Simulation of fast electron dynamics using an Ehrenfest approach with DD-vMCG (QuEh): Application to charge migration driven nuclear dynamics

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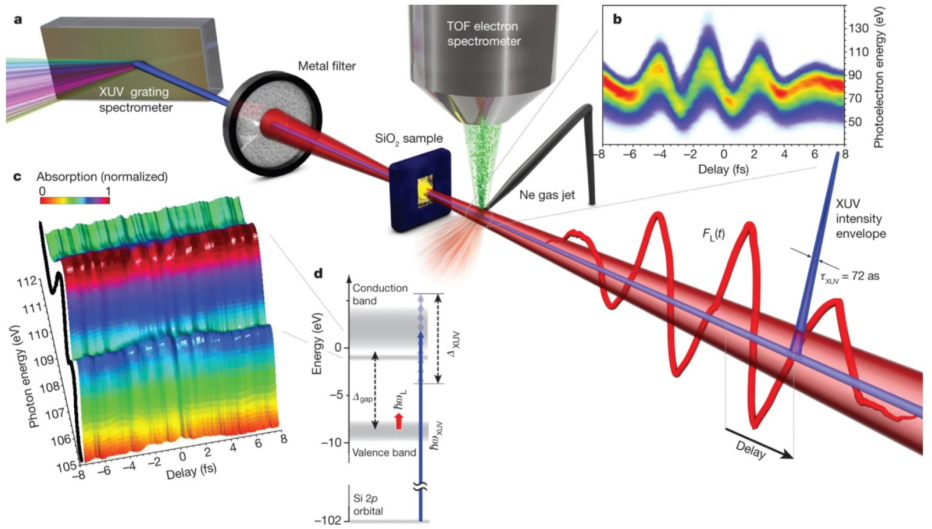
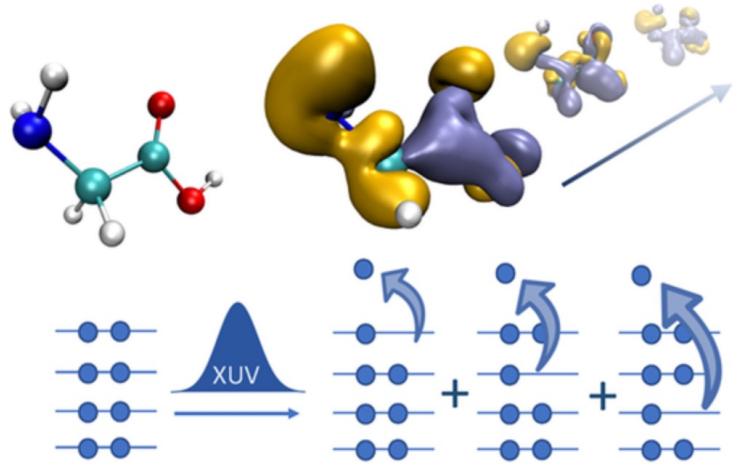
Motivation

Attosecond spectroscopy:

- Pump pulse from HHG or XFEL source
  - ⇒Photoionize the molecule
  - ⇒Generate electronic wavepacket on a "coherent" superposition of cationic states

- Subsequent (probe) pulse can affect the dynamics outcome
  - ⇒Different photoproducts observed
  - ⇒Time-delay and CEP offer potential control scheme





Schultze *et al.*, *Nature*, 493, **2013**, 75-78
Nisoli *et al.*, *Chem. Rev.*, 117, **2020**, 10760-10825
Schüppel *et al.*, *J. Chem. Phys.*, 153, **2020**, 224307
Palacios *et al.*, *WIREs Comput. Mol. Sci.*, 10, **2020**, e1430

Charge Migration

Simulating Intramolecular Charge Migration on Attosecond timescale (SICMA):

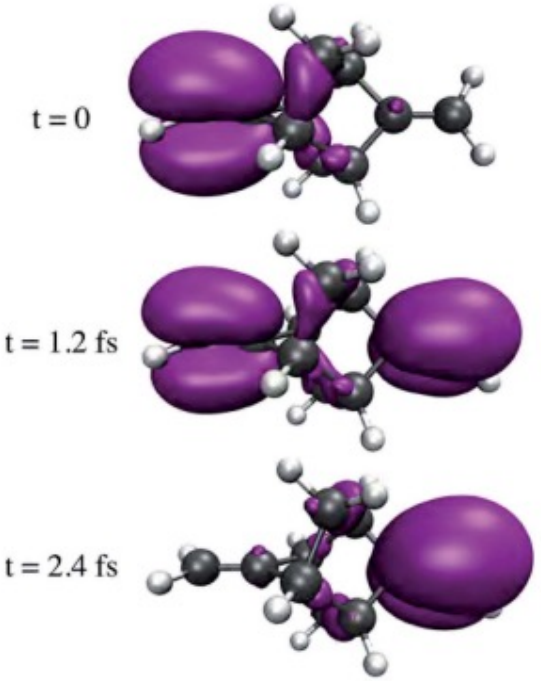
- Coherent superposition of state <-> Localized hole
- Non-stationary wavefunction <-> Electron dynamics

How does the electron dynamics affect the nuclear dynamics?
Control of the correlated motion ? (charge-directed reactivity)

Design specific superposition of states?

How long is the coherence?

How pulse affect the coupled nuclear-electron motion?



Vacher *et al.*, *Faraday Discuss.*, 194, **2016**, 95-115.

