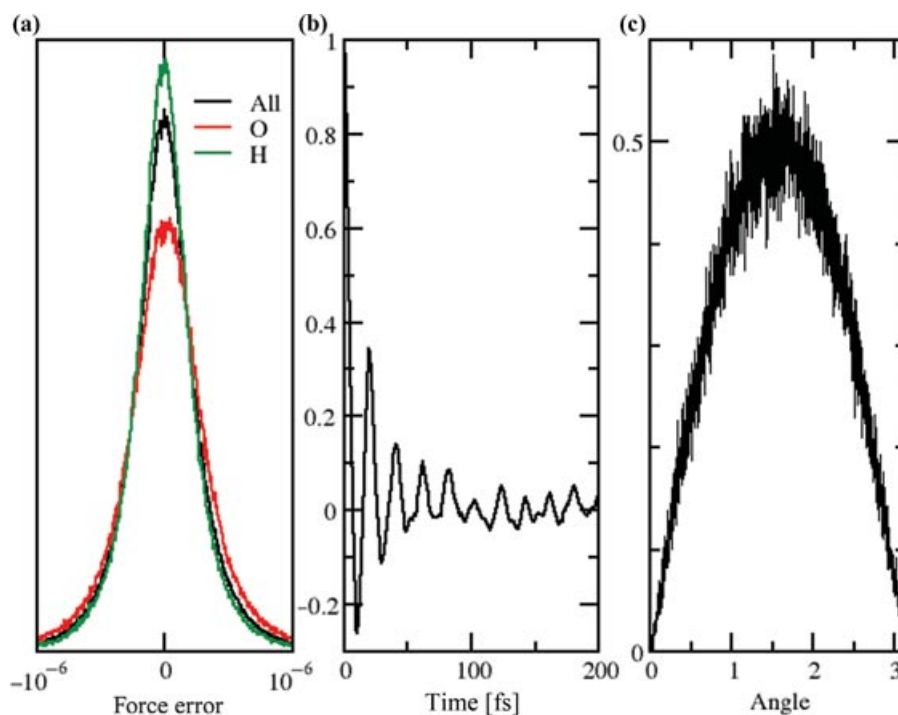


FIGURE 3 | Analysis of error in forces on nuclei from a 1 ps trajectory of 64 water molecules. The error is defined as the difference between a fully converged calculation and a calculation stopped at $\epsilon = 10^{-5}$ (root mean square of orbital transformation gradient⁴⁸). (a) Distribution of error in atomic units on hydrogen (green line), oxygen atoms (red line), and all atoms (black line). (b) Autocorrelation function for the force error vectors. (c) Distribution of angle between force error and atomic velocities.

force $F_{\text{BO}} - F_{\text{inc}}$ can then be approximated to a high degree by

$$-\int \text{d}\mathbf{r} \left\{ \left[\left(\frac{\partial V_{\text{XC}}[\rho_{\text{in}}]}{\partial \rho_{\text{in}}} \right) \Delta\rho + V_{\text{H}}[\Delta\rho] \right] \nabla_I \rho_{\text{in}} \right\}, \quad (25)$$

where $\Delta\rho$ is the difference between input ρ_{in} and output density, and V_{XC} and V_{H} are the exchange–correlation and Hartree potential, respectively.

This method has been applied in a number of applications.^{55,57} The largest gains were achieved for metallic systems but also for the simulation of liquid water the Langevin dynamics provides additional efficiency. The Langevin dynamics method for AIMD is not yet fully explored. The parameter γ_D used in the method has to be investigated further. It is reasonable to expect that γ_D should change if the system undergoes large changes, for example, in phase transitions or global chemical reactions. For heterogeneous systems, one would also expect that γ_D should be position dependent. This can already be seen in Figure 3 where for water slightly different error distributions in the forces on oxygen and hydrogen atoms are reported. A scheme that would dynamically adjust atomic friction forces would probably be the ultimate goal.

SUMMARY

The combination of classical molecular dynamics with on-the-fly calculation of atomic interaction potentials from electronic structure theory has become an important simulation technique in many branches of computational molecular science.⁴ The method introduced by Car and Parrinello¹ in 1985 completely changed the way the AIMD method was looked at and transformed it from a theoretical concept to an applicable tool. The concept of mapping classical molecu-

lar dynamics and self-consistent field electronic structure method onto a two-component classical system proved to be much more than just a clever trick. It was the first realization of a wider class of methods that allow the stable and efficient molecular dynamics simulation of atomistic systems with first principles interaction potentials. Only in recent years has time-reversible BO dynamics,³³ another realization of the same underlying general idea, surpassed the CP method. It provides higher accuracy, meaning follows the BO surface closer, and easier access to dynamical properties, while keeping the same stability and efficiency standards. The Langevin method⁵⁵ was created to further increase computational efficiency by compensating the effect of slightly inaccurate forces with a dissipative term in the nuclear dynamics. Despite impressive applications, it is not yet clear if this new method will be applicable for general systems.

The impact of AIMD simulations and with it of the CP method on the simulation community cannot be overestimated. Besides opening a new way of solving an important class of problems, it introduced statistical mechanics beyond simple transition-state theory to the electronic structure community and made systems that undergo rearrangements in the electronic structure accessible to the molecular dynamics community. Progress in theoretical predictions of heterogeneous,⁵⁹ homogeneous,⁶⁰ and enzymatic catalysis⁶¹ is tightly connected to AIMD as is for example the prediction of the structure of matter under extreme conditions.⁶² Algorithmic advances in combination with increased computational resources have made AIMD simulations available to the extended scientific community, and AIMD has finally completed the transition from a specialty method to a standard tool of computational molecular science.

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