● Comparison #1

Liu and coworkers' Appendix 3 of the WCMS article :

$$\hat{K}_{\mathrm{ele}}^{\mathrm{SU}(F)}(\boldsymbol{\theta},\boldsymbol{\varphi};s)=(1+F)^{(1+s)/2}\,|\boldsymbol{\theta},\boldsymbol{\varphi}\rangle\langle\boldsymbol{\theta},\boldsymbol{\varphi}|+\frac{\hat{\mathbf{I}}}{F}\left(1-(1+F)^{(1+s)/2}\right),\quad s\in\mathbb{R} \qquad \text{S41}$$

$$\hat{K}_{\mathrm{ele}}^{\mathrm{SU}(F),(\lambda)}(\boldsymbol{\theta},\boldsymbol{\varphi};s)=\lambda\,|\boldsymbol{\theta},\boldsymbol{\varphi}\rangle\langle\boldsymbol{\theta},\boldsymbol{\varphi}|+\frac{\hat{I}}{F}\left(1-(1+F)^{\frac{1+s}{2}}\right). \qquad \text{S52}$$

Eq S41 is a reformulation of the work of Tilma and Nemoto in 2012 [*J. Phys. A Math. Theor.* 45, 015302 (2012)], though in their work they did not use the outer product form $\left|\boldsymbol{\theta},\boldsymbol{\varphi}\right\rangle\left\langle\boldsymbol{\theta},\boldsymbol{\varphi}\right|$. Here, s is not limited only for the P, Q, and W representations of Stratonovich phase space. Parameter s can be chosen in a continuous range, which has been indicated in our CMM approach [*J. Chem. Phys.* 151, 024105 (2019); *J. Phys. Chem. Lett.* 12, 2496-2501 (2021)]:

> Hamiltonian requests only $\gamma \in (-1/F,\ \infty)$. When such a constraint is applied, we establish a novel and general formulation for constructing exact mapping models in the Cartesian phase space (for the electronic DOFs). Although the

We further introduce variable λ [*variable* rather than *parameter*] in eq S52, to form a one-to-one correspondence mapping between manifold $(\lambda,\psi,\boldsymbol{\theta},\boldsymbol{\varphi})$ and manifold $(\mathbf{x},\mathbf{p})$, where ψ is the global phase that is not constant as time evolves.

All these equations (eq S41 and eq S52) were based on our own previous work. [E.g., Youhao Shang's notes uploaded to Evernote on **Aug 26, 2021** and **March 16, 2022** (Note-on-August26-2021-BeijingTime.pdf and Note-On-Mar16-2022-BeijingTime.pdf)].

Huo and coworkers's JCP22-AR-01244 :

$$\hat{w}_{\mathrm{s}}(\boldsymbol{\Omega})=\frac{1-r_{\mathrm{s}}}{N}\hat{\mathcal{I}}+r_{\mathrm{s}}|\boldsymbol{\Omega}\rangle\langle\boldsymbol{\Omega}|. \qquad (26)$$

It is a reformulation inherited from Runeson and Richardson's previous work [*J. Chem. Phys.* 152, 084110 (2020)]:

$$\hat{w}_{\mathrm{Q}}(\Omega)=\frac{1}{N}\hat{\mathcal{I}}+2\sum_{i=1}^{N^2-1}\langle\Omega|\hat{S}_i|\Omega\rangle\hat{S}_i, \qquad (17\text{a})$$

$$\hat{w}_{\mathrm{P}}(\Omega)=\frac{1}{N}\hat{\mathcal{I}}+2(N+1)\sum_{i=1}^{N^2-1}\langle\Omega|\hat{S}_i|\Omega\rangle\hat{S}_i, \qquad (17\text{b})$$

$$\hat{w}_{\mathrm{W}}(\Omega)=\frac{1}{N}\hat{\mathcal{I}}+2\sqrt{N+1}\sum_{i=1}^{N^2-1}\langle\Omega|\hat{S}_i|\Omega\rangle\hat{S}_i, \qquad (17\text{c})$$

The coherent state used by Huo and coworkers and that by Runeson and Richardson are highly similar, with same pattern of θ_n and some difference for φ_n. Both can be traced back to Nemoto's definition of coherent state [*J. Phys. A Math. Gen.* 33, 3493-3506 (2000)] with θ_n replaced by $\theta_n / 2$.