Nonadiabatic Dynamics

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

Ansatz to solve the TDSE

Born-Huang

$$\Psi(\boldsymbol{R},\boldsymbol{r},t) = \sum_s A_s(t)\,\chi_s(\boldsymbol{R},t)\,\psi_s(\boldsymbol{r};\boldsymbol{R})$$

- Set of time-independent PES
- Gradient of adiabatic/diabatic electronic states

Exact Factorization

$$\Psi(\boldsymbol{R},\boldsymbol{r},t) = \chi(\boldsymbol{R},t)\,\psi(\boldsymbol{r},t;\boldsymbol{R})$$

- Time-dependent PES
- Gradient of an effective single electronic state

Agostini and Curchod, *WIREs Comput. Mol. Sci.*, 9, **2019**, e1417.
Ibele *et al.*, *J. Phys. Chem. A*, 126, **2022**, 1263-1281.
Abedi *et al.*, *Phys. Rev. Lett.*, 105 **2010**, 123002.

DD-vMCG

$$\chi(\boldsymbol{R},t) = \sum_j \sum_s A_{j,s}(t)\, g_j(\boldsymbol{R},t)\,|s\rangle$$

- Expand the nuclear wavefunction as a sum of frozen width Gaussian wavepackets (in the single-set formalism)

QUANTICS

A suite of programs for molecular QUANTum dynamICS simulations.

Variational trajectories

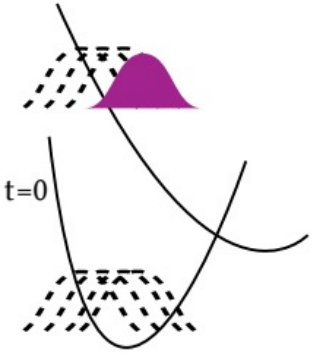
from the Dirac-Frenkel variational principle:

$$i\dot{A}_j = \sum_{lm} [S_{jl}]^{-1}(H_{lm} - i\tau_{lm})A_m,$$

$$i\dot{\boldsymbol{\Lambda}} = \boldsymbol{X} + \boldsymbol{C}^{-1}\boldsymbol{Y}_R$$

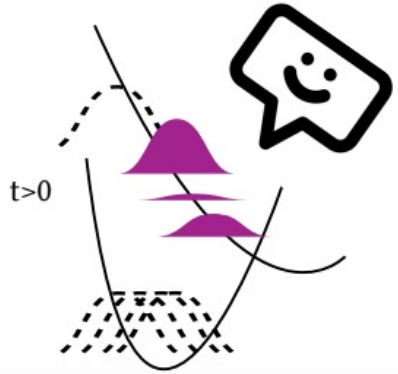
optimal set of gaussian parameters and coefficients

No sampling of initial conds



vertical projection of ground state HO eigenstate

Not adaptive nor independent gaussian basis



Database of Electronic Structure points

- No need to repeat time-consuming QC calculations
- Interpolation between points, Hessian Update
- Allows faster convergence towards number of gaussians

Credit: Dr. Sandra Gómez

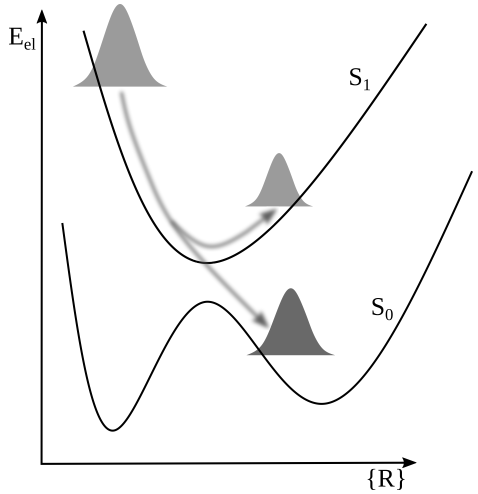
Worth *et al.*, *Mol. Phys.*, 106, **2008**, 2077-2091.
Worth, *Comp. Phys. Comm.*, 248, **2020**, 107040.

QuEh

Quantum-Ehrenfest method:

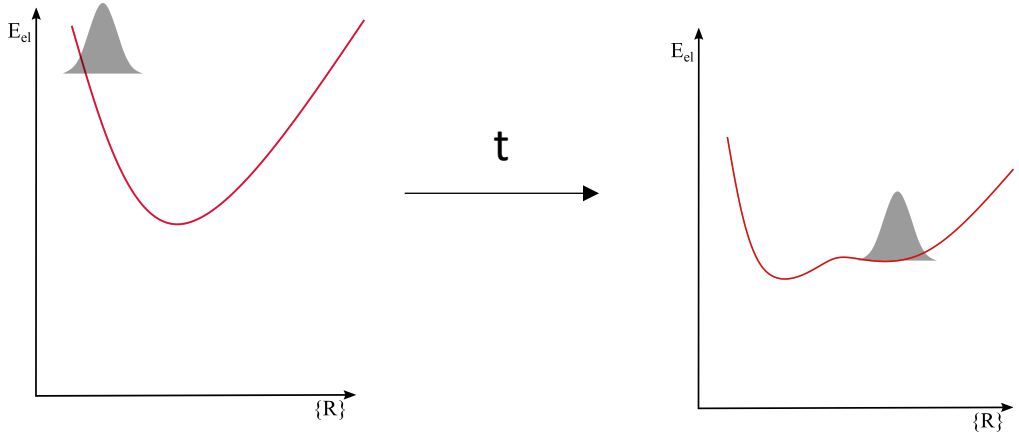
$$\chi(\boldsymbol{R},t) = \sum_j A_j(t) g_j(\boldsymbol{R},t) \,|j\rangle$$

$$\psi_j(\boldsymbol{r},t;\boldsymbol{R}) = \sum_s c_s(t)\psi_s(\boldsymbol{r};\boldsymbol{R})$$



Equation-of-Motions for electron dynamics:

$$i\dot{c}_s(t) = \sum_t H^{el}_{st} c_t(t)$$



Jenkins *et al.*, *J. Chem. Phys.*, 149, **2018**, 094108.

