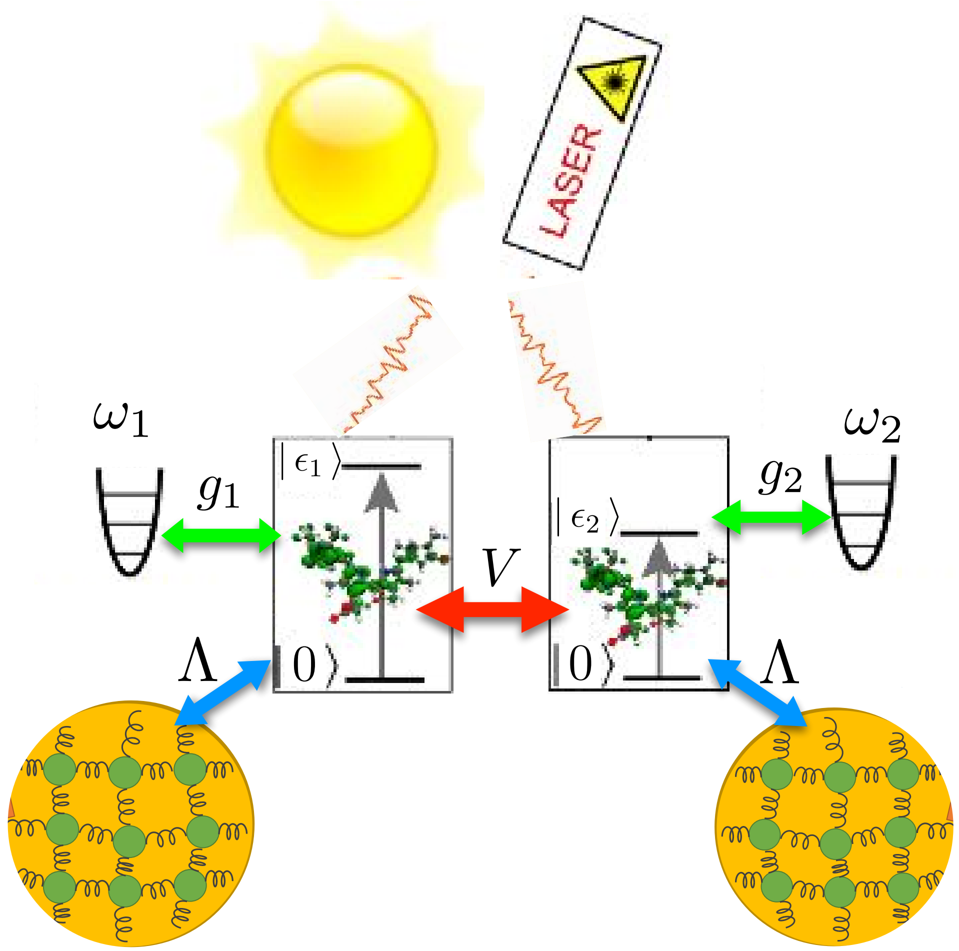
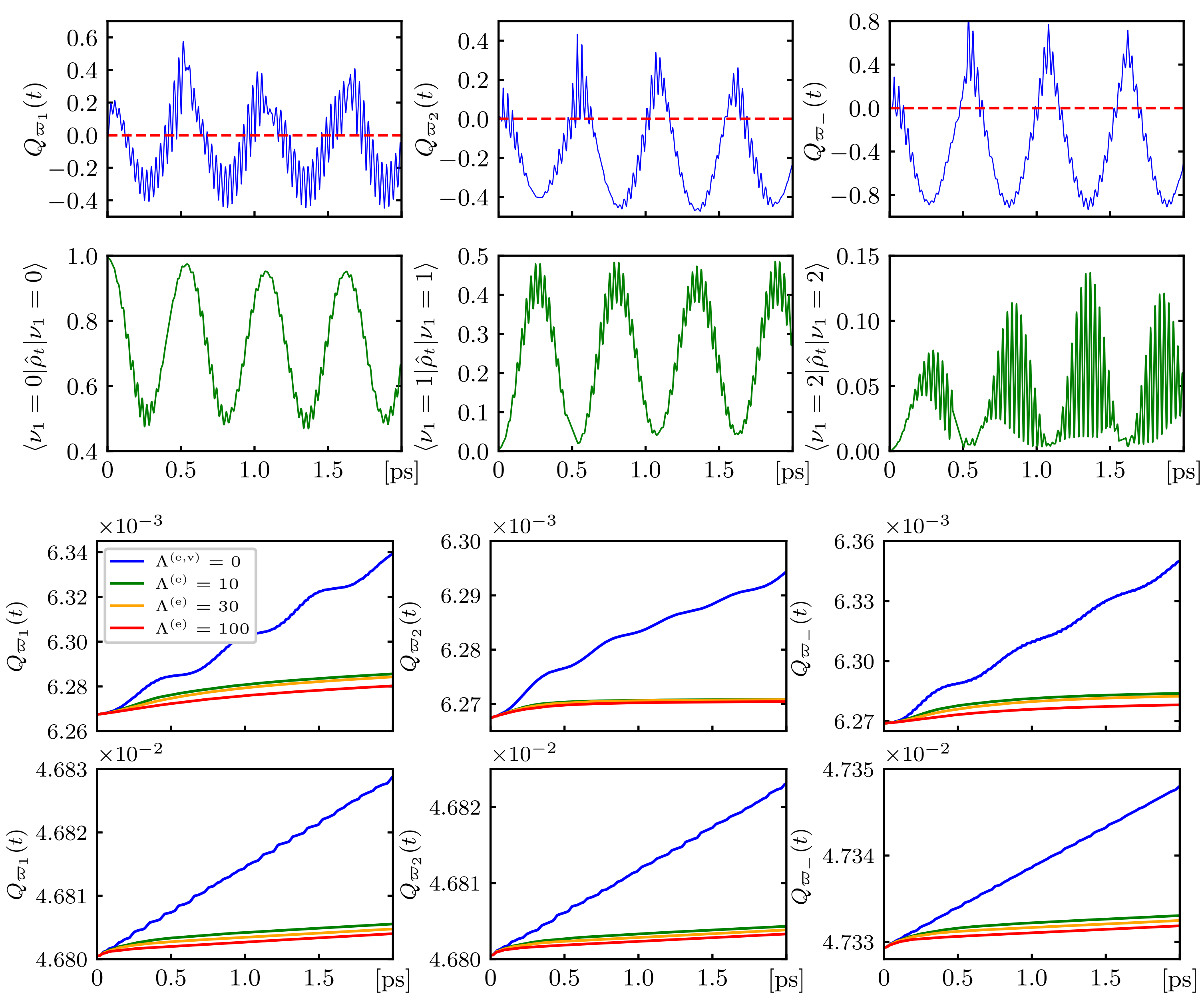
Universidad Industrial de Santander

