Vibronic Spectra without Born-Oppenheimer Surfaces

VISTA 13 Seminar

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Max Planck Institute for the Structure and Dynamics of Matter
Hamburg, Germany

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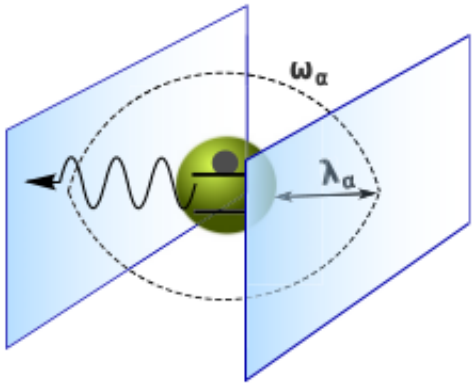
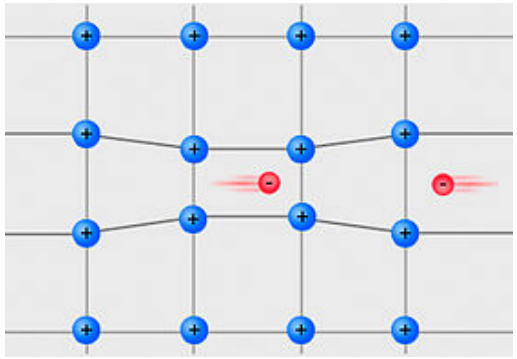
Overview

1. Motivation
   - Mixed Species Dynamics Approaches
   - Escaping the Born Oppenheimer Picture
2. Ehrenfest Dynamics
3. Vibronic Absorption Spectra
   - With Born Oppenheimer
   - Without Born Oppenheimer
4. Interacting Conditional Wavefunction Ansatz

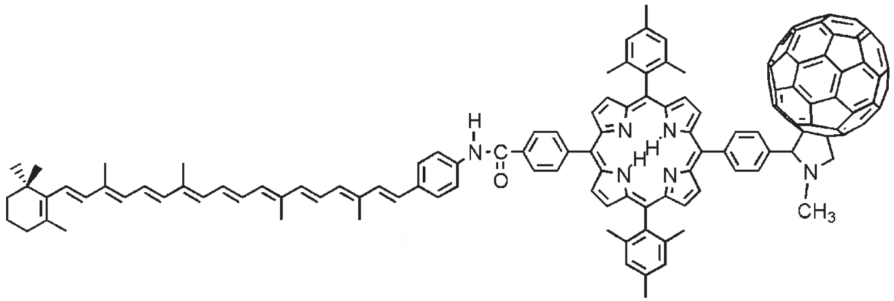
Motivation



Electron-Photon[1]



Electron-Phonon

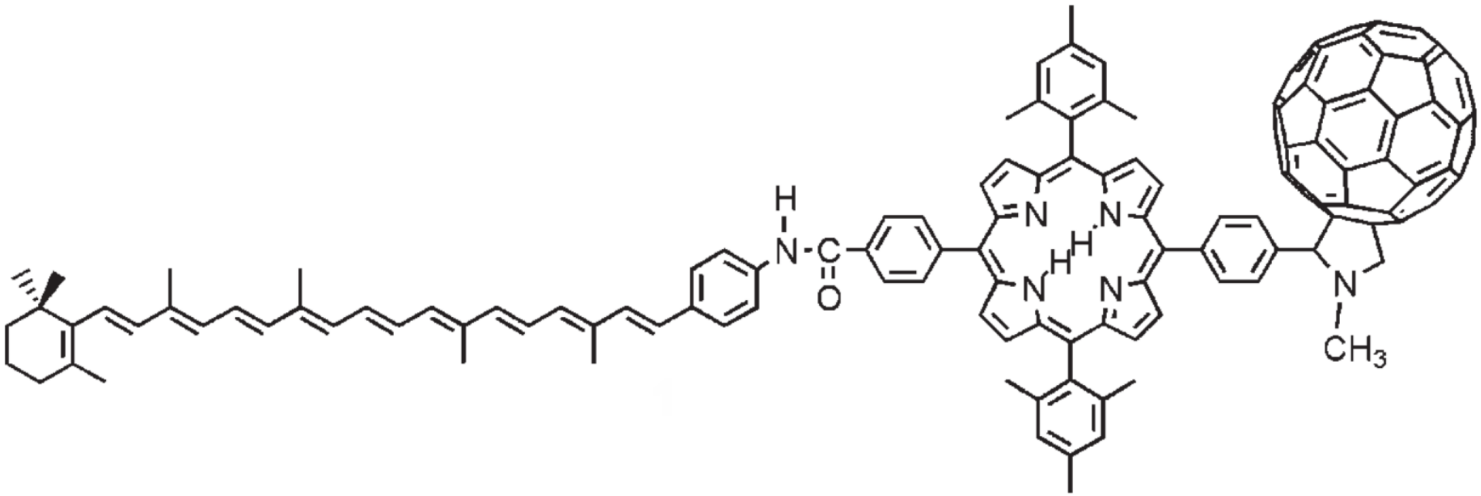


Electron-Nuclei

[1]Hoffmann, N. et al *Phys. Rev. A* 2019 99

Electron-Nuclear Dynamics

Nuclear motion changes charge migration



Light Harvesting Molecule

Kodis, G. et al *J. Phys. Org. Chem* 2004 17

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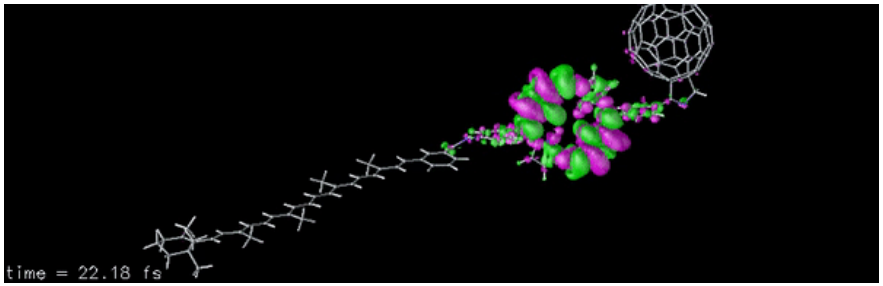

Charge Migration with
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Andrea Rozzi et al. *Nature Communications* 2013, 4

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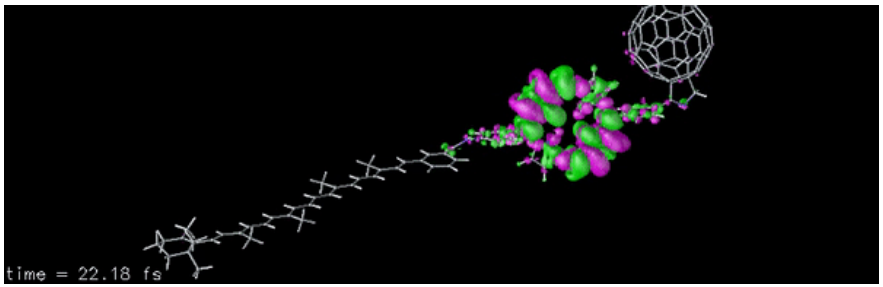

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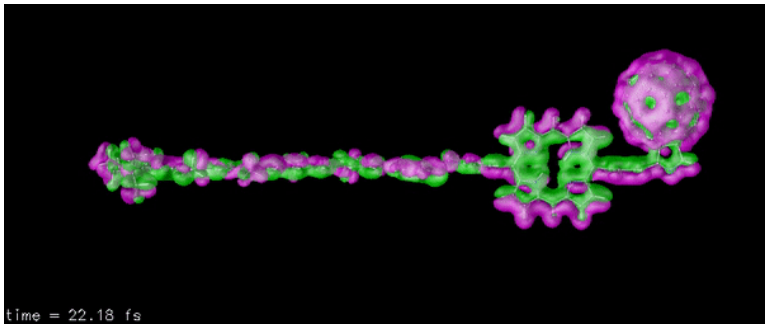
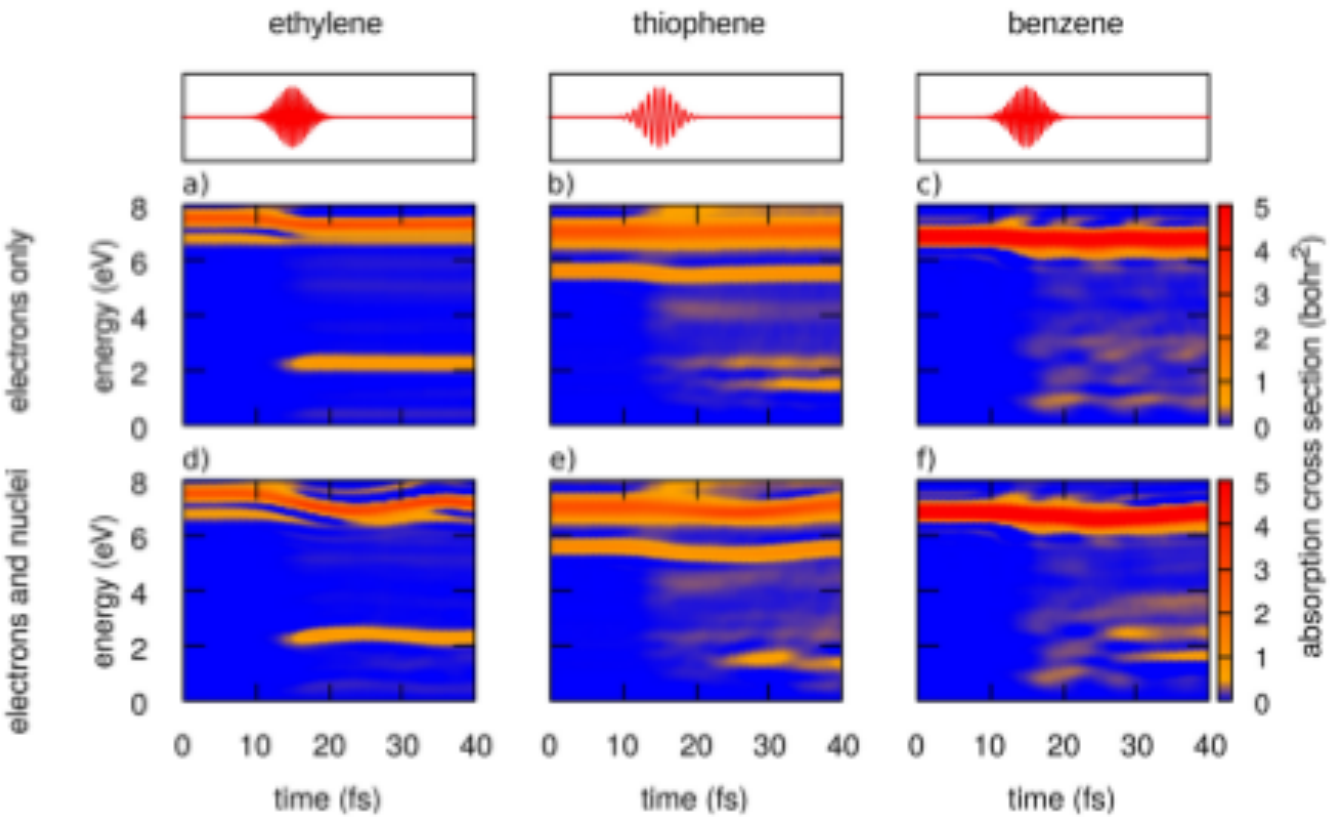


