Collective Non-Adiabatic Interactions through Light-Matter Coupling in a Cavity

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PHYSIKALISCH-CHEMISCHES INSTITUT

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Center for Quantum Dynamics

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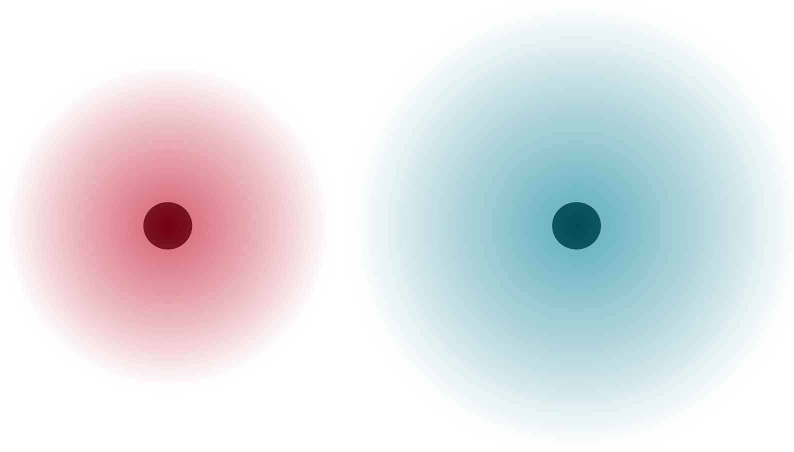
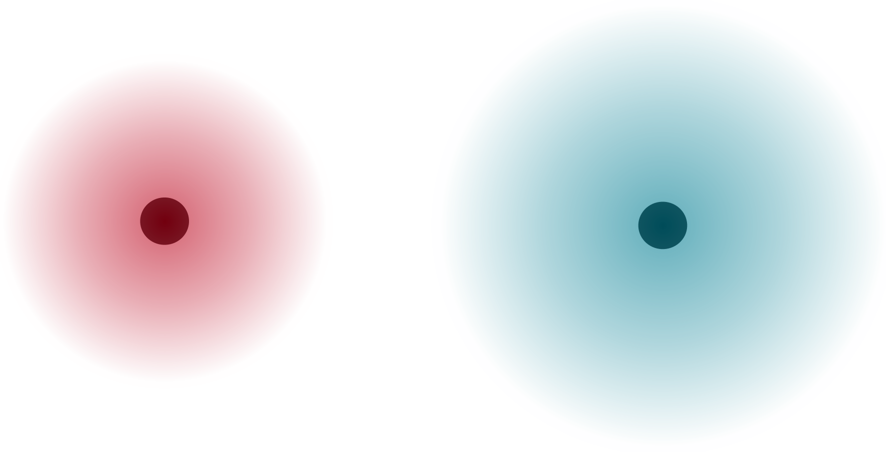
MOLECULAR POLARITONICS 2019
Theoretical and numerical approaches

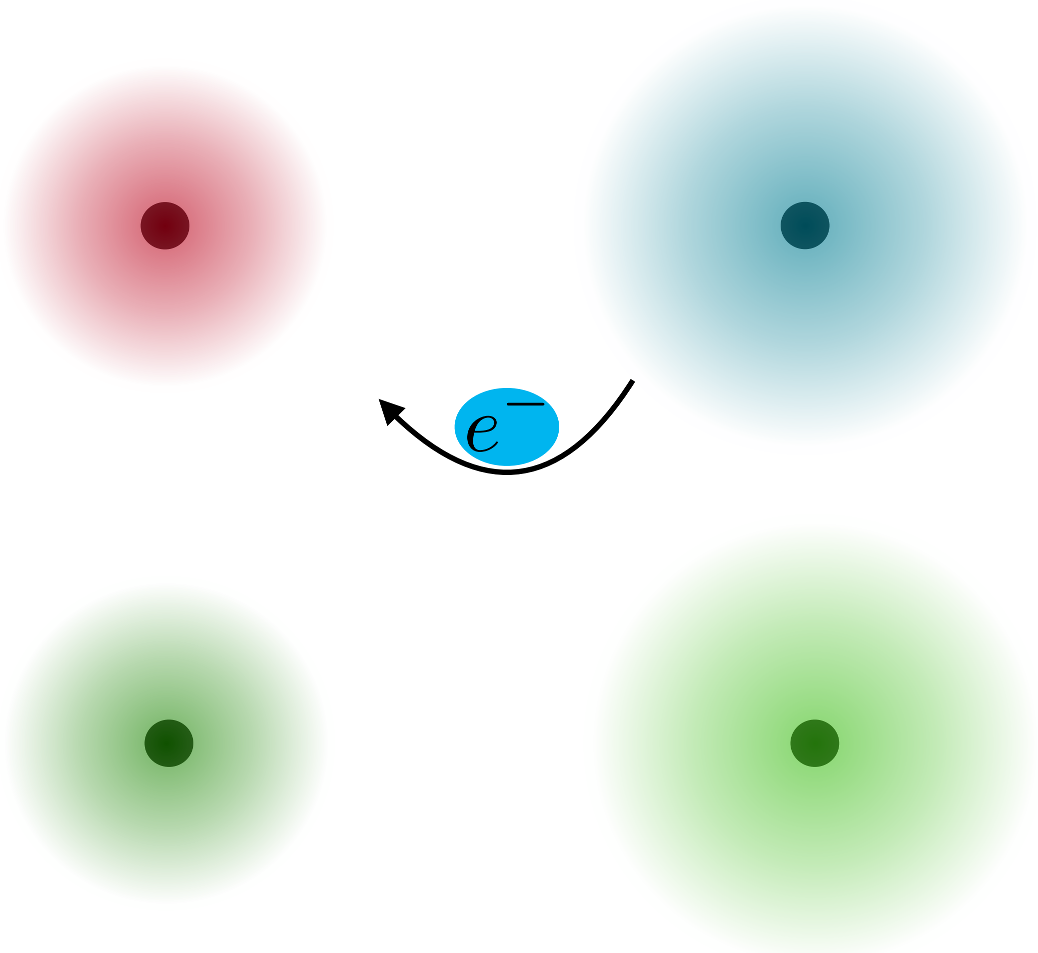
Non-adiabatic effects in molecules



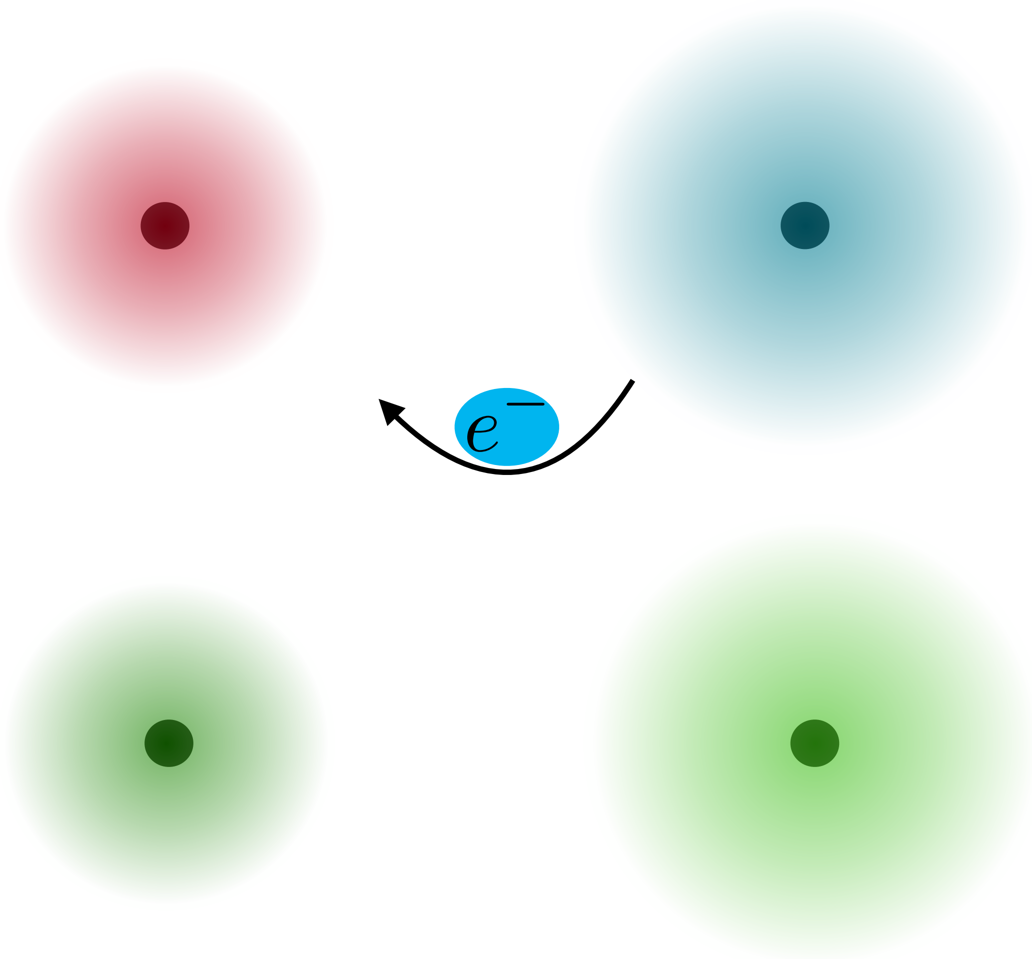
Non-adiabatic effects in molecules

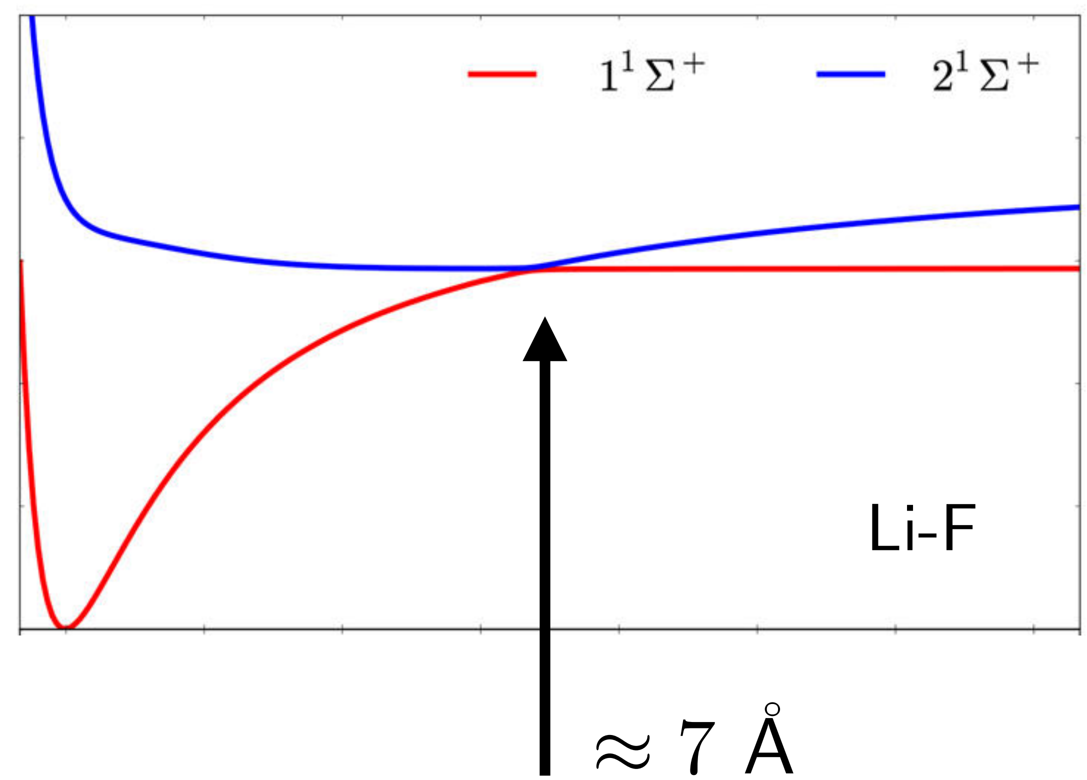


Non-adiabatic effects in molecules

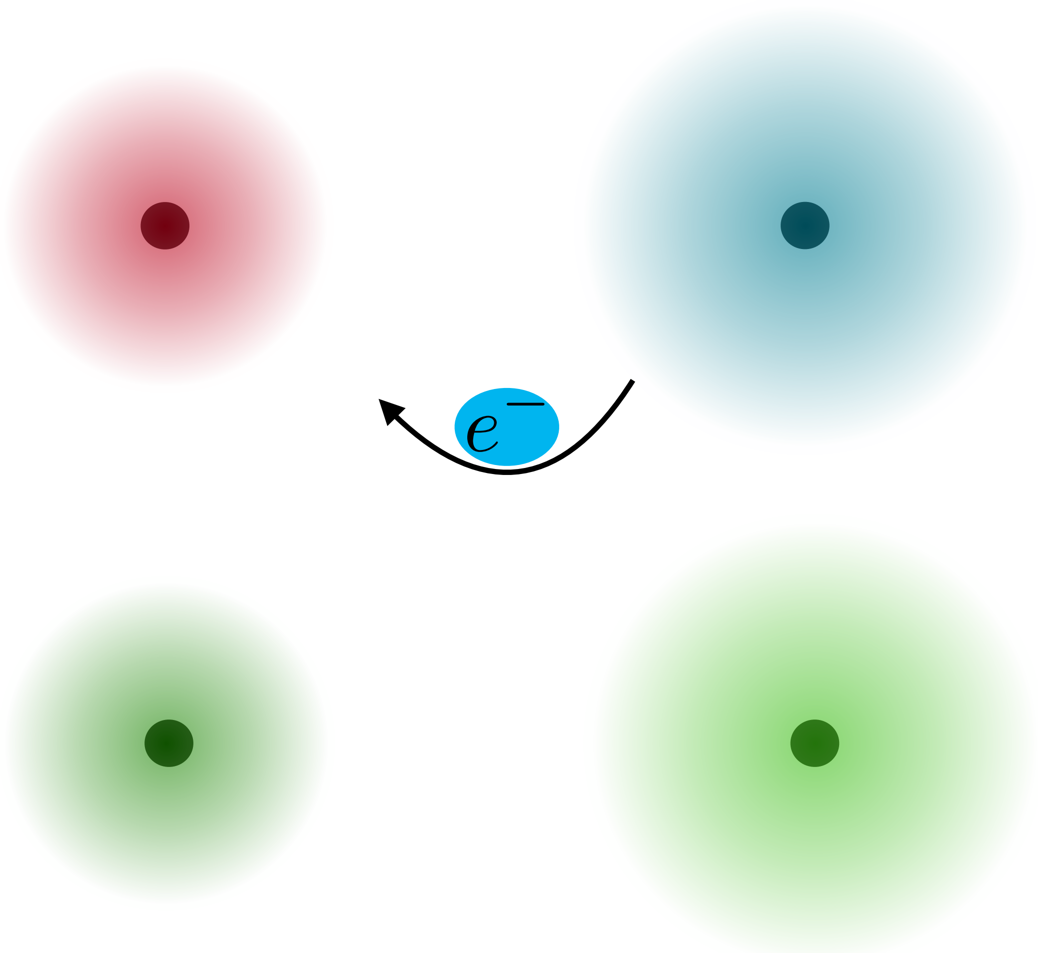


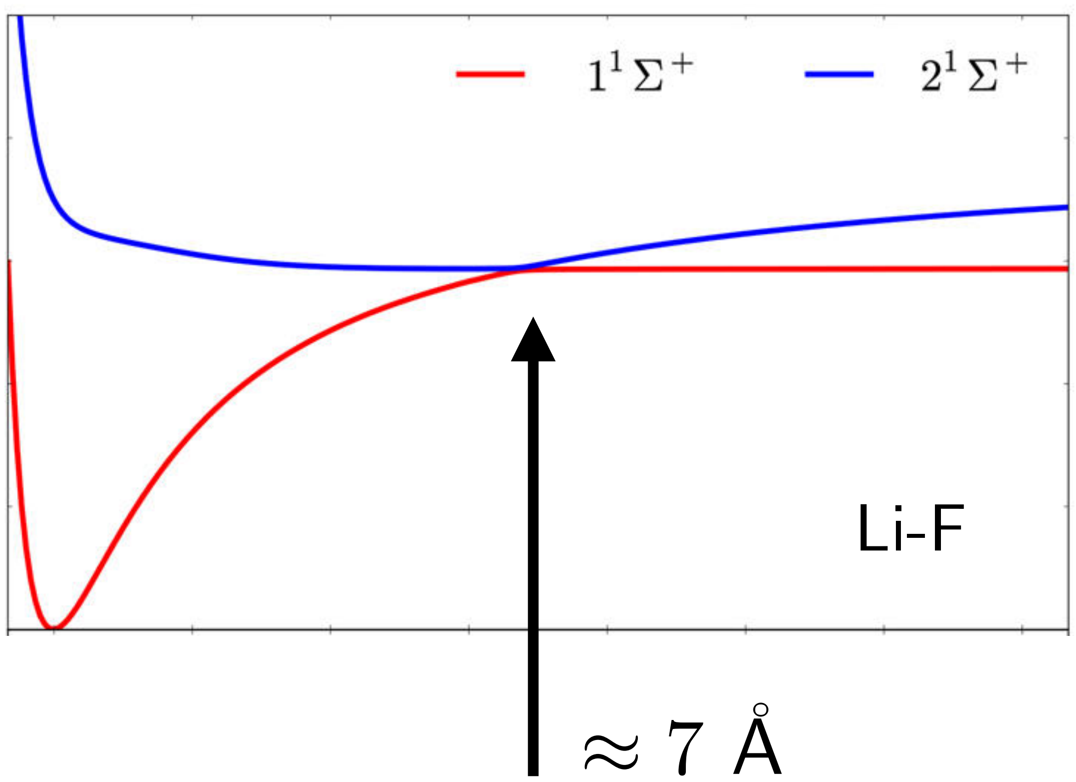
Non-adiabatic effects in molecules





Non-adiabatic effects in molecules





$$\hat{H} = \hat{T}_n + \hat{H}_e$$

$$\hat{H}_e \Phi_j(\mathbf{r}; \mathbf{R}) = V_j(\mathbf{R}) \Phi_j(\mathbf{r}; \mathbf{R})$$

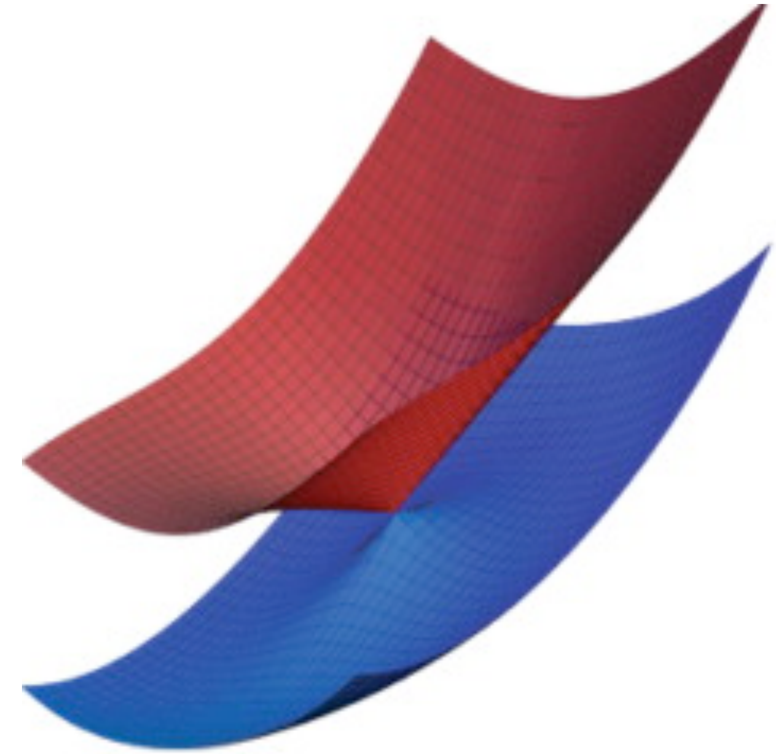
Quantum non-adiabatic dynamics

$$\Psi(\mathbf{r},\mathbf{R},t) = \sum_i \chi_i(\mathbf{R},t)\Phi_i(\mathbf{r};\mathbf{R})$$

Plug into TDSE

$$i\hbar\frac{\partial\chi_j}{\partial t} = (T_N + V_j)\chi_j - \sum_{i\neq j}\Lambda_{ji}\chi_i$$

M. Born and R. Oppenheimer, *Ann. Phys.*, **84**, 457 (1927)
M. Born and K. Huang, Book: *Oxford University Press,* [Appendix VIII] (1954)



- Photo-acidity
- DNA photo-protection
- …

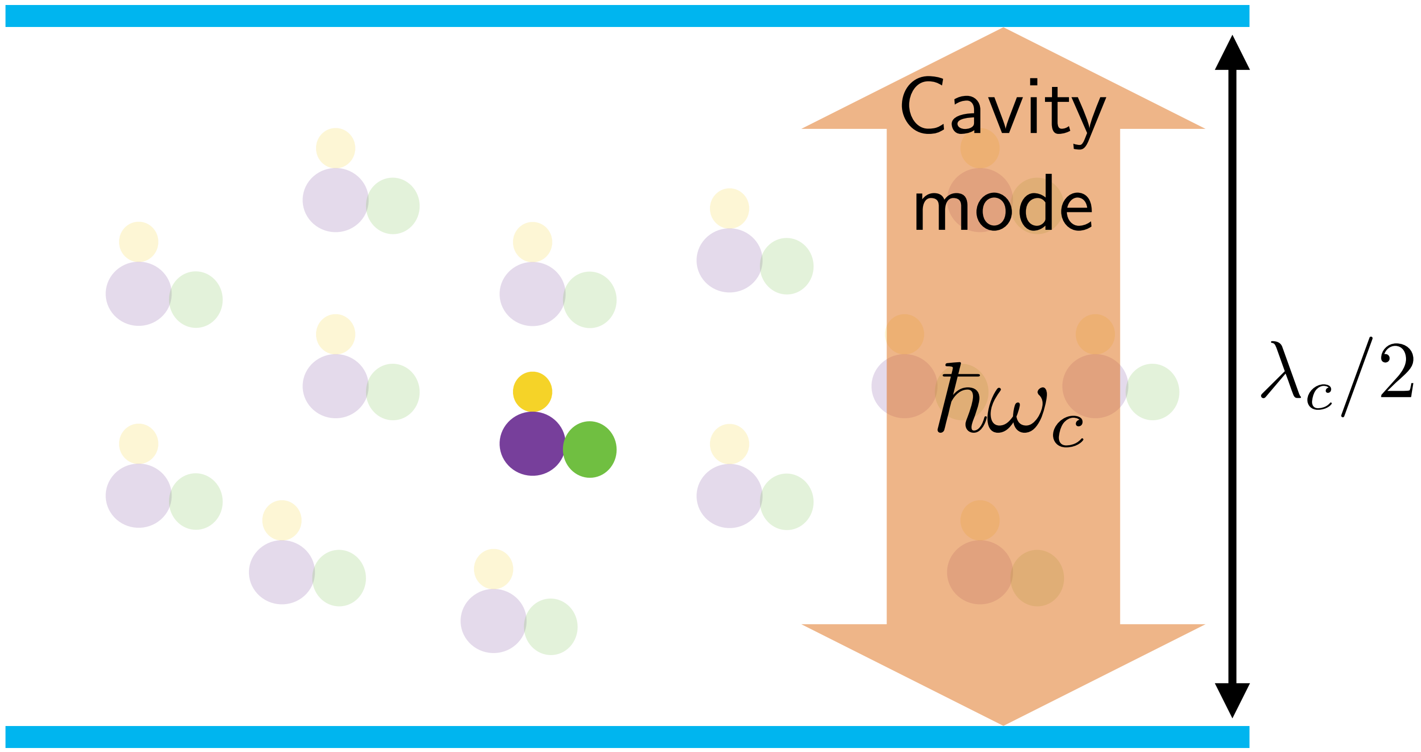
$$\Lambda_{ji} = \frac{1}{2M}(2\langle\Phi_j|\nabla\Phi_i\rangle\nabla + \langle\Phi_j|\nabla^2\Phi_i\rangle)$$

$$\langle\Phi_j|\nabla\Phi_i\rangle = \frac{\langle\Phi_j|(\nabla\hat{H}_{el})|\Phi_i\rangle}{V_i - V_j}$$

In practical applications it is often advantageous to use a **diabatic** representation.

Polaritonic chemistry

- The chemistry of molecular ensembles coupled to confined electromagnetic modes



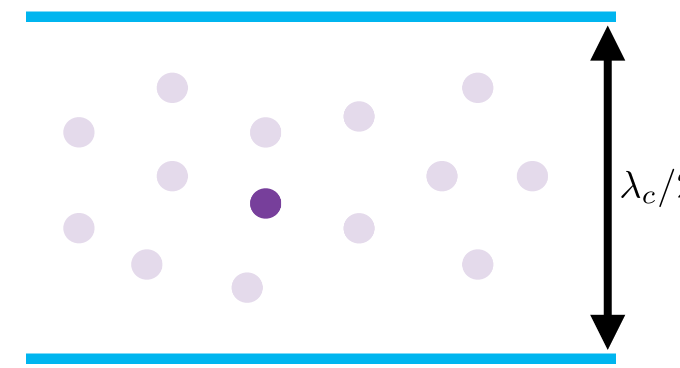
- Effects of the cavity on reaction rates, structure, absorption and emission properties, etc.

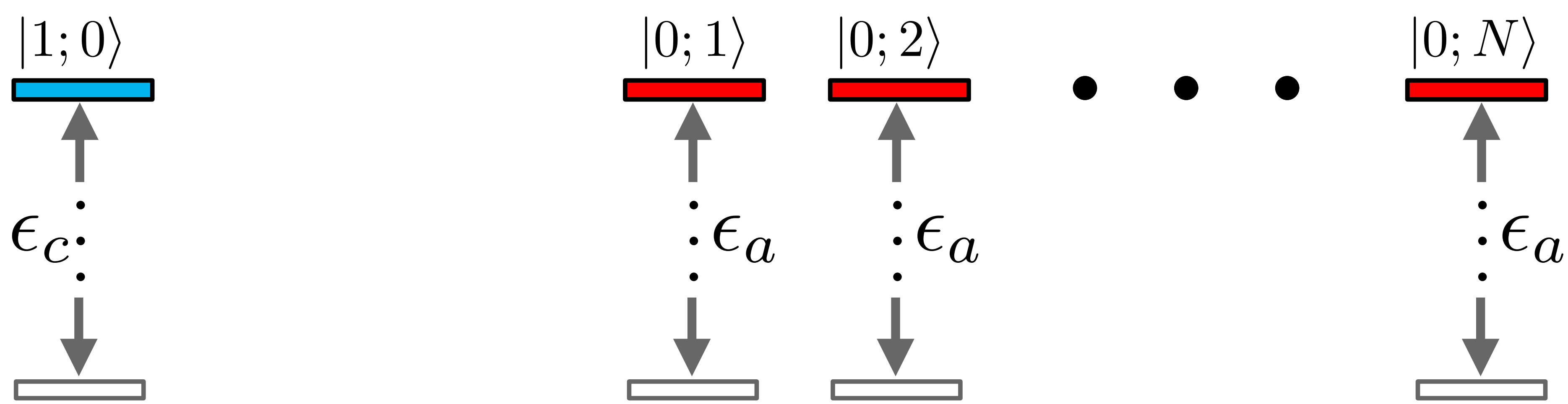
- Single molecule vs collective effects

Ensemble of 2-level atoms coupled to a cavity-mode

$$\begin{pmatrix} \epsilon_c & \gamma & \gamma & \gamma & \cdots \\ \gamma & \epsilon_a & 0 & 0 & \cdots \\ \gamma & 0 & \epsilon_a & 0 & \cdots \\ \gamma & 0 & 0 & \epsilon_a & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$$\gamma = g\langle 1;0|\hat{D}\hat{E}|0;m\rangle$$





M Tavis & FW Cummings, *Phys. Rev. A* **25**, 714 (1967)

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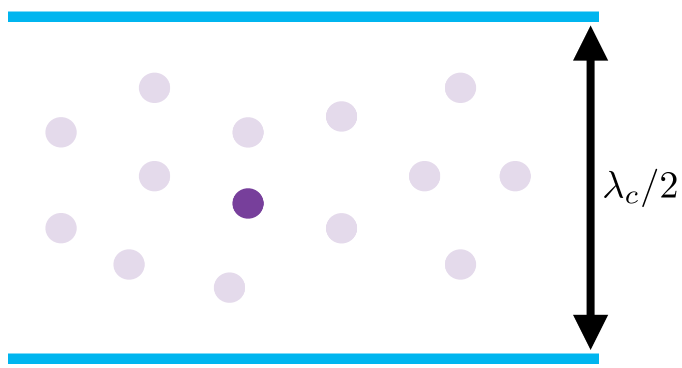
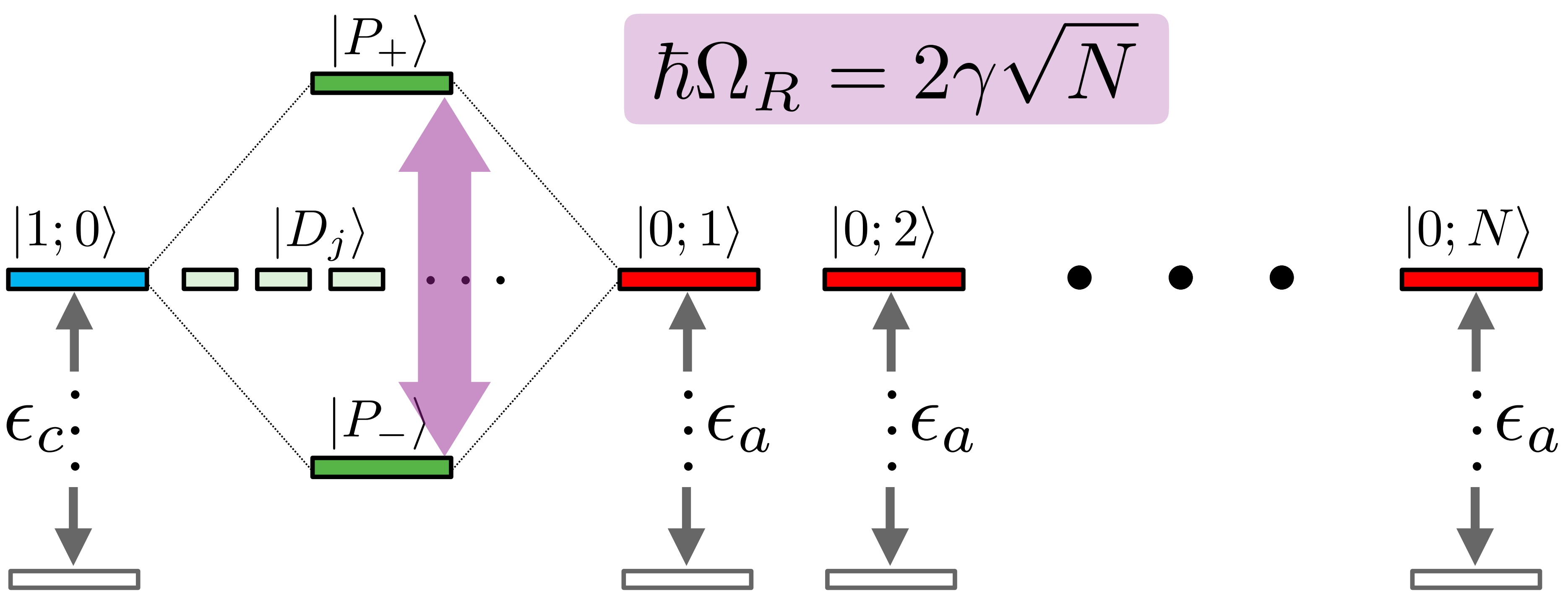


$$\hbar\Omega_R = 2\gamma\sqrt{N}$$



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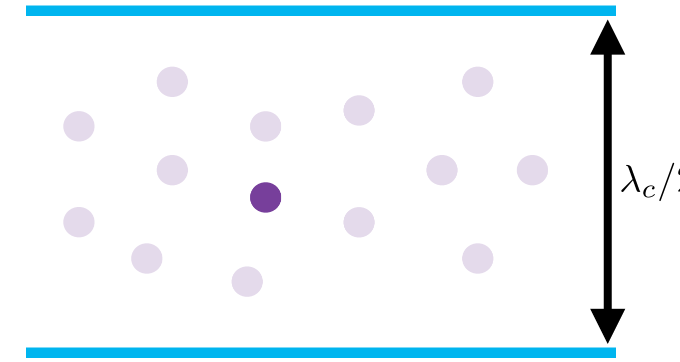

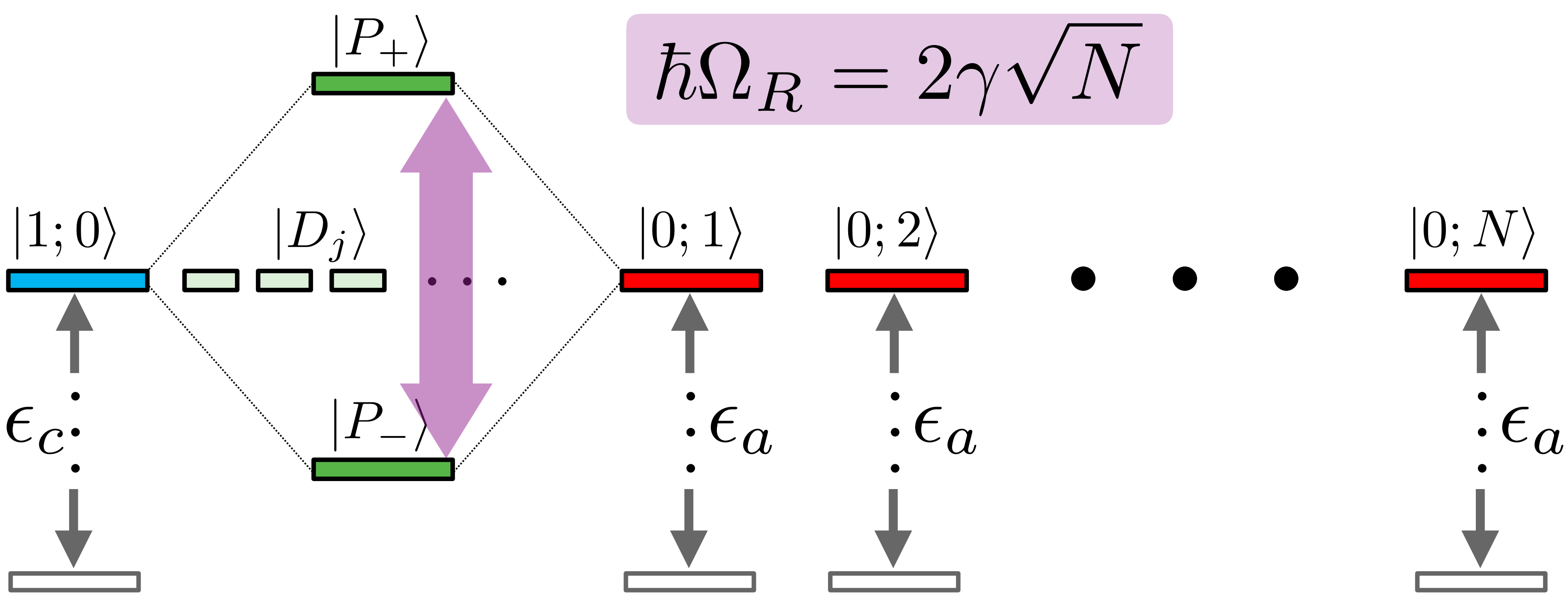

$$\hbar\Omega_R = 2\gamma\sqrt{N}$$

$$|P_\pm\rangle = \frac{1}{\sqrt{2}}\left(|1;0\rangle \mp \frac{1}{\sqrt{N}}\sum_{m=1}^{N}|0;m\rangle\right)$$

M Tavis & FW Cummings, *Phys. Rev. A* **25**, 714 (1967)

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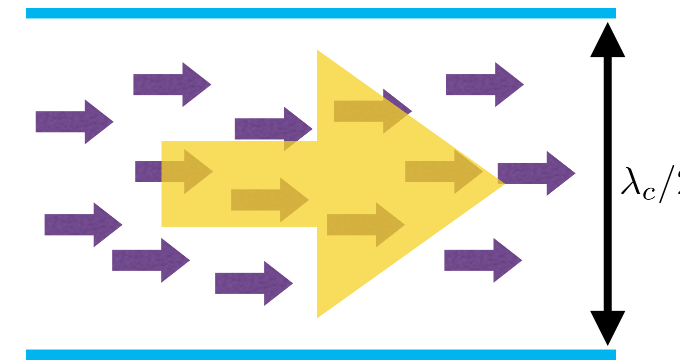

