Efficient Formalism for Large-Scale *Ab Initio* Molecular Dynamics based on Time-Dependent Density Functional Theory

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A new "on the fly" method to perform Born-Oppenheimer *ab initio* molecular dynamics (AIMD) simulations is presented. Inspired by Ehrenfest dynamics in time-dependent density functional theory, the electronic orbitals are evolved by a Schrödinger-like equation, where the orbital time derivative is multiplied by a parameter. This parameter controls the time scale of the fictitious electronic motion and speeds up the calculations with respect to standard Ehrenfest dynamics. In contrast with other methods, wave function orthogonality needs not be imposed as it is automatically preserved, which is of paramount relevance for large-scale AIMD simulations.

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Ab initio molecular dynamics (AIMD) on the ground state Born-Oppenheimer (gsBOMD) potential energy surface for the nuclei has become a standard tool for simulating the conformational behavior of molecules, bio- and nanostructures, and condensed matter systems from first principles [1]. However, gsBOMD (in the DFT [2] picture) requires that the Kohn-Sham (KS) energy functional be minimized for each value of the nuclei positions. As this minimization can be very demanding, Car and Parrinello (CP) [3] proposed an elegant and efficient "on the fly" scheme in which the KS orbitals are propagated with a fictitious dynamics that mimics gsBOMD. Although the CP method has had a tremendous impact in many scientific areas [4,5], and recently new methods have been reported to reduce the computational expenses even more [6], the cost associated with the wave function orthogonalization is still a potential bottleneck for both gsBOMD and CP that hinders the application of these methods to large-scale simulations, such as those of interest in biochemistry or materials science.

Time-dependent density functional theory (TDDFT) [7,8] has been for a long time recognized as an orthogonalization-free alternative for both ground state [9] and excited state AIMD. In its simplest implementation, Ehrenfest TDDFT, the ions are treated classically following electronic Hellmann-Feynman forces. For systems where the gap between the ground and the first excited state is large, Ehrenfest tends to gsBOMD and can mimic adiabatic dynamics [1]. However, the rapid movement of the electrons in TDDFT requires the use of a very small time step, which, in many occasions, renders its numerical application nonpractical [10].

In this Letter, we borrow some of the ideas of CP and introduce a new TDDFT Ehrenfest dynamics that reduces the cost of AIMD simulations while keeping the accuracy of the results in tolerable levels, similar to CP. The whole scheme can be obtained from the following Lagrangian (atomic units are used throughout this Letter):

$$\mathcal{L} = i\frac{\mu}{2}\sum_{j=1}^{N}\int(\phi_j^*\dot{\phi}_j - \dot{\phi}_j^*\phi_j)d\boldsymbol{r} + K_I - E[\phi, R], \quad (1)$$

where $K_I = \frac{1}{2}\sum_I M_I\dot{\boldsymbol{R}}_I\cdot\dot{\boldsymbol{R}}_I$ is the kinetic energy of the nuclei, M_I their masses and E the KS energy. Note that the major modification with respect to TDDFT is the scaling of the electronic velocities by a parameter μ (TDDFT is recovered when $\mu = 1$). We show in what follows that, in the $\mu \to 0$ limit, the trajectories of the system approach gsBOMD, and practical calculations can be done for values of $\mu \gg 1$, thus allowing for more efficient implementations than TDDFT while retaining its advantageous properties: the conservation of the total energy and of the orthogonality of the orbitals. Also, from the computational point of view, the new scheme is simple and can be easily incorporated into existing codes.

The equations of motion obtained from (1) for the electronic (ϕ_j) and nuclear ($\boldsymbol{R}_I$) degrees of freedom are

$$i\mu\dot{\phi}_j = \frac{\delta E[\phi, R]}{\delta\phi_j^*} = -\frac{1}{2}\nabla^2\phi_j + v_{\text{eff}}(\boldsymbol{r}, t)\phi_j, \quad (2a)$$

$$M_I\ddot{\boldsymbol{R}}_I = -\boldsymbol{\nabla}_I E[\phi, R], \quad (2b)$$

where v_{eff} is the time-dependent KS effective potential.