Charge Migration with Ehrenfest dynamic nuclei

Andrea Rozzi et al. *Nature Communications* 2013, 4

Nuclear Motion Changes Time Resolved Spectra



Krumland, J. et al *J. Chem Phys.* 2020, 153

Goal

- Describe driven, non-perturbative system response

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- Include quantum nature of nuclear dyamics

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How is this usually done?

Mixed Species Quantum Dynamics, $\partial_t |\Psi\rangle = -i\hat{H} |\Psi\rangle$

Born Oppenheimer/Huang Framework

$$|\Psi(R,t)\rangle = \sum_n \chi_n(R,t) |\Phi_n(R)\rangle$$

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Major Problem

1. $R \in \mathbb{R}^{3N_n}$, N_n : Number of nuclei
2. Terms like $\langle \Phi_n | \partial_R | \Phi_{n'} \rangle$ can be very expensive!

Dynamics Approaches

Broadly speaking

Variational Wavefunction Ansätz

Mixed-Quantum Classical

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Goal: **Dynamics without multiple BO states**

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- **Interacting Conditional Wavefunctions**

Mixed-Quantum Classical

- Path Integral MD
- Mapping approaches
- Surface Hopping
- **Real Space Multi-trajectory Ehrenfest**

Goal: **Dynamics without multiple BO states**

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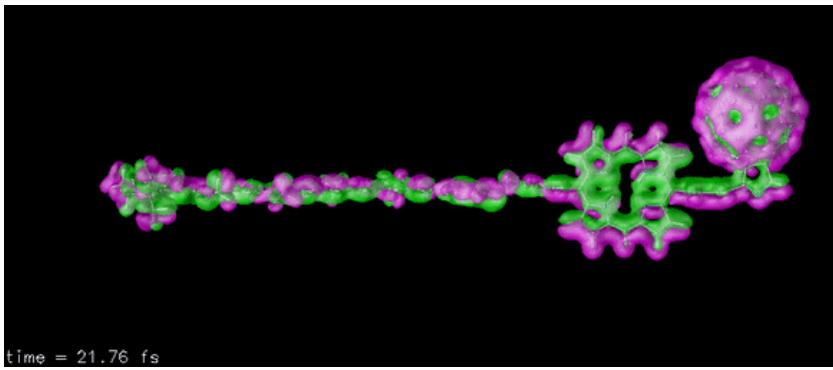

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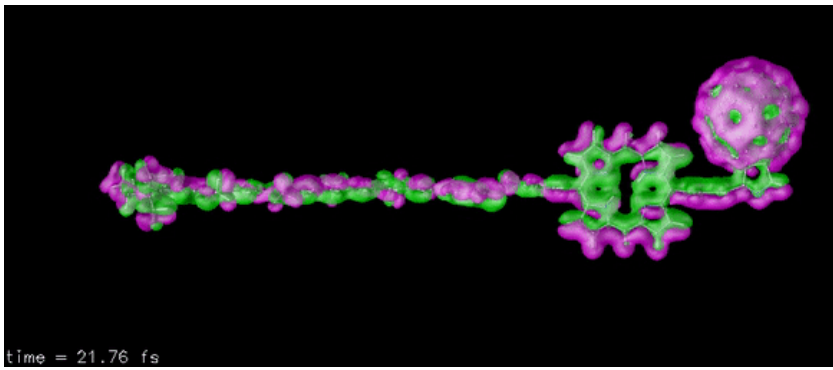
- No Quantum effects from nuclei



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Goal: Calculate absorption spectra $I(\omega)$, via dipole operator $\hat{\mu}$

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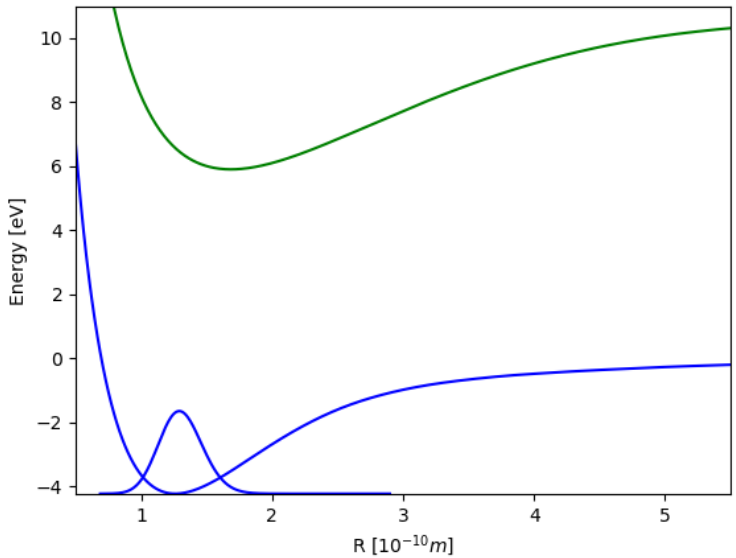

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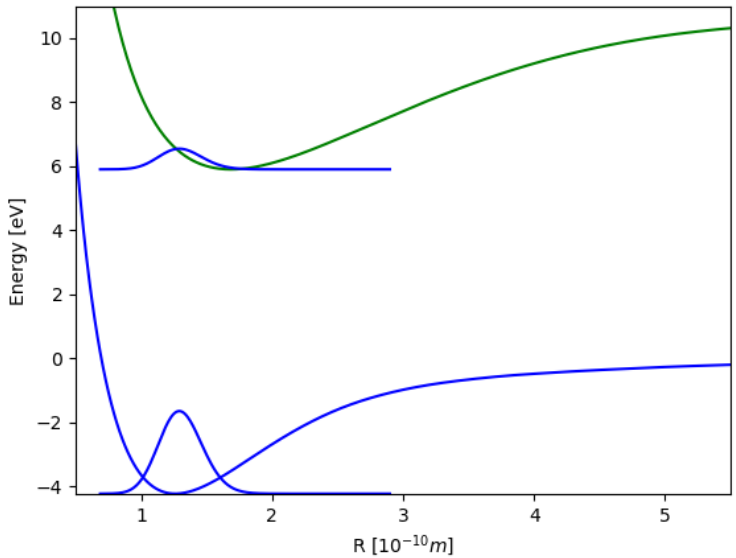

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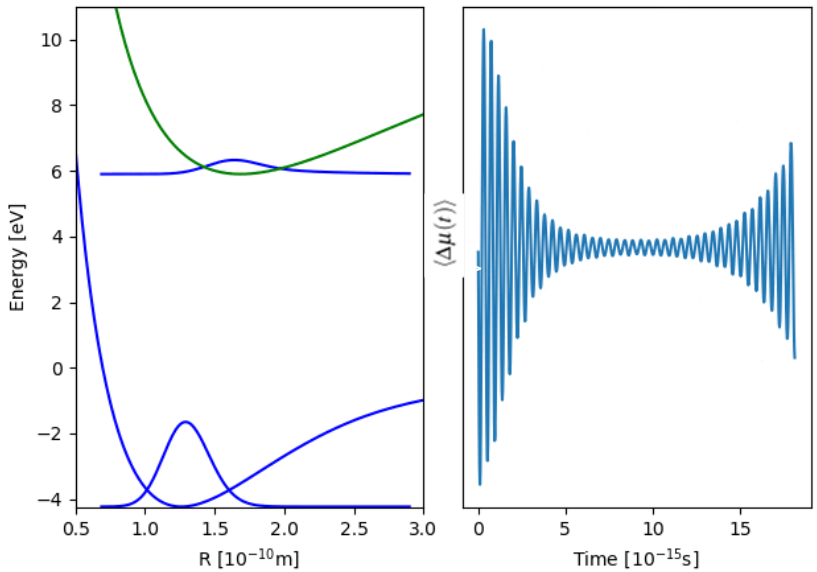

