

Response to “Comment on ‘Curvy-steps approach to constraint-free extended-Lagrangian *ab initio* molecular dynamics, using atom-centered basis functions: Convergence toward Born–Oppenheimer trajectories’ ” [J. Chem. Phys. 123, 027101 (2005)]

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Recently, we introduced a formulation of extended-Lagrangian molecular dynamics (ELMD) that we call “curvy-steps” ELMD, and went on to characterize the conditions under which this method affords a faithful representation of classical molecular dynamics on the Born–Oppenheimer potential-energy surface.¹ In their Comment,² Iyengar *et al.* dispute neither our data nor the conclusions drawn from them, but suggest that we have either overlooked or misrepresented certain aspects of their work on a related method called “atom-centered density matrix propagation” (ADMP; consult Ref. 2 for a complete bibliography). Here we respond briefly to their points.

Iyengar *et al.* first take issue with our abasement of the quantity $dT_f/dt \equiv d\mathcal{H}_{\text{fict}}/dt$, the time derivative of the fictitious kinetic energy, as an “adiabaticity index” for ELMD simulations, citing several rigorous bounds that relate $|dT_f/dt|$ to the electronic gradient, which characterizes the deviation from converged Born–Oppenheimer molecular dynamics. Unfortunately, each of these bounds depends not only on dT_f/dt but also on the density matrix velocity, $\mathbf{W} \equiv \dot{\mathbf{P}}$, so although it is clearly desirable that $|dT_f/dt|$ remain small (in some sense), there exists no simple, quantitative relationship between this index alone and deviations from the Born–Oppenheimer surface. Moreover, T_f itself is ultimately the figure of merit, because this quantity directly measures how much energy is siphoned out of the real nuclear dynamics. A thorough analysis of T_f , dT_f/dt , and other quality-control metrics for ELMD simulations reveals that the most incisive measure of the extent of nuclear-electronic coupling is the separation of nuclear and electronic time scales.¹

A main result in our paper¹ is the characterization and quantification of the extent to which ELMD vibrational frequencies depend upon the fictitious mass parameter. This is one aspect of ELMD that has not, in our opinion, been sufficiently advertised or appreciated, though it has been noted^{3–5} prior to our own work, in the context of Car–Parrinello molecular dynamics (CPMD). Though the importance of maintaining separation of time and energy scales is often mentioned in the ELMD literature,^{6–8} one is sometimes left with the impression that the mere existence of a time-scale (or spectral) gap ensures that ELMD is a faithful representation of Born–Oppenheimer molecular dynamics. For example, Iyengar *et al.*⁷ state that “The fact that fundamental

properties such as vibrational frequencies are independent of the fictitious mass is an important advantage of our ADMP scheme.” Although Iyengar *et al.*² cite various ADMP studies using different fictitious masses, the fact remains that the only comparison of ADMP vibrational frequencies to those obtained from exact (Born–Oppenheimer) molecular dynamics is for NaCl, in Ref. 7. Although the ionic nature of NaCl makes this molecule a difficult test case for plane-wave CPMD,⁵ in Gaussian basis sets NaCl is rather benign, as both pseudopotential and all-electron calculations unequivocally demonstrate.¹ A thorough study of vibrational frequencies using curvy-steps ELMD (Ref. 1) reveals that molecules containing hydrogen atoms are difficult test cases for both plane-wave and Gaussian-orbital-based ELMD, because the extent of nuclear-electronic coupling increases with the highest nuclear vibrational frequency. It is therefore noteworthy that Iyengar *et al.*⁷ use the same set of simulation parameters for H₂CO, C₂H₂O₂, and Cl[−](H₂O)₂₅ as they used for NaCl, without further scrutiny of vibrational frequencies, because simulation parameters that work well for NaCl may afford significantly redshifted frequencies for H-atom stretching motions.¹ The effect on other observables such as intramolecular energy flow is presently unclear.