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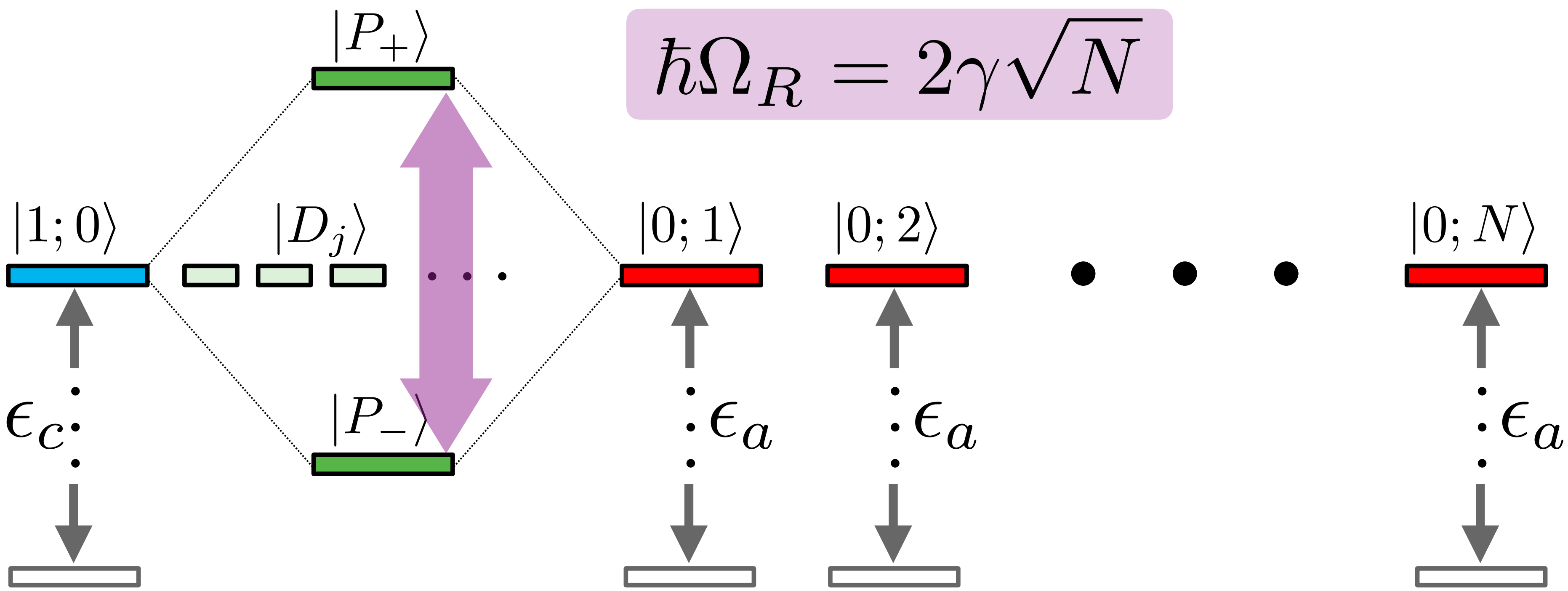

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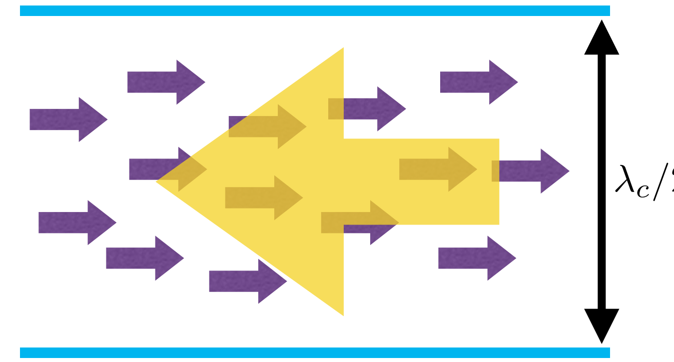

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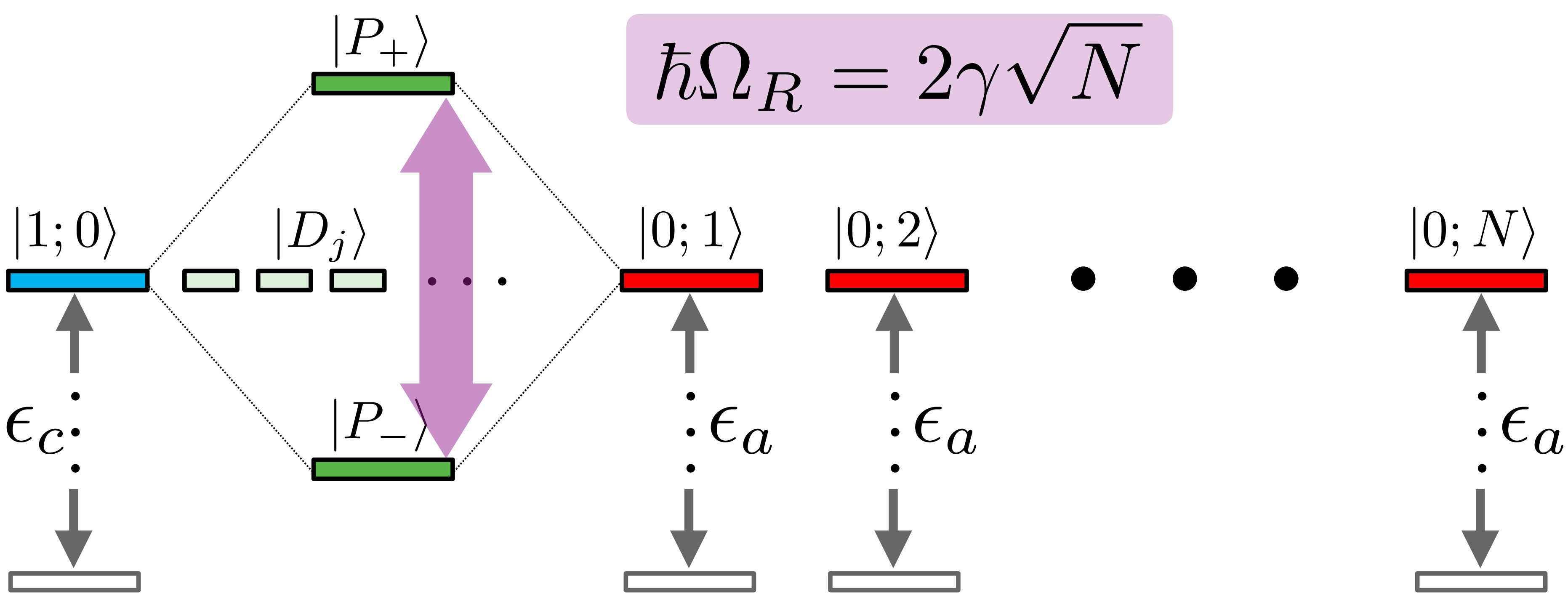

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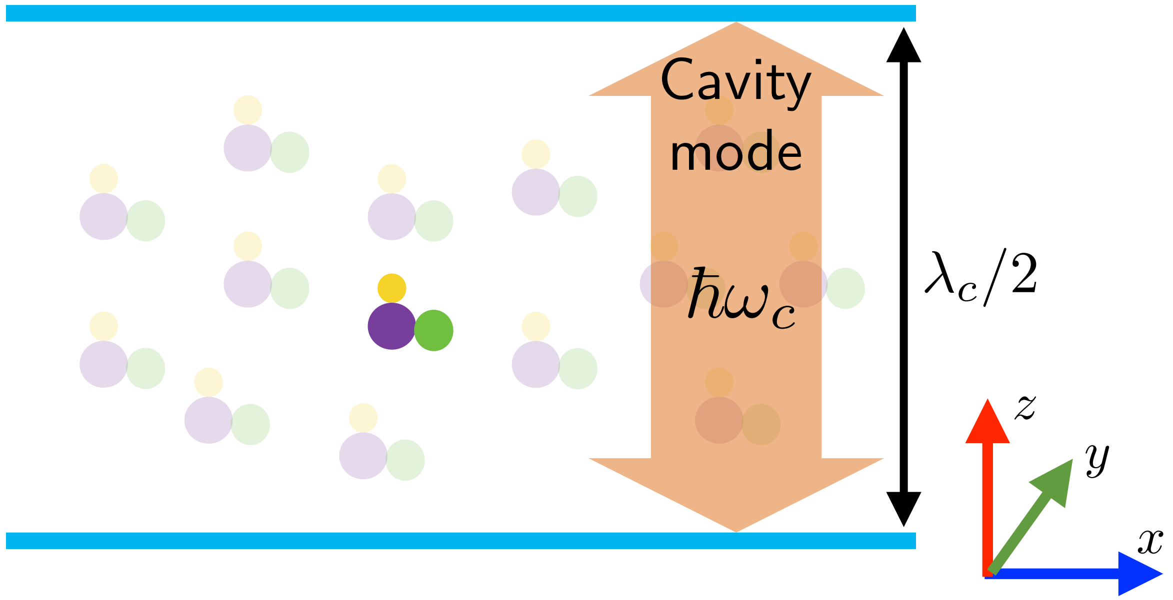
Ensemble-cavity Hamiltonian

$$\hat{H} = \sum_{m=1}^{N} \left(\hat{T}_n^{(m)} + \hat{H}_e^{(m)} \right) + \hat{H}_{\text{cav}}$$

$$\hat{H}_{\text{cav}} = \hbar\omega_c \left(\frac{1}{2} + \hat{a}^\dagger \hat{a} \right) + g\vec{e}_y \cdot \hat{\vec{D}} \left(\hat{a}^\dagger + \hat{a} \right) \qquad g = \sqrt{\frac{\hbar\omega}{2V\epsilon_0}}$$



F.H.M. Faisal, *Theory of multiphoton processes*, Plenum press NY, 1987

Galego et al., *PRX* **5**, 041022 (2015)

J. Flick et al., *PNAS* **114**, 3026 (2017)

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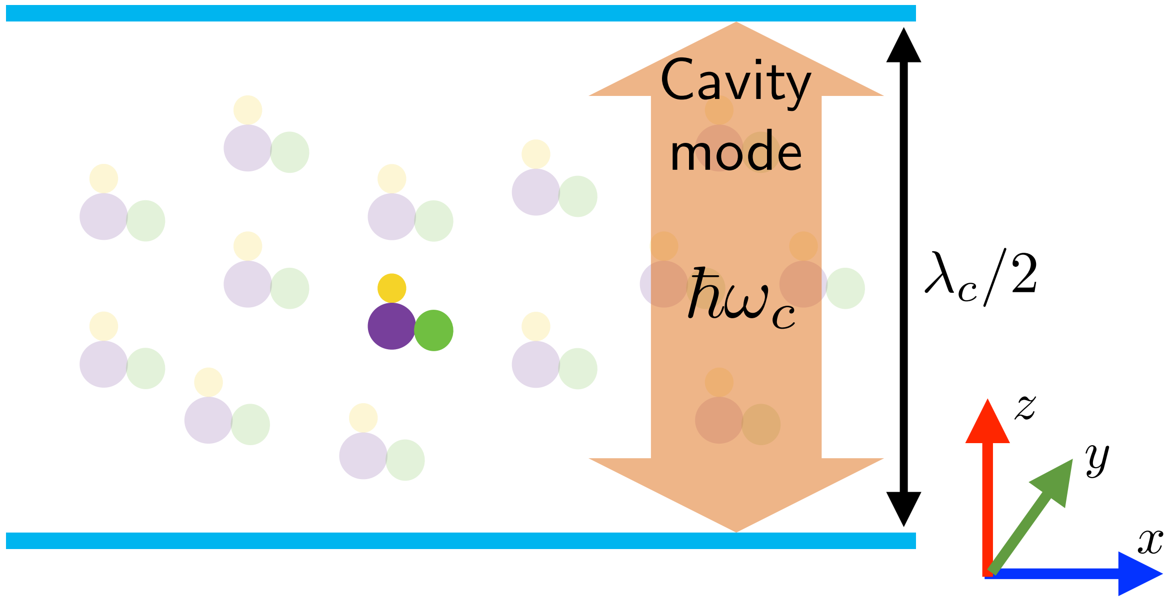
$$\hat{H} = \sum_{m=1}^{N} \left(\hat{T}_n^{(m)} + \hat{H}_e^{(m)} \right) + \hat{H}_{\text{cav}}$$

→ Molecular Tavis-Cummings

$$\hat{H}_{\text{cav}} = \hbar\omega_c \left(\frac{1}{2} + \hat{a}^\dagger \hat{a} \right) + g\vec{e}_y \cdot \hat{\vec{D}} \left(\hat{a}^\dagger + \hat{a} \right)$$

$$g = \sqrt{\frac{\hbar\omega}{2V\epsilon_0}}$$



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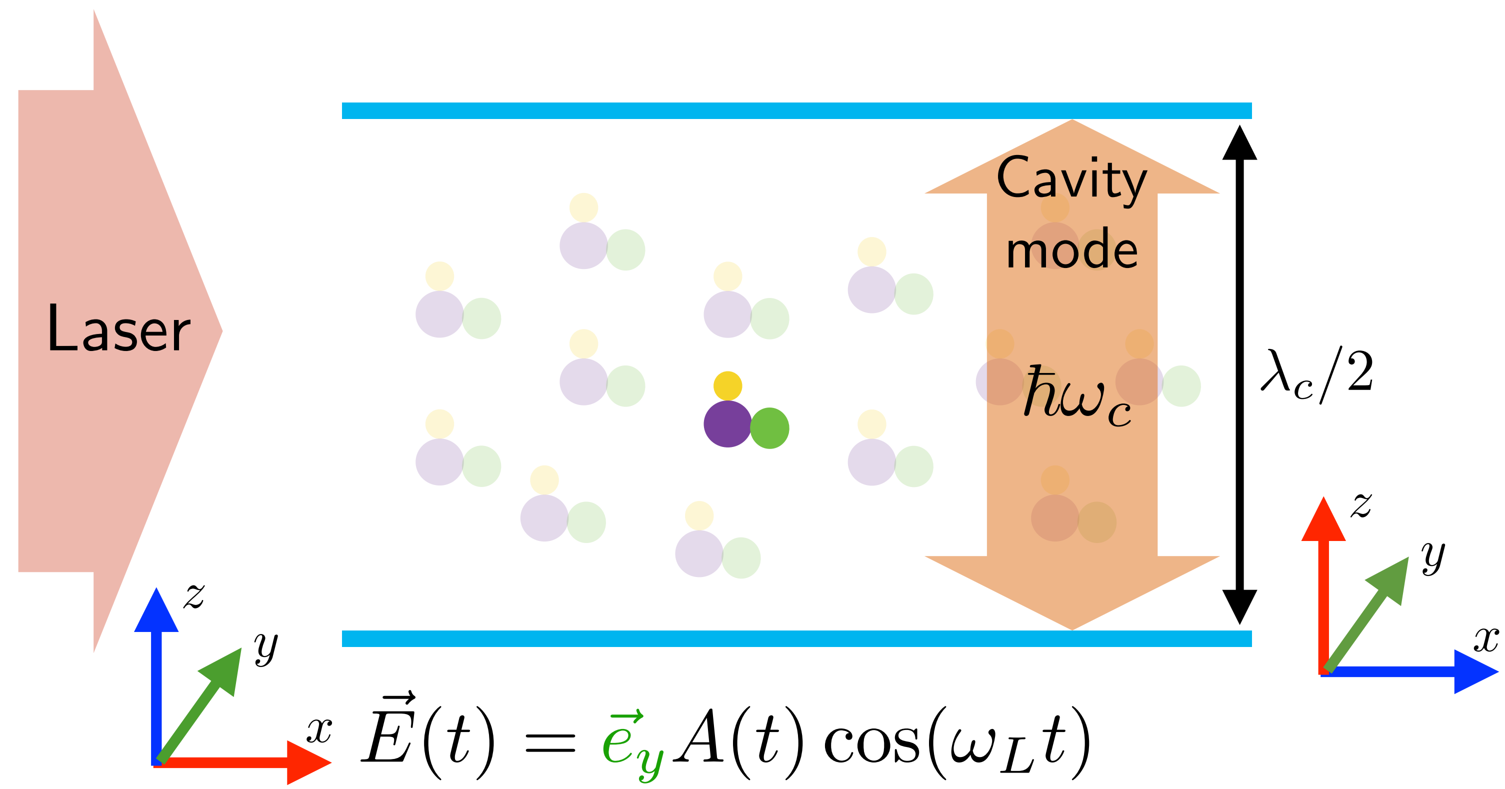
$$\hat{H}_{\text{las}} = \vec{E}(t) \left(\sum_{m=1}^{N} \hat{\vec{D}}^{(m)} \right)$$



$$\vec{E}(t) = \vec{e}_y A(t) \cos(\omega_L t)$$

F.H.M. Faisal, *Theory of multiphoton processes*, Plenum press NY, 1987

Galego et al., *PRX* **5**, 041022 (2015)

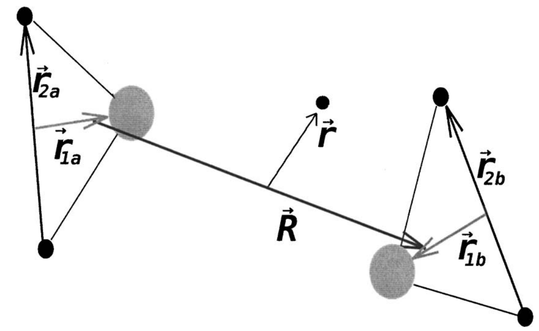
J. Flick et al., *PNAS* **114**, 3026 (2017)

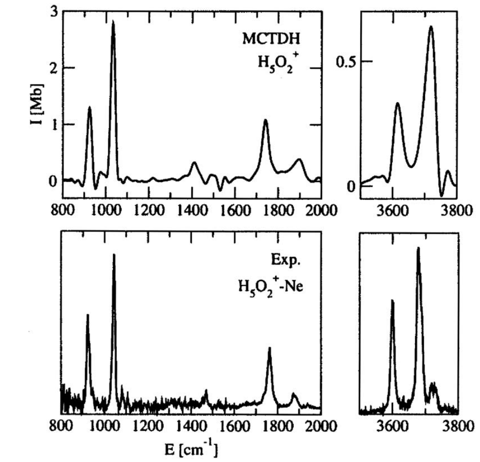
Quantum dynamics toolbox

Multiconfiguration time-dependent Hartree and related methods:

$$\Psi(q_1,\ldots,q_f,t) \equiv \Psi(Q_1,\ldots,Q_p,t)$$
$$= \sum_{j_1}^{n_1}\cdots\sum_{j_p}^{n_p} A_{j_1,\ldots,j_p}(t)\prod_{\kappa=1}^{p}\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t)$$
$$= \sum_J A_J\Phi_J,$$

15 D Zundel cation





OV, F Gatti, H-D Meyer, Angew. Chem. Int. Ed (VIP) 2007
OV, F Gatti, H-D Meyer, Angew. Chem. Int. Ed (VIP) 2009

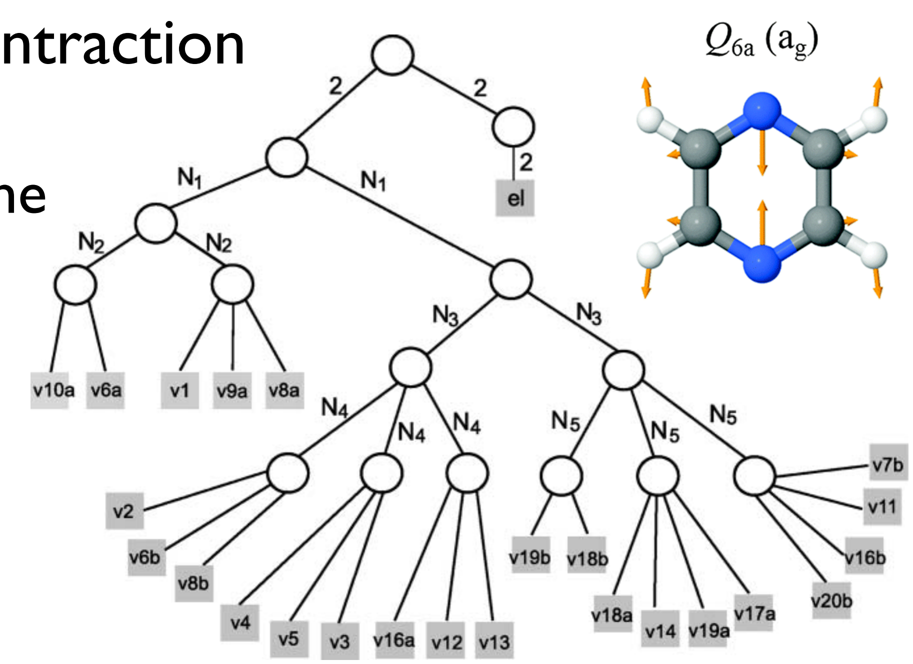
MCTDH propagation of electrons in Fock space

$$H(t) = \sum_{ij\sigma} t_{ij}(t)\, c_{i\sigma}^{\dagger} c_{j\sigma} + U(t)\sum_i \left(n_{i\uparrow}-\frac{1}{2}\right)\left(n_{i\downarrow}-\frac{1}{2}\right)$$

K Balzer, Z Li, OV, M Eckstein, PRB 2015

Multilayer MCTDH: tensor network contraction

24 D pyrazine

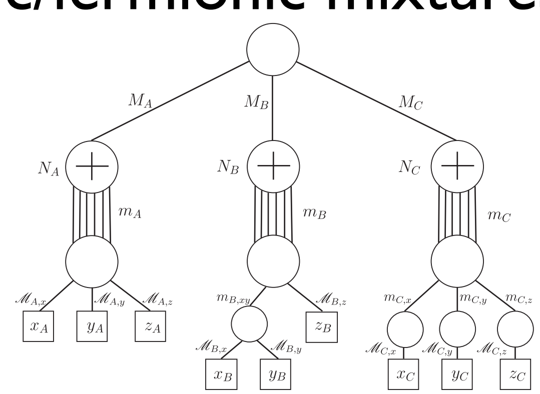


1500 D Henon-Heiles

$$\hat{H} = \frac{\omega}{2}\sum_{\kappa=1}^{f}\left(-\frac{\partial^2}{\partial q_\kappa^2}+q_\kappa^2\right)+\lambda\sum_{\kappa=1}^{f-1}\left(q_\kappa^2\, q_{\kappa+1}-\frac{1}{3}q_{\kappa+1}^3\right)$$

OV, H-D Meyer, *JCP* 2011

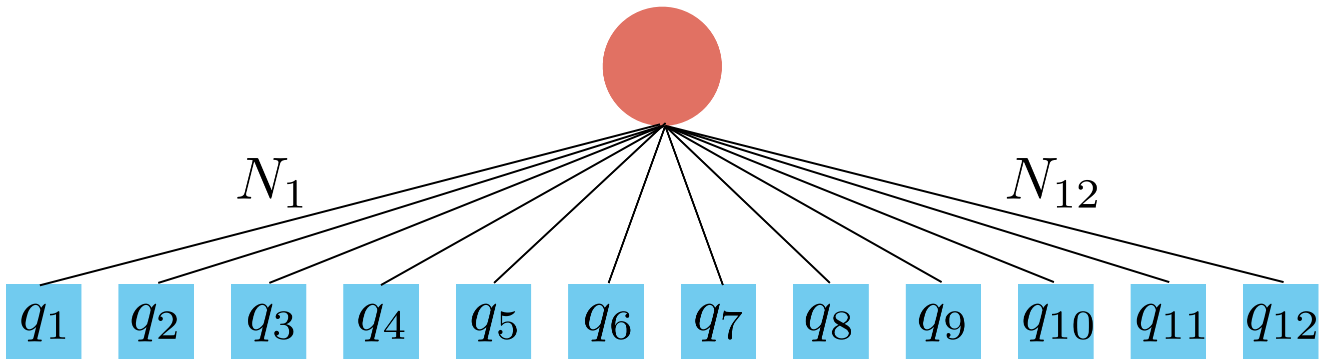
ML-MCTDH-(B/F) for bosonic/fermionic mixtures



L Cao, S Krönke, OV, P Schmelcher, *JCP* 2013
S Krönke, L Cao, OV, P Schmelcher, NJP 2013

Wavepacket dynamics: standard method

12D Example



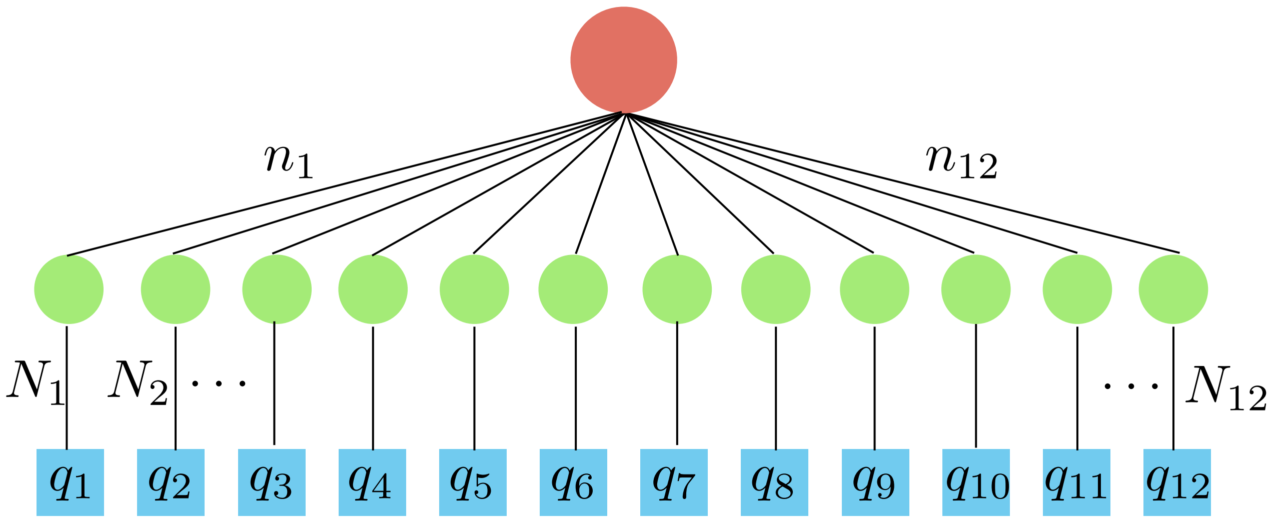
$N_\kappa = 25$

$25^{12} \approx 5.96\,10^{16}$ TD Coeff.

$$\Psi(q_1, \ldots, q_{12}, t) = \sum_{j_1,\ldots,j_{12}}^{N_1,\ldots,N_{12}} A_{j_1,\ldots,j_{12}}(t)\, \chi_{j_1}^{(1)}(q_1) \cdots \chi_{j_{12}}^{(12)}(q_{12})$$

R. Kosloff; *J. Phys. Chem.* **92** , 2087 (1988)

12D Example



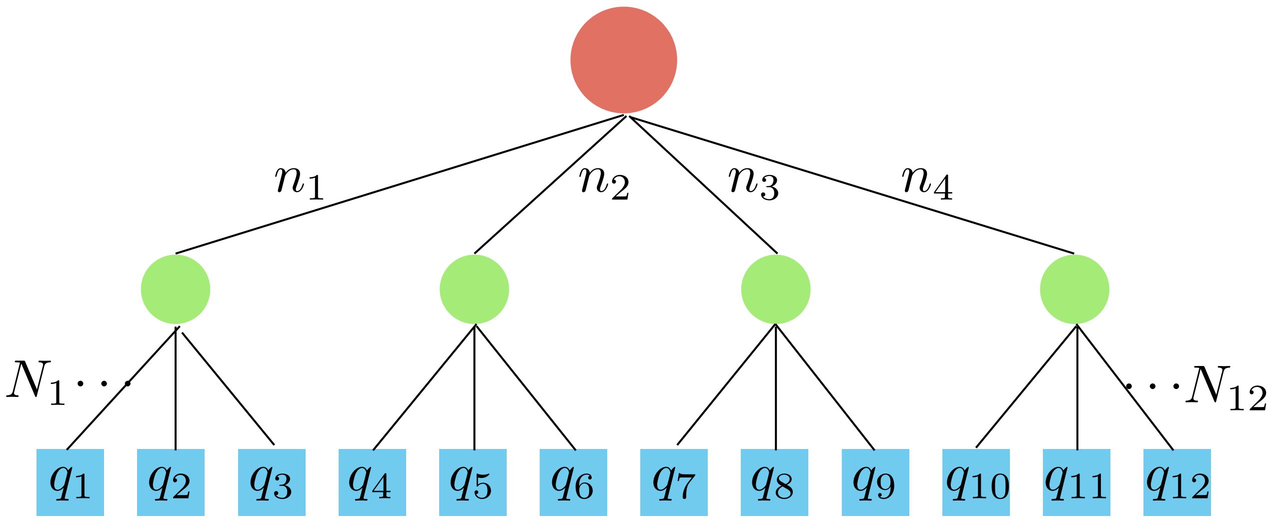
$$n_\kappa = 5$$
$$N_\kappa = 25$$
$$5^{12} + 12 \times (5 \times 25) \approx 2.44\,10^8 \text{ TD Coeff.}$$

$$\Psi(q_1, \ldots, q_{12}, t) = \sum_{j_1,\ldots,j_{12}}^{n_1,\ldots,n_{12}} A_{j_1,\ldots,j_{12}}(t)\, \varphi_{j_1}^{(1)}(q_1, t) \cdots \varphi_{j_{12}}^{(12)}(q_{12}, t)$$

$$\varphi_{j_\kappa}(q_\kappa, t) = \sum_{i=1}^{N_\kappa} B_i^{j_\kappa}(t)\, \chi_i^{(\kappa)}(q_\kappa)$$

H.-D. Meyer, U. Manthe, L.S. Cederbaum; *Chem. Phys. Lett.* **165**, 73 (1990)
M.H. Beck, A. Jäckle, G.A. Worth, H.-D. Meyer; *Phys. Rep.* **324**, 1 (2000)

12D Example



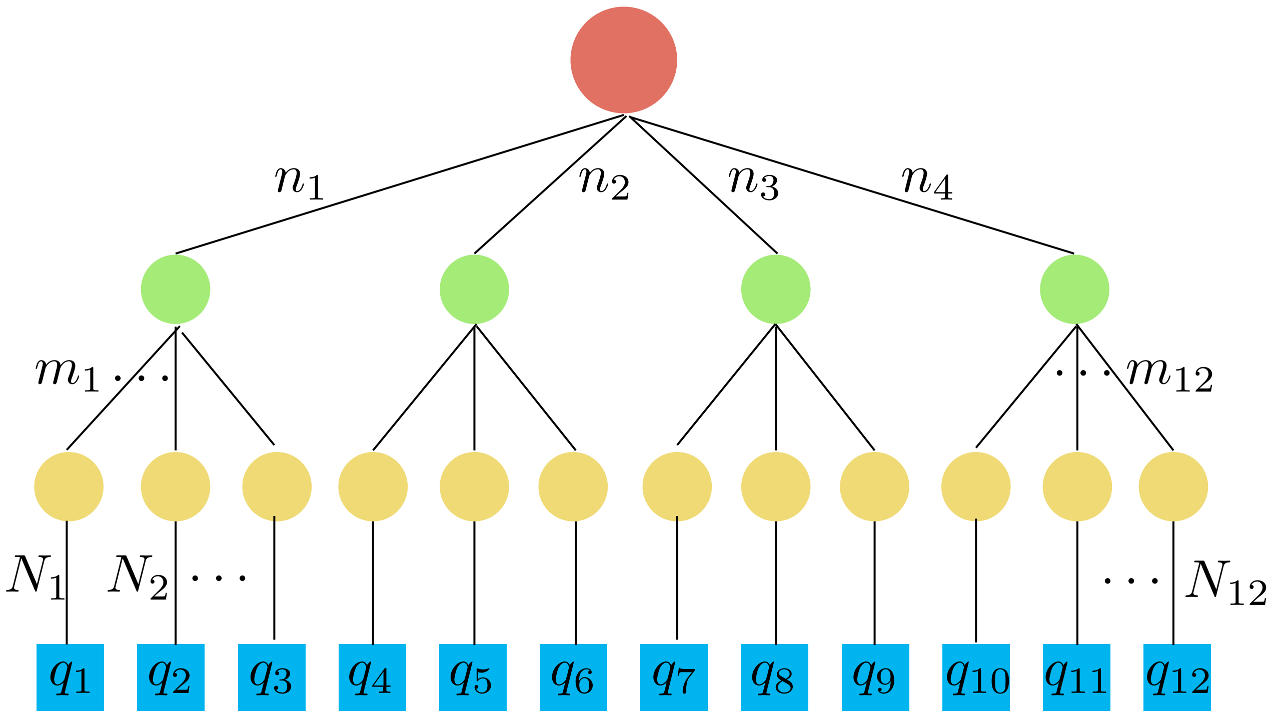
$$n_k = 15$$
$$N_\kappa = 25$$
$$15^4 + 4 \times (15 \times 25^3) \approx 9.88\,10^5 \text{ TD Coeff.}$$

$$\Psi(q_1, \ldots, q_{12}, t) =$$

$$\Psi(Q_1, \ldots, Q_4, t) = \sum_{j_1,\ldots,j_4}^{n_1,\ldots,n_4} A_{j_1,\ldots,j_4}(t)\, \varphi_{j_1}^{(1)}(Q_1, t) \cdots \varphi_{j_4}^{(4)}(Q_4, t)$$

$$\varphi_{j_\kappa}(Q_1, t) = \sum_{i_1,i_2,i_3}^{N_1,N_2,N_3} B_{i_1,i_2,i_3}^{j_\kappa}(t)\, \chi_{i_1}^{(1)}(q_1) \cdots \chi_{i_3}^{(3)}(q_3)$$

12D Example



$$n_{\kappa'} = 15$$
$$m_\kappa = 5$$
$$N_\kappa = 25$$

$$15^4 + 4 \times (15 \times 5^3) + 12 \times (5 \times 25) \approx 5.96\,10^4 \text{ TD Coeff.}$$

$$\Psi(q_1, \dots, q_{12}, t) =$$

$$\Psi(Q_1, \dots, Q_4, t) = \sum_{j_1,\dots,j_4}^{n_1,\dots,n_4} A_{j_1,\dots,j_4}(t)\, \varphi_{j_1}^{(1)}(Q_1, t) \cdots \varphi_{j_4}^{(4)}(Q_4, t)$$

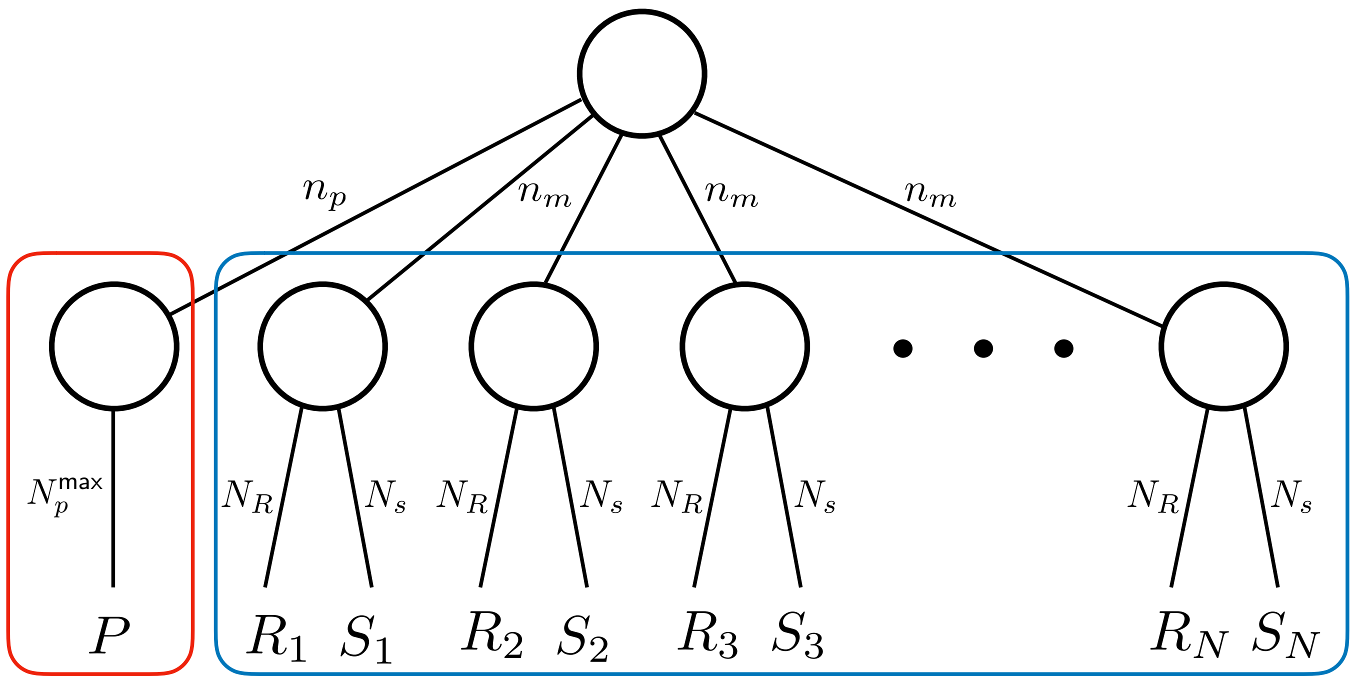
$$\varphi_{j_\kappa}^{(1)}(Q_1, t) = \sum_{i_1,i_2,i_3}^{m_1,m_2,m_3} B_{i_1,i_2,i_3}^{j_\kappa}(t)\, \varphi_{i_1}^{(1;1)}(q_1, t) \cdots \varphi_{i_3}^{(1;3)}(q_3, t)$$

H. Wang, M. Thoss; *J. Chem. Phys.* **119**, 1289 (2003)
U. Manthe; *J. Chem. Phys.* **128**, 164116 (2008) // OV, H.-D. Meyer; *J. Chem. Phys.* **134**, 044135 (2011)

Application of MCTDH

(**M**ulti**c**onfiguration **t**ime-**d**ependent **H**artree)

$$|\Psi(t)\rangle = \left[\prod_{m=1}^{N}\left(\sum_{s_m=1}^{N_s}\phi_{s_m}^{(m)}(\mathbf{R}_m,t)|\psi_{s_m}^{(m)}\rangle\right)\right]\left(\sum_{P=1}^{N_p}B_P(t)|P\rangle\right)$$