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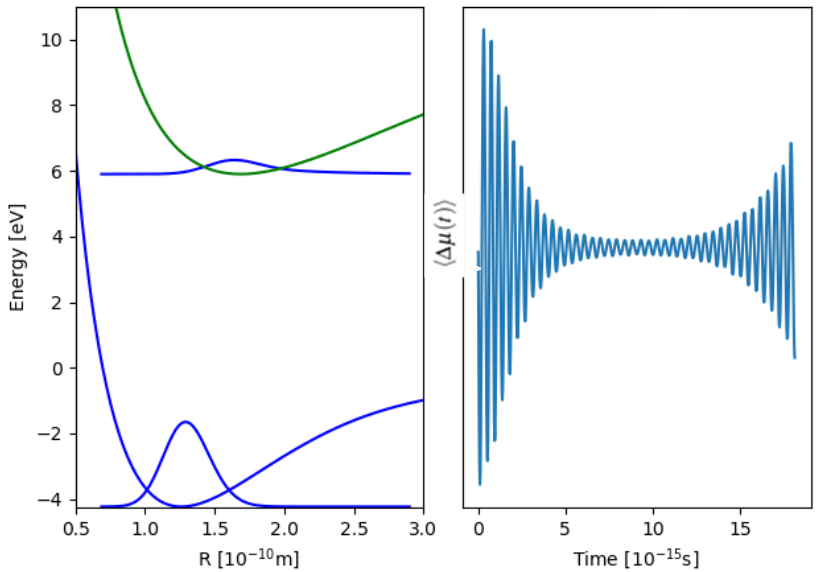
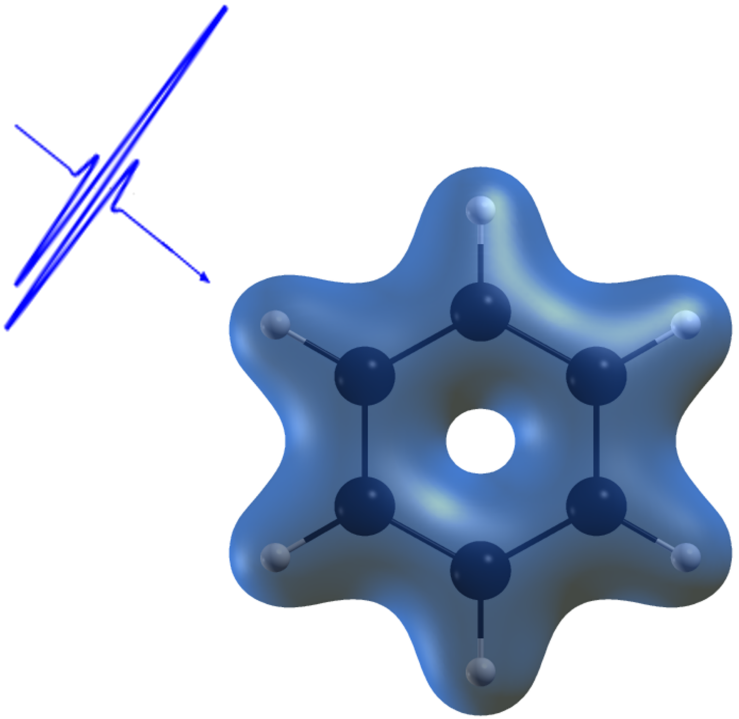
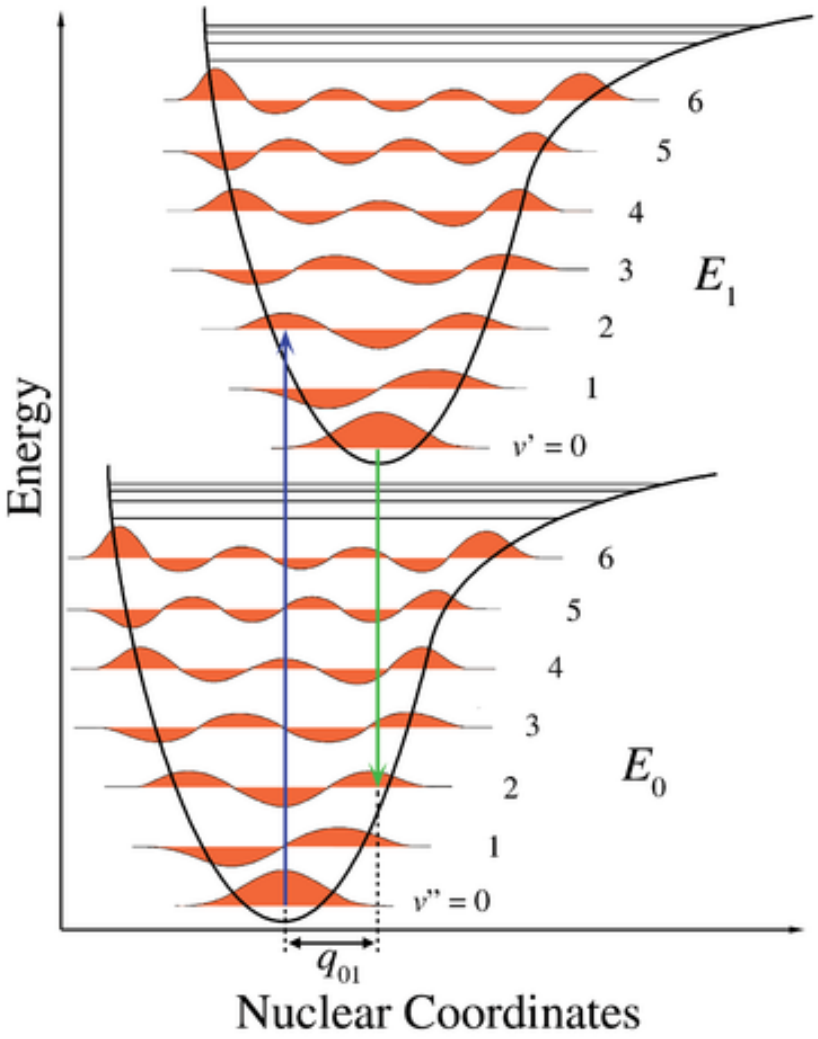
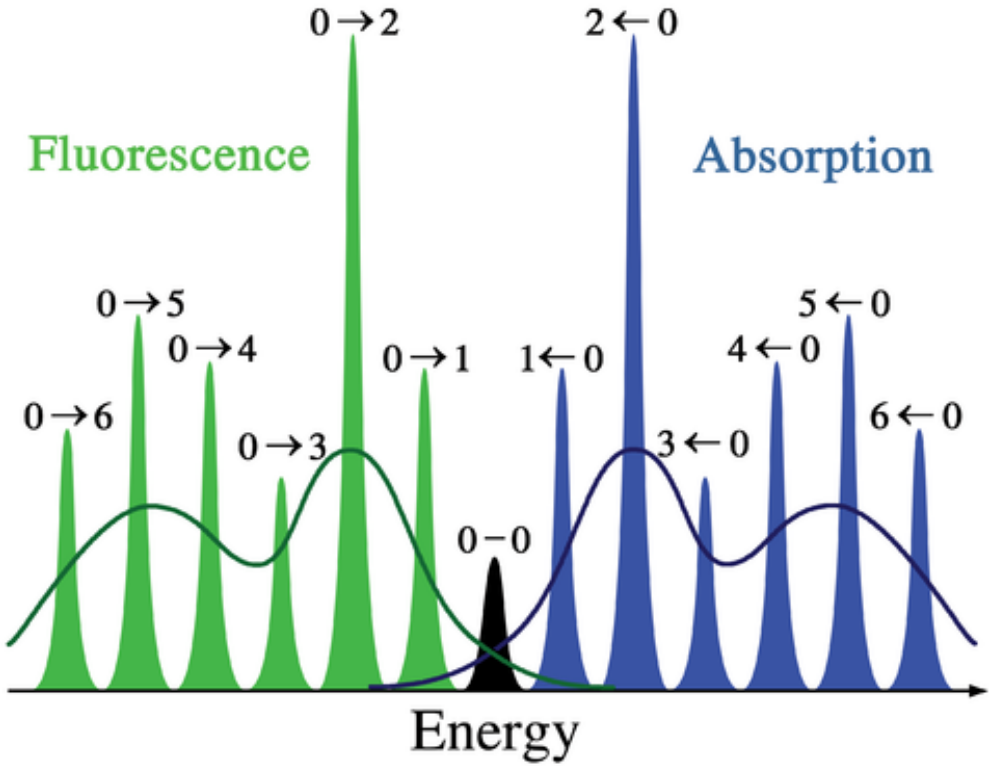


Non BO Option:



Vibronic Spectra: Frank-Condon Principle





Linear Absorption Spectra: MTEF-BO

BO option with MTEF

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$$\partial_t P_i(t) = \sum_n -\partial_R U_n(R_i(t)) \rho_e^{nn'}(t) + \sum_{nn'} \Re \left[\left(U_n(\mathrm{R}_i(t)) \langle \Phi_n | \partial_R | \Phi_{n'} \rangle - c.c. \right) \rho_e^{n'n}(t) \right]$$

Molecular Model

One dimesional H_2

$$\hat{H}(r_1, r_2, R) = -\frac{\partial_R^2}{2\mu_n} - \sum_{i=1}^{2} \frac{\partial_{r_i}^2}{2\mu_e} + \frac{1}{\sqrt{(r_1 - r_2)^2 + 1}} + \frac{1}{R} - \sum_{i=1}^{2} \left(\frac{1}{\sqrt{(r_i + \frac{1}{2}R)^2 + 1}} + \frac{1}{\sqrt{(r_i - \frac{1}{2}R)^2 + 1}} \right)$$

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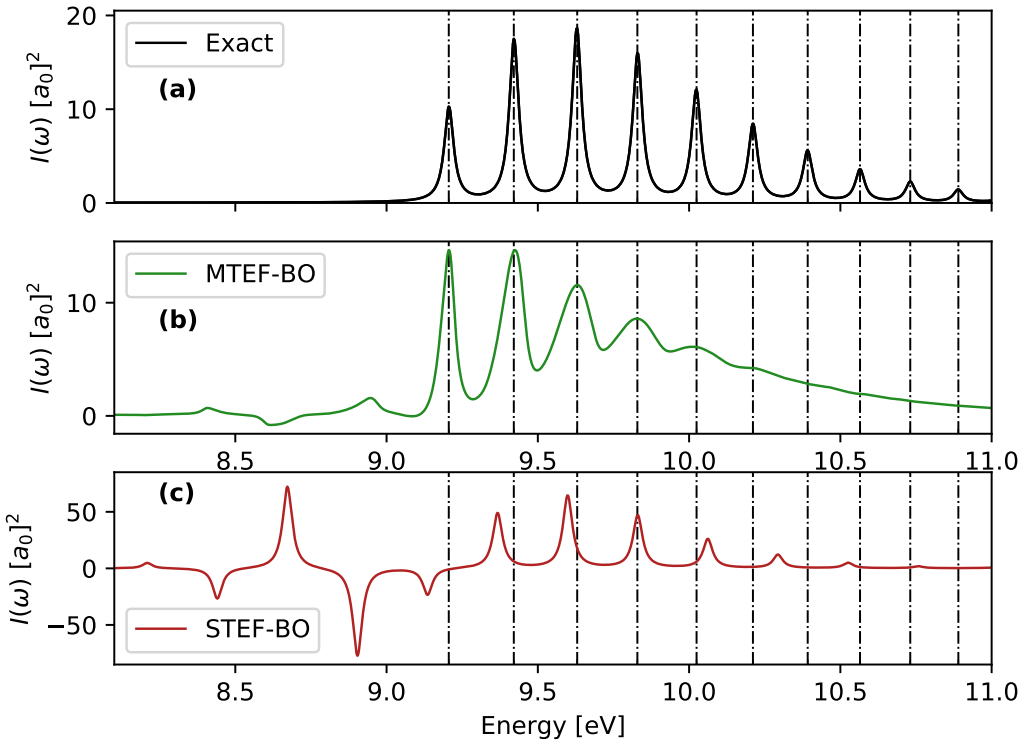
Electronic states solved on grid