SEMINARIO DEL ECOSISTEMA DE POSGRADOS EN FÍSICA

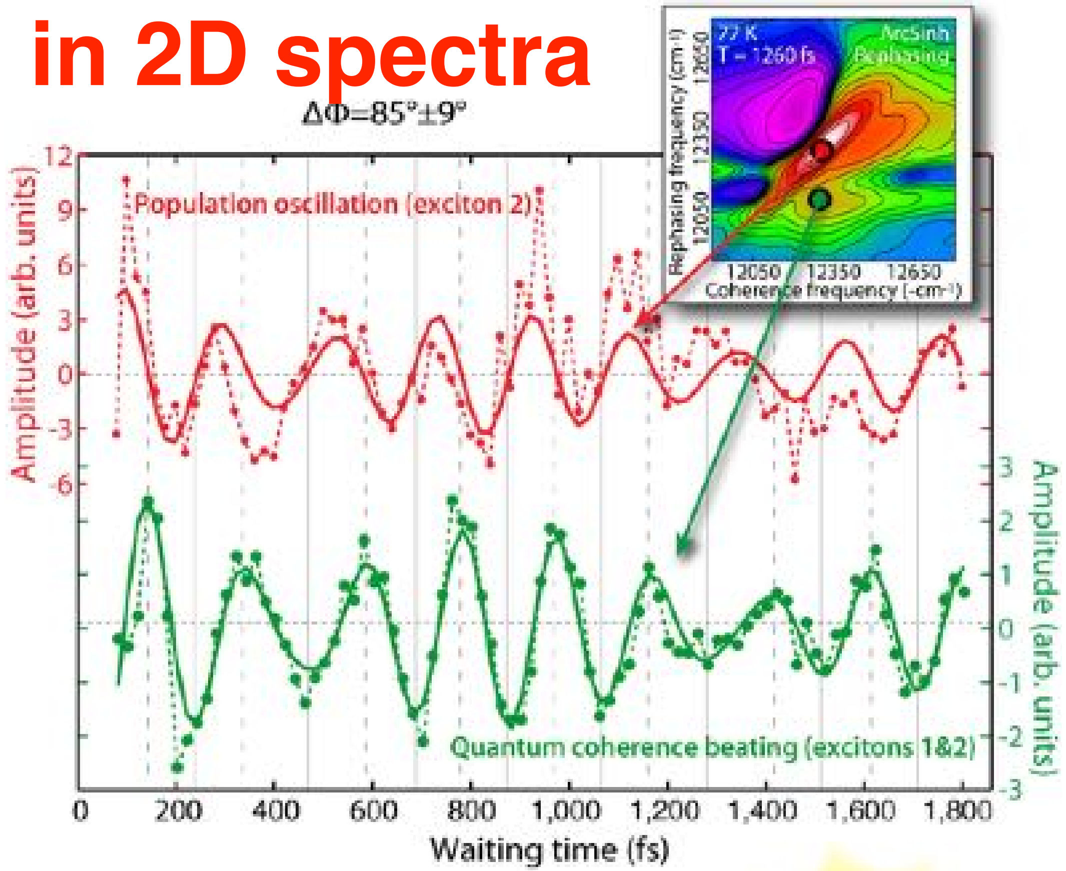
Dinámica de las vibraciones intramoleculares en dímeros fotosintéticos excitados con luz coherente e incoherente





Long-lived oscillations in 2D spectra

Figure taken from Panitchayangkoon et. al., Proc. Natl. Acad. Sci. USA **108**, 52, 20908-20912 (2011)



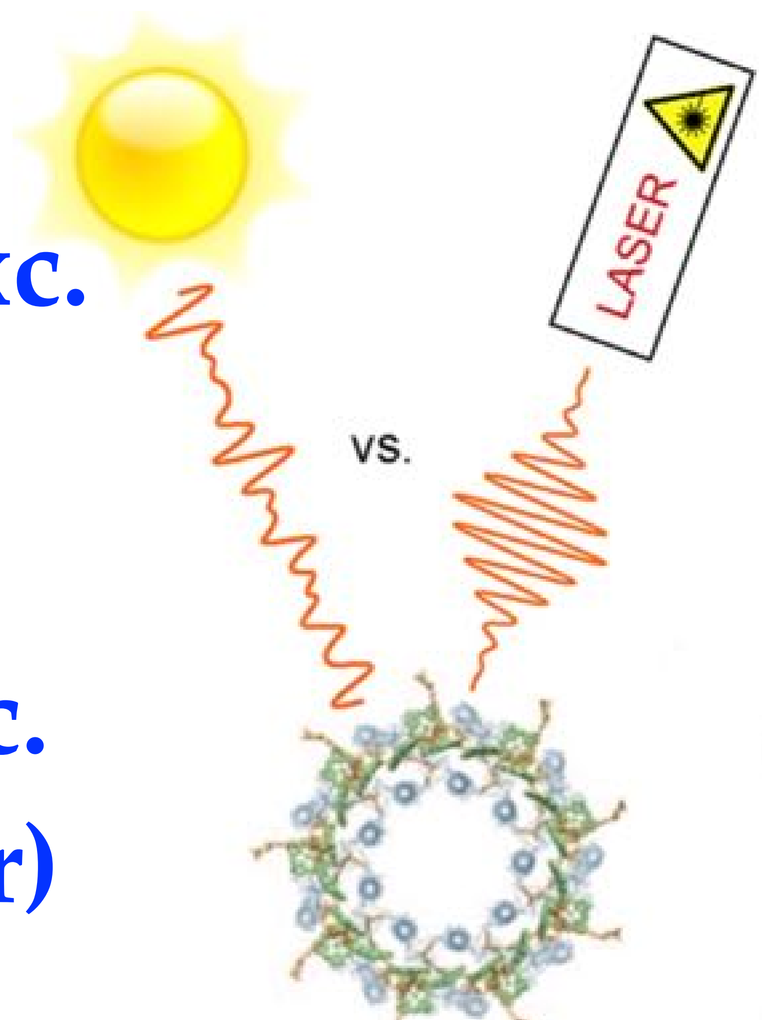
Quantum effects $\xrightarrow{?}$ Efficiency

$$\boxed{\tau_G = \sqrt{\frac{\hbar^2}{2\lambda k_{\mathrm{B}} T}} \qquad \begin{array}{l} T = 77\ \mathrm{K} \rightarrow \tau_G = 45\ \mathrm{fs} \\ T = 294\ \mathrm{K} \rightarrow \tau_G = 23\ \mathrm{fs} \end{array}}$$

Incoherent Exc. (Sunlight)

vs

Coherent Exc. (Pulsed Laser)



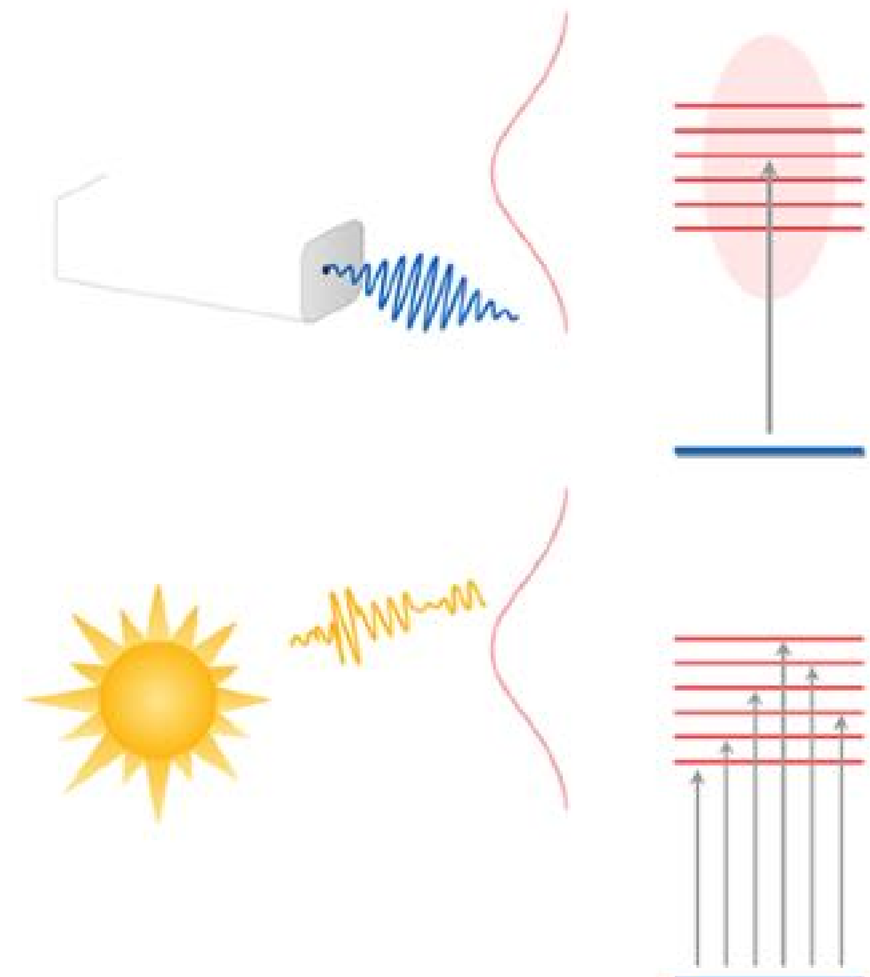
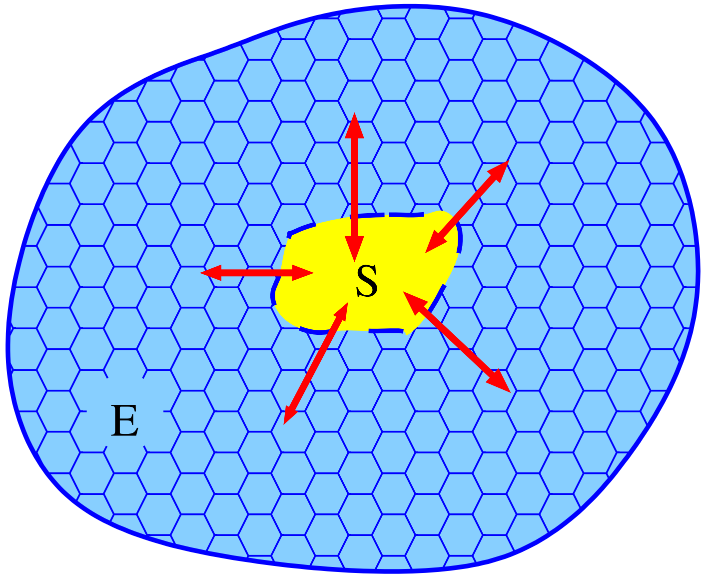