- ## Comparison #2

Liu and coworkers' Appendix 3 of the WCMS article :

$$|\boldsymbol{\theta},\boldsymbol{\varphi}\rangle = \sum_{n=1}^{F} c_n |n\rangle \quad , \tag{S42}$$

Eq S42 follows Tilma and Nemoto's definition of coherent state [*J. Phys. A Math. Theor.* 45, 015302 (2012)], and expansion in $|n\rangle$ basis.

Huo and coworkers's JCP22-AR-01244 :

$$|\boldsymbol{\Omega}\rangle = \sum_{n=1}^{N} |n\rangle\langle n|\boldsymbol{\Omega}\rangle = \sum_{n=1}^{N} c_n |n\rangle, \tag{16}$$

Eq 16 follows Nemoto's definition of coherent state [*J. Phys. A Math. Gen.* 33, 3493-3506 (2000)], with the azimuthal angles φ_n altered *as they said* in the paper. This definition is different from Tilma and Nemoto's work [*J. Phys. A Math. Theor.* 45, 015302 (2012)]. Such expansions are clear in Tilma and Nemoto's works.

- ## Comparison #3

Liu and coworkers' Appendix 3 of the WCMS article :

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_{F-3} \\ c_{F-2} \\ c_{F-1} \\ c_F \end{pmatrix} = \begin{pmatrix} e^{i(\varphi_1+\varphi_2+\cdots+\varphi_{F-1})}\cos(\theta_1)\cos(\theta_2)\cdots\cos(\theta_{F-2})\sin(\theta_{F-1}) \\ -e^{i(-\varphi_1+\varphi_2+\cdots+\varphi_{F-1})}\sin(\theta_1)\cos(\theta_2)\cdots\cos(\theta_{F-2})\sin(\theta_{F-1}) \\ -e^{i(\varphi_3+\varphi_4+\cdots+\varphi_{F-1})}\sin(\theta_2)\cos(\theta_3)\cdots\cos(\theta_{F-2})\sin(\theta_{F-1}) \\ \vdots \\ -e^{i(\varphi_{F-3}+\varphi_{F-2}+\varphi_{F-1})}\sin(\theta_{F-4})\cos(\theta_{F-3})\cos(\theta_{F-2})\sin(\theta_{F-1}) \\ -e^{i(\varphi_{F-2}+\varphi_{F-1})}\sin(\theta_{F-3})\cos(\theta_{F-2})\sin(\theta_{F-1}) \\ -e^{i(\varphi_{F-1})}\sin(\theta_{F-2})\sin(\theta_{F-1}) \\ \cos(\theta_{F-1}) \end{pmatrix}. \tag{S43}$$

Eq S43 exactly follows definition of coherent state in Tilma and Nemoto's work [*J. Phys. A Math. Theor.* 45, 015302 (2012)]:

$\left|(\boldsymbol{\theta},\boldsymbol{\phi})_N^1\right\rangle$ can explicitly be written as

$$\left|(\boldsymbol{\theta},\boldsymbol{\phi})_N^1\right\rangle = \varphi \begin{bmatrix} \mathrm{e}^{\mathrm{i}(\phi_1+\phi_2+\cdots+\phi_{N-2}+\phi_{N-1})}\cos[\theta_1]\cos[\theta_2]\cdots\cos[\theta_{N-2}]\sin[\theta_{N-1}] \\ -\mathrm{e}^{\mathrm{i}(-\phi_1+\phi_2+\cdots+\phi_{N-2}+\phi_{N-1})}\sin[\theta_1]\cos[\theta_2]\cdots\cos[\theta_{N-2}]\sin[\theta_{N-1}] \\ -\mathrm{e}^{\mathrm{i}(\phi_3+\phi_4+\cdots+\phi_{N-2}+\phi_{N-1})}\sin[\theta_2]\cos[\theta_3]\cdots\cos[\theta_{N-2}]\sin[\theta_{N-1}] \\ \vdots \\ -\mathrm{e}^{\mathrm{i}(\phi_{N-3}+\phi_{N-2}+\phi_{N-1})}\sin[\theta_{N-4}]\cos[\theta_{N-3}]\cos[\theta_{N-2}]\sin[\theta_{N-1}] \\ -\mathrm{e}^{\mathrm{i}(\phi_{N-2}+\phi_{N-1})}\sin[\theta_{N-3}]\cos[\theta_{N-2}]\sin[\theta_{N-1}] \\ -\mathrm{e}^{\mathrm{i}\phi_{N-1}}\sin[\theta_{N-2}]\sin[\theta_{N-1}] \\ \cos[\theta_{N-1}] \end{bmatrix}, \qquad (2.10)$$

