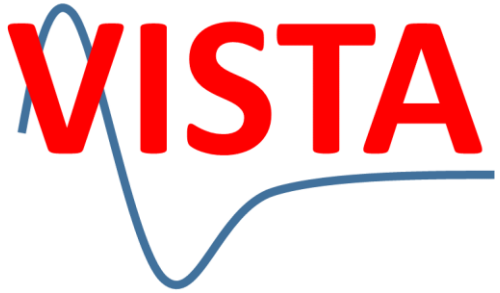

WFOT: A Wave Function Overlap Tool between *Single*- and *Multi*-reference Electronic Structure Methods for Spectroscopy Simulation

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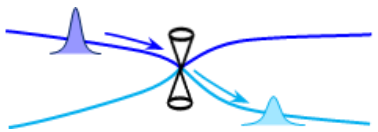
Theoretical basis

I

Cheap, single-reference method

Excited state non-adiabatic dynamics



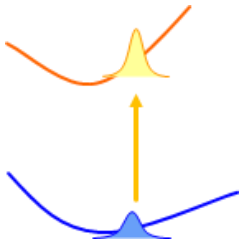
LR-TD-DFT

PBE0

II

Complete, multi-reference method

Compute spectroscopic signals



XMS-CASPT2

(10,8)

Basis set: *cc-pVDZ*

Theoretical basis

$$\Psi_i(r) = \sum_k C_{ik}\Phi_k(r)$$

TDDFT

$$\Psi_i^{DFT}(r) = \sum_a^{N_o}\sum_s^{N_v} C_{ia}^{DFT,s}\Phi_a^{DFT,s}(r)$$

CASPT2

$$\Psi_j^{PT2}(r) = \sum_k C_{jk}\Phi_k(r) = \sum_b^{N_o}\sum_t^{N_v} C_{jb}^{PT2,t}\Phi_b^{PT2,t}(r)$$

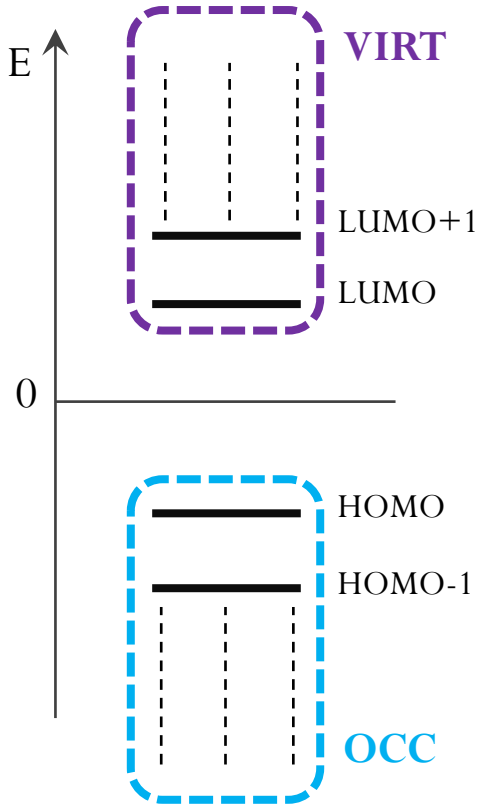
$$\mathbf{WFO} = <\Psi_i^{DFT}(r)|\Psi_j^{PT2}(r)> = \sum_a^{N_o}\sum_s^{N_v}\sum_b^{N_o}\sum_t^{N_v} C_{ia}^{DFT,s}\, C_{jb}^{PT2,t} <\Phi_a^{DFT,s}(r)\,|\,\Phi_b^{PT2,t}(r)>$$