Figure taken from Kassal, et. al. J. Phys. Chem. Lett. **4,** 362-367 (2013)

Figure taken from Brumer, J. Phys. Chem. Lett. **9,** 2946-2955 (2018)

System - Environment

$$\hat{H} = \hat{H}_{\mathrm{S}} \otimes \hat{1}_{\mathrm{E}} + \hat{1}_{\mathrm{S}} \otimes \hat{H}_{\mathrm{E}} + \hat{H}_{\mathrm{I}}$$



$$\mathcal{H}_{\mathrm{SE}} = \mathcal{H}_{\mathrm{S}} \otimes \mathcal{H}_{\mathrm{E}}$$

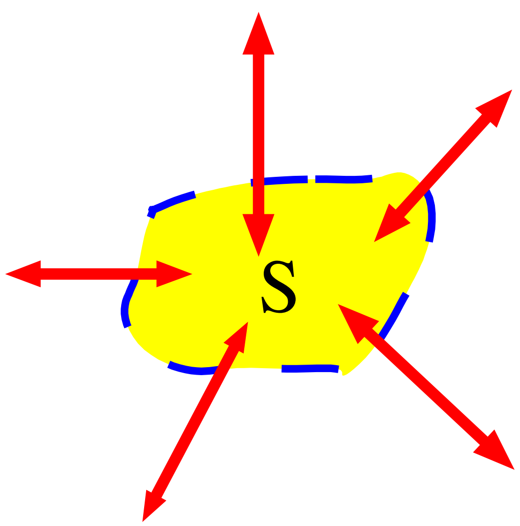
$$\hat{\rho}(t)$$

von-Neumann Equation

$$\frac{d\hat{\rho}(t)}{dt} = -\frac{\mathrm{i}}{\hbar}\left[\hat{H}(t), \hat{\rho}(t)\right]$$

$$\langle \hat{\mathcal{O}} \rangle = \mathrm{Tr}\{\hat{\rho}\hat{\mathcal{O}}\}$$

Open quantum system



$$\mathcal{H}_{\mathrm{S}}$$

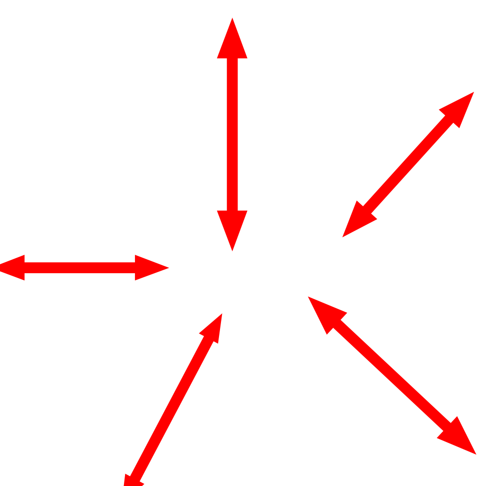
$$\hat{\rho}_{\mathrm{S}}(t)$$

Reduced density operator

$$\hat{\rho}_{\mathrm{S}}(t) = \mathrm{Tr}_{\mathrm{E}}\, \hat{\rho}(t)$$

$$\frac{d\hat{\rho}_{\mathrm{S}}(t)}{dt} = -\frac{\mathrm{i}}{\hbar}\mathrm{Tr}_{\mathrm{E}}\left[\hat{H}(t), \hat{\rho}(t)\right]$$

$$\langle \hat{\mathcal{A}} \rangle = \mathrm{Tr}_{\mathrm{S}}\{\hat{\mathcal{A}}\hat{\rho}_{\mathrm{S}}\}$$



- Dissipation
- Fluctuations
- Decoherence

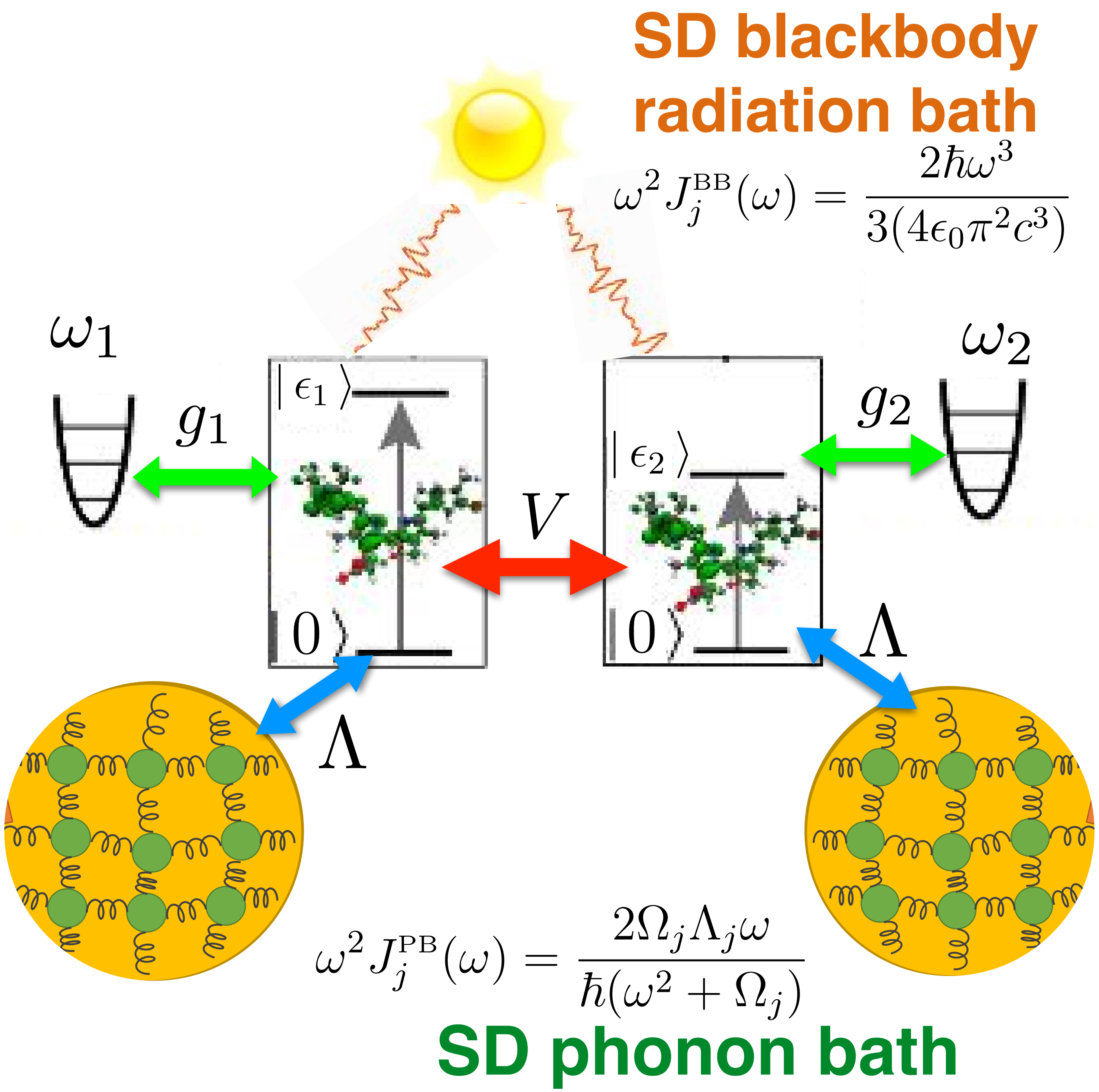
Redfield Master Equation

$$\frac{\mathrm{d}\rho_{ab}(t)}{\mathrm{d}t} = -\mathrm{i}\omega_{ab}\rho_{ab}(t) - \sum_{cd} R_{ab,cd}\,\rho_{cd}(t)$$

$$\hat{H}_{\rm S} = \sum_{i=1}^{N} \left(E_{{\rm g}_i}\hat{1}_i + \epsilon_i \sigma_i^+ \sigma_i^-\right) + \sum_{i\neq j}^{N} V_{ij}\sigma_i^+\sigma_j^- + \sum_{i=1}^{N} \hbar g_i \sigma_i^+\sigma_i^- \left(\hat{b}_i^\dagger + \hat{b}_i\right) + \sum_{i=1}^{N} \hbar\varpi_i \hat{b}_i^\dagger \hat{b}_i$$

$$\hat{H}_{\rm SB} = \sum_{i,l} \hbar g_{il}\sigma_i^+\sigma_i^- \left(\hat{b}_l^{(i)} + \hat{b}_l^{(i)\dagger}\right) - \sum_j \hat{\boldsymbol{\mu}}_j \cdot \hat{\mathbf{E}}(t)$$

$$\hat{H}_{\rm B} = \sum_{i,l} \hbar\omega_l^{(i)} \hat{b}_l^{(i)\dagger}\hat{b}_l^{(i)} + \sum_{\mathbf{k},s} \hbar c k \hat{a}_{\mathbf{k},s}^\dagger \hat{a}_{\mathbf{k},s}$$