Linear Absorption Spectra: MTEF-BO



Lively, K.; Albareda, G.; Sato, S.; Kelly, A.; Rubio, A. (Under review)

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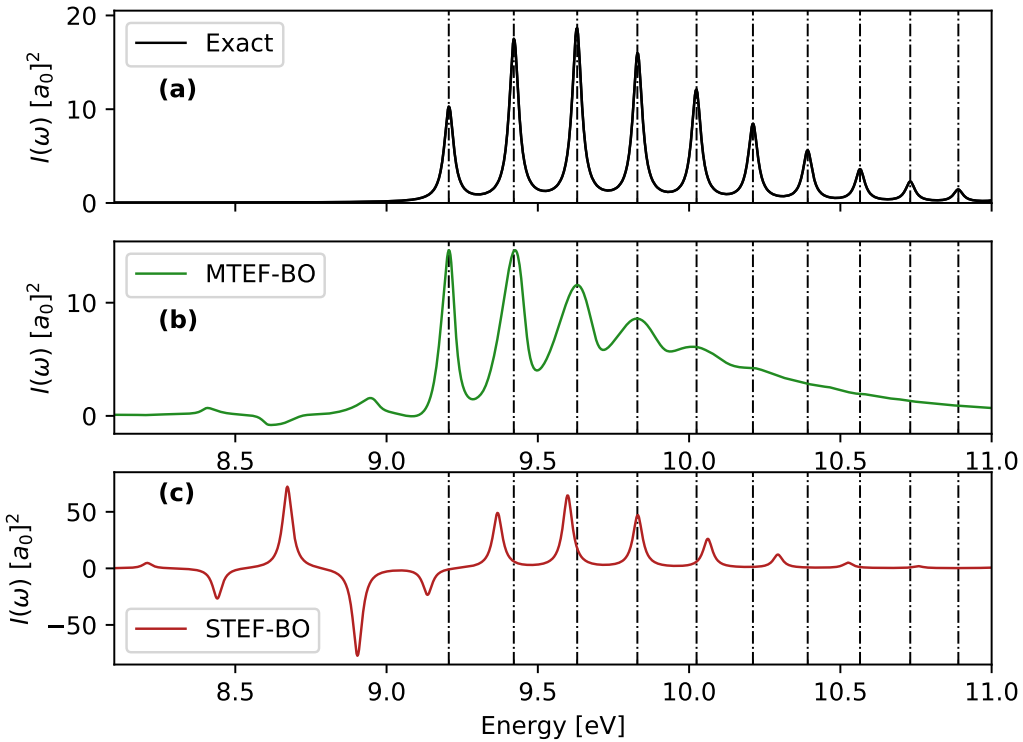

- Nuclei evolve on mean field of BO surfaces

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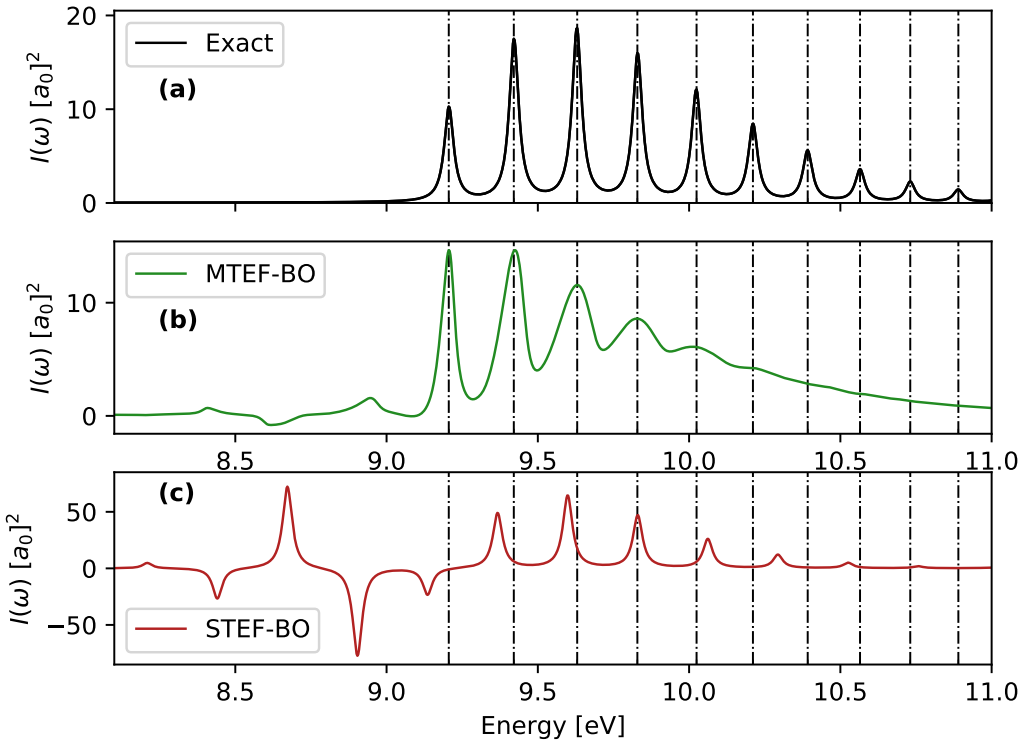

- Nuclei evolve on mean field of BO surfaces
- Separate calculations for each electronic transition

Lively, K.; Albareda, G.; Sato, S.; Kelly, A.; Rubio, A. (Under review)

Linear Absorption Spectra: MTEF-kick

Non BO Option with : MTEF

MTEF-kick

$$I(\omega) \propto \frac{\omega}{\kappa} \Im \int dt e^{i\omega t} \int dR dP \, \langle \hat{\mu}(t) - \hat{\mu}(t=0) \rangle$$

Yabana, K.; Bertsch, G *Physical Review B* 1996, 54

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- All electronic transitions at once

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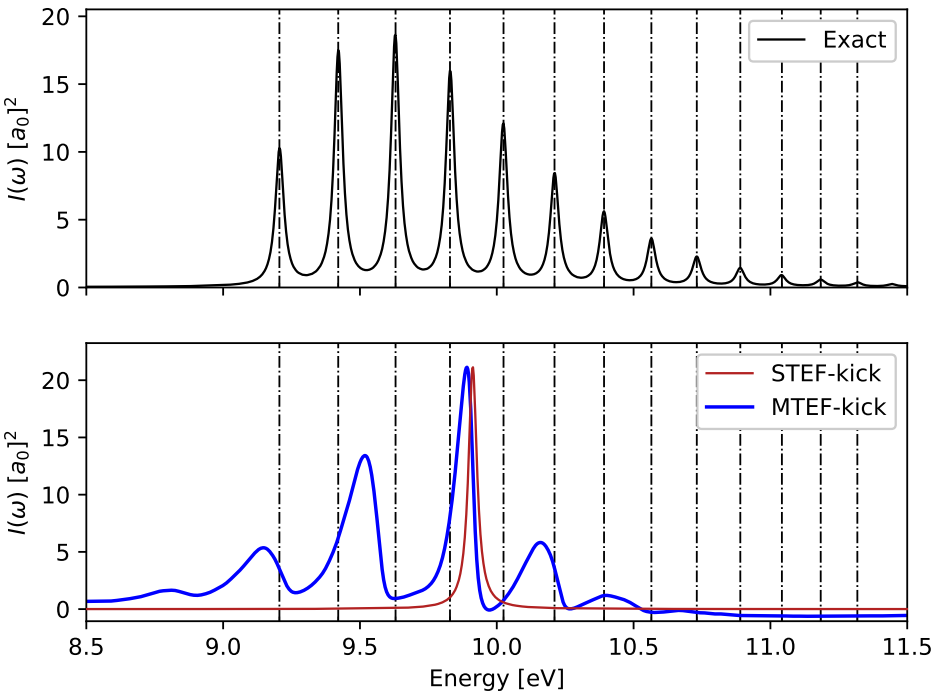
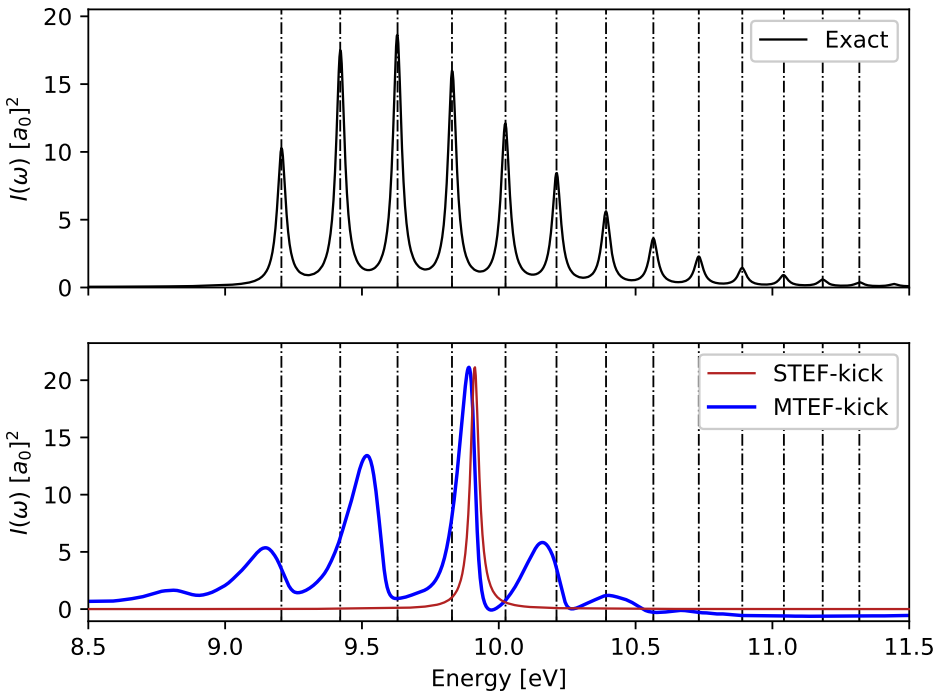


