HOW TO TREAT RADIATIONLESS TRANSITIONS WITH EXACT FACTORIZATION

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Orsay, December 03, 2020

Outline

- Introduction: get into the problem
- Exact factorization
- Inclusion of Spin-Orbit coupling
- Conclusions

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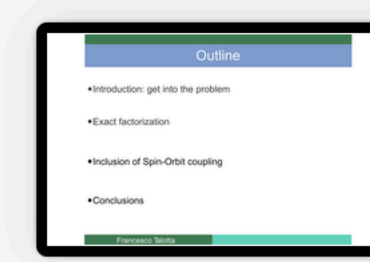
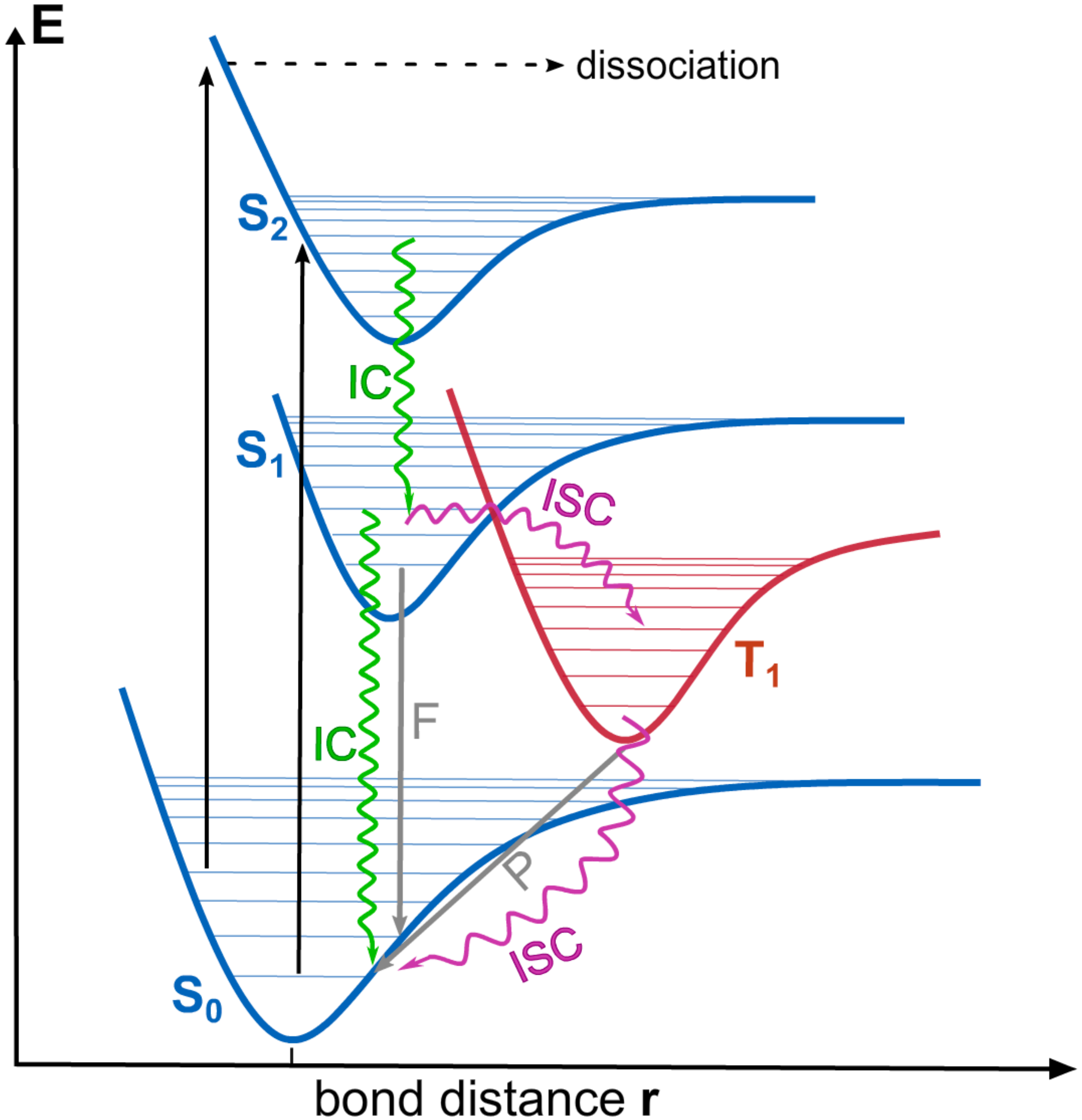


Jablonski diagram



Photochemistry

Excited Molecules

↓

Relaxation phenomena

Radiative transition

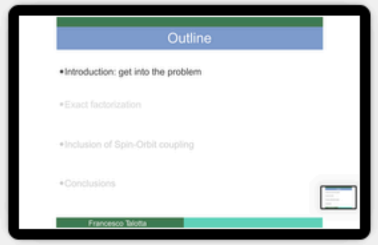
- **Fluorescence**
- **Phosphorescence**

