Quantum State Tomography for Attosecond Ionization of Entangled Many-Electron Systems

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Panofsky Fellowship Seminar, SLAC, Stanford.

10 March 2021

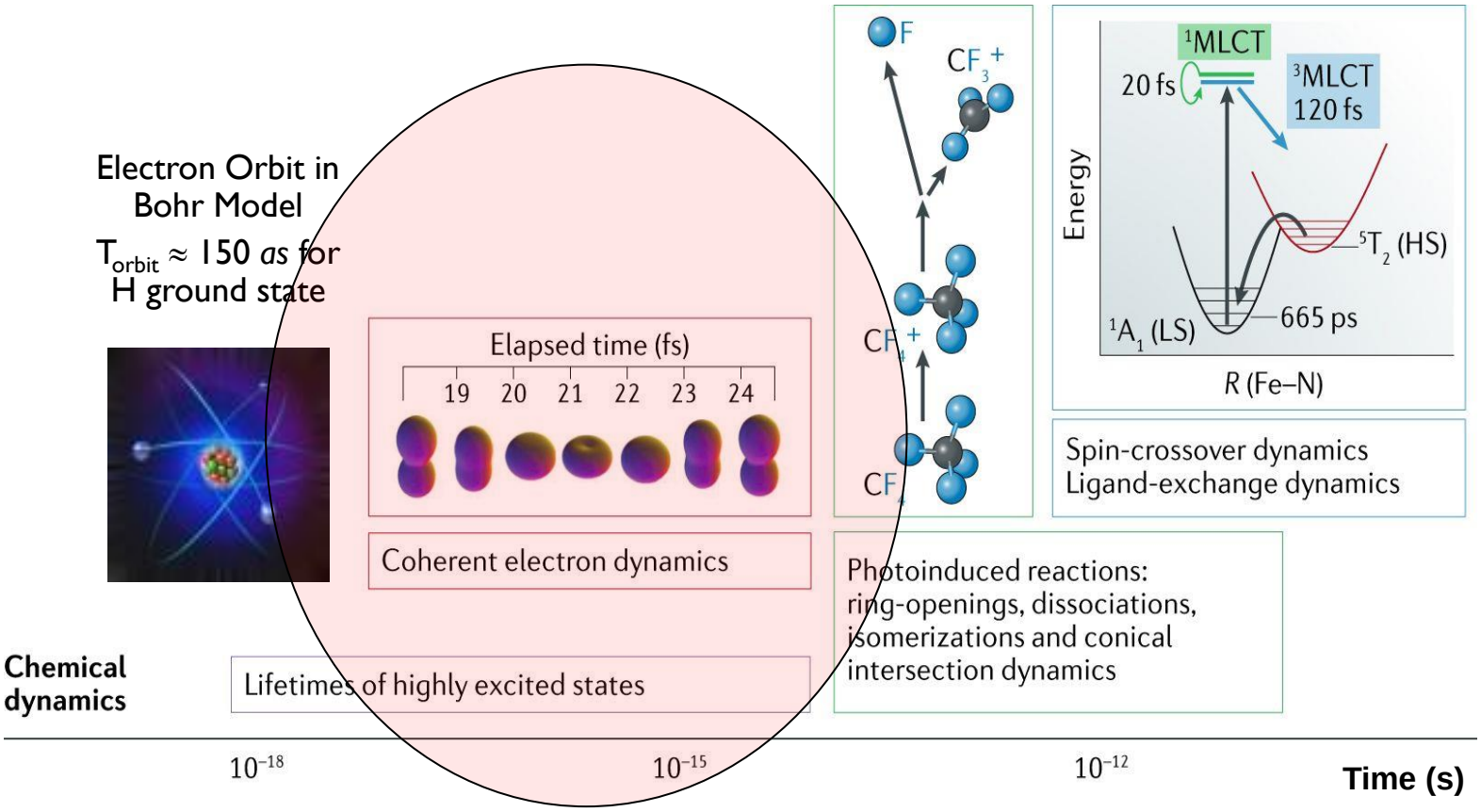
Outline

- Introduction: Quantum **coherence** and **entanglement** upon attosecond ionization of atomic and molecular systems.

- Overview of my theoretical work: the **Time dependent B-spline restricted correlation space (RCS) ADC** *ab initio* method for ionization dynamics of many-electron systems.
  Applications: **mixed state** of the molecular cation prepared by strong-field and attosecond ionization; **fully *ab initio* simulation of attosecond pump–probe experiment in polyatomic molecules**; mapping of the X-ray observables to the pump-prepared quantum electronic coherences in molecular cation.

- Research vision and program for Panofsky Fellowship: **quantum-information-theory** based perspective on attosecond physics.

Attosecond many-electron quantum dynamics in matter



Many-electron motion on timescales of 0.01fs- 10 fs

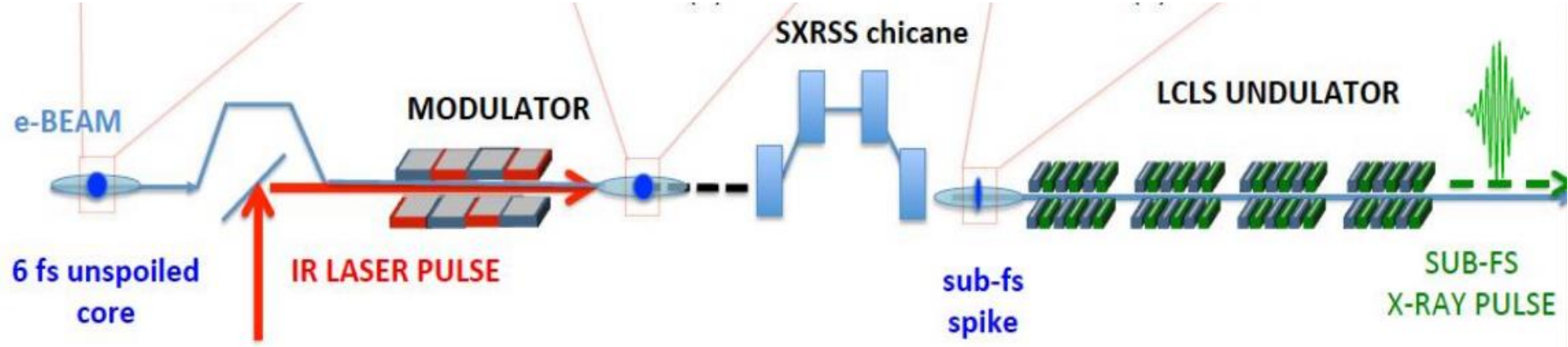
In a photophysical or photochemical process electronic and nuclear quantum dynamics will occur in a highly correlated fashion – we need tools that track this by observing the full dynamics of system i.e. both photoelectron and residual ion/neutral sub-states

Scientific Importance of Understanding Quantum Coherence and Electron-Nuclear Coupling in Photo-Excitation/Ionisation

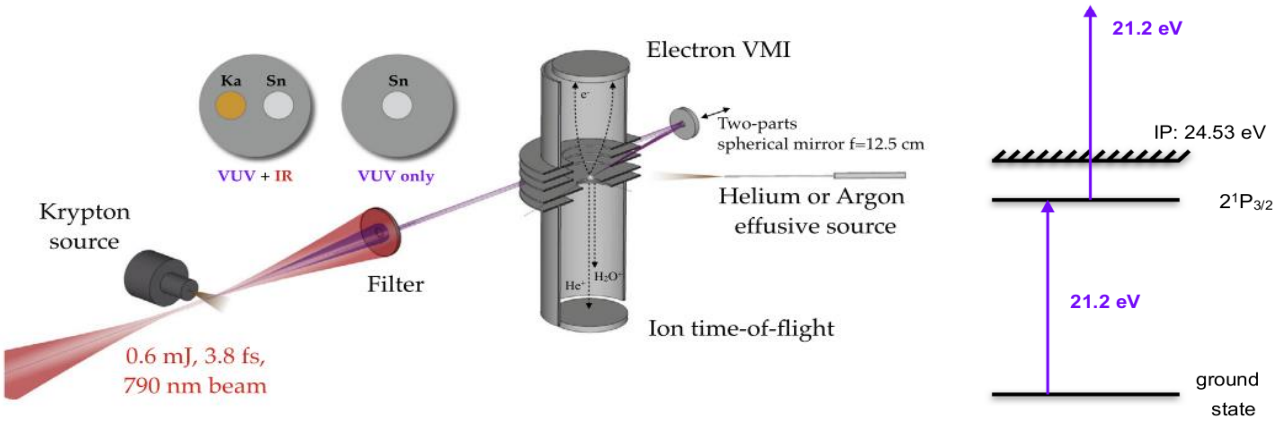
- Photo-excitation/ionisation is primary event in many processes from radiation damage to solar energy devices to photo-catalysed reactions
- Routes to control photo-physical/-chemical processes: *Imagine we can harness these fundamental, inherently quantum-mechanical concepts to develop control strategies of chemical reactivity of excited and ionized molecules by acting on the electronic degrees of freedom on attosecond time scale.*
- An experimental test-bed for quantum information in open multi-partite quantum systems: *entanglement* and *decoherence*
- Test our theories of *charge migration*, *electron-nuclear coupling* and *charge transfer* in quantum chemistry

X-ray FEL source development opens the door for attosecond pump – attosecond probe spectroscopy

From synchrotron radiation towards **attosecond X-ray pulses at LCLS-II**



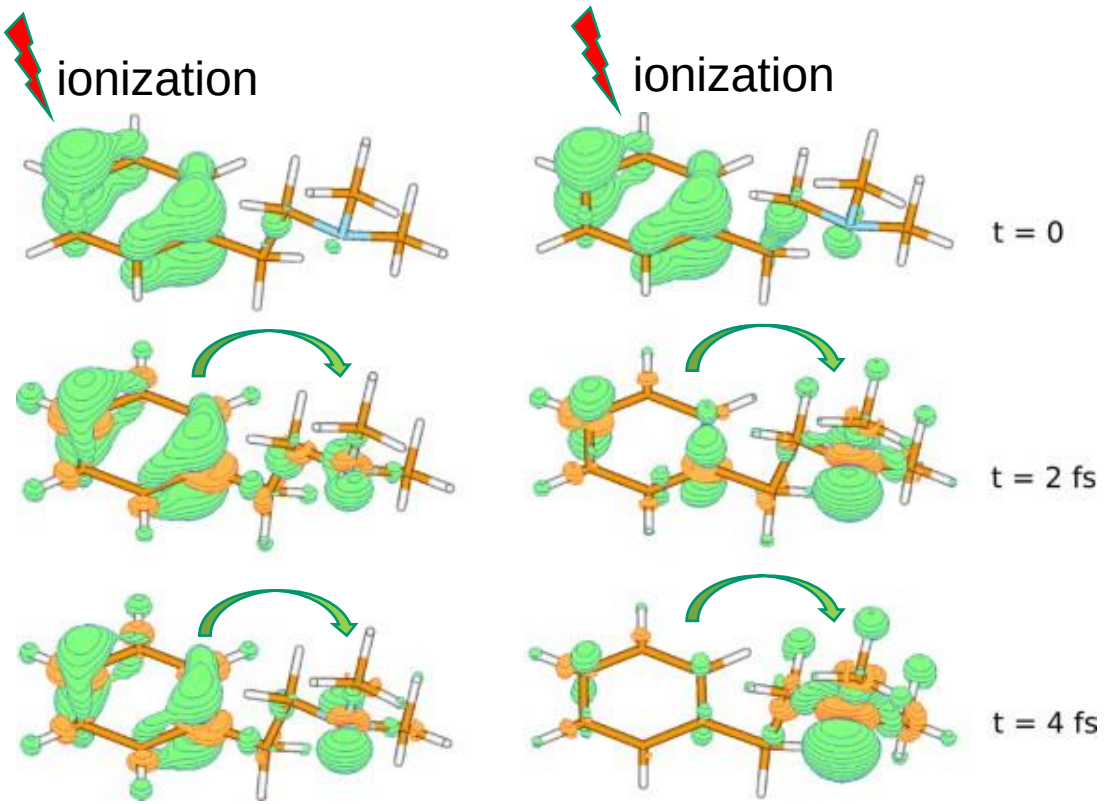
X-LEAP: 0.5 fs duration pulses, [Pellegrini 2017, Duris 2020]



HHG-based sources: [Tisch and co., Chem. Phys. Lett. **683** (2017) 38]

Hole migration: ultrafast bound-state charge dynamics following molecular ionization

- Valence photo-ionization can create a non-stationary state of molecular ion
- This leads to oscillations of the electron hole across the molecule that we call **hole migration**
- Purely electronic process. Eventually damped by nuclear motion



[Lünnemann, Kuleff & Cederbaum, Chem. Phys. Lett. **450**, 232 (2008)]

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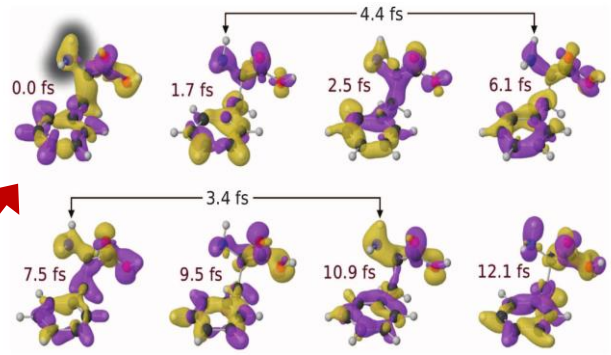
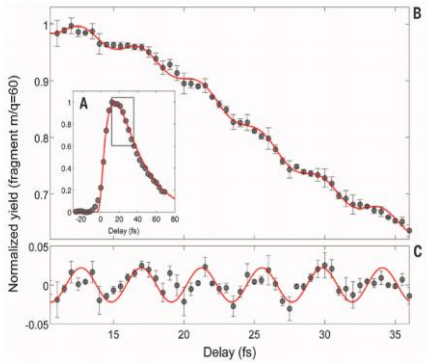
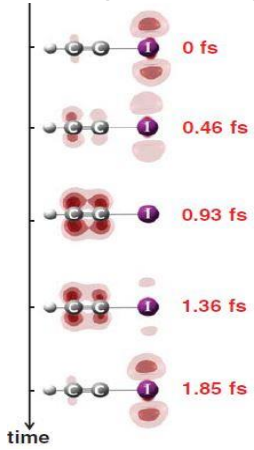
First attempts of time-resolved observation

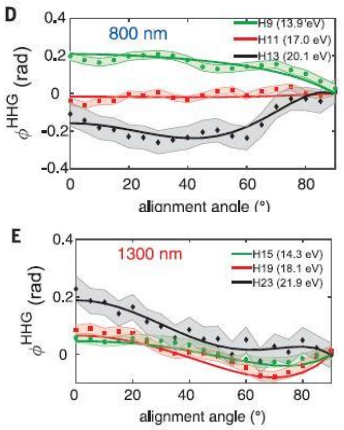
1) using attosecond pump – IR probe spectroscopy: [*Belshaw et al., J. Phys. Chem. Lett.* ***3****, 3751 (2012); Calegari et al., Science* ***346****, 336 (2014)]*

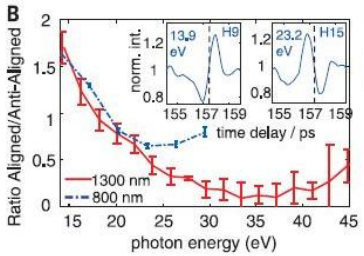




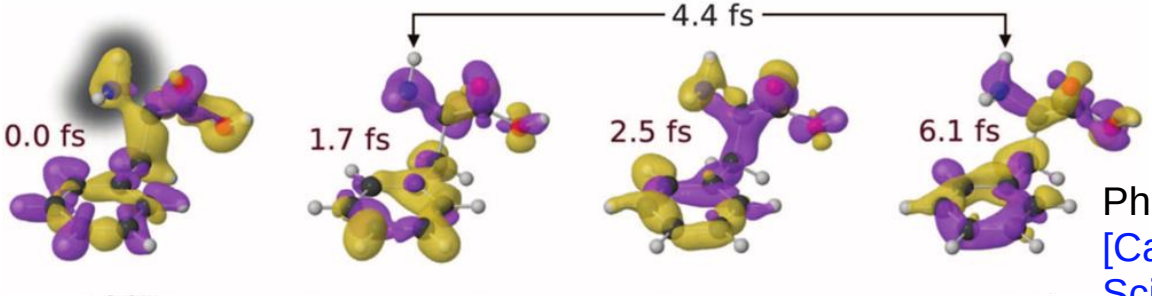
2) using HHG spectroscopy: *[Kraus et al., Science* ***350****, 790, (2015)]*





