# Nonadiabatic effects within condensed-phase systems: a novel partially linearized spin-mapping approach

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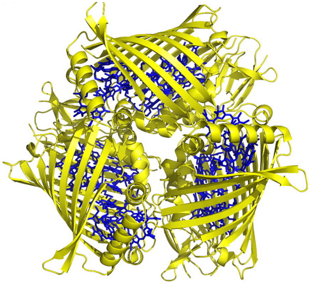
# Background and Motivation



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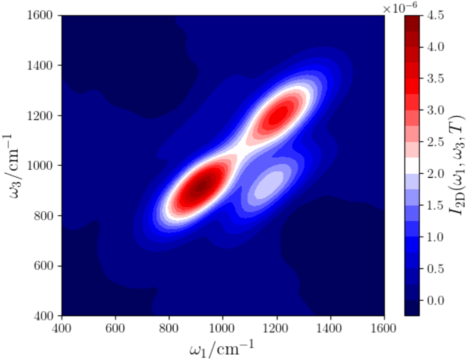
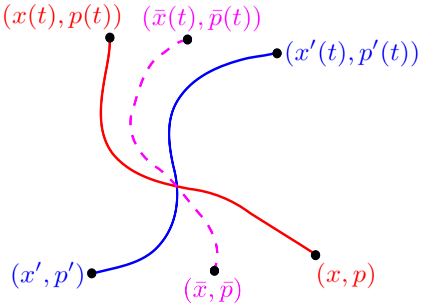



$$C_{AB}(t) = \mathrm{Tr}\left[\hat{\rho}_{\mathrm{b}}\hat{A}\,\mathrm{e}^{i\hat{H}t}\,\hat{B}\,\mathrm{e}^{-i\hat{H}t}\right]$$

$$R(t_1, t_2, t_3) = \mathrm{Tr}\left[\hat{\rho}_{\mathrm{b}}\hat{A}\,\mathrm{e}^{i\hat{H}(t_1+t_2)}\,\hat{B}\,\mathrm{e}^{i\hat{H}t_3}\,\hat{C}\,\mathrm{e}^{-i\hat{H}(t_2+t_3)}\,\hat{D}\,\mathrm{e}^{-i\hat{H}t_1}\right]$$

# Classical Nuclear Limit

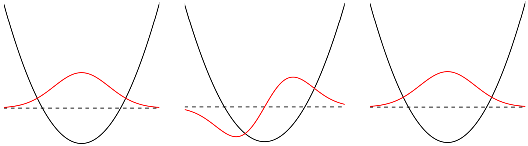
$$C_{AB}(t) = \mathrm{Tr}\left[\hat{\rho}_\mathrm{b} \hat{A}\, \mathrm{e}^{i\hat{H}t} \hat{B}\, \mathrm{e}^{-i\hat{H}t}\right]$$




$$\hat{\rho}_\mathrm{b} \to \rho_\mathrm{b}^\mathrm{W}(\bar{x}, \bar{p}) = \frac{1}{2\pi} \int \mathrm{d}z \, \langle \bar{x} + \tfrac{z}{2} | \hat{\rho}_b | \bar{x} - \tfrac{z}{2} \rangle \, \mathrm{e}^{-i\bar{p}z}$$

$$\frac{\mathrm{d}\bar{x}}{\mathrm{d}t} = \frac{\bar{p}}{m}, \qquad \frac{\mathrm{d}\bar{p}}{\mathrm{d}t} = -F(\bar{x})$$

# Meyer-Miller-Stock-Thoss Mapping

$|2\rangle \rightarrow$ 

$$\hat{a}_m \rightarrow \frac{1}{\sqrt{2}}\left(\hat{X}_m + i\hat{P}_m\right)$$

The classical limit:

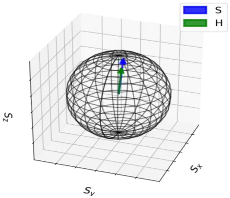
$$\hat{A} \rightarrow A^{\mathrm{W}}(X, P)$$