[See Youhao Shang's notes uploaded to Evernote on **Aug 26, 2021** and **March 16, 2022** (Note-on-August26-2021-BeijingTime.pdf and Note-On-Mar16-2022-BeijingTime.pdf)].

Huo and coworkers's JCP22-AR-01244 :

$$\langle n|\boldsymbol{\Omega}\rangle = \begin{cases} \cos\frac{\theta_1}{2}e^{-i\frac{\varphi_1}{2}} & n=1, \\ \cos\frac{\theta_n}{2}e^{-i\frac{\varphi_n}{2}}\prod_{l=1}^{n-1}\sin\frac{\theta_l}{2}e^{i\frac{\varphi_l}{2}} & 1<n<N, \\ \prod_{l=1}^{N-1}\sin\frac{\theta_l}{2}e^{i\frac{\varphi_l}{2}} & n=N. \end{cases} \qquad (17)$$

Eq (17) follows the definition of coherent state in Nemoto's work (with additional symmetrized splitting of φ_n angles as they said) [*J. Phys. A Math. Gen.* 33, 3493-3506 (2000)]:

$$\boldsymbol{n}_3 = (\mathrm{e}^{\mathrm{i}\varphi}\cos\theta, \mathrm{e}^{\mathrm{i}\varphi_1}\sin\theta\cos\xi_1, \mathrm{e}^{\mathrm{i}\varphi_2}\sin\theta\sin\xi_1)$$

Actually, these two definitions are *not* the same if you check them carefully. The differences among these definitions will *sensitively* affect the final equations of motion of angle variables.

- **Comparison #4**

Liu and coworkers' Appendix 3 of the WCMS article :

$$\hat{K}_{\text{ele}}(\mathbf{x},\mathbf{p};\gamma) = \sum_{m,n=1}^{F}\left[\frac{(x^{(m)}-\mathrm{i}p^{(m)})(x^{(n)}+\mathrm{i}p^{(n)})}{2}-\gamma\delta_{mn}\right]|n\rangle\langle m| = |\mathbf{x},\mathbf{p}\rangle\langle\mathbf{x},\mathbf{p}| - \gamma\hat{\mathbf{1}}, \qquad \text{S44}$$

where the non-normalized state $|\mathbf{x},\mathbf{p}\rangle$ is

$$\sum_{n=1}^{F}\frac{x^{(n)}+\mathrm{i}p^{(n)}}{\sqrt{2}}|n\rangle. \qquad \text{S45}$$

Eqs S44 and S45 follow our CMM framework [*J. Chem. Phys.* 151, 024105 (2019); *J. Phys. Chem. Lett.* 12, 2496-2501 (2021)]:

$$\hat{K}(\mathbf{x},\mathbf{p}) = \sum_{n,m=1}^{F}\left[\frac{1}{2}(x^{(n)}+ip^{(n)})(x^{(m)}-ip^{(m)})-\gamma\delta_{nm}\right]|n\rangle\langle m| \qquad (7)$$

[See Youhao Shang's note uploaded to Evernote on **March 16, 2022** (Note-On-Mar16-2022-BeijingTime.pdf)].

Huo and coworkers's JCP22-AR-01244 :

$$\hat{w}_s = \frac{1-r_s}{N}\hat{\mathcal{I}} + r_s\sum_{a,b} c_a c_b^* |a\rangle\langle b| \qquad (49)$$
$$= \frac{1-r_s}{N}\hat{\mathcal{I}} + \frac{1}{2}\sum_{a,b}(q_a+ip_a)(q_b-ip_b)|a\rangle\langle b|,$$

Eq (49) just reformulates their specified coherent state to fit within the CMM framework [*J. Chem. Phys.* 151, 024105 (2019); *J. Phys. Chem. Lett.* 12, 2496-2501 (2021)] as Huo and coworkers claimed.