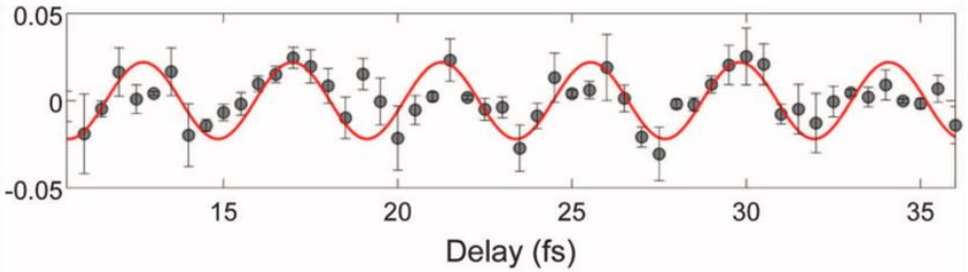


Hole migration: ultrafast bound-state charge dynamics following molecular ionization



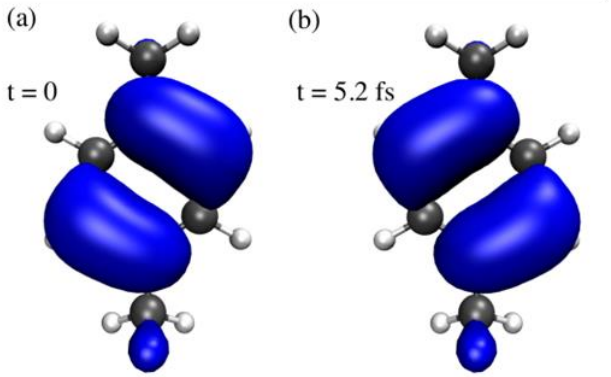
Phenylalanine
[Calegari *et al.*, Science **346**, 336 (2014)]

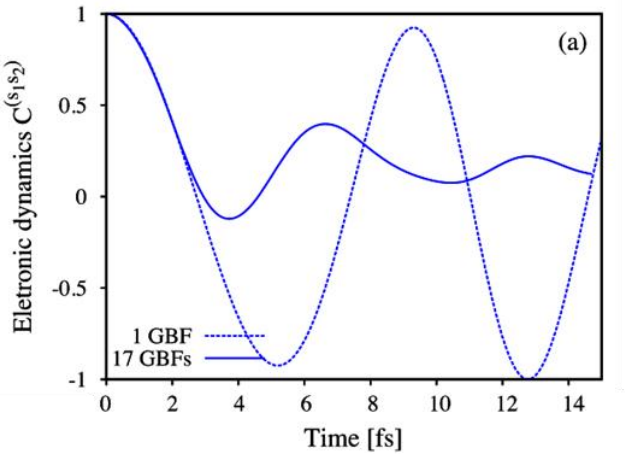
Example of ultrafast consequences of coupling of electronic and nuclear states



☆ Paraxylene dipeptide - Theory suggests nuclear motion damps the oscillations much faster than the 2014 experiment implies...

[Vacher *et al.*, PRL **118,** 083001 (2017)]





Hole migration: problem solved?

- Hole migration is a simple effect of the coherent population of ionic eigenstates...

- But the coherence of ionic state population is a highly non-trivial consequence of several photoionization mechanisms and is poorly understood.

- We need a theoretical tool to model molecular photoionization and predict to what extent can the resulting ion be described by a wavefunction!

Needed:

ab initio framework for

1- designing the
upcoming attosecond pump-probe studies through
reliable simulations

2- interpretation of the
ongoing mixed attosecond/femtosecond pump-probe studies
through reliable simulations

A strong coupling between theoretical, computational and experimental efforts is key for the success of attosecond science

Goals (…Attochemistry...?)

- **Electronic quantum coherence**
- ultrafast electronic charge dynamics (100 as – 30 fs)
- couplings between electrons and nuclei degree of freedom
- rearrangement of the molecular structure:

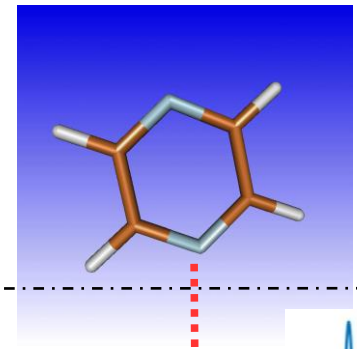
  bond breaking, dissociation, **chemical change**

1) Preparation of **quantum electronic coherences**

2) Probing of **quantum electronic coherences**

3) Control of (and by means of) **quantum electronic coherences**

Ionic coherence after photoionization?



$$\Psi^{N}_{Bound}(1,2,3,.....,N)$$

Is the final wave-function **separable** into the product of an ionic and photo-electron component, i.e. the prepared **ionic subsystem** describable as a **pure state**?

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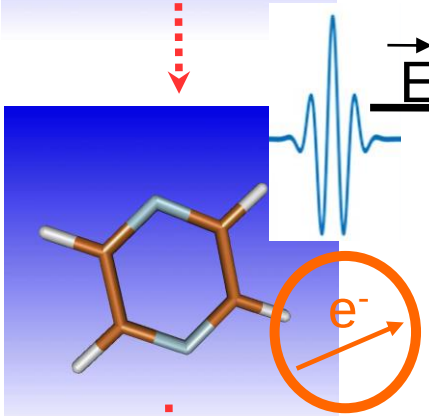
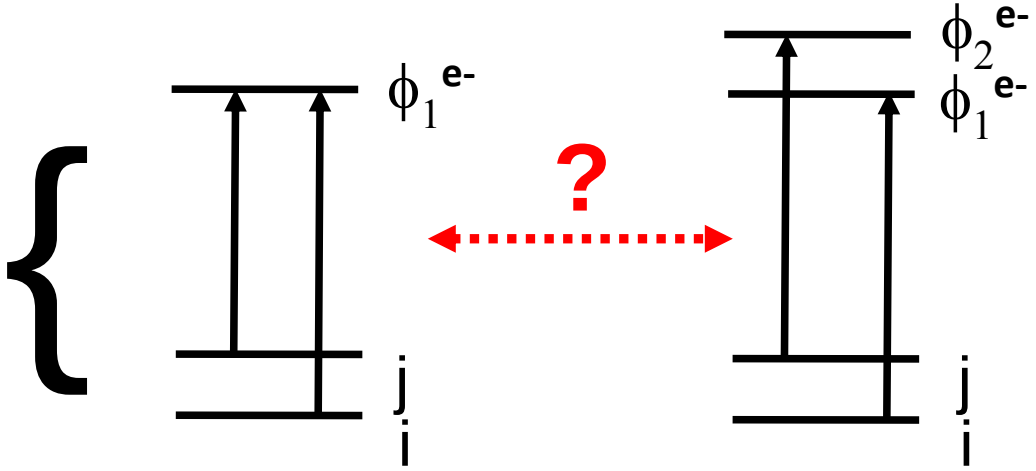
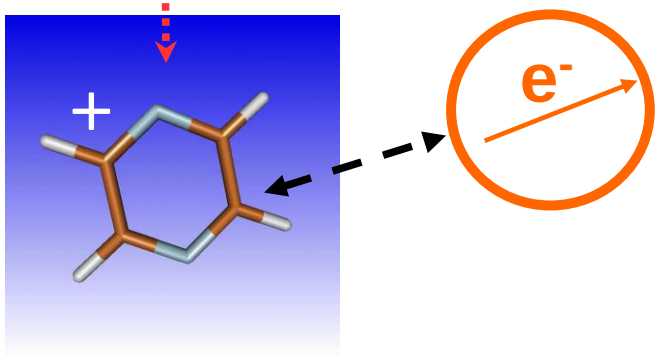




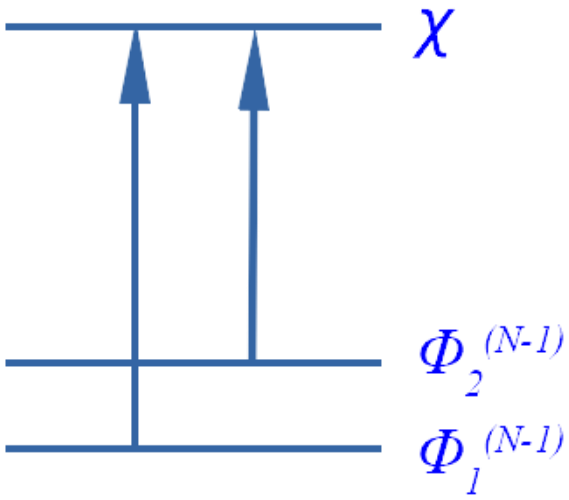


$$\simeq A\left[\sum_{\mathbf{n}}\left(\Phi^{N-1}_{\mathbf{n}}(1,2,3,.....,N-1)\times\phi^{e^-}_{\mathbf{n}}(N)\right)\right]$$

?

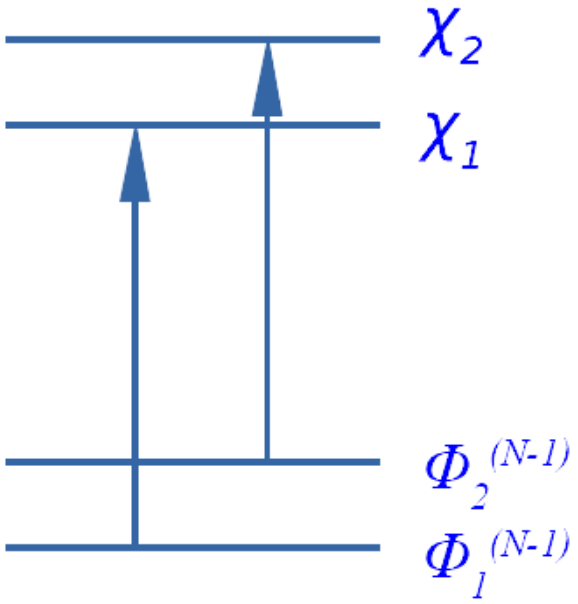
$$\approx A\left[\left(\sum_{\mathbf{n}} c_{\mathbf{n}}\Phi^{N-1}_{\mathbf{n}}(1,2,3,.....,N-1)\right)\times\phi^{e^-}(N)\right]$$

Ionic coherence after ionization?



$$\Psi = [C_1 \Phi_1^{(N-1)} + C_2 \Phi_1^{(N-1)}]\,\chi$$

(N-1)-electron ion has got a [...] wavefunction – coherent population of ionic states



$$\Psi = C_1 \Phi_1^{(N-1)} \chi_1 + C_2 \Phi_1^{(N-1)} \chi_2$$

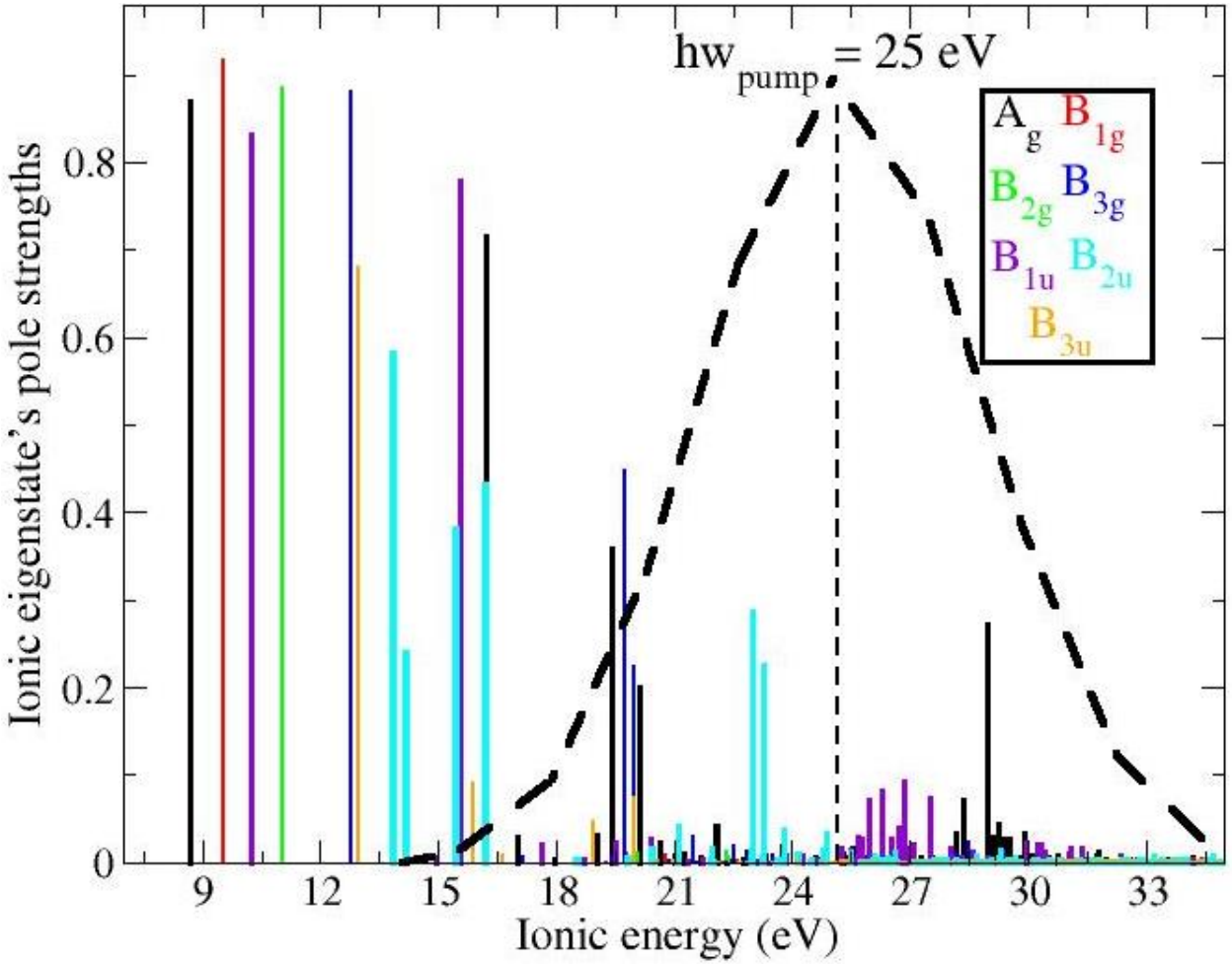
Only the full N-electron system has got a wavefunction – incoherent population of ionic states.

Ion-photoelectron entanglement!

The complete information is contained in the full N-electron wavefunction.