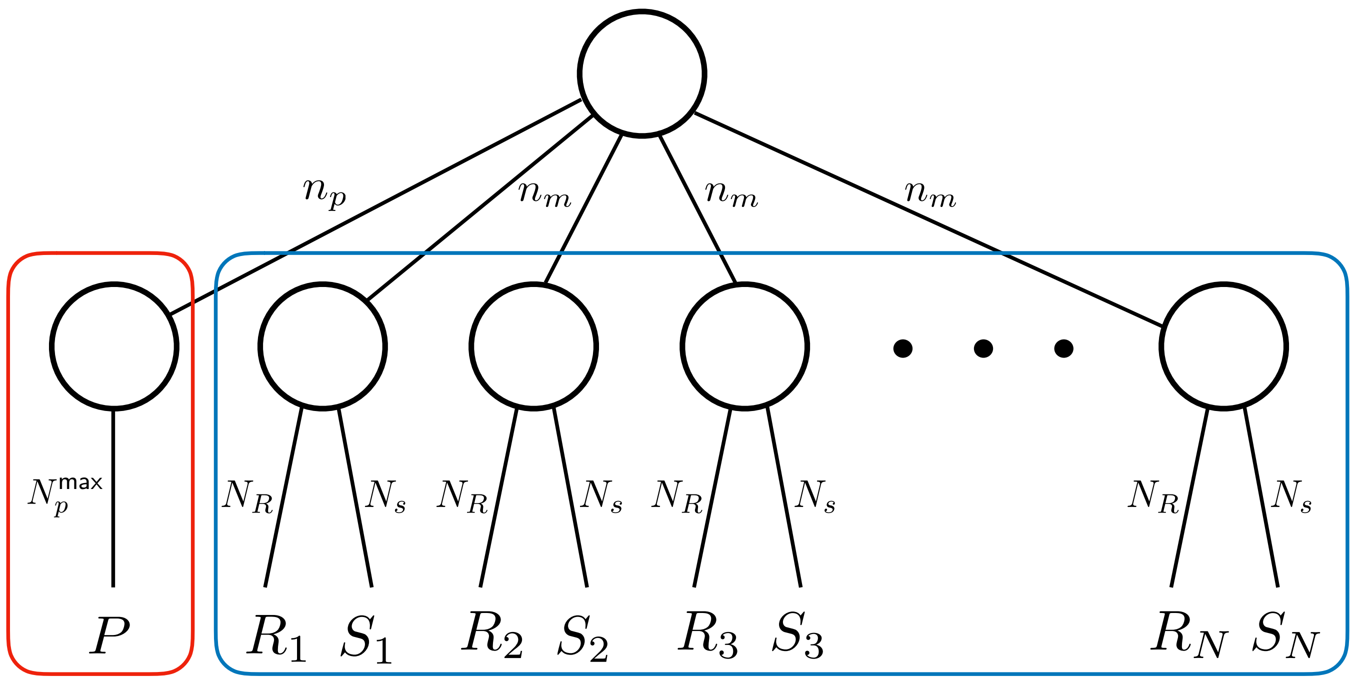


O.V., *Chem. Phys.* **509**, 55 (2018)

Application of MCTDH

(**M**ulti**c**onfiguration **t**ime-**d**ependent **H**artree)

$$|\Psi(t)\rangle = \sum_{j_1,\ldots,j_N,j_p}^{n_1,\ldots,n_N,n_p} A_{j_1,\ldots,j_N,j_p}(t) \cdot \left[\prod_{m=1}^{N}\left(\sum_{s_m=1}^{N_s} \phi^{(m)}_{s_m,j_m}(\mathbf{R}_m,t)|\psi^{(m)}_{s_m}\rangle\right)\right]\left(\sum_{P=1}^{N_p} B_{P,j_p}(t)|P\rangle\right)$$



O.V., *Chem. Phys.* **509**, 55 (2018)

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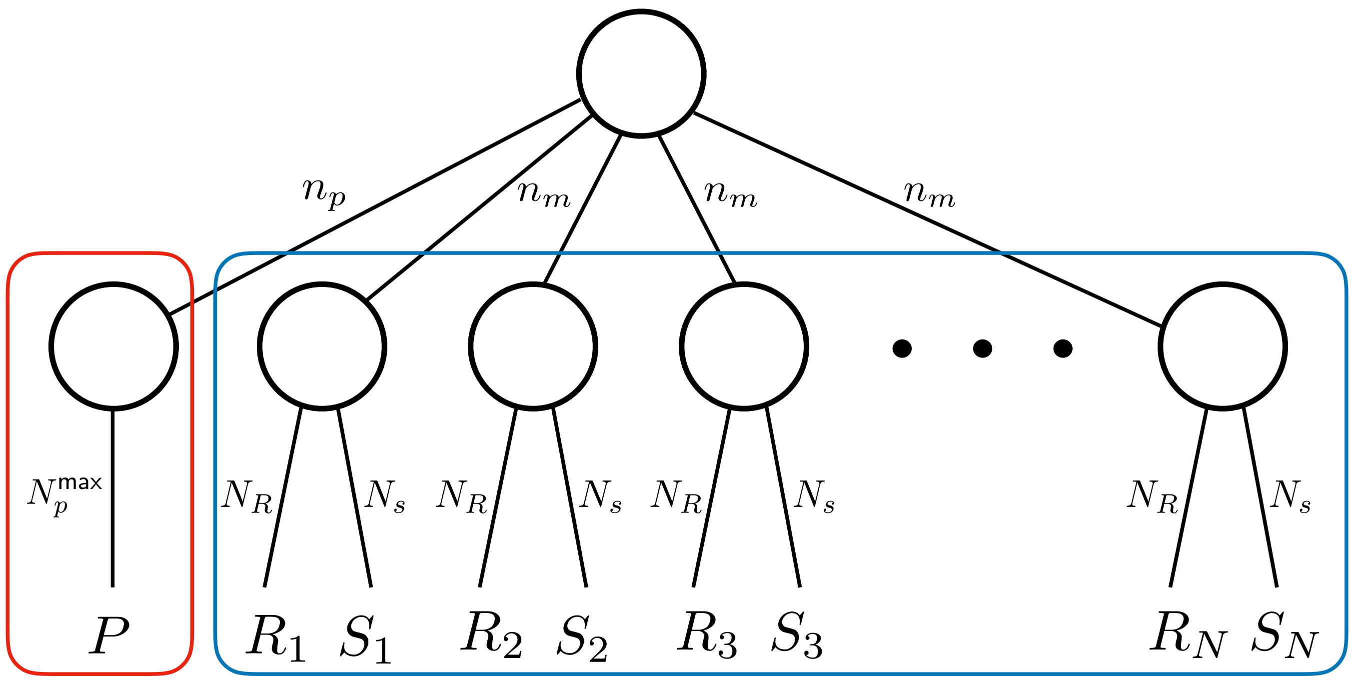


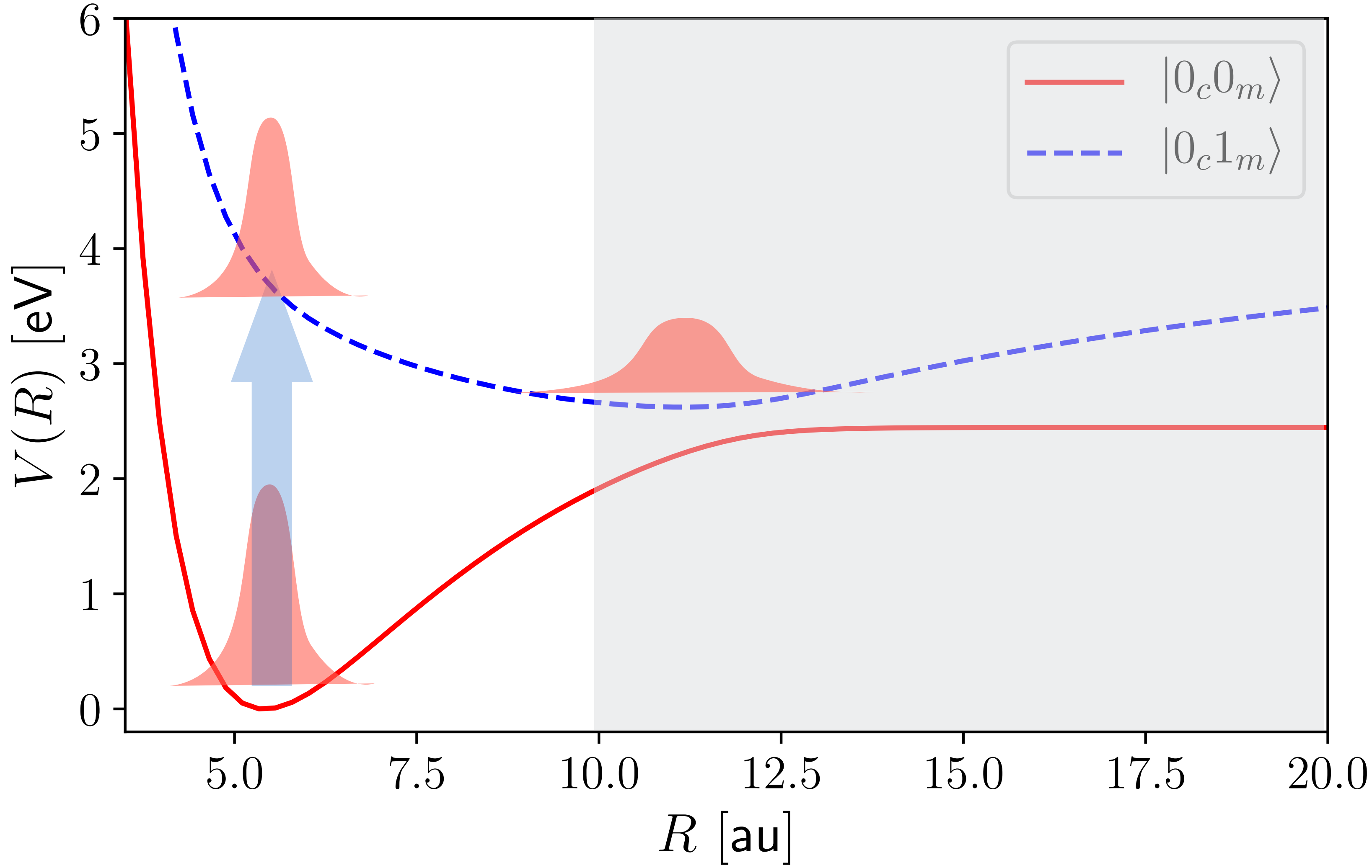
- Multiple excitations / cavity photons naturally treated in the *Ansatzt*

- Exact quantum description of molecule-cavity coupling within the electronic-states included for each molecule.

- Large ensembles / complex molecules addressed through multilayer MCTDH.

O.V., *Chem. Phys.* **509**, 55 (2018)

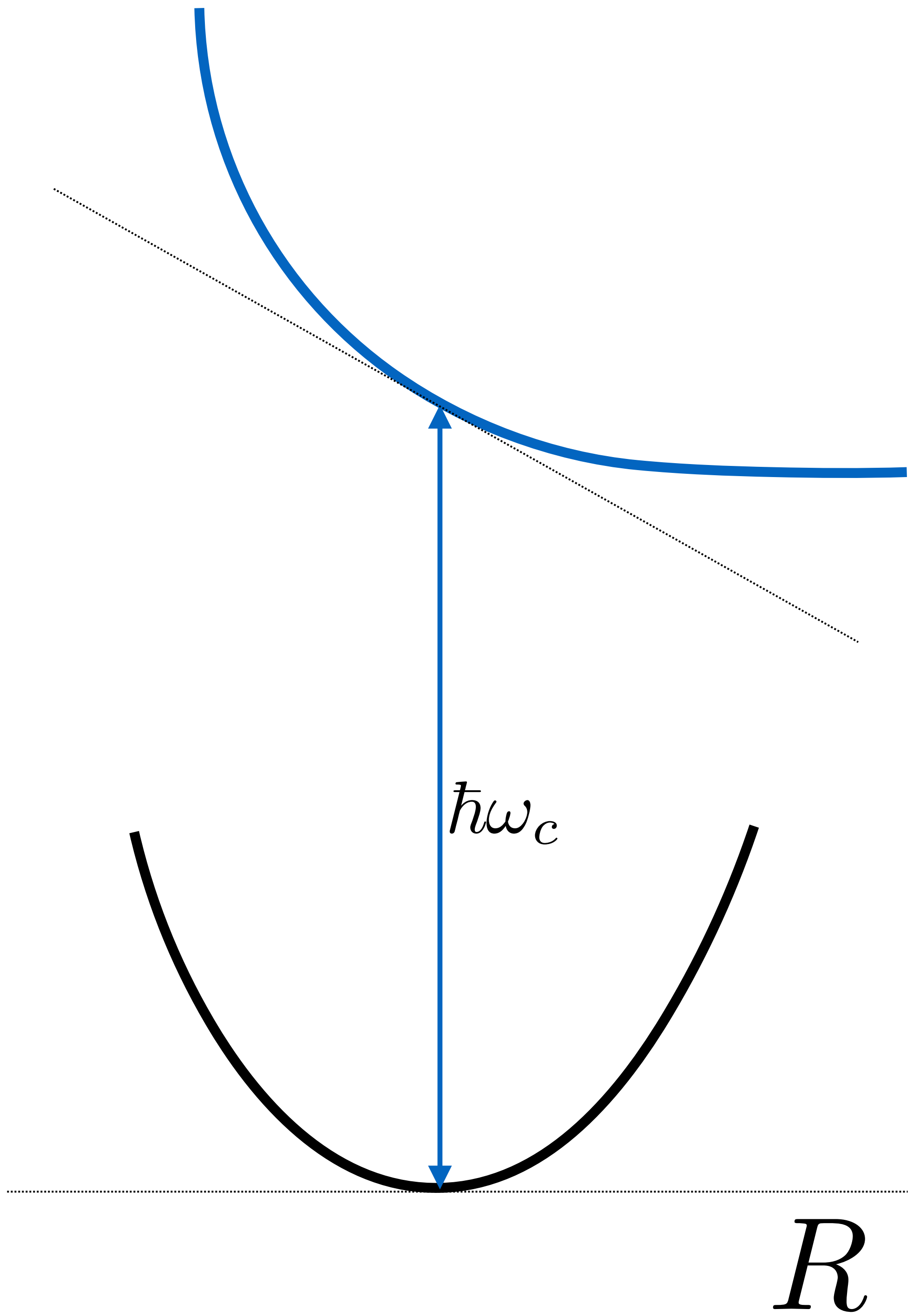
Simple photochemical process: photodissociation



- $$\begin{cases} A = 0.0005 \text{ au} \approx 10^{10} \text{ W/cm}^2 \\ \hbar\omega_L = 3.4 - 4.1 \text{ eV} \\ T_L = 30 \text{ fs} \end{cases}$$

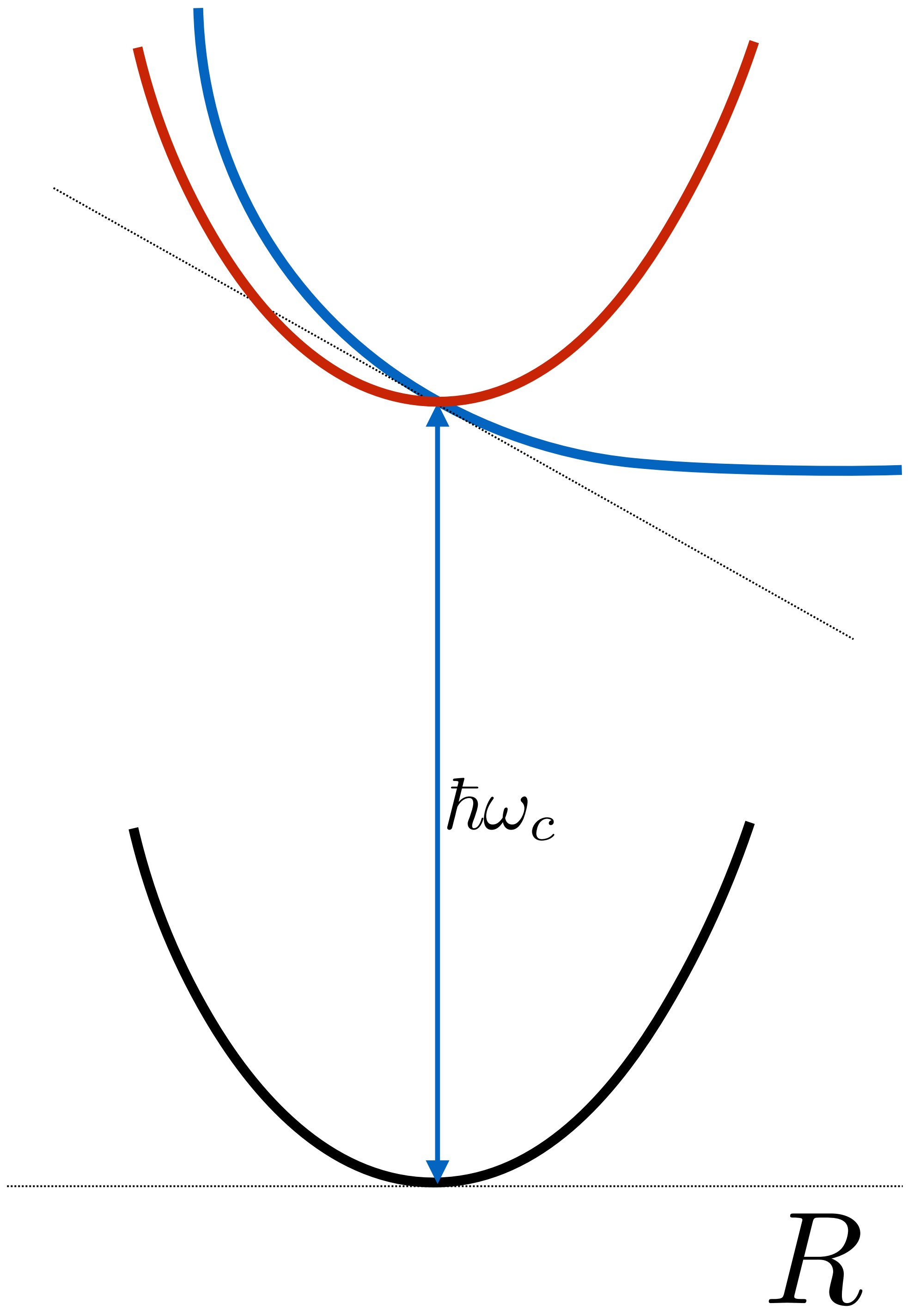
O.V., *Phys. Rev. Lett.* **121** *253001* (2018)

Photo-chemistry of polaritonic states



$$\mathcal{H}_{\text{el}} = \begin{pmatrix} V_0(R) & 0 \\ 0 & V_1(R) \end{pmatrix}$$

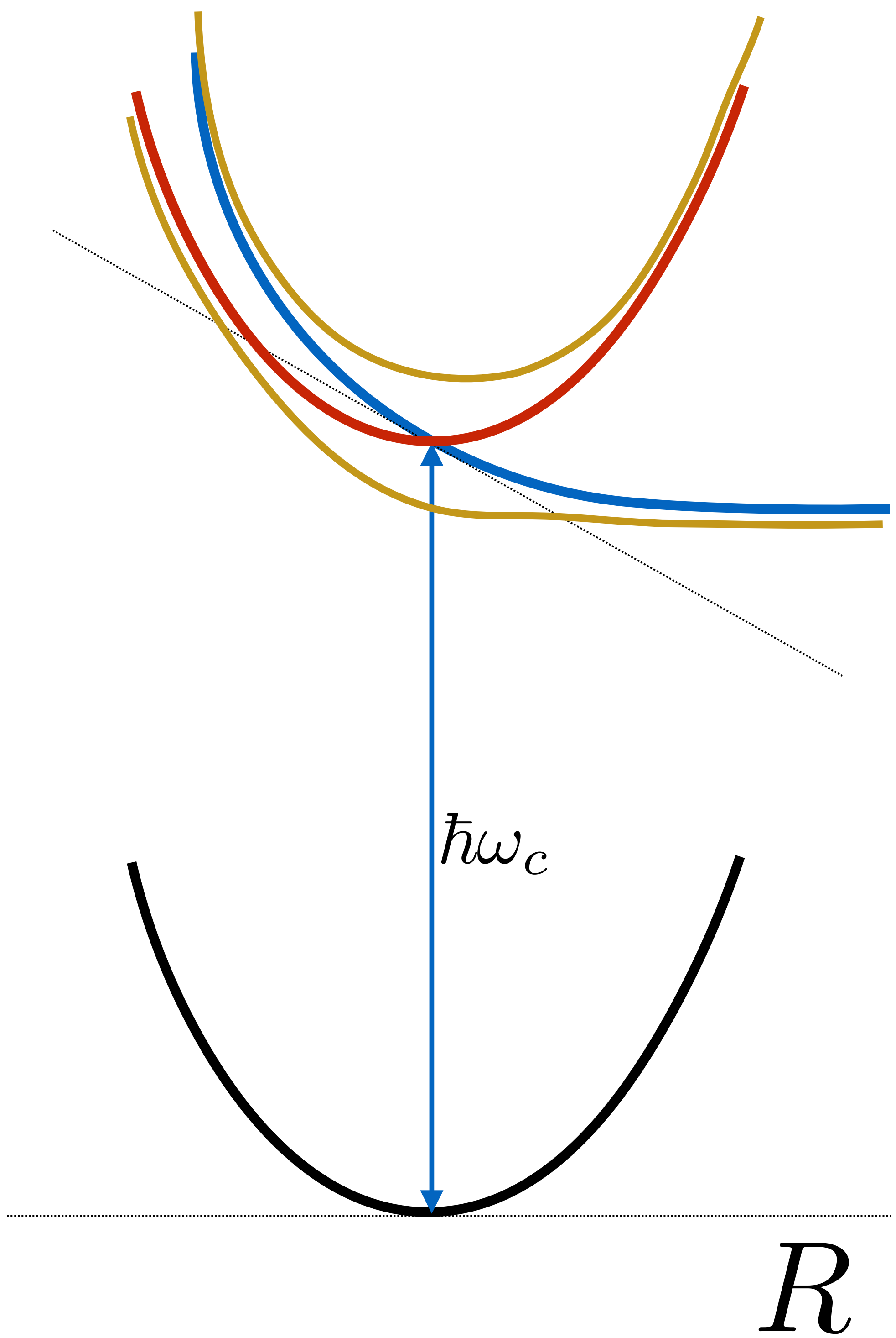
Photo-chemistry of polaritonic states



$$\mathcal{H}_{\mathsf{el}} = \begin{pmatrix} V_0(R) & 0 \\ 0 & V_1(R) \end{pmatrix}$$

$$\mathcal{H}_{\mathsf{el-cav}} = \begin{pmatrix} V_0(R) & 0 & 0 \\ 0 & V_1(R) & \gamma \\ 0 & \gamma & \hbar\omega_c + V_0(R) \end{pmatrix}$$

Photo-chemistry of polaritonic states



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$$\mathcal{H}_{\mathsf{el-cav}} = \begin{pmatrix} V_0(R) & 0 & 0 \\ 0 & V_1(R) & \gamma \\ 0 & \gamma & \hbar\omega_c + V_0(R) \end{pmatrix}$$

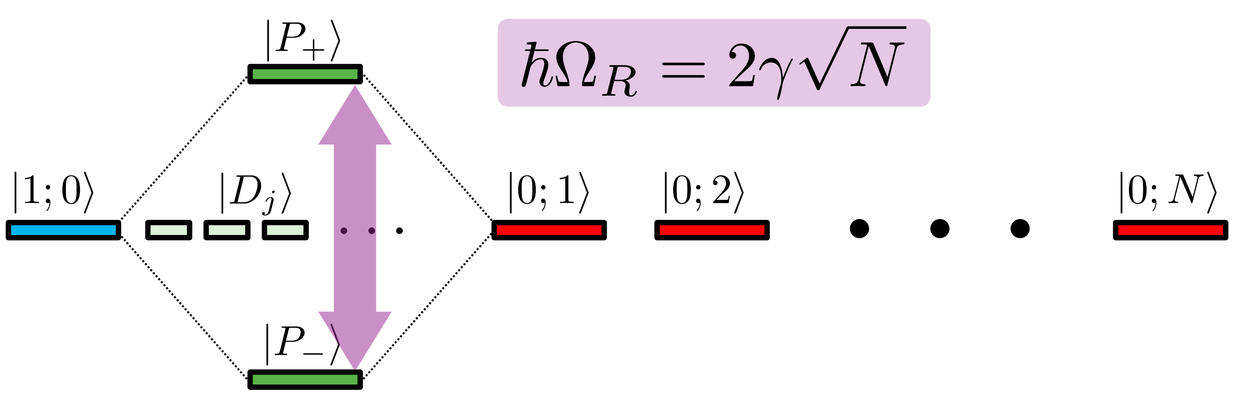
Molecular Tavis-Cummings Hamiltonian

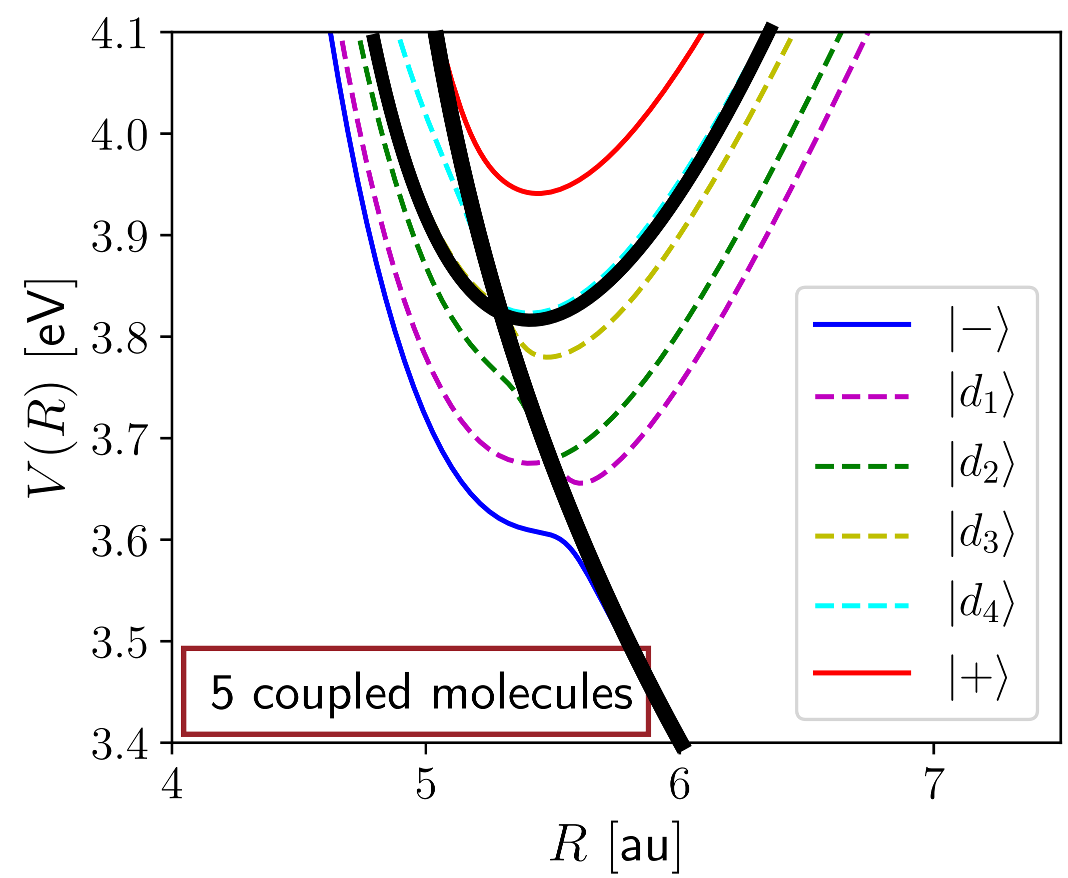
$$\hat{H} = \sum_{m=1}^{N} \left(\hat{T}_n^{(m)} + \hat{H}_e^{(m)} \right) + \hat{H}_{\text{cav}}$$

→ Molecular Tavis-Cummings

$$\begin{pmatrix} \epsilon_c & \gamma & \gamma & \gamma & \cdots \\ \gamma & \epsilon_a & 0 & 0 & \cdots \\ \gamma & 0 & \epsilon_a & 0 & \cdots \\ \gamma & 0 & 0 & \epsilon_a & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

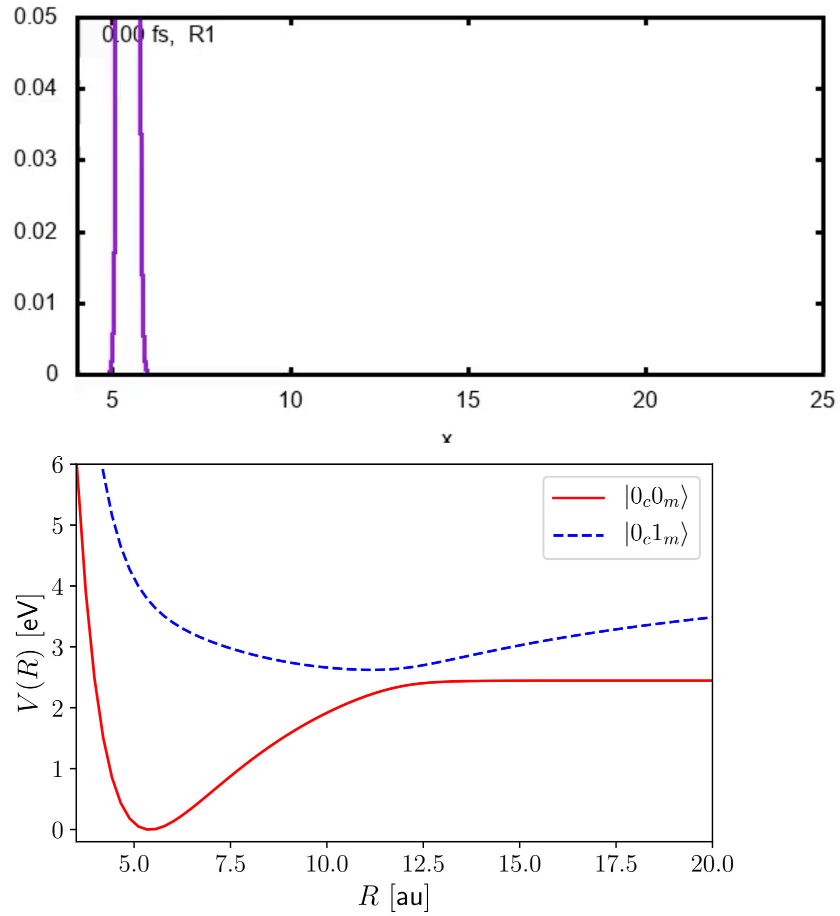
$$\begin{pmatrix} \hbar\omega_c & \gamma^{(1)}(R_1) & \gamma^{(2)}(R_2) & \gamma^{(3)}(R_3) & \cdots \\ \gamma^{(1)}(R_1) & \Delta^{(1)}(R_1) & 0 & 0 & \cdots \\ \gamma^{(2)}(R_2) & 0 & \Delta^{(2)}(R_2) & 0 & \cdots \\ \gamma^{(3)}(R_3) & 0 & 0 & \Delta^{(3)}(R_3) & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

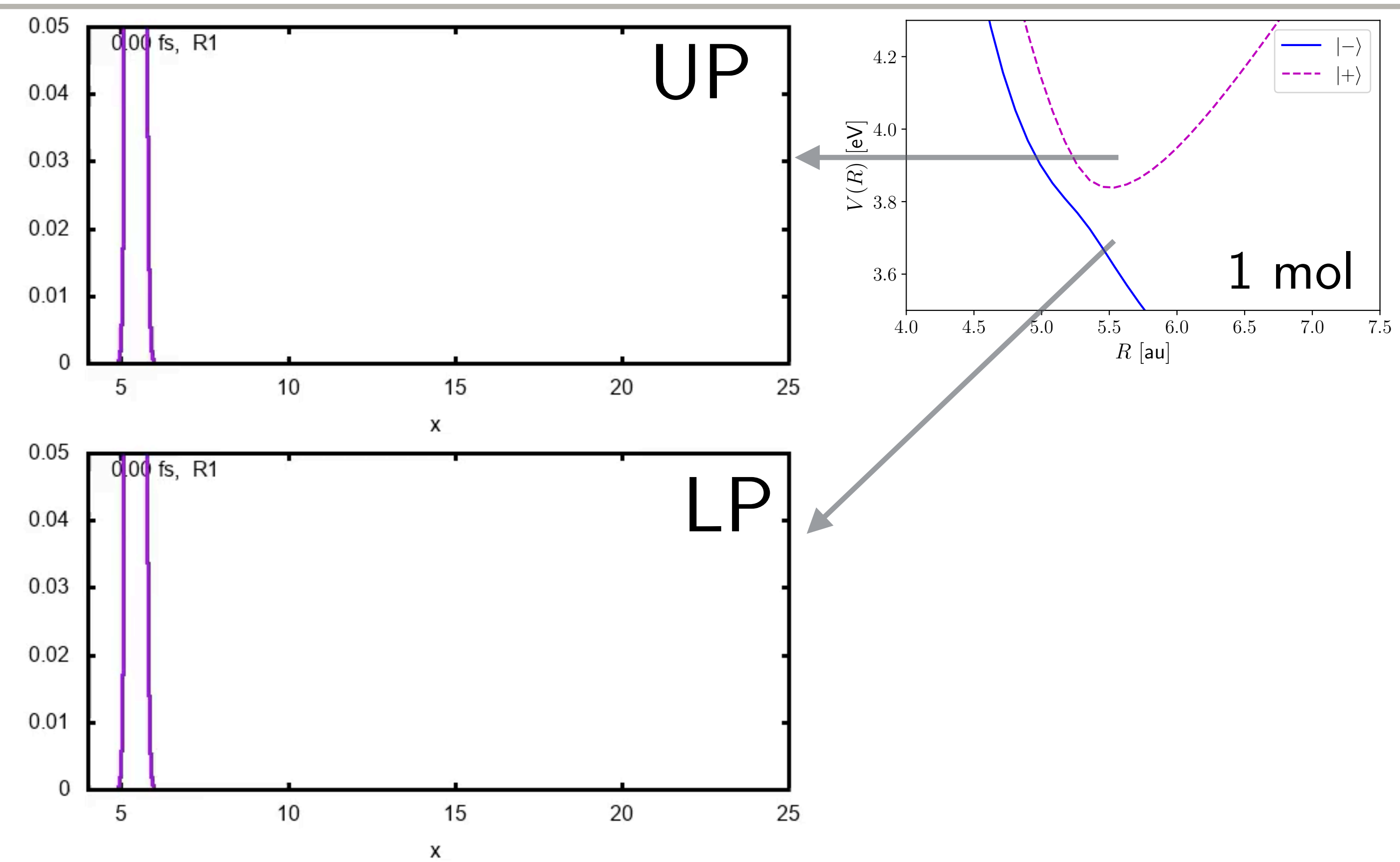


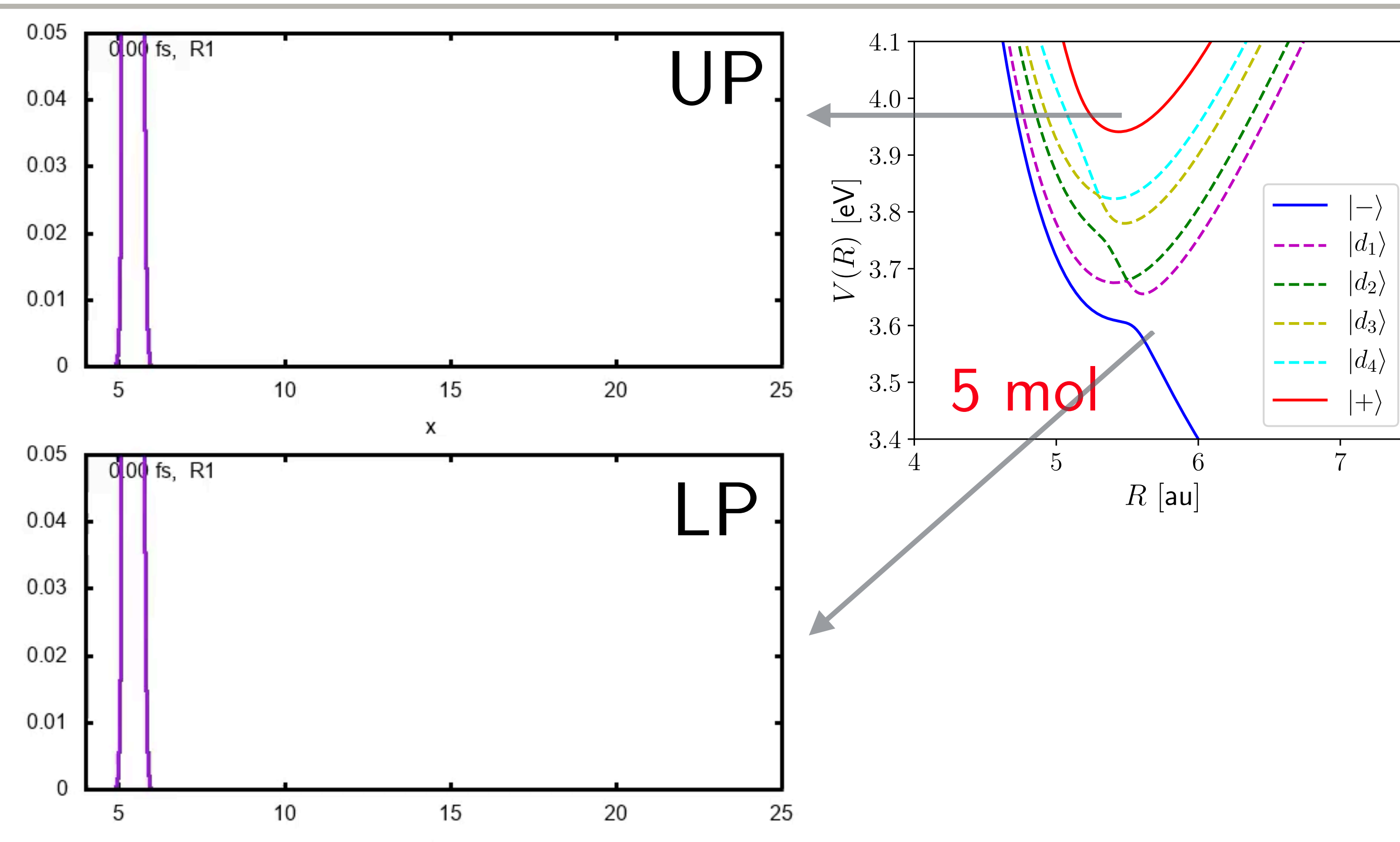


Cavity-modified photodissociation

No cavity







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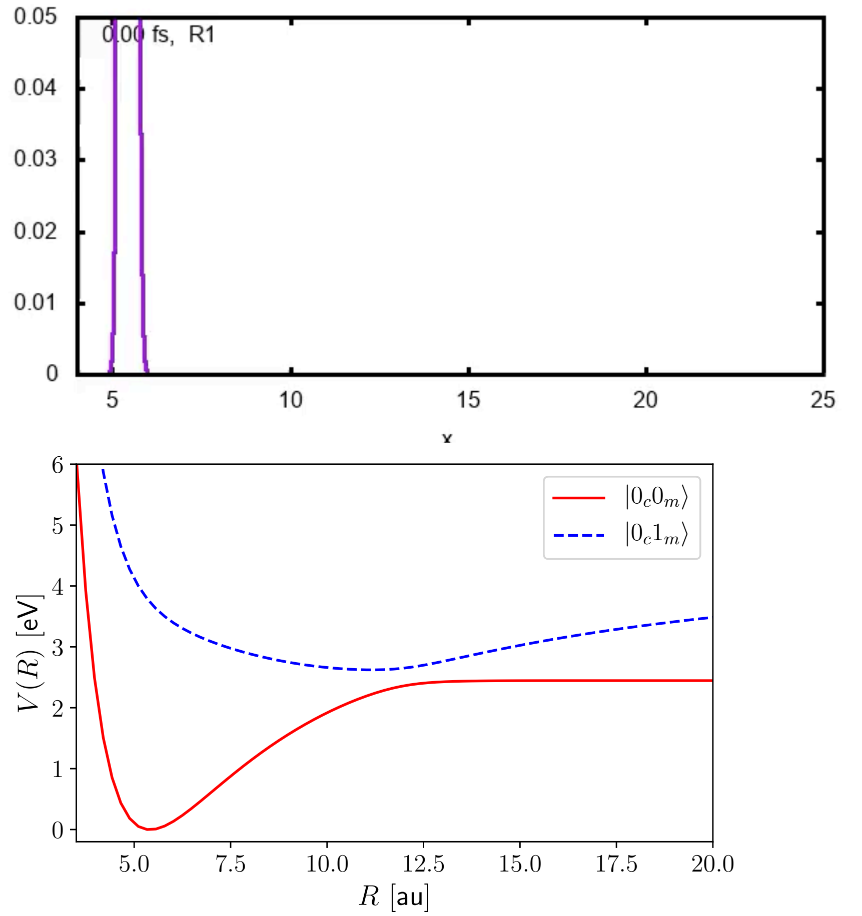