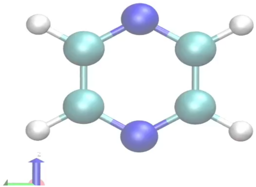
$$\frac{\mathrm{d}X_n}{\mathrm{d}t} = \sum_m \langle n|\hat{H}|m\rangle\, P_m, \qquad \frac{\mathrm{d}P_n}{\mathrm{d}t} = -\sum_m \langle n|\hat{H}|m\rangle\, X_m$$

Problems:

- Unphysical regions of the mapping space
- $\mathcal{I}^{\mathrm{W}}(X, P) = \frac{1}{2}\sum_m (X_m^2 + P_m^2 - 1) \neq 1$

# Spin-Mapping



Video produced by Johan Runeson

$$A(\boldsymbol{S}) = \mathrm{tr}\left[\hat{A}\hat{w}(\boldsymbol{S})\right], \qquad \hat{w}(\boldsymbol{S}) = \tfrac{1}{2}\hat{\mathcal{I}} + S_x\hat{\sigma}_x + S_y\hat{\sigma}_y + S_z\hat{\sigma}_z = \tfrac{1}{2}\hat{\mathcal{I}} + \boldsymbol{S}\cdot\hat{\boldsymbol{\sigma}}$$

$$\frac{\mathrm{d}\boldsymbol{S}}{\mathrm{d}t} = \boldsymbol{H} \times \boldsymbol{S}, \qquad \hat{H} = H_0\hat{\mathcal{I}} + \boldsymbol{H}\cdot\hat{\boldsymbol{\sigma}}$$

Advantages:

- Unphysical regions of the mapping space significantly reduced
- $\mathcal{I}(\boldsymbol{S}) = 1$

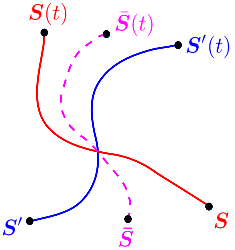
# Fully vs Partially Linearized Methods

$$C_{AB}(t) = \mathrm{Tr}\left[\hat{A}\,\mathrm{e}^{i\hat{H}t}\,\hat{B}\,\mathrm{e}^{-i\hat{H}t}\right]$$

Spin-LSC:

$$C_{AB}(t) = \left\langle A(\bar{\mathbf{S}})B(\bar{\mathbf{S}}(t))\right\rangle$$

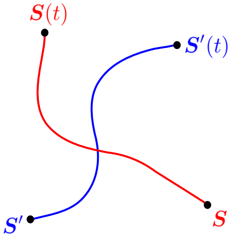
$$F_{\mathrm{e}}(\bar{\mathbf{S}}, x) = -\nabla V(\bar{\mathbf{S}})$$



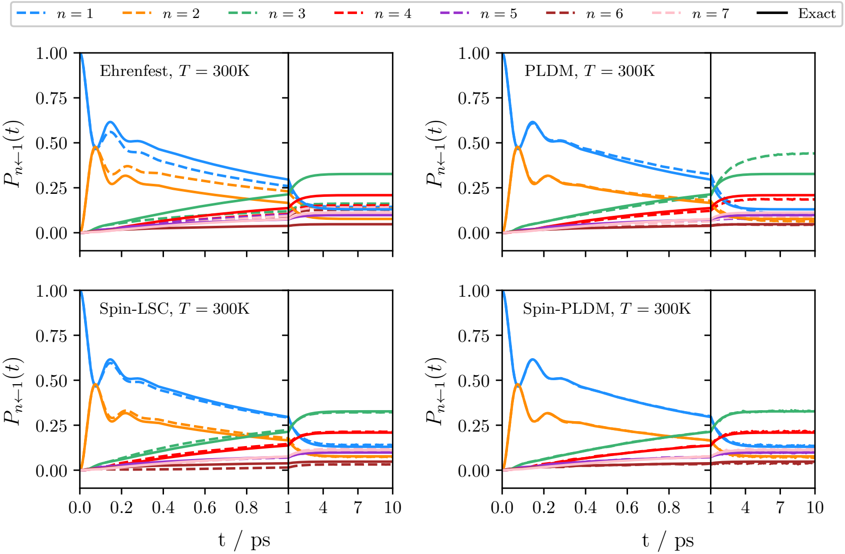

Spin-PLDM:

$$C_{AB}(t) = \left\langle \mathrm{tr}\left[\hat{A}\hat{w}^{\dagger}(\mathbf{S}', t)\hat{B}\hat{w}(\mathbf{S}, t)\right]\right\rangle$$

