Supplementary Information to the "Modeling Irreversible Molecular Internal Conversion Using the Time-dependent Variational Approach with sD$_2$ Ansatz"

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Derivation of the equations of motion

Here we will describe the derivation of the equations of motion of the presented model. Let us first define certain tensors, which will make the derivation more compact and straightforward:

$$\varOmega_n(\boldsymbol{x}) = \varPhi_n^\star(\boldsymbol{x})\varPhi_n(\boldsymbol{x}) \ , \tag{1}$$

$$f_{\alpha\beta} = \theta_\alpha^\star\theta_\beta S_{\alpha\beta} \ , \tag{2}$$

$$\mathrm{U}_{nmq}(\boldsymbol{x}) = V_{nmq}\varPhi_m(\boldsymbol{x}) \ , \tag{3}$$

$$\mathrm{K}_{nq}(\boldsymbol{x}) = \frac{\omega_q}{2}\frac{\partial^2\varPhi_n(\boldsymbol{x})}{\partial(\boldsymbol{x}_q)^2} \ , \tag{4}$$

$$\mathrm{T}^{(\mathrm{I})}_{\alpha\beta p} = \lambda^\star_{\alpha p} + \lambda_{\beta p} \ , \tag{5}$$

$$\mathrm{T}^{(\mathrm{II})}_{\alpha\beta p} = \left(\lambda^\star_{\alpha p} + \lambda_{\beta p}\right)^2 + 1 \ , \tag{6}$$

$$\mathrm{T}^{(\mathrm{III})}_{\alpha\beta p} = \lambda^\star_{\alpha p}\lambda_{\beta p} + \frac{1}{2} \ , \tag{7}$$

$$S_{\alpha\beta} = \exp\left\{\sum_p \lambda^\star_{\alpha p}\lambda_{\beta p} - \frac{1}{2}\left(|\lambda_{\alpha p}|^2 + |\lambda_{\beta p}|^2\right)\right\} \ , \tag{8}$$

$$g^{(\mathrm{I})}_{\alpha\beta np} = w_p\left(\mathrm{T}^{(\mathrm{III})}_{\alpha\beta p} - \frac{s_{np}}{\sqrt{2}}\mathrm{T}^{(\mathrm{I})}_{\alpha\beta p}\right) \ , \tag{9}$$

$$g^{(\mathrm{II})}_{\alpha\beta nqp}(\boldsymbol{x}) = \left(k^{(1,1)}_{nqp}x_q + k^{(2,1)}_{nqp}x_q^2\right)\frac{\mathrm{T}^{(\mathrm{I})}_{\alpha\beta p}}{\sqrt{2}} + k^{(1,2)}_{nqp}x_q\frac{\mathrm{T}^{(\mathrm{II})}_{\alpha\beta p}}{2} \ , \tag{10}$$

$$h^{(\mathrm{I})}_{np} = \sum_{i,j} f_{ij}g^{(\mathrm{I})}_{ijnp} \ , \tag{11}$$

$$h^{(\mathrm{II})}_{nqp}(\boldsymbol{x}) = \sum_{i,j} f_{ij}g^{(\mathrm{II})}_{ijnqp}(\boldsymbol{x}) \ . \tag{12}$$

In order to deduce the defined sD$_2$ *ansatz*

$$|\Psi_{\mathrm{sD}_2}(t)\rangle = \sum_n^N \int_{\boldsymbol{x}^{\min}}^{\boldsymbol{x}^{\max}} \mathrm{d}\boldsymbol{x}\varPhi_n(\boldsymbol{x},t)|n,\boldsymbol{x}\rangle \times \sum_\alpha^M \theta_\alpha(t)\prod_p^P|\lambda_{\alpha p}(t)\rangle \ , \tag{13}$$

free parameter $\xi_i(t) = \varPhi_n(\boldsymbol{x},t), \theta_\alpha(t), \lambda_{\alpha p}(t)$ time evolution using the Euler-Lagrange equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial\mathcal{L}(t)}{\partial\dot{\xi}_i^\star(t)}\right) - \frac{\partial\mathcal{L}(t)}{\partial\xi_i^\star(t)} = 0 \ , \tag{14}$$

we first have to calculate Lagrangian $\mathcal{L}(t)$ of the model

$$\mathcal{L}(t) = \frac{\mathrm{i}}{2}\left(\langle\Psi_{\mathrm{sD}_2}(t)|\dot{\Psi}_{\mathrm{sD}_2}(t)\rangle - \langle\dot{\Psi}_{\mathrm{sD}_2}(t)|\Psi_{\mathrm{sD}_2}(t)\rangle\right) - \langle\Psi_{\mathrm{sD}_2}(t)|\hat{H}|\Psi_{\mathrm{sD}_2}(t)\rangle \ , \tag{15}$$