Non-mixing approximation

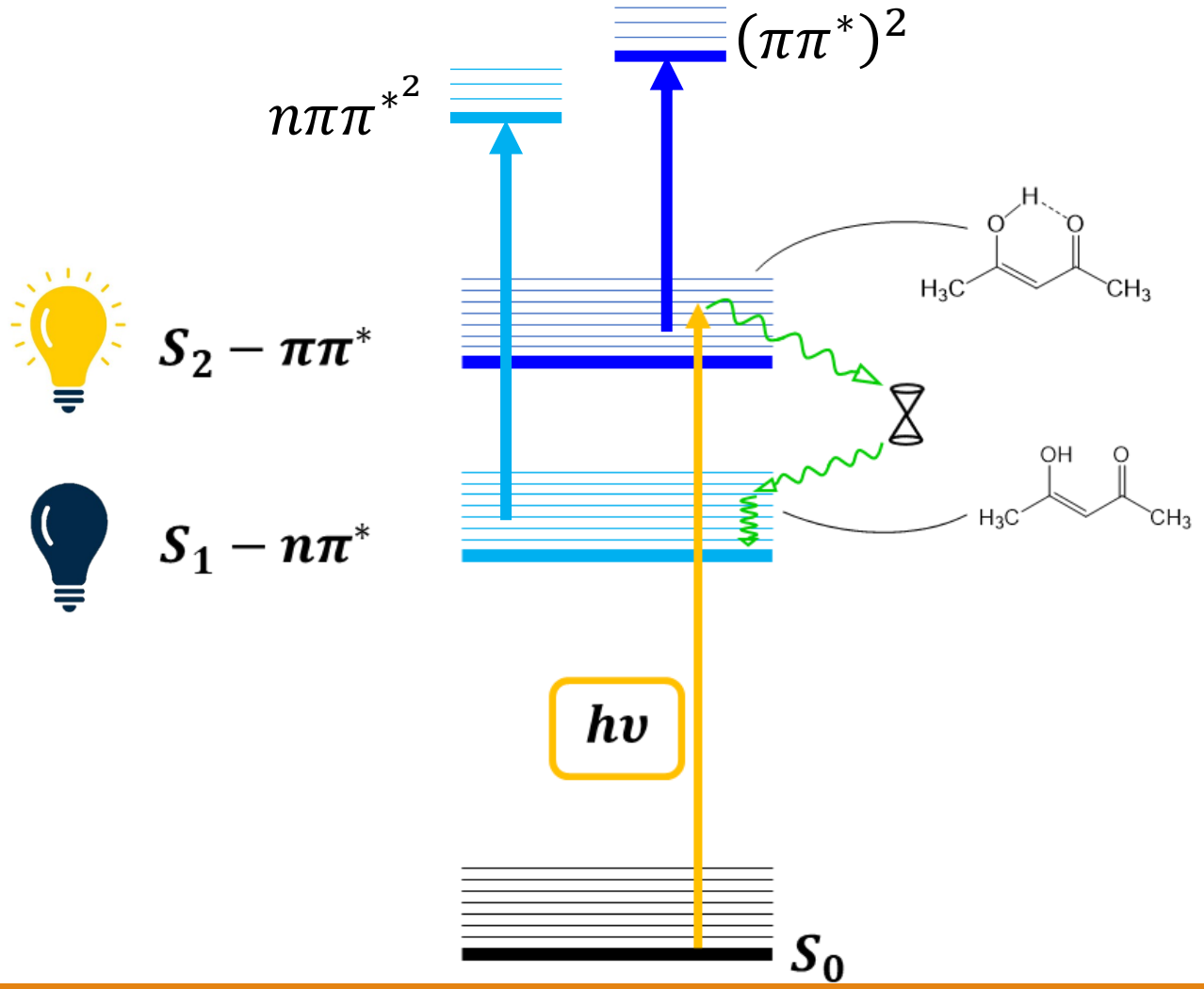
$$< \Phi_a^{DFT,s}(r) \mid \Phi_b^{PT2,t}(r) > = \delta_{ab}\delta_{st}$$

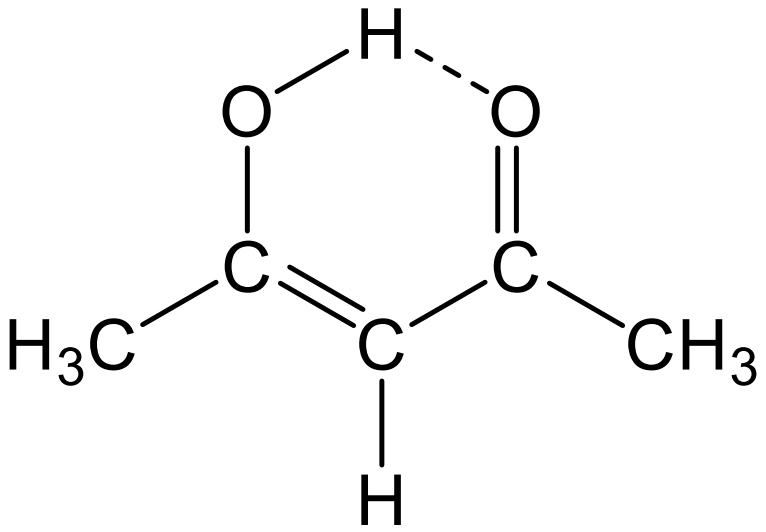
$$< \Psi_i^{DFT}(r) \mid \Psi_j^{PT2}(r) > = \sum_a^{N_o} \sum_s^{N_v} C_{ia}^{\prime DFT,s} C_{ja}^{PT2,s}$$