● Comparison #5

Liu and coworkers' Appendix 3 of the WCMS article :

$$\begin{pmatrix} x^{(n)} \\ p^{(n)} \end{pmatrix} = \sqrt{2(1+F\gamma)}\begin{pmatrix} \cos\psi & -\sin\psi \\ \sin\psi & \cos\psi \end{pmatrix}\begin{pmatrix} \mathrm{Re}\langle n|\boldsymbol{\theta},\boldsymbol{\varphi}\rangle \\ \mathrm{Im}\langle n|\boldsymbol{\theta},\boldsymbol{\varphi}\rangle \end{pmatrix} . \qquad \text{S47}$$

$$\begin{pmatrix} x^{(n)} \\ p^{(n)} \end{pmatrix} = \sqrt{2\lambda}\begin{pmatrix} \cos\psi & -\sin\psi \\ \sin\psi & \cos\psi \end{pmatrix}\begin{pmatrix} \mathrm{Re}\langle n|\boldsymbol{\theta},\boldsymbol{\varphi}\rangle \\ \mathrm{Im}\langle n|\boldsymbol{\theta},\boldsymbol{\varphi}\rangle \end{pmatrix} , \qquad \text{S54}$$

Eq S47 (or eq S54) is the one-to-one correspondence mapping from SU(F)/U(F-1) Stratonovich phase space [with *additional* λ variable (or γ factor) and a global phase variable] to constraint coordinate-momentum phase space. [See Youhao Shang's note uploaded to Evernote on **March 16, 2022** (Note-On-Mar16-2022-BeijingTime.pdf)].

Huo and coworkers's JCP22-AR-01244 :

$$q_n = \sqrt{2r_s}\cdot \mathrm{Re}[\langle n|\boldsymbol{\Omega}\rangle] \qquad (113a)$$
$$p_n = \sqrt{2r_s}\cdot \mathrm{Im}[\langle n|\boldsymbol{\Omega}\rangle], \qquad (113b)$$

This formulation is directly from Runeson and Richardson's work [*J. Chem. Phys.* 152, 084110 (2020)]. It misses the global phase and just treats r_s as a *parameter* other than a *variable* (although r_s or λ variable keeps constant here, to get the EOMs of $(\mathbf{x},\mathbf{p})$ variables, we must include the derivation over r_s or λ variable); It is not a one-to-one correspondence mapping from the SU(F)/U(F-1) Stratonovich phase space to constrained coordinate-momentum phase space (which yields the Meyer-Miller mapping Hamiltonian that leads to linear equations of motion for electronic DOFs).

● Comparison #6

Liu and coworkers' Appendix 3 of the WCMS article :

$$\begin{cases} \dot{\theta}_i = -\sum_{j=1}^{F-1} \frac{A_{ji}}{(1+F)^{(1+s)/2}} \frac{\partial H_C}{\partial \varphi_j} \\ \dot{\varphi}_i = +\sum_{j=1}^{F-1} \frac{A_{ij}}{(1+F)^{(1+s)/2}} \frac{\partial H_C}{\partial \theta_j} \end{cases} . \qquad \text{S48}$$

$$A_{ij} = \begin{cases} \frac{1}{2}\csc(2\theta_1)\csc^2\theta_{F-1}\prod_{k=2}^{F-2}\sec^2\theta_k, & i=j=1; \\ -\frac{1}{2}\cot(2\theta_1)\csc^2\theta_{F-1}\prod_{k=2}^{F-2}\sec^2\theta_k, & (i-1)=j=1; \\ \csc(2\theta_i)\csc^2\theta_{F-1}\prod_{k=i+1}^{F-2}\sec^2\theta_k, & 2\le i=j\le F-2; \\ -\frac{1}{2}\cot(\theta_i)\csc^2\theta_{F-1}\prod_{k=i+1}^{F-2}\sec^2\theta_k, & 2\le (i-1)=j\le F-2; \\ -\csc(2\theta_{F-1}), & i=j=(F-1). \end{cases} . \qquad \text{S49}$$

Eqs S48-S49 give equations of motion in angle variables, which are derived by the symplectic structure of the SU(F)/U(F-1) Stratonovich phase space manifold, parameterized by $\boldsymbol{\theta}$ & $\boldsymbol{\varphi}$.