Electronic Structure Method

PES evaluated with the Complete Active Space Configuration Interaction method (CAS-CI):

- No full orbitals optimization (single step relaxation)
- Arbitrary initial electronic wavefunction
- Local Harmonic Approximation for the Ehrenfest state
- Ehrenfest state propagation within the electronic structure program

Expanding the limits of computational chemistry

External electric field interaction included in the one-electron operator (dipole approximation) : WIP

- Integral evaluated in the AO basis and converted to MO

$$h_{el}(t) = < i|h_0|j > + < i|\vec{r}|j > \cdot \vec{E}(t)$$

Vacher *et al.*, *Theor. Chem. Acc.*, 133, **2014**, 1505.
Tran *et al.*, *J. Chem. Phys.*, 153, **2020**, 031102.

Superposition of States

General solution for the electronic TDSE (2-state problem):

$$\psi(t) = c_1(t)e^{-iE_1(t)t}\phi_1(t) + c_2(t)e^{-iE_2(t)t}\phi_2(t)$$

Time evolution of the density when both state are populated:

$$\begin{aligned}&|\psi(t)|^2 \\ &= |c_1(t)|^2|\phi_1(t)|^2 + |c_2(t)|^2|\phi_2(t)|^2 \\ &+ 2\Re\left(c_1(t)^* c_2(t) e^{i\left(E_1(t)-E_2(t)\right)t}\phi_1(t)^*\phi_2(t)\right)\end{aligned}$$

- Oscillation period depends on energy difference (small energy => longer oscillation time)

Gradient and Symmetry

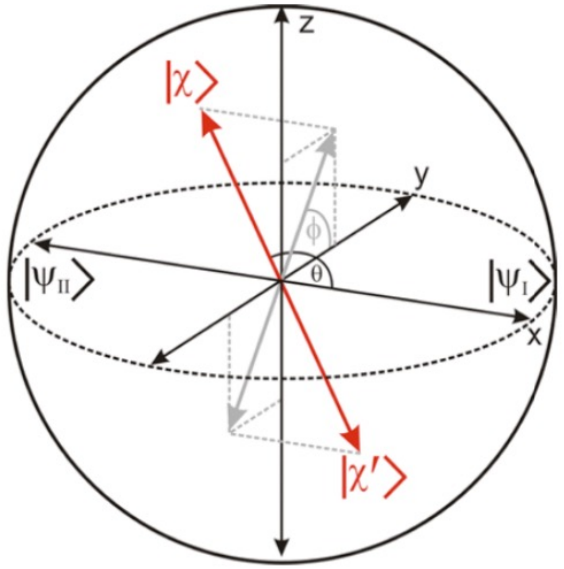
Gradient for a superposition of 2 electronic states *I, II*:

$$\nabla_R \langle \psi_{el}|\hat{H}_{el}|\psi_{el}\rangle \approx \langle \psi_{el}|\nabla \hat{H}_{el}|\psi_{el}\rangle$$

$$\approx \cos^2\left(\frac{\theta}{2}\right) \langle \psi_I|\nabla \hat{H}_{el}|\psi_I\rangle \quad \text{intrastate}$$

$$+ \sin^2\left(\frac{\theta}{2}\right) \langle \psi_{II}|\nabla \hat{H}_{el}|\psi_{II}\rangle \quad \text{intrastate}$$

$$+ \sin(\theta)\cos(\phi) \langle \psi_I|\nabla \hat{H}_{el}|\psi_{II}\rangle \quad \text{interstate}$$



$$\alpha^I \otimes \alpha^{Q_i^{\alpha_i}} \otimes \alpha^{II} = A_{1g}$$

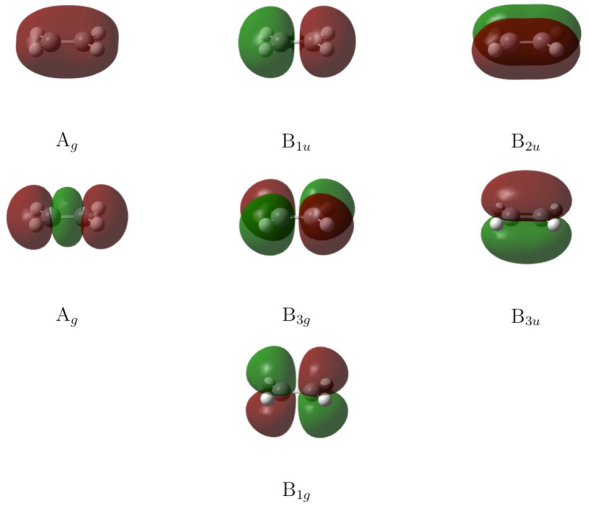
- Dynamics display conical intersection like behaviour
- Upon displacement along non-symmetric mode, symmetry group lower and more motion become symmetry allowed

Meisner *et al.*, *J. Chem. Theor. Comput.*, 11, **2015**, 3115-3122.