Vibronic states

$$|\,g_i,\nu_i\,\rangle = \frac{\left(\hat{b}_i^\dagger\right)^{\nu_i}}{\sqrt{\nu_i!}}|\,g_i,0\,\rangle$$

$$|\,\epsilon_i,\nu_i\,\rangle = \sigma_i^+\frac{\left(\hat{b}_i^\dagger\right)^{\nu_i}}{\sqrt{\nu_i!}}|\,g_i,0\,\rangle$$

Open system Eigenstates

$$\hat{H}_{\rm S}|\,\psi_n\,\rangle \; = \; \xi_n|\,\psi_n\,\rangle$$

$$|\,\psi_n^{(\epsilon)}\,\rangle = \sum_{i=1}^{N}\sum_{\nu_i} C_{i,\nu_i}^n|\,\epsilon_i,\nu_i\,\rangle$$

$$\frac{{\rm d}\rho_{ab}(t)}{{\rm d}t} = -{\rm i}\omega_{ab}\rho_{ab}(t) - \sum_{cd} R_{ab,cd}\,\rho_{cd}(t)$$

Redfield Master Equation

$$\frac{\mathrm{d}\rho_{ab}(t)}{\mathrm{d}t} = -\mathrm{i}\omega_{ab}\rho_{ab}(t) - \sum_{cd} R_{ab,cd}\,\rho_{cd}(t)$$

- No-initial correlations S-E
- Weak coupling S-E
- Markov approximation

Population transfer $(a = b,\ c = d)$

Coherences-Populations transfer $(a = b,\ c \neq d,\ c = d,\ a \neq b)$

Coherence dephasing $(a = c,\ b = d,\ a \neq b)$

Coherence transfer (None of the above)

$$R^{\mathrm{PB,BB}}_{ab,cd} = \delta_{ac}\sum_e \Gamma^{\mathrm{PB,BB}}_{be,ed}(\omega_{de}) + \delta_{b,d}\sum_e \Gamma^{\mathrm{PB,BB}}_{ae,ec}(\omega_{ce}) - \Gamma^{\mathrm{PB,BB}}_{ca,bd}(\omega_{db}) - \Gamma^{\mathrm{PB,BB}}_{db,ac}(\omega_{ca})$$

$$\Gamma^{\mathrm{PB,BB}}_{ab,cd}(\omega) = \sum_{u,v}\int_0^\infty \mathrm{d}\tau \mathrm{e}^{\mathrm{i}\omega\tau} C^{\mathrm{PB,BB}}_{u,v}(\tau)\hat{K}^{\mathrm{PB,BB}}_{u,ab}\hat{K}^{\mathrm{PB,BB}}_{v,cd}$$

$$C^{\mathrm{PB,BB}}_{u,v}(\tau) = \tfrac{1}{\hbar^2}\left\langle \hat{\Phi}^{\mathrm{PB,BB}}_{u,ab}(t)\hat{\Phi}^{\mathrm{PB,BB}}_{v,ab}(0)\right\rangle_{\mathrm{PB,BB}}$$

$$C^{\mathrm{PB,BB}}_i(t) = \int_0^\infty \mathrm{d}\omega\omega^2 J^{\mathrm{PB,BB}}_i(\omega)\left[\coth\left(\frac{\hbar\omega\beta}{2}\right)\cos(\omega t) - \mathrm{i}\sin(\omega t)\right]$$

Spectral densities (SD)

$$\omega^2 J^{\mathrm{PB}}_j(\omega) = \frac{2\Omega_j\Lambda_j\omega}{\hbar(\omega^2+\Omega_j)}$$ **SD phonon bath**

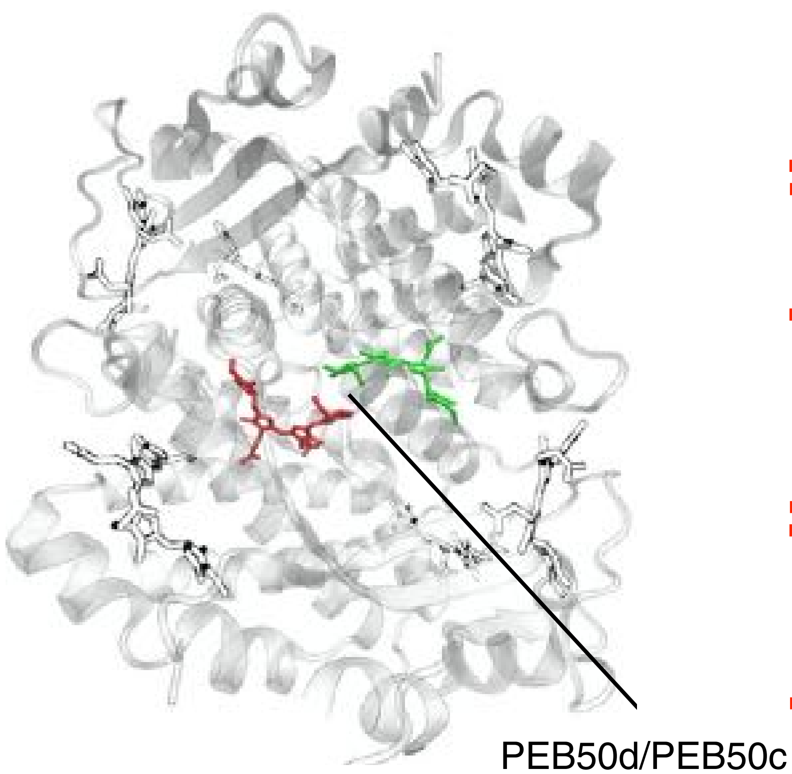
$$\omega^2 J^{\mathrm{BB}}_j(\omega) = \frac{2\hbar\omega^3}{3(4\epsilon_0\pi^2c^3)}$$ **SD blackbody radiation bath**