In contrast to CP, the new dynamics conserves the physical energy $E_{\text{phys}} := K_I + E[\phi, R]$ as well as the scalar product among the orbitals ϕ_j. The first is a direct consequence of $\mathcal{L}$ being linear in the velocities $\dot{\phi}_j$ and $\dot{\phi}_j^*$, and not depending explicitly on t. The conservation of

the scalar product requires more attention due to the nonlinear character of the term $\delta E/\delta\phi_j^*$. To prove it, note that $E[\phi, R]$ is invariant under any unitary transformation mixing the orbitals $\phi \rightarrow U\phi$, with $U = e^{-i(\varepsilon/\mu)A}$, being A an $N \times N$ Hermitian matrix. From this invariance and Eq. (2), we have

$$\begin{aligned}\frac{d}{dt}\int A_{jk}\phi_j^*\phi_k d\boldsymbol{r} &= \int (A_{jk}\dot{\phi}_j^*\phi_k + A_{jk}\phi_j^*\dot{\phi}_k)d\boldsymbol{r} \\ &= -\frac{i}{\mu}\int\left(A_{jk}\frac{\delta E}{\delta\phi_j}\phi_k - A_{jk}\phi_j^*\frac{\delta E}{\delta\phi_k^*}\right)d\boldsymbol{r} \\ &= \frac{d}{d\varepsilon}E[e^{-i(\varepsilon/\mu)A}\phi, R]|_{\varepsilon=0} \\ &= 0. \end{aligned} \tag{3}$$

Now, since $\int A_{jk}\phi_j^*\phi_k d\boldsymbol{r}$ is constant for all $A = A^\dagger$, the scalar product of any pair ϕ_j, ϕ_k is a constant as well. Hence, starting from an orthonormal set, we will not have to reorthonormalize the orbitals during the MD simulation. Numerically, this means that the formal scaling of the new scheme is quadratic with the number of atoms, while for CP and gsBOMD it is cubic [11]. In addition, the time propagation is naturally parallelizable by distributing the orbitals in different processors, as the evolution of each orbital is almost independent from that of the others.

An important question is whether the new method reproduces gsBOMD. We show that the $\mu \rightarrow 0$ limit accounts for this solution. To do so, we recall that the BO Lagrangian reads

$$\mathcal{L}_{\mathrm{BO}} = K_I - E[\phi, R] + \sum_{jk}\Lambda_{jk}^{\mathrm{BO}}\left(\int \phi_j^*\phi_k d\boldsymbol{r} - \delta_{jk}\right), \tag{4}$$

where $\Lambda_{jk}^{\mathrm{BO}}$ are the Lagrange multipliers which ensure the orthonormality of the orbitals. Clearly, as the orthonormality is automatically satisfied by the propagator in our approach, the limit $\mu \rightarrow 0$ gives the BO Lagrangian without the Λ^{BO} term. Note, however, that one could have started from a different Lagrangian $\mathcal{L}' = \mathcal{L} + \sum_{jk}\Lambda_{jk}(\int \phi_j^*\phi_k d\boldsymbol{r} - \delta_{jk})$ for which the $\mu \rightarrow 0$ limit is $\mathcal{L}_{\mathrm{BO}}$, and then, using (for $\mu \neq 0$) the gauge symmetry of $\mathcal{L}'$ ($\phi' = e^{iA}\phi$ and $\Lambda' = e^{iA}\Lambda e^{-iA} - i\mu e^{iA}\frac{d}{dt}e^{-iA}$), where A is a time-dependent Hermitian matrix, one can send Λ' to zero recovering the dynamics of $\mathcal{L}$.