$$C_i^{\prime DFT} = U_{occ}^T C_i^{DFT} U_{virt}$$

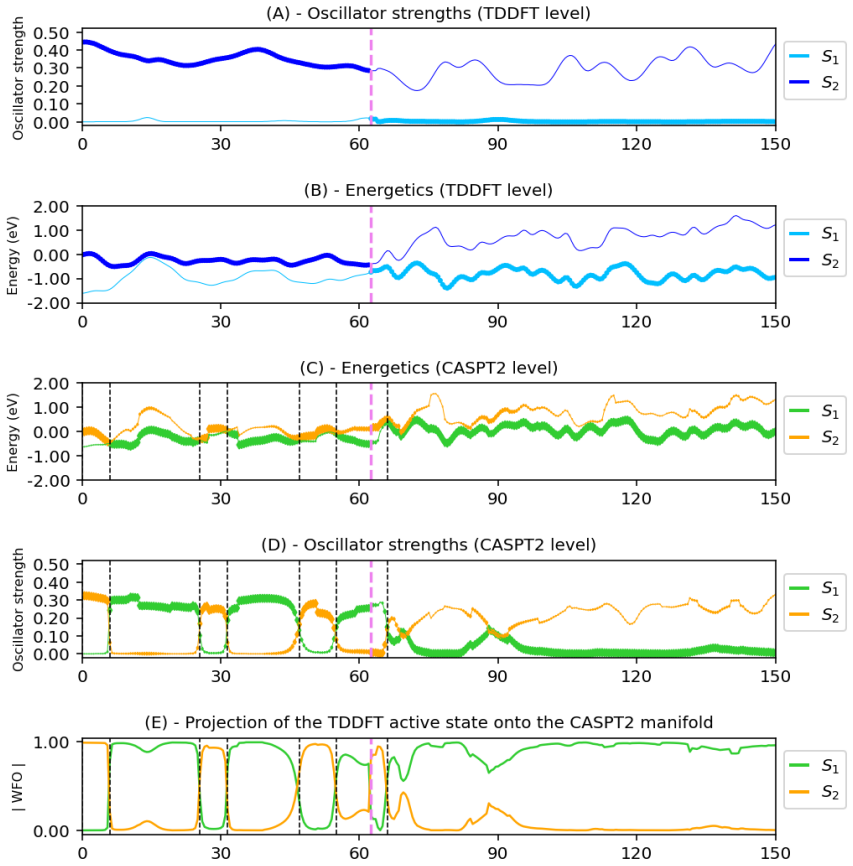


Case study - Acetylacetone

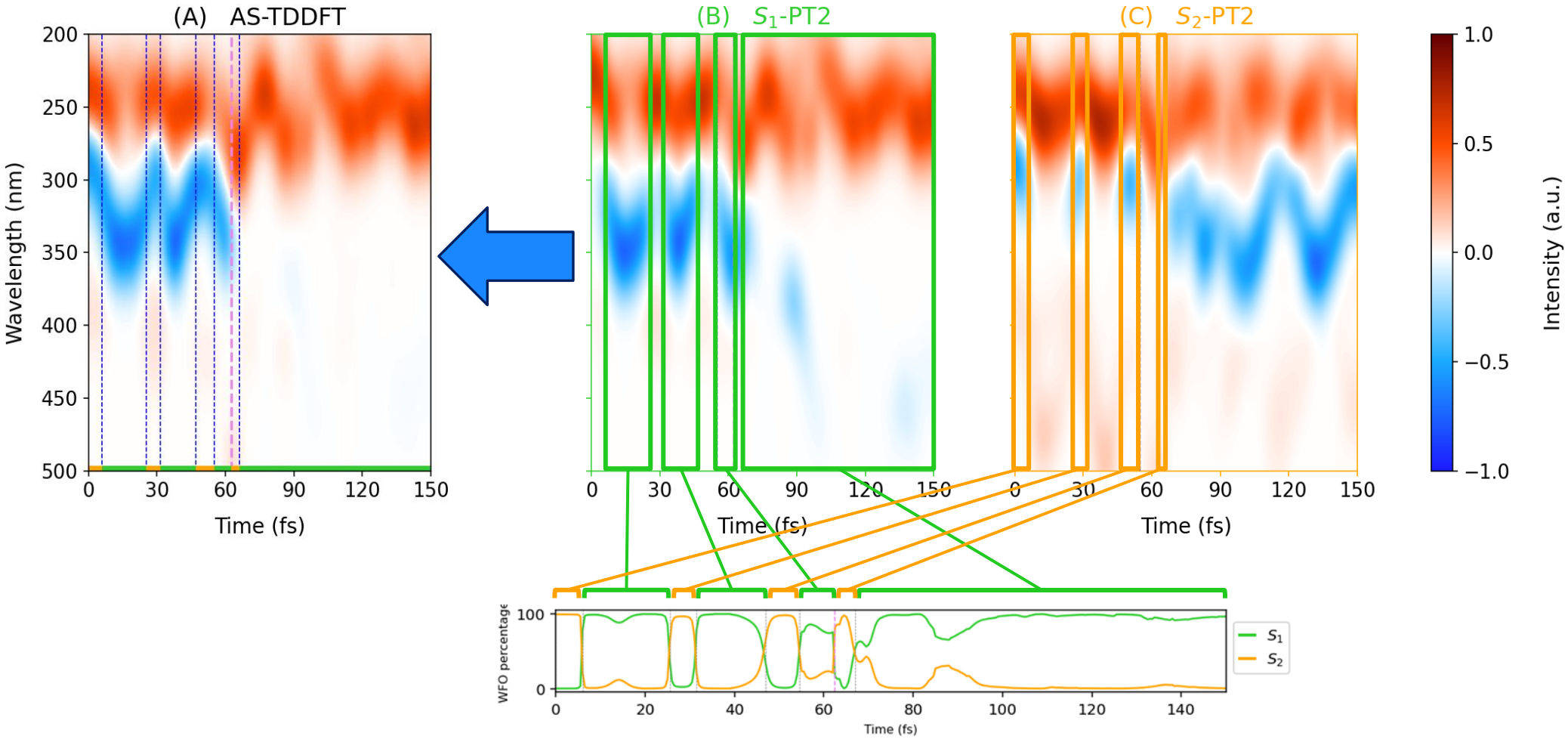




Single trajectory example



Single trajectory signals



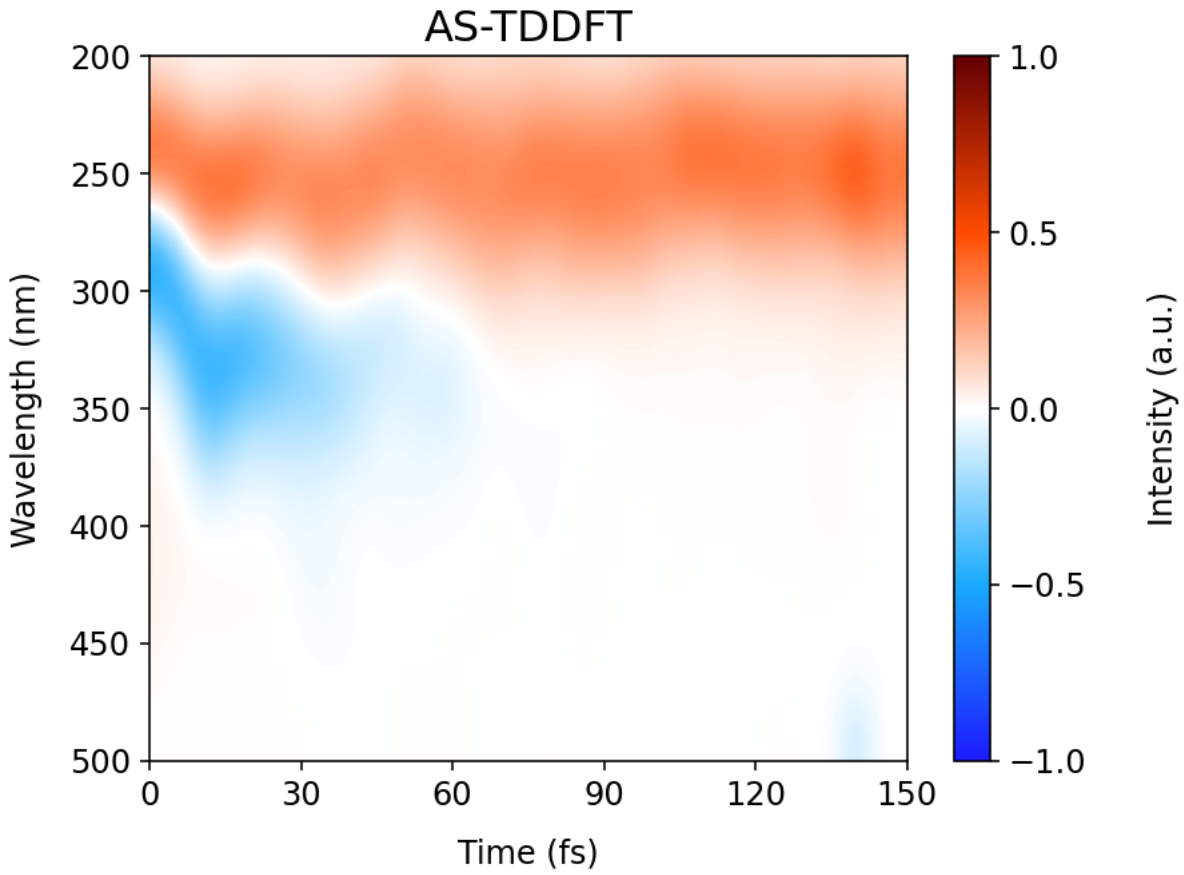
Transient absorption

