Erratum: "Non-adiabatic Mapping Dynamics in the Phase Space of the $SU(N)$ Lie Group" [J. Chem. Phys. 157, 084105 (2022)]

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I. CORRECTION ON THE SURFACE HOPPING RESULTS IN FIG. 4

After publishing the paper (Ref. 1), unfortunately, we noticed an error generated when we digitize the fewest switches surface hopping (FSSH) result from Ref. 2. This digitization error leads to an incorrect FSSH result in Fig. 4c of the original paper in Ref. 1. Here, we provide the correct version of this figure. The only change made in this figure is the FSSH result, shown in dashed lines in panel c of Fig. 1. Compared to the original version of Fig. 4 in Ref. 1, the state 3 population (green dashed curve in panel c) obtained from FSSH is closer to the exact results (green solid curve in panel c). Our main conclusion drawn in the original paper (Ref. 1), which is that the spin mapping (SM) approach (panels b and d) outperforms the FSSH method (in panel c) for this particular model system, remains unaffected, as the FSSH result (in Ref. 2) provides significantly less accurate population dynamics for state 1 (red dashed line in panel c) and 2 (blue dashed line in panel c).

II. CLARIFICATION ON THE NUMERICAL ALGORITHM USED TO PROPAGATE DYNAMICS

We want to clarify the actual numerical algorithm used to propagate the EOMs, which we have used to generate all numerical results presented in the paper.

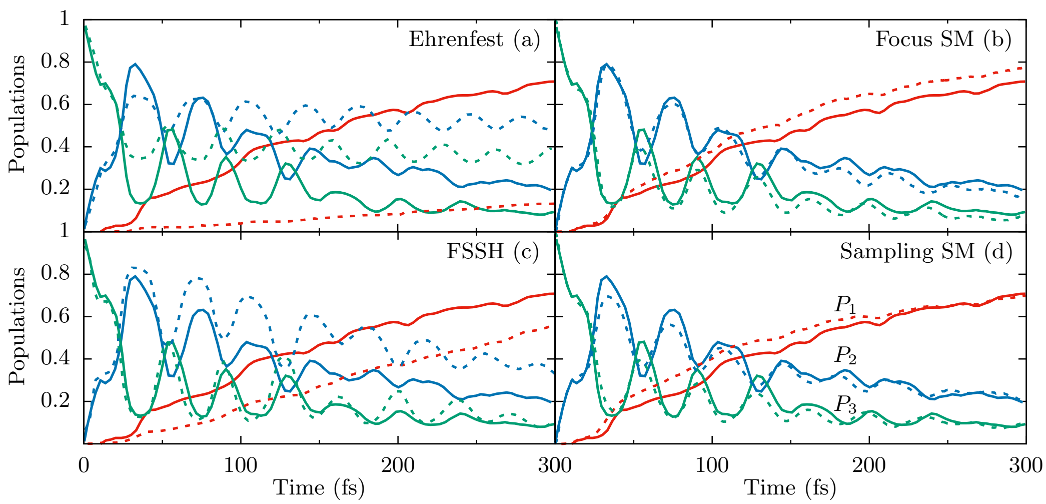

FIG. 1. Corrected version of Fig. 4 in the paper. A correction is made only for the results of the FSSH populations dynamics in panel (c), which is now correctly digitized from Ref. 2.

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As opposed to Eq. 106 in the main text, the actual numerical algorithm we used to generate all numerical results is actually based on the following integration of $\{\theta_n, \varphi_n\}$

$$\boldsymbol{\theta}\big(t+\frac{\Delta t}{4}\big) = \boldsymbol{\theta}(t) + \dot{\boldsymbol{\theta}}(t)\frac{\Delta t}{4}, \tag{1a}$$

$$\boldsymbol{\varphi}\big(t+\frac{\Delta t}{2}\big) = \boldsymbol{\varphi}(t) + \dot{\boldsymbol{\varphi}}\big(t+\frac{\Delta t}{4}\big)\frac{\Delta t}{2}, \tag{1b}$$

$$\boldsymbol{\theta}\big(t+\frac{\Delta t}{2}\big) = \boldsymbol{\theta}\big(t+\frac{\Delta t}{4}\big) + \dot{\boldsymbol{\theta}}\big(t+\frac{\Delta t}{2}\big)\frac{\Delta t}{4}, \tag{1c}$$