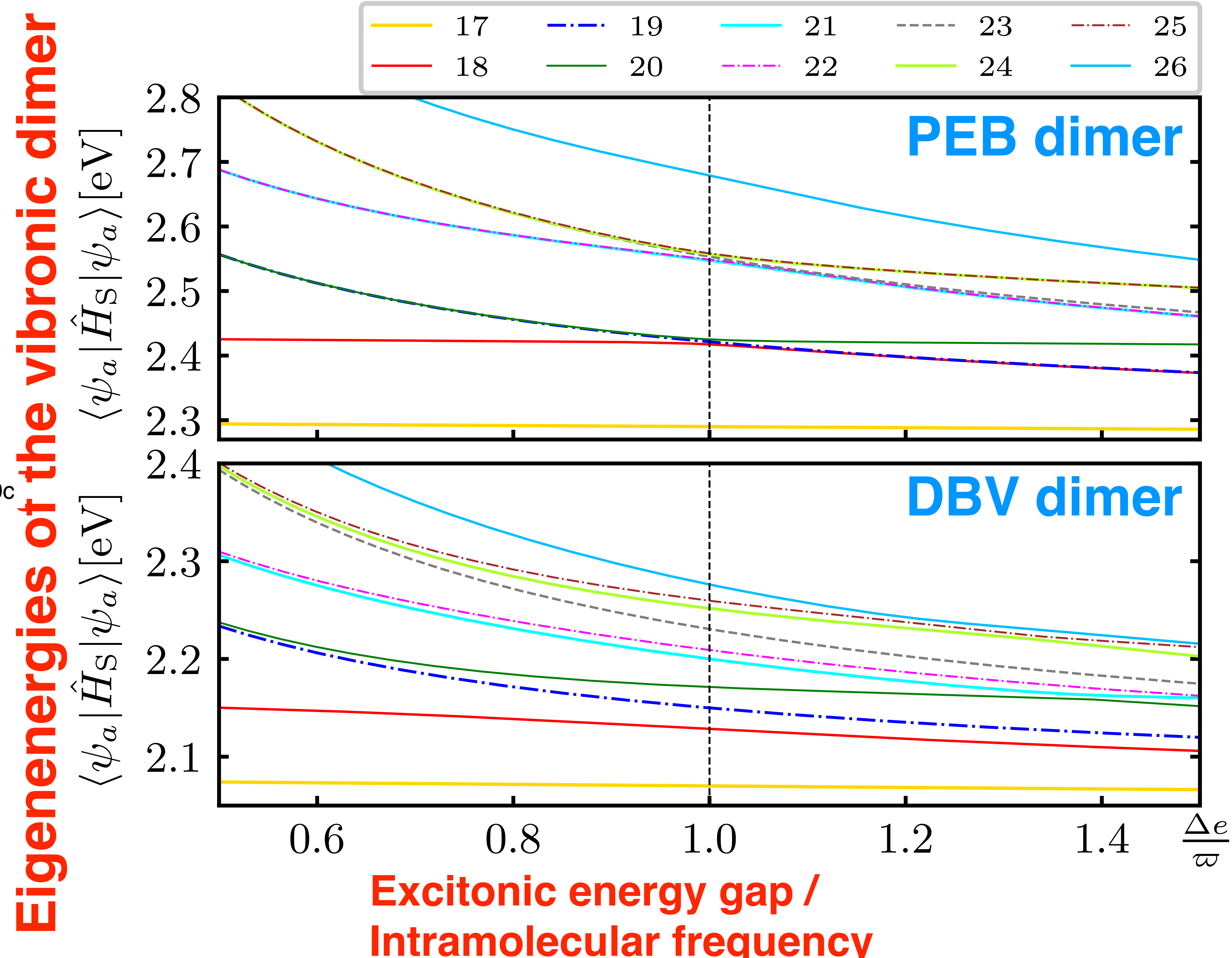
Dimer	TDM[a] (D)	$\Delta\epsilon$[b] (cm^{-1})	V[c] (cm^{-1})	Δe[d] (cm^{-1})
PEB	11.87, 12.17	1042	92	1058
DBV	13.1, 13.2	73	319.4	643

[a] Transition dipole moments.
[b] Site energy difference.
[c] Electronic coupling.
[d] Exciton energy splitting.

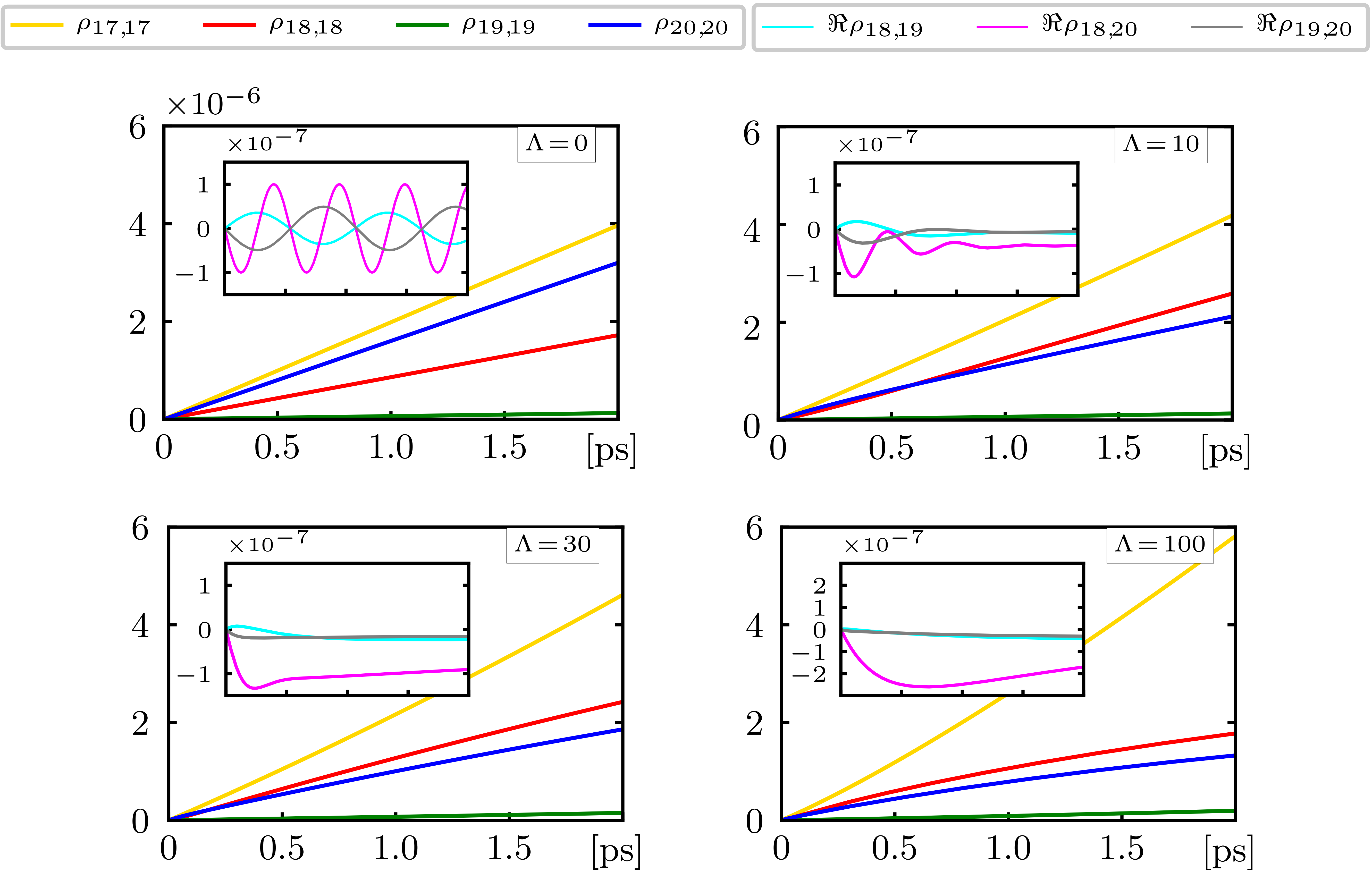
$$T_{\mathrm{PB}} = 300\,\mathrm{K},\ T_{\mathrm{BB}} = 5600\,\mathrm{K}.$$