$S_2 \leftarrow S_0$

Linear Absorption Spectra: MTEF-kick



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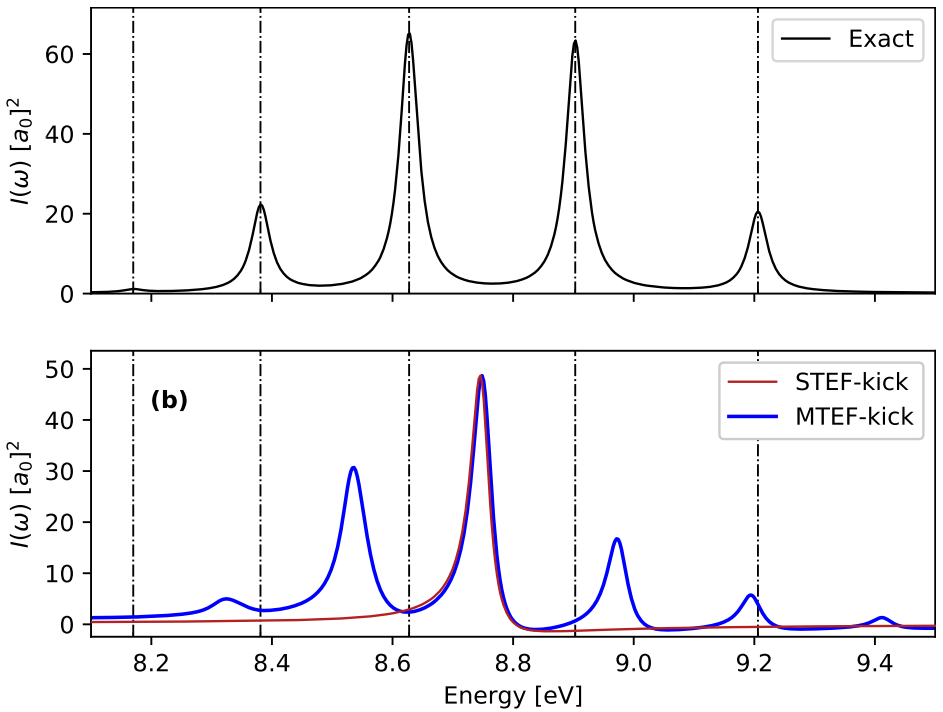

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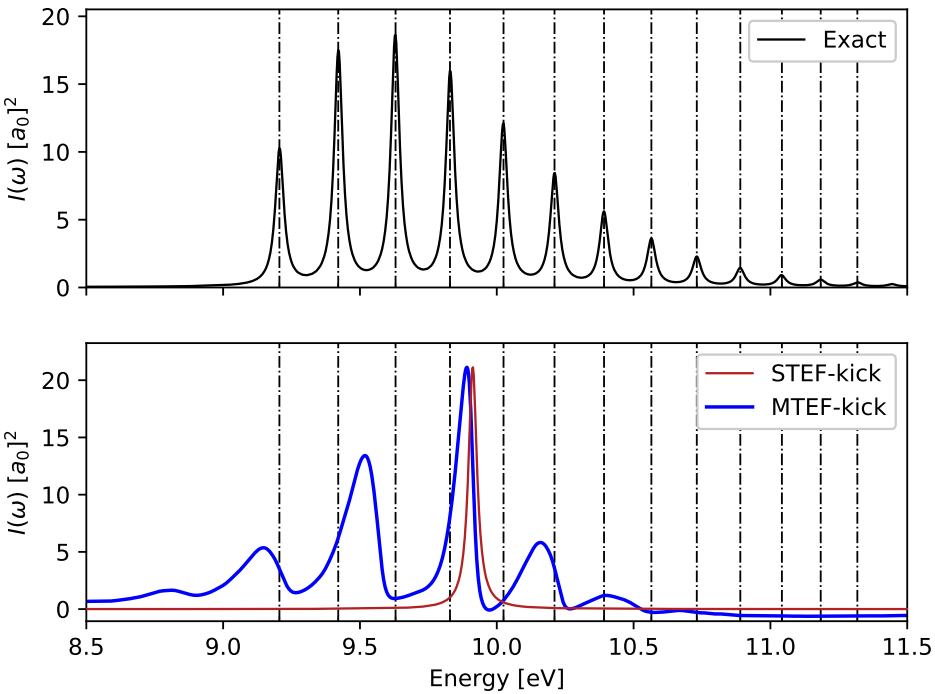

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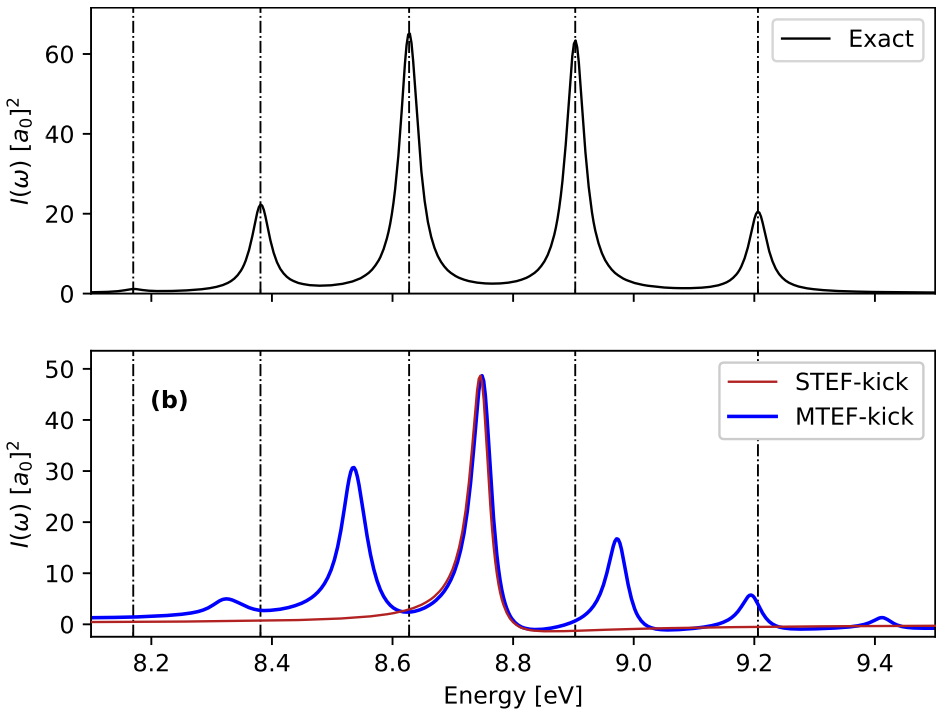

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- Vibronic character

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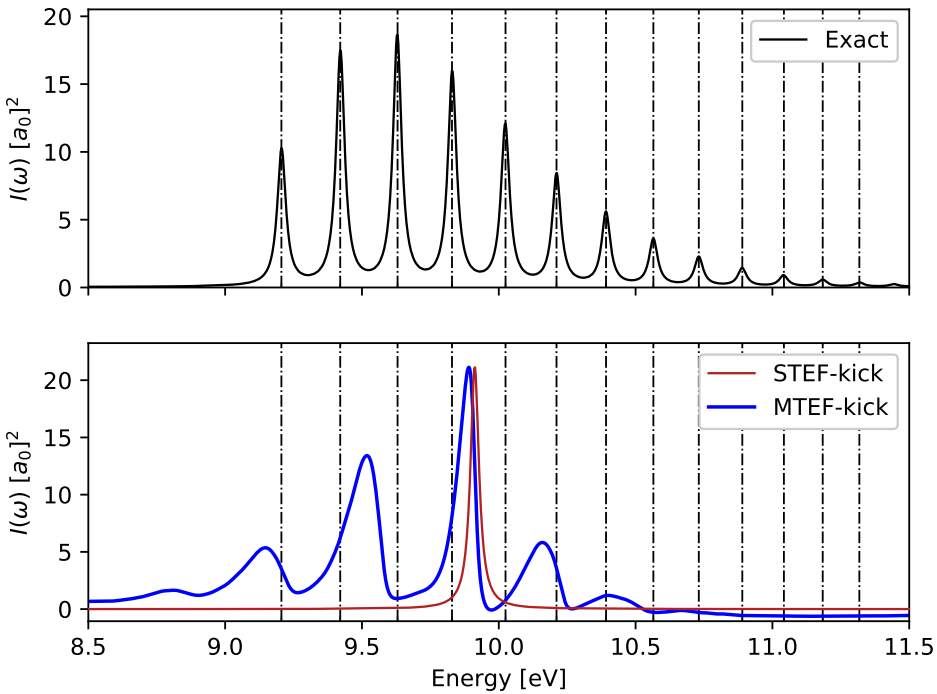

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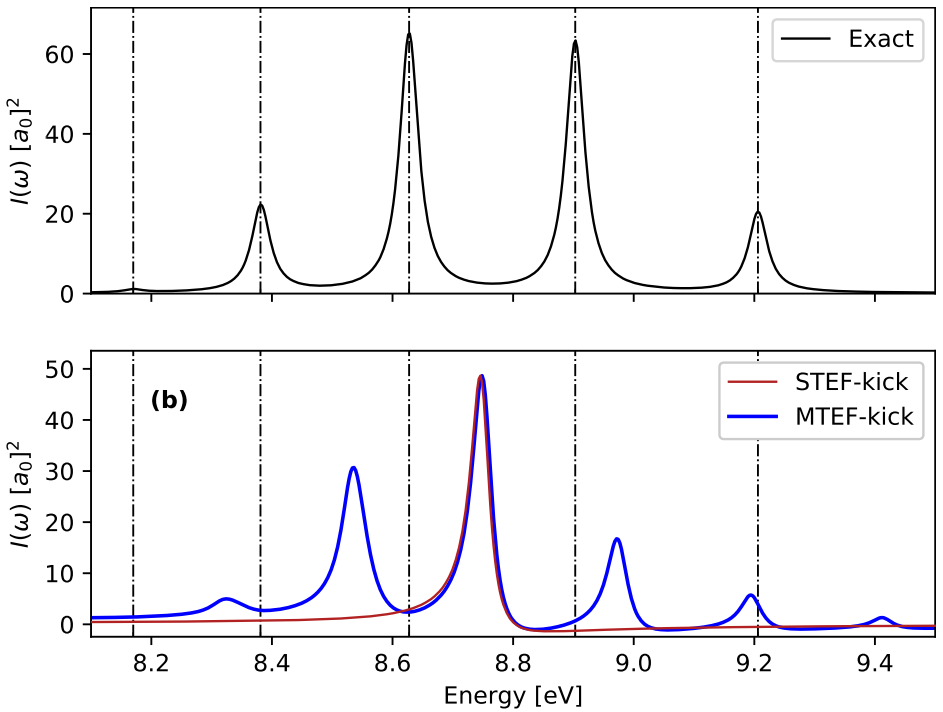


