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. **121**, 11542 (2004)]

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In Ref. 1 the authors discuss the curvy-extended-Lagrangian molecular dynamics (curvy-ELMD) approach to *ab initio* molecular dynamics,[2] which is similar to our atom-centered density-matrix propagation (ADMP),[3–6] but differs in not requiring the idempotency constraints to be numerically enforced. In this Comment, we address several misleading remarks in Refs. 1 and 7.

In Ref. 1, while studying HF, the authors have stated that the adiabaticity index "… falls flat, utterly failing to detect the impending disaster in the ELMD forces for μ =360 a.u." This conclusion regarding the performance of the adiabaticity index is erroneous. In Ref. 4, page 10296, in the paragraphs that follow Eq. (49) (which is the adiabaticity index), we have noted that there are *two* conditions that the index must satisfy in order that the dynamics from ADMP approximate a Born–Oppenheimer molecular-dynamics (BOMD) trajectory. (a) The quantity in Eq. (49) must be *smaller* than some user-defined threshold. This essentially places an upper bound on the instantaneous value of the adiabaticity index. (b) The index must be oscillatory which is also satisfied by requiring that a time average of the quantity be close to zero [Ref. 4, Eq. (51)]. Herbert and Head-Gordon have overlooked the first condition and only tested for the second condition which has lead them to their incorrect conclusion. Furthermore, an important connection between adiabaticity index and the Frobenius norm $\|[\mathbf{F},\mathbf{P}]\|_F$ is provided by Eq. (24) of Ref. 6.

Regarding the choice of the fictitious mass, in Ref. 5, page 8696, we state "the fictitious mass is chosen so that the density oscillations are an order of magnitude higher than the highest-frequency nuclear motions." This is essentially the same conclusion that Herbert and Head-Gordon have arrived at. Under these conditions, the vibrational frequencies are indeed independent of the fictitious mass.[5] Herbert and Head-Gordon[1] incorrectly attribute to us a broader statement that the vibrational frequencies in ADMP are independent of the fictitious mass regardless of the ratio of the electronic and nuclear time scales and regardless of the behavior of the adiabaticity index or the commutator $[\mathbf{F},\mathbf{P}]$. The choice of NaCl in Ref. 5 was governed by (a) its ionic character, considered important,[8] and (b) presence of second-row elements with rapidly moving core electrons that would be a challenge when pseudopotentials are not used. Our analysis considered many different fictitious mass values,[5] some very high and never used in ADMP simulations involving lighter atoms.[9–11] Here we also respond to a related Comment:[7] "It is therefore noteworthy that Iyengar *et al.* use the same set of simulation parameters for H_2CO, $C_2H_2O_2$, and $Cl^-(H_2O)_{25}$ they used for NaCl, without further scrutiny of vibrational frequencies." In Refs. 4 and 5, we used μ=180, 360, and, 720 a.u. to study NaCl. For $Cl^-(H_2O)_{25}$, μ=180 and 360 a.u. were used[4] to reveal a larger error for 360 a.u. Similarly, H_2CO was tested with simulations involving μ in the range of 45–720 a.u. This study lead to the conclusion:[5] "For the very rapid dissociation reactions of formaldehyde and glyoxal, we choose a maximum fictitious mass of μ=182 a.u." This is the result of a detailed study involving a number of fictitious masses for these systems, and ADMP studies involving light atoms use μ=180 a.u.[9–11]

Regarding the Comment:[1] "From a geometrical point of view, ADMP propagates the density matrix along straight-line trajectories, as opposed to curved ones, and such linear updates cannot remain on the Grassmann manifold."[12] We stress that at every instant of ADMP dynamics, idempotency of the density matrix is conserved to better than 10^{-12}. Since *N*-representability implies existence of a set of orthonormal molecular orbitals (MOs) for a given idempotent single-particle density matrix, ADMP density matrices are on the Grassmann manifold, by definition. In regard to "straight-line trajectories," we note that the density matrix at each step

of ADMP is first updated using its velocity and acceleration. The result is used as an initial guess for a purification process, Eq. (36) of Ref. 4, that conserves idempotency up to good numerical accuracy and is nonlinear. Generally, idempotency is maintained with about ten iterations of this scheme for large systems.[3–6,9–11] Furthermore, there exists a direct relation between ADMP and curvy-ELMD as discussed in the Appendix.

Finally, curvy-ELMD necessitates resetting $\boldsymbol{\Delta}$ to zero at every time step, since the energy derivative with reference to $\boldsymbol{\Delta}$ is obtained[1] for $\boldsymbol{\Delta}=0$. This implies that the classical dynamics in the $\{\mathbf{R},\boldsymbol{\Delta}\}$ phase space is not strictly smooth. This does not have numerical bearings on the results in Ref. 1. However, this also implies that curvy-ELMD does not *strictly* conserve the "total" energy of the system. In response,[7] Herbert and Head-Gordon state that this statement is "correct, and also wholly irrelevant." We note that the derivation of Euler–Lagrange equations in classical mechanics assume a formally conserved Hamiltonian and corresponding Lagrangian.[13] Hence, the total energy within an extended-Lagrangian framework does have a practical value. In ADMP, this is not a problem, since the dynamical variables move on a strictly smooth surface, smoothness being limited only by numerical precision and the total energy is formally conserved.[4]