Next, to provide an estimation of the performance improvements of our method in comparison with Ehrenfest dynamics, we write the left-hand side of (2a) as $\mu(d\phi/dt) = d\phi/dt_e$. With this transformation, (2a) can be seen as a standard TDDFT propagation, and the maximum time step for our method in terms of μ is $\Delta t = \mu\Delta t_e$, where Δt_e is the maximum electronic time step, determined by the system and the propagation scheme. In the case of CP, on the other hand, $\Delta t \propto \sqrt{\mu_{\mathrm{CP}}}$. Note, however, that this difference does not imply anything about the relative performance of both methods, since the two parameters are not directly comparable (e.g., they have different dimensions). The dependence of the accuracy on μ must also be taken into account, as we show later. Additionally, the ionic motion imposes a constraint in the maximum value of Δt, but usually this limit is much higher.

Now, although our method approaches the reference gsBOMD as $\mu \rightarrow 0$, this limit is not practical from a numerical point of view because it implies a time step $\Delta t \rightarrow 0$. But, as $\mu = 1$ is already close to gsBOMD for large gap systems, we shall mainly focus on how close we can stay to this limit for $\mu \gg 1$. In this regime, numerical simulations are in principle μ times faster than standard TDDFT, so we first made a detailed study of how large can μ be in CP and Ehrenfest for a simple two-band model (see supplementary material [12]), to conclude that the new scheme shows a performance similar to CP.

To further investigate in real systems the efficiency of the new approach, we implemented it, together with CP, in the first principle OCTOPUS code [13]. For Ehrenfest dynamics, the approximated enforced time reversal symmetry method [14] is used to propagate the electronic wave functions. In the case of CP, the electronic part is integrated by a RATTLE velocity verlet algorithm described in Ref. [15]. In both cases, the velocity Verlet algorithm is used for the ionic equations of motion. The ions are represented using norm-conserving pseudopotentials and the exchange correlation term is approximated by the adiabatic local-density approximation (LDA) functional.

With respect to implementation there are some differences to remark. For Ehrenfest, the propagation must be performed using complex wave functions while for CP it can be performed using real wave functions for finite systems or for gamma point supercell calculations in periodic systems. Also, due to the second order dynamic of CP, two sets of wave functions must be propagated while only one is needed for Ehrenfest. Finally, in the velocity Verlet algorithm, a temporary third set of wave functions is required to store the previous time step.

In parallel architectures, CP methods are known to scale very well based on domain descomposition [16]. This also applies to Ehrenfest dynamics and, on top of that, we can add a new level of parallelization by distributing groups of different states among processors. As the evolution of each state is independent, this is a very effective approach where communication is only required to calculate quantities that involve sums over all states, like the density or the forces. As these operations are performed only once per time step, it can scale efficiently even over slow interconnections. In the case of CP, due to orthogonalization between states, this parallelization scheme is more complex to implement [17] and requires much more communication.

The first real system we simulated was the nitrogen molecule (see supplementary material [12]). We observed that, for $\mu = 20$, the simulation remains steadily close to the BO potential energy surface, and there is only a 3.4% deviation of the vibrational frequency. For $\mu = 30$ the

TABLE I. Selected vibrational frequencies (in cm^{-1}) for the benzene molecule, obtained using different values of μ.

$\mu = 1$	398	961	1209	1623	3058
$\mu = 5$	396	958	1204	1620	3040
$\mu = 10$	391	928	1185	1611	2969
$\mu = 15$	381	938	1181	1597	2862

system starts to strongly separate from the gsBO surface by mixing with higher BO surfaces.

Next, we applied the method to the benzene molecule. We set up the atoms in the equilibrium geometry with a random Maxwell-Boltzmann distribution for 300 K. Each run was propagated for a period of time of ~400 fs with a time step of $\mu \times 0.001$ fs (that provides a reasonable convergence in the spectra). In Table I, we show some low, medium, and high frequencies of benzene as a function of μ. The general trend is a redshift of the frequencies with a maximum deviation of 7% for $\mu = 15$. Still, to make a direct comparison with experiment, we computed the infrared spectra. In Fig. 1, we show how the spectra changes with μ. For large μ, besides the redshift, spurious peaks appear above the higher vibrational frequency (not shown). We performed equivalent CP calculations for different values of μ_{CP}, and found that, as shown in Fig. 1, it is possible to compare the physical error induced in both methods and establish and a relation between μ and μ_{CP}.