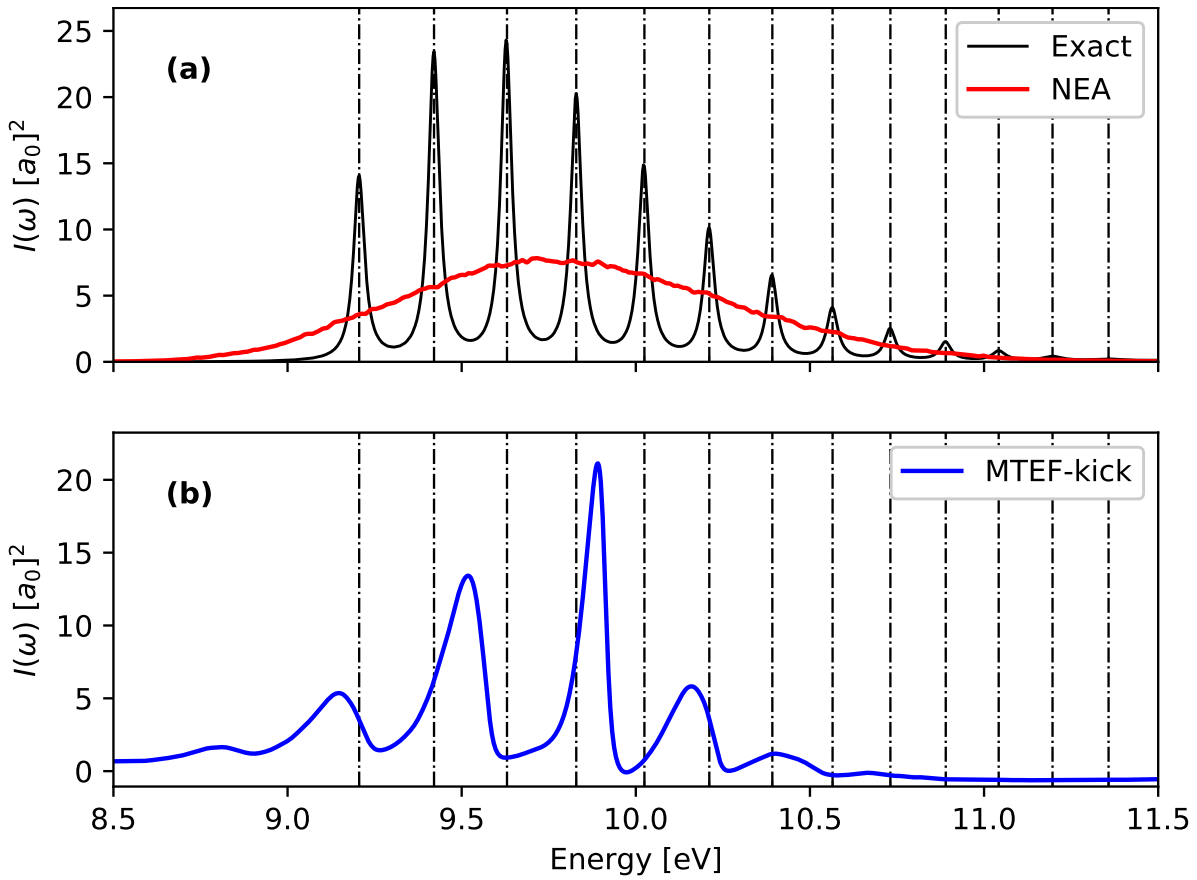
$S_0 \leftarrow S_2$

- Vibronic character
- Mean field dominated by initial electronic state

Dynamics is More than Statistics

NEA[1]

Static nuclei sampled from the Wigner distribution.

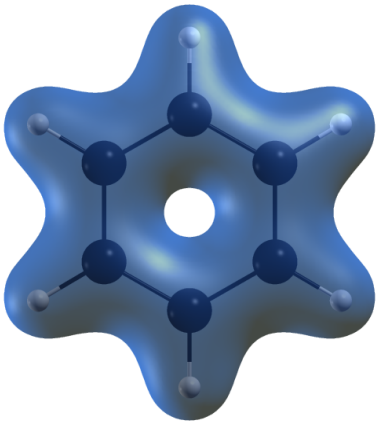


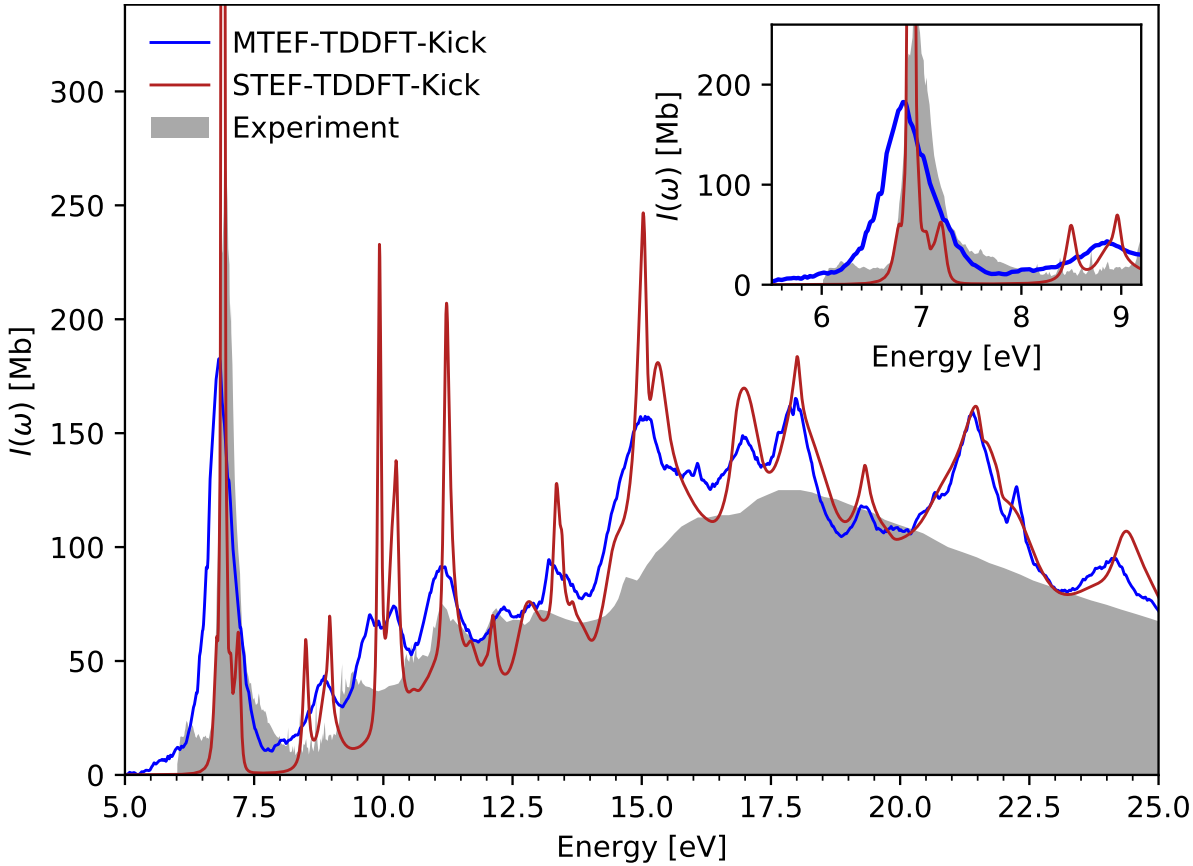
[1] Crespo-Otero, R.; Barbatti, M. *Theoretical Chemistry Accounts* 2012, 131

Application to Ab-initio System: Benzene

TDDFT

$$\phi(r) \rightarrow \rho_e(r)$$





Lively, K.; Albareda, G.; Sato, S.; Kelly, A.; Rubio, A. (Under review)