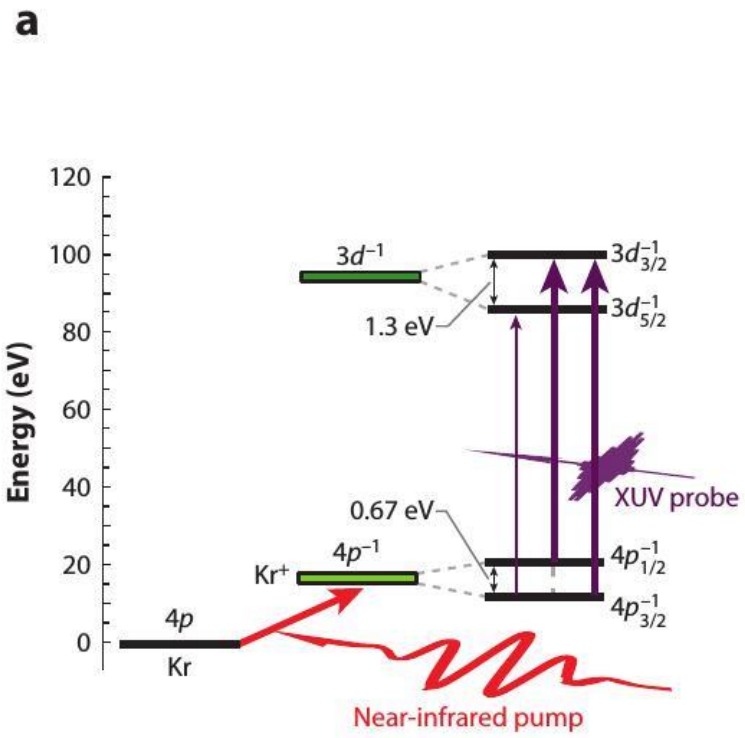
Regimes of Coherent Hole-State Wavepacket Formation: Dependence on Photon Energy & Bandwidth

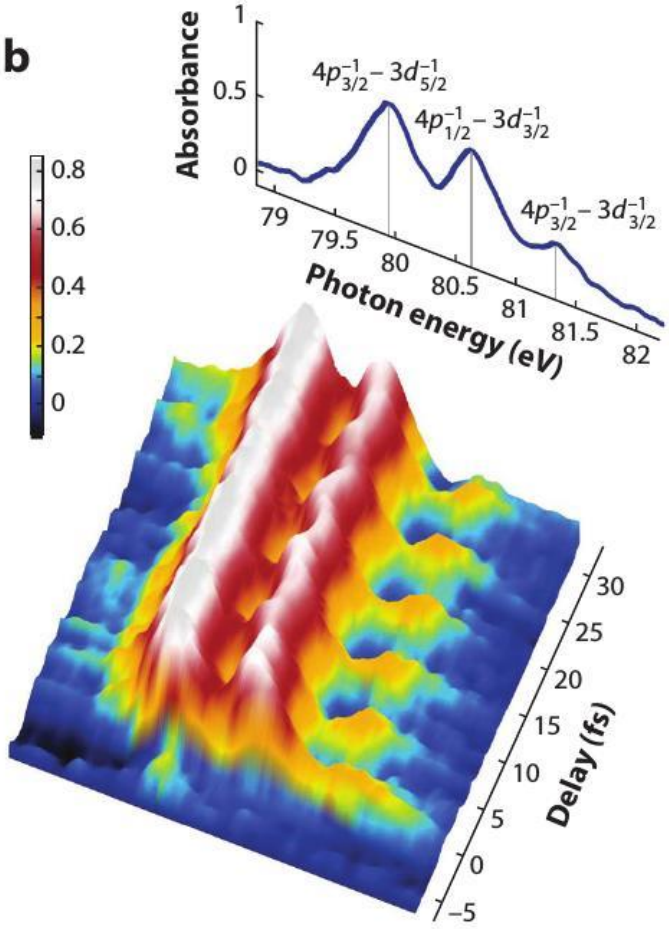
Central Pump photon energy = 25 eV **Bandwidth FWHM = 7 eV**



Measuring ionic coherence: the atomic Kr spin-orbit two-level case

Coherence between different spin-orbit states upon strong-field IR ionization of Kr atom

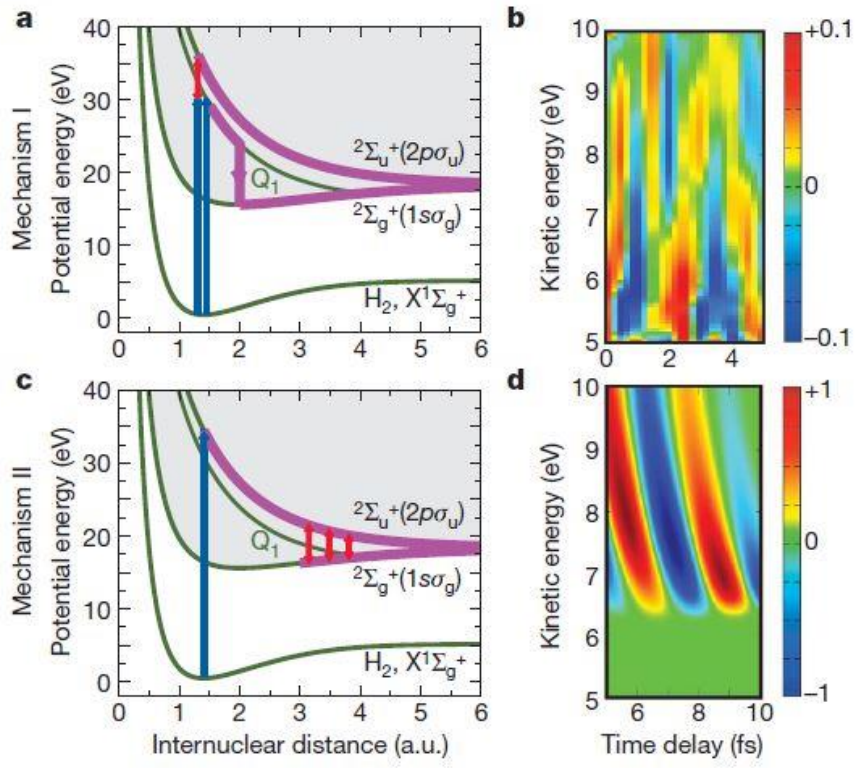




[E. Goulielmakis *et al.*, *"Real-time observation of valence electron motion"*, Nature **466**, 739 (2010)]

Effects of coherence: electron localization in XUV-IR dissiocative photoionization of H_2

"H_2 and D_2 are dissociatively ionized by a sequence comprising an isolated attosecond ultraviolet pulse and an intense few-cycle infrared pulse, and a localization of the electronic charge distribution within the molecule is measured that depends—with attosecond time resolution—on the delay between the pump and probe pulses."



Asymmetry in EUV-IR dissociative ionization of H_2

↓

Electron localization in H_2^+
Coherent superposition of *gerade* and *ungerade* ionic states

Electron localization in the ion is influenced by the interaction between the IR field and the photoelectron

[Sansone et al., *Electron localization following attosecond molecular photoionization,* Nature **465**, 763 (2010)]

Summary

- Quantum **coherence** and **entanglement** are key concepts in attosecond science. For example, these competing phenomena underpin/destroy electronic hole migration in molecular ions.

- We are only at the very beginning of appreciating *the role of ultrafast quantum electronic coherences and entanglement in the photoinduced physical & chemical change of matter.*

- A full quantum-information perspective on attoscience is thus far unexplored and the role of electron-nuclear coupling in this game is even more obscure – *how would an interaction with or a measurement performed on the photoelectron affect the chemical process (dissociation, rearrangement, ...) in the ion that this electron left behind?*

- There is a room for a new field to be born: **quantum attoscience**.

Ionic wavefunction...?
The "Sudden Approximation"

Assuming perfect coherence

$$\Psi^{N}_{Final}(1,2,3,.....,N) \sim A\left[\Psi^{N-1}_{Bound}(1,2,3,.....,N-1)\times\phi^{e^-}(N)\right]$$

$$\Psi^{N-1}_{Bound}(1,2,3,.....,N-1) = \sum_n c_n \Phi^{N-1}_n(1,2,3,.....,N-1)$$

$$c_n = c_n\left(E_{field}\right) = ?$$

? Dependence on laser pulse parameters ?

Sudden approximation
ansatz for the initial state

$$|\Psi^{N-1}_{initial}\rangle \sim a_i \; |\Psi^{N}_{0}\rangle$$

when is it valid...?

We need a theoretical tool to model molecular photo-ionization beyond sudden approximation, including electron correlation

(Ionic wavefunction...?)
Beyond The "Sudden Approximation":
TD B-spline RCS-ADC theory

New ***ab initio*** method:

Time-dependent (TD) multicentre- **B-spline** restricted correlation space **(RCS) –** algebraic diagrammatic construction **ADC**

$$i\hbar \frac{\partial \mid \Psi^N(t)\rangle}{\partial t} = \hat{H}^N(t) \mid \Psi^N(t)\rangle$$

Time-dependent many-electron Schrodinger equation

$$\mid \Psi^N(t)\rangle = \sum_m \left\{ \sum_\mu c_{m\mu}(t)\, \hat{c}^\dagger_\mu \mid \Psi^{(N-1)}_m \rangle^{[n]} \right\} + \sum_{I_{RCS}} c_{I_{RCS}}(t) \mid \tilde{\Psi}^N_{I_{RCS}} \rangle^{[n]} + c_0(t) \mid \Psi^{RCS}_0 \rangle^{[n]}$$

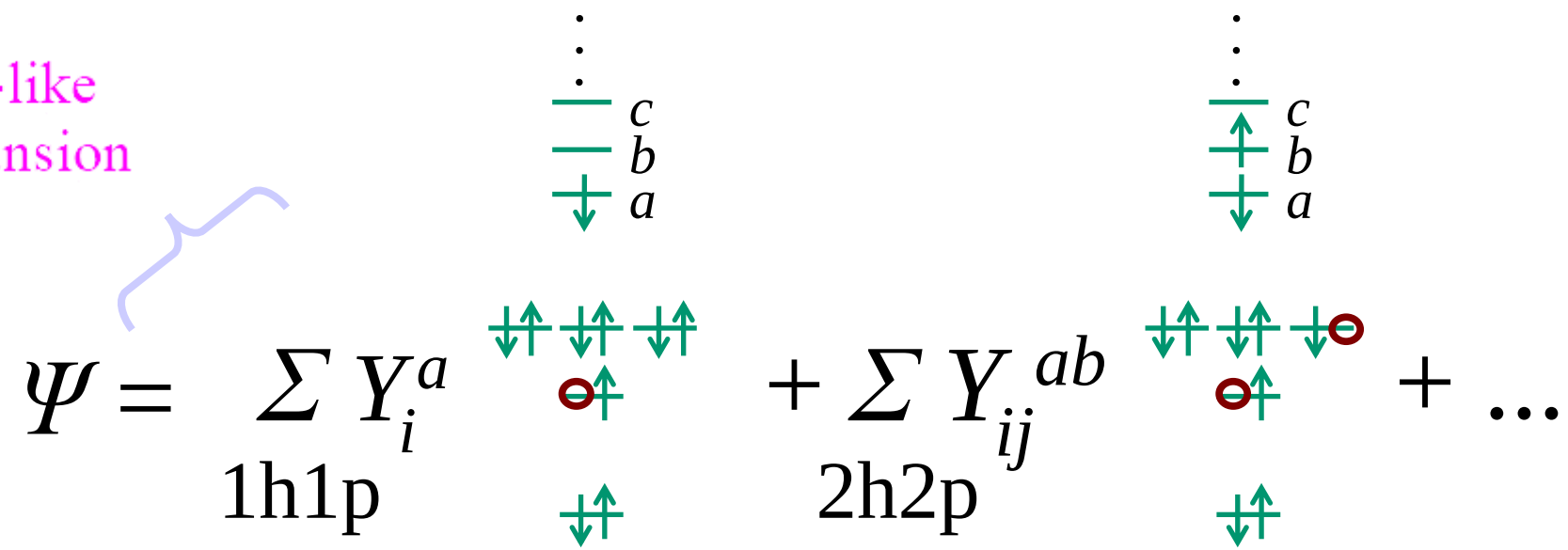
continuum/delocalised

bound/localised

[M. Ruberti, Journal of Chemical Theory and Computation, **14**, 4991 (2019)]

Algebraic Diagrammatic Construction (ADC) in the Intermediate State Representation (ISR)

CI-like expansion



$$\Psi = \sum_{1h1p} Y_i^a + \sum_{2h2p} Y_{ij}^{ab} + \ldots$$

$$\Psi_i^{a'(0)} = c_a^\dagger c_i \Psi_0$$

$$\Psi_{ij}^{ab'(0)} = c_a^\dagger c_b^\dagger c_i c_j \Psi_0$$

$$\Psi_0 = \Phi_0^{\mathrm{HF}} + \Psi_0^{(1)} + \Psi_0^{(2)} + \ldots$$

many-body PT for the ground state

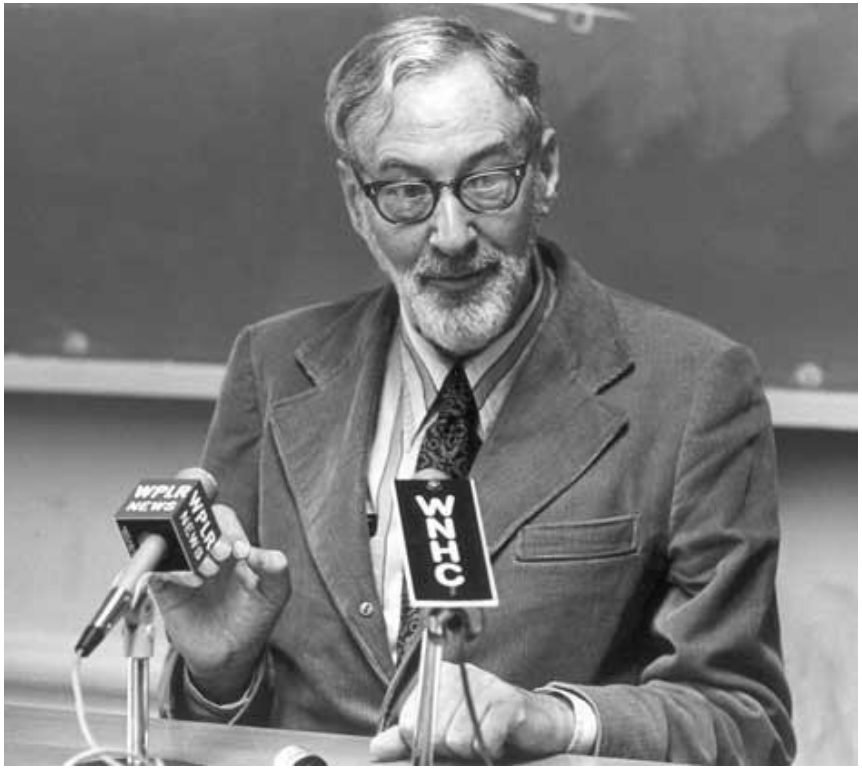
Arnoldi-Lanczos time-propagation scheme

Traditionally, standard *Gaussian* single-electron basis sets are employed, but here I use *B-splines*

Analogous formulation for *singly-ionised* states is available

[Cederbaum, Schirmer and co-workers; Using B-splines: Ruberti, Decleva & Averbukh (2014)]

Simple theory of electron holes: Koopmans theorem

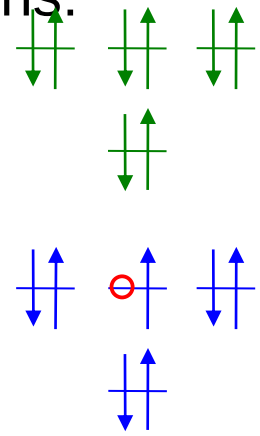


Tjalling C. Koopmans (Nobel prize winner in *economics*, 1975)

If both the ground state of the neutral and the eigenstate of the cation are well approximated by Single HF configurations:

$$\Psi_0^{(N)} = \Phi_0^{HF}$$

$$\Psi_0^{(N-1)} = \hat{a}_i \Phi_0^{HF}$$



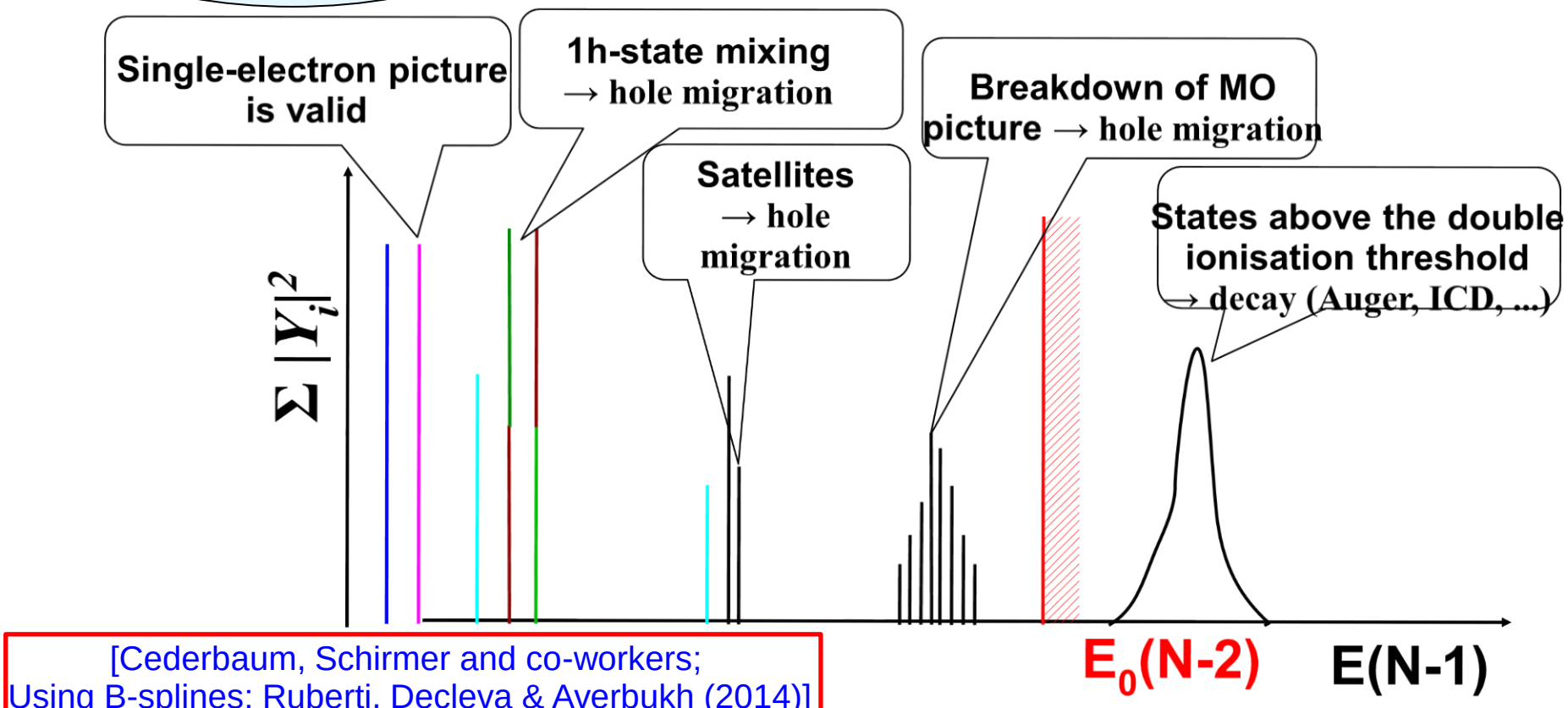
then the corresponding ionization potential is given by the HF orbital energy:

$$\mathbf{IP} = E_i(N-1) - E_0(N) = -\varepsilon_i$$

(Ionic wavefunction...?)
ADC ionic states:
Electron holes beyond Koopmans

$$|\tilde{\Psi}^N_{\mu,n}\rangle = \hat{c}^\dagger_\mu |\Psi^{N-1}_n\rangle$$

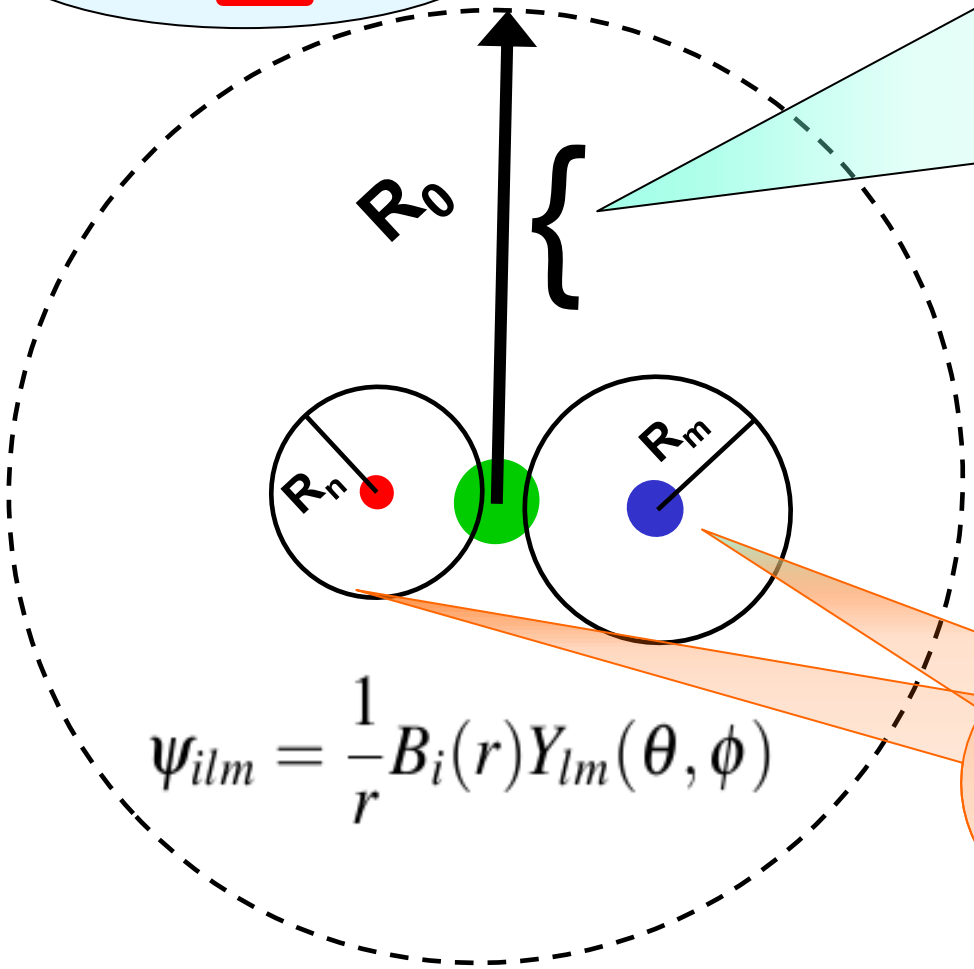
$$\Psi^{(N-1)} = \underset{\text{1h}}{\sum Y_i \Psi_i} + \underset{\text{2h1p}}{\sum Y_{ij}^{\ a} \Psi_{ij}^{\ a}} + \underset{\text{3h2p}}{\sum Y_{ijk}^{\ ab} \Psi_{ijk}^{\ ab}} + \ldots$$



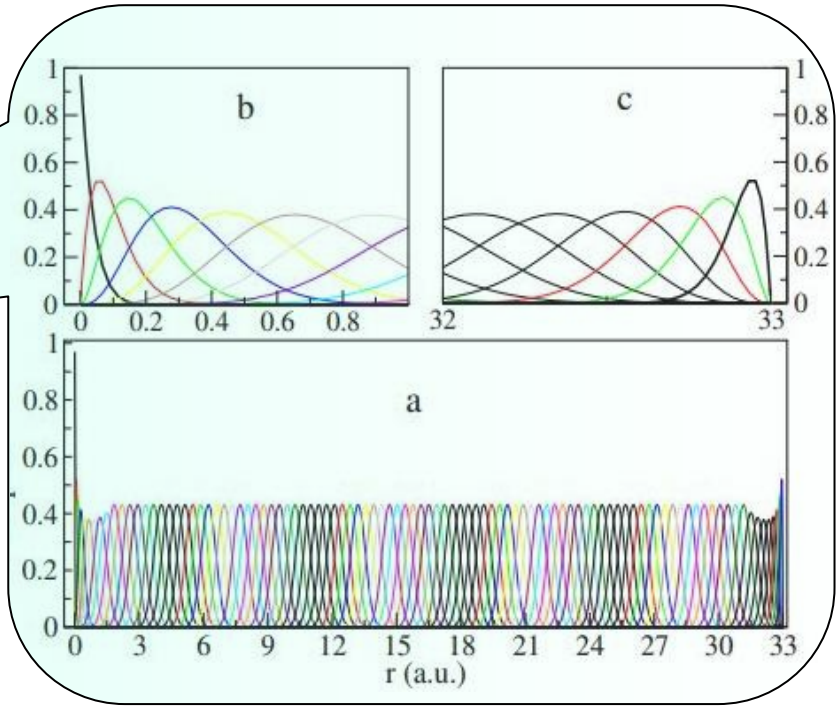
[Cederbaum, Schirmer and co-workers;
Using B-splines: Ruberti, Decleva & Averbukh (2014)]

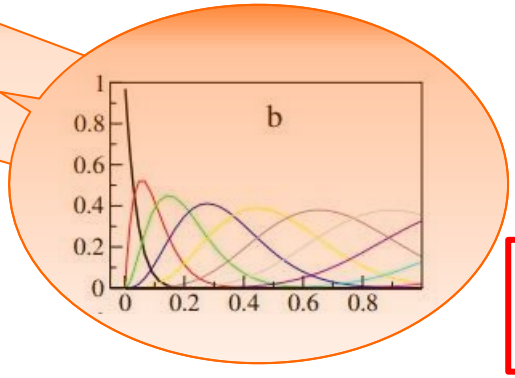
Single-electron basis set: Multicentre B-splines

$$|\tilde{\Psi}^N_{\mu,n}\rangle = \hat{c}^\dagger_\mu |\Psi^{N-1}_n\rangle$$



$$\psi_{ilm} = \frac{1}{r} B_i(r) Y_{lm}(\theta, \phi)$$





[D. Toffoli & P. Decleva Chem. Phys. (2002)]

TD B-spline RCS-ADC theory

$$H^{\hat{N}}(t) = \hat{H}^{N}_{RCS-ADC(n)} + \hat{D}^{N}_{RCS-ADC(n)} E(t) - i\hat{W}$$

Dipole approximation

Length Gauge

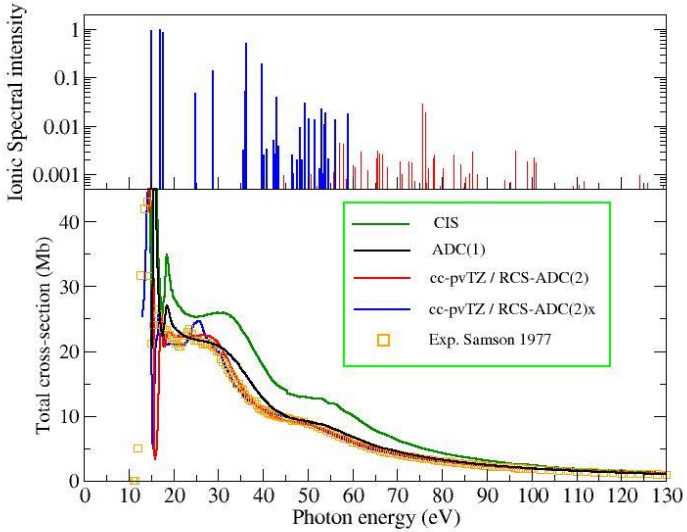
Complex **A**bsorbing **P**otential **(CAP)**

$$\mathbf{H}^{\text{RCS-ADC}(n)} = \begin{pmatrix} \mathbf{H}^{\text{ADC}(n)}_{\text{RCS}} & \left\langle \tilde{\Psi}^{N}_{I_{\text{RCS}}} \middle| \hat{\tilde{H}} \hat{c}^{\dagger}_{\nu} \middle| \Psi^{N-1}_{m} \right\rangle^{\text{ADC}(n)} \\ \left\langle \Psi^{N-1}_{m} \middle| \hat{c}_{\mu} \hat{\tilde{H}} \middle| \tilde{\Psi}^{N}_{I_{\text{RCS}}} \right\rangle^{\text{ADC}(n)} & \left\langle \Psi^{N-1}_{m} \middle| \hat{c}_{\mu} \hat{\tilde{H}} \hat{c}^{\dagger}_{\nu} \middle| \Psi^{N-1}_{n} \right\rangle^{\text{ADC}(n)} \end{pmatrix}$$

$$\mathbf{D}^{\text{RCS-ADC}(n)} = \begin{pmatrix} \mathbf{D}^{\text{ADC}(n)}_{\text{RCS}} & \left\langle \tilde{\Psi}^{N}_{I_{\text{RCS}}} \middle| \hat{D} \hat{c}^{\dagger}_{\nu} \middle| \Psi^{N-1}_{m} \right\rangle^{\text{ADC}(n)} \\ \left\langle \Psi^{N-1}_{m} \middle| \hat{c}_{\mu} \hat{D} \middle| \tilde{\Psi}^{N}_{I_{\text{RCS}}} \right\rangle^{\text{ADC}(n)} & \left\langle \Psi^{N-1}_{m} \middle| \hat{c}_{\mu} \hat{D} \hat{c}^{\dagger}_{\nu} \middle| \Psi^{N-1}_{n} \right\rangle^{\text{ADC}(n)} \end{pmatrix}$$

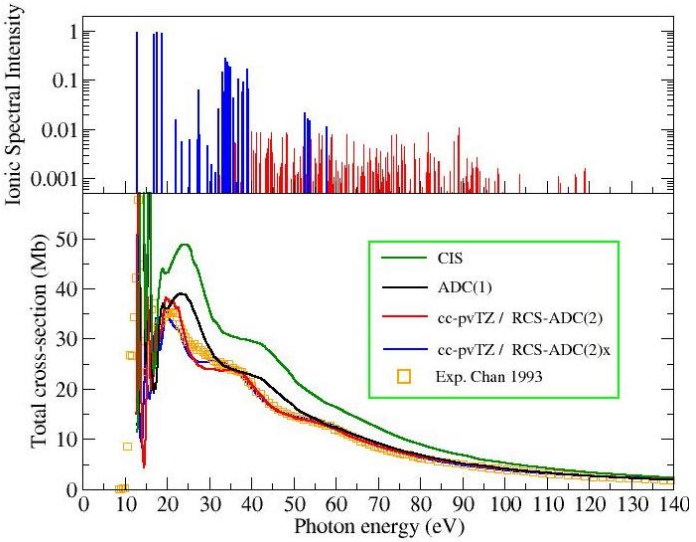
$$\left\langle \Psi^{\text{RCS}}_{0} \middle| \hat{D} \hat{c}^{\dagger}_{\mu} \middle| \Psi^{N-1}_{n} \right\rangle = \sum_{\gamma \in \text{RCS}} d_{\gamma\mu} \left\langle \Psi^{\text{RCS}}_{0} \middle| \hat{c}^{\dagger}_{\gamma} \middle| \Psi^{N-1}_{n} \right\rangle = \sum_{\gamma \in \text{RCS}} d_{\gamma\mu} x_{\gamma n}$$

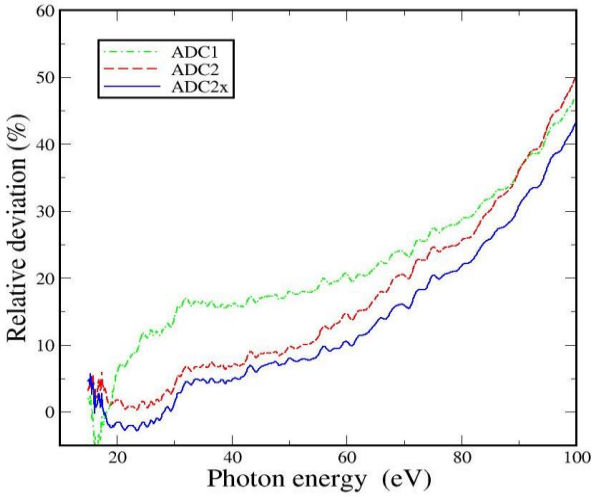
Benchmark calculations: atomic and molecular total photoionization cross-sections



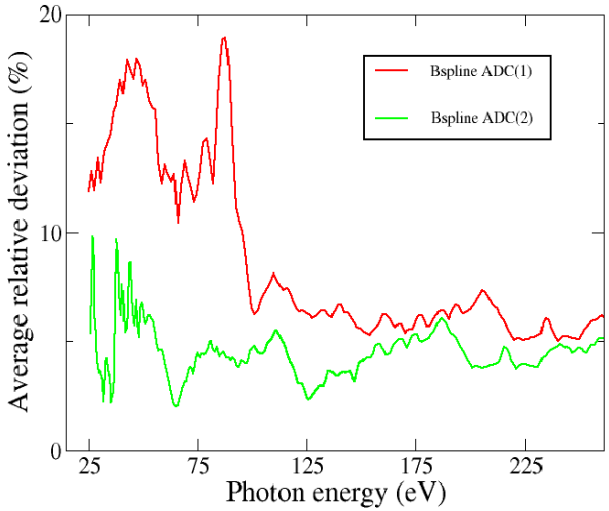
N_2

CO_2

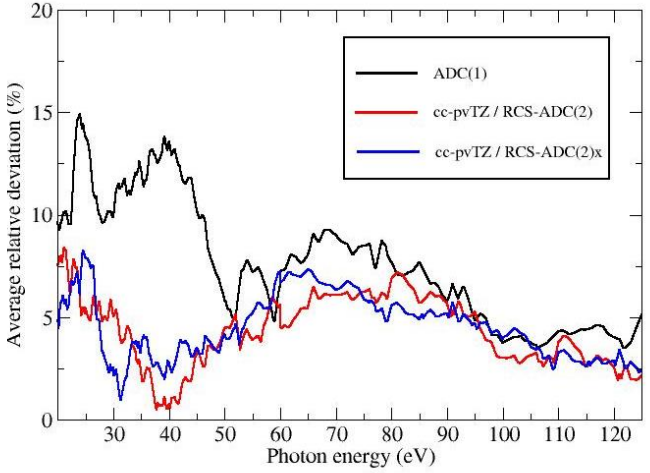




[Ruberti *et al.*, JCP **139**, 144107 (2013)]



[Ruberti, Decleva and Averbukh, JCP **141**, 164126 (2014)]



[Ruberti, JCTC **15**, 6, 3635 (2019)]

