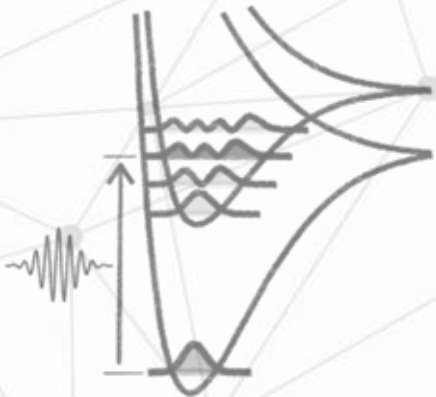


ON THE INTERPRETATION OF MOLECULAR PHOTOEXCITATION WITH LONG AND ULTRASHORT LASER PULSES

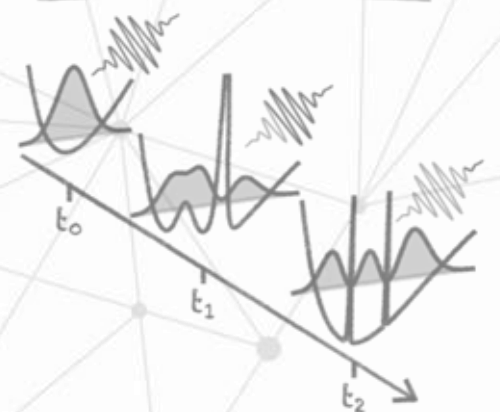
JIŘÍ JANOŠ

BORN-HUANG



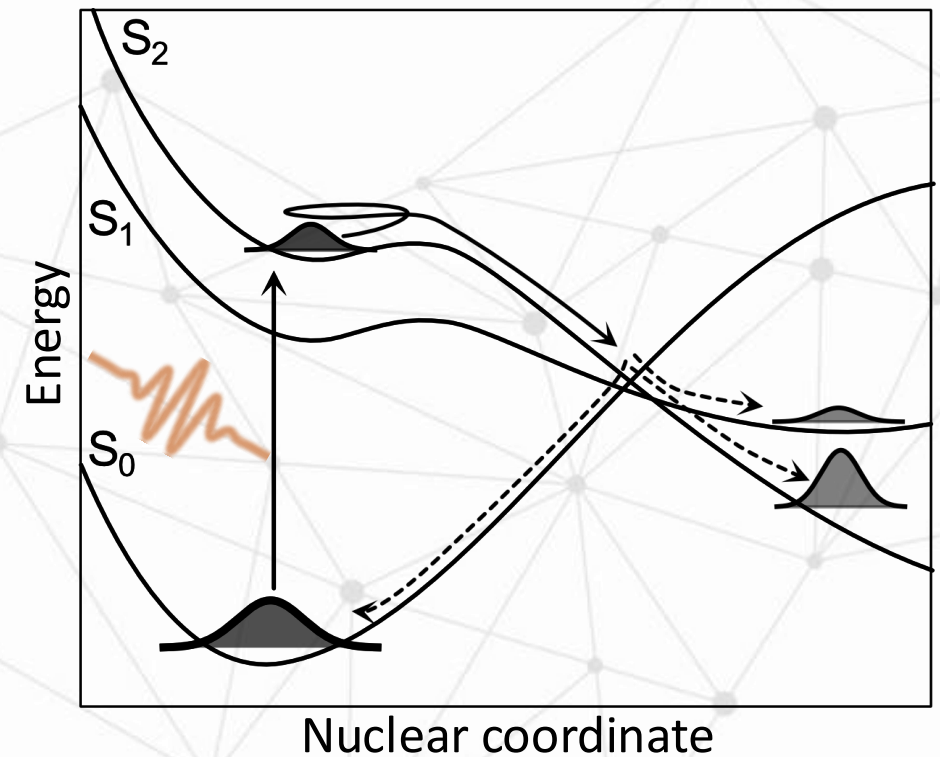
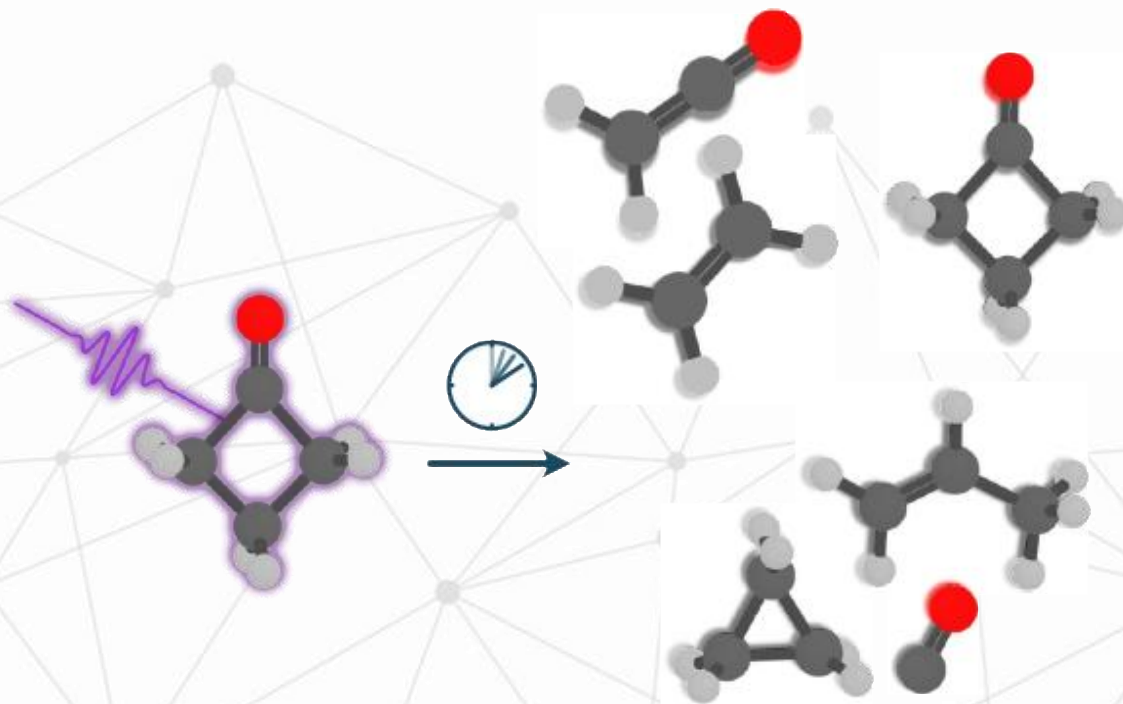
19.10.2026