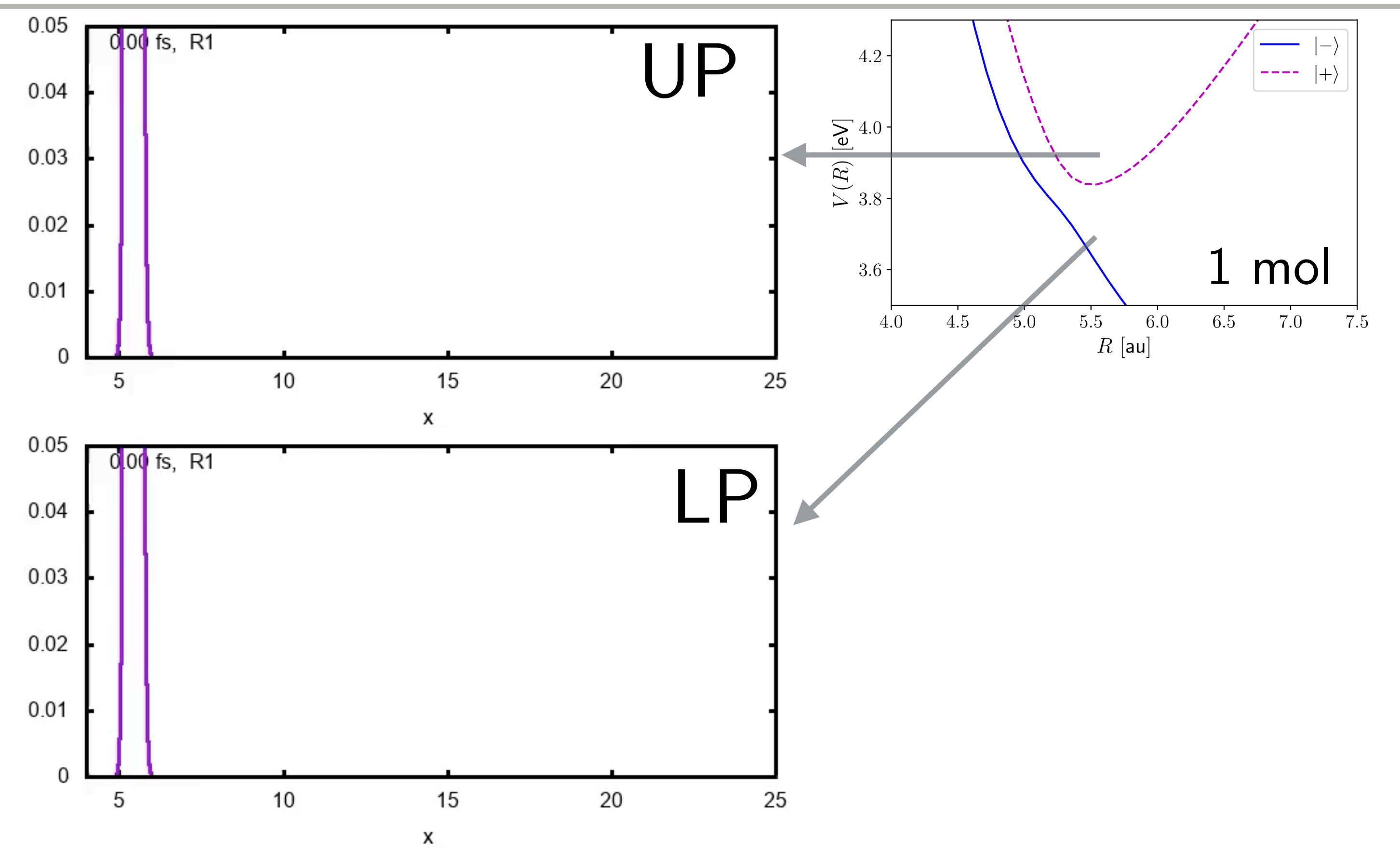

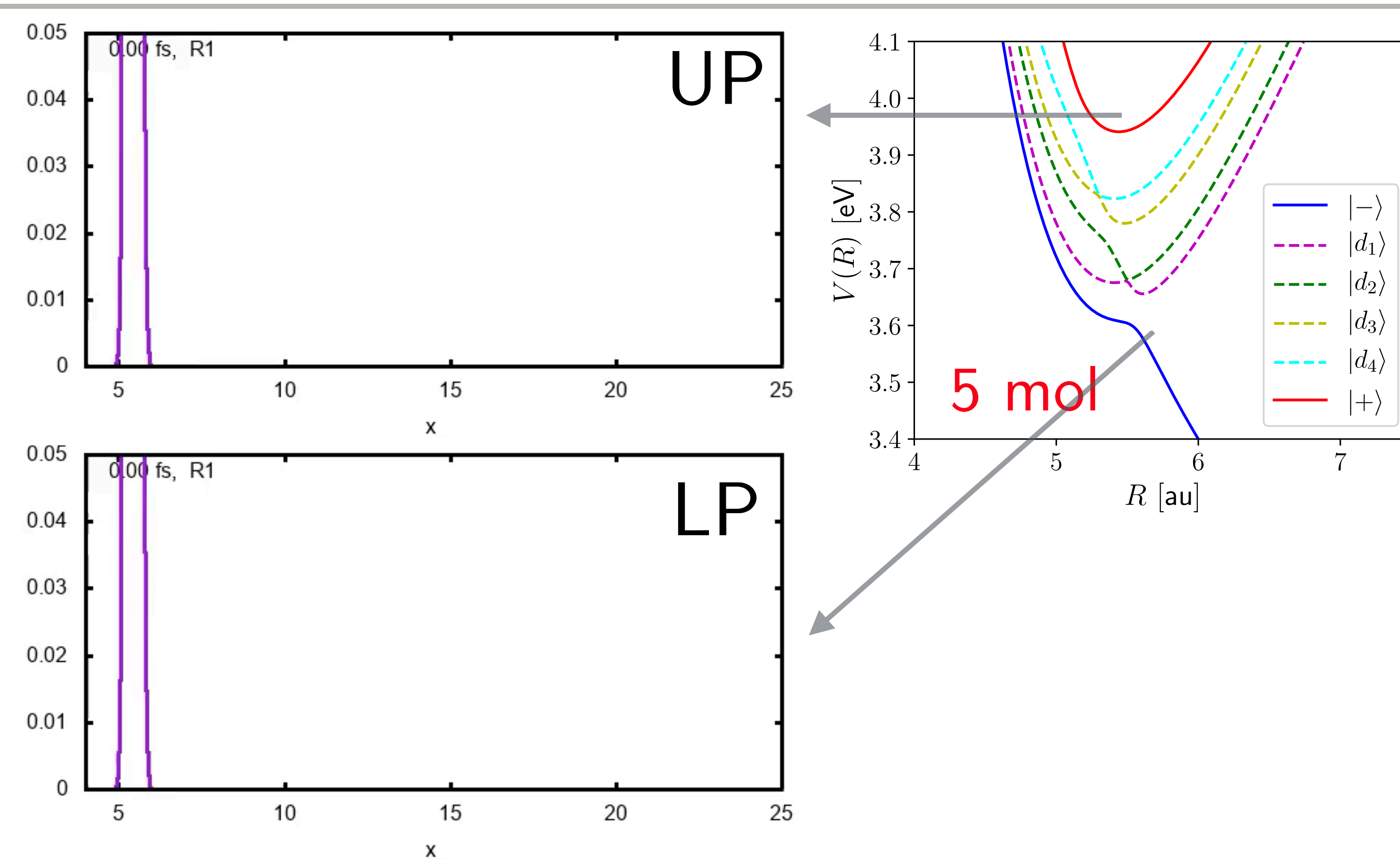

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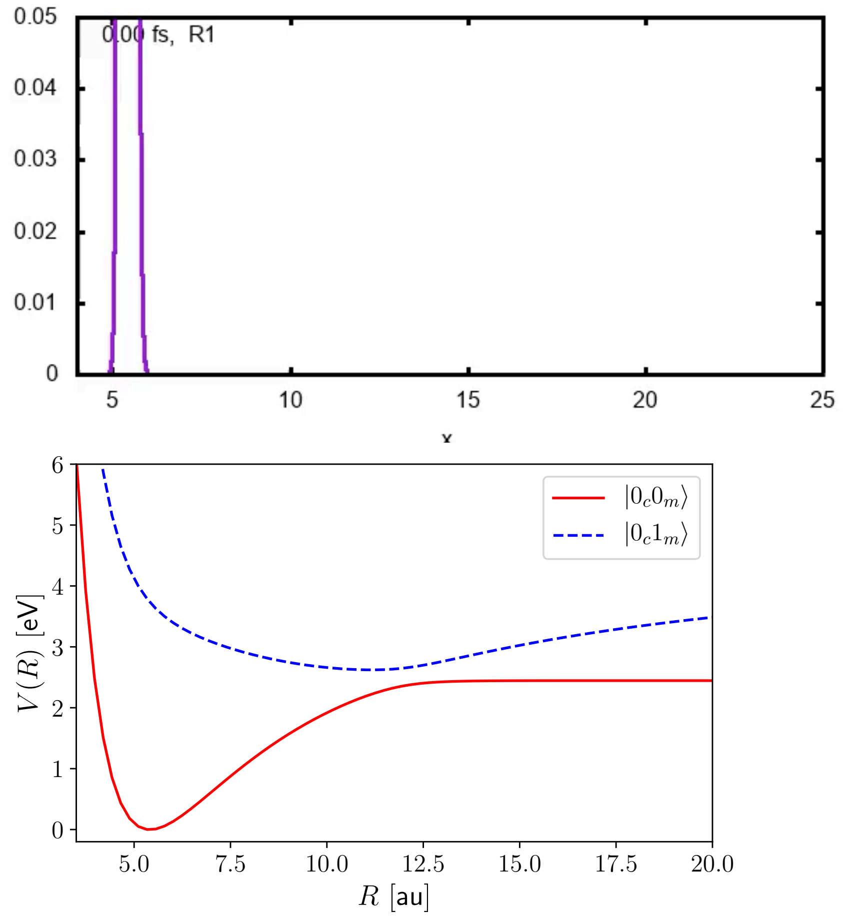

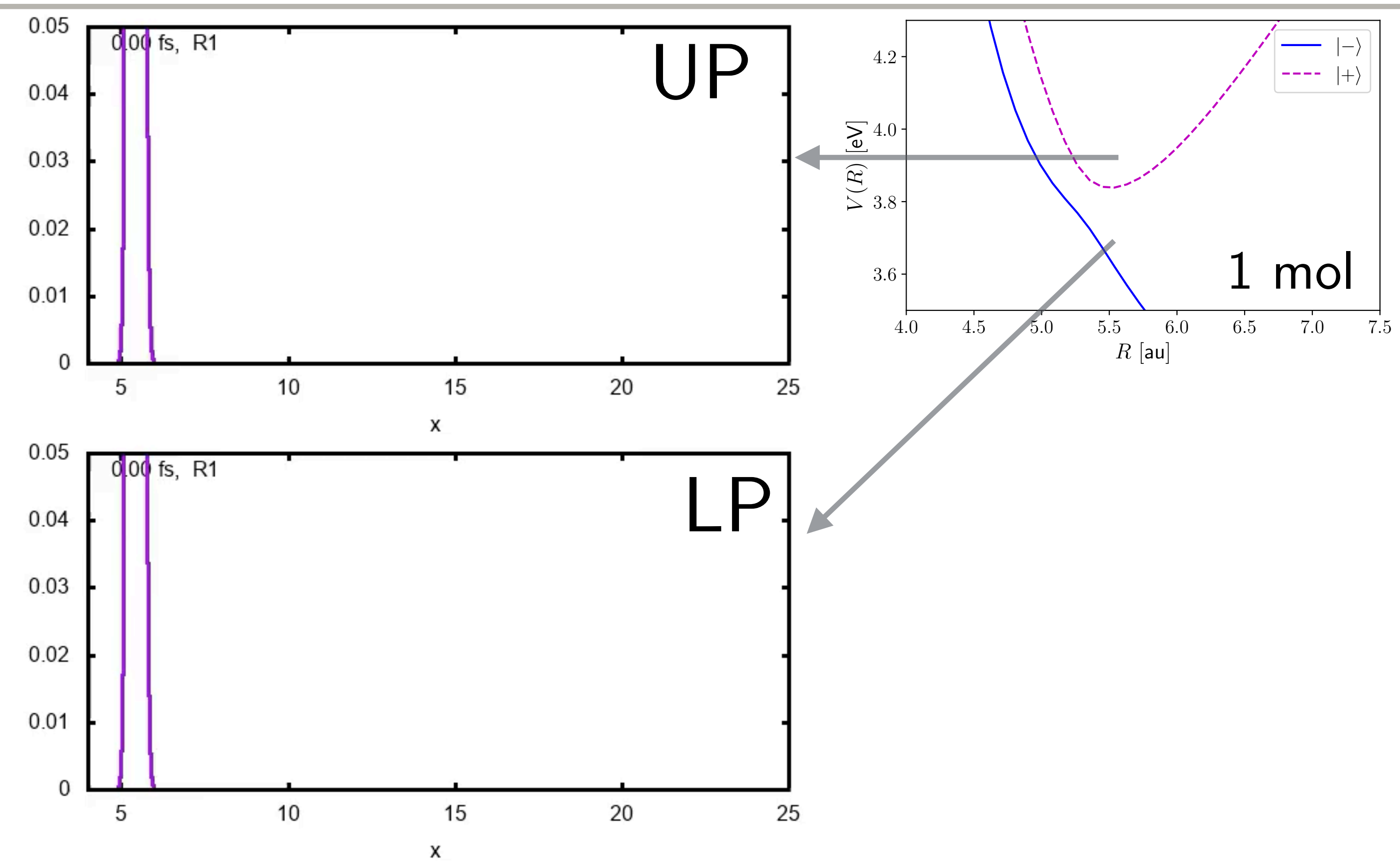

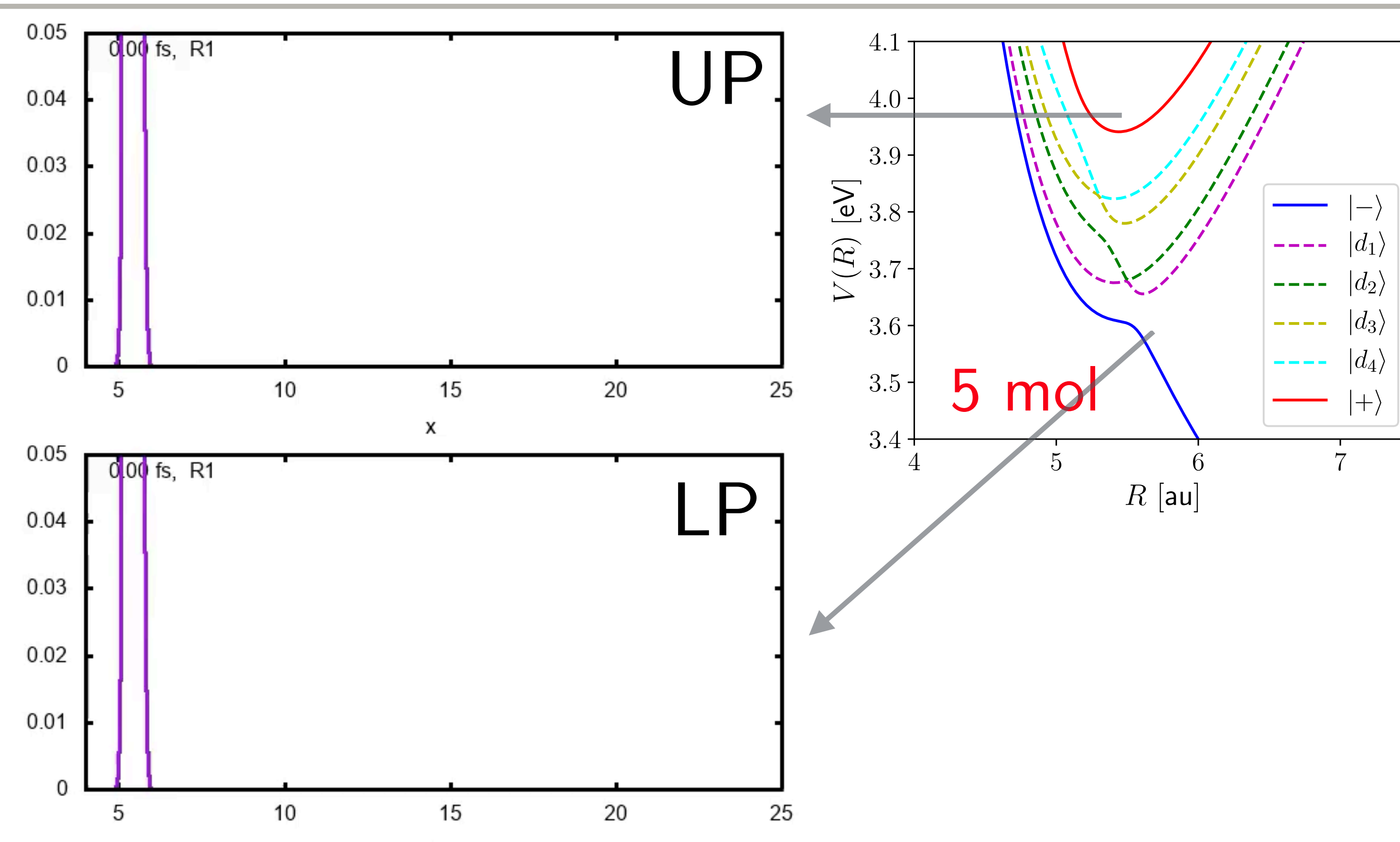

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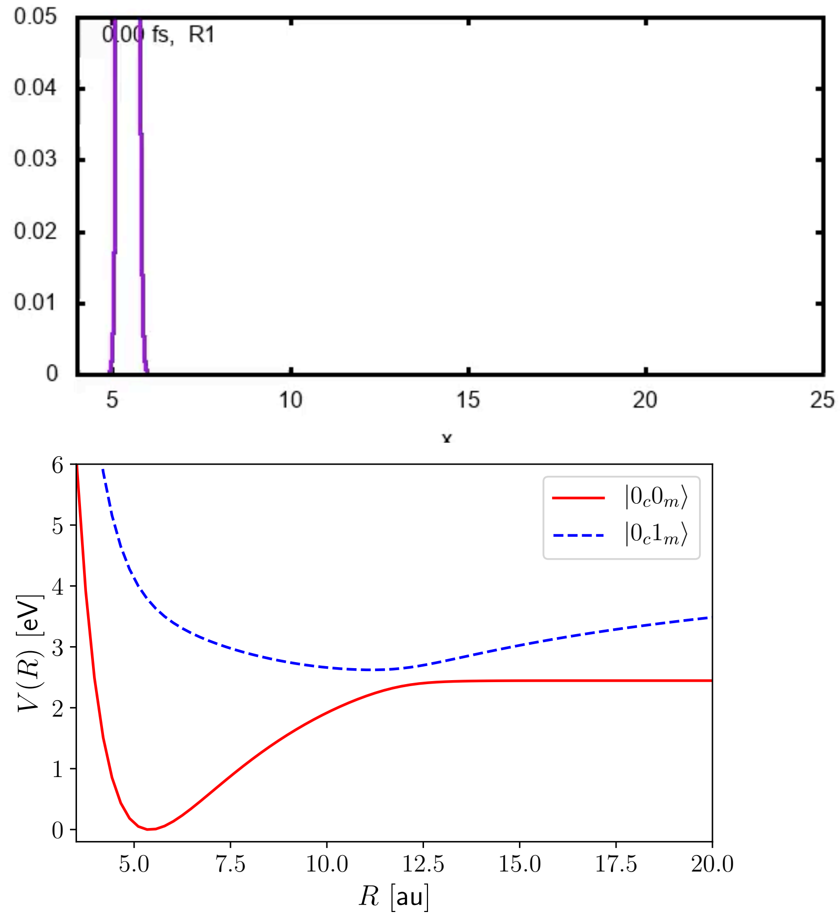
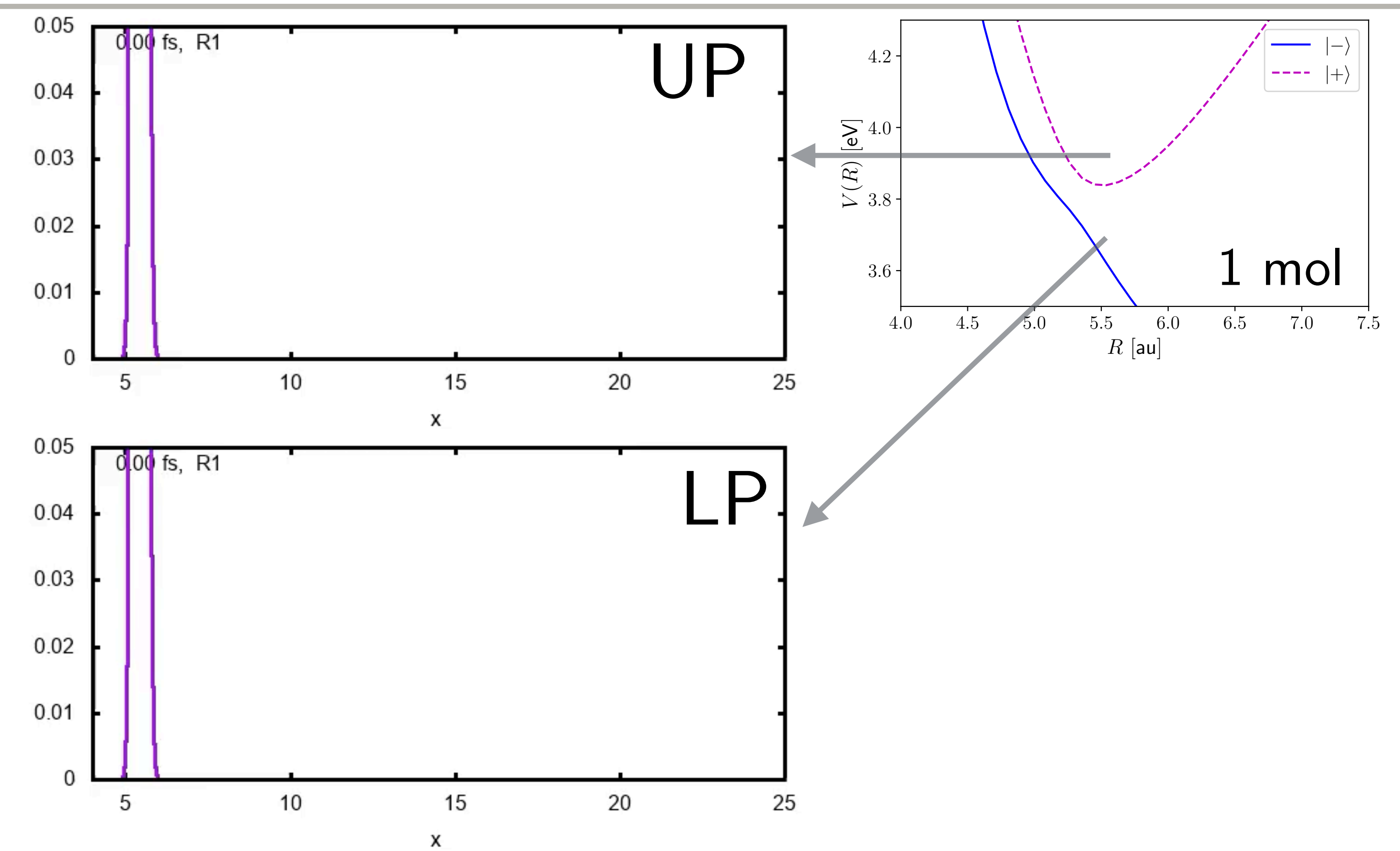
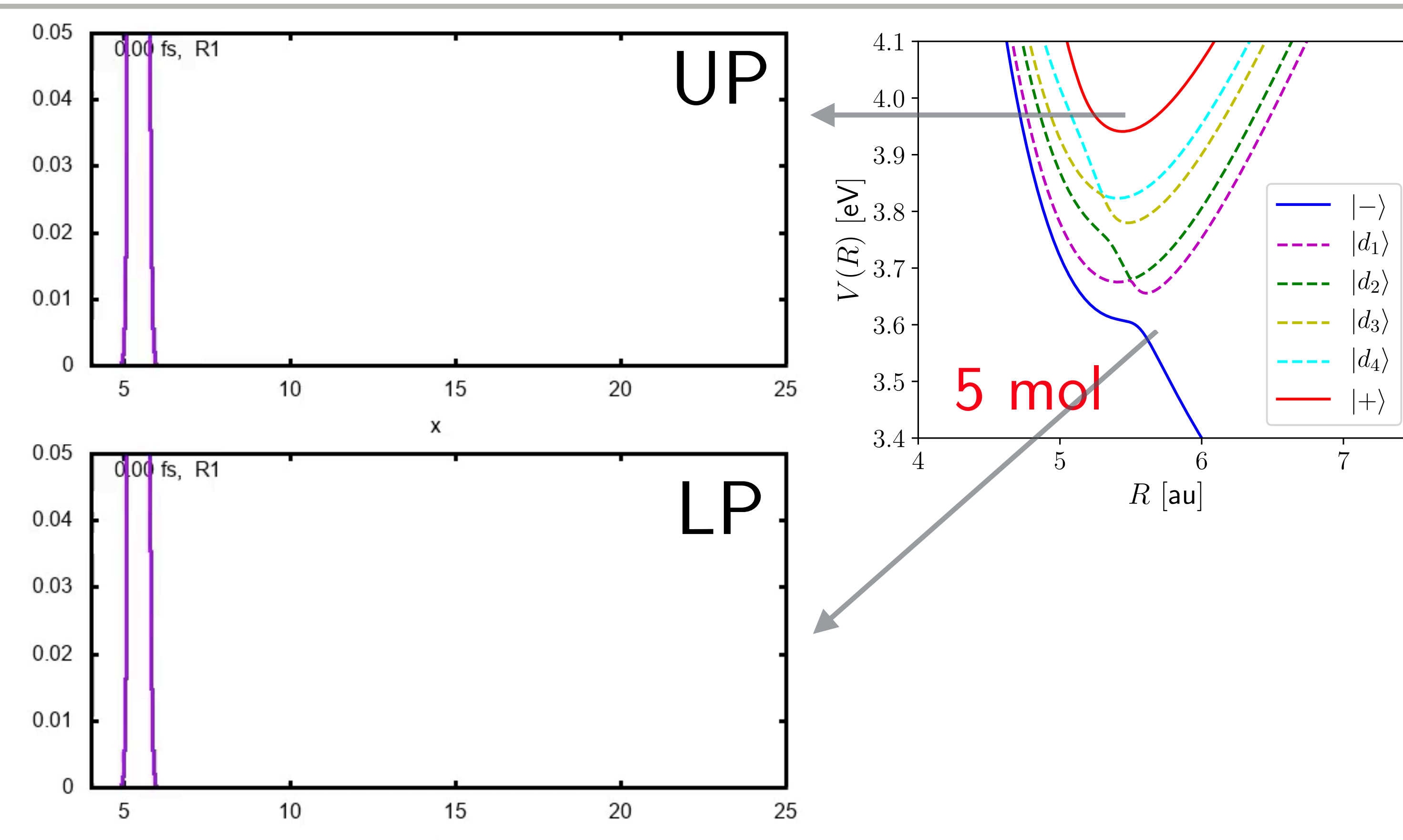
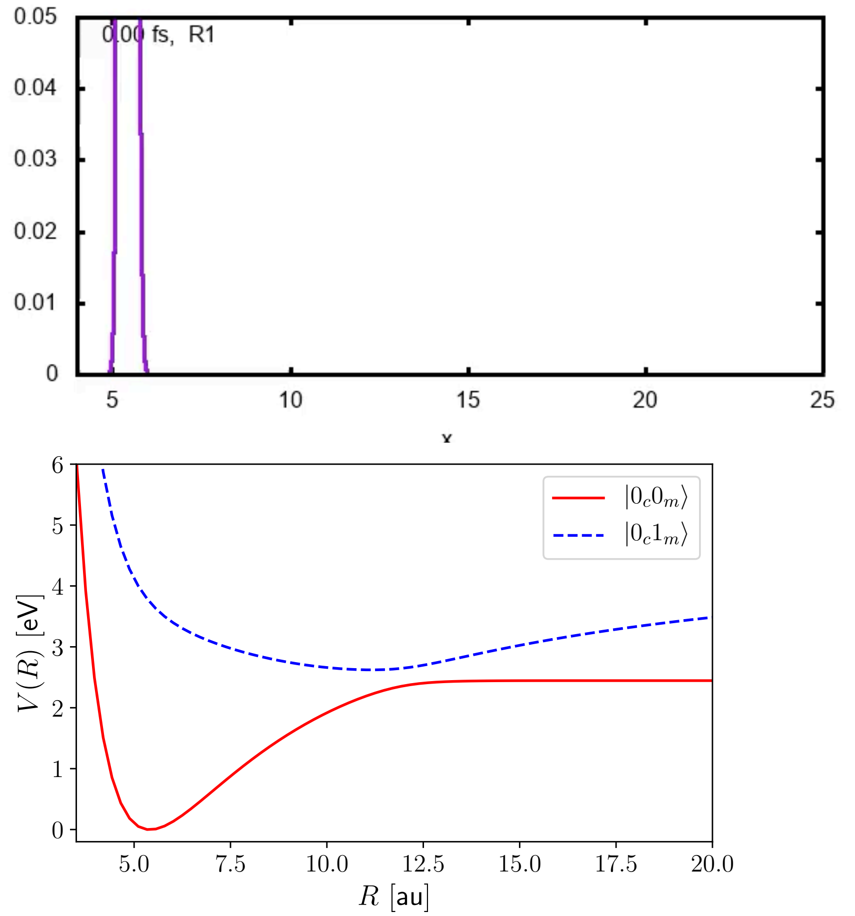