(Ionic wavefunction…no!)
Reduced Ionic Density Matrix

Reduced ionic density matrix (R-IDM):
trace over the **unobserved** photo-electron states

$$\hat{\rho}(t) = |\,\Psi^N(t)\rangle\langle\Psi^N(t)\,| \qquad \hat{\rho}^{R-IDM}(t) = Tr_\mu[\hat{\rho}(t)]$$

$$\hat{\rho}^{\text{R-IDM}}(t) = \sum_{m=1,N}\sum_{n=1,N} \rho_{mn}^{\text{R-IDM}}(t)\left|\Psi_m^{N-1}\right\rangle\left\langle\Psi_n^{N-1}\right|$$

Ionic density matrix
from TD B-spline RCS-ADC theory

$$\rho_{mn}^{R-IDM}(t) = \sum_\mu \langle\tilde{\Psi}_{\mu,m}^N \,|\, \Psi^N(t)\rangle\langle\Psi^N(t) \,|\, \tilde{\Psi}_{\mu,n}^N\rangle = \sum_\mu c_{m\mu}(t)\, c_{n\mu}^*(t)$$

[M. Ruberti, P. Decleva and V. Averbukh, JCTC **14**, 4991-5000 (2018)]

[M. Ruberti, Phys. Chem. Chem. Phys., 2019, **21**, 17584-17604 PCCP HOT Article Collection 2019]

Reduced Ionic Density Matrix

Populations

of ionic state ***n***

$$P_n(t) = |\rho_{nn}(t)|$$

Degrees of coherence

between pair of populated ionic states ***m*** and ***n***

$$G_{mn}(t) = \frac{|\rho_{mn}(t)|}{\sqrt{P_m(t) * P_n(t)}}$$

Maximum quantum coherence between two states corresponds to $G_{mn} = 1$

Purity

$$Tr\left(\hat{\hat{\rho}}^2(t)\right) \neq Tr\left(\hat{\hat{\rho}}(t)\right) \leq 1 \quad mixed\ state,$$

$$Tr\left(\hat{\hat{\rho}}^2(t)\right) = Tr\left(\hat{\hat{\rho}}(t)\right) = 1 \quad pure\ state.$$

von Neumann entropy of entanglement

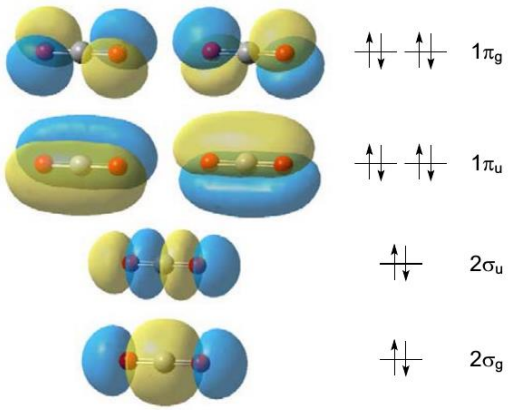
$$s^{Ion}(t) = -ln\left(\frac{1}{N}\right) \quad statistical\ mixture,$$

$$s^{Ion}(t) = 0 \quad pure\ state.$$

[M. Ruberti, P. Decleva and V. Averbukh, JCTC **14**, 4991-5000 (2018)]

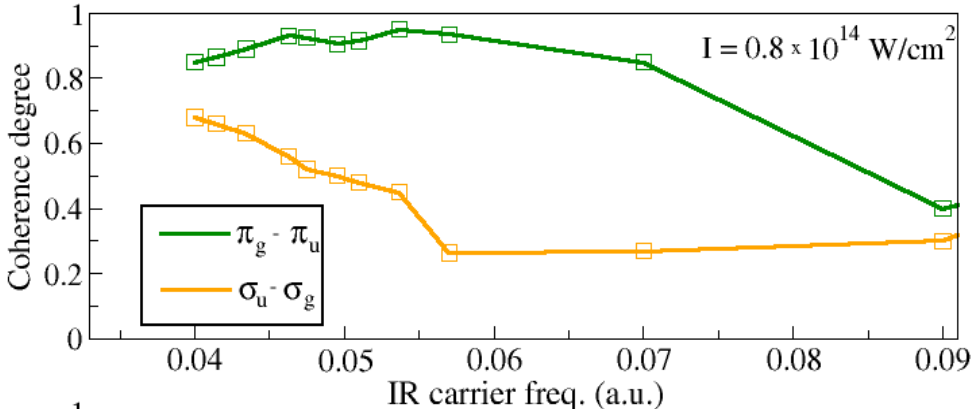
[M. Ruberti, Phys. Chem. Chem. Phys., 2019, **21**, 17584-17604 PCCP HOT Article Collection 2019]

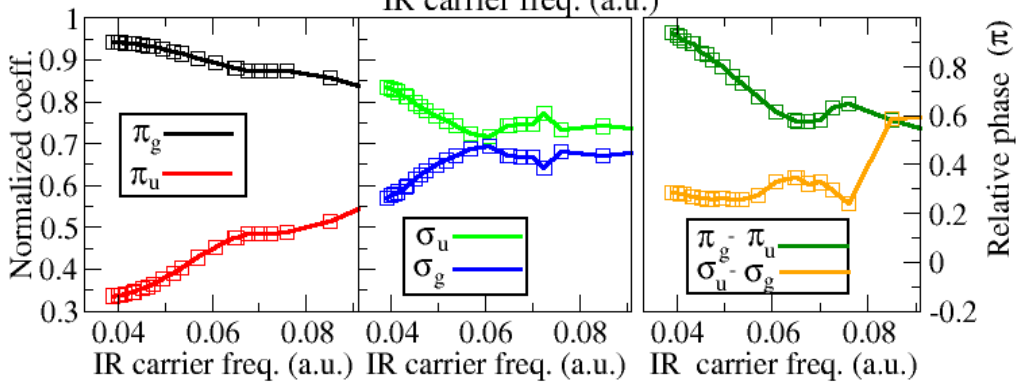
Ionic coherence upon IR strong-field ionization of aligned CO_2 molecules:



State	Experimental I.P.s (eV)	HF B-splines basis set I.P.s (eV)
$\vert \pi_g \rangle^{-1}$	13.8	15.03
$\vert \pi_u \rangle^{-1}$	17.3	18.81
$\vert \sigma_u \rangle^{-1}$	18.1	19.6
$\vert \sigma_g \rangle^{-1}$	19.36	20.7

Carrier-frequency dependence of the **degree of coherence** and of the **ionic wave-packet parameters**



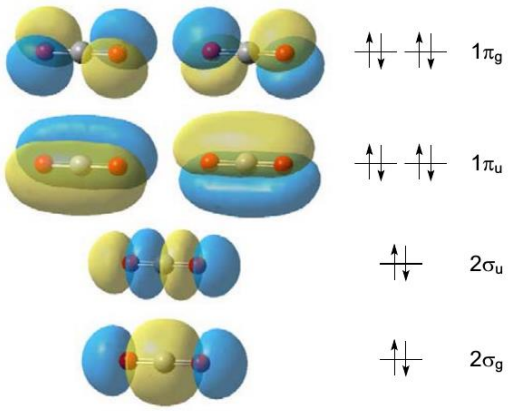


Ultra-short 2 cycles pulse.
Linear polarization along the molecular axis.
Peak intensity: 0.8 x 10^{14} W/cm^2
Σ states Energy Gap = **1.26 eV**
Π states Energy Gap = **3.518 eV**

$$\Psi^{\Sigma}(t) = C_{\Sigma_u} \mid \sigma_u^{-1} \rangle + C_{\Sigma_g} e^{-i(E_{\Sigma_g} - E_{\Sigma_u})t} e^{-i\phi_{\Sigma_u - \Sigma_g}} \mid \sigma_g^{-1} \rangle$$

[M. Ruberti, P. Decleva and V. Averbukh, JCTC **14**, 4991-5000 (2018)]

Ionic coherence upon IR strong-field ionization of aligned CO_2 molecules:



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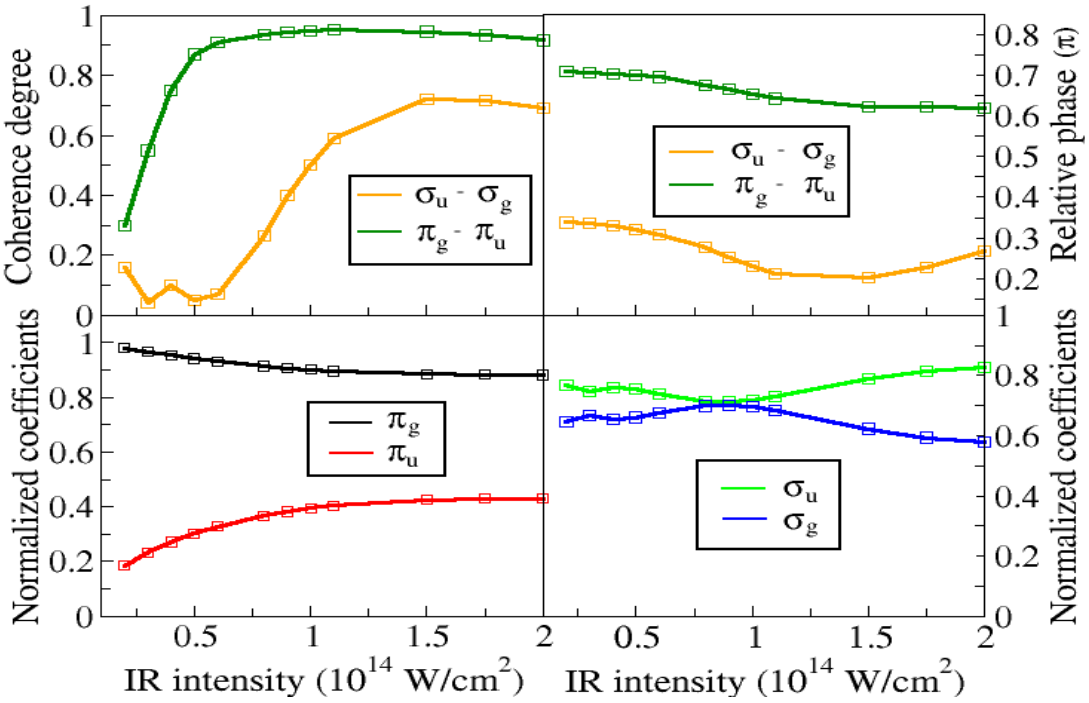
$\|\sigma_u\rangle^{-1}$	18.1	19.6
$\|\sigma_g\rangle^{-1}$	19.36	20.7

IR intensity dependence of the **degree of coherence** and of the **ionic wave-packet parameters**

Ultra-short 2 cycles pulse.
Linear polarization along the molecular axis.
IR wavelength: 800 nm
Σ states Energy Gap = **1.26 eV**
Π states Energy Gap = **3.518 eV**

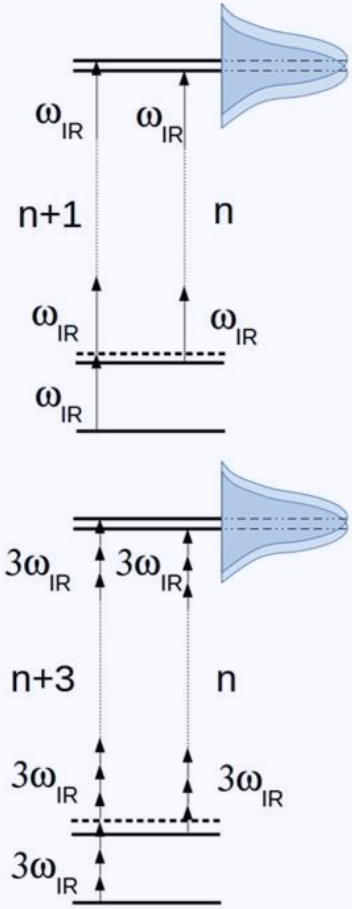
$$\Psi^{\Sigma}(t) = C_{\Sigma_u} \mid \sigma_u^{-1} \rangle + C_{\Sigma_g} e^{-i(E_{\Sigma_g} - E_{\Sigma_u})t} e^{-i\phi_{\Sigma_u - \Sigma_g}} \mid \sigma_g^{-1}$$



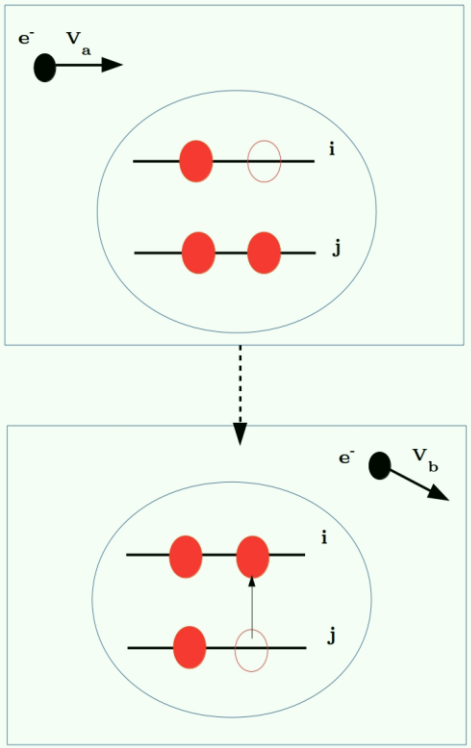
[M. Ruberti, P. Decleva and V. Averbukh, JCTC **14**, 4991-5000 (2018)]

Mechanisms of coherence formation in molecular IR strong-field ionization

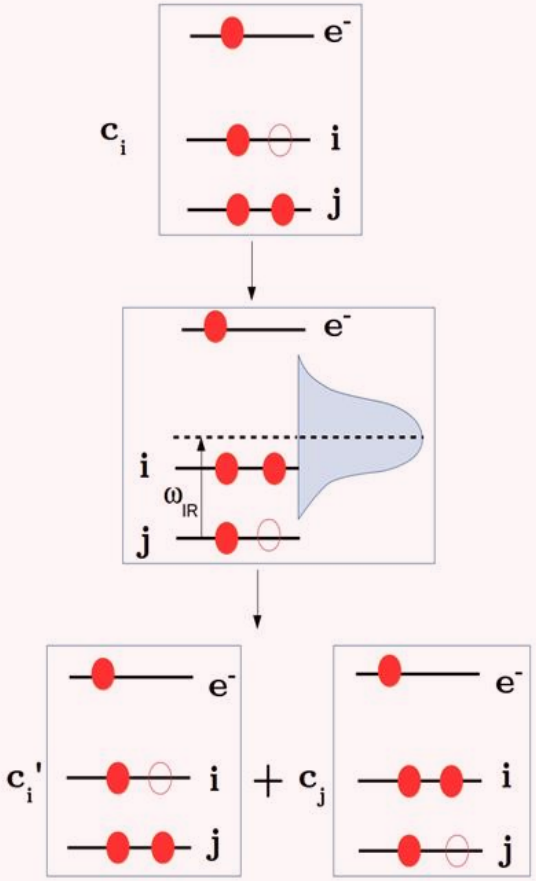
Direct ionisation into the same continuum state