where $\hat{H} = \hat{H}_{\mathrm{S}} + \hat{H}_{\mathrm{B}} + \hat{H}_{\text{E-B}} + \hat{H}_{\text{V-B}}$ is the full Hamiltonian operator of the model. The first two Lagrangian terms are equal to

$$\langle\Psi_{\mathrm{sD}_2}(t)|\dot{\Psi}_{\mathrm{sD}_2}(t)\rangle = \sum_{n,\alpha\beta}\int \mathrm{d}\boldsymbol{x}f_{\alpha\beta}\varPhi_n^\star(\boldsymbol{x})\dot{\varPhi}_n(\boldsymbol{x}) + \sum_{n,\alpha\beta}\int \mathrm{d}\vec{x}\varOmega_n(\boldsymbol{x})S_{\alpha\beta}\theta^\star_\alpha\dot{\theta}_\beta$$
$$+ \sum_{n,\alpha,\beta}\int \mathrm{d}\boldsymbol{x}\varOmega_n(\boldsymbol{x})f_{\alpha\beta}\sum_p\left(\lambda^\star_{\alpha p}\dot{\lambda}_{\beta p} - \frac{1}{2}\frac{\partial}{\partial t}|\lambda_{\beta p}|^2\right) \ , \tag{16}$$

$$\langle\dot{\Psi}_{\mathrm{sD}_2}(t)|\Psi_{\mathrm{sD}_2}(t)\rangle = \left(\langle\Psi_{\mathrm{sD}_2}(t)|\dot{\Psi}_{\mathrm{sD}_2}(t)\rangle\right)^\star \ , \tag{17}$$

and the Hamiltonian operator terms are equal to

$$\langle\Psi_{\mathrm{sD}_2}|\hat{H}_{\mathrm{S}}|\Psi_{\mathrm{sD}_2}\rangle=\sum_{n,\alpha,\beta}\int\mathrm{d}\boldsymbol{x}f_{\alpha\beta}\left[\varepsilon_n\Omega_n\left(\boldsymbol{x}\right)-\Phi_n^\star\left(\boldsymbol{x}\right)\sum_q\left(\mathrm{K}_{nq}\left(\boldsymbol{x}\right)-\sum_m\mathrm{U}_{nmq}\left(\boldsymbol{x}\right)\right)\right]\ ,\tag{18}$$

$$\langle\Psi_{\mathrm{sD}_2}|\hat{H}_{\mathrm{B}}|\Psi_{\mathrm{sD}_2}\rangle=\sum_{n,\alpha,\beta}\int\mathrm{d}\boldsymbol{x}\Omega_n\left(\boldsymbol{x}\right)f_{\alpha\beta}\sum_p\mathrm{T}^{(\mathrm{III})}_{\alpha\beta p}\ ,\tag{19}$$

$$\langle\Psi_{\mathrm{sD}_2}|\hat{H}_{\mathrm{E\text{-}B}}|\Psi_{\mathrm{sD}_2}\rangle=\sum_{n,\alpha,\beta}\int\mathrm{d}\boldsymbol{x}\Omega_n\left(\boldsymbol{x}\right)f_{\alpha\beta}\sum_p w_p\left(\frac{1}{2}s_{np}^2-\frac{s_{np}}{\sqrt{2}}\mathrm{T}^{(\mathrm{I})}_{\alpha\beta p}\right)\ ,\tag{20}$$

$$\langle\Psi_{\mathrm{sD}_2}|\hat{H}_{\mathrm{V\text{-}B}}|\Psi_{\mathrm{sD}_2}\rangle=\sum_{n,\alpha,\beta}\int\mathrm{d}\boldsymbol{x}\Omega_n\left(\boldsymbol{x}\right)f_{\alpha\beta}\sum_{q,p}g^{(\mathrm{II})}_{\alpha\beta nqp}\left(\boldsymbol{x}\right)\ .\tag{21}$$