→ **hν**

Non-radiative transition

- **Internal Conversion**
- **Intersystem Crossing**

Dissociation



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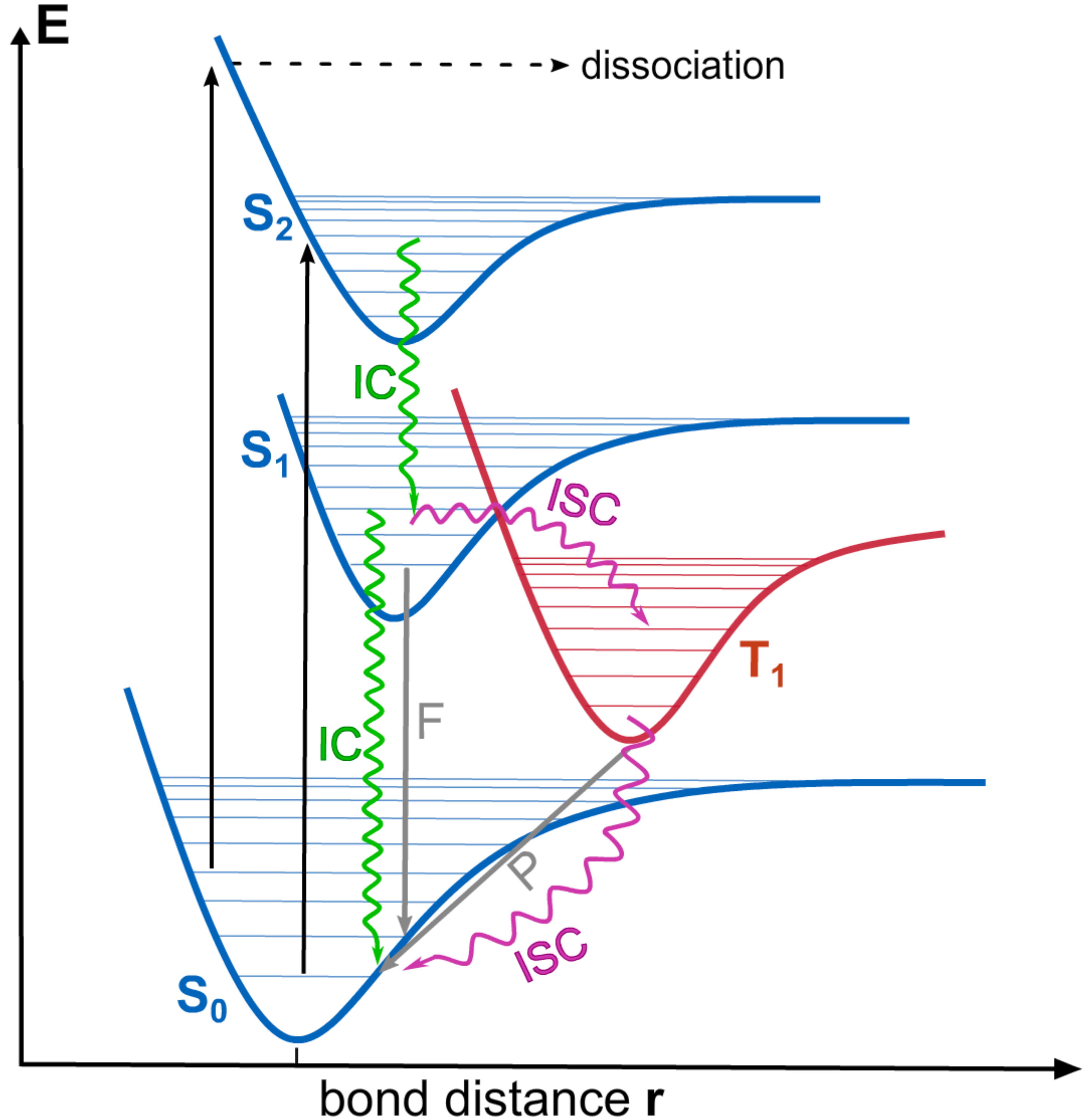

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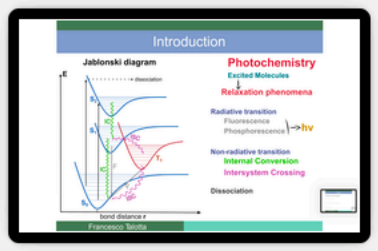

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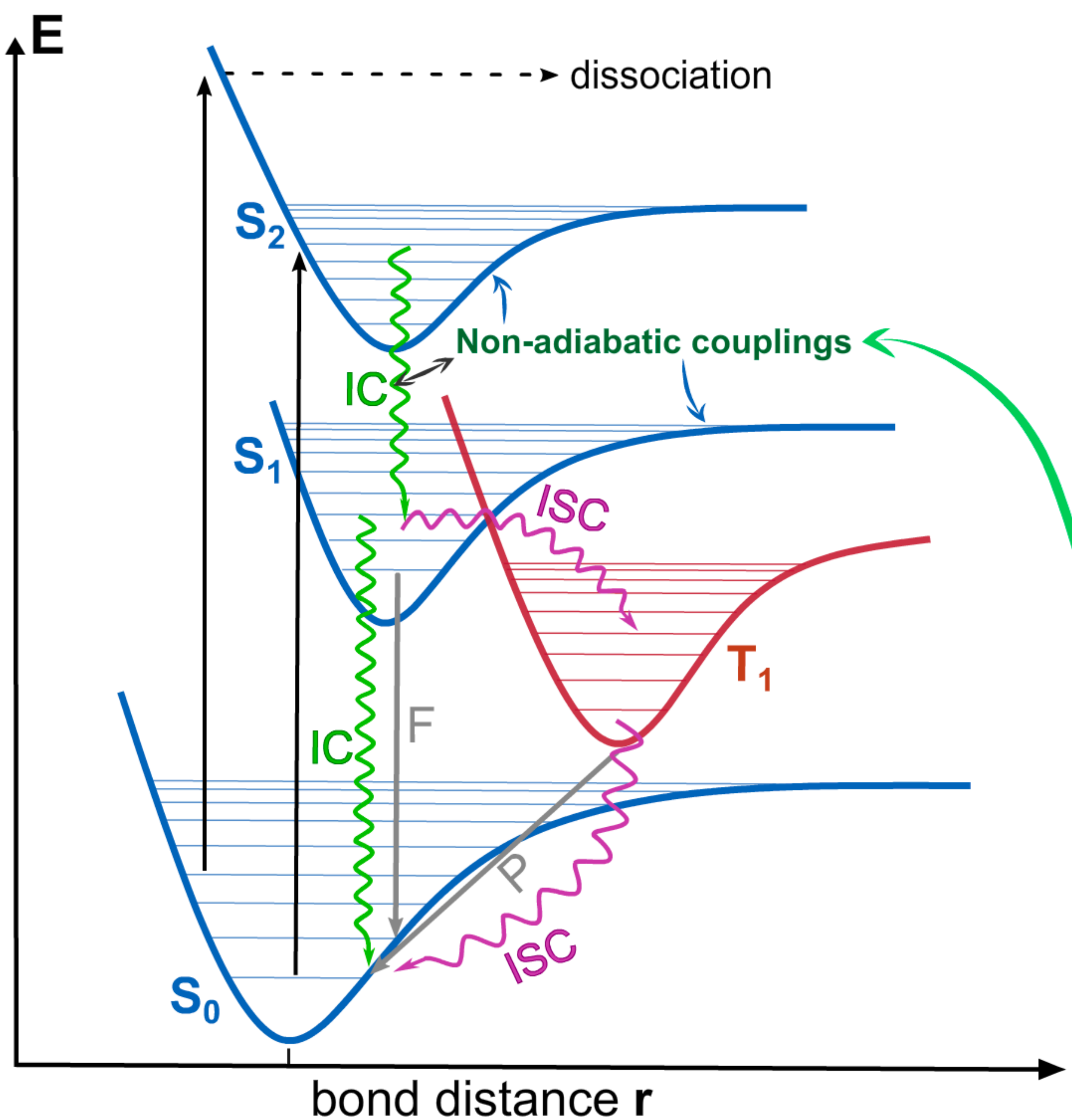

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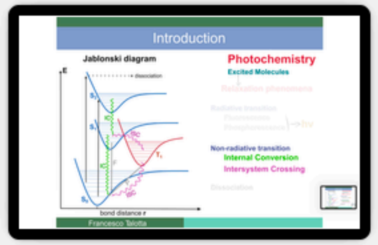