To integrate the above equations, we need the expressions of the time-derivatives of θ_n and φ_n(Eq. E9)

$$\dot{\theta}_n = \Big(\frac{\partial H_\mathrm{s}}{\partial \varphi_n}\frac{2}{\sin\theta_n} - \frac{\partial H_\mathrm{s}}{\partial \varphi_{n-1}}\tan\frac{\theta_n}{2}\Big)\Big/\Big(r_\mathrm{s}\prod_{j=1}^{n-1}\sin^2\frac{\theta_j}{2}\Big), \tag{2a}$$

$$\dot{\varphi}_n = \frac{\dot{\Omega}_{\beta_{n+1,n}}\Omega_{\alpha_{n+1,n}} - \Omega_{\beta_{n+1,n}}\dot{\Omega}_{\alpha_{n+1,n}}}{\Omega^2_{\alpha_{n+1,n}} + \Omega^2_{\beta_{n+1,n}}}, \tag{2b}$$

where for $n = 1$ the denominator is replaced by r_s because there is no θ_0 variable and the numerator only has the term that includes $\frac{\partial H_\mathrm{s}}{\partial \varphi_n}$ as there is no φ_{n-1}.

To compute those derivatives, we use Eq. C2 of the paper

$$-\frac{\partial H_\mathrm{s}}{\partial \varphi_n} = r_{\bar{\mathrm{s}}}\sum_{j=n+1}^{N}\sum_{k=1}^{n}\big(\mathcal{H}_{\alpha_{jk}}\Omega_{\beta_{jk}} - \mathcal{H}_{\beta_{jk}}\Omega_{\alpha_{jk}}\big), \tag{3}$$

which itself requires Eq. C5 of the paper

$$\begin{aligned}\dot{\Omega}_{\alpha_{k,n}} =& \frac{1}{\hbar}\Big[\sqrt{\frac{n-1}{2n}}\big(\mathcal{H}_{\gamma_n}\Omega_{\beta_{kn}} - \mathcal{H}_{\beta_{kn}}\Omega_{\gamma_n}\big) - \sqrt{\frac{n+1}{2n}}\big(\mathcal{H}_{\gamma_k}\Omega_{\beta_{kn}} - \mathcal{H}_{\beta_{kn}}\Omega_{\gamma_k}\big)\\ &+ \frac{1}{2}\sum_{j=1}^{n-1}\big(\mathcal{H}_{\beta_{nj}}\Omega_{\alpha_{kj}} - \mathcal{H}_{\alpha_{kj}}\Omega_{\beta_{nj}} - \mathcal{H}_{\alpha_{nj}}\Omega_{\beta_{kj}} + \mathcal{H}_{\beta_{kj}}\Omega_{\alpha_{nj}}\big)\\ &+ \frac{1}{2}\sum_{l=n+2}^{N}\big(\mathcal{H}_{\alpha_{ln}}\Omega_{\beta_{lk}} - \mathcal{H}_{\beta_{lk}}\Omega_{\alpha_{ln}} - \mathcal{H}_{\beta_{ln}}\Omega_{\alpha_{lk}} + \mathcal{H}_{\alpha_{lk}}\Omega_{\beta_{ln}}\big)\Big].\end{aligned} \tag{4}$$

as well as Eq. C6 of the paper

$$\begin{aligned}\dot{\Omega}_{\beta_{kn}} =& \frac{1}{\hbar}\Big[\sqrt{\frac{n+1}{2n}}\big(\mathcal{H}_{\gamma_k}\Omega_{\alpha_{kn}} - \mathcal{H}_{\alpha_{kn}}\Omega_{\gamma_k}\big) - \sqrt{\frac{n-1}{2n}}\big(\mathcal{H}_{\gamma_n}\Omega_{\alpha_{kn}} - \mathcal{H}_{\alpha_{kn}}\Omega_{\gamma_n}\big)\\ &+ \frac{1}{2}\sum_{j=1}^{n-1}\big(\mathcal{H}_{\alpha_{nj}}\Omega_{\alpha_{kj}} - \mathcal{H}_{\alpha_{kj}}\Omega_{\alpha_{nj}} + \mathcal{H}_{\beta_{nj}}\Omega_{\beta_{kj}} - \mathcal{H}_{\beta_{kj}}\Omega_{\beta_{nj}}\big)\\ &+ \frac{1}{2}\sum_{l=n+2}^{N}\big(\mathcal{H}_{\alpha_{ln}}\Omega_{\alpha_{lk}} - \mathcal{H}_{\alpha_{lk}}\Omega_{\alpha_{ln}} + \mathcal{H}_{\beta_{ln}}\Omega_{\beta_{lk}} - \mathcal{H}_{\beta_{lk}}\Omega_{\beta_{ln}}\big)\Big].\end{aligned} \tag{5}$$