EXACT FACTORIZATION



Introduction

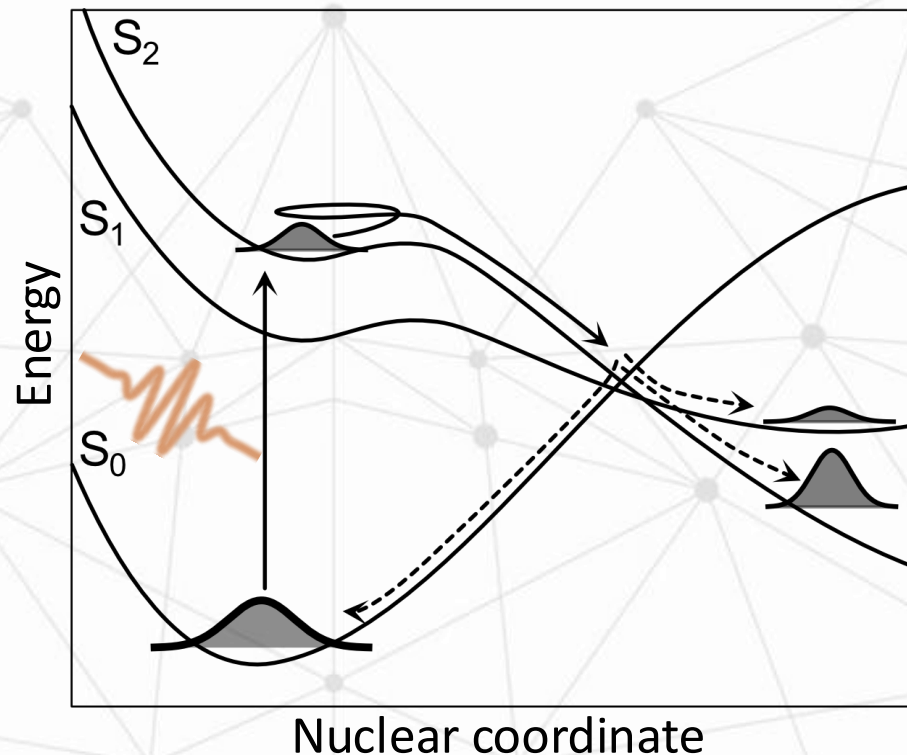
Photoexcitation is the initial step of any photochemical reaction



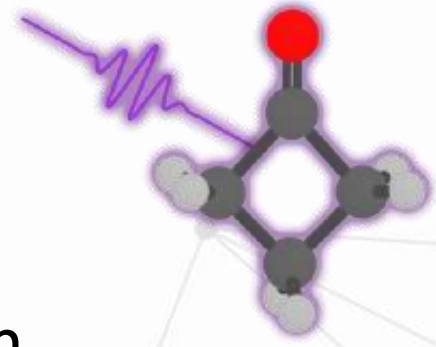
Introduction

Photoexcitation is the initial step of any photochemical reaction

Conceptual understanding of **photoexcitation** and **photochemistry** rooted in the **Born–Huang representation**