Having established this link, we address the numerical performance of our new method compared to CP in terms of system size. To do this, we simulate several benzene molecules in a cell. For the new scheme, a value of $\mu = 15$ is used while for CP $\mu_{CP} = 750$, (values that yield a similar deviation from the BO surface, according to Fig. 1). The time steps used are 3.15 and 7.26 a.u., respectively. The results are shown in Fig. 2. In the serial case, CP is 3.5 times faster for small systems, but the difference reduces to only 1.7 times faster for the larger ones. Extrapolating the results, we predict that the new dynamics will become less demanding than CP for around 1100 atoms. In the parallel case, the difference is reduced, CP being only 2 times faster than our method for small systems, and with a crossing point below 750 atoms. This is due to the better scalability of the Ehrenfest approach, as seen on Fig. 2(c). Moreover, memory requirements for our approach are lower than for CP: in the case of 480 atoms the ground state calculation requires a maximum of

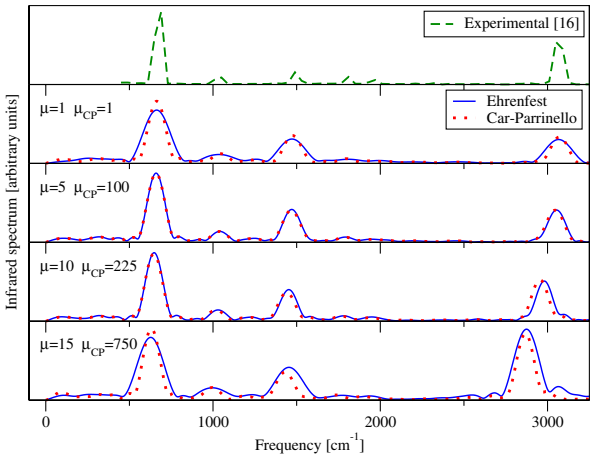

FIG. 1 (color online). Calculated infrared spectrum for benzene for different values of μ, compared to CP dynamics and to experiment [19].