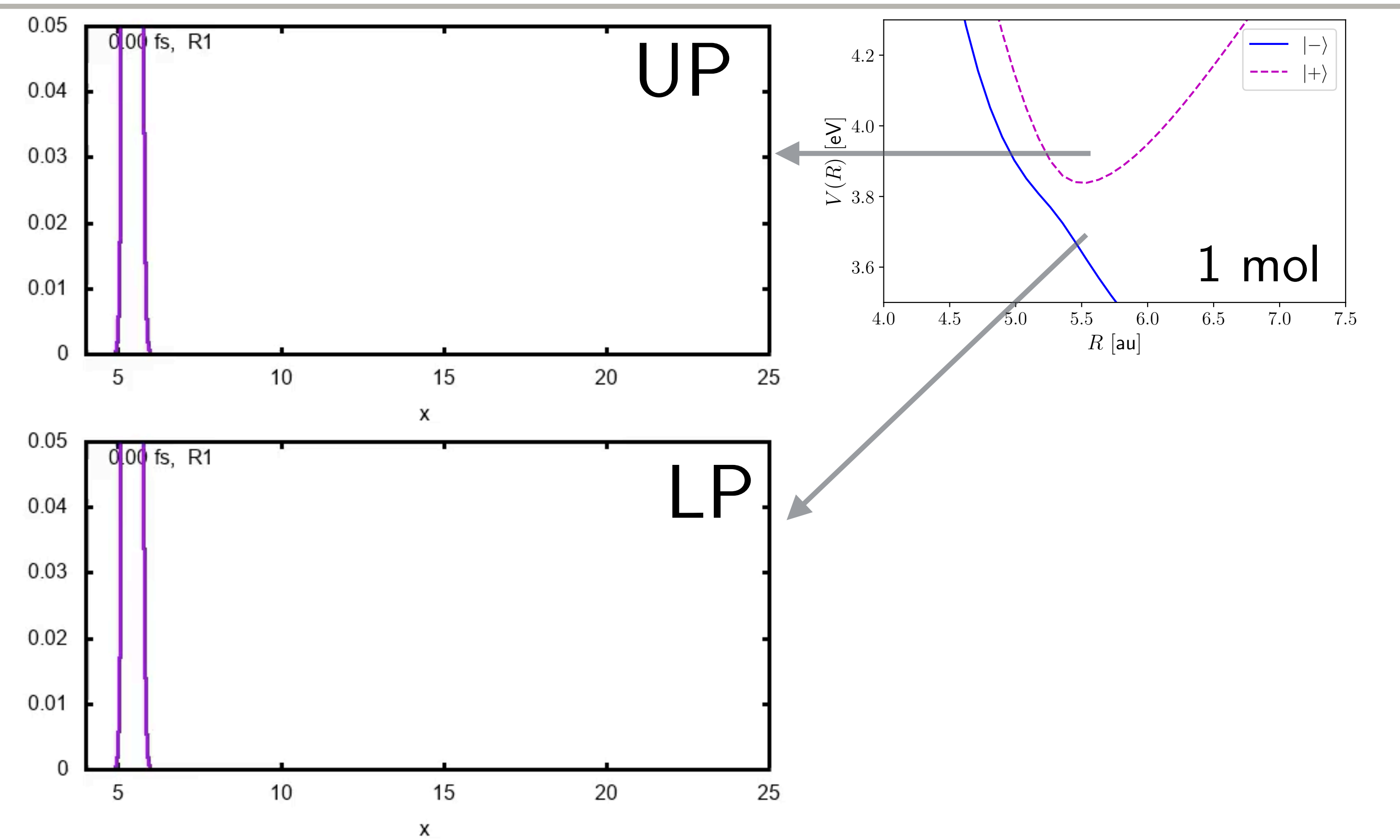


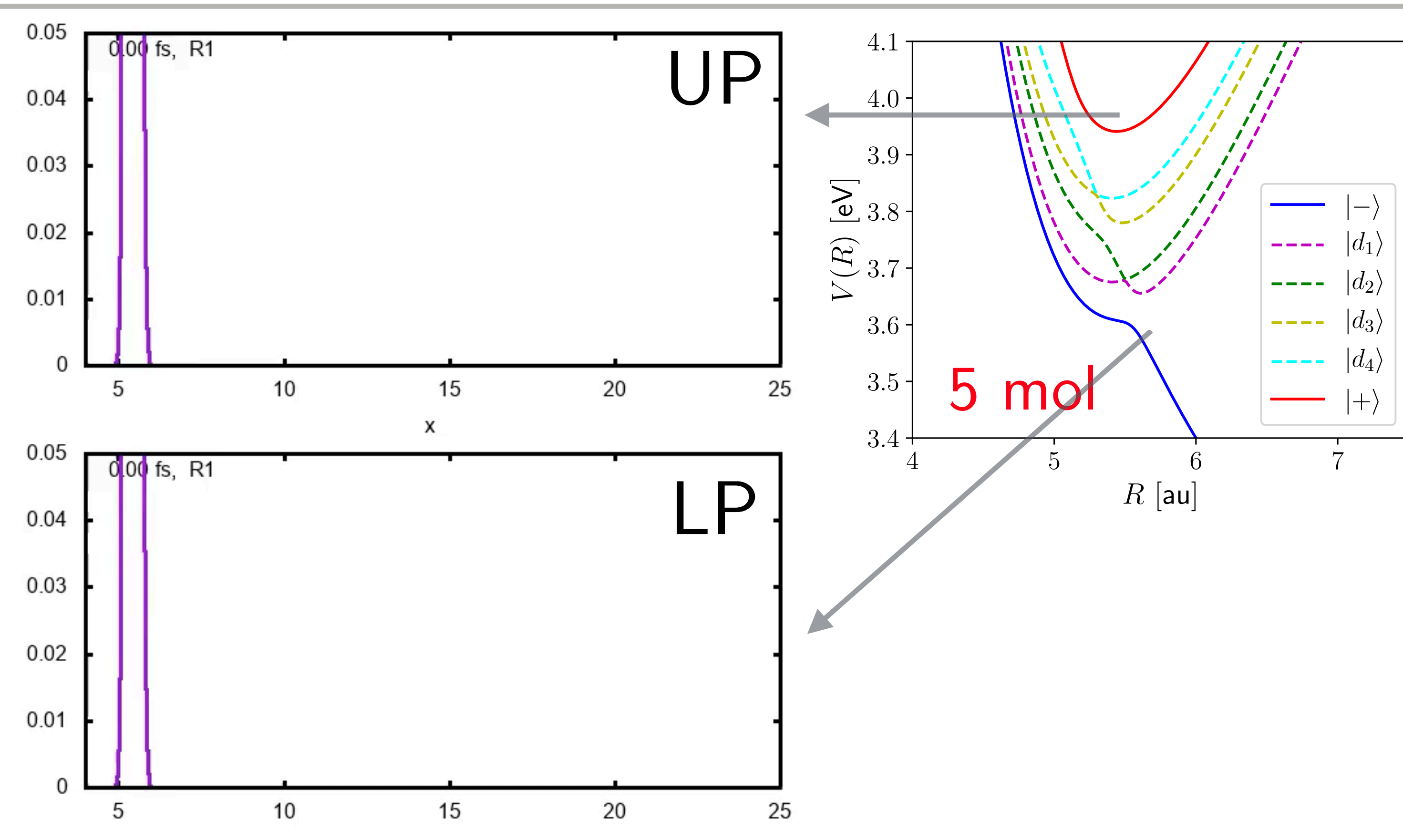


Cavity-modified photodissociation

No cavity







Cavity-modified photodissociation

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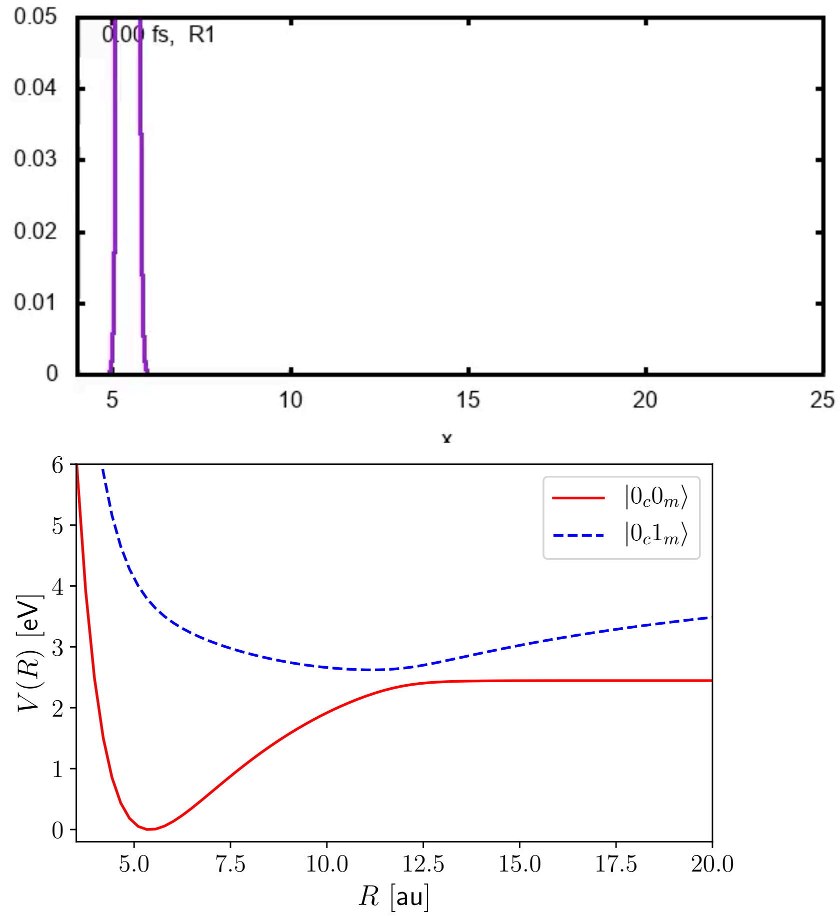
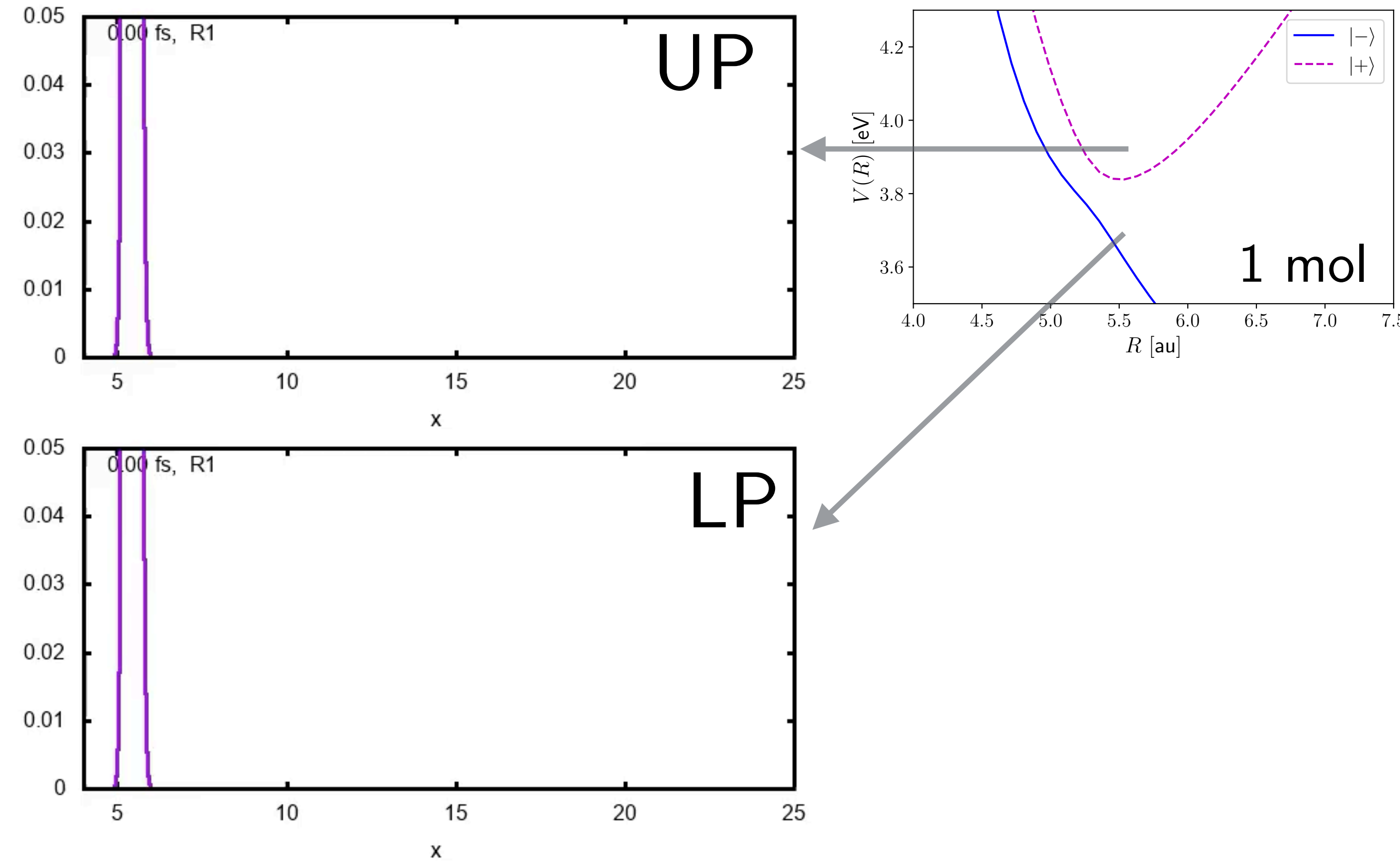
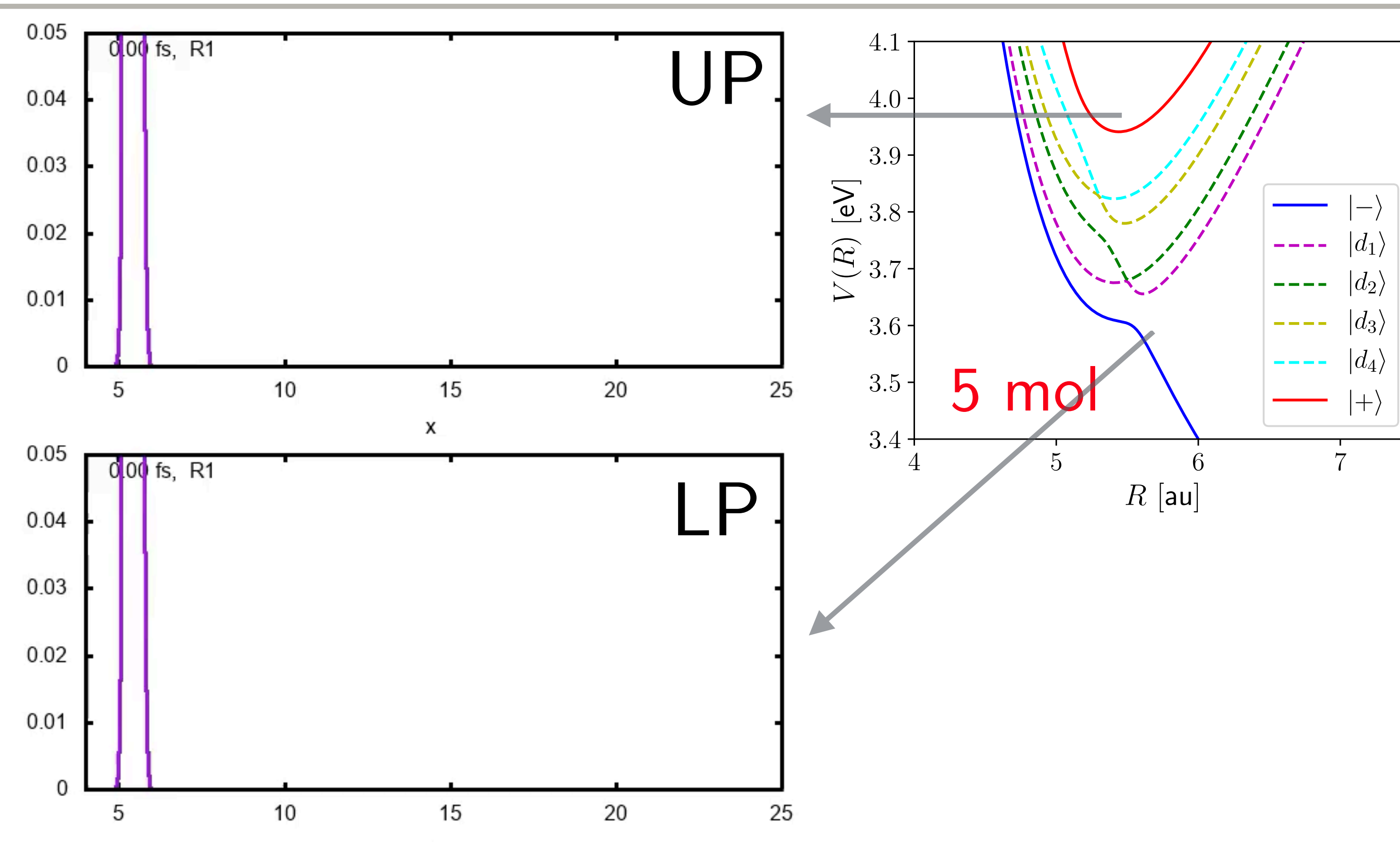
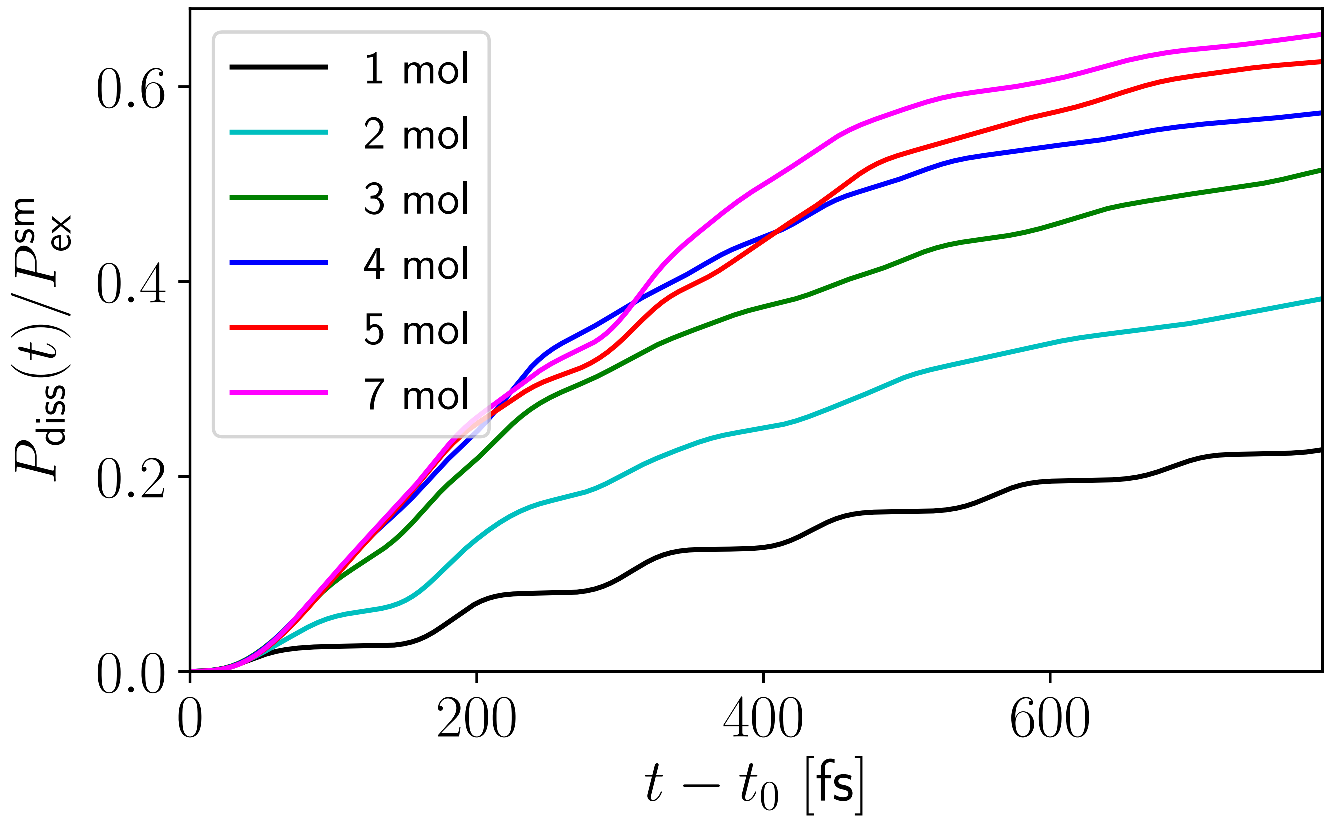






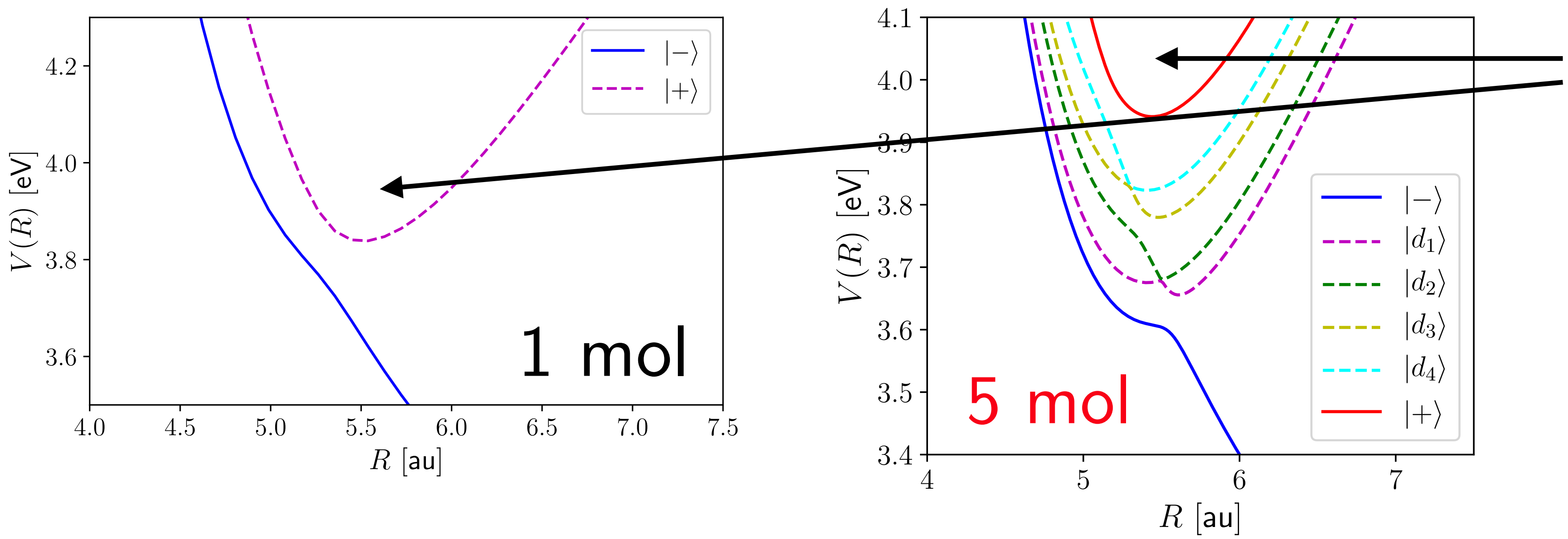
Photodissociation from the upper polariton



N	$\hbar\omega_L$ [eV]	$P_{\text{ex}}^{\text{sm}}$	$1/\Gamma_N$ [fs]
1	3.92	0.089	2903
2	3.94	0.10	1555
3	3.96	0.091	1037
4	3.97	0.10	880
5	3.99	0.10	763
7	4.01	0.11	707

$$\frac{P_{\text{dis}}(t)}{P_{\text{ex}}^{\text{sm}}} = 1 - e^{(t-t_0)\Gamma_N}$$

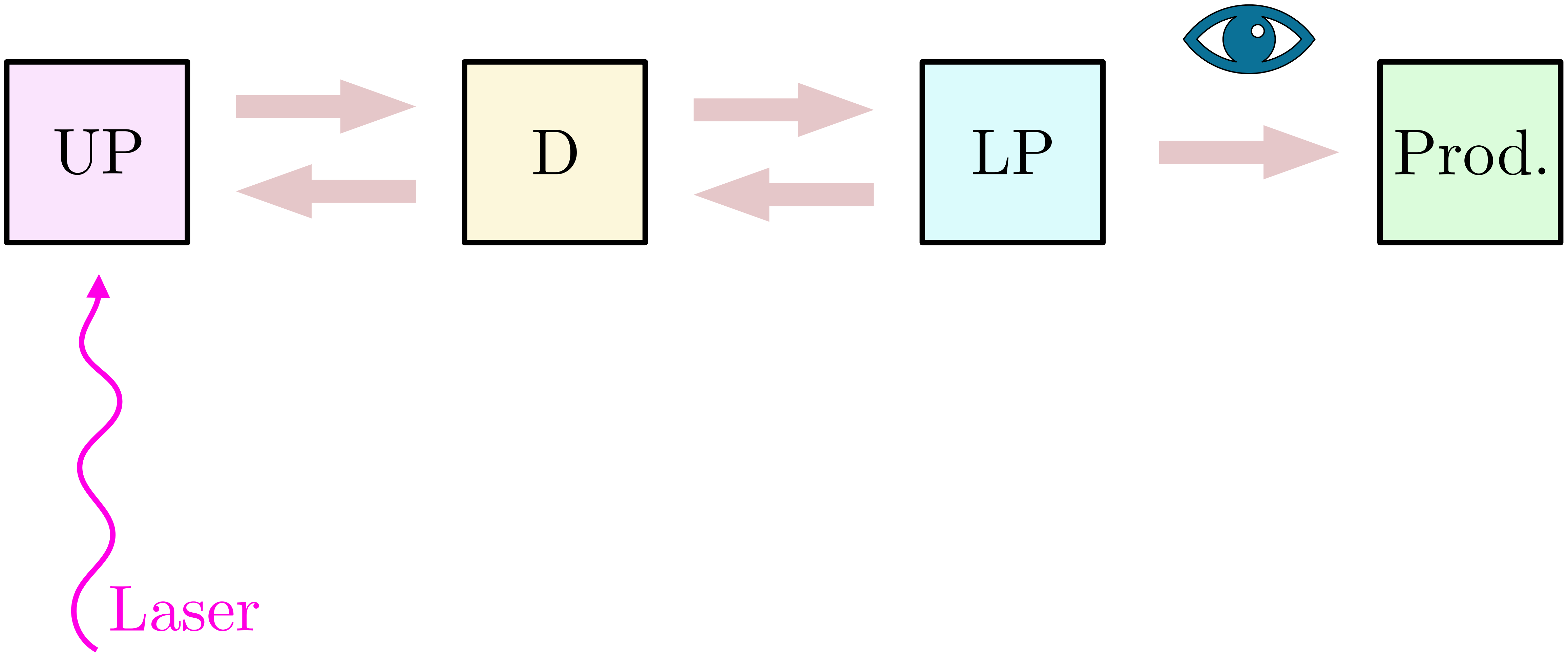
$g/\omega_c = 0.01$



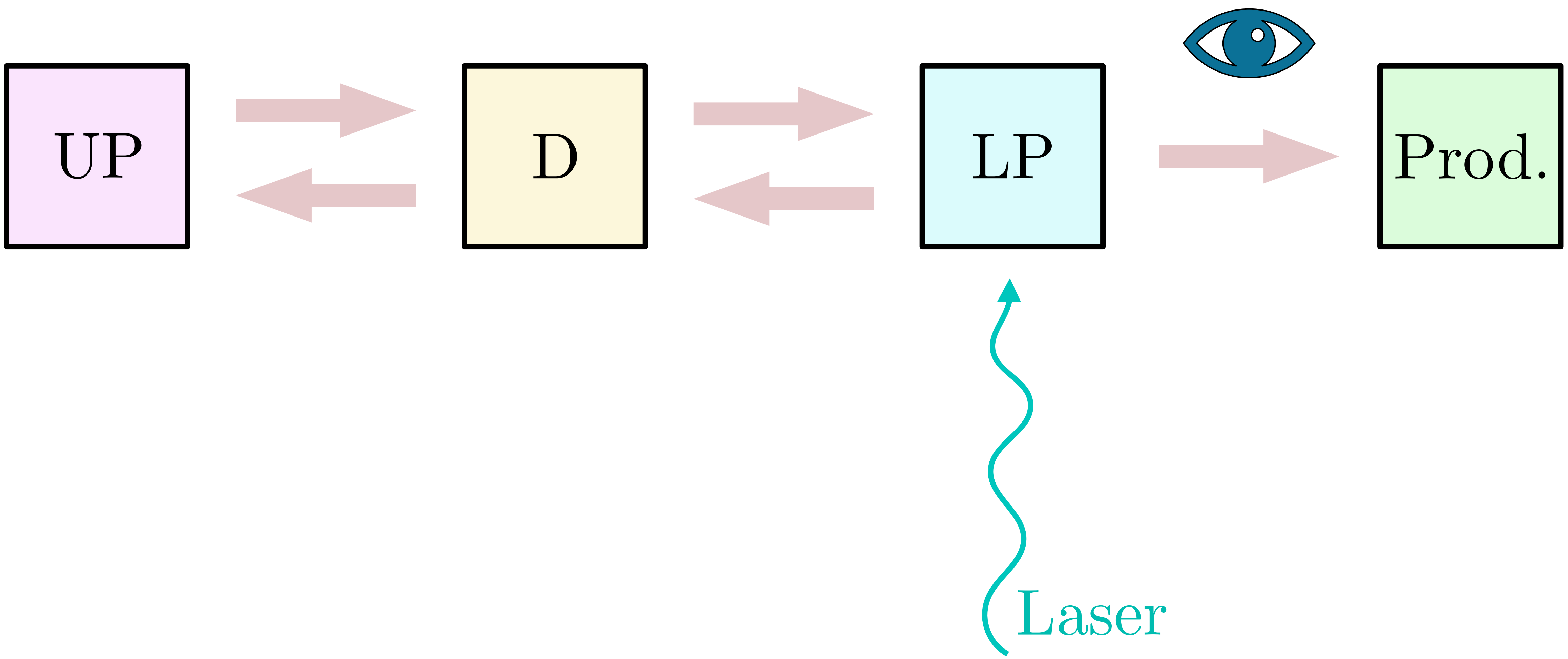
Photodissociation slowed down from the upper polaritonic state.

O.V., *Phys. Rev. Lett.* **121** *253001* (2018)

Tuning the rate of photo-chemical processes



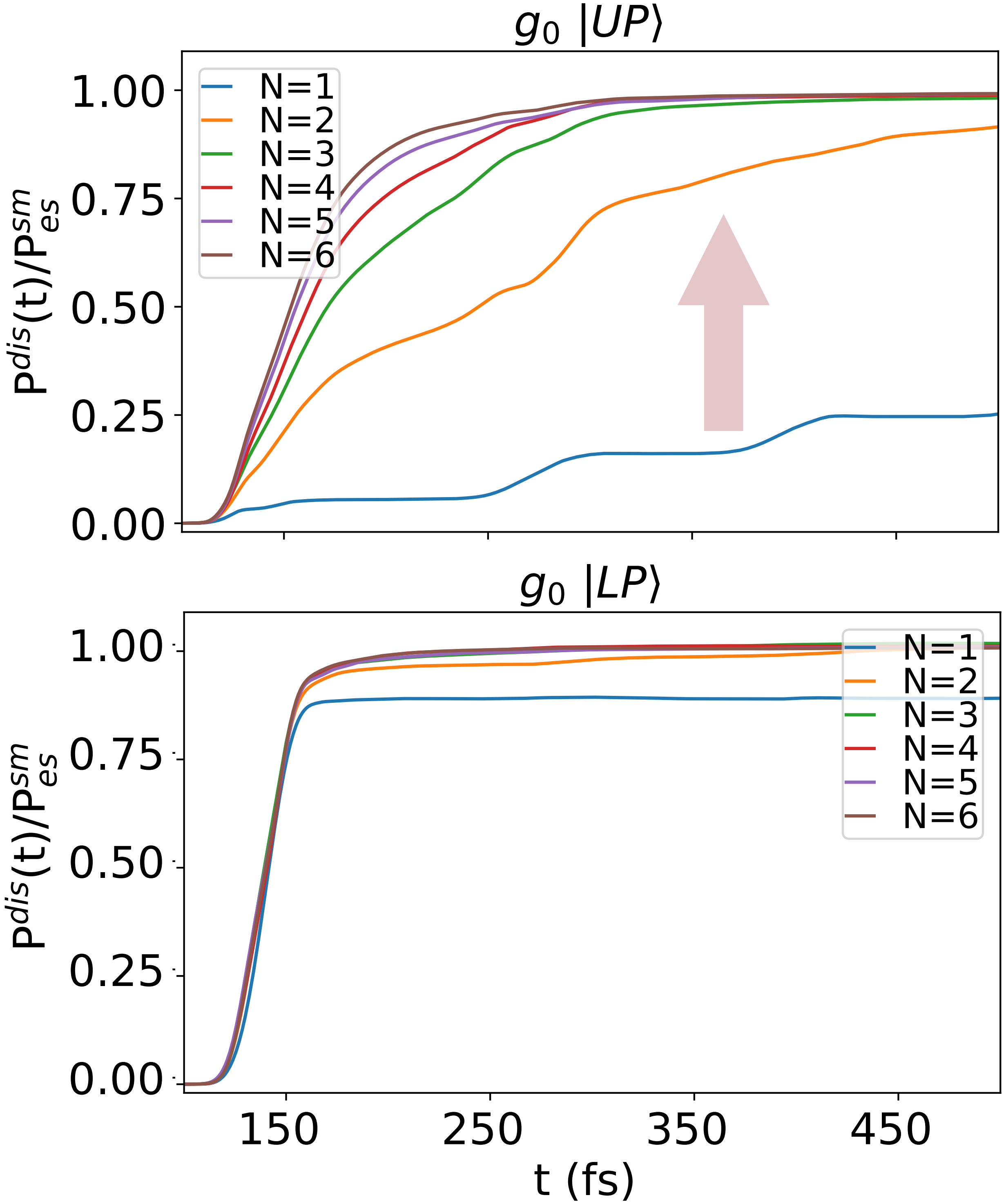
Tuning the rate of photo-chemical processes



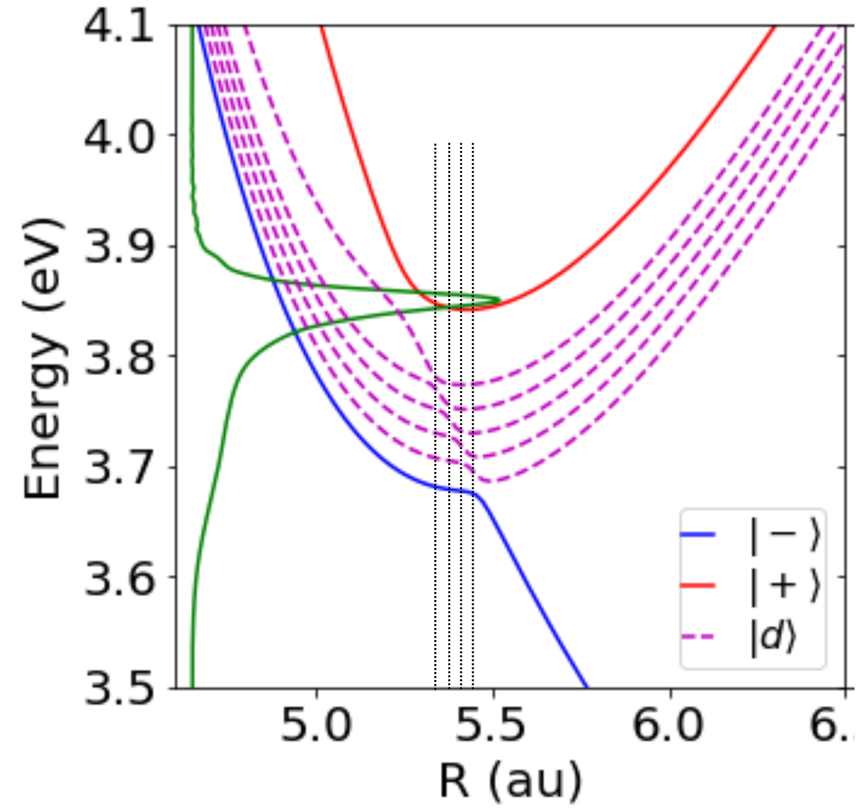
Tuning the rate of photo-chemical processes

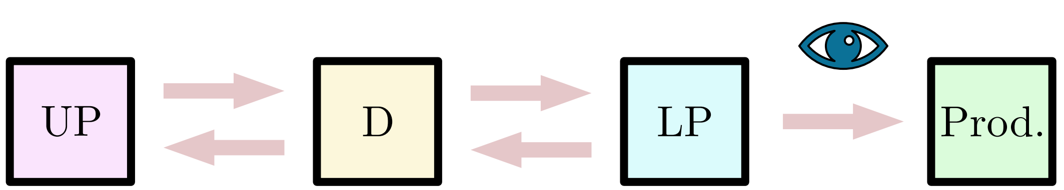
Rabi splitting **constant**: $\hbar\Omega_R \approx 0.13$ eV

Molecular coupling **varies**: $g = \hbar\Omega_R / 2\sqrt{N}$



N Molecules





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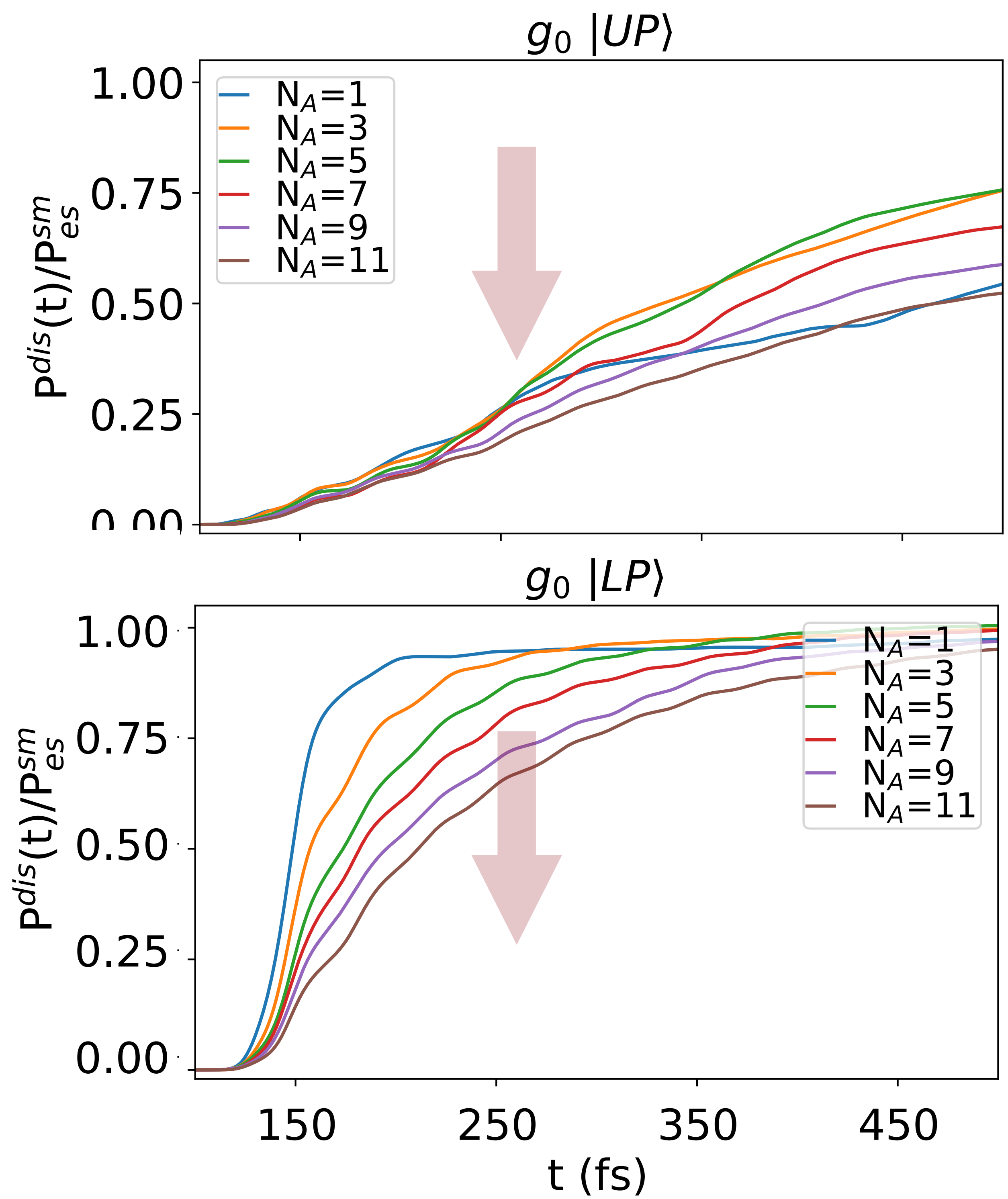
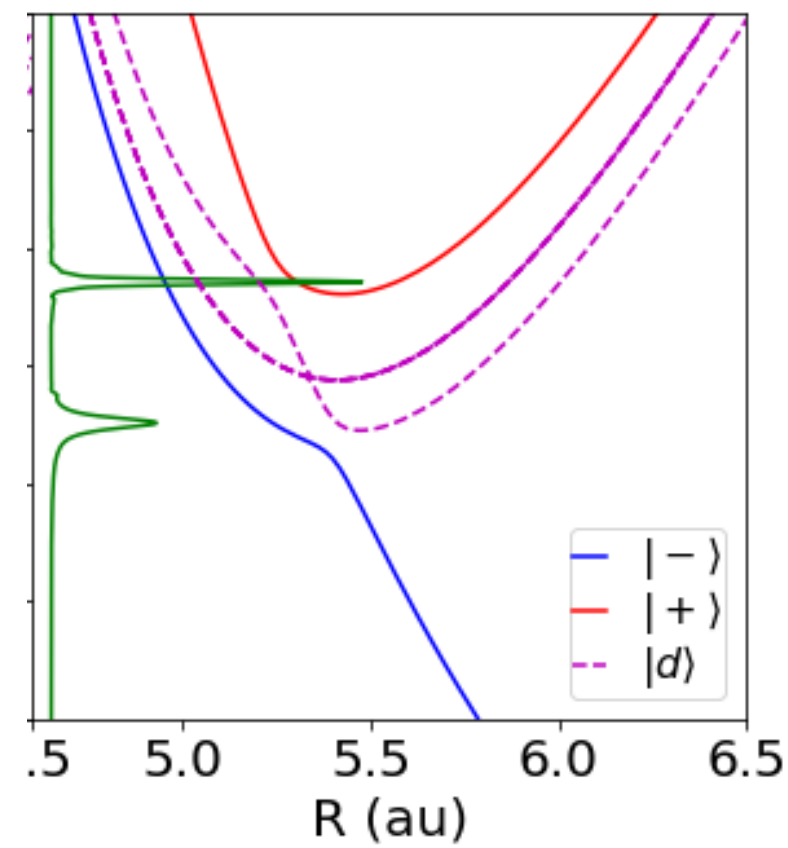
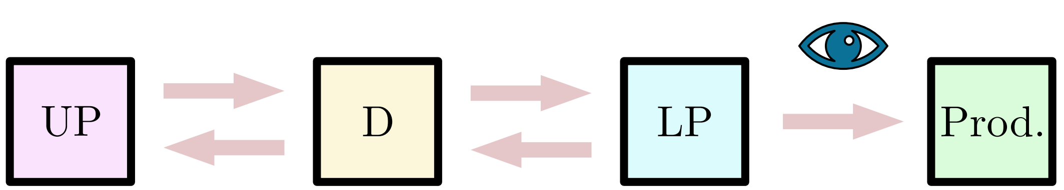