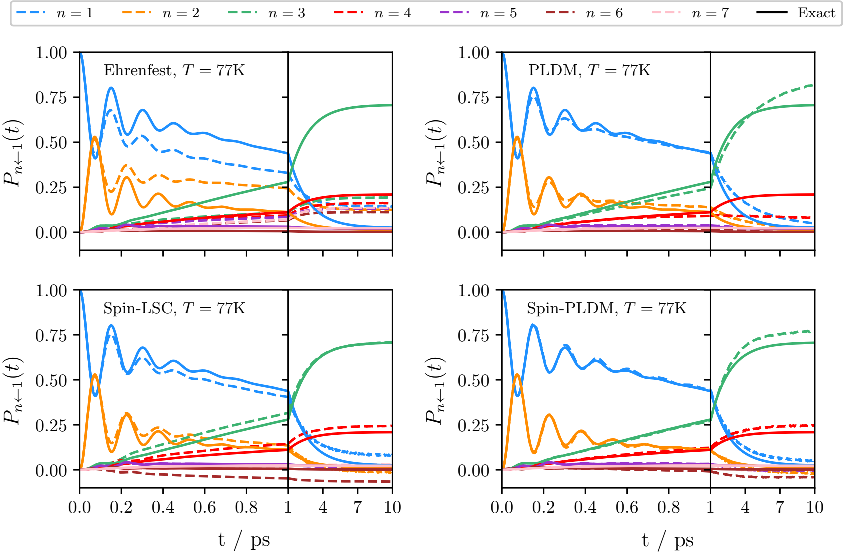
$$F_{\mathrm{e}}(\mathbf{S}', \mathbf{S}, x) = -\frac{1}{2}\left[\nabla V(\mathbf{S}') + \nabla V(\mathbf{S})\right]$$



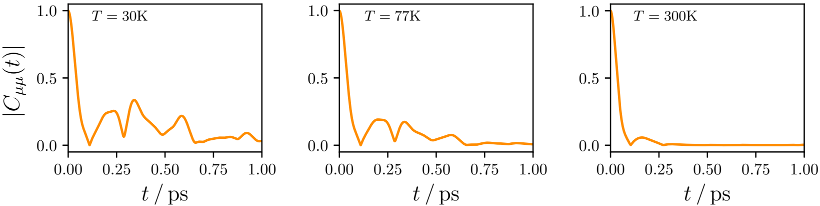
# Fenna-Matthews-Olsen Complex



# Fenna-Matthews-Olsen Complex



# Electronic Spectroscopy

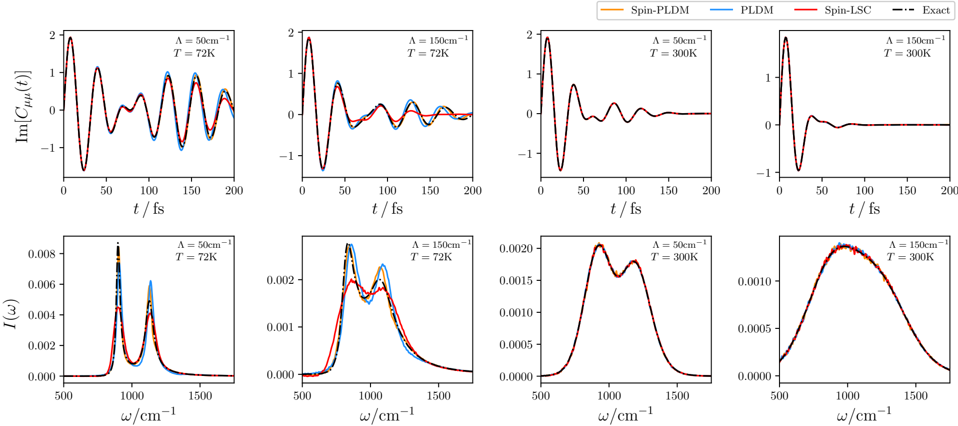



$$\hat{\mu} = \sum_{\mathrm{e}} \mu_{\mathrm{ge}} \left( |\mathrm{e}\rangle\langle\mathrm{g}| + |\mathrm{g}\rangle\langle\mathrm{e}| \right)$$