Introduction

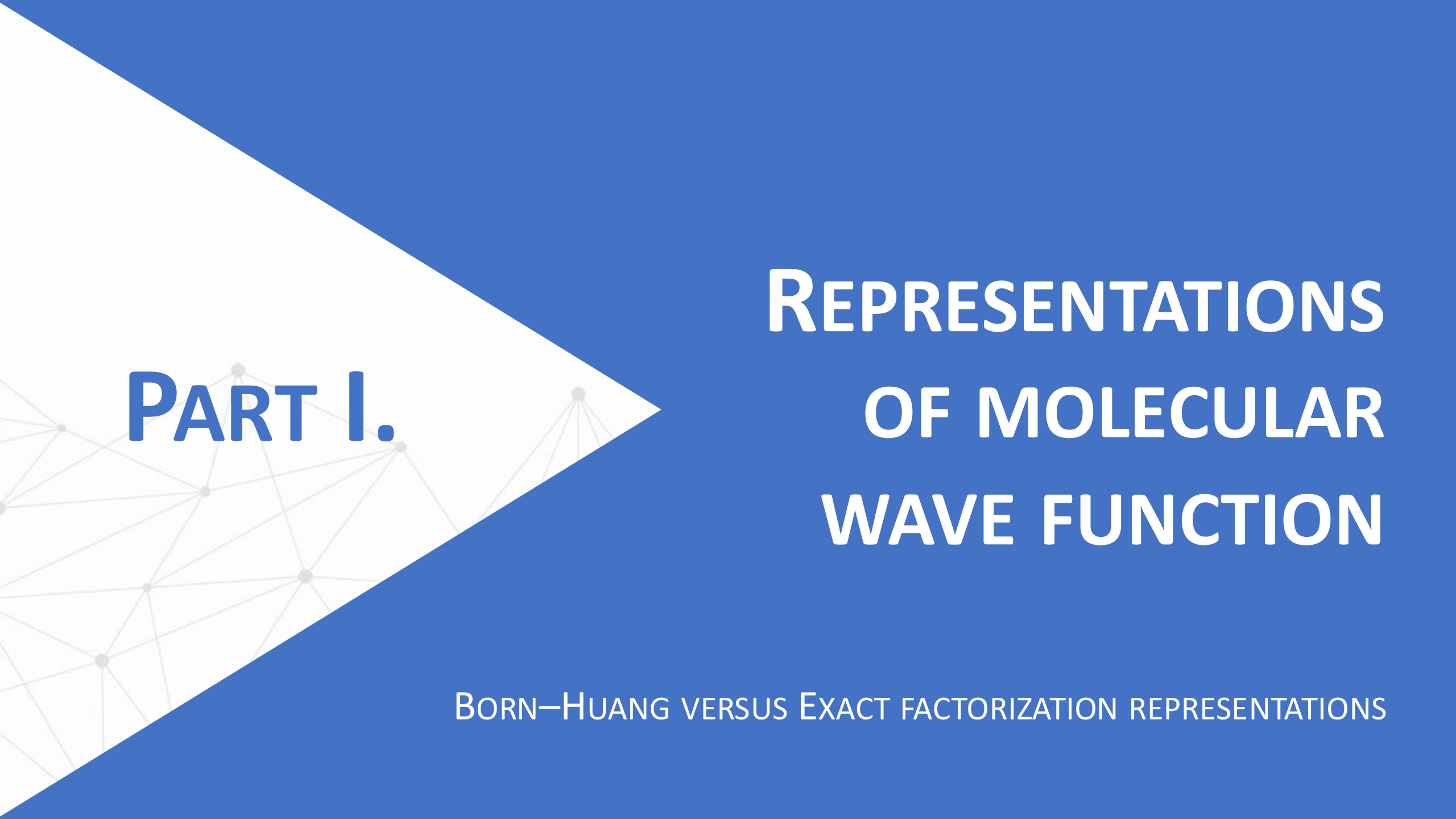


Photoexcitation is the initial step of any photochemical reaction

Conceptual understanding of **photoexcitation** and **photochemistry** rooted in the **Born–Huang representation**

Can we **improve our understanding** of photoexcitation by **changing the perspective?**

Alternative representation: **exact factorization** of the molecular wave function



PART I.

REPRESENTATIONS OF MOLECULAR WAVE FUNCTION

BORN–HUANG VERSUS EXACT FACTORIZATION REPRESENTATIONS

Representations of molecular wave function

Molecular wave function

$$\Psi(\mathbf{r}, \mathbf{R}; t)$$

$\mathbf{r}$... electrons

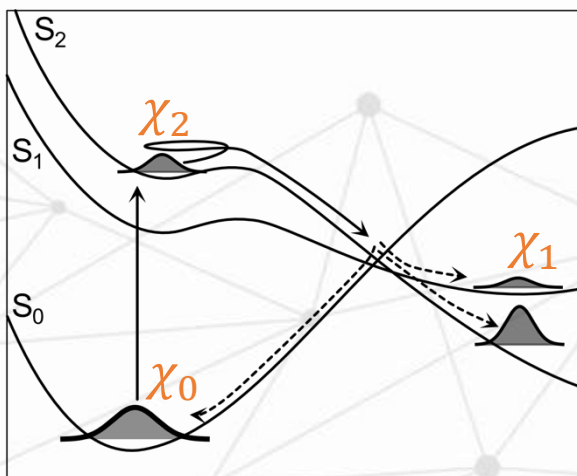
$\mathbf{R}$... nuclei

t ... time

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

Born–Oppenheimer approximation

$$\Psi(\mathbf{r}, \mathbf{R}; t) \approx \chi(\mathbf{R}; t) \phi(\mathbf{r}; \mathbf{R})$$



Born–Huang expansion

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \sum_j \chi_j(\mathbf{R}; t) \phi_j(\mathbf{r}; \mathbf{R})$$

Exact factorization

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \chi(\mathbf{R}; t) \phi(\mathbf{r}; t, \mathbf{R})$$

$$\text{PNC: } \langle \phi(t, \mathbf{R}) | \phi(t, \mathbf{R}) \rangle_{\mathbf{r}} = 1 \quad \forall \mathbf{R}, t$$

Representations of molecular wave function

Born–Huang

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \sum_j \chi_j(\mathbf{R}; t) \phi_j(\mathbf{r}; \mathbf{R})$$

$$\hat{H}_{\text{el}} \phi_j(\mathbf{r}; \mathbf{R}) = \varepsilon_j(\mathbf{R}) \phi_j(\mathbf{r}; \mathbf{R})$$

$$i\hbar \frac{\partial}{\partial t} \chi_j(\mathbf{R}; t) = \sum_k \left[\left(-\frac{\hbar^2 \nabla^2}{2M} + \varepsilon_k(\mathbf{R}) \right) \delta_{jk} + \hat{D}_{jk}(\mathbf{R}) + \hat{V}_{jk}^{\text{int}}(\mathbf{R}, t) \right] \chi_k(\mathbf{R}; t)$$

Coupled PESs

Exact factorization

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \chi(\mathbf{R}, t) \phi(\mathbf{r}, t; \mathbf{R})$$

$$i\hbar \frac{\partial}{\partial t} \phi(\mathbf{r}, t; \mathbf{R}) = [\hat{H}_{\text{el}} + \hat{V}_{jk}^{\text{e}}(\mathbf{R}, t) + \hat{U}_{\text{en}}[\chi, \phi] - \varepsilon(\mathbf{R}, t)] \phi(\mathbf{r}, t; \mathbf{R})$$

$$i\hbar \frac{\partial}{\partial t} \chi(\mathbf{R}; t) = \left[\frac{(-i\hbar \vec{\nabla} + \vec{A}(\mathbf{R}, t))^2}{2M} + \varepsilon(\mathbf{R}, t) + \hat{V}_{jk}^{\text{n}}(\mathbf{R}, t) \right] \chi(\mathbf{R}; t)$$

One time-dependent PES

One time-dependent vector potential

EXCITATION WITH A LONG LASER PULSE

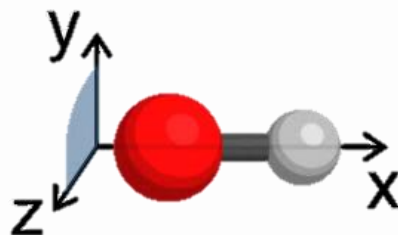
FROM STATIONARY STATE TO STATIONARY STATE