[See Youhao Shang's note uploaded to Evernote on **March 16, 2022** (Note-On-Mar16-2022-BeijingTime.pdf)].

Please note that the methodology of Liu and coworkers is capable of dealing with any definitions of the phase space variables of the SU(F)/U(F-1) manifold.

Huo and coworkers's JCP22-AR-01244 :

$$\langle n|\boldsymbol{\Omega}\rangle = \begin{cases} \cos\frac{\theta_1}{2}e^{-i\frac{\varphi_1}{2}} & n=1, \\ \cos\frac{\theta_n}{2}e^{-i\frac{\varphi_n}{2}}\prod_{l=1}^{n-1}\sin\frac{\theta_l}{2}e^{i\frac{\varphi_l}{2}} & 1<n<N, \\ \prod_{l=1}^{N-1}\sin\frac{\theta_l}{2}e^{i\frac{\varphi_l}{2}} & n=N. \end{cases} \qquad (17)$$

$$\dot{\theta}_n = \left(\frac{\partial H_s}{\partial \varphi_n}\frac{2}{\sin\theta_n} - \frac{\partial H_s}{\partial \varphi_{n-1}}\tan\frac{\theta_n}{2}\right) \Big/ \left(r_s \prod_{j=1}^{n-1}\sin^2\frac{\theta_j}{2}\right), \tag{105c}$$

$$\dot{\varphi}_n = \frac{\dot{\Omega}_{\beta_{n+1,n}}\Omega_{\alpha_{n+1,n}} - \Omega_{\beta_{n+1,n}}\dot{\Omega}_{\alpha_{n+1,n}}}{\Omega^2_{\alpha_{n+1,n}} + \Omega^2_{\beta_{n+1,n}}}. \tag{105d}$$

This formulation is based on their assumption that the conjugate variable of φ_n is a linear combination of Ω_{γ_n}. Ironically, Eqs (105c-d) in fact *mismatched* their definition of coherent state in eq (17). [See Page 49 of /JCP-manuscript/Explicit_comments_on_JCP22-AR-01244.pdf]

- ## Comparison #7

Liu and coworkers' Appendix 3 of the WCMS article :

$$\begin{cases} \dot{\lambda} = \dfrac{\partial}{\partial \psi} H_C^{(\lambda)}(\boldsymbol{\theta},\boldsymbol{\varphi};s) = 0 \\ \dot{\psi} = \left[-\dfrac{\partial}{\partial \lambda} + \dfrac{\tan\theta_{F-1}}{2\lambda}\dfrac{\partial}{\partial \theta_{F-1}}\right] H_C^{(\lambda)}(\boldsymbol{\theta},\boldsymbol{\varphi};s) \\ \dot{\theta}_i = -\sum_{j=1}^{F-1}\dfrac{A_{ji}}{\lambda}\dfrac{\partial}{\partial \varphi_j} H_C^{(\lambda)}(\boldsymbol{\theta},\boldsymbol{\varphi};s) - \delta_{i,F-1}\dfrac{\tan\theta_{F-1}}{2\lambda}\dfrac{\partial}{\partial \psi} H_C^{(\lambda)}(\boldsymbol{\theta},\boldsymbol{\varphi};s) \\ \dot{\varphi}_i = +\sum_{j=1}^{F-1}\dfrac{A_{ij}}{\lambda}\dfrac{\partial}{\partial \theta_j} H_C^{(\lambda)}(\boldsymbol{\theta},\boldsymbol{\varphi};s) \end{cases} \tag{S53}$$

Eq S53 involves extra λ and global phase ψ variables, and is capable of mapping the EOMs on the SU(F)/U(F-1) Stratonovich phase space to the EOMs on constrained coordinate-momentum phase space. (The exact one-to-one correspondence manifold mapping should include an evolving global phase). [See Youhao Shang's note uploaded to Evernote on **March 16, 2022** (Note-On-Mar16-2022-BeijingTime.pdf)]

Please note that it is impossible to transform the EOMs with whatever 2F-2 variables on the SU(F)/U(F-1) Stratonovich phase space to the EOMs of the Meyer-Miller model with 2F variables, because an *evolving* global phase (not a *frozen* global phase!) is indispensable.