Those expressions are written in terms of $\{\Omega_n\}$, which are entirely related to the $\{\theta_n, \varphi_n\}$ angles through Eqs. B2-B4 of the paper,

$$\hbar\Omega_{\alpha_{nm}} = \hbar\prod_{j=1}^{m-1}\sin^2\frac{\theta_j}{2}\cos\frac{\theta_m}{2}\prod_{k=m}^{n-1}\sin\frac{\theta_k}{2}\cos\frac{(1-\delta_{nN})\theta_n}{2}\cos\Big(\sum_{l=m}^{n-1}\varphi_l\Big), \tag{6}$$

where $1 \le m < n \le N$. When $m = 1$, $\prod_{j=1}^{m-1}\sin^2\frac{\theta_j}{2}$ is replaced by 1.

$$\hbar\Omega_{\beta_{nm}} = \hbar\prod_{j=1}^{m-1}\sin^2\frac{\theta_j}{2}\cos\frac{\theta_m}{2}\prod_{k=m}^{n-1}\sin\frac{\theta_k}{2}\cos\frac{(1-\delta_{nN})\theta_n}{2}\sin\Big(\sum_{l=m}^{n-1}\varphi_l\Big), \tag{7}$$

when $m=1$, the term $\prod_{j=1}^{m-1}\sin^2\frac{\theta_j}{2}$ is replaced by 1.

$$\hbar\Omega_{\gamma_n}=\frac{\hbar}{\sqrt{2n(n-1)}}\Big(\sum_{j=1}^{n-1}\cos^2\frac{\theta_j}{2}\prod_{k=1}^{j-1}\sin^2\frac{\theta_k}{2}+(1-n)\cos^2\frac{(1-\delta_{nN})\theta_n}{2}\prod_{j=1}^{n-1}\sin^2\frac{\theta_j}{2}\Big), \tag{8}$$

where $\prod_{k=1}^{j-1}\sin^2\frac{\theta_k}{2}$ is replaced by 1 when $n=2$ (or $j=1$). The above equations allow transforming the variables at each time-step to compute the time-derivatives. Note that the $N=2$ special case of this algorithm has already been used in our previous work of spin-mapping NRPMD (see Appendix B of Ref. 3).

To compute the population dynamics, we use the estimator expressed in terms of $\{\theta_n\}$, which is Eq. 62 of the paper

$$\big[|n\rangle\langle n|\big]_{\mathrm{s}}=\frac{1}{N}+r_{\mathrm{s}}\Big(-\frac{1}{N}+\cos^2\frac{\theta_n}{2}\prod_{k=1}^{n-1}\sin^2\frac{\theta_k}{2}\Big). \tag{9}$$

As we have already emphasized in the paper, an *alternative* but *numerically simpler* way to propagate dynamics is to directly propagate the EOMs with the MMST variables (see Eq. 95 of the paper). This is an *easier approach to implement into computer code*, because these equations (Eq. 95 of the paper) are simpler than the corresponding EOMs for $\{\varphi_n,\theta_n\}$. In addition, there are several previously developed symplectic integrators[4,5] to propagate these EOMs, which one can take advantage of. Our numerical tests confirm that identical results are obtained using this approach. This is an independent test of the validity of the algorithm in Eqs. 1-9.

We also want to explain the algorithm we expressed in Eq. 106 of the paper. When we developed the algorithm in Eq. 1-Eq 9 to generate the numerical results presented in the paper, we have not yet derived the analytic equations in Eq. C8 of the paper, which only involved $\{\Theta_n,\varphi_n\}$. Because $\{\Theta_n,\varphi_n\}$ are conjugate variables, they can also be integrated directly, using

$$\mathbf{\Theta}\big(t+\frac{\Delta t}{4}\big)=\mathbf{\Theta}(t)+\dot{\mathbf{\Theta}}(t)\frac{\Delta t}{4}, \tag{10a}$$

$$\boldsymbol{\varphi}\big(t+\frac{\Delta t}{2}\big)=\boldsymbol{\varphi}(t)+\dot{\boldsymbol{\varphi}}\big(t+\frac{\Delta t}{4}\big)\frac{\Delta t}{2}, \tag{10b}$$

$$\mathbf{\Theta}\big(t+\frac{\Delta t}{2}\big)=\mathbf{\Theta}\big(t+\frac{\Delta t}{4}\big)+\dot{\mathbf{\Theta}}\big(t+\frac{\Delta t}{2}\big)\frac{\Delta t}{4}, \tag{10c}$$

which is Eq. 106 of the paper. The variables $\dot{\Theta}_n$ and $\dot{\varphi}_n$ are obtained (based on Eq. C8 in the paper) as

$$\dot{\Theta}_n=-\frac{\partial H_{\mathrm{s}}}{\partial\varphi_n}=2\sum_{l=n+1}^{N}\sum_{m=1}^{n}V_{lm}(R)\sqrt{\Big(\Theta_l-\Theta_{l-1}+\frac{r_{\mathrm{s}}}{N}\Big)}\sqrt{\Big(\Theta_m-\Theta_{m-1}+\frac{r_{\mathrm{s}}}{N}\Big)}\cdot\sin\left(\sum_{k=m}^{l-1}\varphi_k\right), \tag{11a}$$