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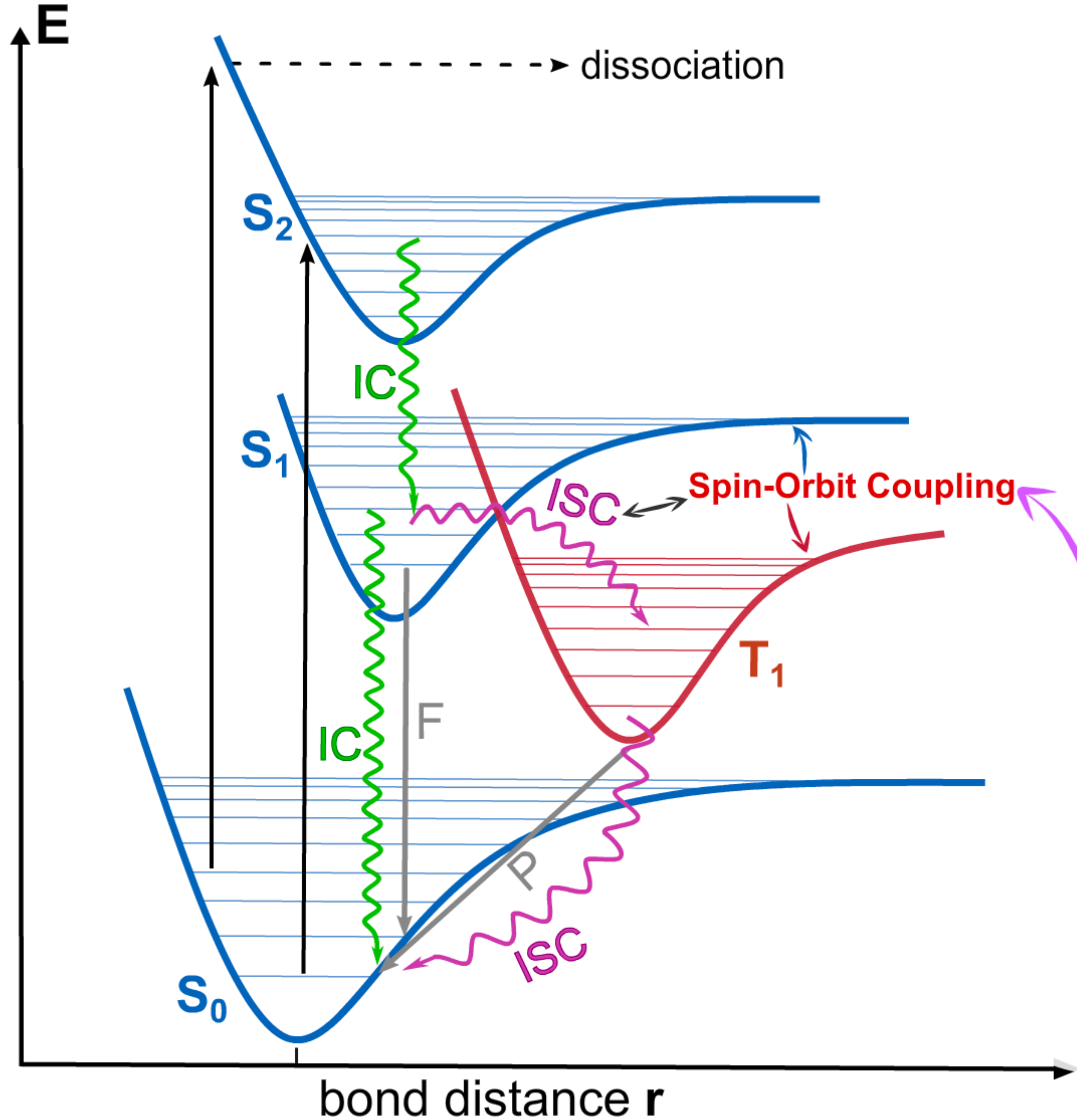

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→ hν

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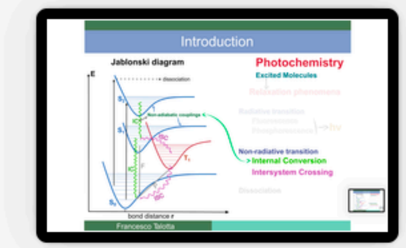
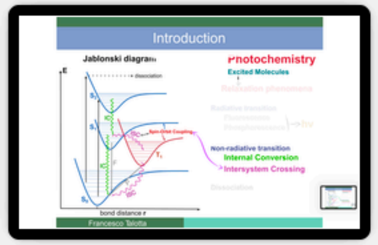


Introduction

Non-radiative transitions

- **Internal Conversion**
- **Intersystem Crossing**



Introduction

Non-radiative transitions

Internal Conversion

Intersystem Crossing

Biological Phenomena:

Introduction

Non-radiative transitions

Internal Conversion

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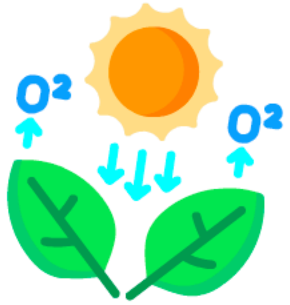
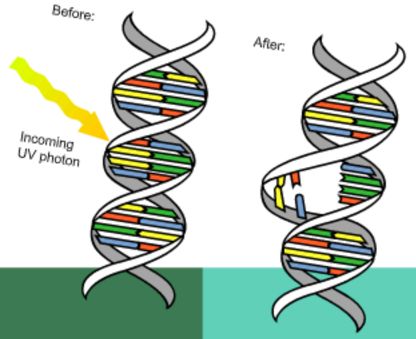
Biological Phenomena:

- Visual perception 
- Photosynthesis 

- Bioluminescence 
- DNA photodamage and repair 

Introduction

Non-radiative transitions

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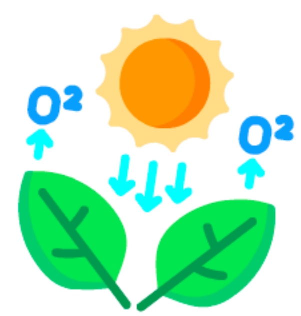
Intersystem Crossing

→ **Numerical Simulations**

Biological Phenomena:

- **Visual perception** 
- **Photosynthesis** 

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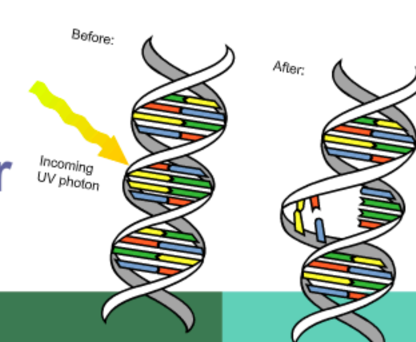
- **DNA photodamage and repair** 