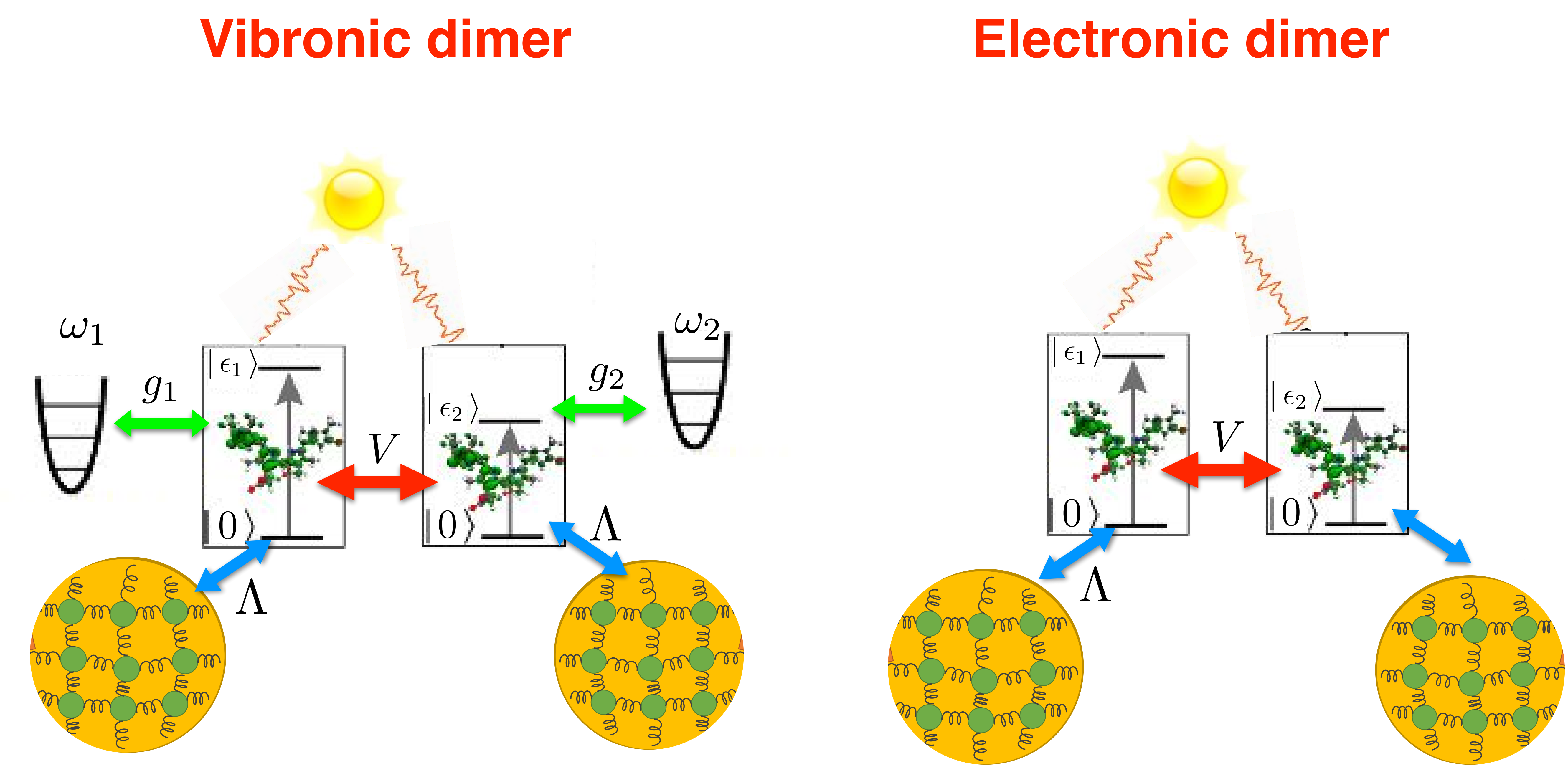
$$\rho(t_0) = \rho_{\mathrm{S}}(t_0) \otimes \rho_{\mathrm{BB}}(t_0) \otimes \rho_{\mathrm{TB}}(t_0)$$





PEB dimer - Vibronic exciton basis dynamics

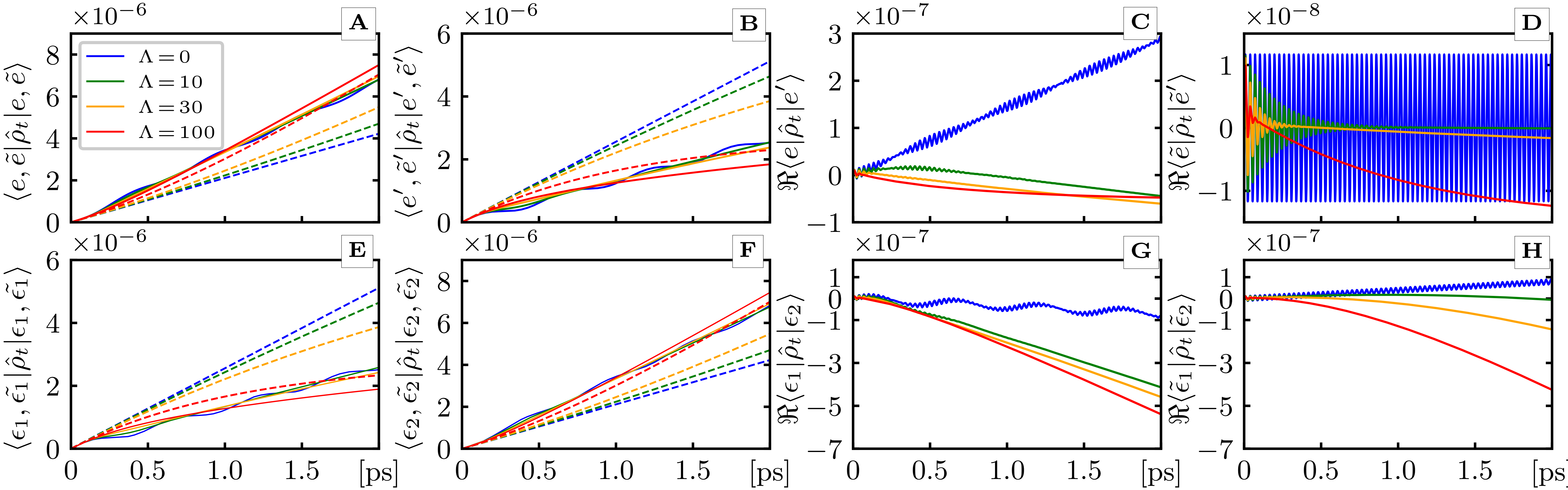




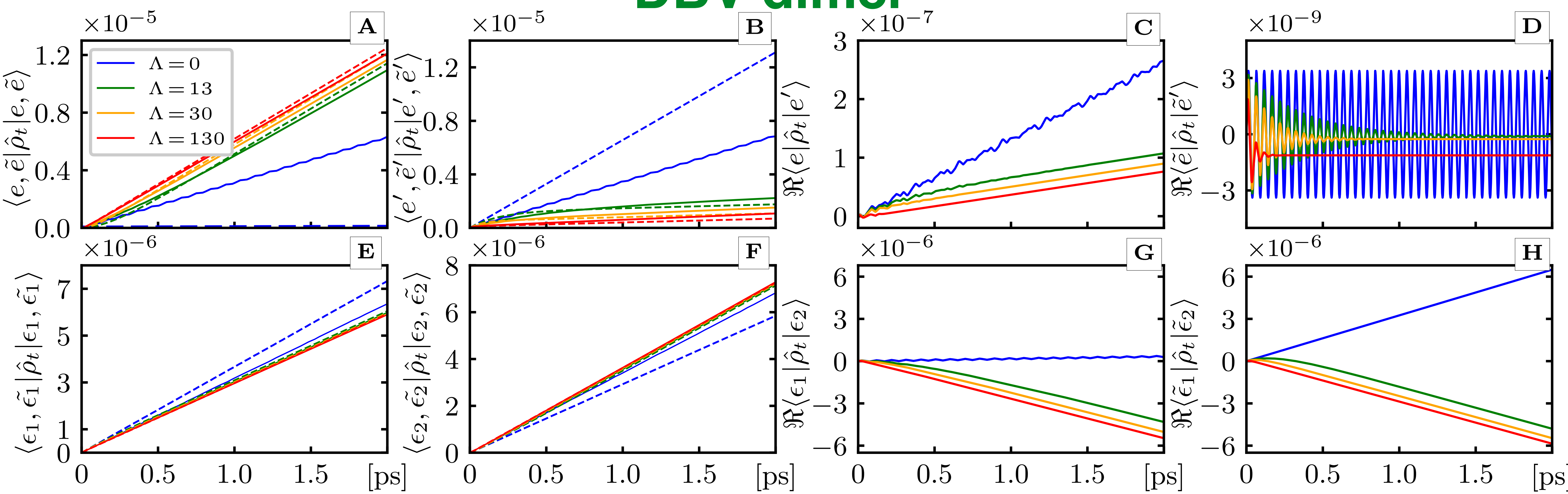
Vibronic dimer
Electronic dimer
ω_1
g_1
$|\epsilon_1\rangle$
$|0\rangle$
V
$|\epsilon_2\rangle$
$|0\rangle$
g_2
ω_2
Λ
Λ
$|\epsilon_1\rangle$
$|0\rangle$
V
$|\epsilon_2\rangle$
$|0\rangle$
Λ

Dynamics in the exciton and site bases

PEB dimer



DBV dimer



Non-classicality of bosonic fields

Fock (Number) states

$$\hat{H} = \hbar\omega\left(\hat{n} + \frac{1}{2}\right)$$

$$\hat{n}\left|n\right\rangle = n\left|n\right\rangle; \quad n = 0, 1, 2, 3, \ldots, \infty.$$

$$\hat{n} = \hat{a}^\dagger \hat{a}$$

$$\left|n\right\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}\left|0\right\rangle$$

$$\left\langle n|n'\right\rangle = \delta_{nn'}, \quad \sum_{n=0}^{\infty} |n\rangle\langle n| = 1$$