Next, let us comment on the geometry of the ADMP algorithm versus that of curvy-steps ELMD. First, note that the mathematical disquisition of Iyengar *et al.*² rests upon the assumption (in deriving a relationship between Δ and δ) that $\mathbf{W} = \dot{\Delta}$, which holds trivially at $t=0$ when the electronic velocities are initialized to zero (the usual choice), but does not hold at subsequent times. Order-by-order comparison of ADMP and curvy-steps ELMD is therefore more complicated than the analysis in Ref. 2 suggests. In a broader sense, the mathematical rhetoric in Ref. 2 is superfluous, as the key fact is evident in their first equation: ADMP employs a linear update of the density matrix at each time step, $\mathbf{P} \rightarrow \mathbf{P} + \delta$, which cannot preserve idempotency. This linear update of the electronic variables is followed (as in CPMD) by an auxiliary, nonlinear purification process that iteratively *restores* idempotency, rather than *maintaining* idempotency as in curvy-steps ELMD. The McWeeny⁹ purification procedure exploited in ADMP contains no energy information and constitutes, in the limit of an infinitesimal idempotency violation, a return to the Grassmann manifold along a direction normal to this manifold.¹⁰ (Note that motion along orthogo-

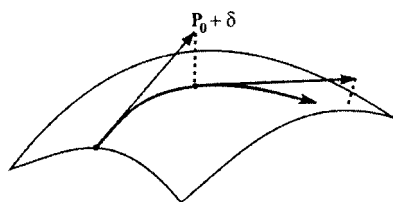


FIG. 1. Sketch of the Grassmann manifold of one-electron density matrices, illustrating a curvy step along the geodesic $\exp(-\mathbf{\Delta})\mathbf{P}_0\exp(\mathbf{\Delta})$ vs a linear update $\mathbf{P}_0 + \delta$ of an initially idempotent density matrix \mathbf{P}_0 . Broken lines indicate purification back to the manifold along McWeeny pathways (Ref. 10).

nal directions does not change the energy.¹¹) In contrast, the nonlinear density-matrix updates that are the heart of curvy-steps ELMD incorporate idempotency preservation into the dynamical propagation itself; in curvy-steps ELMD, every update of the density matrix serves to lower the electronic energy.

The difference between our density-matrix updates and those used in ADMP is illustrated schematically in Fig. 1. Our test calculations indicate that ADMP works because the fast electronic degrees of freedom limit the step size to be small, thus the density matrix never strays too far from the Grassmann manifold. Our philosophy, however, is that it is better not to depart this manifold in the first place.

Finally, Iyengar *et al.*² criticize the fact that, by resetting the curvy-steps rotation angles Δ_{ij} to zero at every time step, our method fails to provide continuous dynamics in the extended phase space that includes the electronic degrees of freedom. This is correct, and also wholly irrelevant: the electronic degrees of freedom are fictitious constructs, and as such may be abused with impunity so long as the impact on nuclear observables is tolerable. Despite the discontinuous resetting of $\mathbf{\Delta}$, the total energy in our simulations—that is, the value of the Hamiltonian \mathcal{H} associated with the extended

Lagrangian \mathcal{L} —is conserved,¹ up to the usual small fluctuations induced by finite time steps. The assertion of Iyengar *et al.*² notwithstanding, this is in no way inconsistent with the derivation of Euler–Lagrange equations of motion, because the electronic energy and its derivatives are evaluated in terms of \mathbf{P} , $\dot{\mathbf{\Delta}}$, and the nuclear variables R_I and \dot{R}_I , all of which evolve continuously in time. (In particular, $\dot{\mathbf{\Delta}}$ is not reset.) Curvy-steps ELMD simulations of up to 7 ps in length exhibit no evidence of drift or discontinuous changes in $\mathcal{H}(t)$.¹

We conclude with the maxim that we hope was evident in our original paper: any change in simulation parameters, including the fictitious mass or the propagation algorithm, *will* alter the simulated nuclear dynamics. Only careful benchmark studies can place bounds on the *extent* to which observables are affected by various tricks employed to accelerate the calculations.

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