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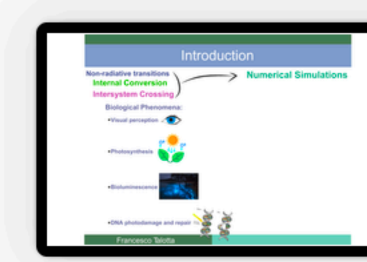

Exact Factorization

Time-Dependent Schroedinger Equation

$$\hat{H}(\boldsymbol{r},\boldsymbol{R})\Psi(\boldsymbol{r},\boldsymbol{R},t) = i\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{r},\boldsymbol{R},t)$$

Molecular Hamiltonian

$$\hat{H}(\boldsymbol{r},\boldsymbol{R}) = \sum_{K=1}^{N_n}\frac{-\hbar^2}{2M_K}\nabla_K^2 + \hat{T}_e(\boldsymbol{r}) + \hat{V}_{ee}(\boldsymbol{r}) + \hat{V}_{nn}(\boldsymbol{R}) + \hat{V}_{en}(\boldsymbol{r},\boldsymbol{R})$$

Exact Factorization of the total wavefunction

Ansatz $$\Psi(\boldsymbol{r},\boldsymbol{R},t) = \Xi(\boldsymbol{R},t)\Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$

Nuclear Wavefunction

Electronic Wavefunction

Agostini et al., *Eur. Phys. J. B*, **2018**, 91:139

Exact Factorization

Equations of motion

Two coupled equations, one for the electrons and one for the nuclei

$$\left[\hat{H}_{BO}(\boldsymbol{r},\boldsymbol{R}) + \hat{U}_{en}\left[\Phi_{\boldsymbol{R}},\Xi\right] - \epsilon(\boldsymbol{R},t)\right]\Phi_{\boldsymbol{R}}(\boldsymbol{r},t) = i\hbar\frac{\partial}{\partial t}\Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$

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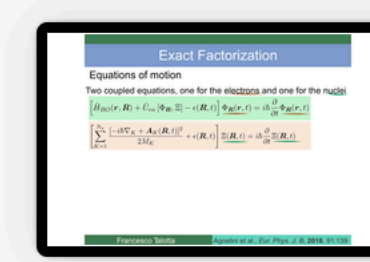

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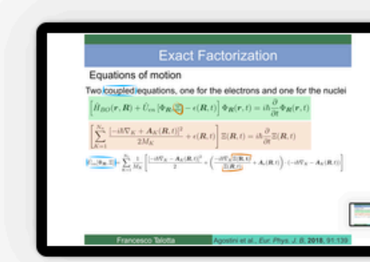
Time-dependent vector potential

Time-dependent potential energy surface

$$\boldsymbol{A}_K(\boldsymbol{R},t) = \langle\Phi_{\boldsymbol{R}}(t)| - i\hbar\nabla_K\,\Phi_{\boldsymbol{R}}(t)\rangle_{\boldsymbol{r}}$$

$$\epsilon(\boldsymbol{R},t) = \langle\Phi_{\boldsymbol{R}}(t)|\,\hat{H}_{BO} + \hat{U}_{en} - i\hbar\frac{\partial}{\partial t}\,|\Phi_{\boldsymbol{R}}(t)\rangle_{\boldsymbol{r}}$$



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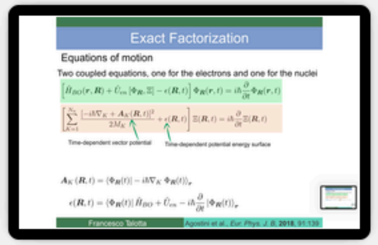
BO Framework

$$\boldsymbol{A}_K\left(\boldsymbol{R},t\right) = \langle\Phi_{\boldsymbol{R}}(t)|-i\hbar\nabla_K\,\Phi_{\boldsymbol{R}}(t)\rangle_{\boldsymbol{r}}$$

NACs

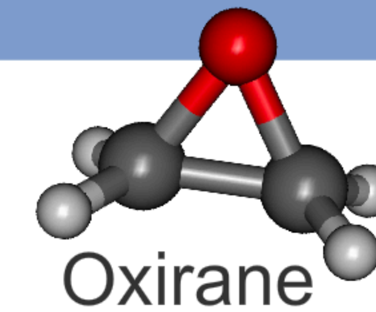
$$\epsilon(\boldsymbol{R},t) = \langle\Phi_{\boldsymbol{R}}(t)|\,\hat{H}_{BO} + \hat{U}_{en} - i\hbar\frac{\partial}{\partial t}\,|\Phi_{\boldsymbol{R}}(t)\rangle_{\boldsymbol{r}}$$

PES



TRAJECTORY-BASED EQUATIONS

Exact solution: impossible for big systems



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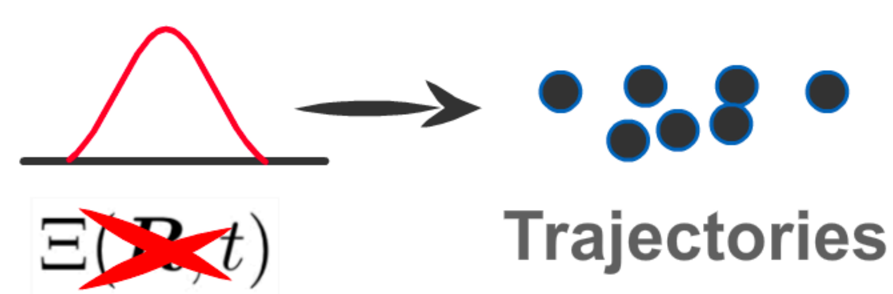
Find a classical solution for the Nuclear equation

$$\left[\sum_{K=1}^{N_n}\frac{\left[-i\hbar\nabla_K + \boldsymbol{A}_K(\boldsymbol{R},t)\right]^2}{2M_K} + \epsilon(\boldsymbol{R},t)\right]\Xi(\boldsymbol{R},t) = i\hbar\frac{\partial}{\partial t}\Xi(\boldsymbol{R},t)$$



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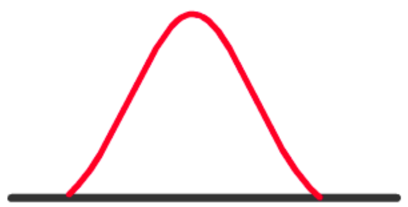
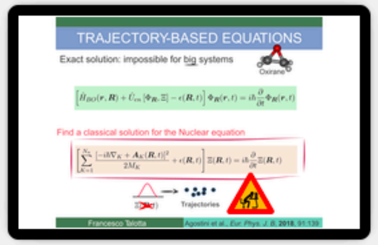