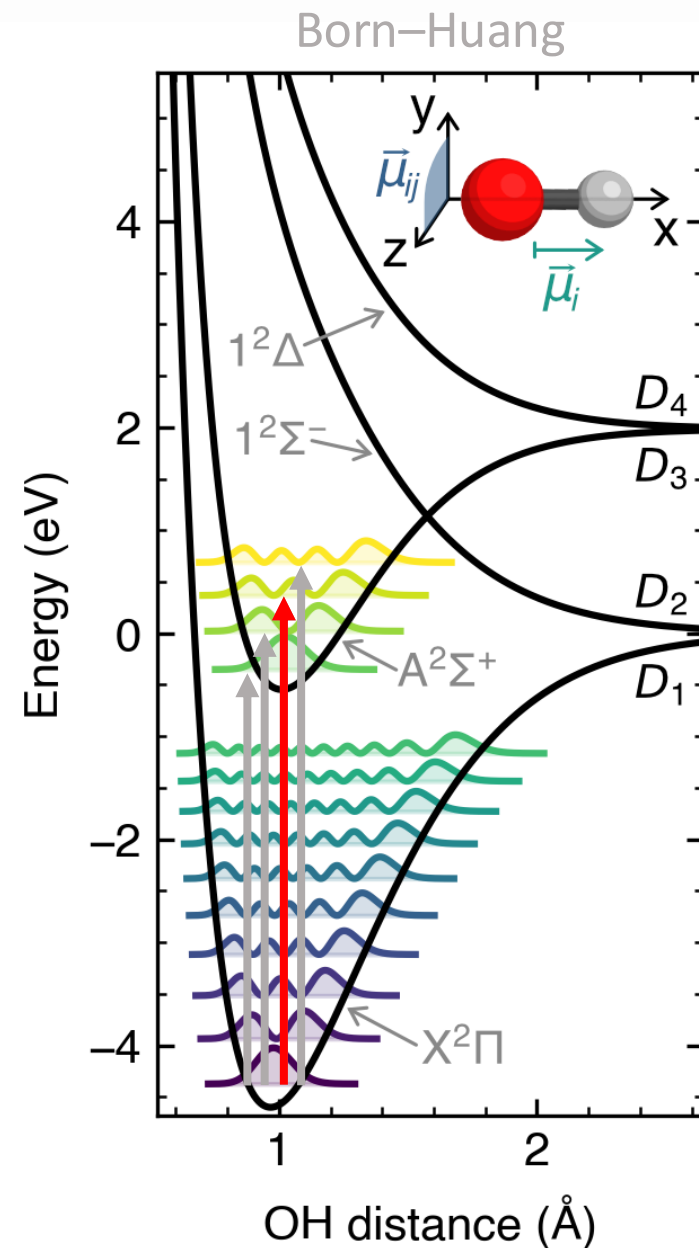
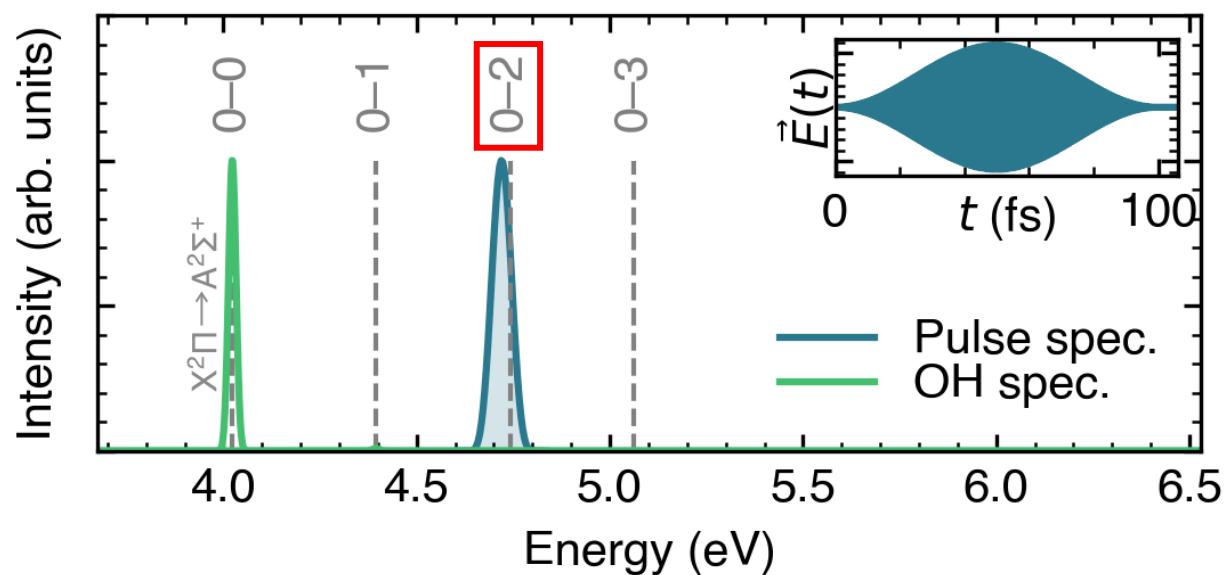
PART II.