Coherent states

$$\hat{a}\left|\alpha\right\rangle = \alpha\left|\alpha\right\rangle$$

$$\left|\alpha\right\rangle = \mathrm{e}^{-\frac{1}{2}|\alpha|^2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}}\left|n\right\rangle$$

$$\left\langle \hat{n}^2\right\rangle - \langle\hat{n}\rangle^2 = \langle\hat{n}\rangle$$

$$\frac{1}{\pi}\int |\alpha\rangle\langle\alpha|\,\mathrm{d}^2\alpha = 1, \quad \alpha = x + \mathrm{i}y, \quad \mathrm{d}^2\alpha = \mathrm{d}x\mathrm{d}y, \quad -\infty \le x, y \le \infty.$$

$$\left\langle \alpha|\beta\right\rangle = \exp\left(\alpha^*\beta - \frac{1}{2}|\alpha|^2 - \frac{1}{2}|\beta|^2\right)$$

Diagonal coherent state representation

$$\hat{\rho} = \int P(\alpha)\,|\alpha\rangle\langle\alpha|\,\mathrm{d}^2\alpha, \quad \int P(\alpha)\mathrm{d}^2\alpha = 1.$$

Quantum states with $P(\alpha) \geq 0$ are considered "classical"

$$P(\alpha) = \frac{1}{\pi^2}\mathrm{e}^{|\alpha|^2}\int \langle -\beta|\hat{\rho}|\beta\rangle\,\mathrm{e}^{|\beta|^2-(\beta\alpha^*-\beta^*\alpha)}\mathrm{d}^2\beta.$$

$$\left\langle \hat{a}^{\dagger m}\hat{a}^n \right\rangle = \int P(\alpha)\alpha^{*m}\alpha^n\mathrm{d}^2\alpha = \left\langle \alpha^{*m}\alpha^n \right\rangle_P.$$

Mandel Parameter

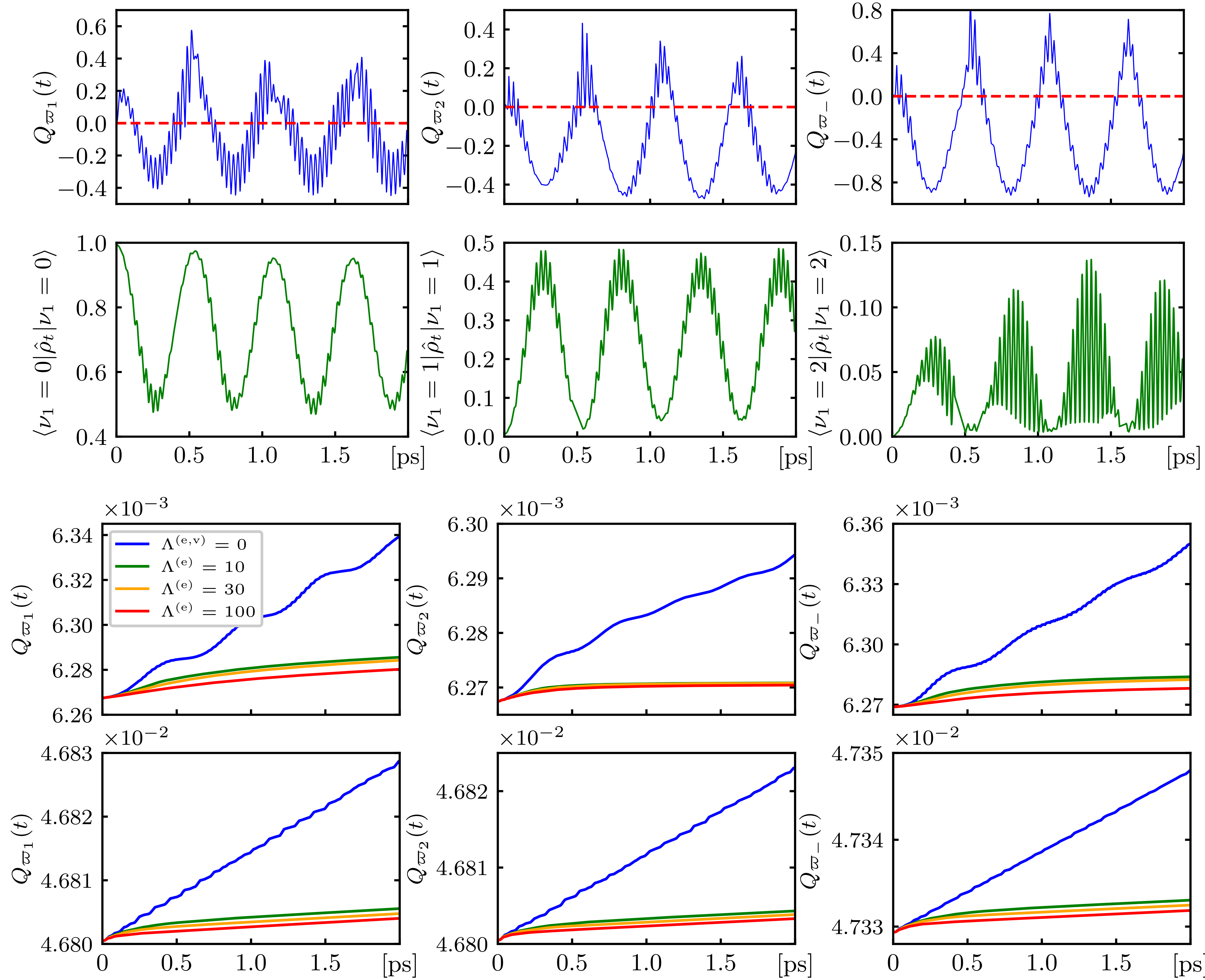
$$Q_M = \frac{\langle \hat{n}^2\rangle - \langle \hat{n}\rangle^2}{\langle \hat{n}\rangle} - 1 = \frac{\left\langle (\hat{a}^\dagger\hat{a})^2\right\rangle - \left\langle \hat{a}^\dagger\hat{a}\right\rangle^2 - \left\langle \hat{a}^\dagger\hat{a}\right\rangle}{\left\langle \hat{a}^\dagger\hat{a}\right\rangle}.$$

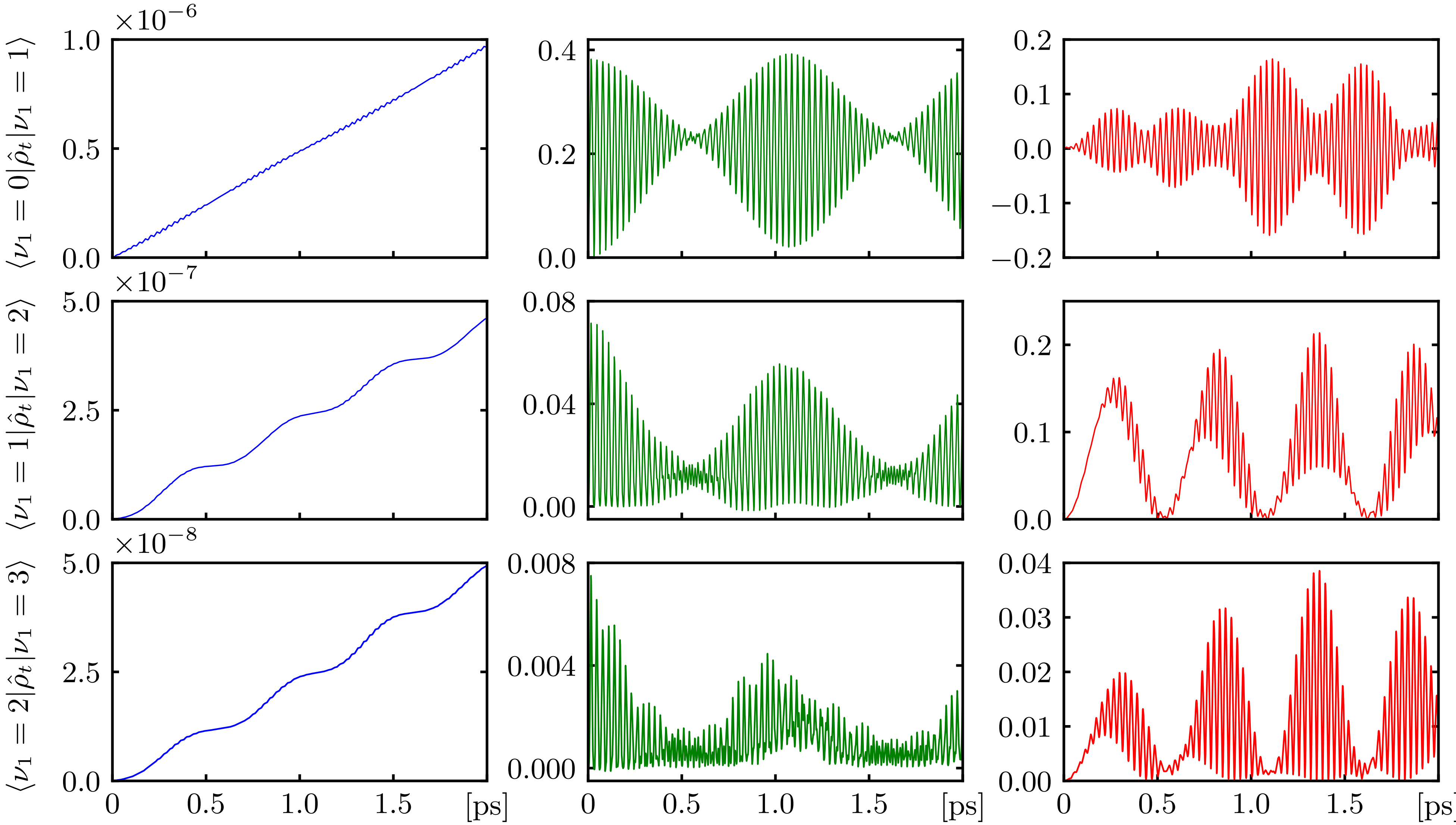
Mandel established that the photon number distribution for the case of a coherent state corresponds to a Poisson distribution, and therefore any distribution that is narrower than this must correspond to a non-classical state.