$\Xi(\boldsymbol{R},t)$

$$\Xi(\boldsymbol{R},t) = |\Xi(\boldsymbol{R},t)|e^{(i/\hbar)S(\boldsymbol{R},t)}$$

modulus

phase



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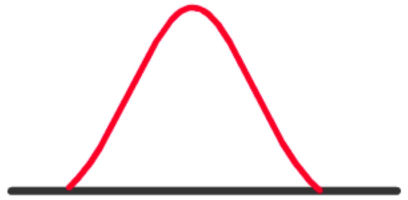
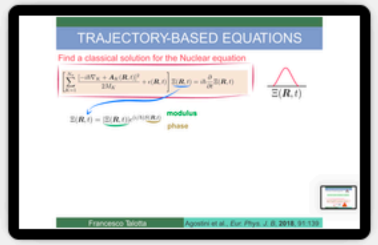


$$\Xi(\boldsymbol{R},t) = |\Xi(\boldsymbol{R},t)|e^{(i/\hbar)S(\boldsymbol{R},t)}$$

$$\left.\frac{d}{dt}\boldsymbol{P}_K(t)\right|_{\boldsymbol{R}^{(I)}(t)} = \left.\frac{d}{dt}\boldsymbol{A}_K(\boldsymbol{R},t)\right|_{\boldsymbol{R}^{(I)}(t)}$$

$$\left.\frac{d}{dt}\boldsymbol{R}_K(t)\right|_{\boldsymbol{R}^{(I)}(t)} = \left.\frac{\boldsymbol{P}_K(t)}{M_K}\right|_{\boldsymbol{R}^{(I)}(t)}$$



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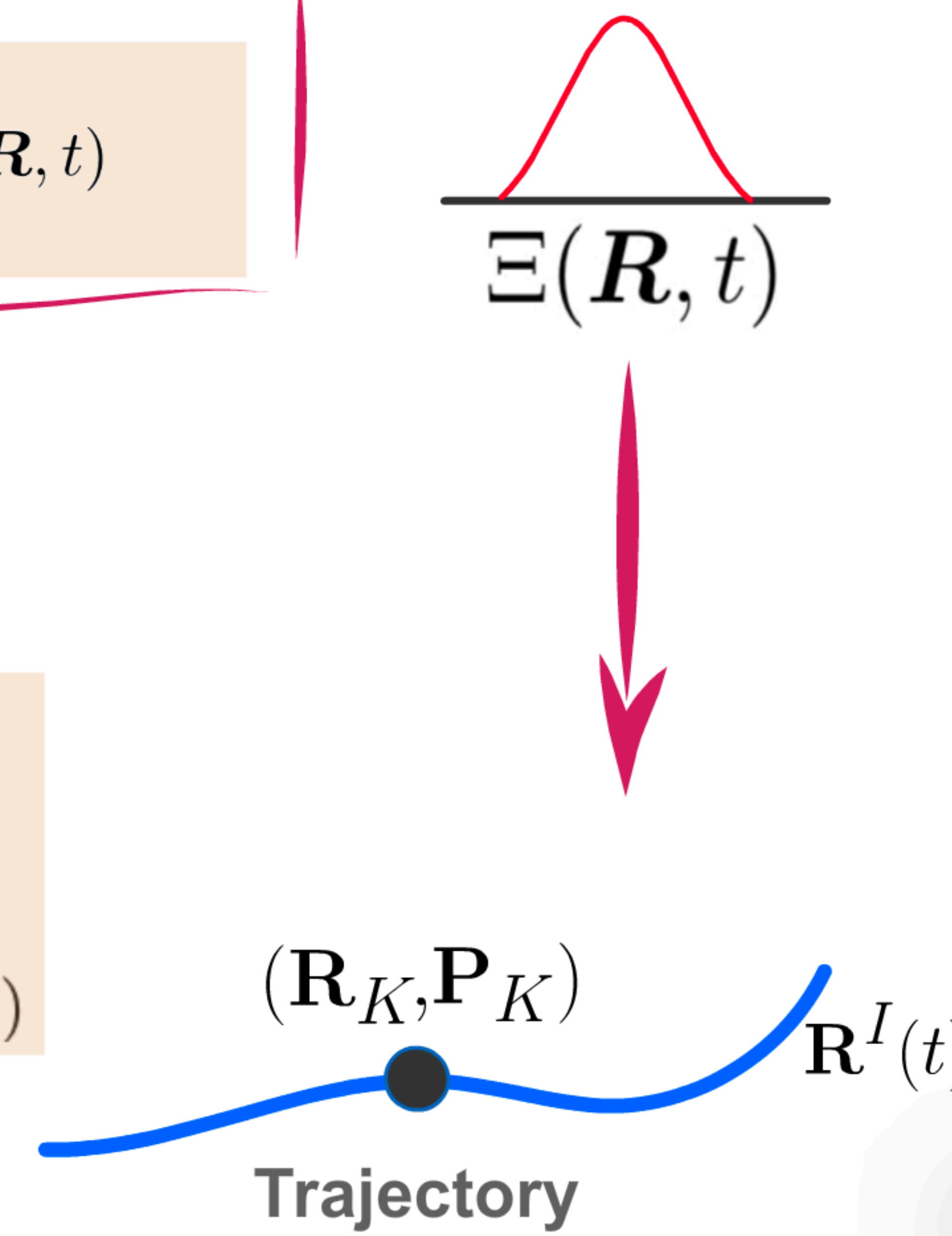

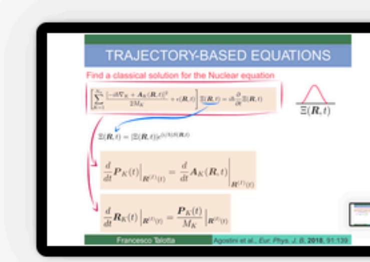

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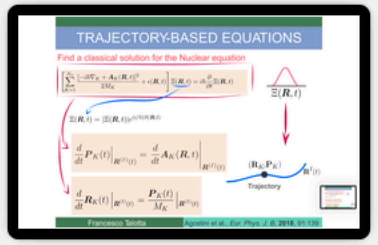

Inclusion of the Spin-Orbit Coupling

$$\hat{H}_{BO}(\boldsymbol{r},\boldsymbol{R}) \longrightarrow \hat{H}_{BO}(\boldsymbol{r},\boldsymbol{R}) + \hat{H}_{SO}(\boldsymbol{r},\boldsymbol{R},\boldsymbol{\sigma})$$