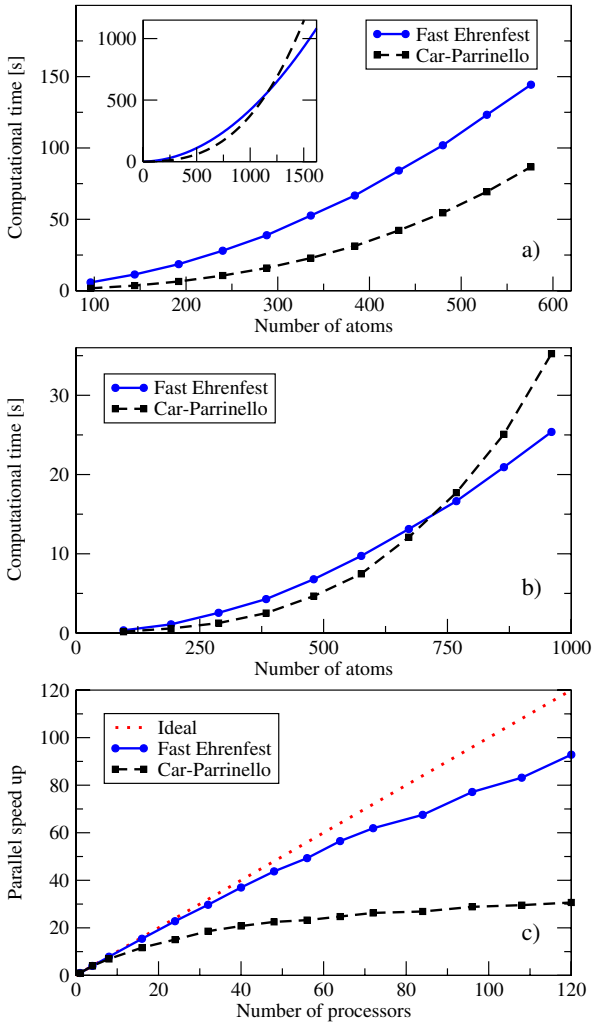

FIG. 2 (color online). Computational performance comparisons of our method and CP for an array of benzene molecules with finite boundary conditions and a spacing of 0.6 a.u. Performance is measured as the computational time required to propagate 1 a.u. of time. (a) Single processor computational cost for different system sizes. (Inset) Polynomial extrapolation for larger systems. Performed in one core of an Intel Xeon E5435 processor. (b) Parallel computational cost for different system sizes. Performed in 32 × Intel Itanium 2 (1.66 GHz) processor cores of a SGI Altix. (c) Parallel scaling with respect to the number of processor for a system of 480 atoms in a SGI Altix system. In both cases a mixed states-domain parallelization is used to maximize the performance.

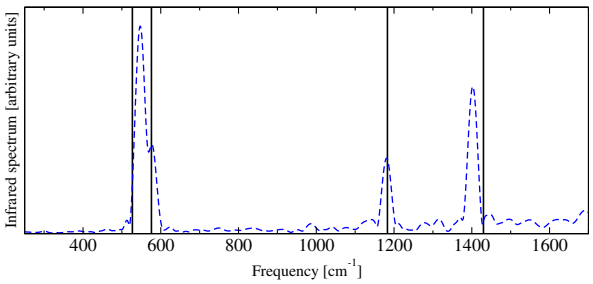

FIG. 3 (color online). Infrared spectrum of C_{60}. The (blue) dashed line corresponds to the calculated one ($\mu = 5$ and 2 ps of time) while the black bars are the experimental values from Ref. [20].

3.5 GB, whereas in the MD, Ehrenfest requires 5.6 GB and CP 10.5 GB.

Finally, we illustrate our method (using $\mu = 5$) for the calculation of the infrared spectrum of a prototype molecule, C_{60}. The calculated IR spectra is in very good agreement with the experiment (see Fig. 3) for low and high energy peaks (which are the most sensitive to μ as seen in Fig. 1). The result is robust and independent of the initial condition of the simulation. The low energy splitting of IR spectrum starts to be resolved for simulations longer than 2 ps.

In conclusion, we have presented a new approach to AIMD based on a generalization of TDDFT Ehrenfest dynamics. Our approach introduces a parameter μ that controls the trade-off between the closeness of the simulation to the gsBO surface and the numerical cost of the calculation, analogously to the role of the fictitious electronic mass in CP. We have made direct comparisons of the numerical performance with CP, proving that our method can outperform CP in some relevant cases, namely, for large-scale systems that can only be studied from first principles MD in massively parallel computers. To increase its applicability, it would also be important to study if the improvements developed to optimize CP can be combined with our approach [6], in particular, techniques to treat small-gap or metallic systems [18]. Finally, note that the introduction of the parameter μ changes the time scale of the motion of the electrons with respect to the Ehrenfest case, which implies a shift in the electronic excitation energies. This must be taken into account when we extend the applicability of our method for non-adiabatic MD and MD under electromagnetic fields, in particular, for the case of Raman spectroscopy, general resonant vibrational spectroscopy, and laser induced molecular bond rearrangement (work in progress).

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[11] Assuming no linear scaling techniques are used. Note that these techniques could also be combined with our method, where the orthogonalization-free propagation would be reflected in a smaller scaling prefactor.
[12] See EPAPS Document No. E-PRLTAO-101-060836 for a PDF document containing simulations in simple systems (a toy model and the N2 molecule) that complement the more intensive calculations found in the Letter. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
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