A negative value of Q represents a sufficient condition for a state to be considered non-classical.

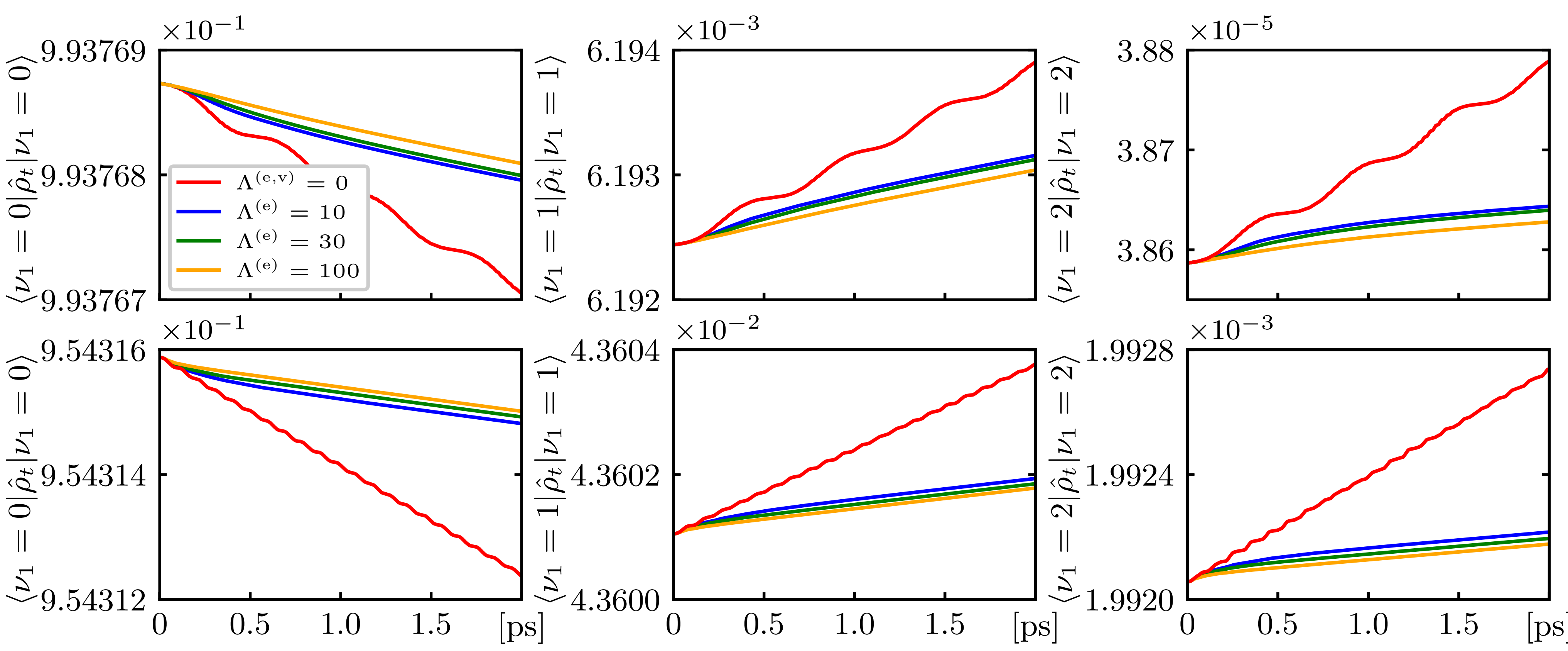
$$Q_M = \frac{\left\langle \hat{a}^{\dagger 2}\hat{a}^2\right\rangle - \left\langle \hat{a}^\dagger\hat{a}\right\rangle^2}{\left\langle \hat{a}^\dagger\hat{a}\right\rangle} = \frac{\left\langle \alpha^{*2}\alpha^2\right\rangle_P - \langle \alpha^*\alpha\rangle_P^2}{\langle \alpha^*\alpha\rangle_P} = \frac{\left\langle (\alpha^*\alpha - \langle \alpha^*\alpha\rangle_P)^2\right\rangle_P}{\langle \alpha^*\alpha\rangle_P}.$$

$$\hat{H}_{\mathrm{S}} = \epsilon_1 \hat{\sigma}_1^+ \hat{\sigma}_1^- + \epsilon_2 \hat{\sigma}_2^+ \hat{\sigma}_2^- + V_{12}\left(\hat{\sigma}_1^+ \hat{\sigma}_2^- + \hat{\sigma}_2^+ \hat{\sigma}_1^-\right) + \hbar\varpi\left(\hat{b}_1^\dagger \hat{b}_1 + \hat{b}_2^\dagger \hat{b}_2\right)$$
$$+ \hbar g\left[\hat{\sigma}_1^+ \hat{\sigma}_1^- \left(\hat{b}_1^\dagger + \hat{b}_1\right) + \hat{\sigma}_2^+ \hat{\sigma}_2^- \left(\hat{b}_2^\dagger + \hat{b}_2\right)\right].$$





$\langle \nu_1 = 0|\hat{\rho}_t|\nu_1 = 1\rangle$
$\langle \nu_1 = 1|\hat{\rho}_t|\nu_1 = 2\rangle$
$\langle \nu_1 = 2|\hat{\rho}_t|\nu_1 = 3\rangle$
$\times 10^{-6}$
$\times 10^{-7}$
$\times 10^{-8}$
1.0
0.5
0.0
5.0
2.5
0.0
5.0
2.5
0.0
0.4
0.2
0.0
0.08
0.04
0.00
0.008
0.004
0.000
0.2
0.1
0.0
−0.1
−0.2
0.2
0.1
0.0
0.04
0.03
0.02
0.01
0.00
0
0.5
1.0
1.5
[ps]



$\langle \nu_1 = 0|\hat{\rho}_t|\nu_1 = 0\rangle$
$\langle \nu_1 = 1|\hat{\rho}_t|\nu_1 = 1\rangle$
$\langle \nu_1 = 2|\hat{\rho}_t|\nu_1 = 2\rangle$
$\times 10^{-1}$
$\times 10^{-3}$
$\times 10^{-5}$
$\times 10^{-2}$
9.93769
9.93768
9.93767
6.194
6.193
6.192
3.88
3.87
3.86
9.54316
9.54314
9.54312
4.3604
4.3602
4.3600
1.9928
1.9924
1.9920
$\Lambda^{(\mathrm{e,v})} = 0$
$\Lambda^{(\mathrm{e})} = 10$
$\Lambda^{(\mathrm{e})} = 30$
$\Lambda^{(\mathrm{e})} = 100$
0
0.5
1.0
1.5
[ps]