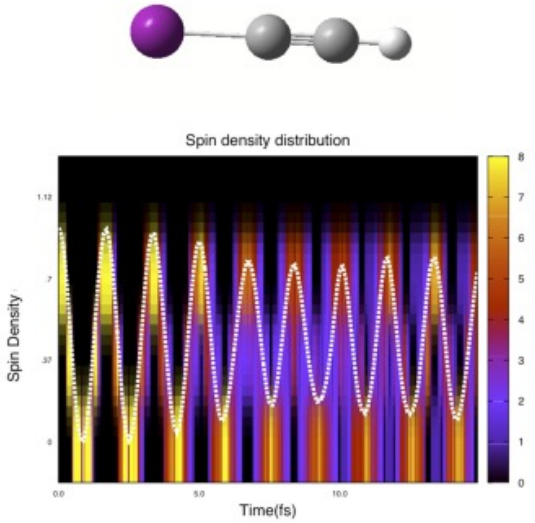
Data Analysis

Electron dynamics

Ref. MO for quasi-diabatic states

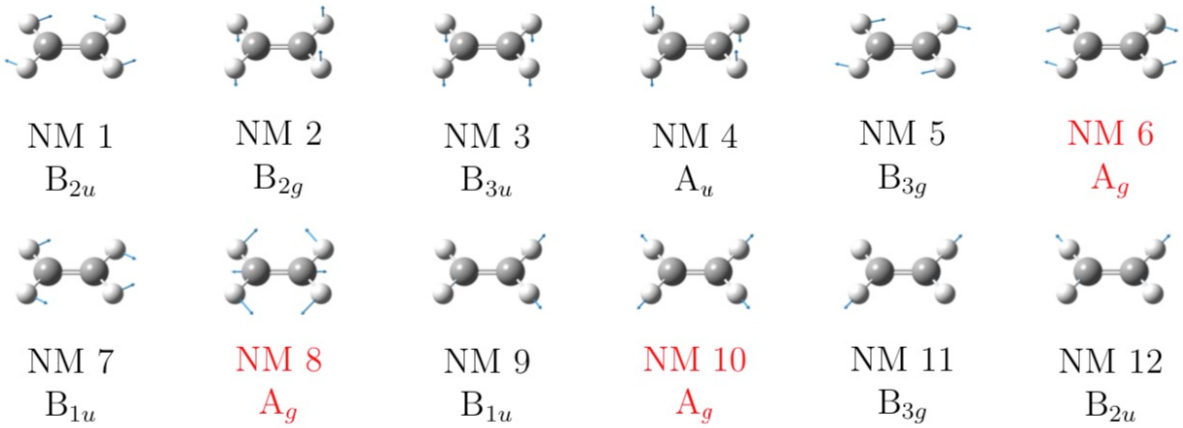


Mulliken spin density



Nuclear dynamics

Normal mode at a ref. geometry

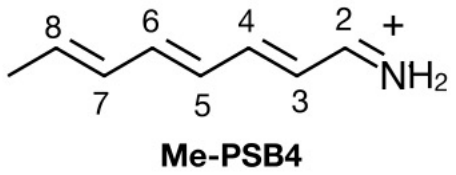


Average calculated with Gross Gaussian Population:

$$\mathrm{GGP}_i^{(s)}(t) = \mathrm{Re}\left\{ \sum_j S_{ij}^{(s)}(t) A_j^{(s)*}(t) A_i^{(s)}(t) \right\}$$

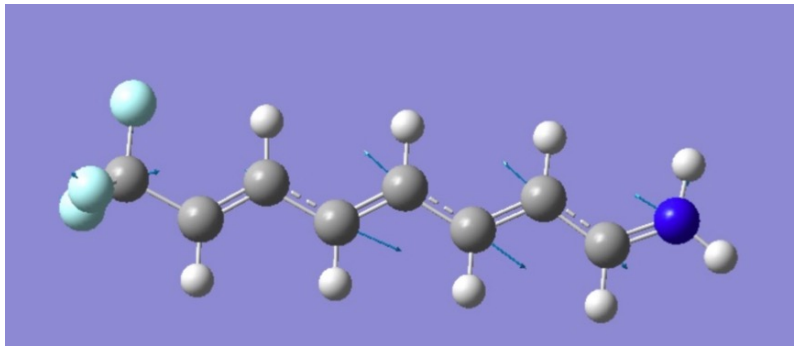
Polyak *et al.*, *Int. J. Quantum Chem.*, 118, **2018**, e25559.
Jenkins *et al.*, *J. Chem. Phys.*, 149, **2018**, 094108.
Allan *et al.*, *J. Phys. Chem. A*, 114, **2010**, 8713-8729.