Huo and coworkers's JCP22-AR-01244 :

$$\dot{\theta}_n = \left(\frac{\partial H_s}{\partial \varphi_n}\frac{2}{\sin\theta_n} - \frac{\partial H_s}{\partial \varphi_{n-1}}\tan\frac{\theta_n}{2}\right) \Big/ \left(r_s \prod_{j=1}^{n-1}\sin^2\frac{\theta_j}{2}\right), \tag{105c}$$

$$\dot{\varphi}_n = \frac{\dot{\Omega}_{\beta_{n+1,n}}\Omega_{\alpha_{n+1,n}} - \Omega_{\beta_{n+1,n}}\dot{\Omega}_{\alpha_{n+1,n}}}{\Omega^2_{\alpha_{n+1,n}} + \Omega^2_{\beta_{n+1,n}}}. \tag{105d}$$

This formulation is based on their statement that the conjugate variable of φ_n is a linear combination of Ω_{γ_n}. They did not include an *evolving* global phase, and their deductions (Eq 105c-d) *mismatch* with their definition of coherent state.

● Comparison #8

Liu and coworkers' Appendix 3 of the WCMS article :

$$\begin{aligned} \dot{x}^{(n)} &= +\frac{\partial H_C}{\partial p^{(n)}} \\ \dot{p}^{(n)} &= -\frac{\partial H_C}{\partial x^{(n)}} \end{aligned} \qquad \text{S55}$$

$$\begin{aligned} \dot{x}^{(n)} &= \sum_{i=1}^{2F} \frac{\partial x^{(n)}}{\partial z_i} \dot{z}_i \\ \dot{p}^{(n)} &= \sum_{i=1}^{2F} \frac{\partial p^{(n)}}{\partial z_i} \dot{z}_i \end{aligned} \qquad \text{S56}$$

where $\{z_i\}$ denote variables $\{\lambda, \psi, \boldsymbol{\theta}, \boldsymbol{\varphi}\}$.

These equations follow the Meyer-Miller equations of motion used in our CMM approach [*J. Chem. Phys.* 151, 024105 (2019); *J. Phys. Chem. Lett.* 12, 2496-2501 (2021)]. We clarified the relationship between the Meyer-Miller variables [on constrained coordinate-momentum phase space] and angle variables [on the SU(F)/U(F-1) Stratonovich phase space], and a one-to-one correspondence mapping relation should include λ and ψ (global phase) variables.

[See Youhao Shang's note uploaded to Evernote on **March 16, 2022** (Note-On-Mar16-2022-BeijingTime.pdf)].

Huo and coworkers's JCP22-AR-01244 :

$$\dot{q}_n = \sum_m V_{nm}(R) \cdot p_m = \frac{\partial \mathcal{H}}{\partial p_n}, \qquad (109a)$$

$$\dot{p}_n = -\sum_m V_{nm}(R) \cdot q_m = -\frac{\partial \mathcal{H}}{\partial q_m}. \qquad (109b)$$

Huo and coworkers were not able to derive the Meyer-Miller EOMs from the spin-mapping approach that employs the SU(F)/U(F-1) Stratonovich phase space where only 2F-2 variables are involved.

- **Final Conclusion:**

In Appendix 3, we made efforts to figure out the role of additional *evolving* global phase in *exact point-to-point* mapping of the SU(F)/U(F-1) Stratonovich phase space (by adding the global phase ψ) to constrained coordinate-momentum phase space, and the one-to-one correspondence mapping was also extended to the transform between the EOMs (by including variables λ and ψ). The EOMs on the SU(F)/U(F-1) Stratonovich phase space with 2F-2 variables are highly nonlinear.

In comparison, in JCP22-AR-01244 Huo and his coworkers simply followed the work of Richardson and coworkers, and failed to understand that the global phase is important to obtain the linear EOMs of the Meyer-Miller Hamiltonian from the SU(F)/U(F-1) Stratonovich phase space variables. Without the global phase variable, it was conceptually wrong to show the relation between our CMM approach and Richardson and coworkers' spin mapping method.