Speeding-up \textit{Ab Initio} Molecular Dynamics with Hybrid Functionals using Adaptively Compressed Exchange Operator based Multiple Timestepping

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\textit{Ab initio} molecular dynamics (AIMD) simulations using hybrid density functionals and plane waves are of great interest owing to the accuracy of this approach in treating condensed matter systems. On the other hand, such AIMD calculations are not routinely carried out since the computational cost involved in applying the Hartree Fock exchange operator is very high. In this work, we make use of a strategy that combines adaptively compressed exchange operator formulation and multiple time step integration to significantly reduce the computational cost of these simulations. We demonstrate the efficiency of this approach for a realistic condensed matter system.

\textit{Ab initio} molecular dynamics (AIMD) simulations with density functional theory (DFT) and plane wave (PW) basis set are the methods of choice in studying structural and dynamic properties of condensed matter systems. Usage of density functionals at the level of Generalized Gradient Approximation (GGA) is commonplace for these simulations because more than a million energy and force evaluations are computationally achievable by taking advantage of parallel programs and parallel computing platforms. Contrarily, hybrid density functionals are preferred over GGA functionals for improved accuracy in AIMD simulations. \textsuperscript{2} \textsuperscript{3} Computations of energy and gradients at the hybrid functional level using PW basis set have prohibitively high computational cost resulting from the application of the exact exchange operator on each of the occupied orbitals. One of the ways to increase the efficiency of such AIMD simulations is by making use of multiple time step (MTS) algorithms among others. \textsuperscript{6} \textsuperscript{7} In this respect, the reversible reference system propagator algorithm (r-RESPA) \textsuperscript{4} \textsuperscript{5} has been used by several authors. \textsuperscript{8} \textsuperscript{9} In the r-RESPA MTS approach, artificial time scale separation in the ionic force components due to computationally intensive Hartree Fock exchange (HFX) contribution and the computationally cheaper rest of the terms is made. \textsuperscript{10} \textsuperscript{11} In this manner, MTS scheme allows us to compute HFX contributions less frequently compared to the rest of the contributions to the force, thereby reducing the overall computational cost in performing AIMD simulations.

Here we propose a new way to take advantage of the r-RESPA scheme for performing AIMD using hybrid functionals and PWs. This scheme is based on the recently developed adaptively compressed exchange (ACE) operator approach. \textsuperscript{16} \textsuperscript{17} We exploited some property of the ACE operator to artificially split the ionic forces into fast and slow.

The self consistent field (SCF) solution of hybrid functional based Kohn-Sham (KS) DFT equations requires application of the exchange operator $V_X = -\sum_{j}^{N_{orb}} \frac{|\psi_j\rangle \langle \psi_i|}{(r_{12})}$ on each of the KS orbitals $|\psi_i\rangle$:

$$V_X|\psi_i\rangle = -\sum_{j}^{N_{orb}} |\psi_j\rangle \langle \psi_j| \frac{1}{(r_{12})} |\psi_i\rangle, \quad i = 1, ..., N_{orb}. \quad (1)$$

Here, $N_{orb}$ is the total number of occupied orbitals. The evaluation of $\langle \psi_j| \frac{1}{(r_{12})} |\psi_i\rangle$ is usually done in reciprocal space using Fourier transform (FT). If $N_G$ is the total number of PWs, the computational cost for doing FT scales as $N_G \log N_G$ on using fast Fourier transform (FFT) algorithm. The total computational cost scales as $N_{2_{orb}} N_G \log N_G$, \textsuperscript{18} as operation of $V_X$ on all the KS orbitals requires $N_{2_{orb}}$ times evaluation of $\langle \psi_j| \frac{1}{(r_{12})} |\psi_i\rangle$.

In the recently developed ACE operator formulation, \textsuperscript{16} the full rank $V_X$ operator is approximated by the ACE operator $V_X^{ACE} = -\sum_{k}^{N_{orb}} |P_k\rangle \langle P_k|$ using a low rank decomposition. Here, $\{P_k\}$ is the set of ACE projection vectors which can be computed through a series of simpler linear algebra operations. Now, the evaluation of the action of $V_X^{ACE}$ operator on KS orbitals can be done with $N_{2_{orb}}$ number of simpler inner products as

$$V_X^{ACE}|\psi_i\rangle = -\sum_{k}^{N_{orb}} |P_k\rangle \langle P_k|\psi_i\rangle, \quad i = 1, ..., N_{orb}. \quad (2)$$

The advantage of the ACE approach is that the cost of applying the $V_X^{ACE}$ operator on each KS orbitals is much less as compared to $V_X$ operator. At the first SCF step, $V_X^{ACE}$ operator can be constructed through the computation of $\{V_X|\psi_i\rangle\}$, which is the costliest step ($N_{orb}$ times evaluation of $\langle \psi_j| \frac{1}{(r_{12})} |\psi_i\rangle$). As HFX has only a minor contribution to the total energy, an approximate energy computation is possible by using the previously constructed $V_X^{ACE}$ operator without updating it for the rest of the SCF iterations. It is again stated that, once the $V_X^{ACE}$ operator is constructed, its low rank structure allows the easy computation of $\{V_X^{ACE}|\psi_i\rangle\}$ in the subsequent SCF iterations. We exploit this property of the ACE operator to combine with the r-RESPA scheme.