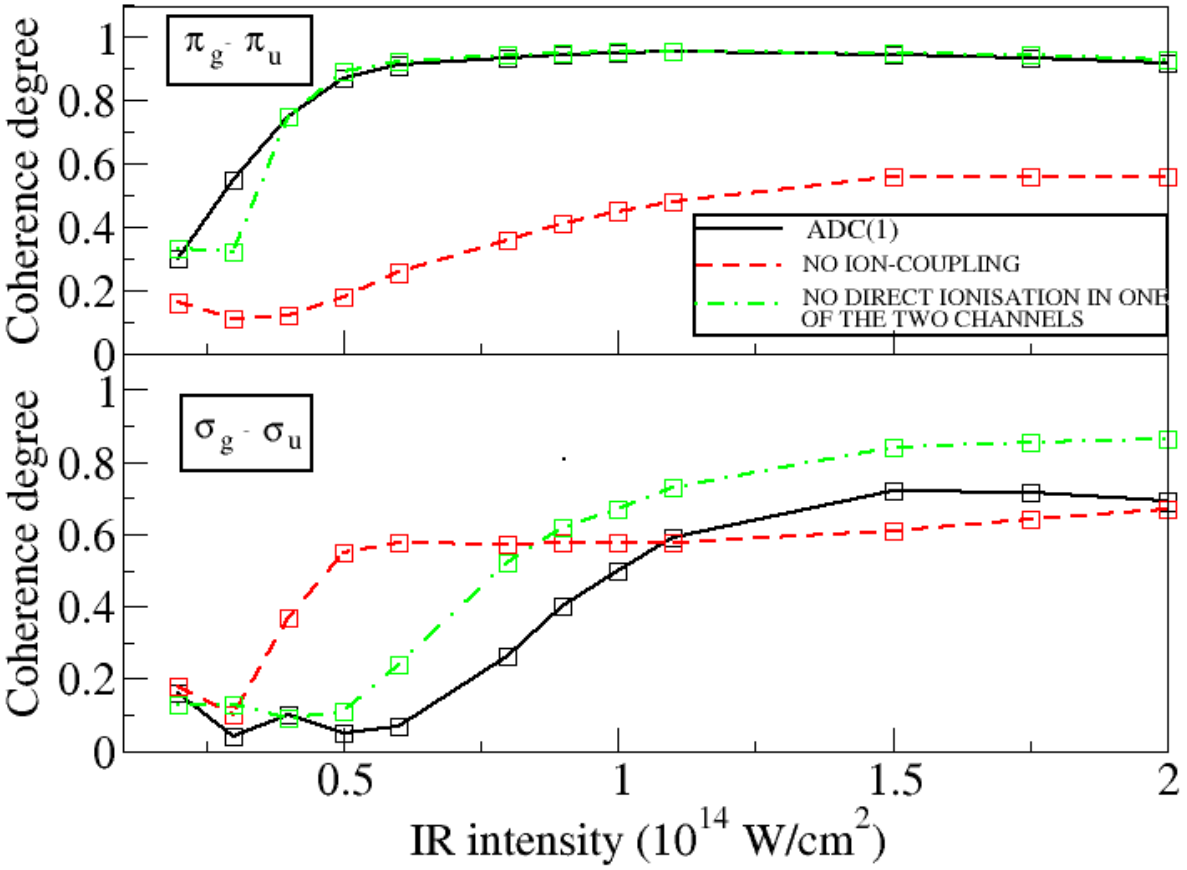
Ion-photoelectron coupling



Dipole coupling of ionised states

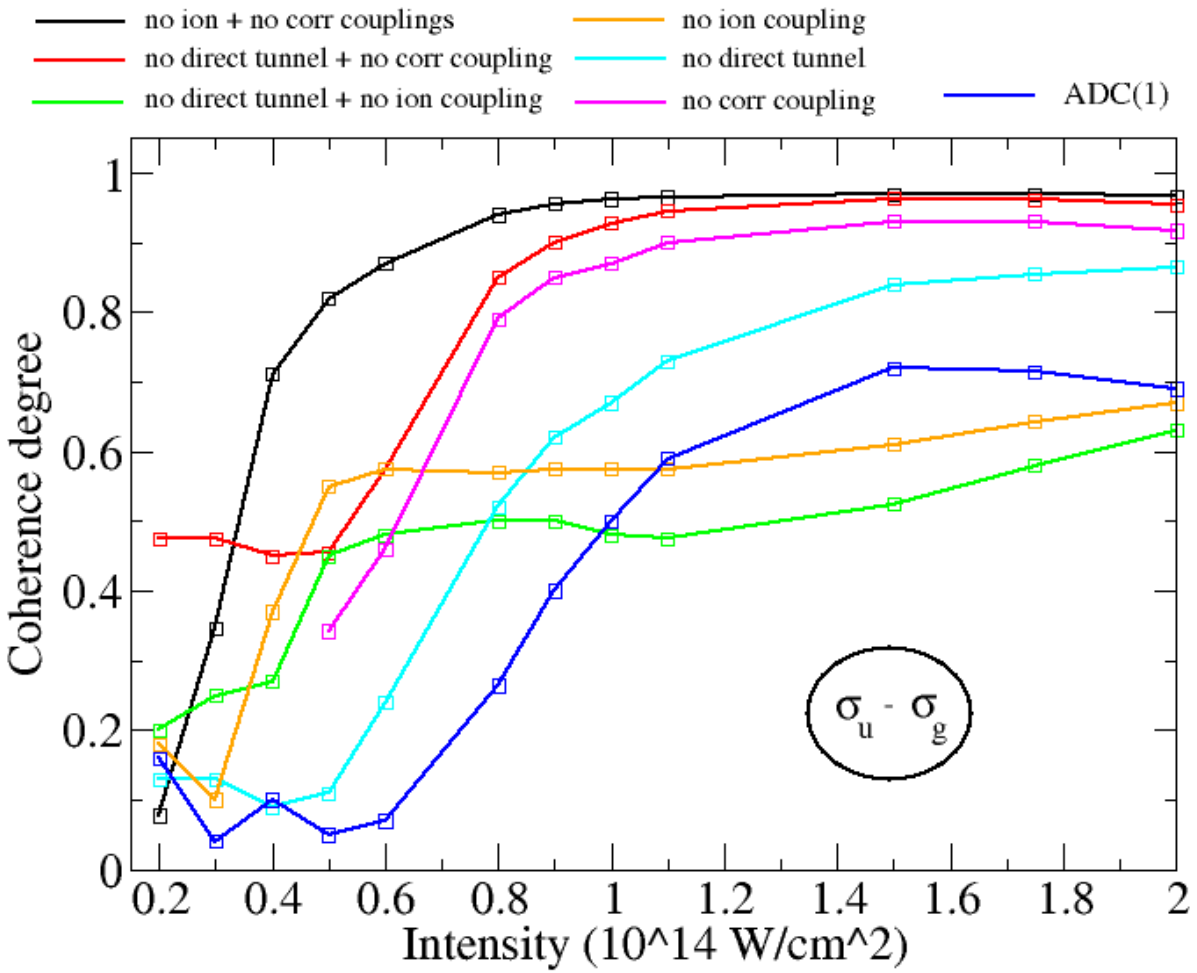


Mechanisms of coherence formation in molecular IR strong-field ionization



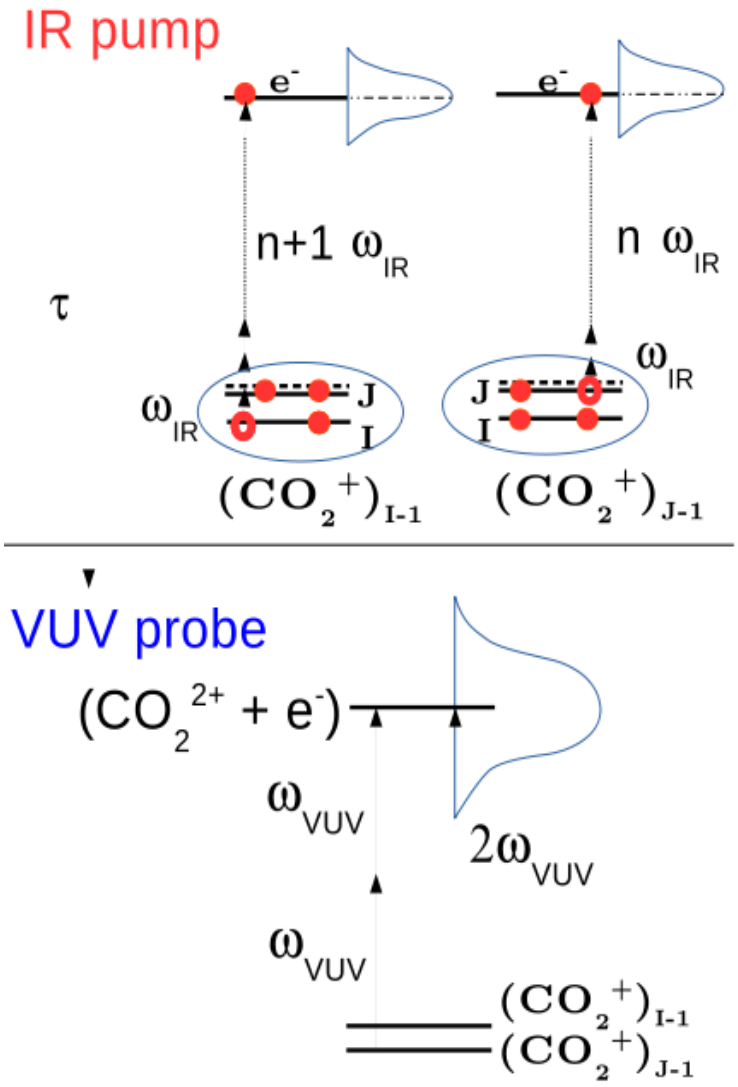
- In some cases, the leading mechanism can be identified

Mechanisms of coherence formation in molecular IR strong-field ionization



- In general, coherence is formed as non-additive superposition of three different effects

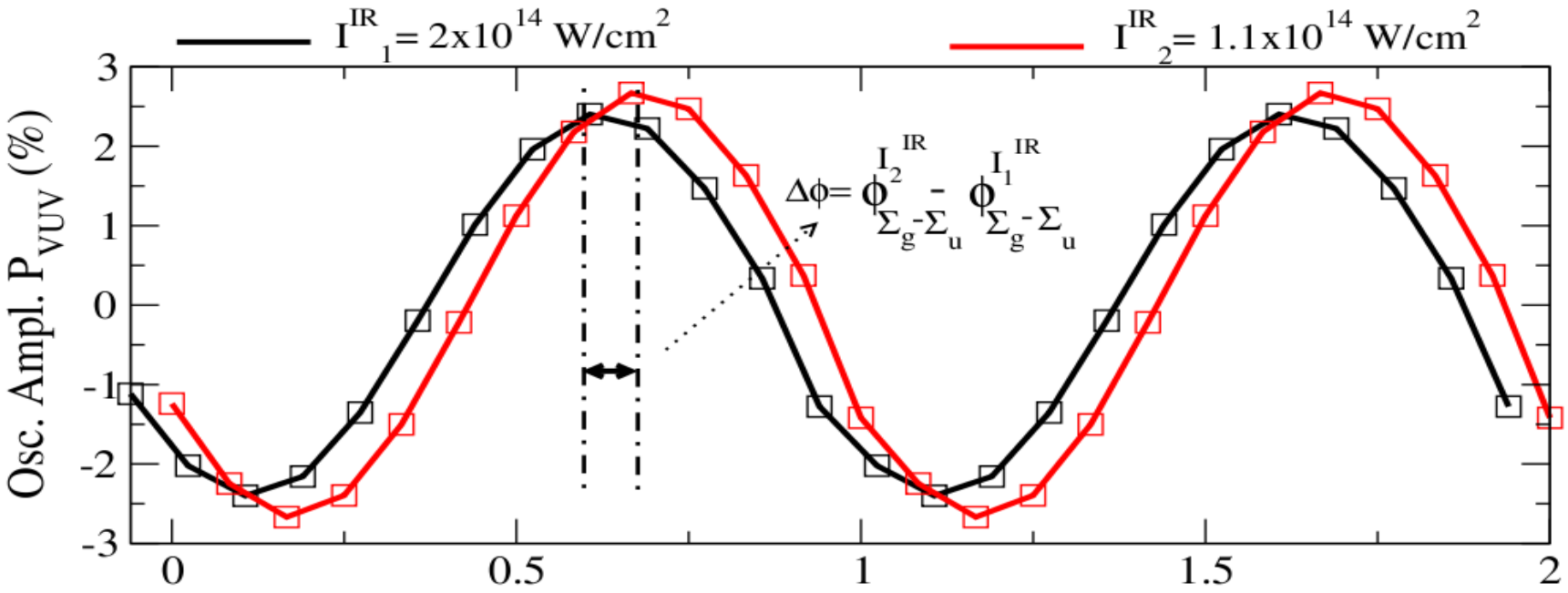
Probing the ionic coherence



- Take the ionic state coefficients from the N-electron ADC(1) wavefunction analysis and plug them into ADC(2)x for (N-1)-electron state to simulate the probe

- ω-2ω probe is required for symmetry reasons, for a general molecule a single-colour probe would work

Probing the ionic coherence

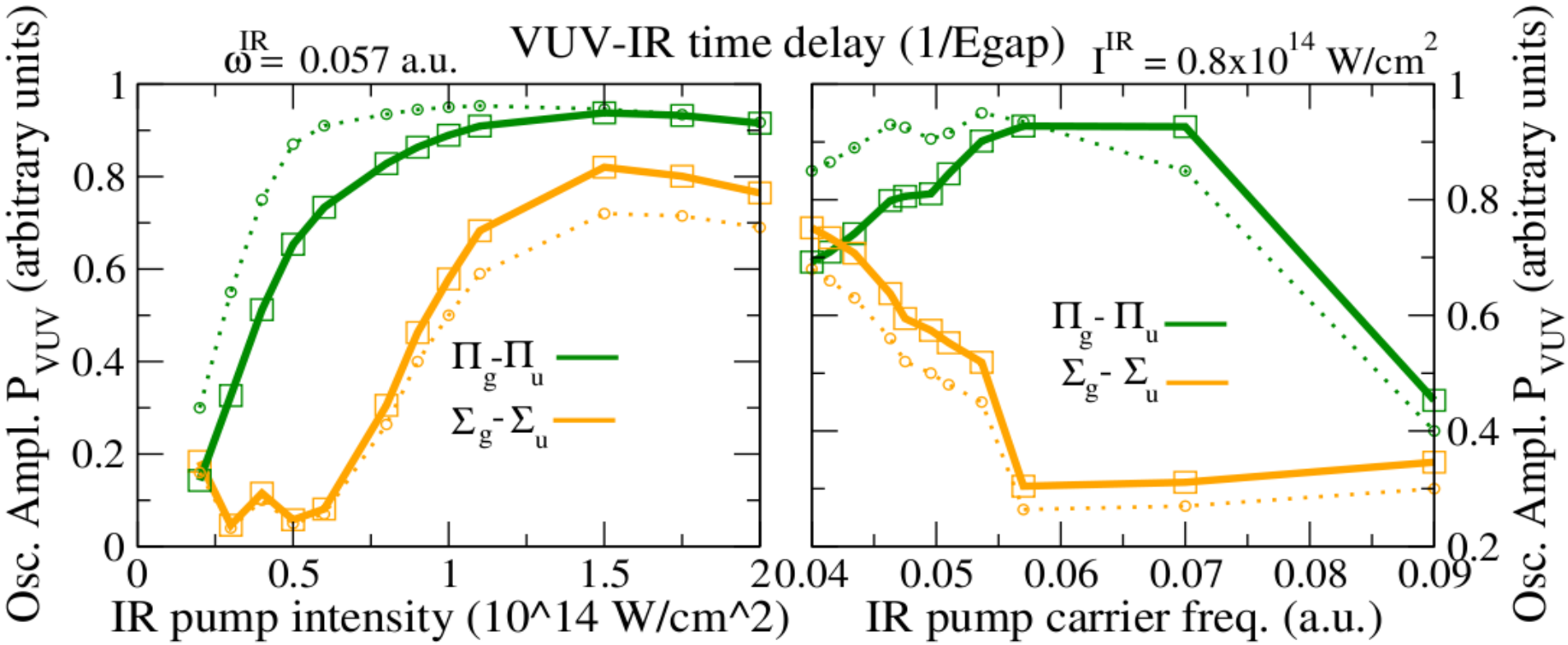


- Total yield of CO_2^{2+} follows the two-state (Σ_g-Σ_u) oscillations

Relative phase of the oscillations at two different pump intensities gives relative phase of the coherent superposition

[M. Ruberti, P. Decleva and V. Averbukh, JCTC **14**, 4991-5000 (2018)]

Probing the ionic coherence



- Degree of coherence achieved at the pump stage (dotted lines) can be inferred from the amplitude of the CO_2^{2+} yield oscillations

[M. Ruberti, P. Decleva and V. Averbukh, JCTC **14**, 4991-5000 (2018)]

First-principles simulation of IR-pump XUV-probe attosecond spectroscopy of molecules: summary

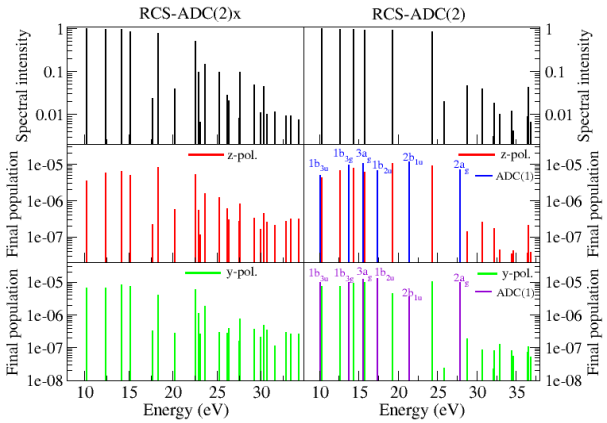
- ✓ Molecular IR pump - XUV probe experiment is simulated fully, with both pump and probe described within the same *ab initio* framework

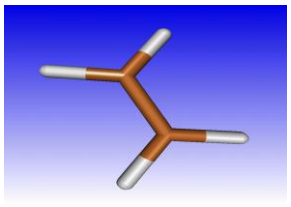
- ✓ Mechanisms of ionic coherence formation identified and their interplay is revealed through numerical experiments