Then the Lagrangian can be written as

$$\begin{aligned}\mathcal{L}=&\frac{\mathrm{i}}{2}\sum_{n,\alpha\beta}\int\mathrm{d}\boldsymbol{x}\left[f_{\alpha\beta}\Phi_n^\star\left(\boldsymbol{x}\right)\dot{\Phi}_n\left(\boldsymbol{x}\right)-f_{\alpha\beta}^\star\Phi_n\left(\boldsymbol{x}\right)\dot{\Phi}_n^\star\left(\boldsymbol{x}\right)+\Omega_n\left(\boldsymbol{x}\right)\left(S_{\alpha\beta}\theta_\alpha^\star\dot{\theta}_\beta-S_{\alpha\beta}^\star\theta_\alpha\dot{\theta}_\beta^\star\right)\right]\\&+\frac{\mathrm{i}}{2}\sum_{n,\alpha,\beta}\int\mathrm{d}\boldsymbol{x}\Omega_n\left(\boldsymbol{x}\right)\sum_p\left[f_{\alpha\beta}\lambda_{\alpha p}^\star\dot{\lambda}_{\beta p}-f_{\alpha\beta}^\star\lambda_{\alpha p}\dot{\lambda}_{\beta p}^\star+\frac{1}{2}\left(f_{\alpha\beta}^\star-f_{\alpha\beta}\right)\left(\lambda_{\beta p}^\star\dot{\lambda}_{\beta p}+\lambda_{\beta p}\dot{\lambda}_{\beta p}^\star\right)\right]\\&-\sum_{n,\alpha,\beta}\int\mathrm{d}\boldsymbol{x}f_{\alpha\beta}\left[\Omega_n\left(\boldsymbol{x}\right)\left(\varepsilon_n+\sum_p\frac{w_ps_{np}^2}{2}\right)-\Phi_n^\star\left(\boldsymbol{x}\right)\sum_q\left(\mathrm{K}_{nq}\left(\boldsymbol{x}\right)-\sum_m\mathrm{U}_{nmq}\left(\boldsymbol{x}\right)\right)\right]\\&-\sum_n\int\mathrm{d}\boldsymbol{x}\Omega_n\left(\boldsymbol{x}\right)\sum_{\alpha,\beta}f_{\alpha\beta}\sum_p\left(g^{(\mathrm{I})}_{\alpha\beta np}+\sum_q g^{(\mathrm{II})}_{\alpha\beta nqp}\left(\boldsymbol{x}\right)\right)\ .\end{aligned}\tag{22}$$

Now, by applying Eq. (14) to the free sD_2 *ansatz* parameters $\xi_i\left(t\right)=\Phi_k\left(\boldsymbol{y},t\right),\theta_\tau\left(t\right),\lambda_{\mu j}\left(t\right)$, we obtain a system of implicit differential equations:

$$\begin{aligned}&\dot{\Phi}_k\left(\boldsymbol{y}\right)+\Phi_k\left(\boldsymbol{y}\right)\sum_{\alpha\beta}\theta_\alpha^\star\dot{\theta}_\beta S_{\alpha\beta}+\Phi_k\left(\boldsymbol{y}\right)\sum_{\alpha\beta}f_{\alpha\beta}H_{\alpha\beta}=\\&-\mathrm{i}\Phi_k\left(\boldsymbol{y}\right)\left(\varepsilon_k+\sum_p\frac{w_ps_{kp}^2}{2}\right)-\mathrm{i}\sum_q\left(\sum_m\mathrm{U}_{kmq}\left(\boldsymbol{y}\right)-\mathrm{K}_{kq}\left(\boldsymbol{y}\right)\right)\\&-\mathrm{i}\Phi_k\left(\boldsymbol{y}\right)\sum_{\alpha,\beta}f_{\alpha\beta}\sum_p\left(g^{(\mathrm{I})}_{\alpha\beta kp}+\sum_q g^{(\mathrm{II})}_{\alpha\beta kqp}\left(\boldsymbol{y}\right)\right)\ \forall\left\{k,\boldsymbol{y}\right\}\ ,\end{aligned}\tag{23}$$

$$\begin{aligned}&\sum_{n,\alpha}\int\mathrm{d}\boldsymbol{x}\theta_\alpha S_{\tau\alpha}\Phi_n^\star\left(\boldsymbol{x}\right)\dot{\Phi}_n\left(\boldsymbol{x}\right)+\sum_\alpha\left(S_{\tau\alpha}\dot{\theta}_\alpha+\theta_\alpha S_{\tau\alpha}H_{\tau\alpha}\right)=\\&-\mathrm{i}\sum_{n,\alpha}\int\mathrm{d}\boldsymbol{x}\theta_\alpha S_{\alpha\tau}^\star\left[\Omega_n\left(\boldsymbol{x}\right)\left(\varepsilon_n+\sum_p\frac{w_ps_{np}^2}{2}\right)-\Phi_n^\star\left(\boldsymbol{x}\right)\sum_q\left(\mathrm{K}_{nq}\left(\boldsymbol{x}\right)-\sum_m\mathrm{U}_{nmq}\left(\boldsymbol{x}\right)\right)\right]\\&-\mathrm{i}\sum_n\int\mathrm{d}\boldsymbol{x}\Omega_n\left(\boldsymbol{x}\right)\sum_\alpha\theta_\alpha S_{\alpha\tau}^\star\sum_p\left(g^{(\mathrm{I})}_{\alpha\tau np}+\sum_q g^{(\mathrm{II})}_{\alpha\tau nqp}\left(\boldsymbol{x}\right)\right)\ \forall\tau\ ,\end{aligned}\tag{24}$$