1 Molecule + buffer



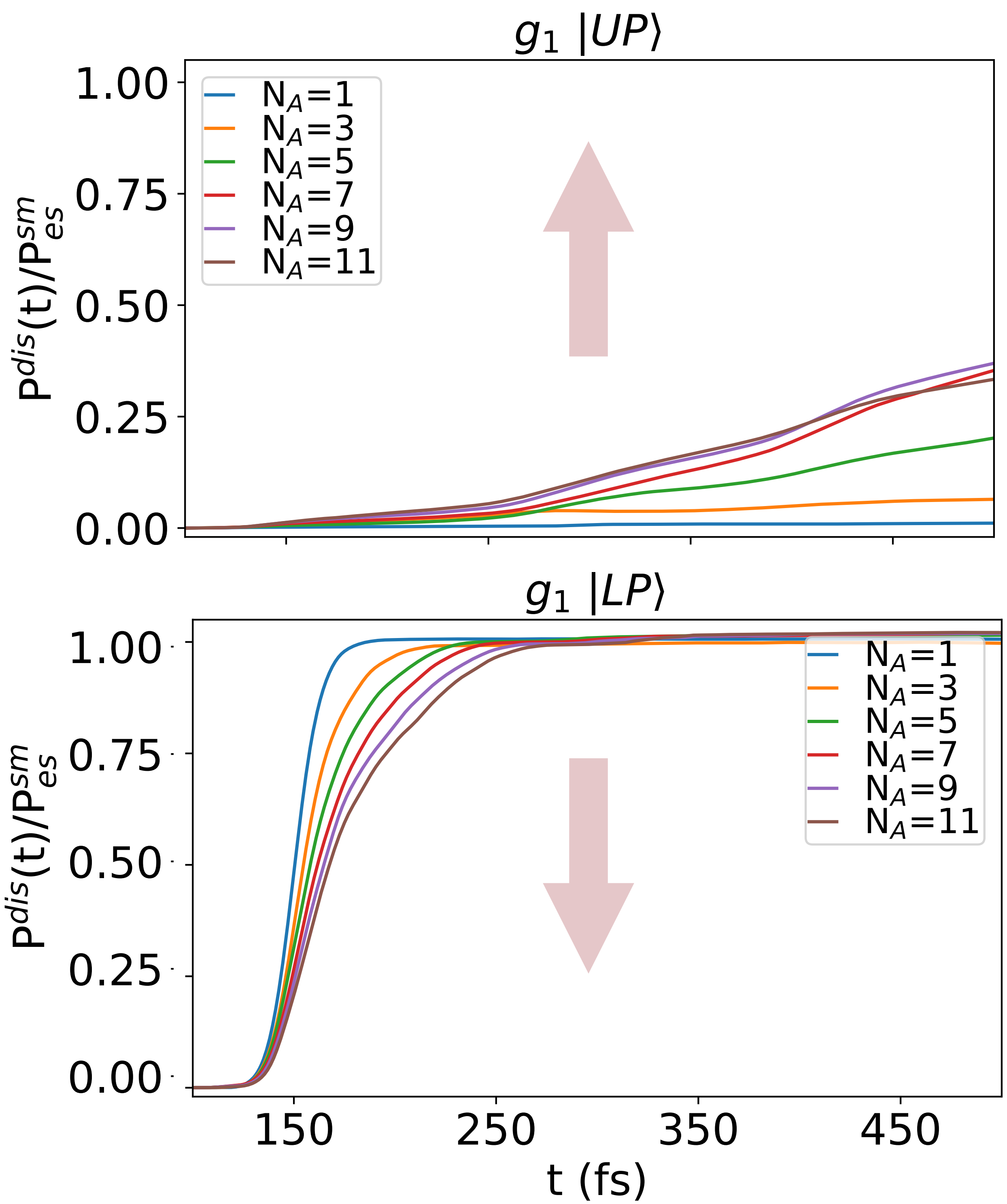


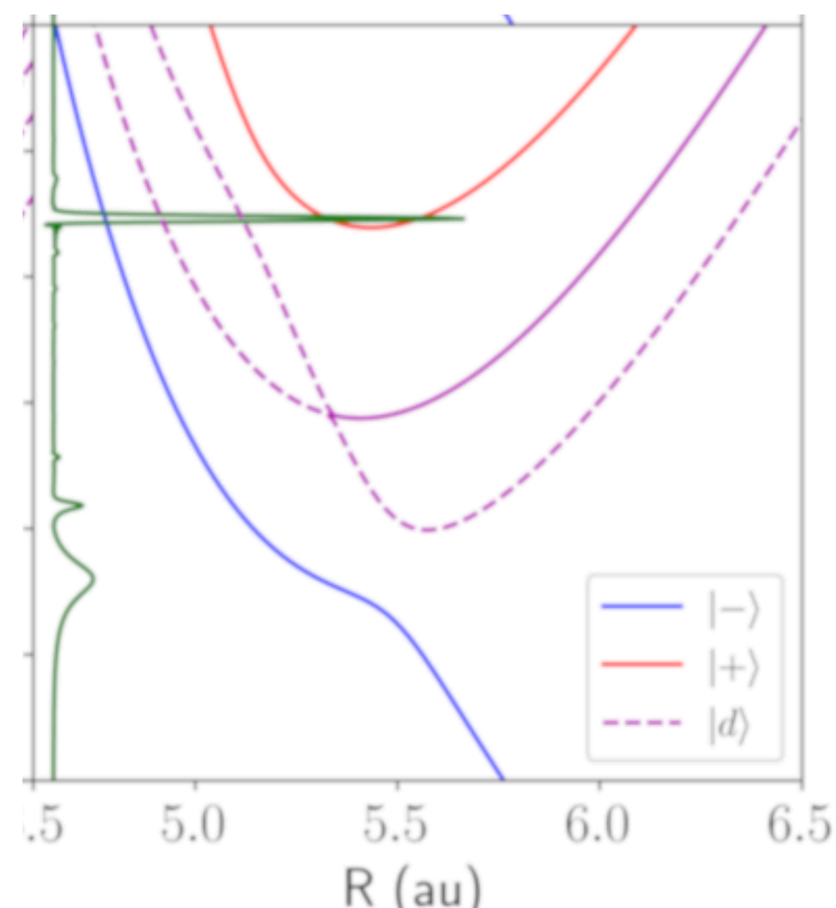
Tuning the rate of photo-chemical processes

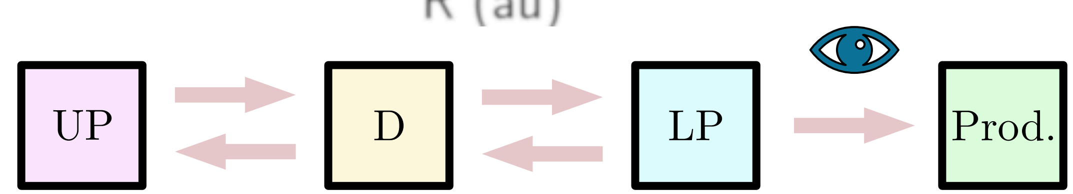
Rabi splitting **constant**: $\hbar\Omega_R \approx 0.30$ eV

Molecular coupling **varies**: $g = \hbar\Omega_R/2\sqrt{N}$

1 Molecule + buffer



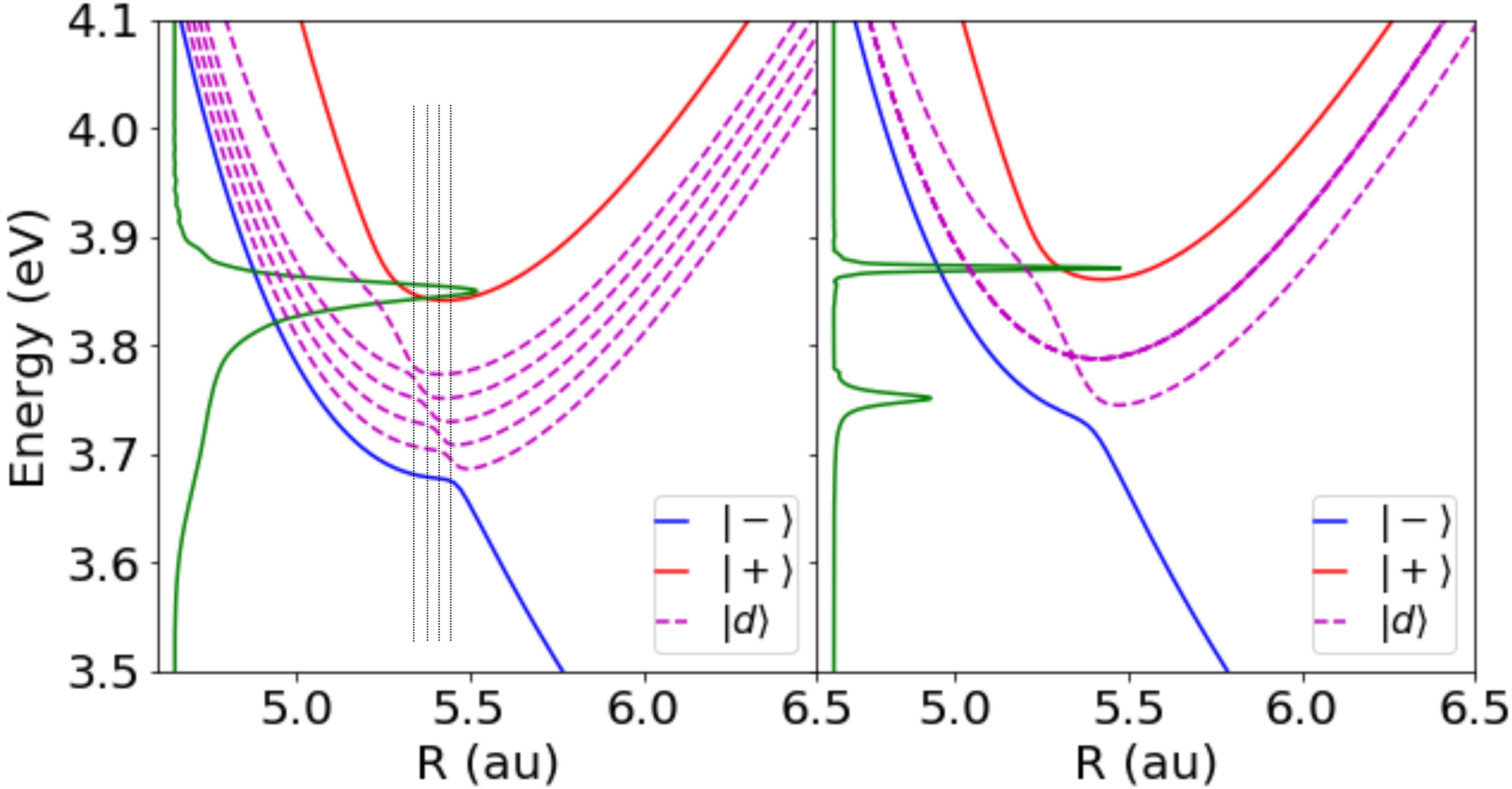




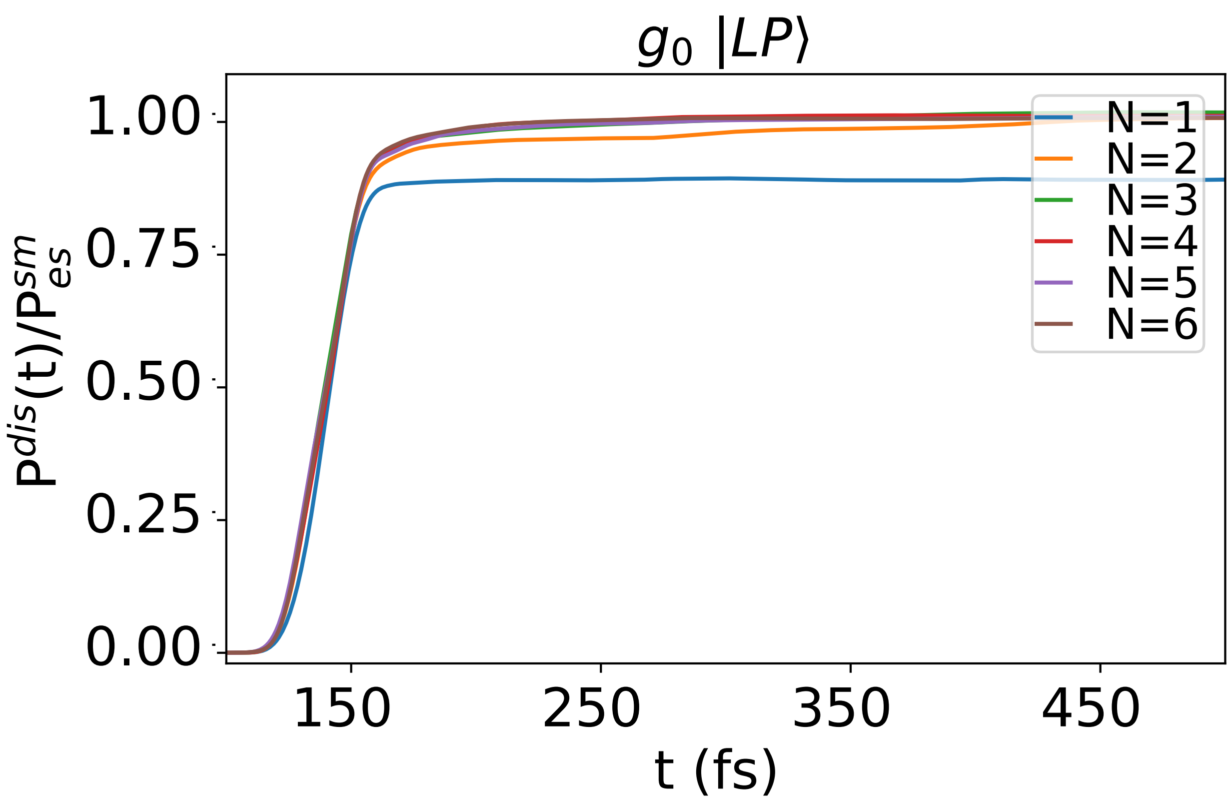
Tuning the rate of photo-chemical processes

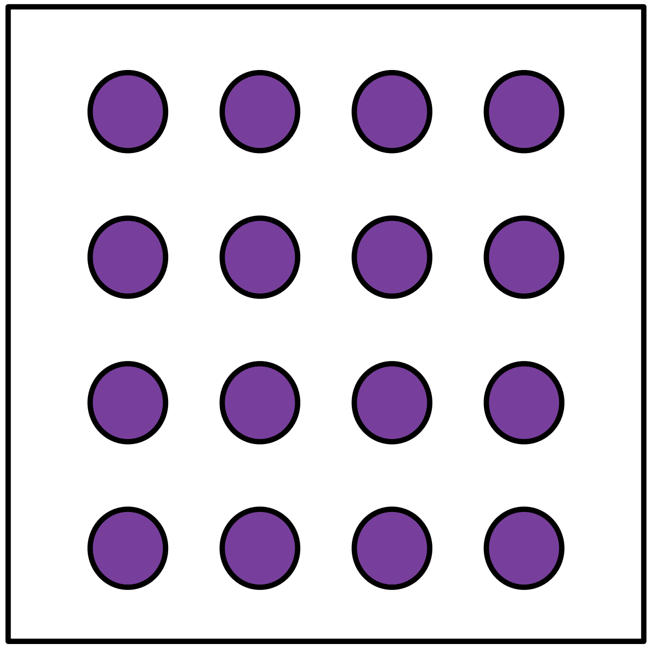
PES cut for 6 molecules,
5 at fixed **different** distances

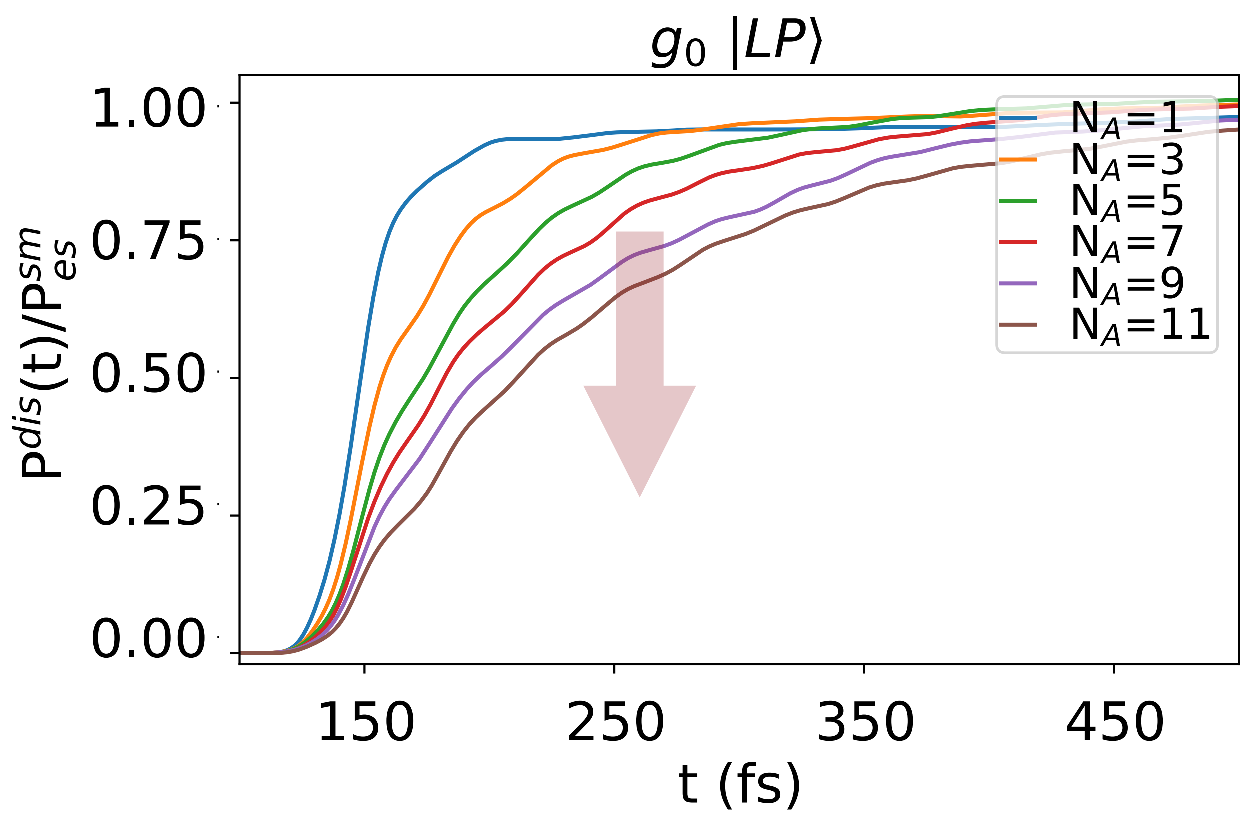
PES cut for 1 molecules +
photonic buffer (5)

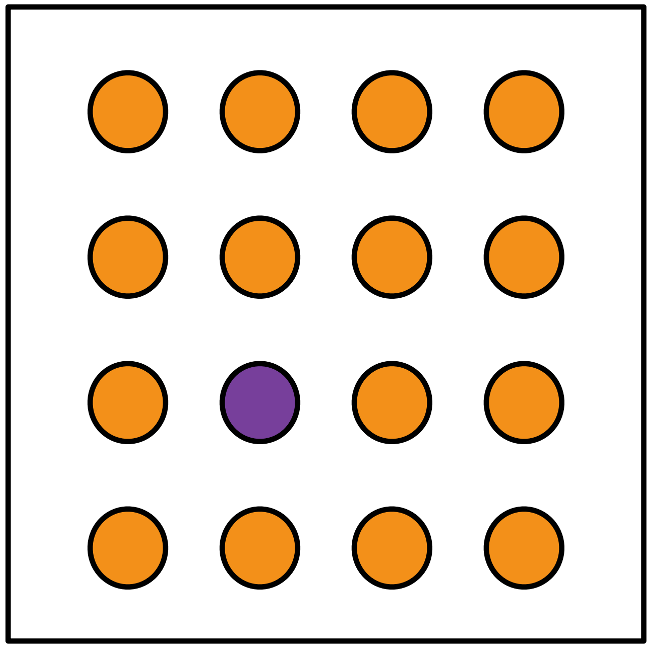


Effect of a photonic buffer



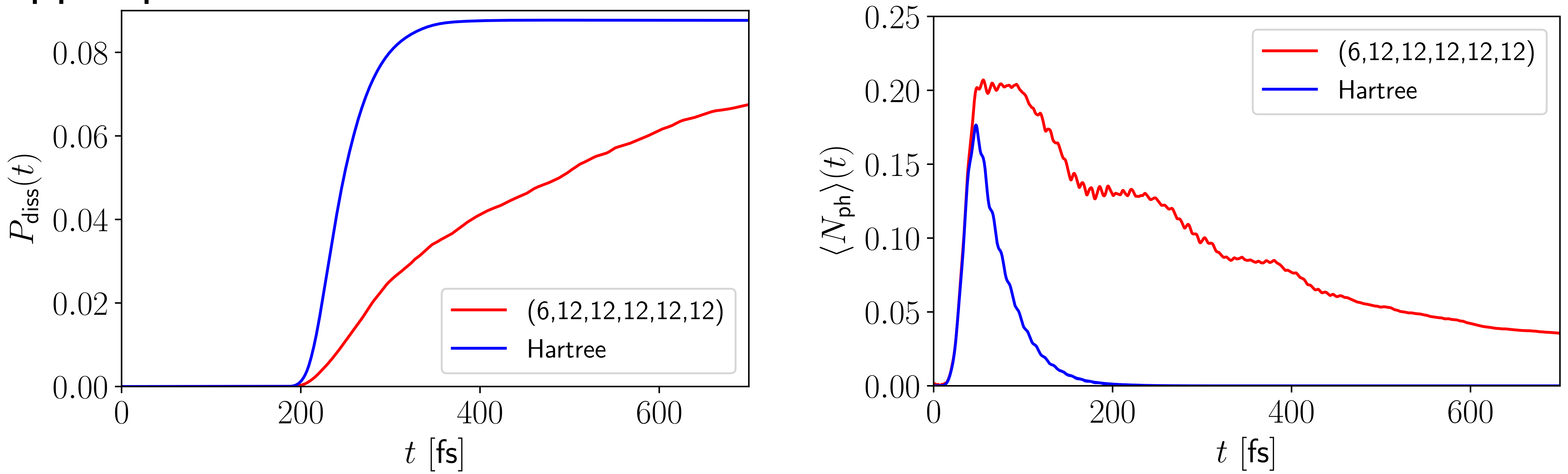




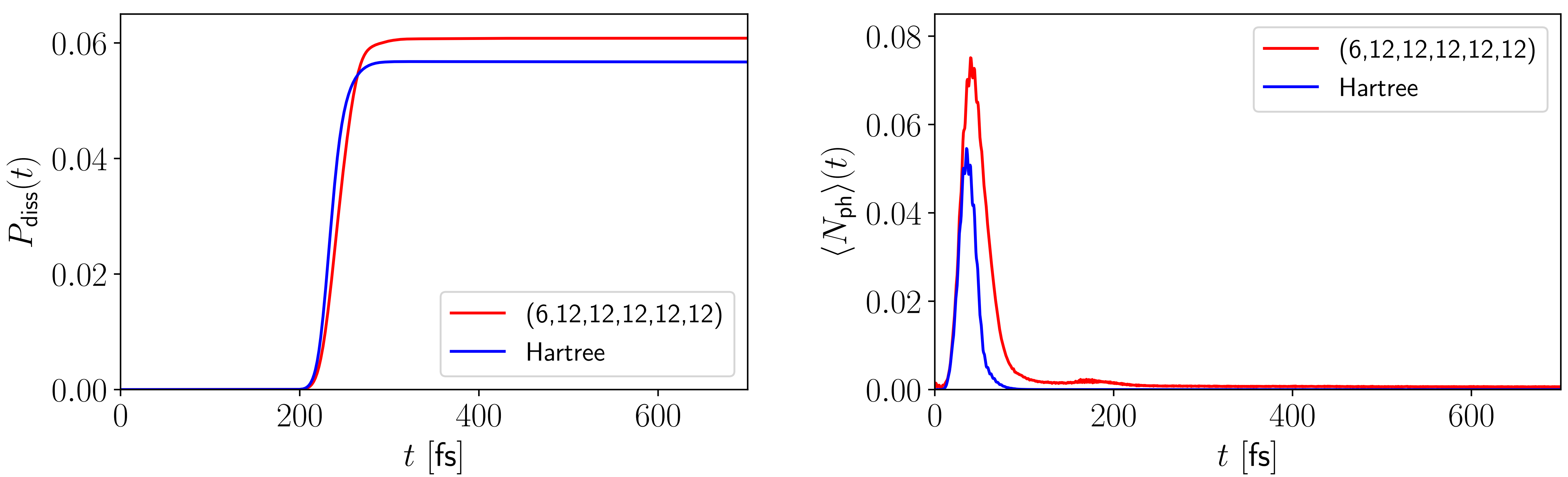


Back to correlations...

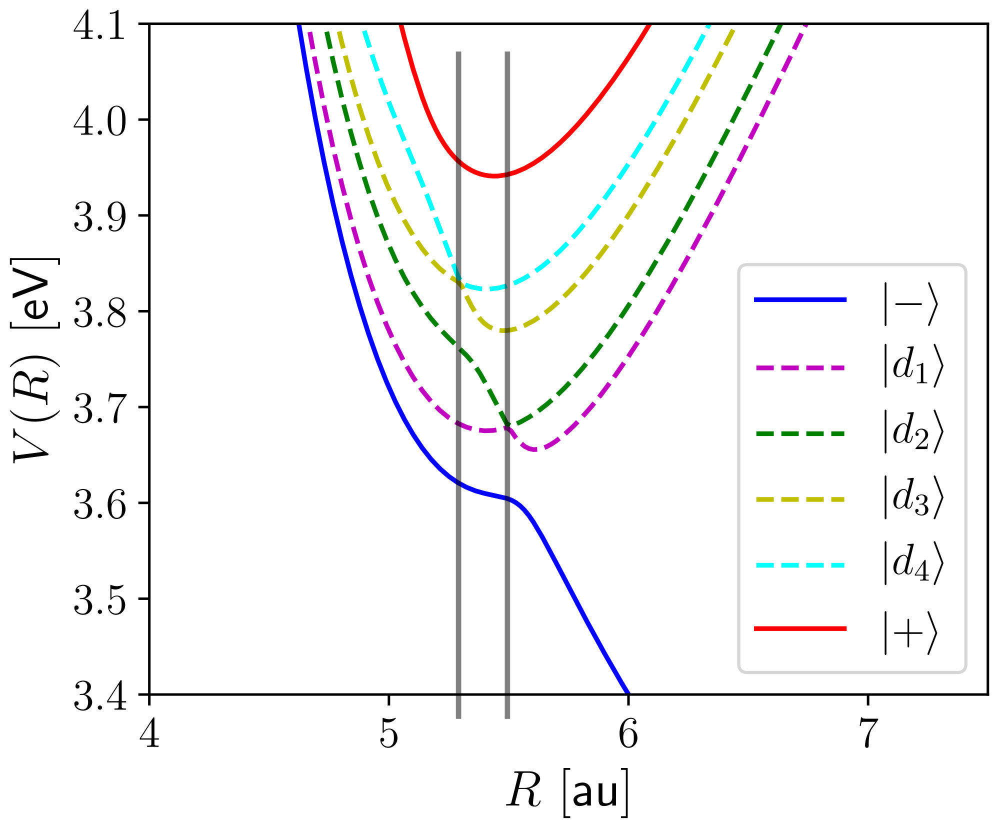
Upper pol.



Lower pol.



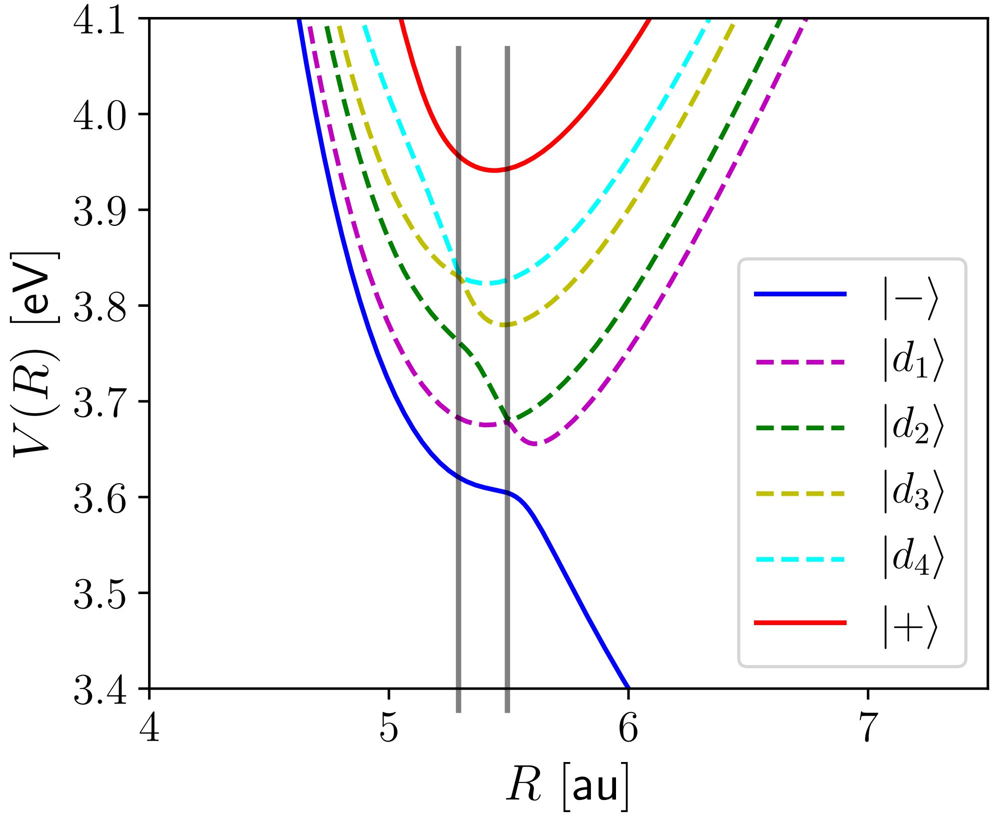
Vibronic coupling and collective conical intersections

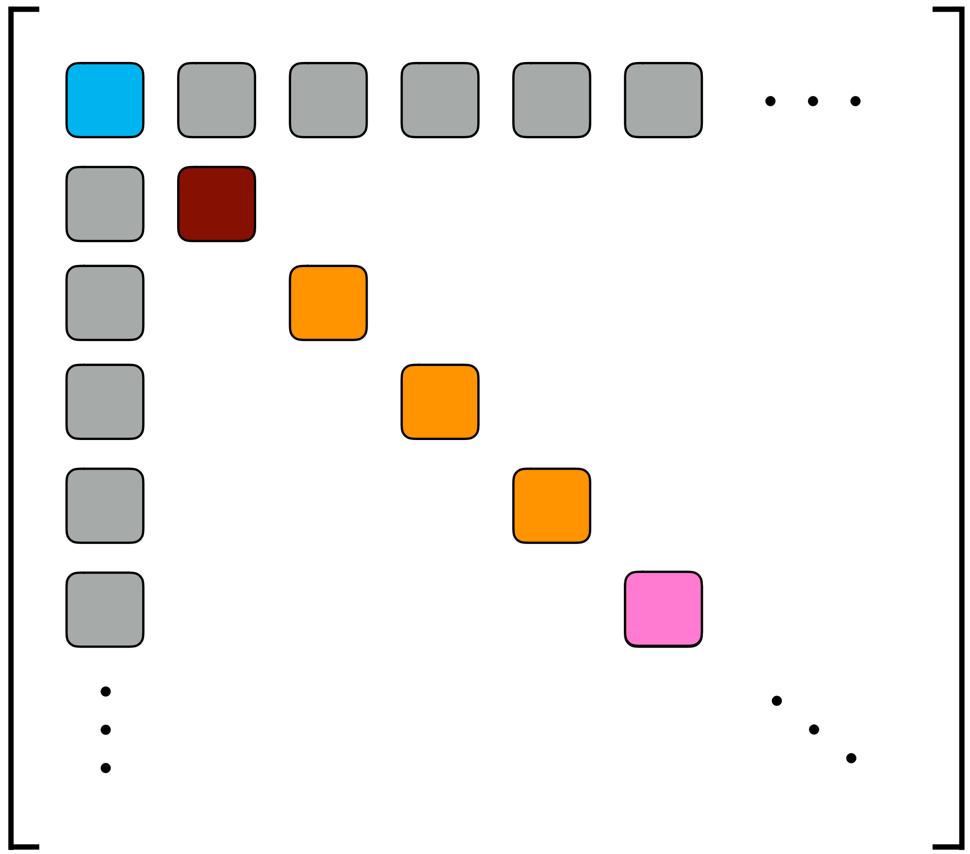


$R_2 = R_3 = 5.30$ au

$R_4 = R_5 = 5.50$ au

O'Leary & Stewart, *J. Comput. Phys.* **90**, 497 (1990)





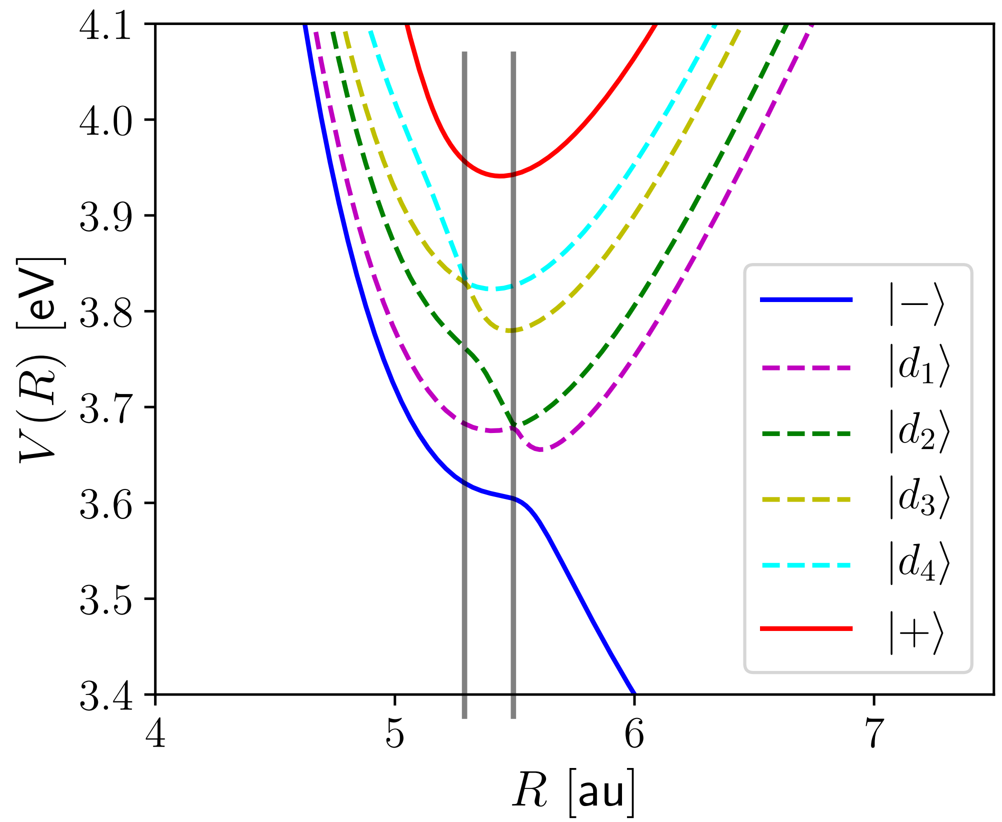
$R_2 = R_3 = 5.30$ au

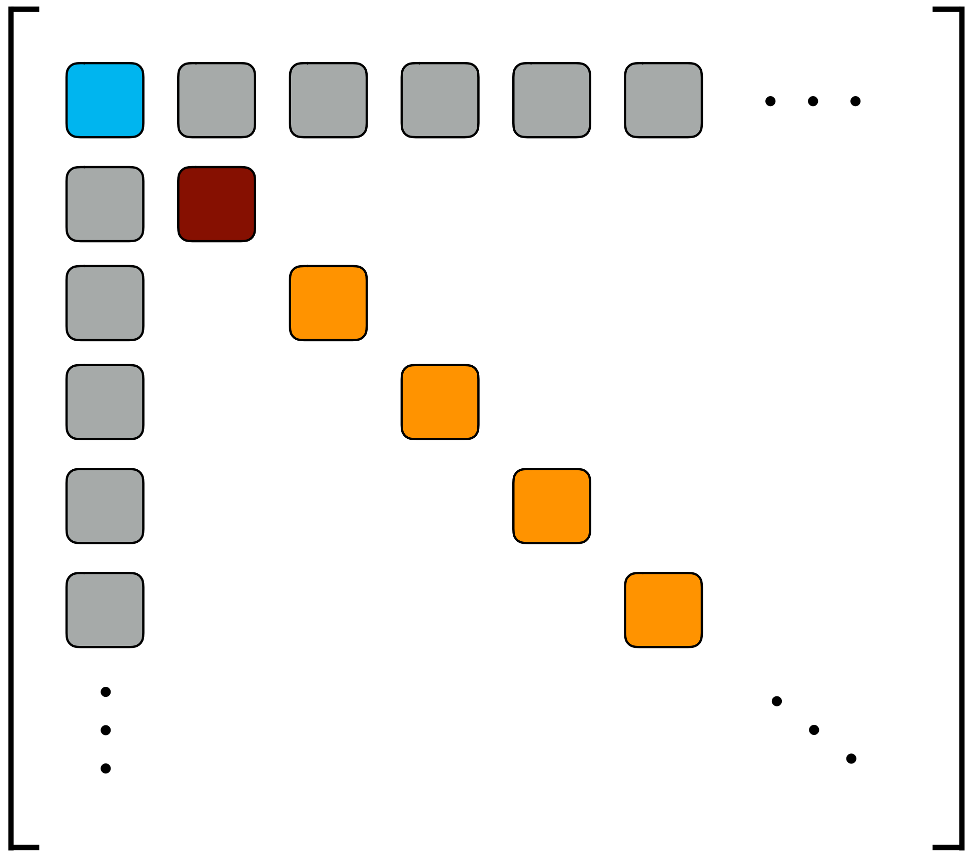
$R_4 = R_5 = 5.50$ au

	Perm. Gr.	Point. Gr.	CCI order	JT equiv.
$R_i = R_j = R_k$	S_3	D_3, C_{3v}	2	$E \otimes e$