Interacting Conditional Wavefunction Ansatz

Wavefunction Ansätz

- **Interacting Conditional Wavefunctions**

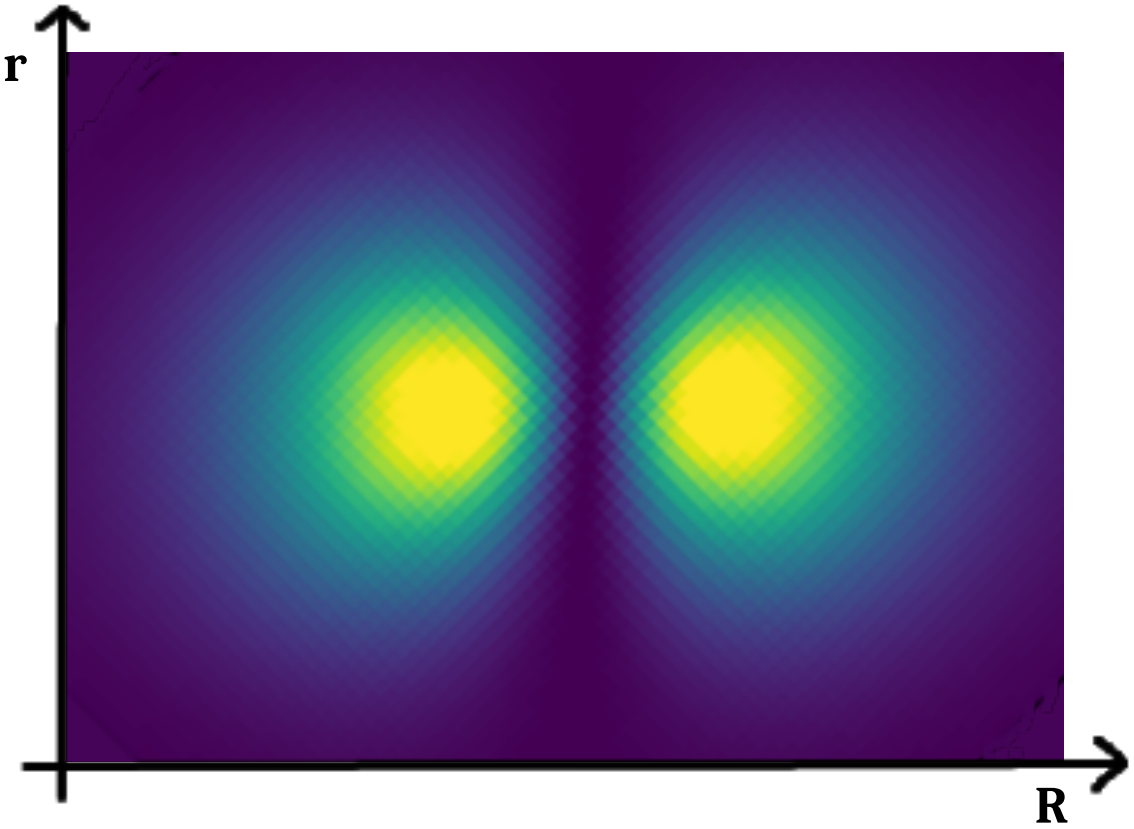
Mixed-Quantum Classical

- **Real Space Multi-trajectory Ehrenfest**

Interacting Conditional Wavefunction Ansatz

Conditional Wavefunctions (CWFs)

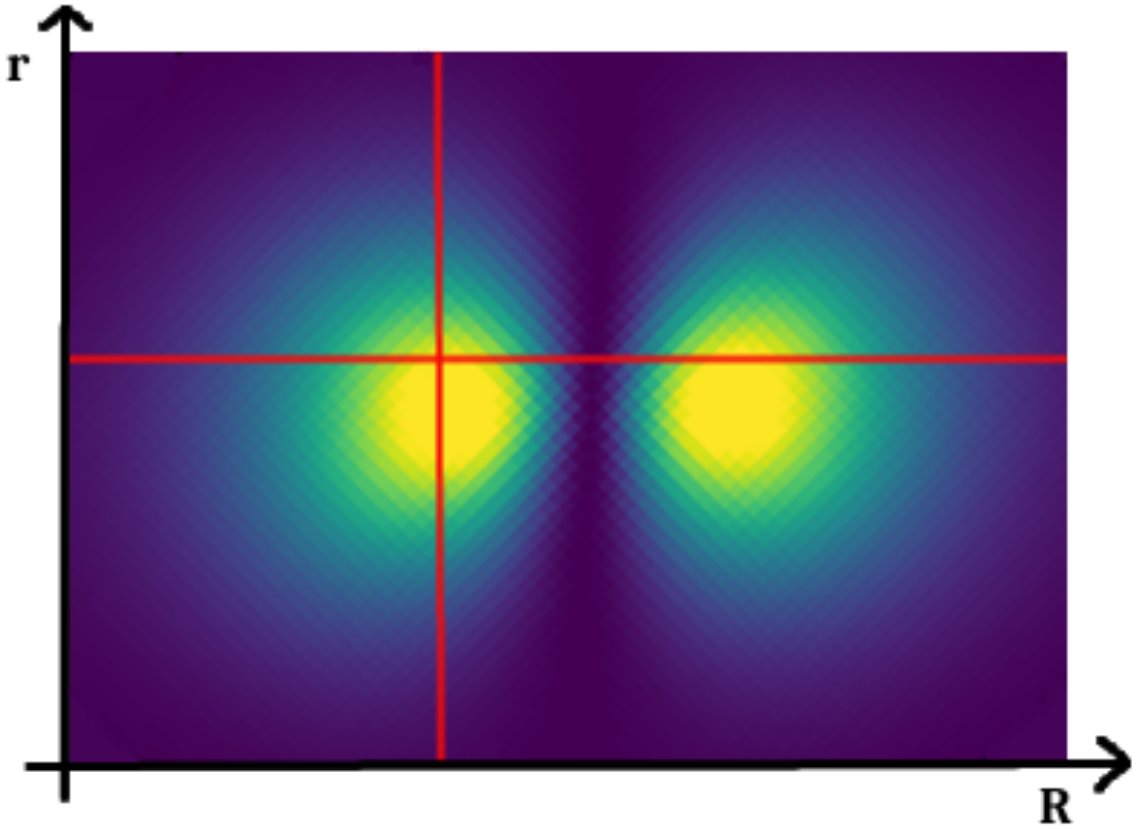
$\Psi(r, R)$



Interacting Conditional Wavefunction Ansatz

Conditional Wavefunctions (CWFs)

$$\int dr \delta(r - r^{\alpha}) \Psi(r, R)$$
$$\int dR \delta(R - R^{\alpha}) \Psi(r, R)$$



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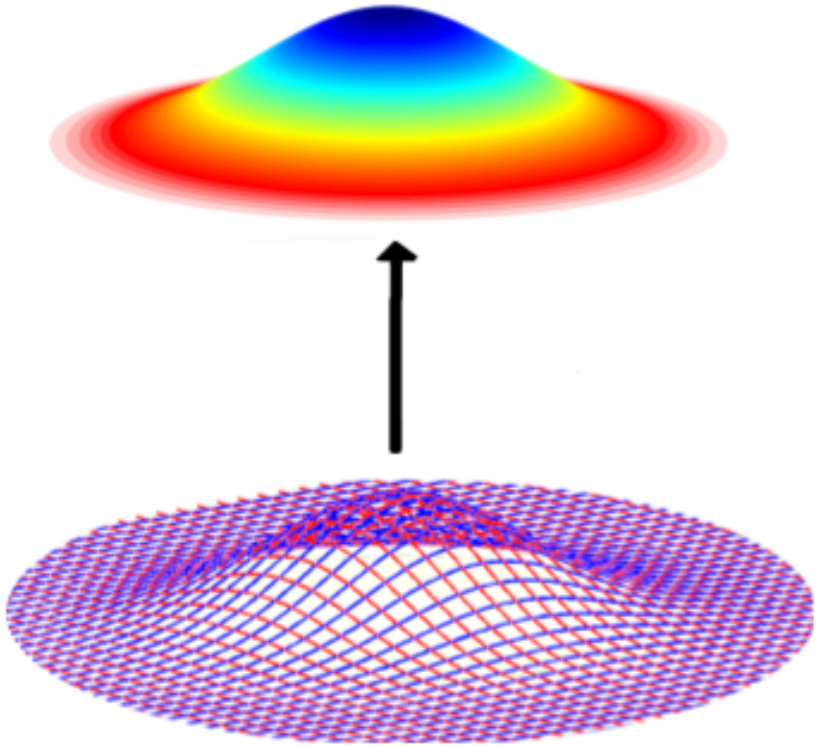

ICWF Ansatz

Conditional Hamiltonians

$$\int dr \delta(r - r^\alpha) H(r, R) = -\frac{\nabla_R^2}{2M} + V_{nn}(R) + V_{en}(R, r^\alpha) + \eta(R, r^\alpha)$$