Model system

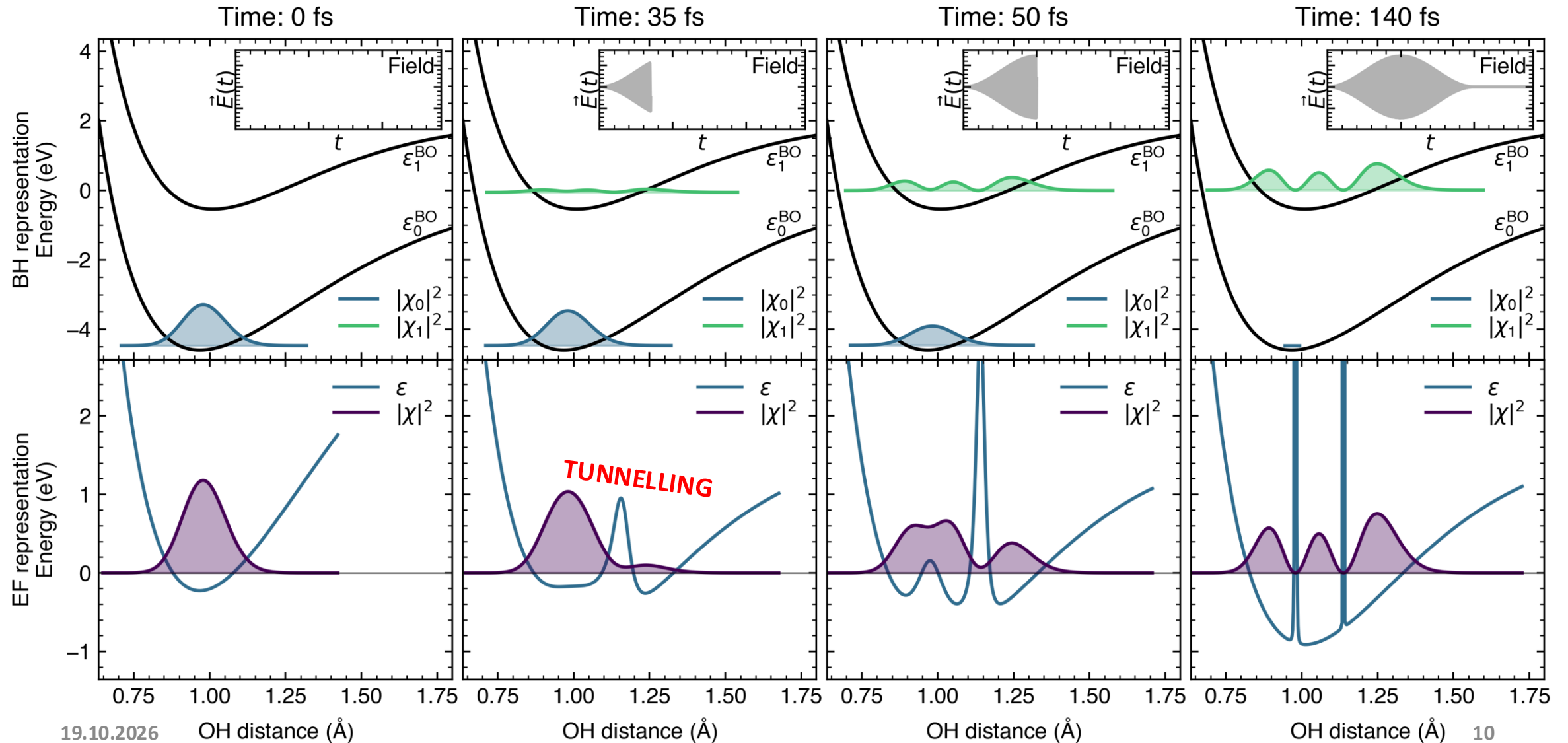
Hydroxyl radical (OH)



100-fs laser pulse



Photoexcitation in different representations

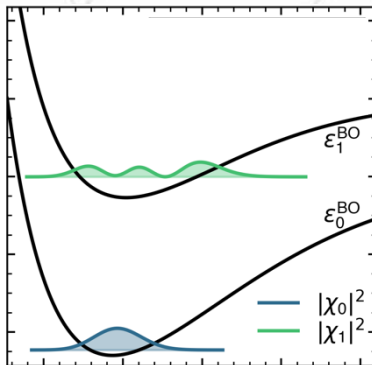


Photoexcitation in different representations

Born–Huang

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \sum_j \chi_j(\mathbf{R}; t) \phi_j(\mathbf{r}; \mathbf{R})$$

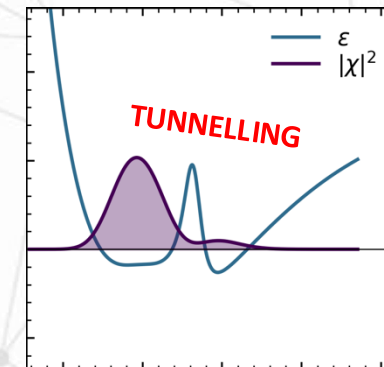
Photoexcitation as **amplitude transfer** between coupled electronic potential energy surfaces