In the r-RESPA method, \textsuperscript{a} symmetric Trotter factorization of the classical time evolution operator is carried out. Let that ionic force can be decomposed into slow and fast
components as $F_K = F_{\text{fast}}^K + F_{\text{slow}}^K$, $K = 1, \ldots, 3N$, for a system containing $N$ atoms. In this case, the Liouville operator $L$ can be written as

$$iL = iL_1^{\text{fast}} + iL_2^{\text{fast}} + iL^{\text{slow}},$$

with

$$iL_1^{\text{fast}} = \sum_{K=1}^{3N} \left[ \dot{X}_K \frac{\partial}{\partial X_K} \right], \quad iL_2^{\text{fast}} = \sum_{K=1}^{3N} \left[ F_K^{\text{fast}} \frac{\partial}{\partial P_K} \right] \quad (4)$$

and

$$iL^{\text{slow}} = \sum_{K=1}^{3N} \left[ F_K^{\text{slow}} \frac{\partial}{\partial P_K} \right]. \quad (5)$$

Here, $\{X_K\}$ and $\{P_K\}$ are the Cartesian coordinates and the conjugate momenta of the particles. Using symmetric Trotter factorization, we arrive at

$$\exp(iL\Delta t) \approx \exp \left( iL^{\text{slow}} \frac{\Delta t}{2} \right) \times \left[ \exp \left( iL_2^{\text{fast}} \frac{\Delta t}{2} \right) \exp \left( iL_1^{\text{fast}} \frac{\Delta t}{2} \right) \exp \left( iL_2^{\text{slow}} \frac{\Delta t}{2} \right) \right]^n \times \exp \left( iL^{\text{slow}} \frac{\Delta t}{2} \right). \quad (6)$$

Here, the large time step $\Delta t$ is chosen according to the time scale of variation of slow forces ($\{F_{\text{slow}}^K\}$) and the smaller time step $\delta t = \Delta t/n$ is chosen according to the time scale of fast forces ($\{F_{\text{fast}}^K\}$).

Now, we split the contribution of ionic forces from the HFX part as

$$F_K^{\text{hybrid}} = F_K^{\text{ACE}} + \Delta F_K, \quad K = 1, \ldots, 3N \quad (7)$$

with $\Delta F_K = \left( F_K^{\text{hybrid}} - F_K^{\text{ACE}} \right)$. Here, $F_K^{\text{hybrid}}$ is the ionic force computed with the full rank exchange operator $V_X$. The term $F_K^{\text{ACE}}$ is the ionic force calculated using the low rank $V_X^{\text{ACE}}$ operator. In Figures (a) and (b) we have shown the components of the $F_K^{\text{ACE}}$ and $\Delta F$ for a realistic molecular system, where $V_X^{\text{ACE}}$ is calculated once at the beginning of a SCF while kept fixed during the remaining SCF cycles. The clear difference in the time scale at which the two forces are varying allowed us to use $F_K^{\text{ACE}}$ as the fast ionic force and $\Delta F$ as the slow ionic force, and combine it with the r-RESPA algorithm. Here, the longer time step $\Delta t$ is chosen according to the time scale of variation of the computationally costly slow forces, whereas the smaller time step $\delta t$ is taken as per the time scale of fast forces that are cheaper to compute. In this way, we get the required speed-up using the r-RESPA algorithm.

To benchmark our implementation, we first compared the fluctuations in total energy using conventional velocity Verlet (VV) integrator and MTS runs (MTS-n) with $n = \Delta t/\delta t$, and $\delta t \approx 0.5$ fs for 32-water in a periodic box treated by PBE0 functional. The magnitude of the total

![FIG. 1. Test results for 32-water system using PBE0 functional](image)

- One of the components of $F_{\text{ACE}}$ and $\Delta F$ on an arbitrarily chosen (a) oxygen and (b) hydrogen atoms; (c) Comparison of potential energy during VV, MTS-5 and MTS-15 simulations in NVE ensemble; (d) $\log_{10}(\Delta E)$ for different $\Delta t$ values in VV and MTS simulations calculated from 5 ps long trajectories.
Figure to the increase in total energy fluctuations as shown in runs, log_{10} \langle \cdot \cdot \cdot \rangle).

In order to show the correctness of our proposed MTS scheme, we compared the fluctuation in potential energy for VV, MTS-5 and MTS-15 runs for a short initial time period for the 32-water system (before the trajectories deviate due to growing numerical differences) in VV/MTS-n runs. This average is calculated over 1000 MD steps.

The quality of the energy conservation in these runs depends on the value of n, which determines how large the outer timestep is compared to the inner timestep. It is clear from Figure 1(d) that MTS-n runs with n up to 15 have total energy conservation comparable to VV run using a timestep 1.4 fs. Although the MTS-30 run (with \Delta t = 14.4 fs) was showing higher total energy fluctuation, it was able to generate stable MD trajectories. Notably, we observed good accuracy in MTS runs with n = 15 (i.e. MTS-15); (see Table II).

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Thus, we conclude that our method gives accurate description of the structural and dynamical properties. In conclusion, we presented a new scheme in using rRESPA to perform hybrid functional based AIMD simulations with PW basis set. This involves artificial splitting in the nuclear forces envisaged by the recently developed ACE approach. Our benchmark results for liquid water show that stable and accurate MD trajectories can be obtained through this procedure. For the specific case of 32-water system, a computational speed-up up to 7 could be obtained. We hope that this approach will enable us to compute long accurate AIMD trajectories at the level of hybrid DFT. Further systematic improvement can be made to speed-up this approach, in particular the construction of ACE operator is beyond the scope of this work.

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