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ICWF Ansatz

Conditional Hamiltonians

$$h_n(R, r^\alpha) = -\frac{\nabla_R^2}{2M} + V_{nn}(R) + V_{en}(R, r^\alpha)$$

$$h_e(r, R^\alpha) = -\frac{\nabla_r^2}{2} + V_{ee}(r) + V_{en}(r, R^\alpha)$$

ICWF Ansatz

Variational ICWF

$$h_e(r, R^\alpha)\phi_e^\alpha(r) = \epsilon_e^\alpha \phi_e^\alpha(r)$$

- Parameter free static basis

ICWF Ansatz

Variational ICWF

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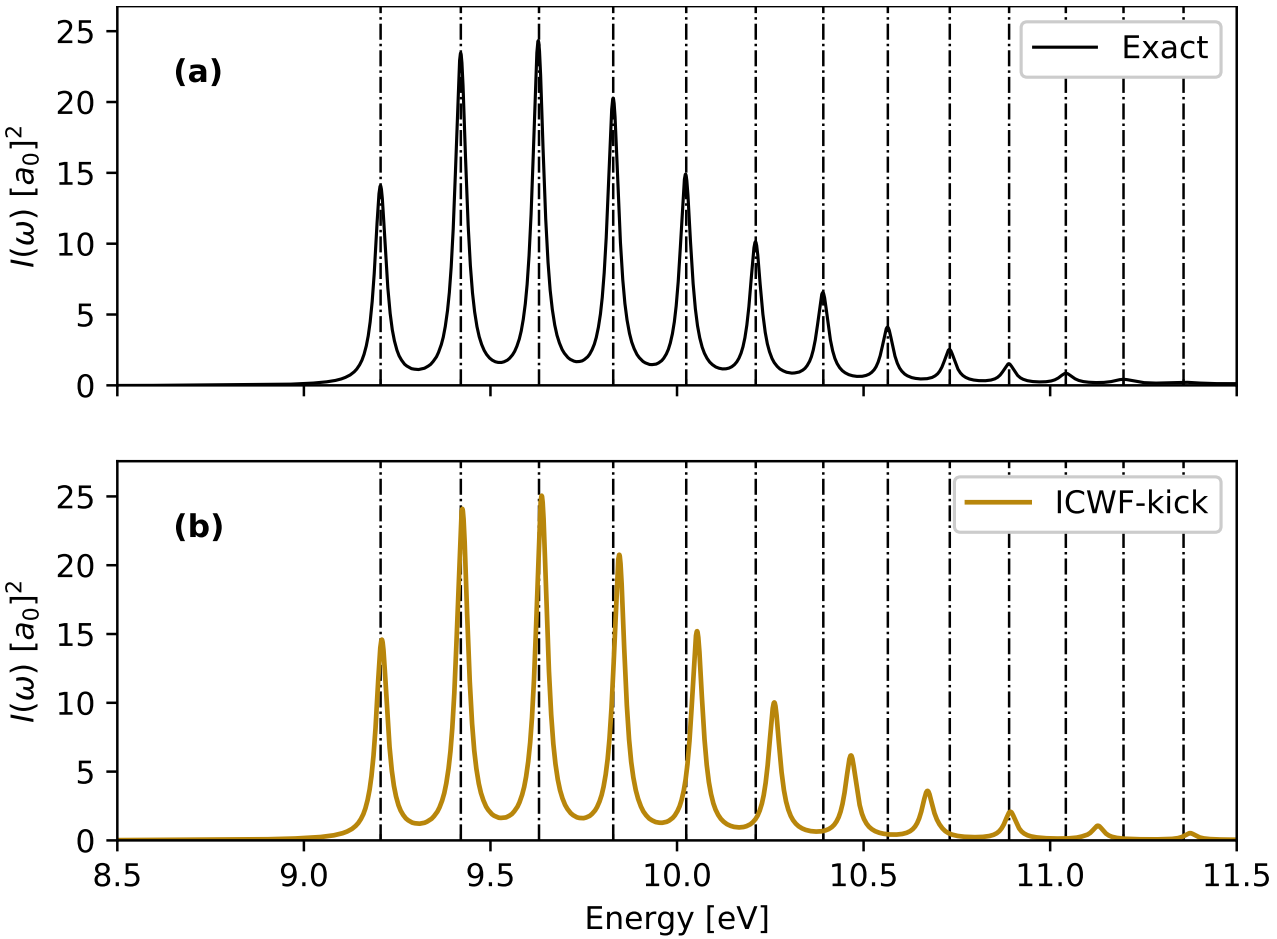
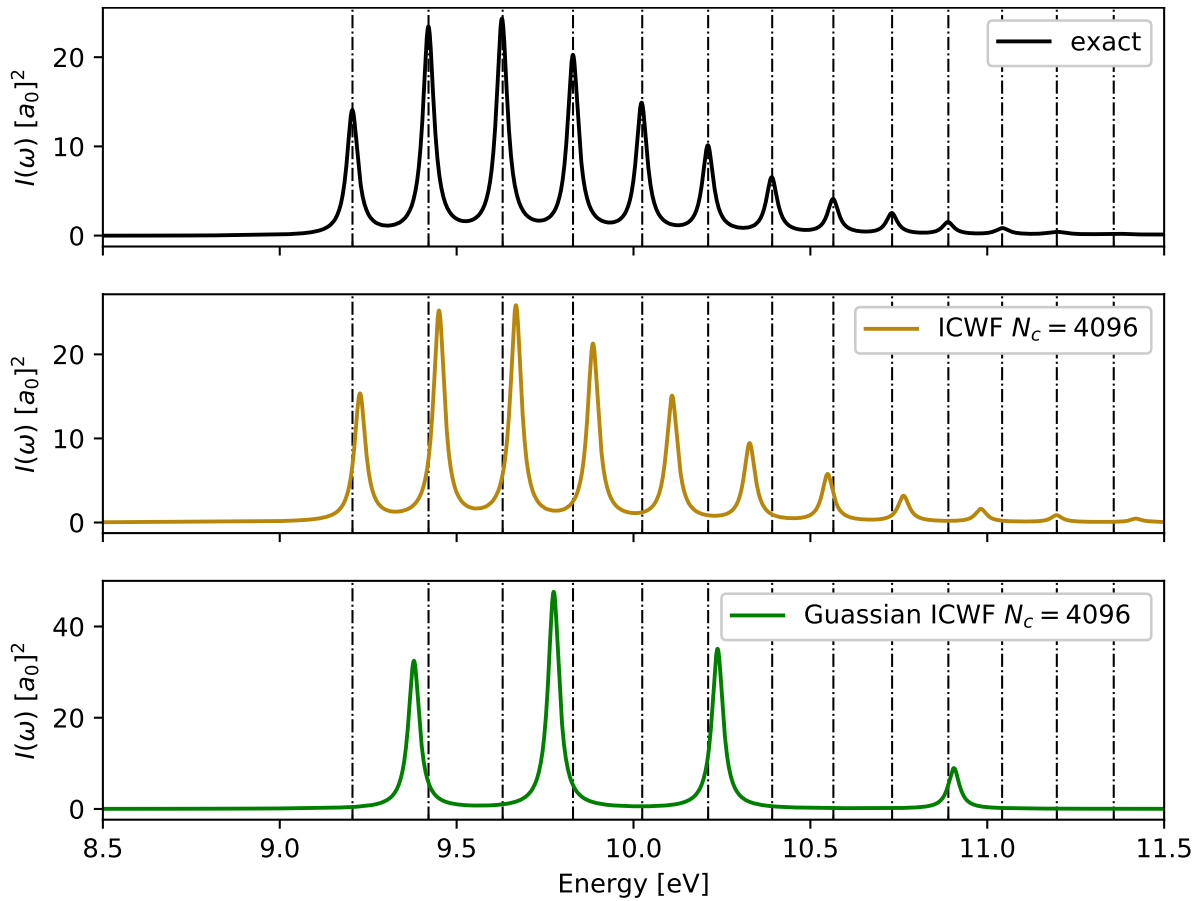
ICWF-kick



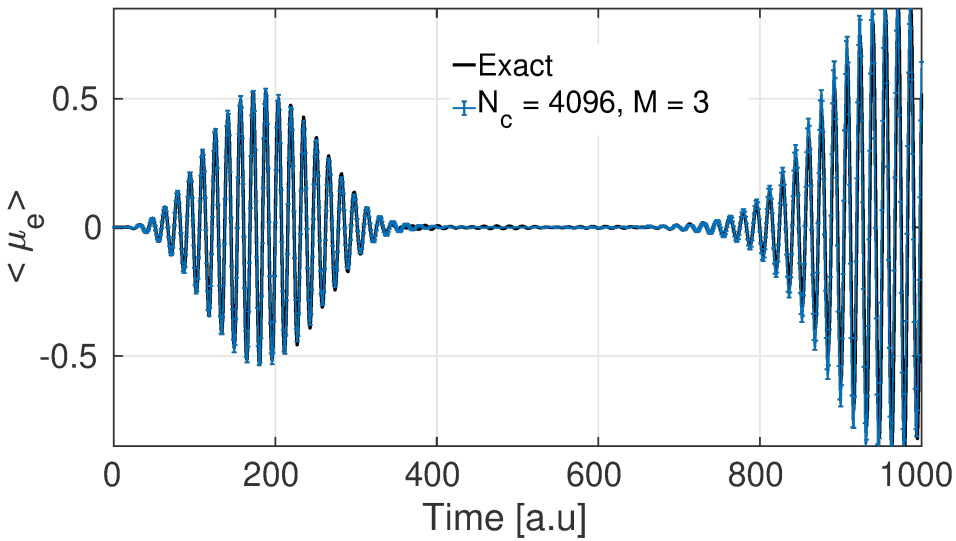
$$S_2 \leftarrow S_0$$

Utility of Conditional Wavefunctions

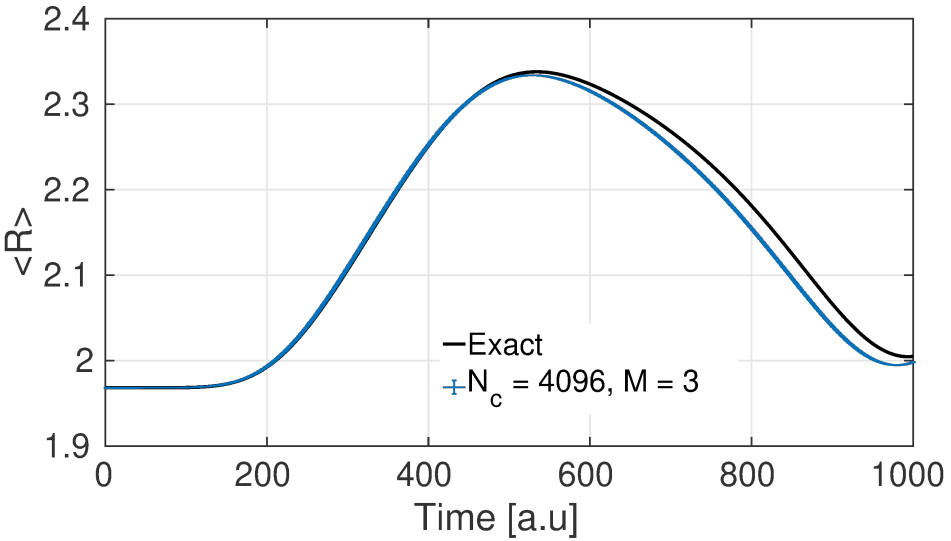
Use gaussian basis with optimized uniform widths instead of CWFs



ICWF under a driving laser field



$\langle \Delta\mu(t) \rangle$



$\langle \Delta R(t) \rangle$

Albareda, G.; Lively, K.; Kelly, A.; Sato, S.; Rubio, A. (In Preparation)

Summary

- Vibronic effects without BO quantites

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  - Accuracy dependent on electron-nuclear dynamics method

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  - Accuracy dependent on electron-nuclear dynamics method
- MTEF captures non-trivial electron-nuclear correlation
  - If you can do one trajectory, do many!
- Foundation for non-perturbative electron-nuclear dynamics without reliance on BO surfaces

Future Directions

- Periodic systems

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Acknowledgements

Dr. Angel Rubio
Dr. Aaron Kelly
Dr. Guillermo Albareda

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Struktur und Dynamik der Materie

Dr. Shunsuke Sato

筑波大学
University of Tsukuba

Thanks for Your Kind Attention!

Questions?

Appendix: Wigner Transform

$$\hat{\rho}_W(R,P) = \int dX e^{-i\frac{PX}{\hbar}} \langle R + X/2|\hat{\rho}|R - X/2\rangle$$

Given QHO ground state: $\chi(R) = \frac{1}{\sqrt[4]{\pi}}\sqrt{\frac{m\omega}{\hbar}}e^{-\frac{m\omega x^2}{4\hbar}}$

$$\chi(R) \rightarrow W(R,P) = \frac{2}{h}\exp(-\frac{P^2}{m\omega\hbar} - \frac{m\omega R^2}{\hbar})$$