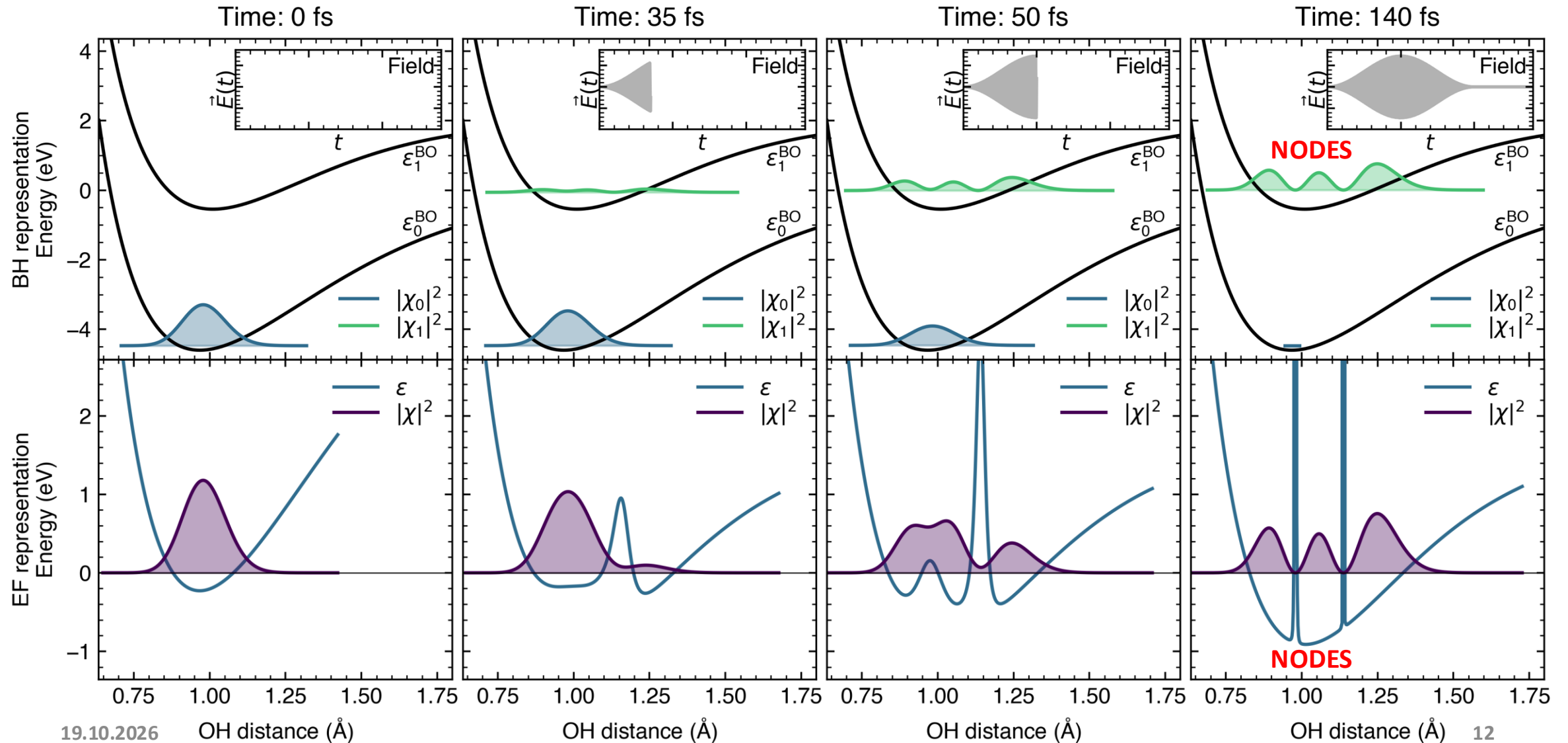
Exact factorization

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \chi(\mathbf{R}; t) \phi(\mathbf{r}; t, \mathbf{R})$$

Photoexcitation as **tunnelling** through the time-dependent electronic potential energy surface



Photoexcitation in different representations

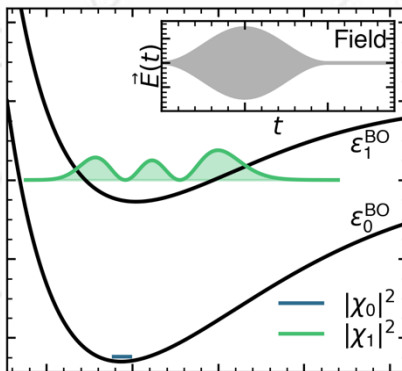


Photoexcitation in different representations

Born–Huang

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \sum_j \chi_j(\mathbf{R}; t) \phi_j(\mathbf{r}; \mathbf{R})$$

Nodes origin naturally from the **orthogonality** of bound vibrational eigenfunctions

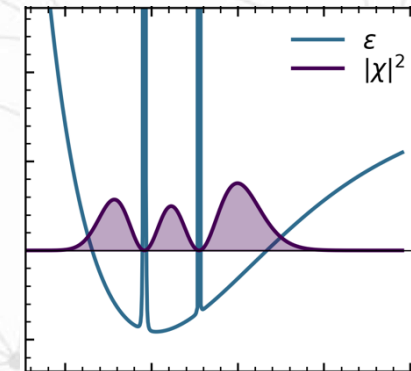


19.10.2026

Exact factorization

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \chi(\mathbf{R}; t) \phi(\mathbf{r}; t, \mathbf{R})$$

Nodes are enforced by the **singularities** in the time-dependent potential energy surface



13



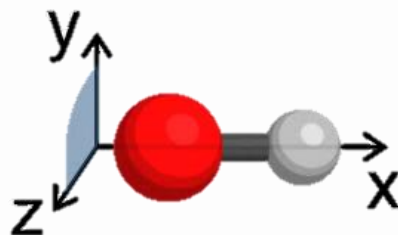
PART III.