Hamiltonian

$$\left[\hat{H}_{BO}(\boldsymbol{r},\boldsymbol{R}) + \hat{U}_{en}[\Phi_{\boldsymbol{R}},\Xi] - \epsilon(\boldsymbol{R},t)\right]\Phi_{\boldsymbol{R}}(\boldsymbol{r},t) = i\hbar\frac{\partial}{\partial t}\Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$

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Talotta et al., *J. Comput. Theor. Chem.*, 16 (8), 4833

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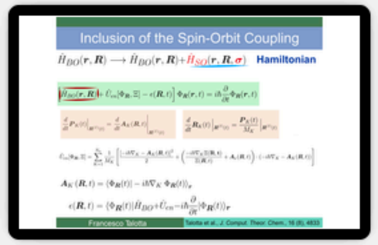

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Hamiltonian

$$\left[\hat{H}_{BO}(\boldsymbol{r}, \boldsymbol{R}) + \hat{H}_{SO}(\boldsymbol{r}, \boldsymbol{R}, \boldsymbol{\sigma}) + \hat{U}_{en}[\Phi_{\boldsymbol{R}}, \Xi] - \epsilon(\boldsymbol{R}, t)\right] \Phi_{\boldsymbol{R}}(\boldsymbol{r}, t) = i\hbar \frac{\partial}{\partial t} \Phi_{\boldsymbol{R}}(\boldsymbol{r}, t)$$

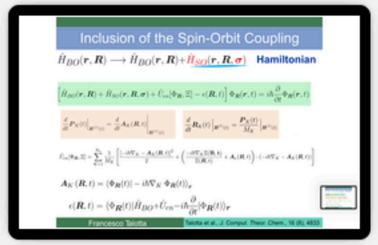
$$\frac{d}{dt} \boldsymbol{P}_K(t)\Big|_{\boldsymbol{R}^{(I)}(t)} = \frac{d}{dt} \boldsymbol{A}_K(\boldsymbol{R}, t)\Big|_{\boldsymbol{R}^{(I)}(t)}$$

$$\frac{d}{dt} \boldsymbol{R}_K(t)\Big|_{\boldsymbol{R}^{(I)}(t)} = \frac{\boldsymbol{P}_K(t)}{M_K}\Big|_{\boldsymbol{R}^{(I)}(t)}$$

$$\hat{U}_{en}[\Phi_{\boldsymbol{R}}, \Xi] = \sum_{K=1}^{N_n} \frac{1}{M_K} \left[\frac{[-i\hbar\nabla_K - \boldsymbol{A}_K(\boldsymbol{R}, t)]^2}{2} + \left(\frac{-i\hbar\nabla_K \Xi(\mathbf{R}, \mathbf{t})}{\Xi(\boldsymbol{R}, t)} + \boldsymbol{A}_\nu(\boldsymbol{R}, t) \right) \cdot (-i\hbar\nabla_K - \boldsymbol{A}_K(\boldsymbol{R}, t)) \right]$$

$$\boldsymbol{A}_K(\boldsymbol{R}, t) = \langle \Phi_{\boldsymbol{R}}(t) | -i\hbar\nabla_K \, \Phi_{\boldsymbol{R}}(t) \rangle_{\boldsymbol{r}}$$

$$\epsilon(\boldsymbol{R}, t) = \langle \Phi_{\boldsymbol{R}}(t) | \hat{H}_{BO} + \hat{H}_{SO} + \hat{U}_{en} - i\hbar \frac{\partial}{\partial t} | \Phi_{\boldsymbol{R}}(t) \rangle_{\boldsymbol{r}}$$



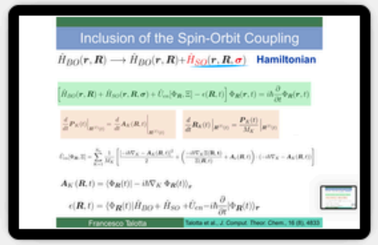
Talotta et al., *J. Comput. Theor. Chem.*, 16 (8), 4833

Inclusion of the Spin-Orbit Coupling

$$\Phi_{\boldsymbol{R}}(\boldsymbol{r}, t) \longrightarrow \Phi_{\boldsymbol{R}}(\boldsymbol{r}, \boldsymbol{\sigma}, t)$$ **Electronic Wavefunction**

Electronic wavefunction expanded in some **spin basis...**

$$\Phi_{\boldsymbol{R}}(\boldsymbol{r}, \boldsymbol{\sigma}, t) = \sum_J C_J(\boldsymbol{R}, t)\varphi_{\boldsymbol{R}}^{(J)}(\boldsymbol{r}, \boldsymbol{\sigma})$$



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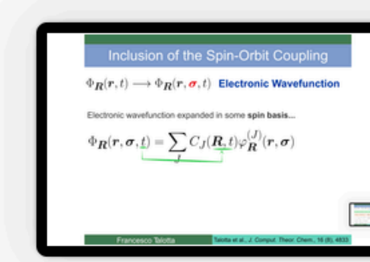

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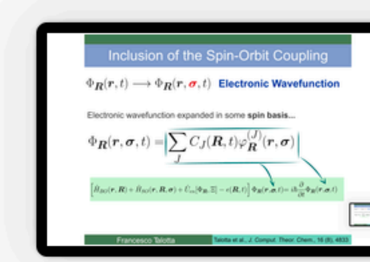
$$\left[\hat{H}_{BO}(\boldsymbol{r}, \boldsymbol{R}) + \hat{H}_{SO}(\boldsymbol{r}, \boldsymbol{R}, \boldsymbol{\sigma}) + \hat{U}_{en}[\Phi_{\boldsymbol{R}}, \Xi] - \epsilon(\boldsymbol{R}, t)\right] \Phi_{\boldsymbol{R}}(\boldsymbol{r}, \boldsymbol{\sigma}, t) = i\hbar\frac{\partial}{\partial t}\Phi_{\boldsymbol{R}}(\boldsymbol{r}, \boldsymbol{\sigma}, t)$$

Get the equation of motion $\frac{d}{dt}C_J(\boldsymbol{R}, t)$



Inclusion of the Spin-Orbit Coupling

$$\Phi_{\boldsymbol{R}}(\boldsymbol{r},\boldsymbol{\sigma},t) = \sum_J C_J(\boldsymbol{R},t)\varphi^{(J)}_{\boldsymbol{R}}(\boldsymbol{r},\boldsymbol{\sigma})$$

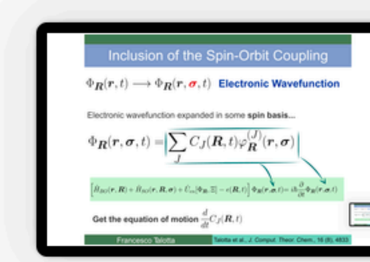
Two ways to tackle the problem:

Spin-Diabatic

- Eigenstates of $\hat{H}_{BO}(\boldsymbol{r},\boldsymbol{R})$
- Eigenstates of $\hat{S}^2$ and $\hat{S}_z$
- **Electronic adiabatic** states **S_0,S_1,S_2,T_1**
- Electronic structure programs provide energies, NACs, SOCs in this representation
- Need to **test** the approximations of the Exact Factorization equations

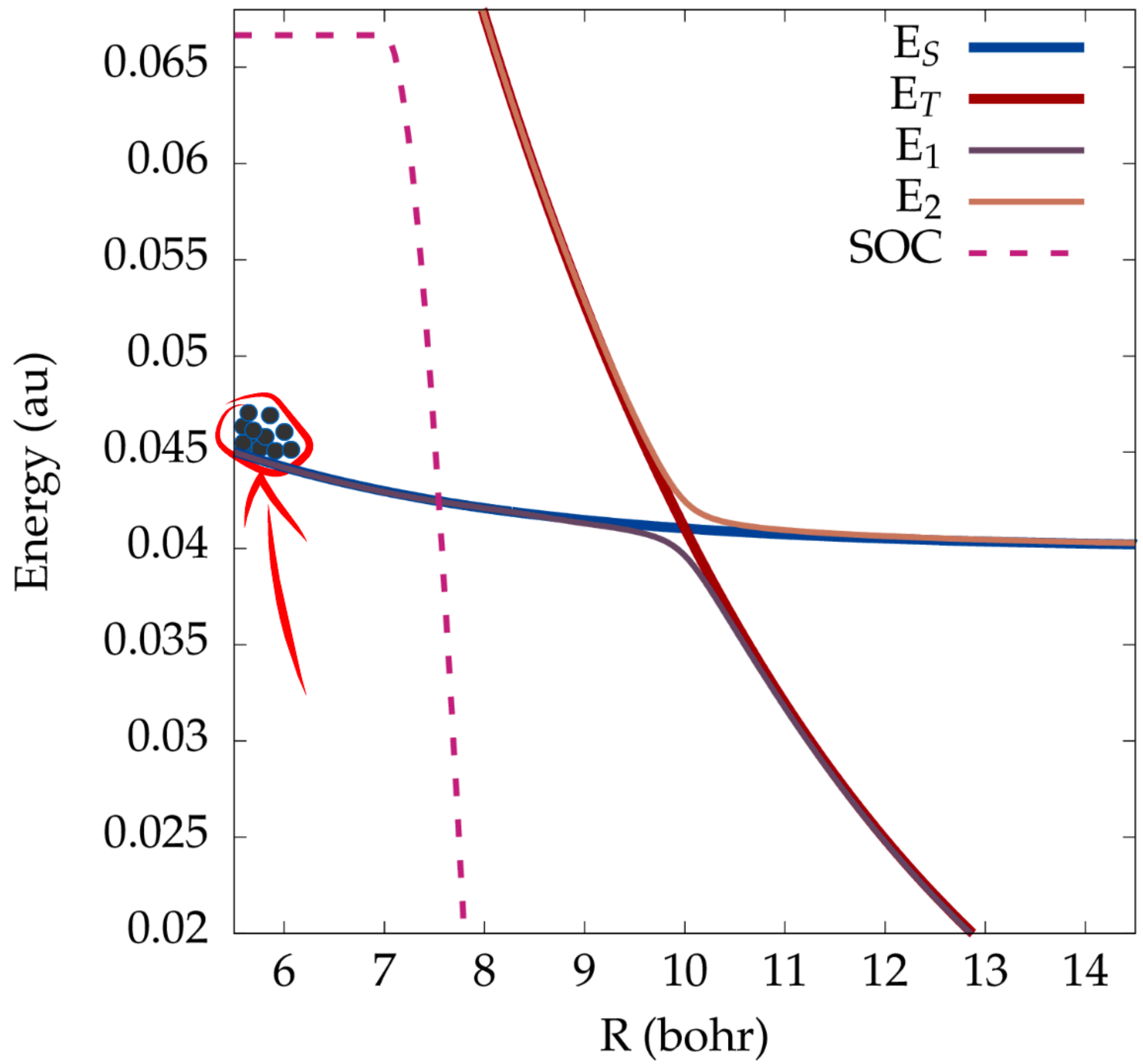
Spin-Adiabatic

- Eigenstates of the full $\hat{H}_{BO}+\hat{H}_{SO}$
- Spin properties depend on $\boldsymbol{R}$
- **Electronic** states have a mixed spin character
- Approximations for the Exact Factorization equations were written in this basis



Inclusion of the Spin-Orbit Coupling

Granucci-Persico-Spighi Model: 1 Singlet, 1 Triplet



Talotta et al., *Phys. Rev. Lett*, 124(33001), **2020**

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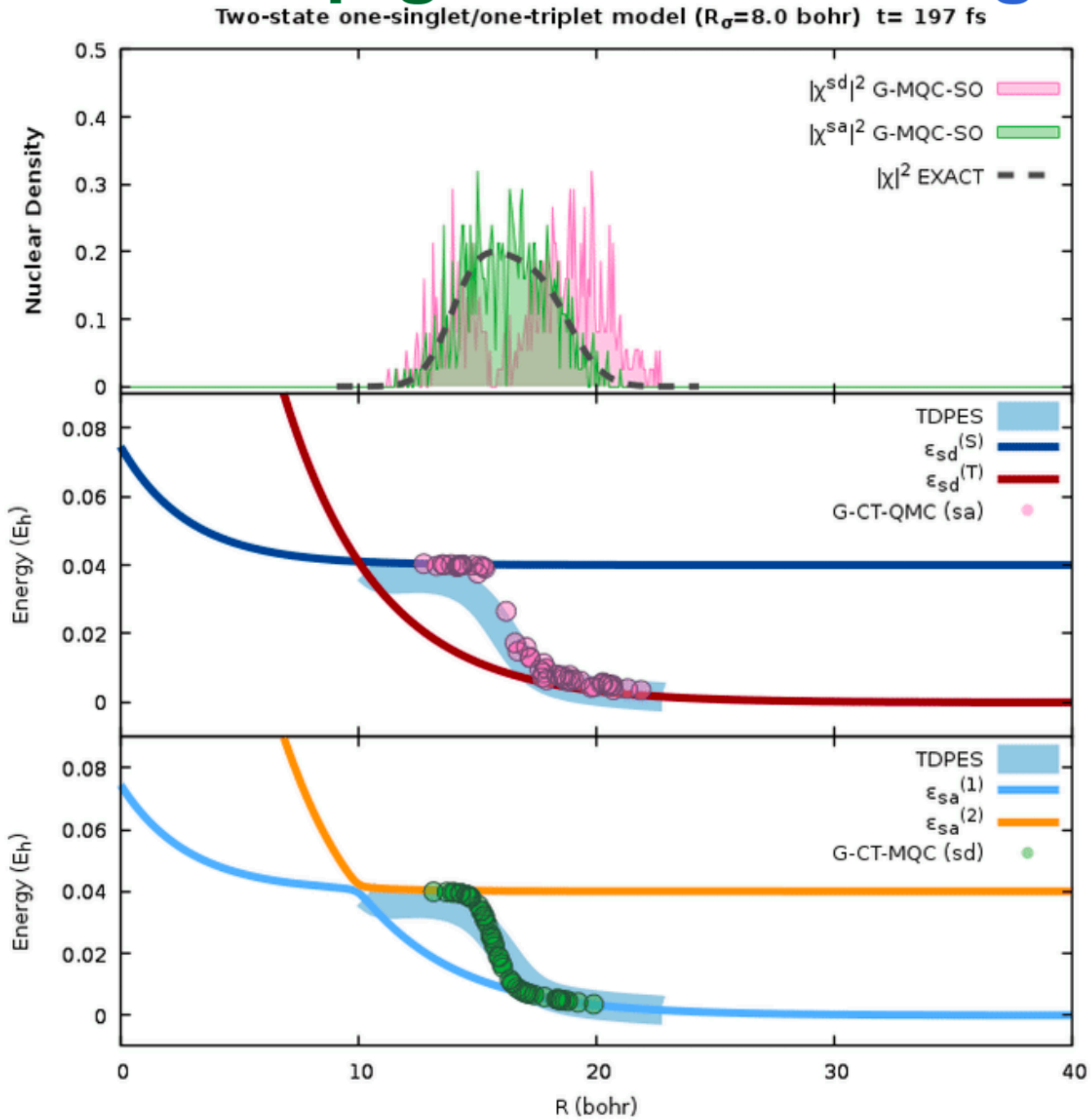