$$\dot{\varphi}_n=\frac{\partial H_{\mathrm{s}}}{\partial\Theta_n}=V_{nn}(R)-V_{n+1,n+1}(R) \tag{11b}$$
$$+\left[\sum_{m\neq n}^{N}V_{nm}(R)\sqrt{\frac{\Theta_m-\Theta_{m-1}+\frac{r_{\mathrm{s}}}{N}}{\Theta_n-\Theta_{n-1}+\frac{r_{\mathrm{s}}}{N}}}\cdot\cos\Big(\sum_{k=\min\{m,n\}}^{\max\{m,n\}-1}\varphi_k\Big)-\sum_{m\neq n+1}^{N}V_{nm}(R)\sqrt{\frac{\Theta_m-\Theta_{m-1}+\frac{r_{\mathrm{s}}}{N}}{\Theta_{n+1}-\Theta_n+\frac{r_{\mathrm{s}}}{N}}}\cdot\cos\Big(\sum_{k=\min\{m,n+1\}}^{\max\{m-1,n\}}\varphi_k\Big)\right].$$

This is the algorithm that we intended to express in the paper in Sec. VII Computational Details. We emphasize that we have *not* used it to perform any numerical simulation. However, because it is analytically equivalent to the EOMs in $\{\theta_n,\varphi_n\}$, it should generate numerically identical results at a single trajectory level if starting with an identical initial condition. This is expected because all the EOMs presented in this work are analytically equivalent, as we have proved in the paper.

III. CLARIFICATION ON THE NOTE IN REF. 65

In our published paper (Ref. 1) we put a note in Ref. 65, stating that "To the best of our knowledge, we do not see this expression in the previous literature". This expression refer to Eq. 27 of the main text in Ref. 1, expressed as follows

$$\hat{w}_{\mathrm{s}}(\mathbf{\Omega})=\frac{1-r_{\mathrm{s}}}{N}\hat{\mathcal{I}}+r_{\mathrm{s}}|\mathbf{\Omega}\rangle\langle\mathbf{\Omega}|. \tag{12}$$

We did not realize until recently that this simple equation was discovered in Ref. 6, which is Eq.(4.7) expressed as

$$\begin{aligned} F_{N,1}^{s'}(\boldsymbol{\theta},\boldsymbol{\varphi}) &= \frac{\Omega(s')}{\Omega(s)}\widetilde{F}_{N,1}^{s}(\boldsymbol{\theta},\boldsymbol{\varphi}) + \frac{1}{N}\mathbb{I}_N, \\ &= \frac{\Omega(s')}{\Omega(s)}\left(F_{N,1}^{s}(\boldsymbol{\theta},\boldsymbol{\varphi}) - \frac{1}{N}\mathbb{I}_N\right) + \frac{1}{N}\mathbb{I}_N, \\ &= \frac{\Omega(s')}{\Omega(s)}F_{N,1}^{s}(\boldsymbol{\theta},\boldsymbol{\varphi}) + \left(1 - \frac{\Omega(s')}{\Omega(s)}\right)\frac{1}{N}\mathbb{I}_N, \end{aligned} \tag{13}$$

where $F_{N,1}^{s}(\boldsymbol{\theta},\boldsymbol{\varphi})$ is the generating kernel of Stratonovich-Weyl correspondence that depends on the value of s. Further, $\Omega(s)$ in Eq. 13 (c.f. Eq.(3.16). of Ref. 6) is expressed as follows

$$\Omega(s) = \begin{cases} \sqrt{N+1} & s = 0, \\ 1 & s = +1, \\ N+1 & s = -1. \end{cases} \tag{14}$$

The above $\Omega(s)$ expression, which defines finite-dimensional Wigner, Q- and P-functions of the $SU(N)$-symmetric quasi-probability distribution, plays the same role as our Bloch sphere radius r_{s} in our work Ref. 1.

If one takes the following substitutions

$$r_{\mathrm{s}'} \equiv \frac{\Omega(s')}{\Omega(s)}, \qquad |\boldsymbol{\Omega}\rangle\langle\boldsymbol{\Omega}| \equiv F_{N,1}^{s}(\boldsymbol{\theta},\boldsymbol{\varphi}), \quad \text{and } s = +1 \tag{15}$$

then Eq.(13) is identical to Eq. (12). We apologize for our limited knowledge at the time when we wrote this particular note in Ref. 65. We want to clarify that Ref. 6 was the first work that discovered this expression. It seems that we may have independently re-discovered the same expression from a different derivation (using Eq. 26 in Ref. 1).

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