EXCITATION WITH A SHORT LASER PULSE

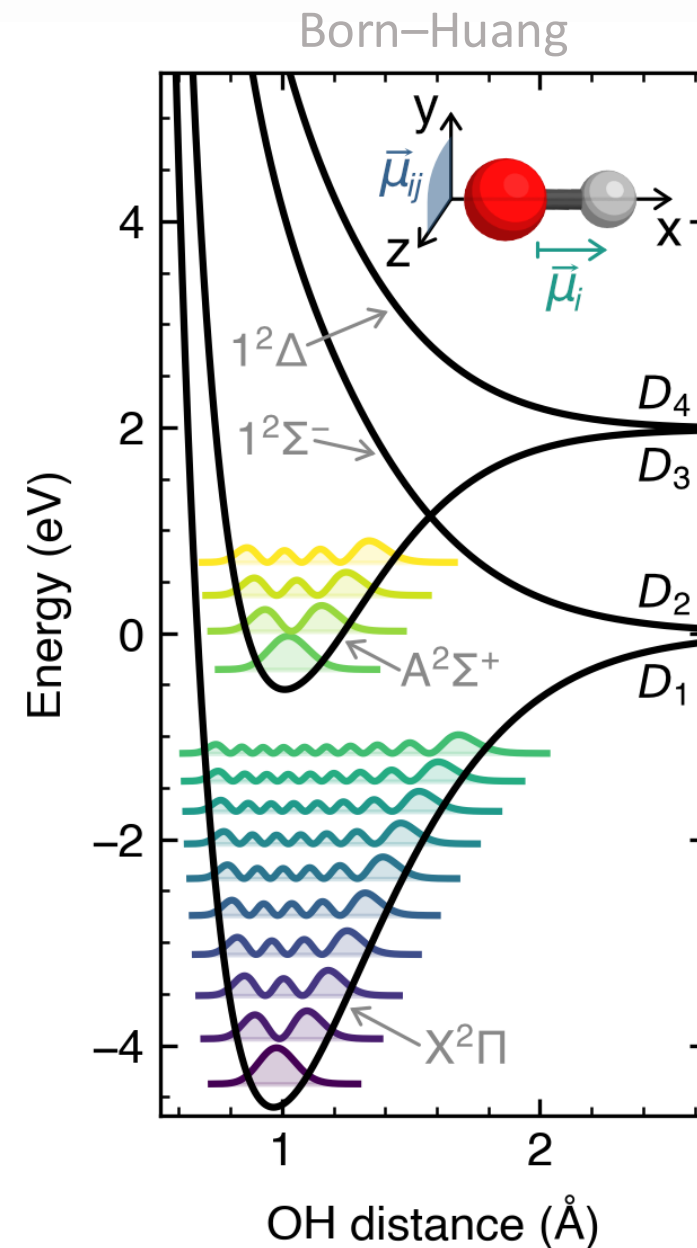
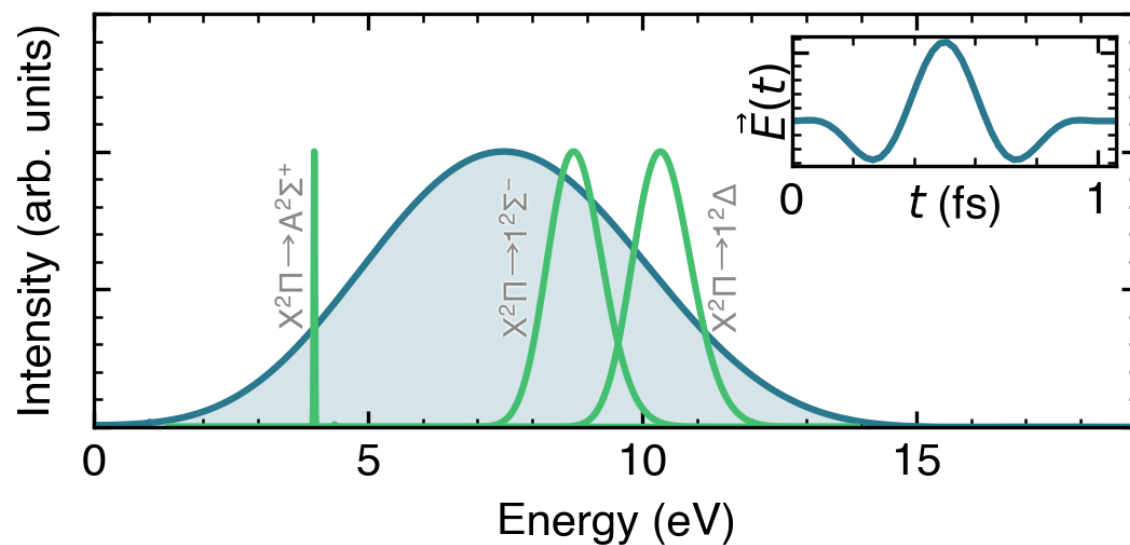
ATTOCHEMISTRY AND COHERENT SUPERPOSITION OF ELECTRONIC STATES

Model system

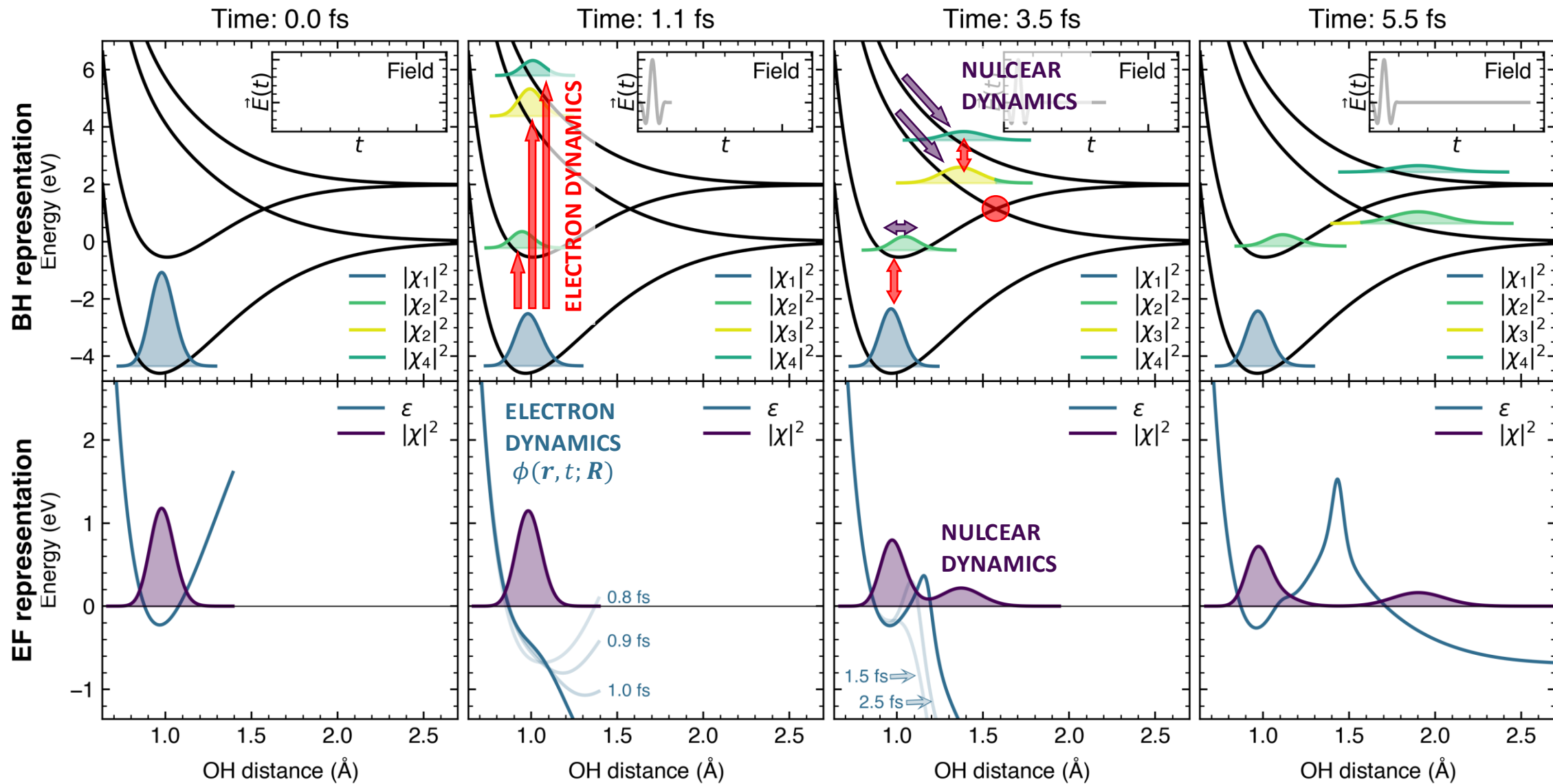
Hydroxyl radical (OH)