Stimulated emission

Complete spectrum

Transient absorption

Stimulated emission



Time convolution

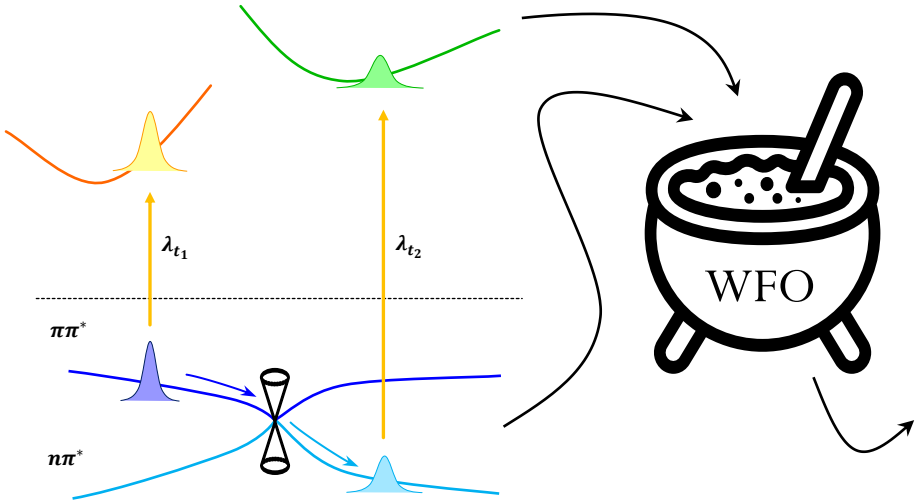
$\sigma = 3\ fs$

Energy convolution

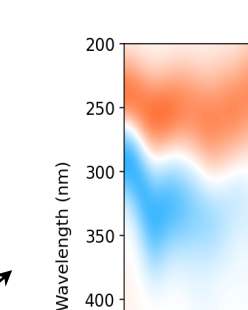
$\sigma = 0.2\ eV$

Conclusions

Transient absorption signals at **CASPT2** level



on-the-fly non adiabatic dynamics at **TDDFT** level



TDDFT/CASPT2 transient spectrum

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https://gitlab.com/cobrammgroup/cobramm

A. Loreti

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