$$
\begin{aligned}
&\sum_{\alpha} \dot{\lambda}_{\alpha j} f_{\mu\alpha} + \frac{1}{2} \sum_{\alpha} \left[\left(\theta^{\star}_{\mu} \dot{\theta}_{\alpha} + \theta_{\alpha} \dot{\theta}^{\star}_{\mu} \right) S_{\mu\alpha} + \left(H_{\mu\alpha} + H^{\star}_{\alpha\mu} \right) f_{\mu\alpha} \right] \lambda_{\alpha j} \\
&- \frac{\mathrm{i}}{2} \sum_{\alpha} \Re \left\{ \left(\theta^{\star}_{\mu} \dot{\theta}_{\alpha} + \theta_{\alpha} \dot{\theta}^{\star}_{\mu} \right) S_{\mu\alpha} + \left(H_{\mu\alpha} + H^{\star}_{\alpha\mu} \right) f_{\mu\alpha} \right\} \lambda_{\mu j} = \\
&- \mathrm{i} \sum_{n} \int \mathrm{d}\boldsymbol{x} \mathit{\Omega}_{n} \left(\boldsymbol{x} \right) \sum_{\alpha} f_{\mu\alpha} \left[w_{j} \left(\lambda_{\alpha p} - \frac{s_{nj}}{\sqrt{2}} \right) + \left(k^{(1,1)}_{nqj} x_{q} + k^{(2,1)}_{nqj} x^{2}_{q} \right) \frac{1}{\sqrt{2}} + k^{(1,2)}_{nqj} x_{q} \mathrm{T}^{(\mathrm{I})}_{\mu\alpha j} \right] \; \forall \left\{ \mu, j \right\} \;, \qquad (25)
\end{aligned}
$$

with auxiliary function $H_{\alpha\beta} = \sum_{p} \left(\lambda^{\star}_{\alpha p} \dot{\lambda}_{\beta p} - \frac{1}{2} \dot{\lambda}_{\beta p} \lambda^{\star}_{\beta p} - \frac{1}{2} \lambda_{\beta p} \dot{\lambda}^{\star}_{\beta p} \right)$. Eq. (24) can be further simplified by constructing a $\sum_{n,\alpha} \int \mathrm{d}\boldsymbol{x} \theta_{\alpha} S_{\tau\alpha} \mathit{\Phi}^{\star}_{n} \left(\boldsymbol{x} \right) \dot{\mathit{\Phi}}_{n} \left(\boldsymbol{x} \right)$ term using the Eq. (23) and inserting it back into Eq. (24). This results in a simplified form of Eq. (24)

$$
\begin{aligned}
&\sum_{\alpha} \left(\dot{\theta}_{\alpha} - \theta_{\alpha} \sum_{ij} \theta^{\star}_{i} \dot{\theta}_{j} S_{ij} + H_{\tau\alpha} \theta_{\alpha} - \sum_{ij} f_{ij} H_{ij} \theta_{\alpha} \right) S_{\tau\alpha} = \\
&- \mathrm{i} \sum_{n} \int \mathrm{d}\boldsymbol{x} \mathit{\Omega}_{n} \left(\boldsymbol{x} \right) \sum_{\alpha} \theta_{\alpha} S_{\tau\alpha} \sum_{p} \left[\left(g^{(\mathrm{I})}_{\alpha\tau np} - h^{(\mathrm{I})}_{np} \right) + \sum_{q} \left(g^{(\mathrm{II})}_{\alpha\tau nqp} \left(\boldsymbol{x} \right) - h^{(\mathrm{II})}_{nqp} \left(\boldsymbol{x} \right) \right) \right] \; \forall \tau \;. \qquad (26)
\end{aligned}
$$

Eqs. (23), (25), (26) then constitute the final system of equations of motion to be solved in order to obtain the model time evolution.