1-fs laser pulse



Photoexcitation in different representations

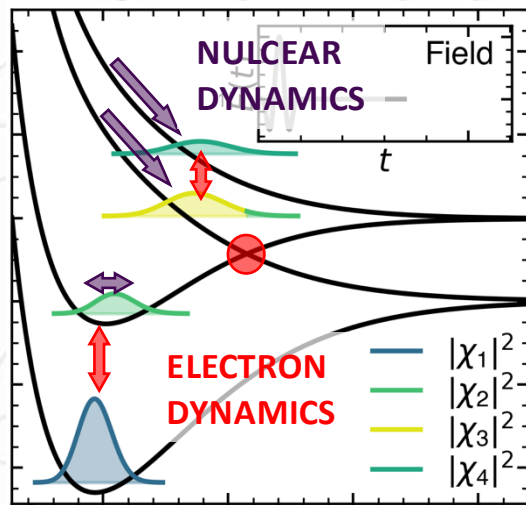


Photoexcitation in different representations

Born–Huang

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \sum_j \chi_j(\mathbf{R}; t) \phi_j(\mathbf{r}; \mathbf{R})$$

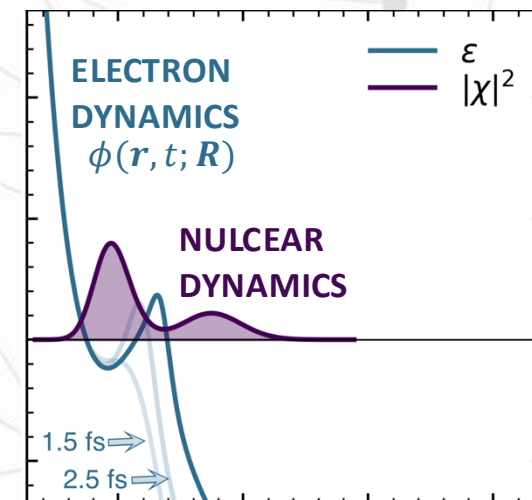
Mixes both **electronic and nuclear dynamics** in the nuclear amplitudes



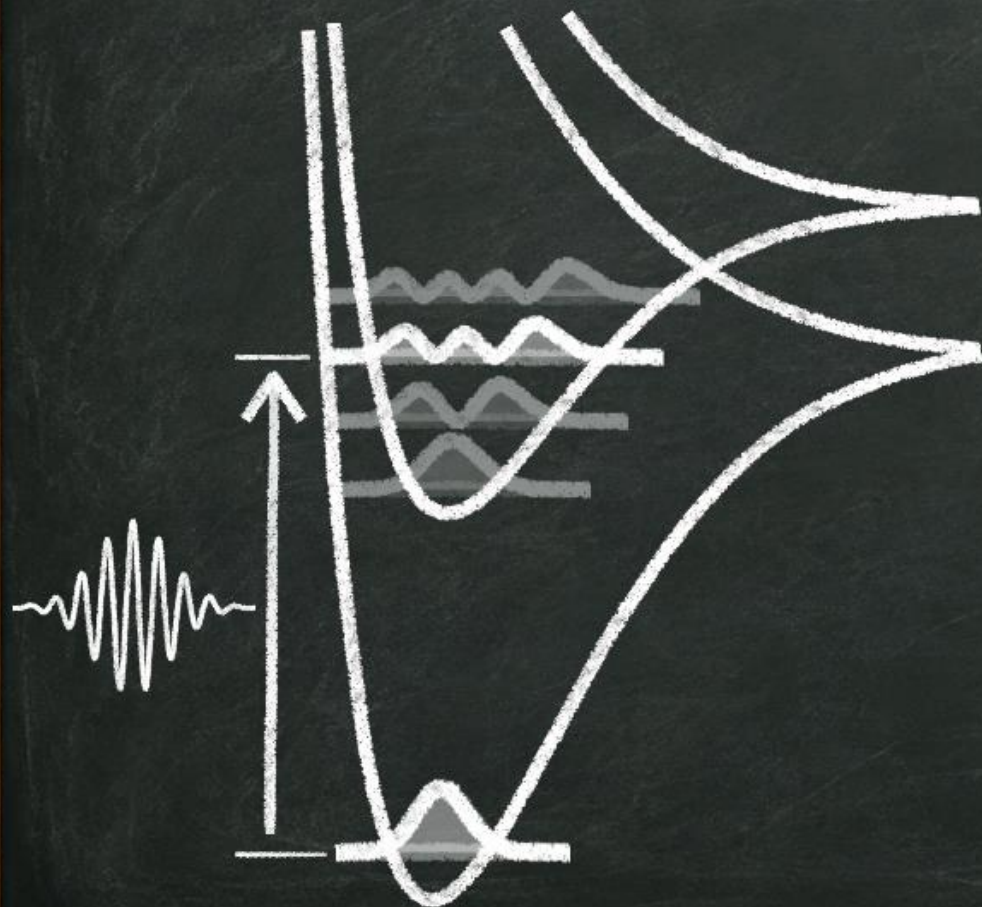
Exact factorization

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \chi(\mathbf{R}; t) \phi(\mathbf{r}; t, \mathbf{R})$$

Separates **electronic and nuclear dynamics** in their respective wave functions



BORN-HUANG



EXACT FACTORIZATION



Conclusions

Photoexcitation from the perspective of **exact factorization** allows us to:

- View photoexcitation as **tunnelling** instead of amplitude transfer
- Interpret origin **nodes in nuclear density** differently
- Easily **decouple electronic and nuclear dynamics**

 > physics > arXiv:2603.06229

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[Submitted on 6 Mar 2026]

On the interpretation of molecular photoexcitation with long and ultrashort laser pulses

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Prof. Basile Curchod



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Ministry of Education,
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