- ✓ Time-dependent B-spline ADC is a powerful *ab initio* tool ready for further attosecond spectroscopy applications

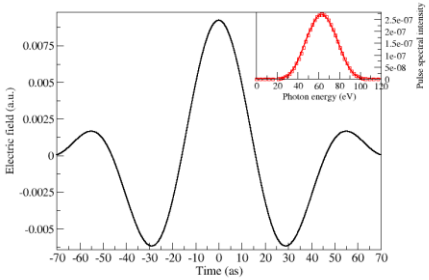
Reduced ionic density matrix upon attosecond XUV ionization of C_2H_4

Ionic populations

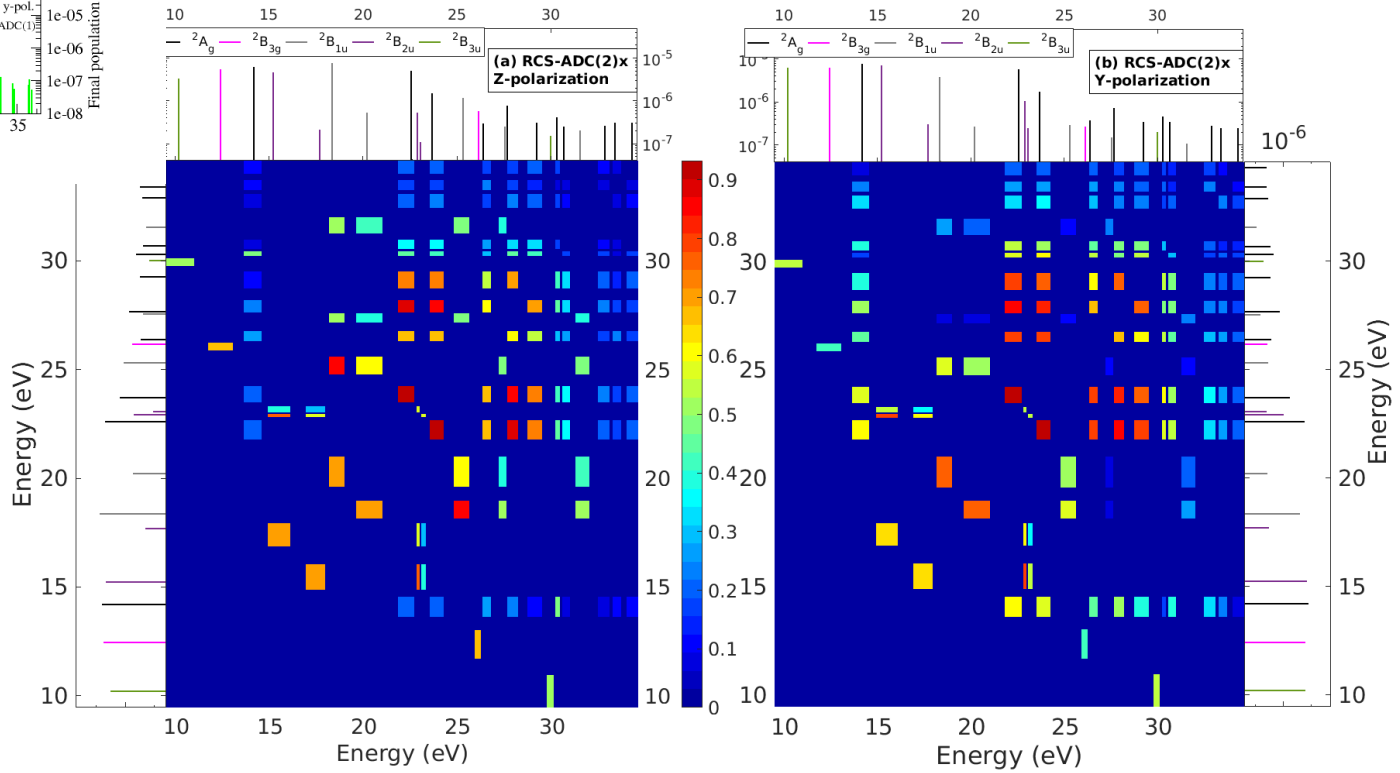




Mean photon energy = 63 eV
Intensity = 3 x 10^{11} W/cm^2



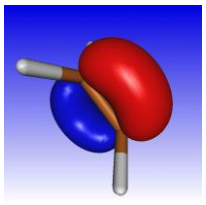
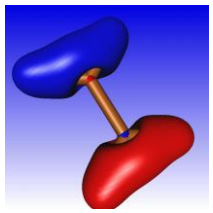
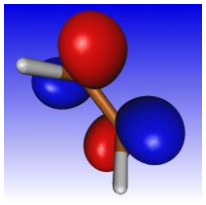
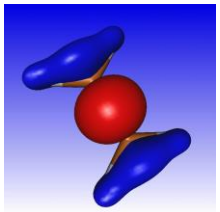
Ionic coherences G_{mn}



[M. Ruberti, Phys. Chem. Chem. Phys., 2019, **21**, 17584-17604 PCCP HOT Article Collection 2019]

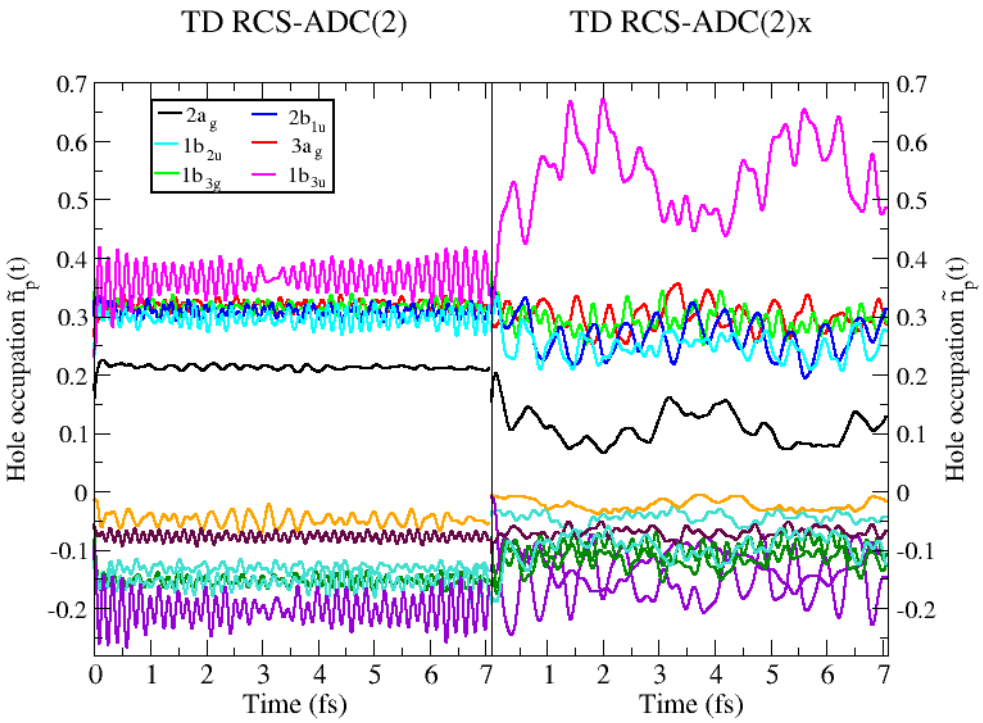
Charge dynamics upon attosecond ionization of C_2H_4

Natural charge orbitals

$$\tilde{Q}(r,t) = \langle \Psi_0^N \mid \hat{Q}(r) \mid \Psi_0^N \rangle - Tr\left(\hat{Q}(r)\,\hat{\tilde{\rho}}(t)\right)$$

$$\tilde{Q}(r,t) = \sum_p \mid \tilde{\phi}_p(r) \mid^2 \tilde{n}_p(t)$$

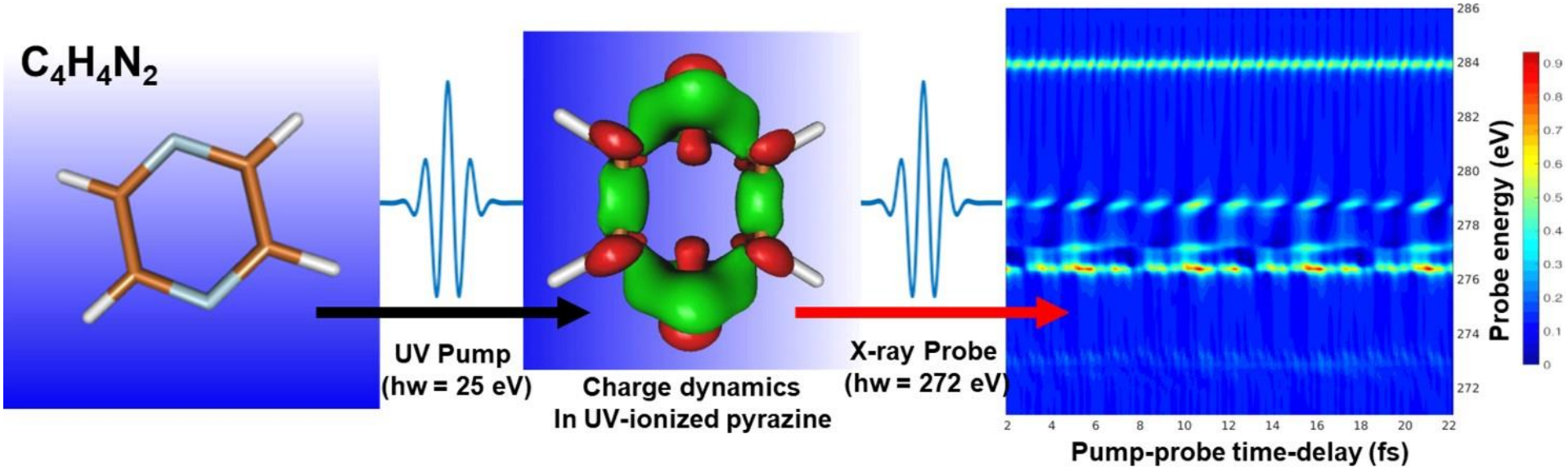


Dominance of correlation-driven charge dynamics

[M. Ruberti, Phys. Chem. Chem. Phys., 2019, **21**, 17584-17604 PCCP HOT Article Collection 2019]

TD B-spline RCS-ADC Theory Applied to Electron Hole Wavepacket Coherence in Pyrazine:

Complete simulation of full attosecond XUV-pump - X-ray-probe experiment in a polyatomic molecule



PUMP: Characterization of ionized system prepared by the XUV pump: Ionic density matrix, coherence and charge dynamics upon attosecond XUV ionization.

PROBE: X-ray attosecond transient absorption spectra.

