An Efficient and Accurate Car-Parrinello-like Approach to Born-Oppenheimer Molecular Dynamics

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We present a new method to accelerate density functional theory-based ab-initio molecular dynamics simulations. In the spirit of the Car-Parrinello [1] approach, the method circumvents the need to perform fully self-consistent electronic structure calculations. However, in contrast to the original scheme, large integration time steps can be used. To achieve this, we propagate the electronic degrees of freedom in terms of the contra-covariant density matrix in a nearly time-reversible manner by applying the always stable predictor-corrector method [2]. The corrector consists of a single preconditioned minimization step using the idempotency conserving orbital transformation method [3]. In this way sizable minimization steps can be taken, which guarantees that the propagation is performed within a small skin very close to its instantaneous ground state.

Although the applied non-self-consistent energy functional is not variational, the energies thus calculated are a strict upper bound. Deviations from the Born-Oppenheimer surface are small and, more importantly constant, which implies that energy differences are portrayed with great accuracy.

In spite of these excellent properties the incomplete energy minimization and the use of a non-symplectic integrator for the electronic degrees of freedom induces a small dissipative drift. Inspired by ideas of Krajewski and Parrinello [4] we show how this can be rigorously corrected using a properly modified Langevin equation, which leads to correct sampling of the Boltzmann distribution. Furthermore the friction term is so small that the dynamics is also properly reproduced. The method works well irrespective of system type and band gap, so it is very efficient even in simulating large metallic systems.

We implemented these ideas in the mixed Gaussian Plane Wave (GPW) [5] code QUICKSTEP [6] which is part of the publicly available suite of programs CP2K [7]. Using this code we performed extensive tests on liquid semiconductors showing that the accuracy can be maintained throughout. The gain in efficiency ranges from one to two orders of magintude depending on the system.

References

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