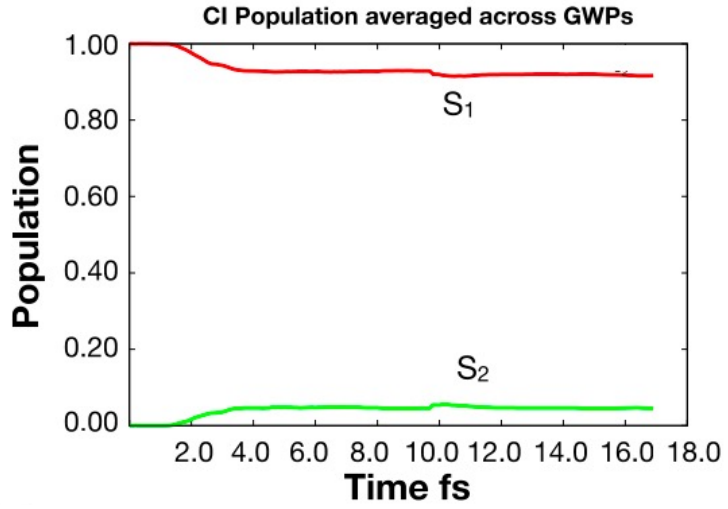
Retinal Protonated Schiff Base

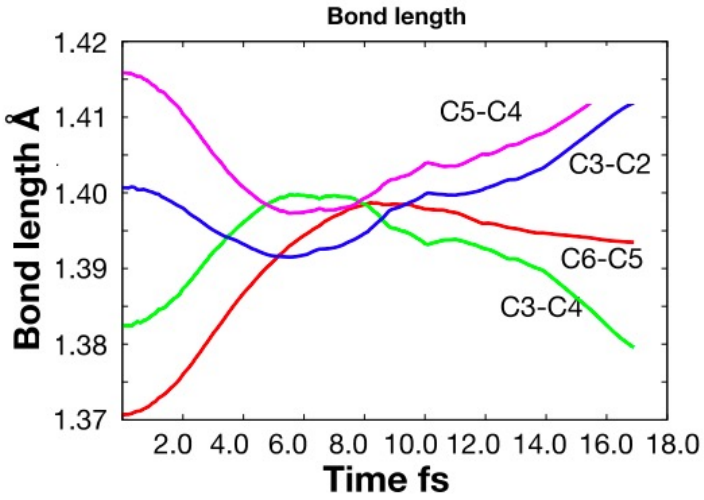


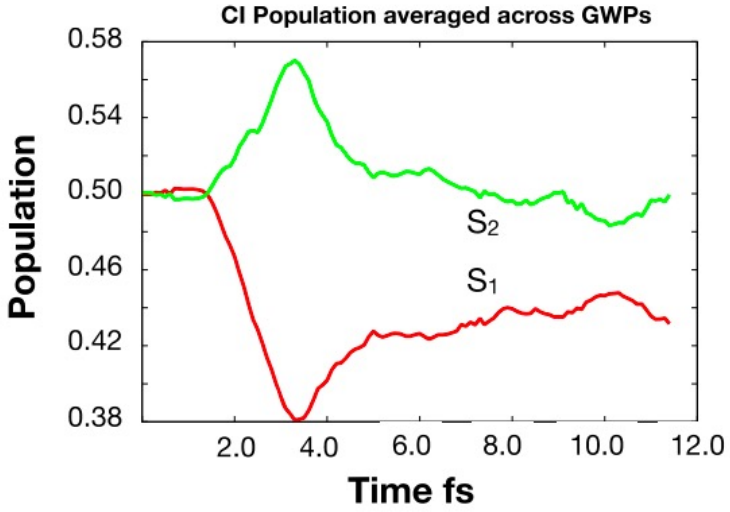
Me-PSB4

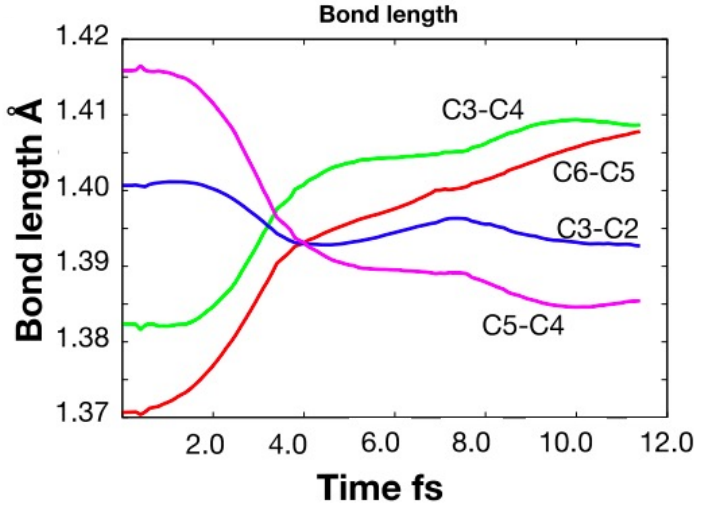