Talotta et al., *Phys. Rev. Lett*, 124(33001), **2020**

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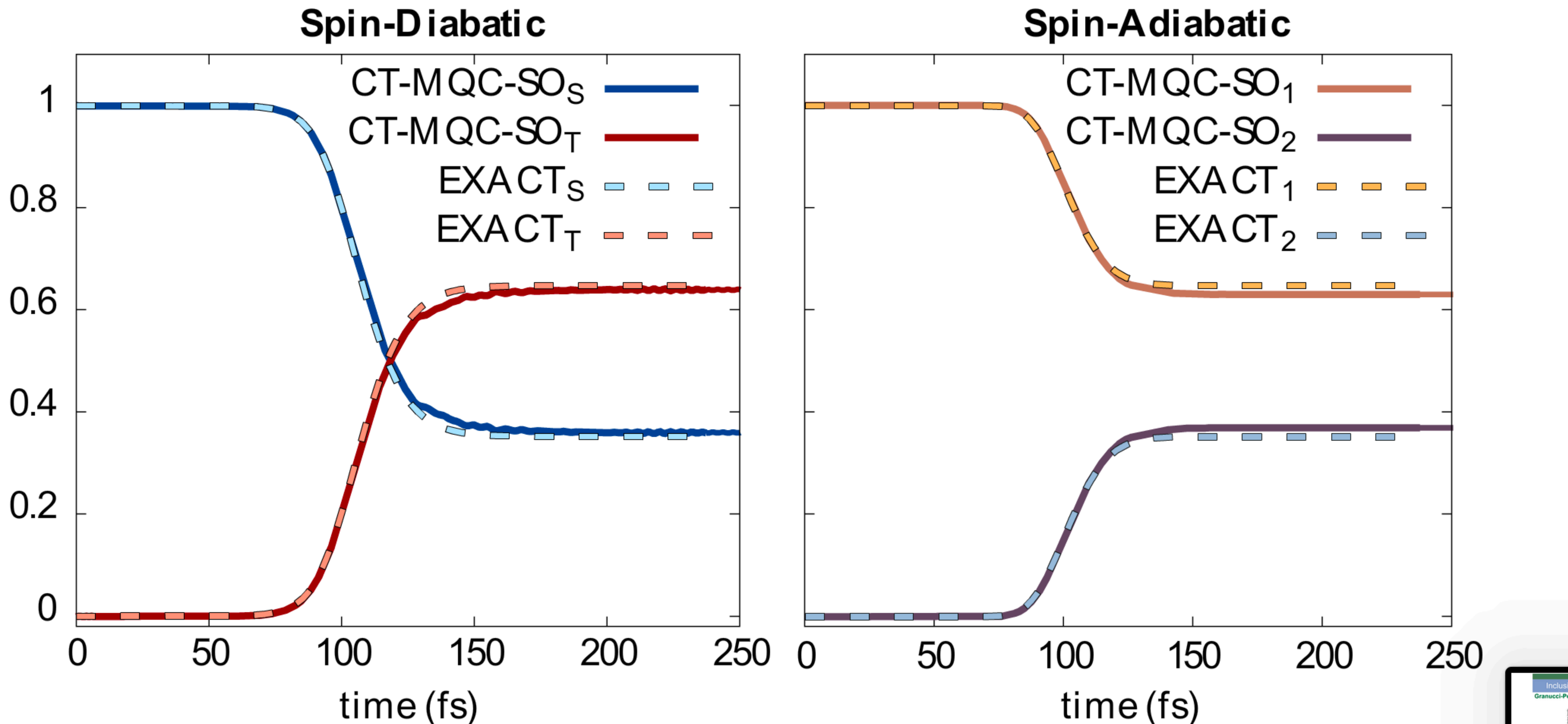
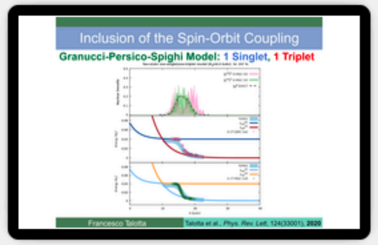


Good agreement with the exact DIA QM calculation

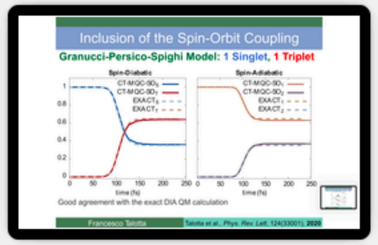


Talotta et al., *Phys. Rev. Lett*, 124(33001), **2020**

Conclusions

- **First working implementation of the spin-orbit coupling in quantum classical algorithm derived from the exact factorization for both spin-diabatic and spin-adiabatic**

- **Perspectives:**
  - Extend the spin-orbit model to N dimensions
  - Interface the algorithm with MOLCAS
  - Comparison with Exact Factorization and Surface-Hopping dynamics



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