APPENDIX: FORMAL CONNECTIONS

The density-matrix propagation in ADMP satisfies

$$\mathbf{P}_{i+1} = \mathbf{P} + \mathbf{W}dt - \frac{dt^2}{2\mu_{\text{ADMP}}}\left.\frac{\partial E}{\partial \mathbf{P}}\right|_{\mathbf{R}} \equiv \mathbf{P} + \delta, \qquad (\text{A1})$$

before idempotency is imposed. In curvy-ELMD, propagation is achieved through exponential transformation: $\mathbf{P}_{i+1} \equiv e^{\boldsymbol{\Delta}_{i+1}}\mathbf{P}e^{-\boldsymbol{\Delta}_{i+1}}$. The anti-Hermitian operator $\boldsymbol{\Delta}_{i+1}$ obeys

$$\boldsymbol{\Delta}_{i+1} = \dot{\boldsymbol{\Delta}}dt - \frac{dt^2}{2\mu_{\text{curvy}}}\left[\frac{\partial E}{\partial \boldsymbol{\Delta}}\right]. \qquad (\text{A2})$$

The energy derivatives are $(\partial E/\partial \mathbf{P})|_{\mathbf{R}}=[[\mathbf{F},\mathbf{P}],\mathbf{P}]$ and $(\partial E/\partial \boldsymbol{\Delta})=[\mathbf{F},\mathbf{P}]$. The occupied–occupied and virtual–virtual blocks of $(\partial E/\partial \mathbf{P})|_{\mathbf{R}}$ and $(\partial E/\partial \boldsymbol{\Delta})$ are zero. The occupied-virtual blocks are related:

$$\mathbf{P}\left.\frac{\partial E}{\partial \mathbf{P}}\right|_{\mathbf{R}}\mathbf{Q} = \mathbf{PFQ} = -\mathbf{P}\frac{\partial E}{\partial \boldsymbol{\Delta}}\mathbf{Q}, \qquad (\text{A3})$$

where $\mathbf{Q}=\mathbf{I}-\mathbf{P}$. Below we assume that at the initial step ($t=0$), ADMP, and curvy-ELMD velocities, $\mathbf{W}$ and $\dot{\boldsymbol{\Delta}}$, are zero. We also assume that the time steps and fictitious masses

are identical. Using Eq. (A3) and its transpose, the ADMP and curvy-ELMD displacement vectorss δ and $\boldsymbol{\Delta}$ are related by $\mathbf{P}\boldsymbol{\Delta}\mathbf{Q}=-\mathbf{P}\delta\mathbf{Q}$ and $\mathbf{Q}\boldsymbol{\Delta}\mathbf{P}=\mathbf{Q}\delta\mathbf{P}$. Hence $\boldsymbol{\Delta}\equiv\mathbf{Q}\delta\mathbf{P}-\mathbf{P}\delta\mathbf{Q}$. In ADMP, idempotency is enforced through iterative purification:[4]

$$\mathbf{P}_{i+1}^{j+1} \leftarrow \mathbf{P}_{i+1}^{j} + \mathbf{PTP} + \mathbf{QTQ}, \qquad (\text{A4})$$

where $\mathbf{T}=3[\mathbf{P}_{i+1}^{j}]^2-2[\mathbf{P}_{i+1}^{j}]^3-\mathbf{P}_{i+1}^{j}$, and $\mathbf{P}_{i+1}^{0}=\mathbf{P}+\delta$. Thus after the first purification iteration

$$\mathbf{P}_{i+1} = \mathbf{P} + \mathbf{P}\delta\mathbf{Q} + \mathbf{Q}\delta\mathbf{P} - \mathbf{P}\delta\mathbf{Q}\delta\mathbf{P} + \mathbf{Q}\delta\mathbf{P}\delta\mathbf{Q}. \qquad (\text{A5})$$

Subsequent idempotency iterations will change the occupied–occupied and virtual–virtual blocks. For curvy-ELMD, an idempotent density matrix is obtained from BCH approximation:

$$\mathbf{P}_{i+1} = e^{\boldsymbol{\Delta}}\mathbf{P}e^{-\boldsymbol{\Delta}} = \mathbf{P} + [\boldsymbol{\Delta},\mathbf{P}] + \frac{1}{2}[\boldsymbol{\Delta},[\boldsymbol{\Delta},\mathbf{P}]] + \cdots$$

$$\equiv \mathbf{P} + \mathbf{P}\delta\mathbf{Q} + \mathbf{Q}\delta\mathbf{P} - \mathbf{P}\delta\mathbf{Q}\delta\mathbf{P} + \mathbf{Q}\delta\mathbf{P}\delta\mathbf{Q} + \cdots. \qquad (\text{A6})$$

Thus, with the same initial densities and corresponding velocities, the two approaches yield the same changes in the density up to second order. These relations, however, hold only for scalar-mass ADMP. For the mass tensorial scheme, the relations are complicated by idempotency contribution to occupied-virtual blocks of density.[4]

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