O'Leary & Stewart, *J. Comput. Phys.* **90**, 497 (1990)

Vibronic coupling and collective conical intersections





$R_2 = R_3 = 5.30$ au

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	Perm. Gr.	Point. Gr.	CCI order	JT equiv.
$R_i = R_j = R_k$	S_3	D_3, C_{3v}	2	$E \otimes e$
$R_i = R_j = R_k = R_l$	S_4	T_d	3	$T_2 \otimes t_2$

O'Leary & Stewart, *J. Comput. Phys.* **90**, 497 (1990)

Vibronic Coupling: Tavis-Cummings *à la* Jahn-Teller

$$\mathcal{H}^{[1]}_{\mathsf{el-cav}}(\mathbf{R}) = \begin{pmatrix} \hbar\omega_c & \gamma^{(1)}(R_1) & \gamma^{(2)}(R_2) & \gamma^{(3)}(R_3) & \cdots \\ \gamma^{(1)}(R_1) & \Delta^{(1)}(R_1) & 0 & 0 & \cdots \\ \gamma^{(2)}(R_2) & 0 & \Delta^{(2)}(R_2) & 0 & \cdots \\ \gamma^{(3)}(R_3) & 0 & 0 & \Delta^{(3)}(R_3) & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

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Vibronic Coupling: Tavis-Cummings *à la* Jahn-Teller

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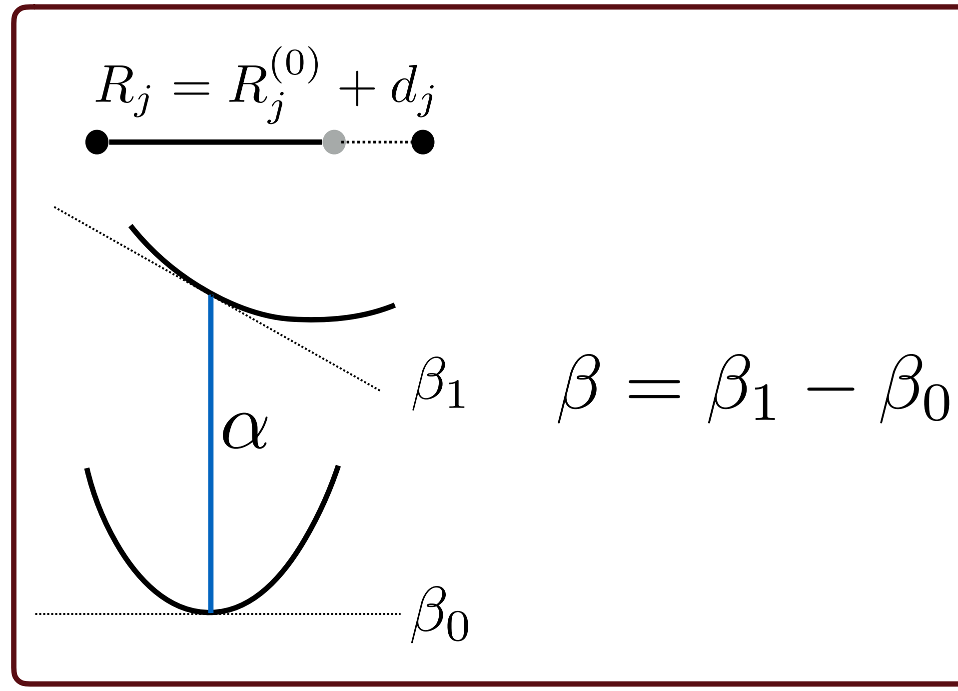
$$\mathcal{H}^{[1]}_{\text{m}=3}(\mathbf{d}) = \begin{pmatrix} \alpha & \gamma & \gamma & \gamma \\ \gamma & \alpha + \beta\, d_1 & 0 & 0 \\ \gamma & 0 & \alpha + \beta\, d_2 & 0 \\ \gamma & 0 & 0 & \alpha + \beta\, d_3 \end{pmatrix}$$



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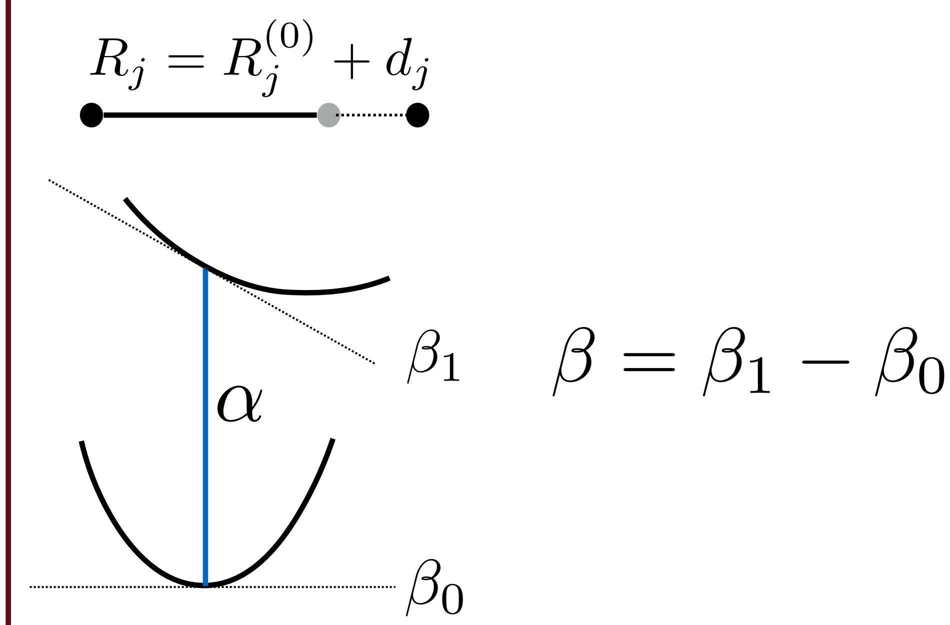
$$\mathcal{H}^{[1]}_{\text{m}=3}(\mathbf{d}) = \begin{pmatrix} \alpha & \gamma & \gamma & \gamma \\ \gamma & \alpha + \beta\, d_1 & 0 & 0 \\ \gamma & 0 & \alpha + \beta\, d_2 & 0 \\ \gamma & 0 & 0 & \alpha + \beta\, d_3 \end{pmatrix}$$



Symmetry-adapted polaritonic states:

$$|\pm\rangle = \frac{1}{\sqrt{2}}|1;0\rangle \pm \frac{1}{\sqrt{6}}\left(|0;1\rangle + |0;2\rangle + |0;3\rangle\right)$$

$$|D_1\rangle = -\frac{\sqrt{6}}{6}|0;1\rangle + \frac{\sqrt{6}}{3}|0;2\rangle - \frac{\sqrt{6}}{6}|0;3\rangle$$

$$|D_2\rangle = -\frac{\sqrt{2}}{2}|0;1\rangle + \frac{\sqrt{2}}{2}|0;3\rangle$$

Symmetry-adapted molecular displacements:

$$\rho = \frac{1}{\sqrt{3}}\left(d_1 + d_2 + d_3\right)$$

$$\nu_1 = -\frac{\sqrt{6}}{6}d_1 + \frac{\sqrt{6}}{3}d_2 - \frac{\sqrt{6}}{6}d_3$$

$$\nu_2 = -\frac{\sqrt{2}}{2}d_1 + \frac{\sqrt{2}}{2}d_3$$

$$\Longrightarrow \quad \langle S_i|\frac{\partial \mathcal{H}^{[1]}}{\partial Q_l}|S_j\rangle$$

O.V., *Phys. Rev. Lett.* **121** *253001* (2018)

Vibronic Coupling: Tavis-Cummings *à la* Jahn-Teller

$$\mathcal{W}(\rho,\nu_1,\nu_2) = \boxed{\mathcal{W}_{[0]}} + \boxed{\mathcal{W}_{[A,A]}(\rho)} + \boxed{\mathcal{W}_{[A,E_1]}(\nu_1) + \mathcal{W}_{[A,E_2]}(\nu_2)} + \boxed{\mathcal{W}_{[E_1,E_2]}(\nu_1,\nu_2)}$$

TC

$$\mathcal{W}_{[0]} = \begin{pmatrix} \alpha+\gamma\sqrt{3} & 0 & 0 & 0 \\ 0 & \alpha & 0 & 0 \\ 0 & 0 & \alpha & 0 \\ 0 & 0 & 0 & \alpha-\gamma\sqrt{3} \end{pmatrix}$$

O.V., *Phys. Rev. Lett.* **121** *253001* (2018)

Vibronic Coupling: Tavis-Cummings *à la* Jahn-Teller

$$\mathcal{W}(\rho,\nu_1,\nu_2) = \boxed{\mathcal{W}_{[0]}} + \boxed{\mathcal{W}_{[A,A]}(\rho)} + \boxed{\mathcal{W}_{[A,E_1]}(\nu_1) + \mathcal{W}_{[A,E_2]}(\nu_2)} + \boxed{\mathcal{W}_{[E_1,E_2]}(\nu_1,\nu_2)}$$

TC

$$\mathcal{W}_{[0]} = \begin{pmatrix} \alpha+\gamma\sqrt{3} & 0 & 0 & 0 \\ 0 & \alpha & 0 & 0 \\ 0 & 0 & \alpha & 0 \\ 0 & 0 & 0 & \alpha-\gamma\sqrt{3} \end{pmatrix}$$

$$\mathcal{W}_{[A,A]}(\rho) = \begin{pmatrix} \rho/2 & 0 & 0 & -\rho/2 \\ 0 & \rho & 0 & 0 \\ 0 & 0 & \rho & 0 \\ -\rho/2 & 0 & 0 & \rho/2 \end{pmatrix} \frac{\beta}{\sqrt{3}}$$

PJT

$$\mathcal{W}_{[A,E_1]}(\nu_1) = \begin{pmatrix} 0 & \nu_1 & 0 & 0 \\ \nu_1 & 0 & 0 & -\nu_1 \\ 0 & 0 & 0 & 0 \\ 0 & -\nu_1 & 0 & 0 \end{pmatrix} \frac{\beta}{\sqrt{6}} \qquad \mathcal{W}_{[A,E_2]}(\nu_2) = \begin{pmatrix} 0 & 0 & \nu_2 & 0 \\ 0 & 0 & 0 & 0 \\ \nu_2 & 0 & 0 & -\nu_2 \\ 0 & 0 & -\nu_2 & 0 \end{pmatrix} \frac{\beta}{\sqrt{6}}$$

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JT $E \otimes e$

$$\mathcal{W}_{[E_1,E_2]}(\nu_1,\nu_2) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \nu_1 & \nu_2 & 0 \\ 0 & \nu_2 & -\nu_1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \frac{\beta}{\sqrt{6}}$$

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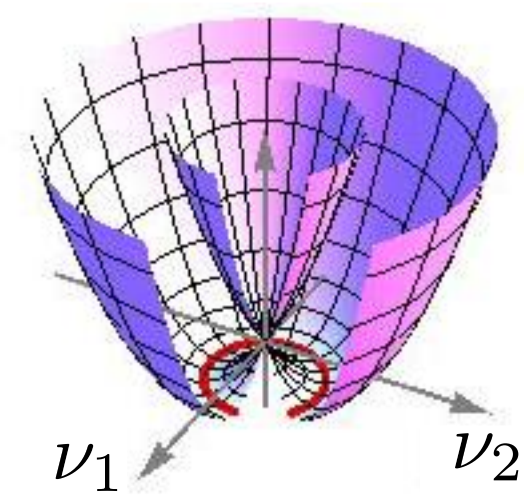

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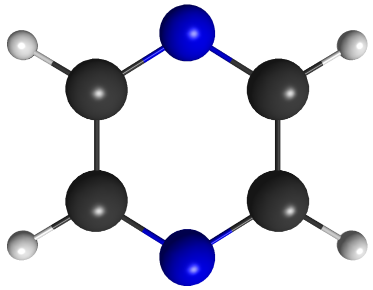
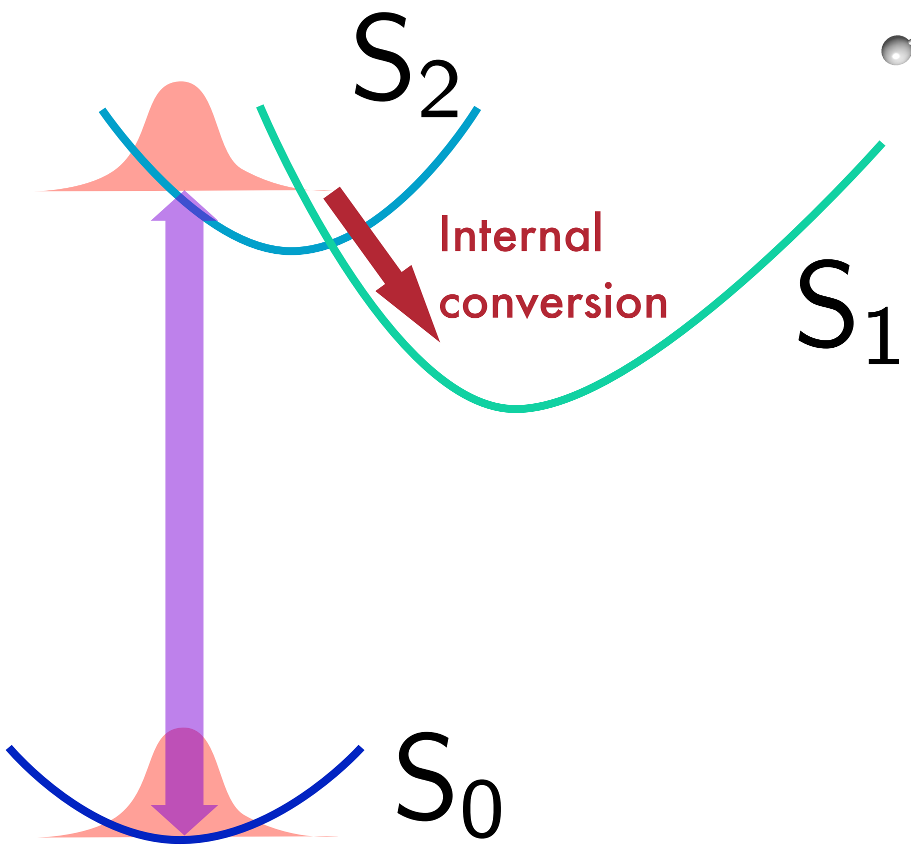
Internal conversion in polyatomic systems: pyrazine

Vibronic coupling Hamiltonian of Raab et al.,
J. Chem. Phys. **110** *936* (1999)





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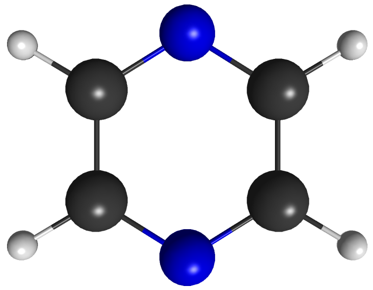

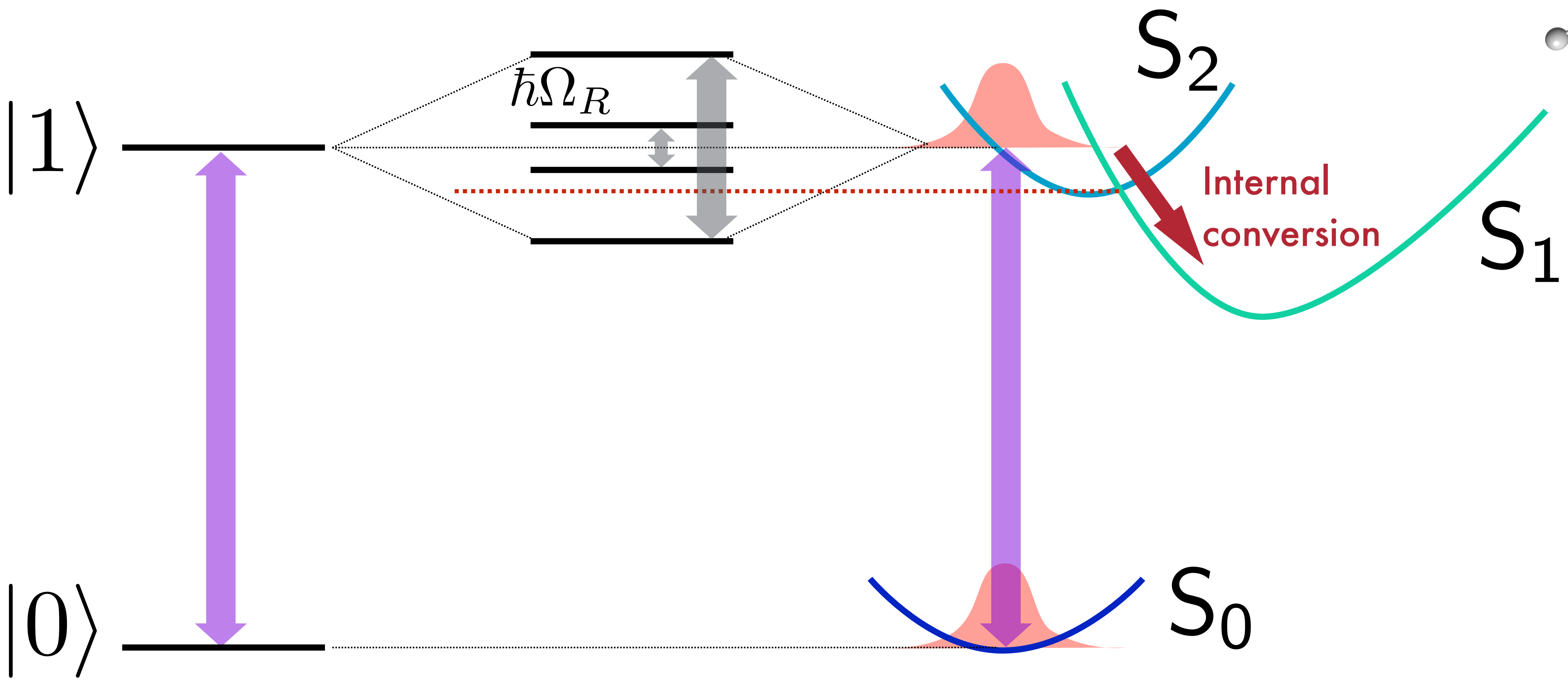

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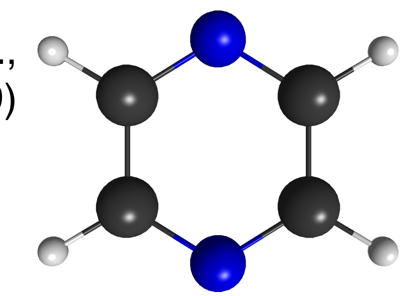

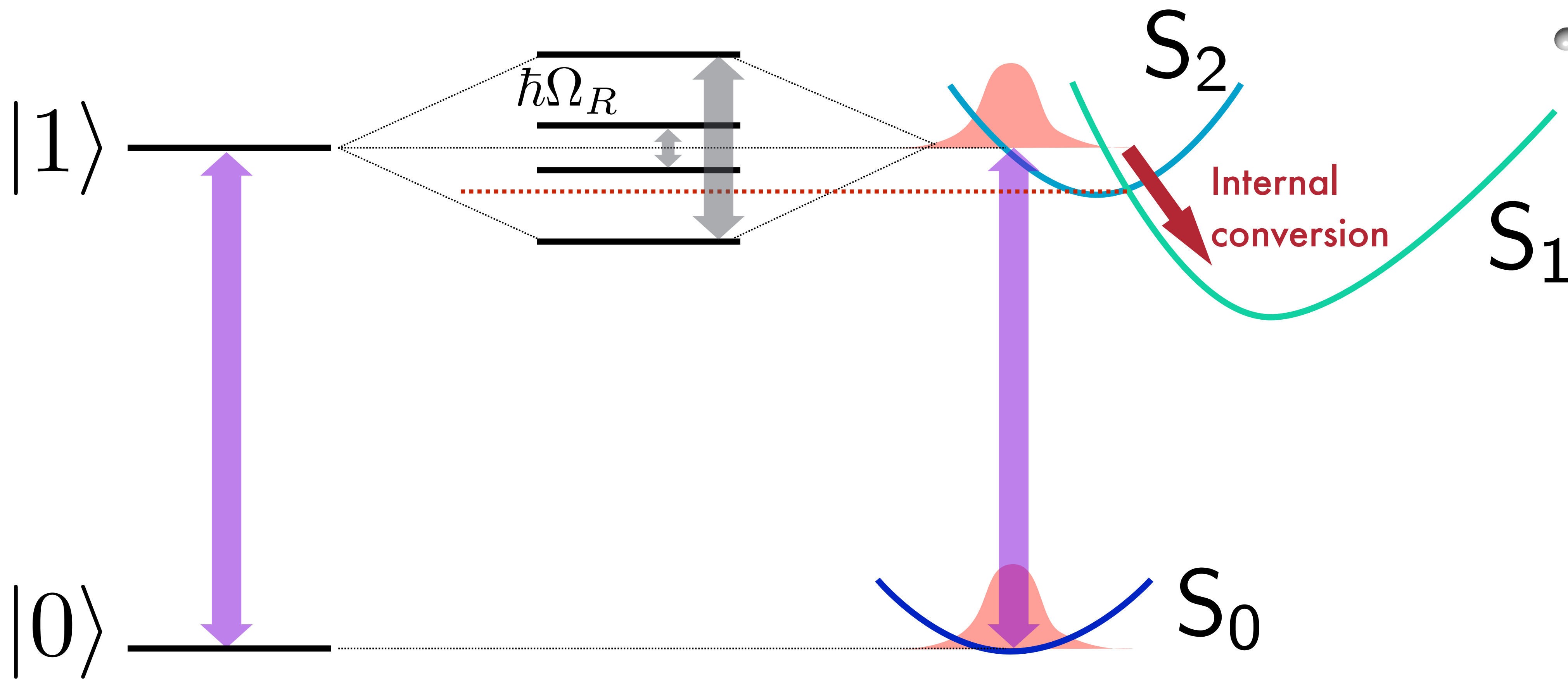

Ground state S_0 coupled to S_2 via the cavity mode:

Large coupling: $E_{LP} < E_{CoIn}$ $\hbar\Omega_R \approx 2.0$ eV

Small coupling: $E_{LP} > E_{CoIn}$ $\hbar\Omega_R \approx 0.95$ eV

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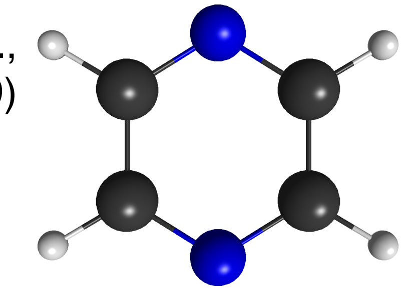
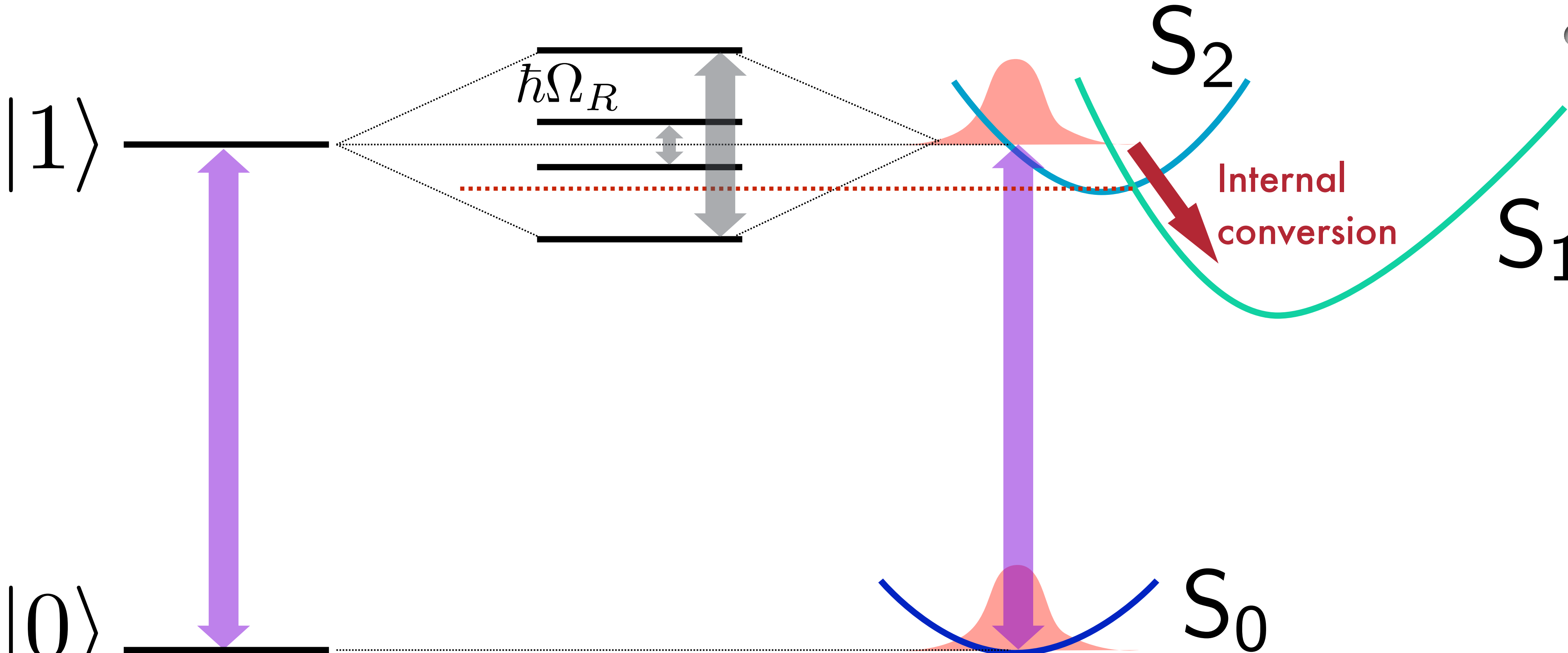
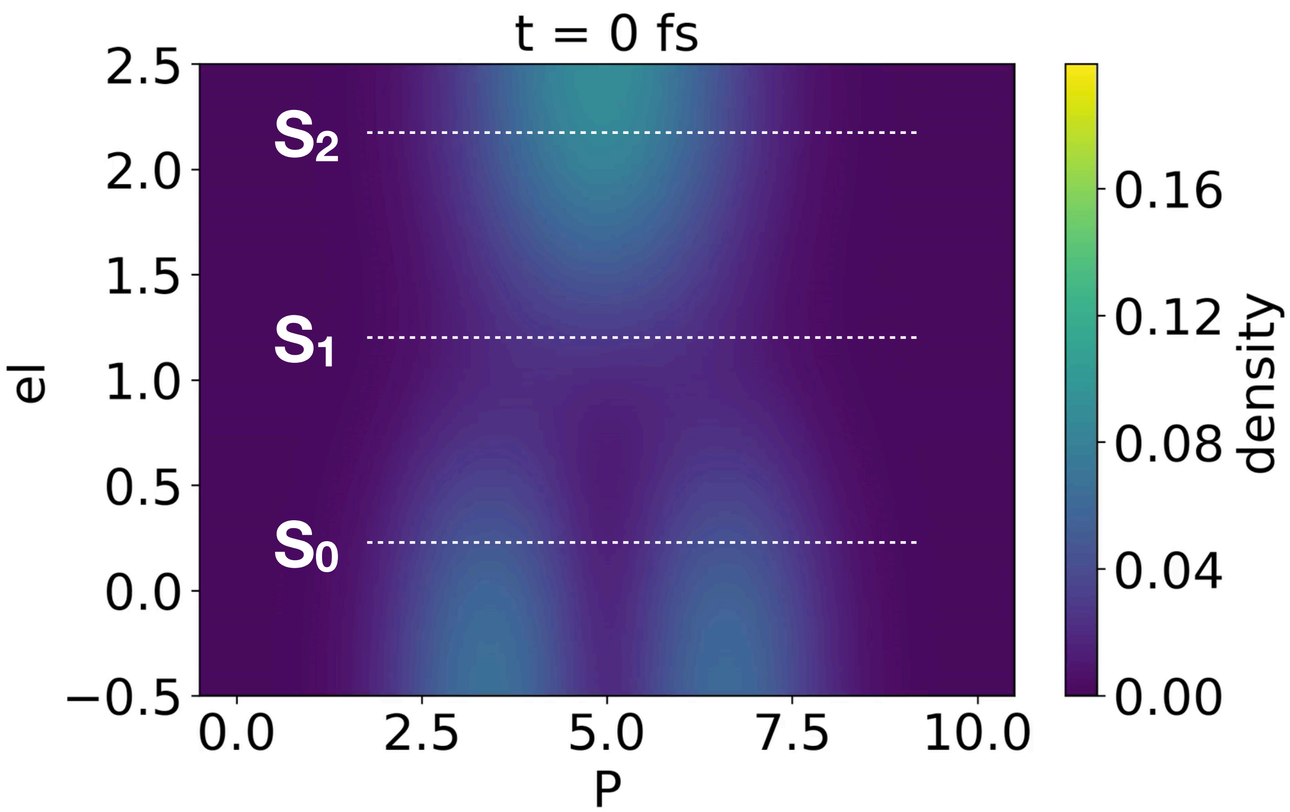




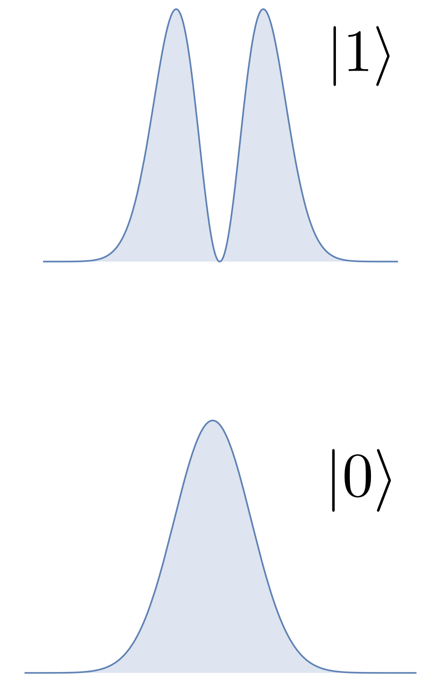
$$\hat{H}_{\text{pyr}} = \sum_i^{n_{\text{modes}}} \frac{\omega_i^2}{2}\left(-\frac{\partial^2 Q_i}{\partial t^2} + Q_i^2\right)\mathbf{1} + \begin{pmatrix} E_0 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_2 \end{pmatrix} + \sum_i^{n_{\text{tun}}} \begin{pmatrix} \kappa_0^i & 0 & 0 \\ 0 & \kappa_1^i & 0 \\ 0 & 0 & \kappa_2^i \end{pmatrix} Q_i$$

$$+ \sum_i^{n_{\text{coupl}}} \begin{pmatrix} 0 & \lambda_{01}^i & \lambda_{02}^i \\ \lambda_{10}^i & 0 & \lambda_{12}^i \\ \lambda_{20}^i & \lambda_{21}^i & 0 \end{pmatrix} Q_i$$

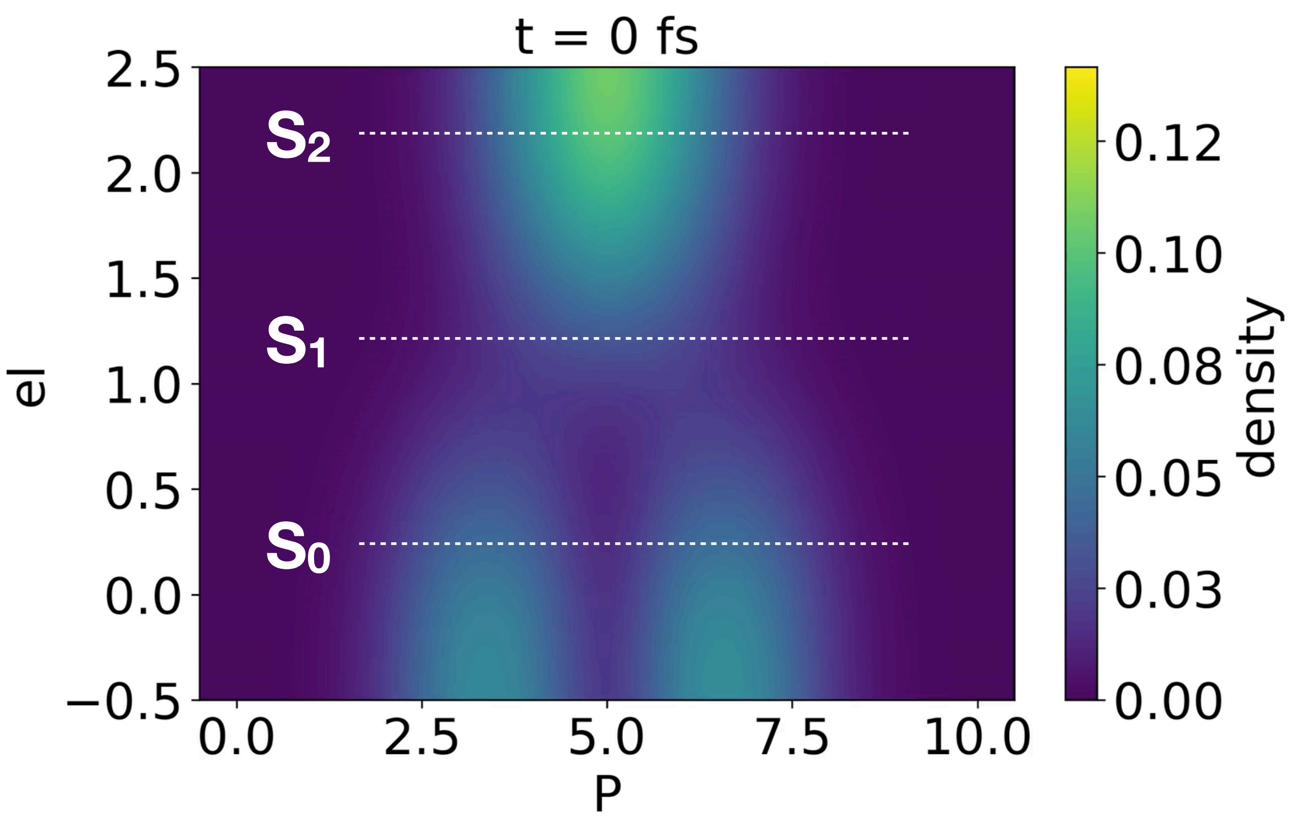
Internal conversion in polyatomic systems: pyrazine



reduced density
for LP



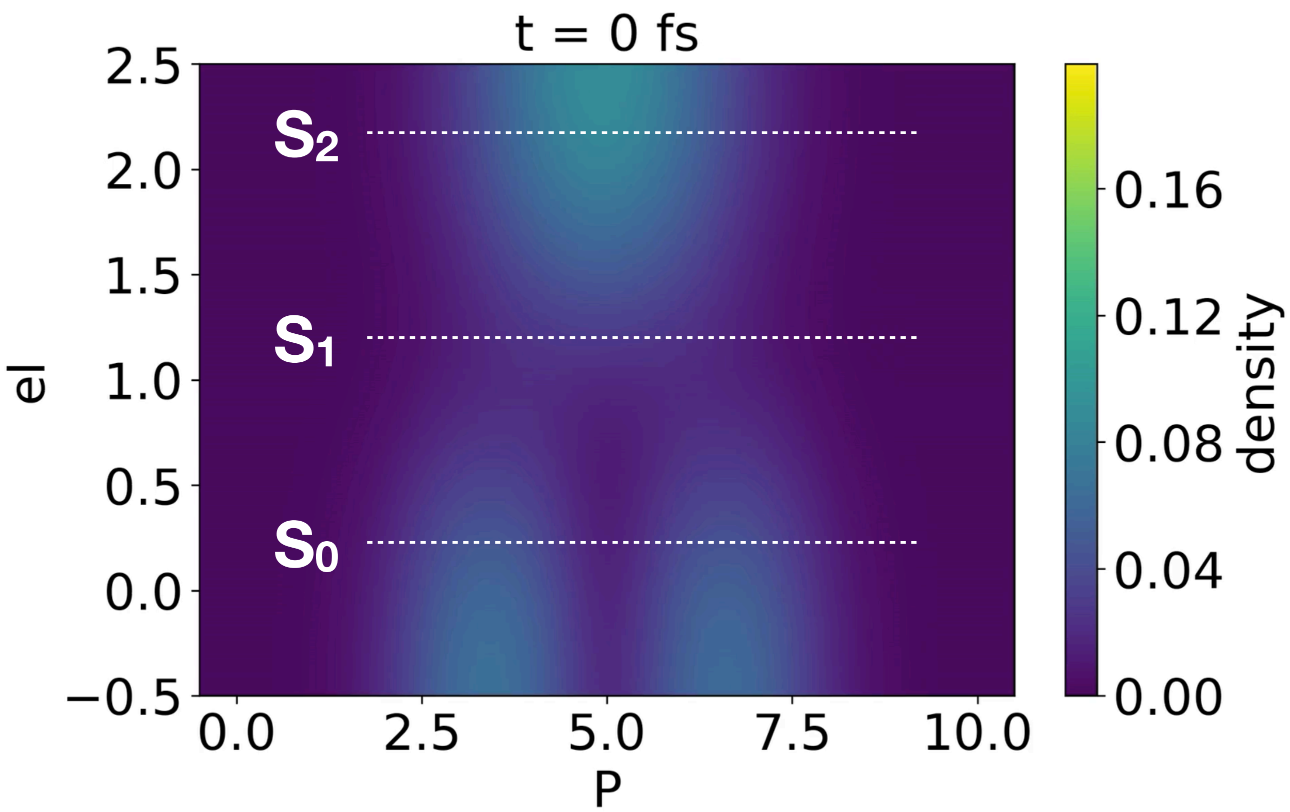
$$|P_\pm\rangle = \frac{1}{\sqrt{2}}\left(|1;S_0\rangle \mp |0;S_2\rangle\right)$$



reduced density
for UP

polariton mode (P) vs
electronic state (el)
N=1

Internal conversion in polyatomic systems: pyrazine



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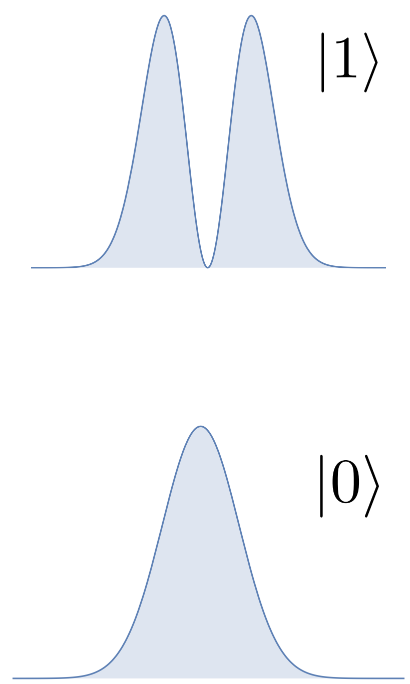