Initial gradient for mix S_2/S_1





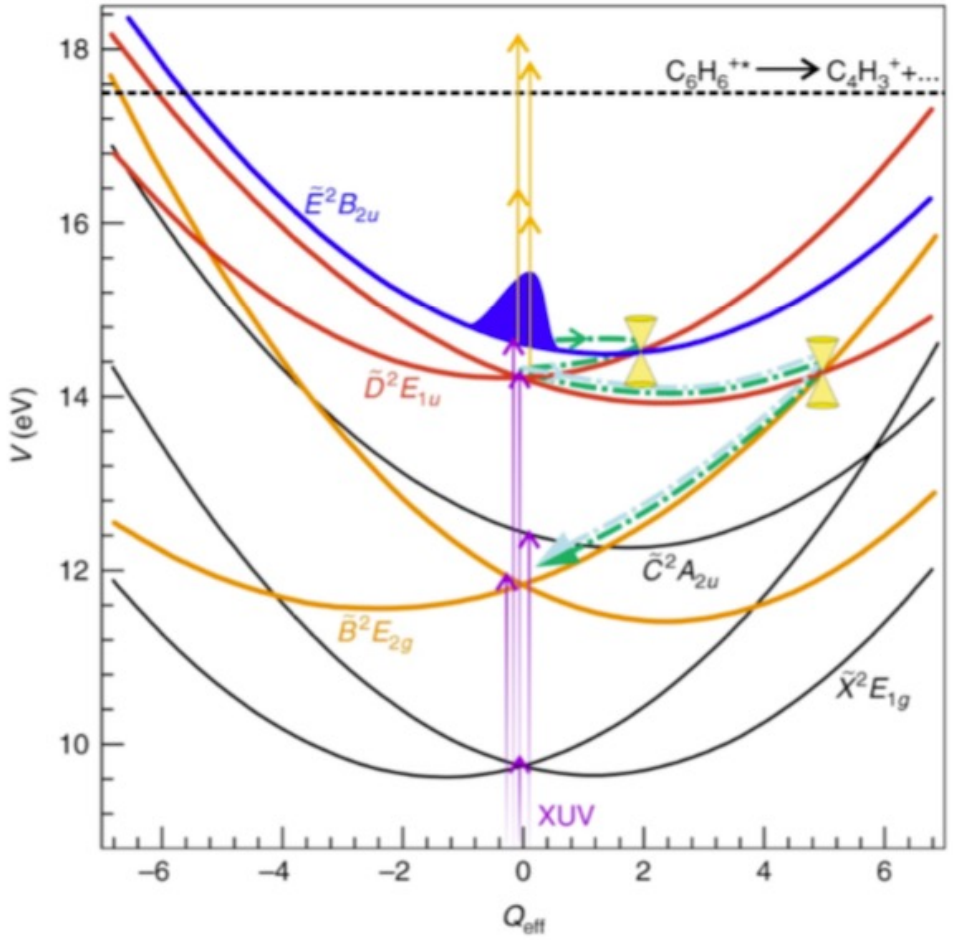




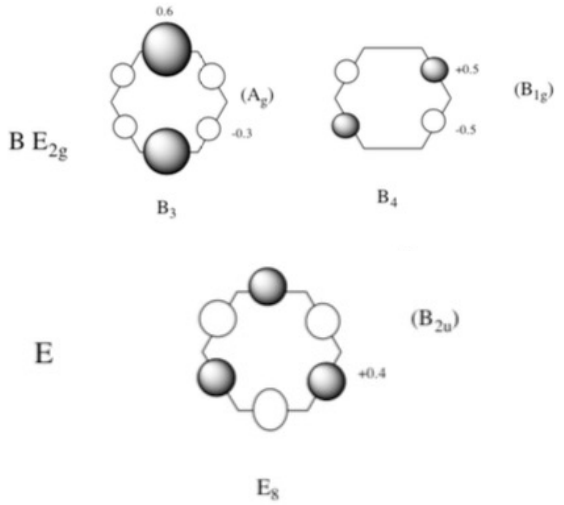


Olivucci *et al.*, *J. Chem. Phys. Lett.,* 12, **2021**, 5639-5643.

