Time-Reversible *ab initio* Molecular Dynamics

Anders M. N. Niklasson, T-1; C. J. Tymczak, Texas Southern University; Matt Challacombe, T-12

In classical molecular dynamics (MD) it is well known that computational schemes are improved significantly by imposing time-reversal symmetry on the integration of Newton's equations of motion. However, in *ab initio* Born-Oppenheimer MD, based on self-consistent field (SCF) theory, a time-reversible integration of the nuclear motion is problematic. In Born-Oppenheimer MD the electronic degrees of freedom, e.g., the density $\rho(t)$, is propagated by an extrapolation from previous time steps, $\rho(t - n\delta t)$. This is necessary to provide an accurate initial guess for the SCF optimization, which constrains the solution to the Born-Oppenheimer potential energy surface. A good initial guess often reduces the computational cost by an order of magnitude. The electron extrapolation from previous time steps combined with the SCF optimization constitutes an adiabatic propagation of the electronic degrees of freedom,

$$\rho(t + \delta t) = SCF[\rho(t), \rho(t - \delta t), \ldots] \,. \qquad (1)$$

Unfortunately, Eq. (1) is inconsistent with a time-reversible dynamics because of the nonlinearity and irreversibility of the SCF procedure. The remedy for this problem was previously to force the SCF optimization to a very high degree of accuracy, which is computationally expensive. At "exact" SCF convergence the optimized density is independent of the input density and there is therefore no longer a "propagation" of the density. However, a more efficient approach would be to keep the electron propagation, but with a restored time-reversal symmetry. This was achieved with the introduction of time-reversible Born-Oppenheimer MD [1].

The principle of lossless time-reversible dual channel integration of the electronic degrees of freedom is illustrated in Fig. 1. The idea is to replace the irreversible adiabatic propagation of the electron density in Eq. (1) by a dual filter procedure with an additional auxiliary density channel denoted by a tilde. The scheme is perfectly reversible, despite the irreversibility of the SCF procedure.

Figure 2 illustrates the effect of replacing a lossy linear extrapolation scheme with a time-reversible lossless linear integration.

The key advantage with time-reversible Born-Oppenheimer MD is the improved global energy stability even under approximate SCF convergence. The computational cost can therefore be substantially reduced.

This work demonstrates a first step toward a new class of time-reversible and symplectic integrators that previously was limited only to classical MD. We hope that further development may lead to new standards for large-scale *ab initio* MD simulations.

For further information contact Anders Niklasson at amn@lanl.gov.

[1] A.M.N. Niklasson, et al., *Phys. Rev. Lett.* **97**, 123001 (2006).

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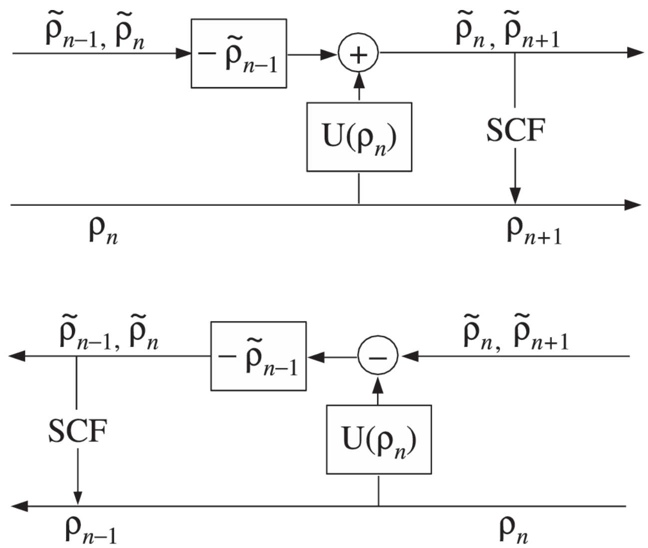

Fig. 1.
The principle of lossless dual-channel filter integration. The propagation is driven by the update filter U, where $\tilde{\rho}_{n+1} = U[\rho n] - \tilde{\rho}_{n-1}$ and $\rho_n = \widetilde{SCF}[\rho_n]$. The filter scheme is perfectly reversible, either by going backwards and changing the ⊕ sign to a – sign, or equivalently, by changing δt to –δt.

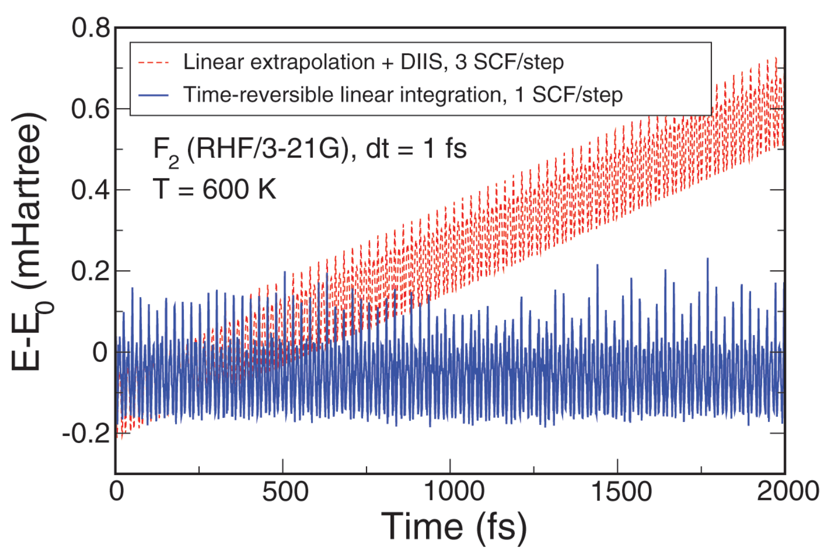

Fig. 2.
The energy fluctuations around the starting energy E_0 as a function of time for a F_2 molecule at a temperature T ≈ 600K (Hartree-Fock theory with a Gaussian basis set RHF/3-21G and time steps δt = 1 fs).