$$C_{\mu\mu}(t) = \sum_{\mathrm{e}\,\mathrm{e}'} \mu_{\mathrm{ge}}\, \mu_{\mathrm{ge}'}\, \mathrm{Tr}\left[ \hat{\rho}_{\mathrm{g}}\, |\mathrm{g}\rangle\langle\mathrm{e}|\; \mathrm{e}^{i\hat{H}_{\mathrm{e}} t}\, |\mathrm{e}'\rangle\langle\mathrm{g}|\; \mathrm{e}^{-i\hat{H}_{\mathrm{g}} t} \right]$$

$$C_{\mu\mu}(t) = \sum_{\mathrm{e}\,\mathrm{e}'} \mu_{\mathrm{ge}}\, \mu_{\mathrm{ge}'} \left\langle \rho_{\mathrm{g}}^{\mathrm{W}}(x, p)\; \langle\mathrm{e}|\hat{w}^{\dagger}(\boldsymbol{S}', t)|\mathrm{e}'\rangle \right\rangle$$

# Biexciton Model Absorption Spectra



# Nonlinear Spectroscopy

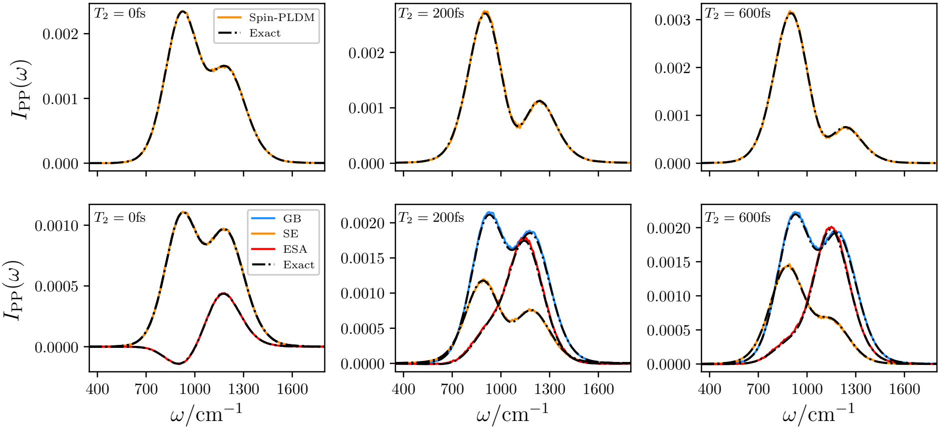
$$\langle \mathrm{e}''|\hat{w}(\boldsymbol{S}, t_2 + t_3)|\mathrm{e}'''\rangle$$

$$R_{\mathrm{SE,RP}}(t_1, t_2, t_3) = \sum_{\mathrm{e}\,\mathrm{e}'\,\mathrm{e}''\,\mathrm{e}'''} \mu_{\mathrm{ge}}\,\mu_{\mathrm{ge}'}\,\mu_{\mathrm{ge}''}\,\mu_{\mathrm{ge}'''}$$

$$\times \mathrm{Tr}\left[\hat{\rho}_{\mathrm{g}}\,|\mathrm{g}\rangle\langle\mathrm{e}|\;\mathrm{e}^{i\hat{H}_{\mathrm{e}}(t_1+t_2)}\,|\mathrm{e}'\rangle\langle\mathrm{g}|\;\mathrm{e}^{i\hat{H}_{\mathrm{g}}t_3}\,|\mathrm{g}\rangle\langle\mathrm{e}''|\;\mathrm{e}^{-i\hat{H}_{\mathrm{e}}(t_2+t_3)}\,|\mathrm{e}'''\rangle\langle\mathrm{g}|\;\mathrm{e}^{-i\hat{H}_{\mathrm{g}}t_1}\right]$$

$$\langle \mathrm{e}|\hat{w}^{\dagger}(\boldsymbol{S}', t_1 + t_2)|\mathrm{e}'\rangle$$

# Biexciton Model Pump Probe Spectra



# Acknowledgements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