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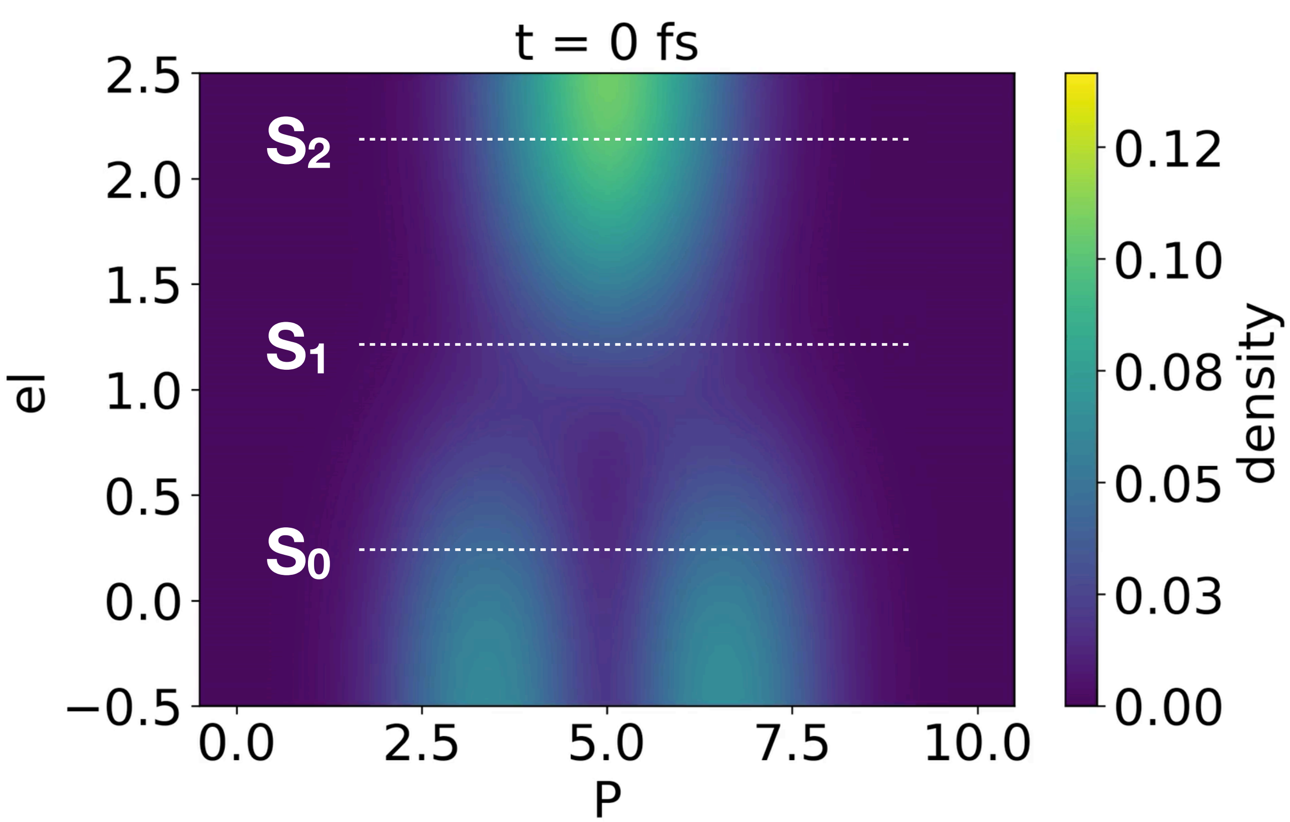

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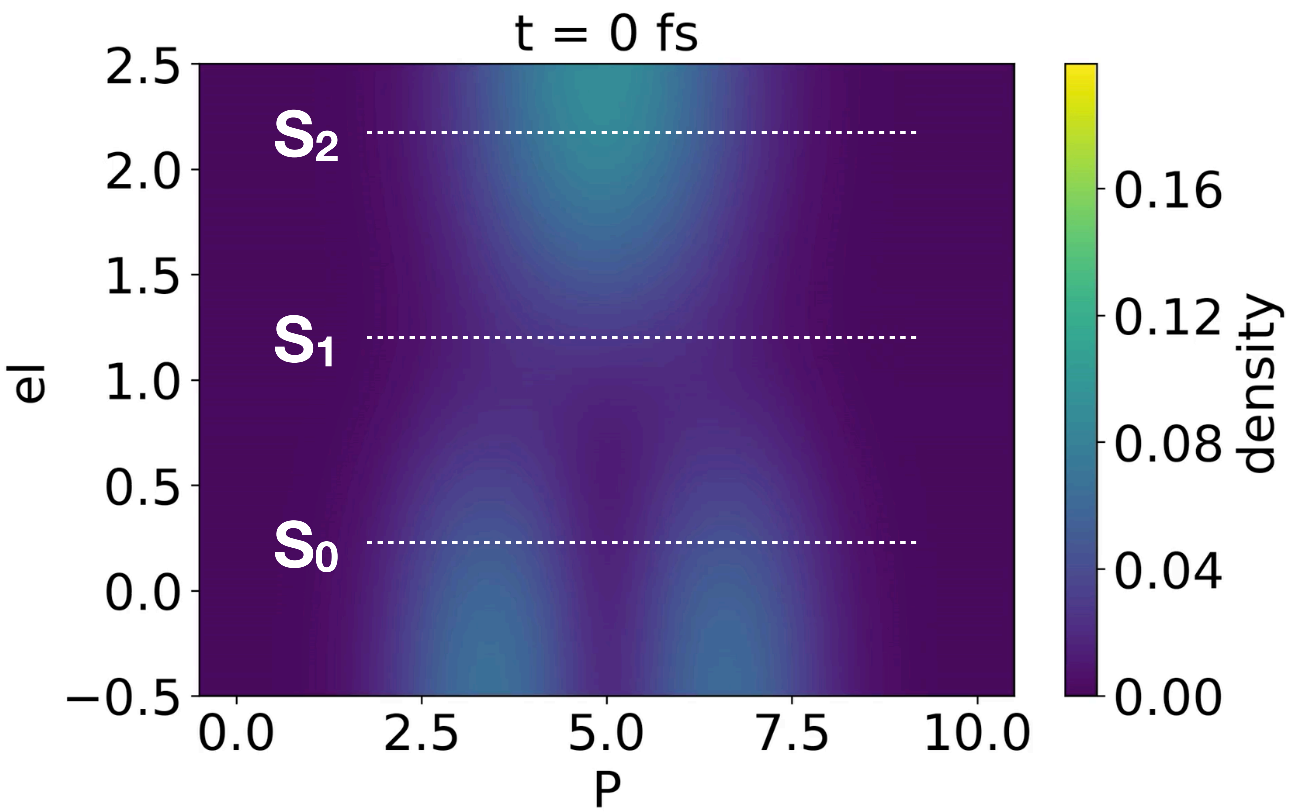
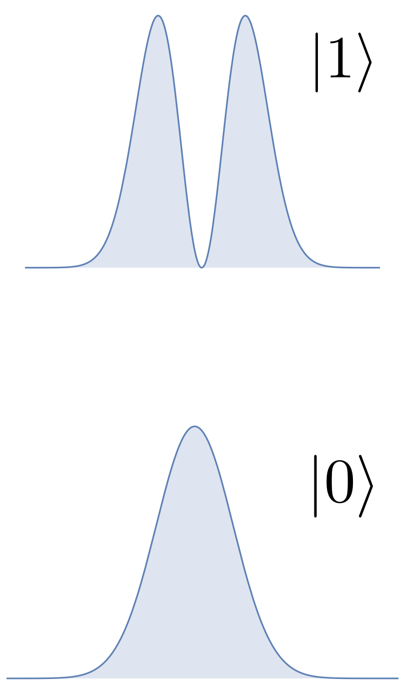


reduced density for LP



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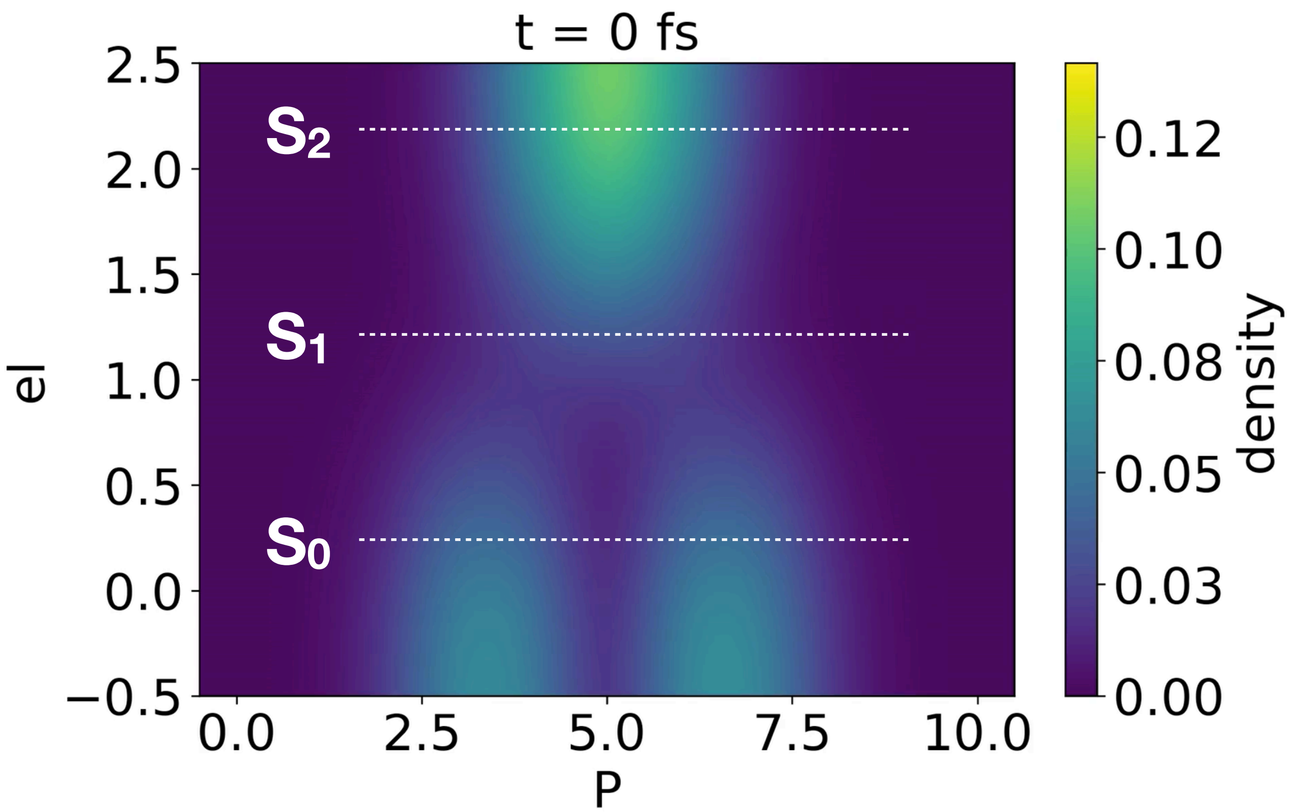
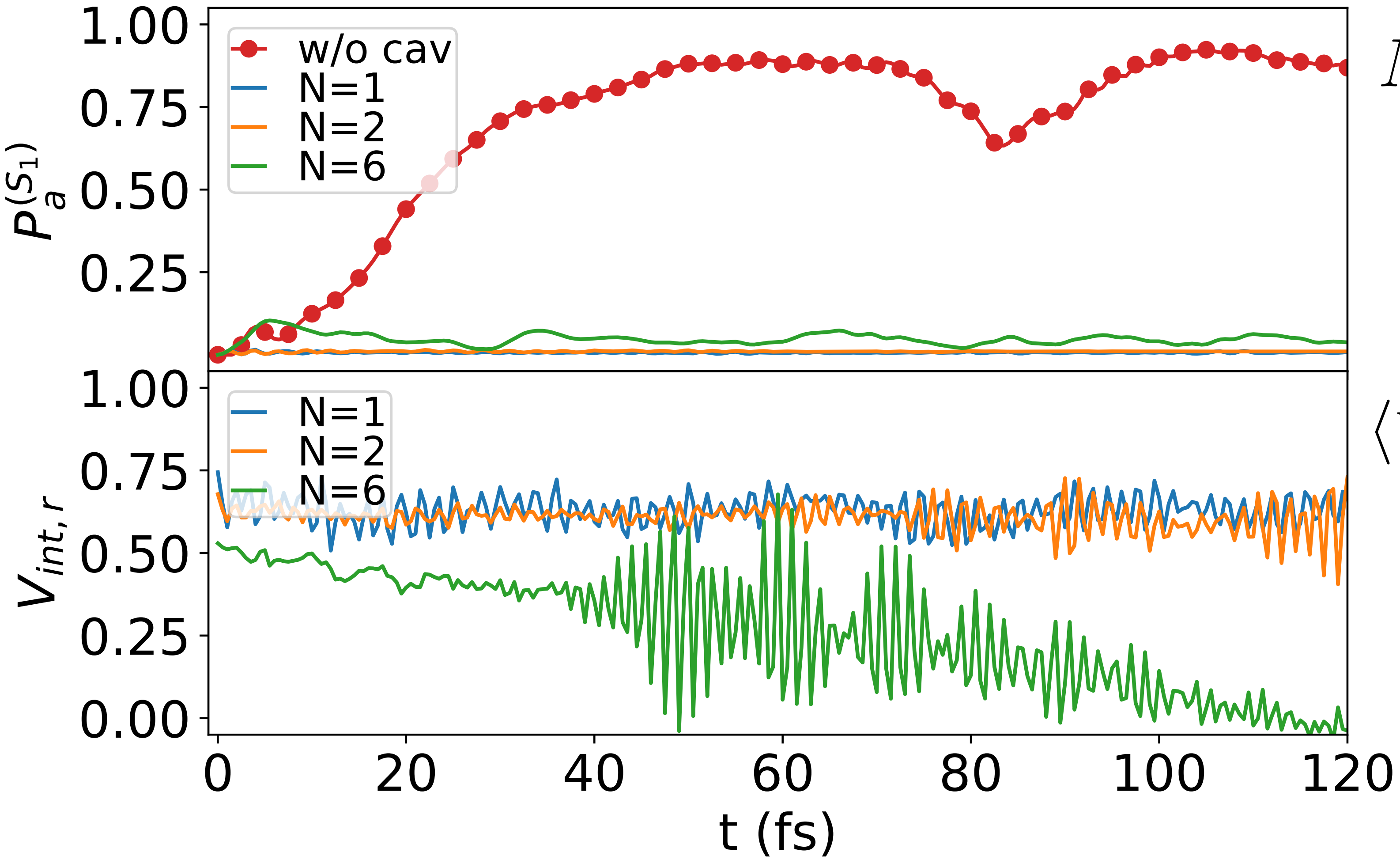


reduced density for UP

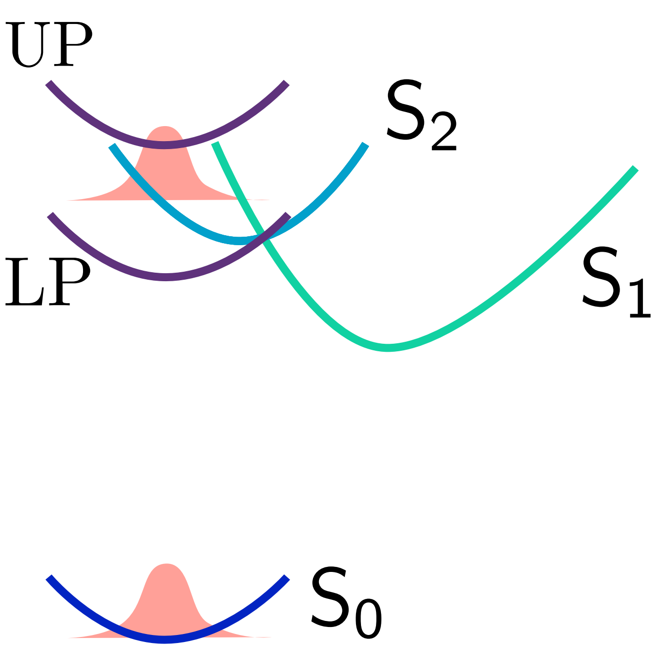
polariton mode (P) vs electronic state (el) N=1

$$|\Psi(0)\rangle = \phi_0(\mathbf{R})|\mathrm{UP}\rangle$$



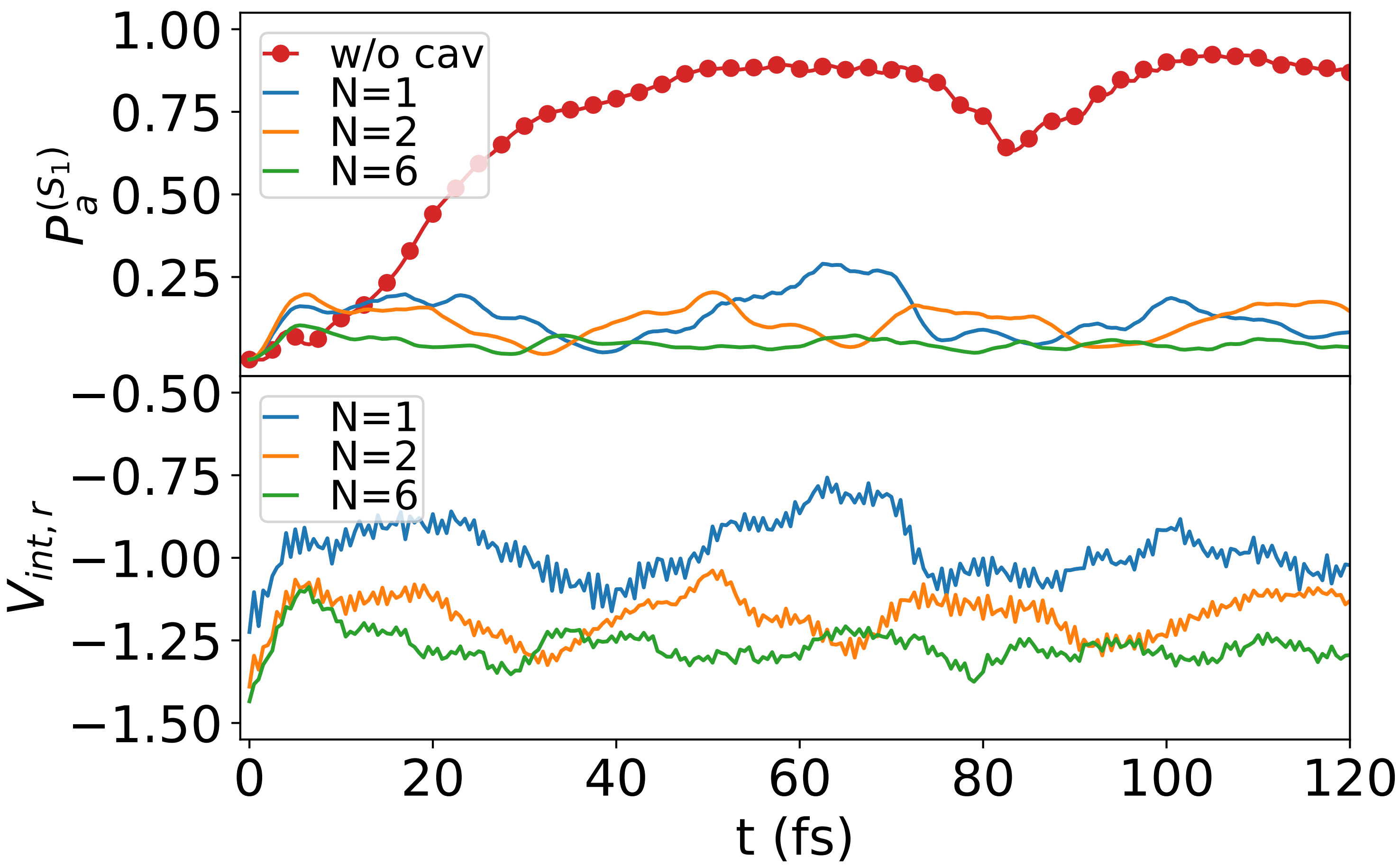
$$N \, |\langle S_1^{(\kappa)}|\Psi\rangle|^2$$

$$\langle\Psi|(\hat{a}^\dagger + \hat{a})\hat{D}|\Psi\rangle$$



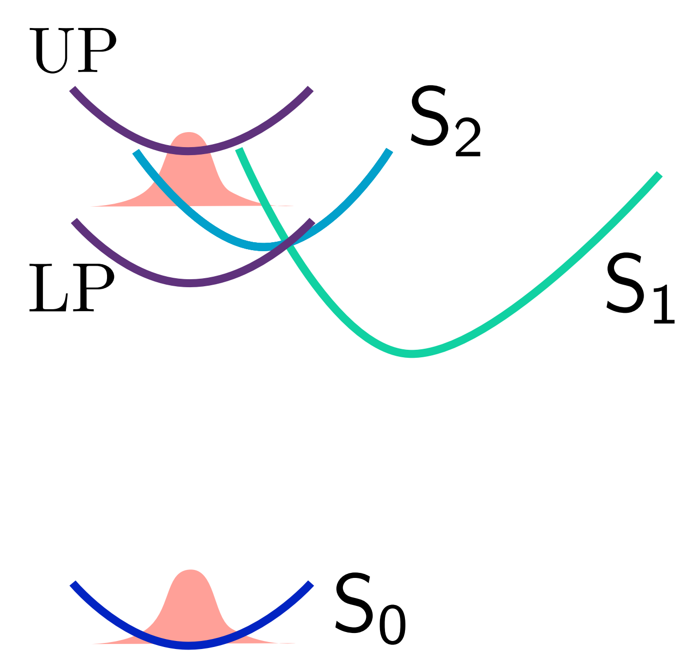
Suppression of radiative decay through large coupling

$$|\Psi(0)\rangle = \phi_0(\mathbf{R})|\mathrm{LP}\rangle$$



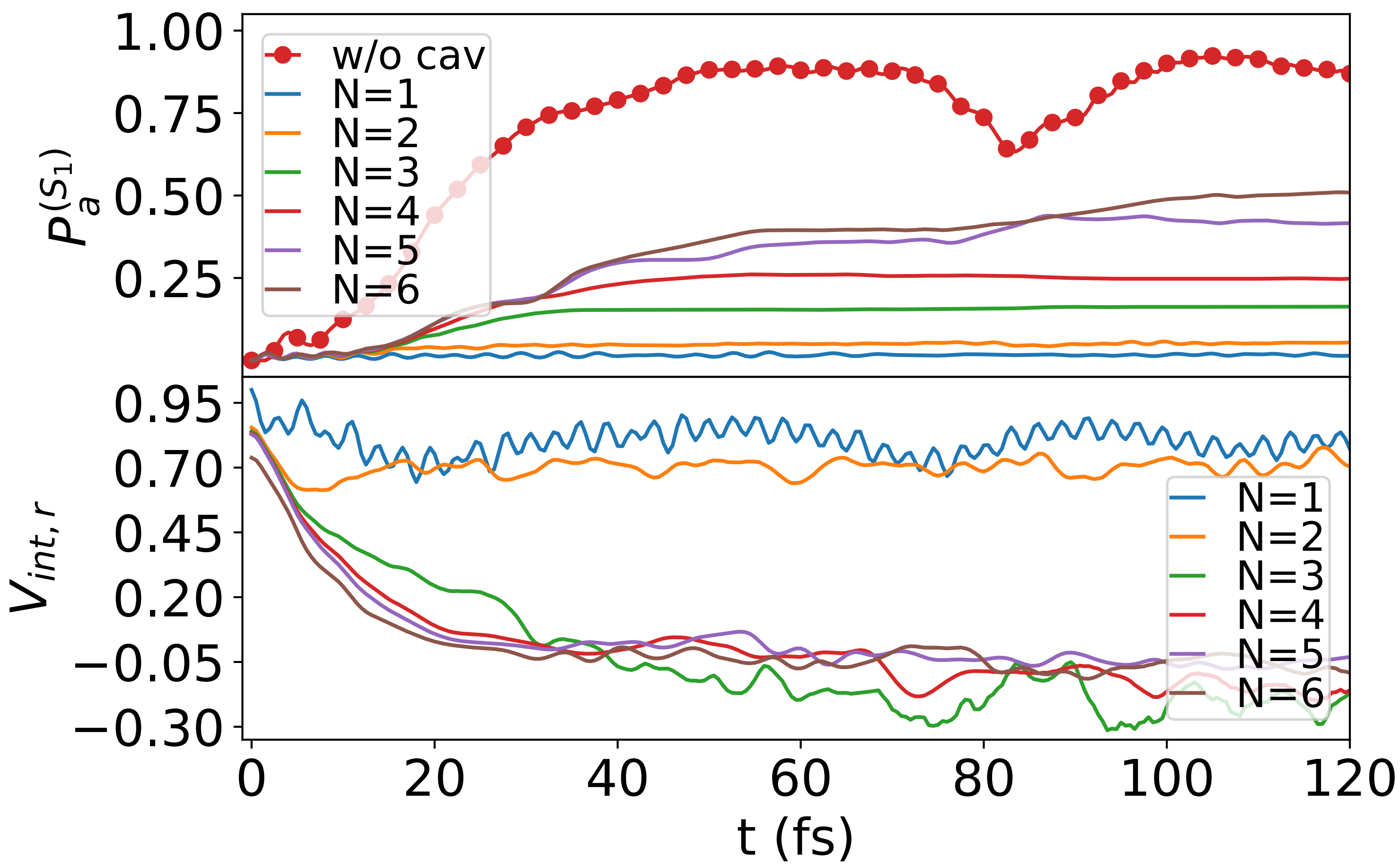
$$N\,|\langle S_1^{(\kappa)}|\Psi\rangle|^2$$

$$\langle\Psi|(\hat{a}^\dagger + \hat{a})\hat{D}|\Psi\rangle$$



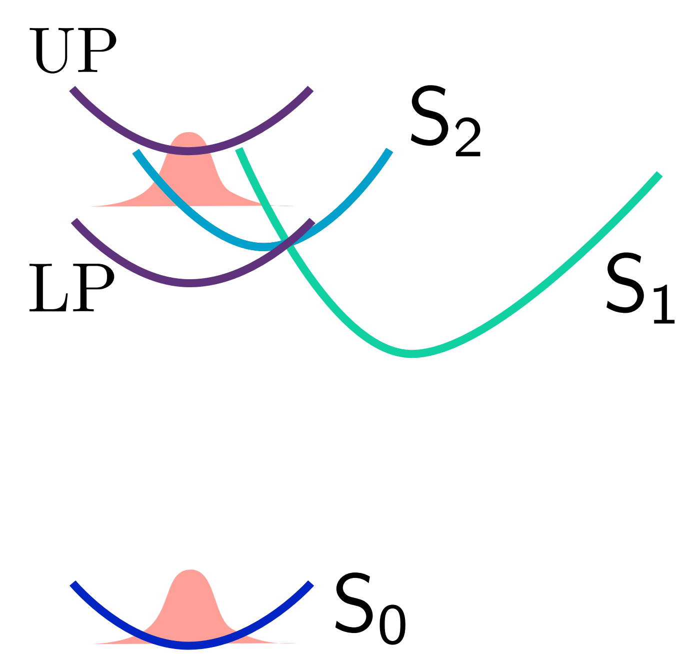
Suppression of radiative decay through small coupling

$$|\Psi(0)\rangle = \phi_0(\mathbf{R})|\mathrm{UP}\rangle$$



$$N\,|\langle S_1^{(\kappa)}|\Psi\rangle|^2$$

$$\langle\Psi|(\hat{a}^\dagger + \hat{a})\hat{D}|\Psi\rangle$$



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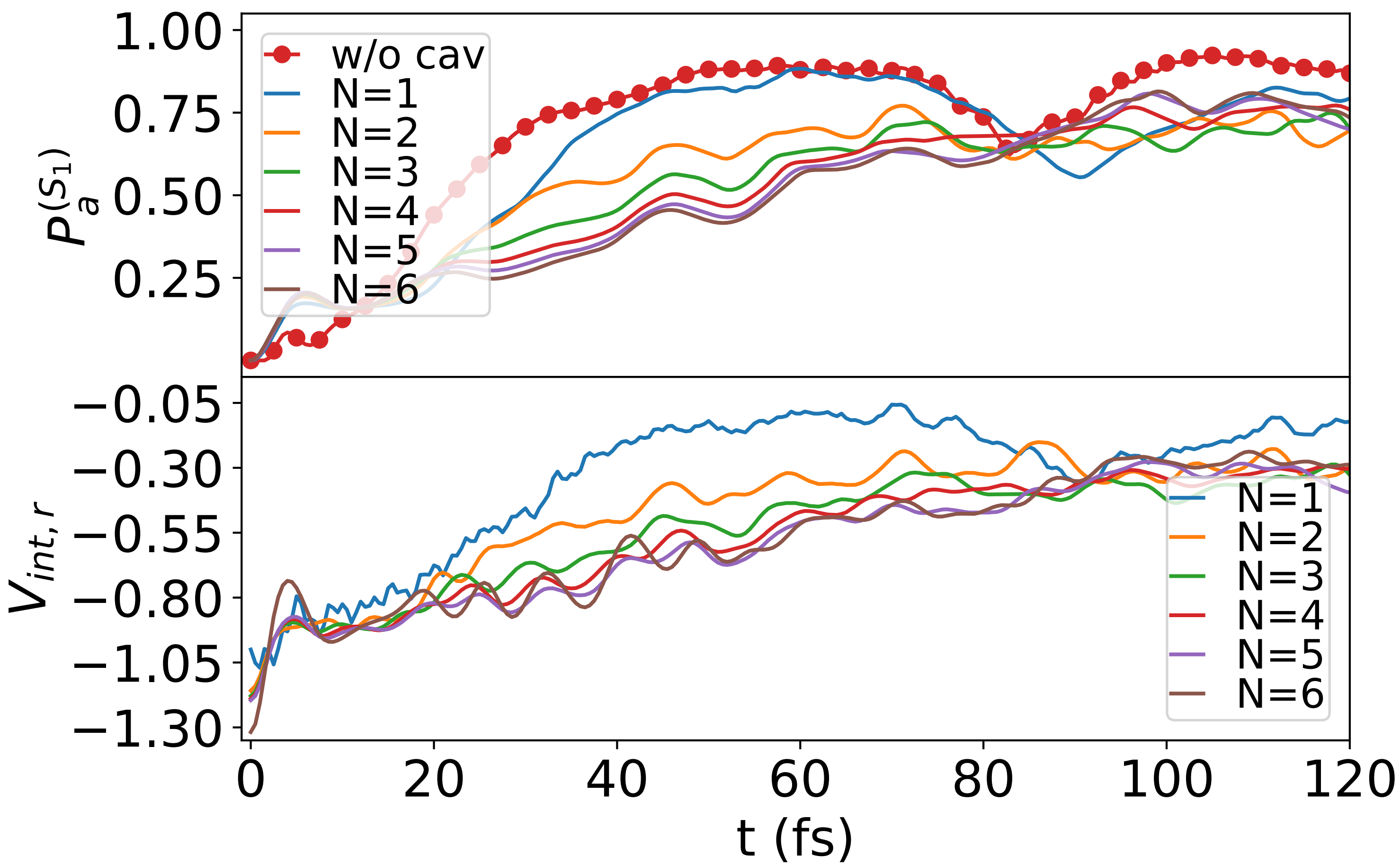
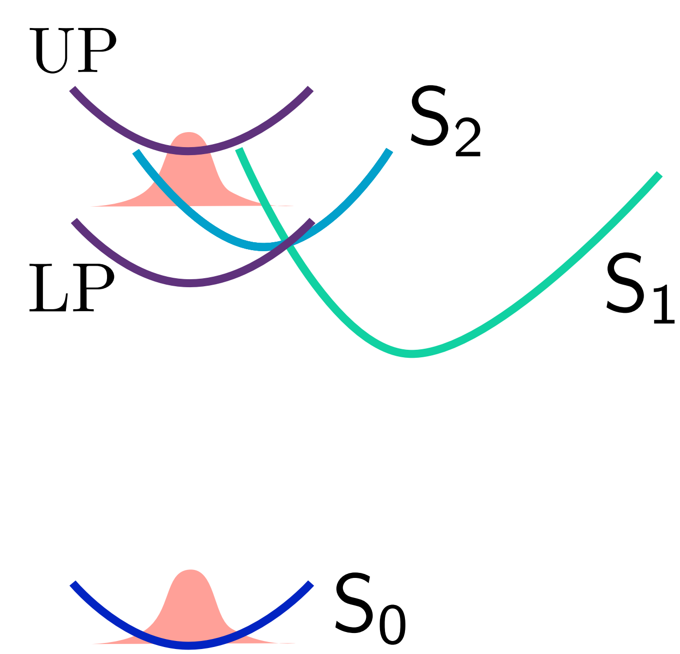
$$|\Psi(0)\rangle = \phi_0(\mathbf{R})|\mathrm{LP}\rangle$$



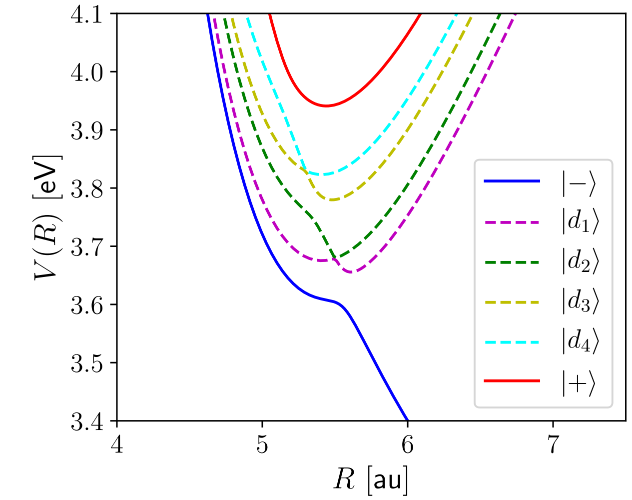
$$N\ |\langle S_1^{(\kappa)}|\Psi\rangle|^2$$

$$\langle\Psi|(\hat{a}^\dagger + \hat{a})\hat{D}|\Psi\rangle$$



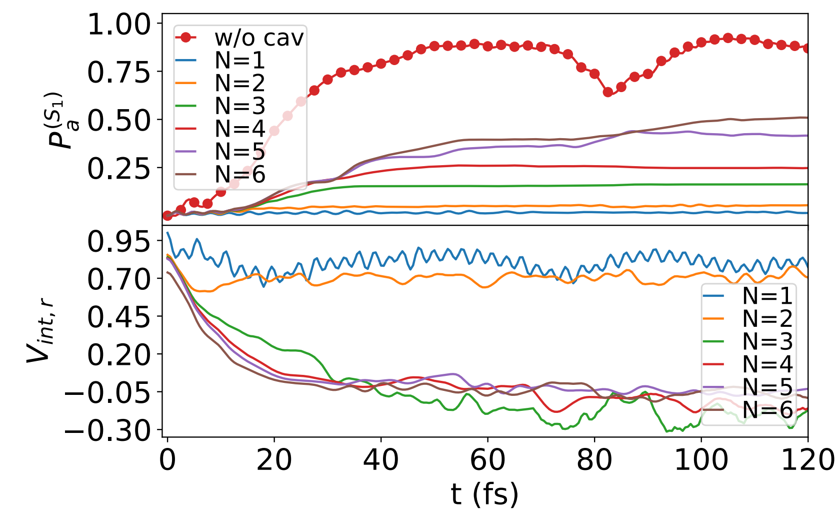
Summary and perspectives

- Upper and lower polaritonic states display different kinds of short-time dynamics. Dynamics started from the upper polaritonic state are delayed due to internal conversion through the dark states.

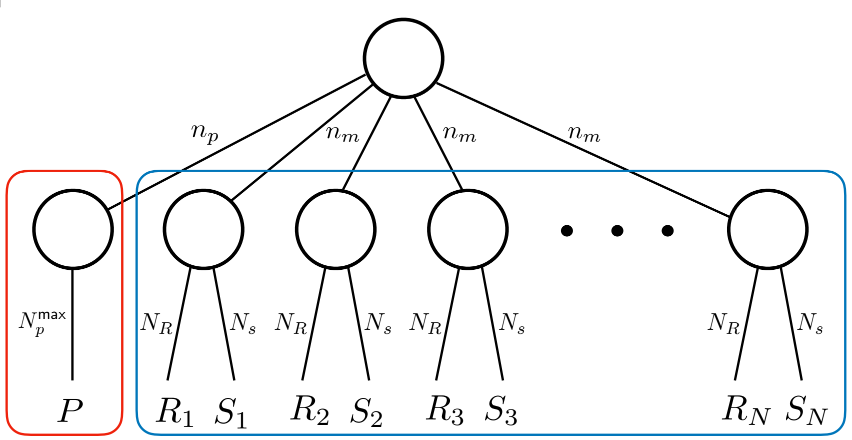


- Photonic buffer systems (vibrationally inactive) can be used to slow down reactive processes in the excited state.

- High dimensional systems get lost in the dark side.



- **MCTDH:** efficient tool to describe the dynamics of molecular ensembles coupled to quantized light.



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