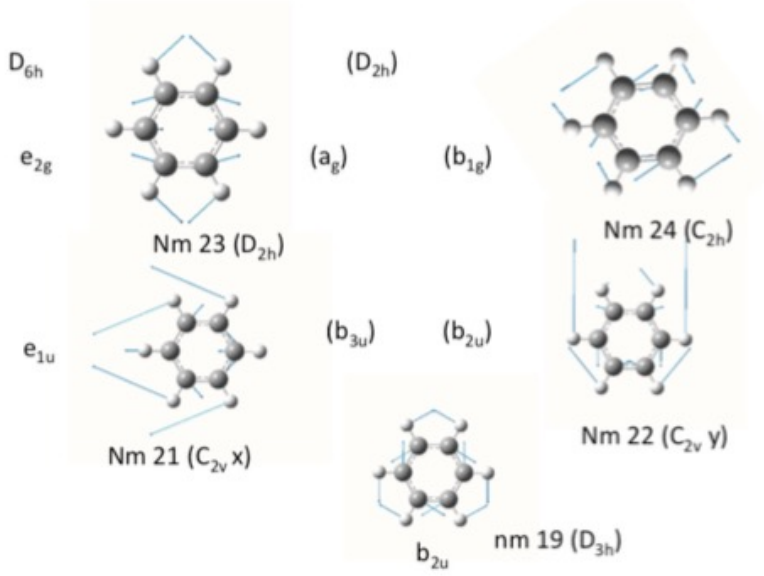
Benzene cation



Electronic state



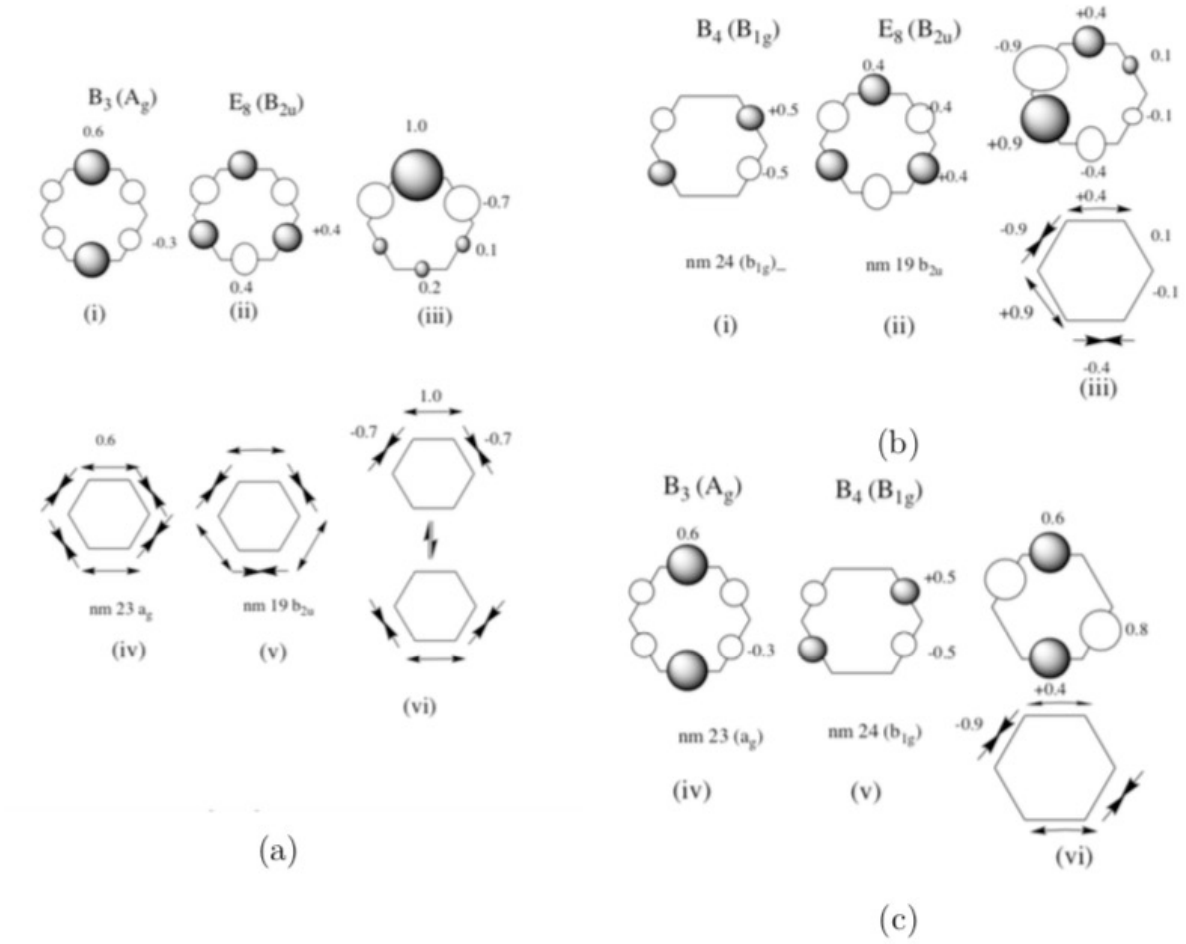
Normal mode



Galbraith *et al.*, *Nat. Commun.*, 8, **2017**, 1018

Benzene cation

E/B symmetry analysis

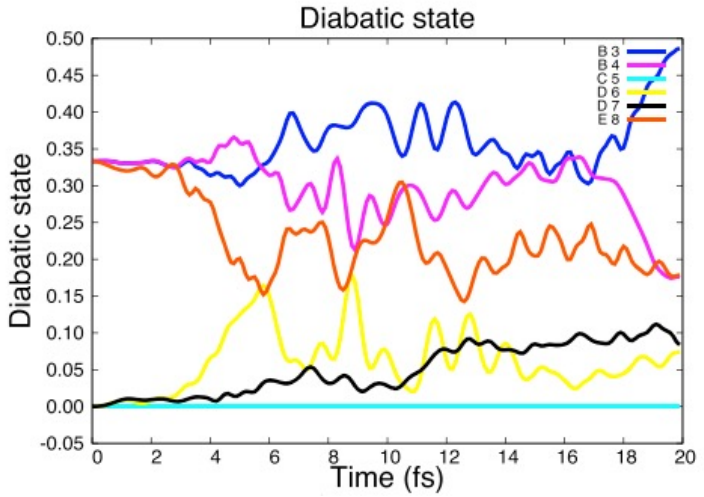


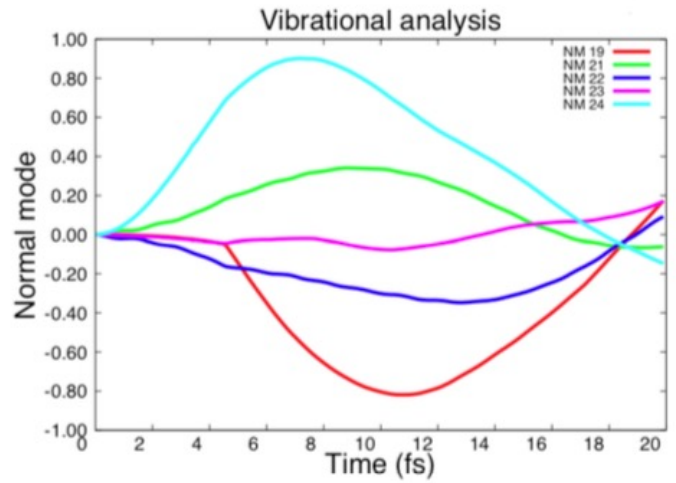
Tran *et al., Commun. Chem.*, 4, **2021**, 48.

Benzene cation

Symmetry analysis

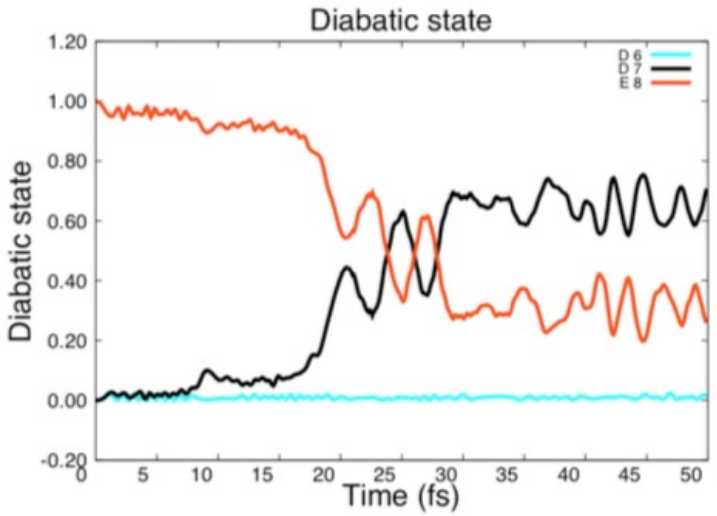
	States	electronic coupling	electron dynamics
E/B mix	E8 B3	19 22	19 23
	E8 B4	21	19 24

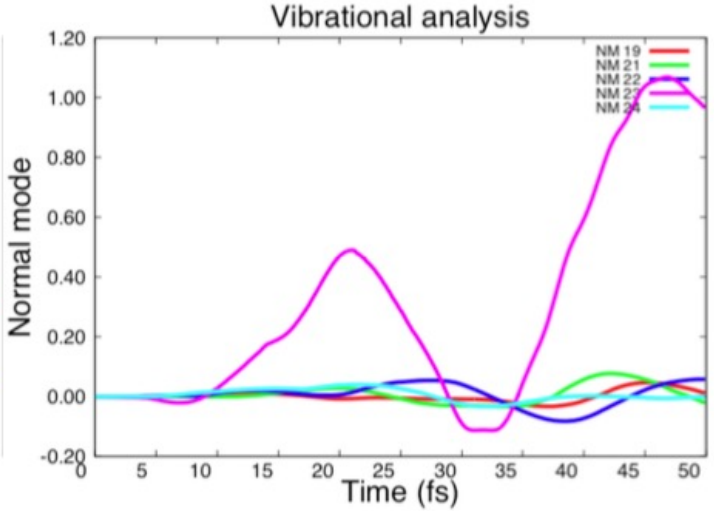




E only

Totally symmetric motion



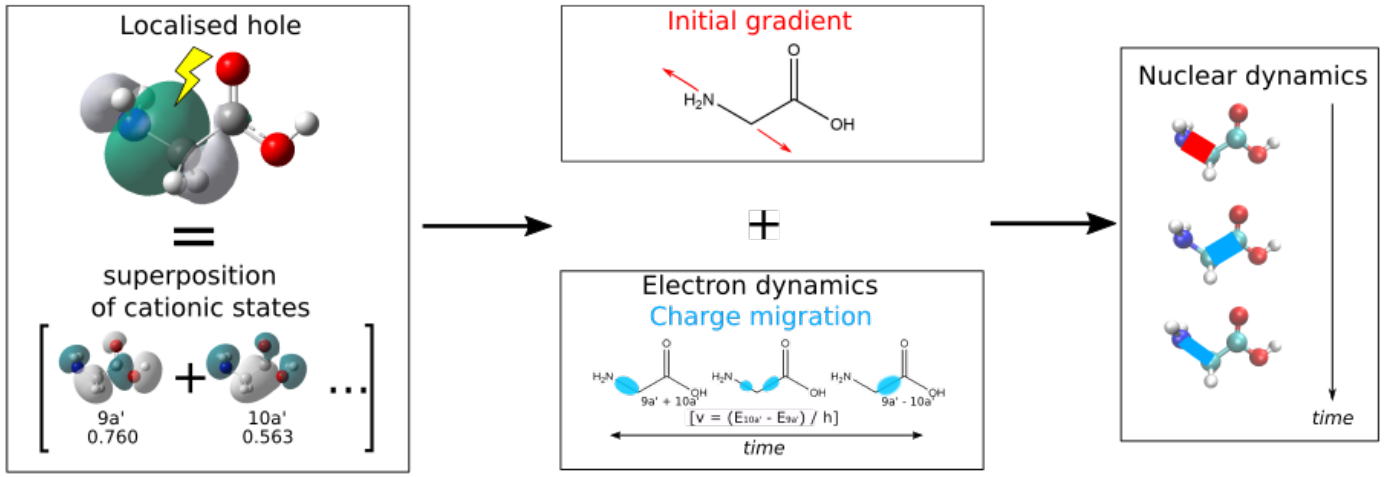


Tran *et al., Commun. Chem.*, 4, **2021**, 48.

Conclusion

- Attosecond pump laser create superposition of states
  - ➢ Fast electron dynamics (i.e. charge migration)

- Possible to create arbitrary coherent superposition of states with QuEh
  - ➢ Coherent superposition leads to heavily coupled nuclear-electron dynamics
  - ➢ Initial dynamics governed by initial gradient and instantaneous force from localized hole
  - ➢ Motion can be rationalized and predicted with symmetry



Credit: Don Danilov

Acknowledgments

Imperial College London

Expanding the limits of computational chemistry