M. Ruberti,
Faraday Discussions (2020)

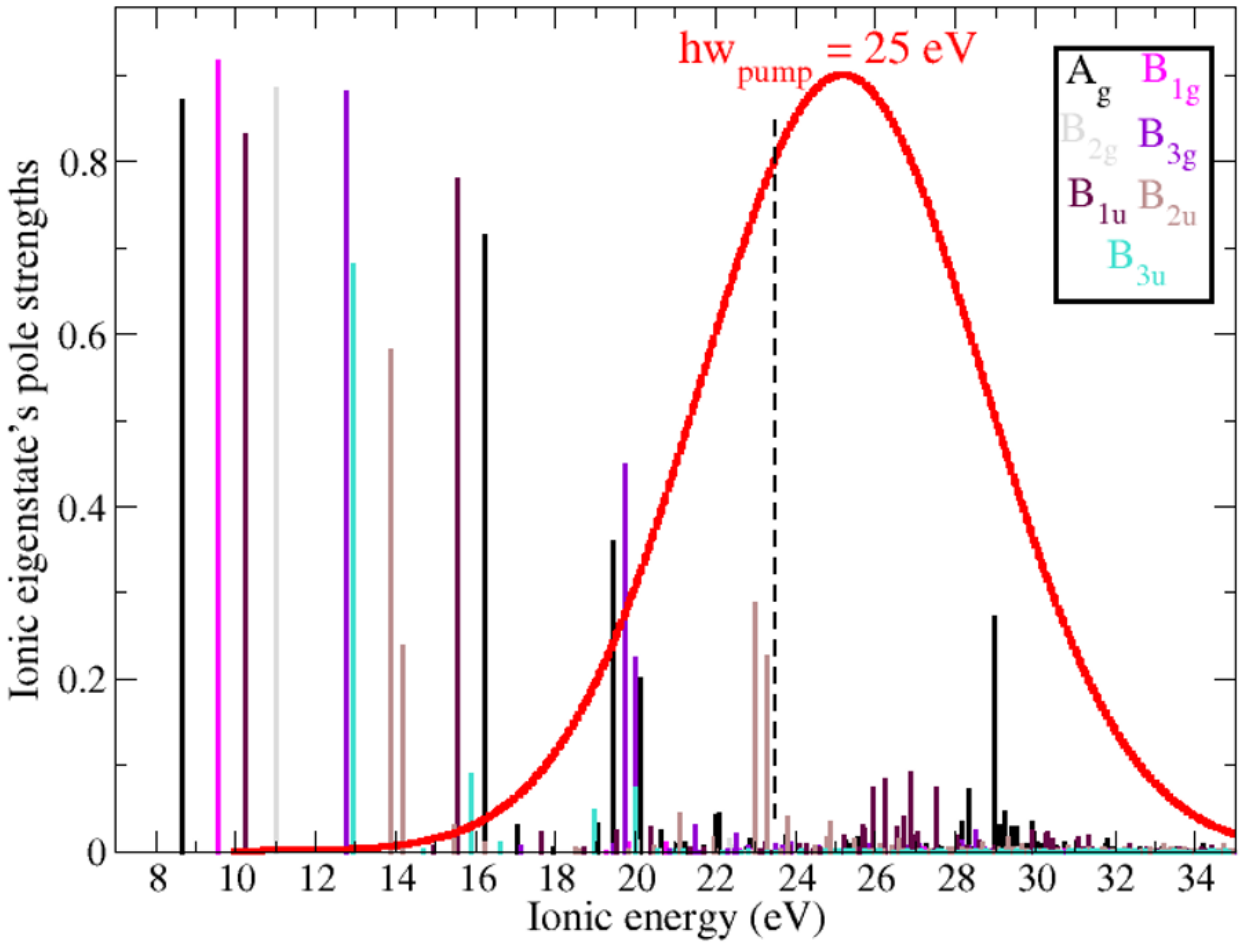
PUMP attosecond ionization of pyrazine

Populations
of ionic state ***n***

$$P_n(t) = |\rho_{nn}(t)|$$

Pump central photon energy
25 eV
Intensity **6 x 10^{11} W/cm^2**

Bandwidth = **7 eV**



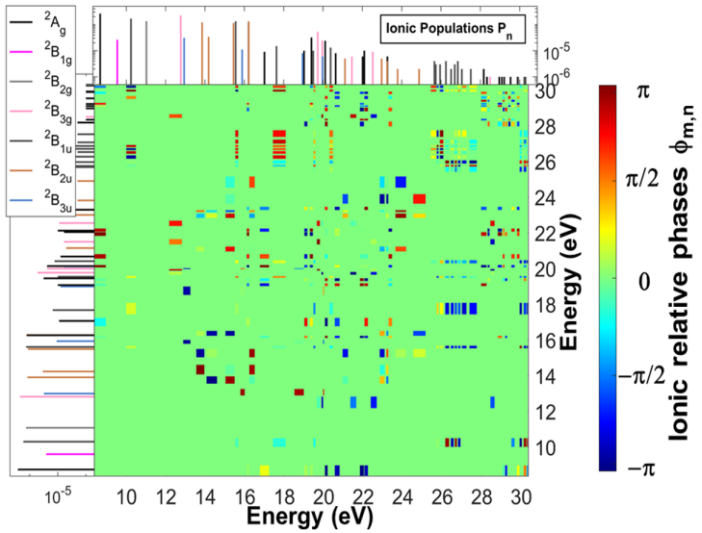
PUMP attosecond ionization of pyrazine

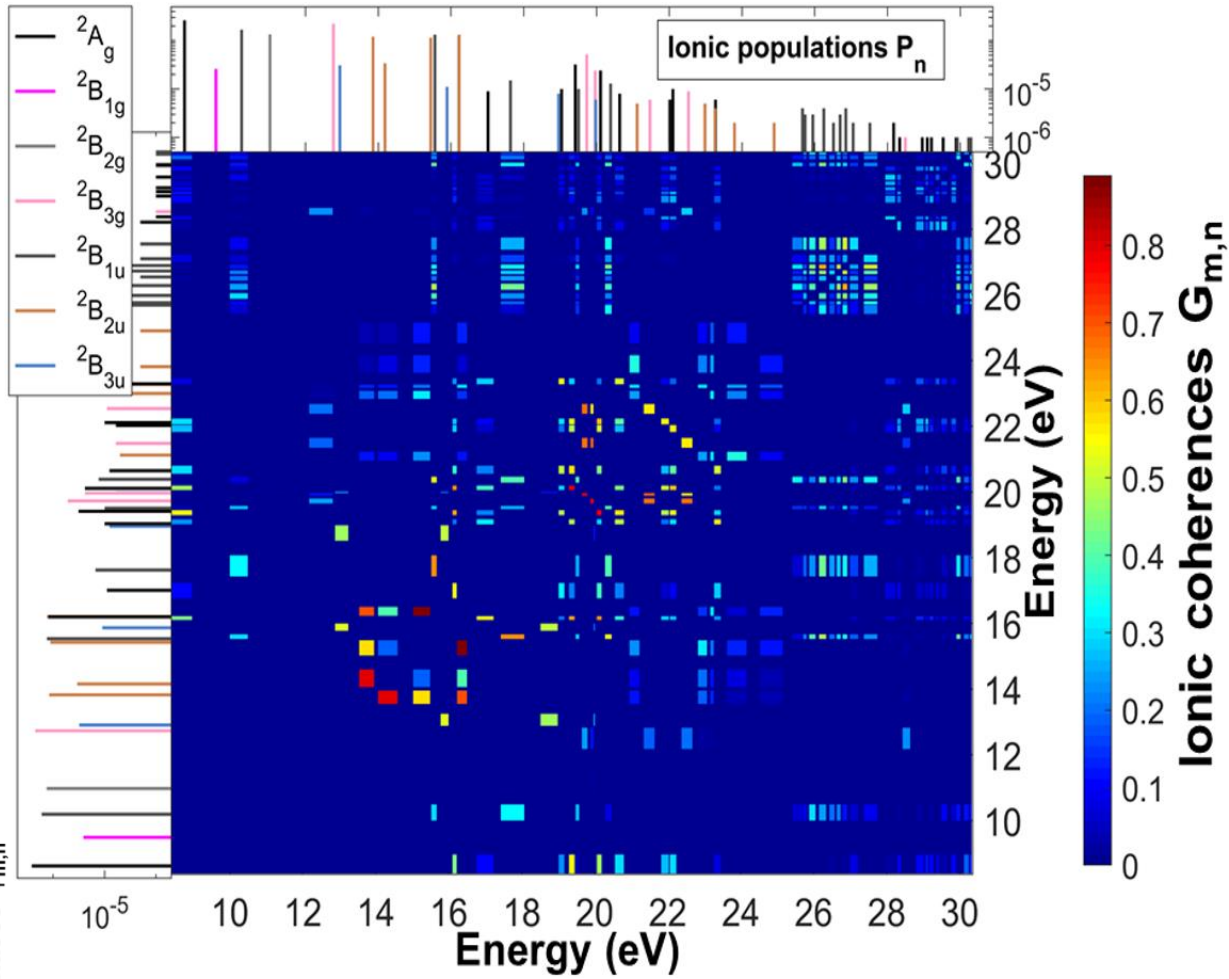
Degrees of coherence
between pair of populated ionic states ***m*** and ***n***

$$G_{mn}(t) = \frac{|\rho_{mn}(t)|}{\sqrt{P_m(t) * P_n(t)}}$$

Maximum quantum coherence corresponds to $G_{mn} = 1$

Ionic relative phases



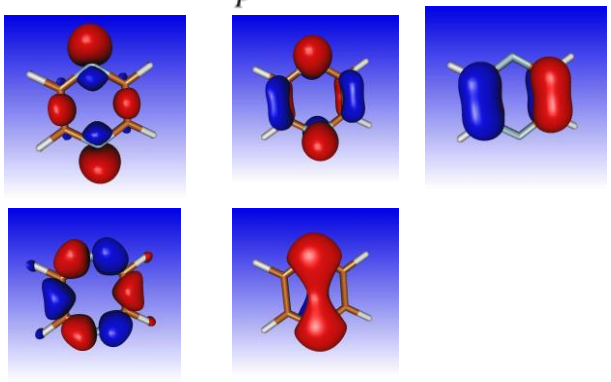


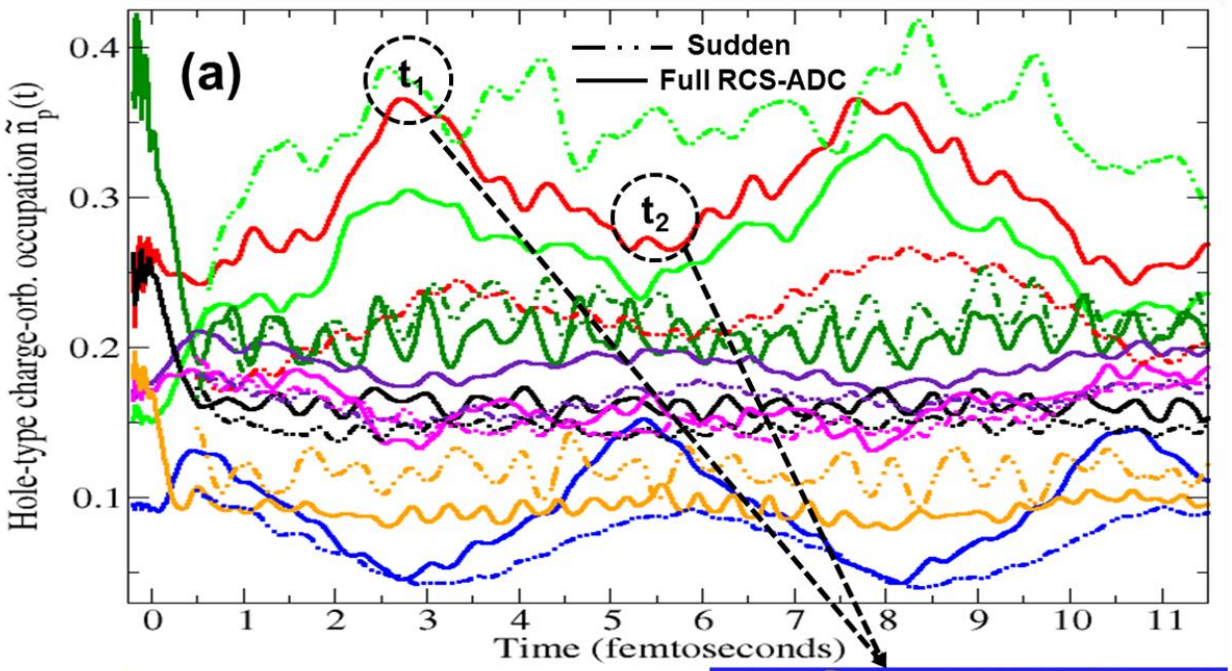
M. Ruberti,
Faraday Discussions (2020)

Deviation from sudden approximation for smaller photon energies: the case of pyrazine

Natural charge orbitals

$$\tilde{Q}(r,t) = \sum_p |\,\tilde{\phi}_p(r)\,|^2\,\tilde{n}_p(t)$$



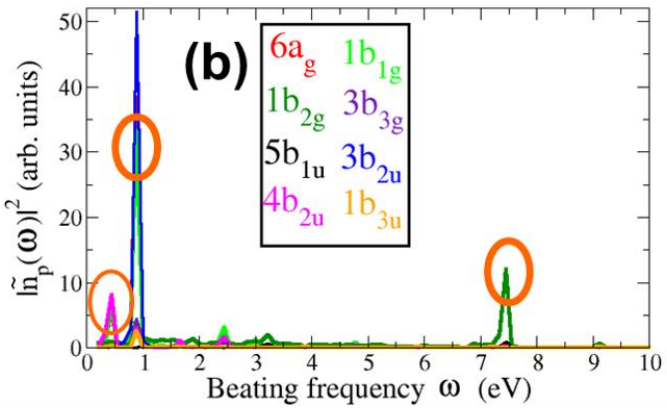


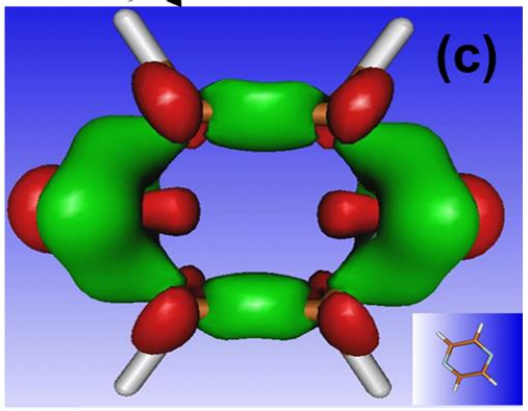
Sudden approximation ansatz for the initial state

? Dependence on laser pulse parameters **?**

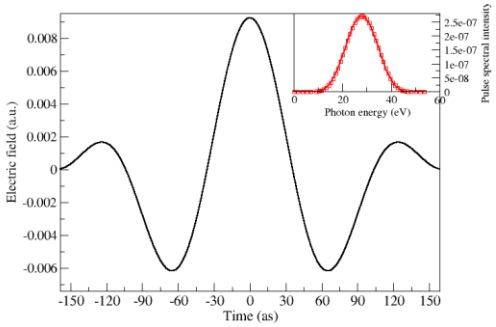
$$|\,\Psi^{N-1}_{initial}\rangle \sim a_i\,|\,\Psi^N_0\rangle$$

when is it valid...?





Ionic coherence evolution upon XUV ionization of pyrazine



Ionic decoherence due to coupling to the emitted photoelectron

Purity

$$Tr\left(\hat{\tilde{\rho}}^2(t)\right) \neq Tr\left(\hat{\tilde{\rho}}(t)\right) \leq 1 \quad mixed\ state,$$

$$Tr\left(\hat{\tilde{\rho}}^2(t)\right) = Tr\left(\hat{\tilde{\rho}}(t)\right) = 1 \quad pure\ state.$$

von Neumann entropy of entanglement

$$s^{Ion}(t) = -ln\left(\frac{1}{N}\right) \quad statistical\ mixture,$$

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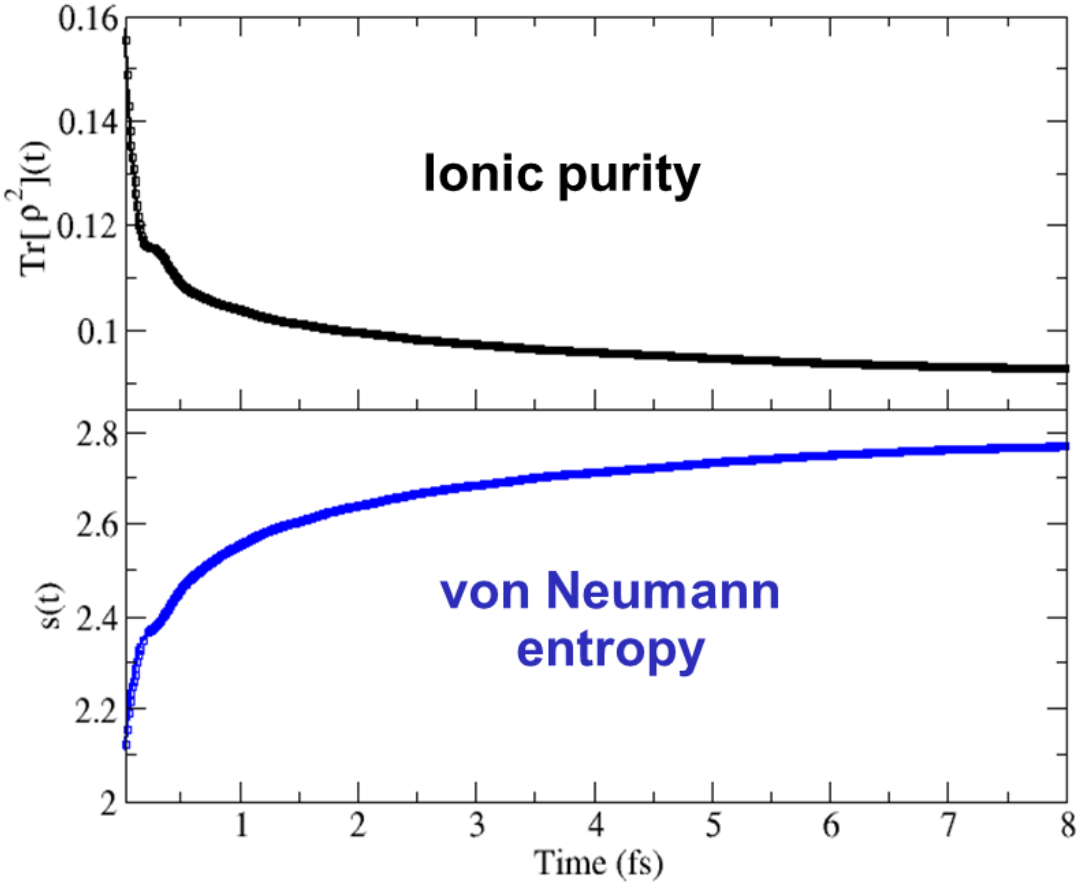
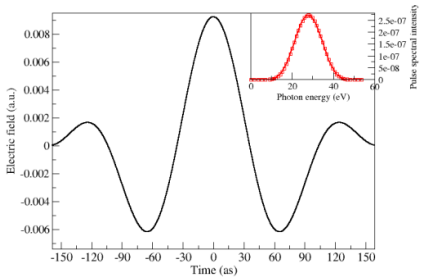
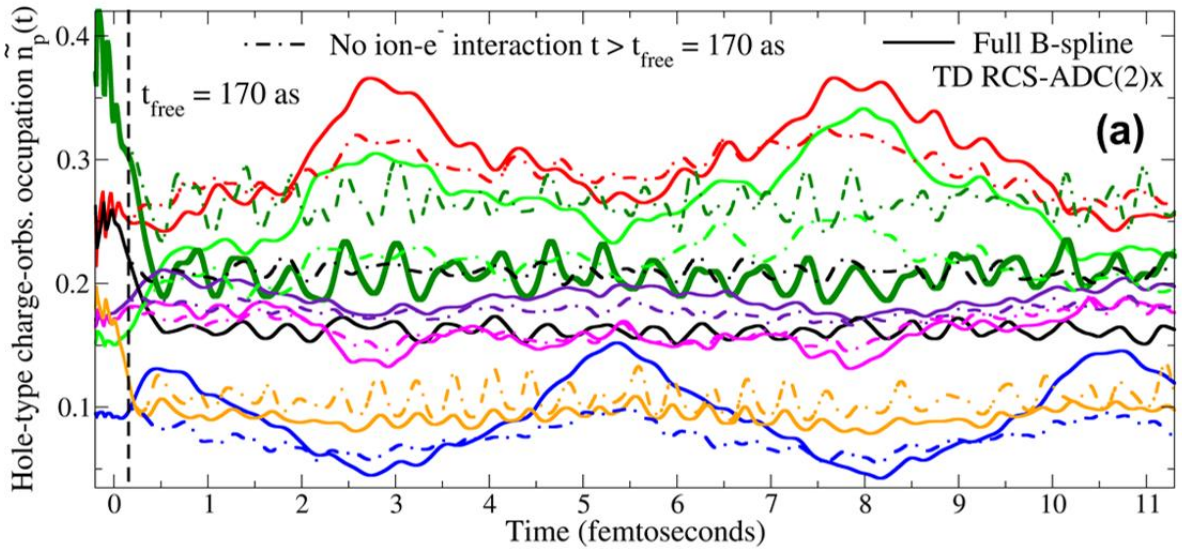


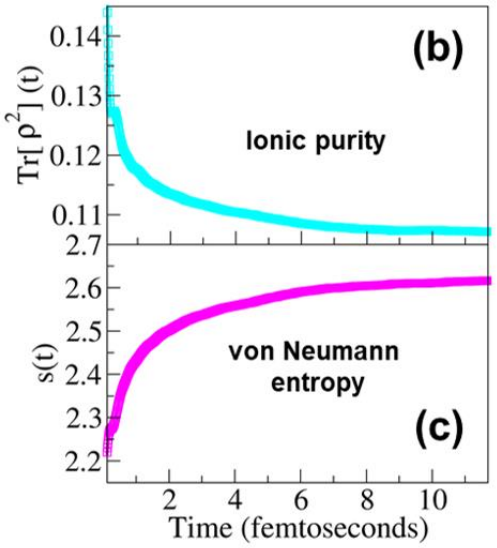
Ionic coherence evolution upon XUV ionization of pyrazine

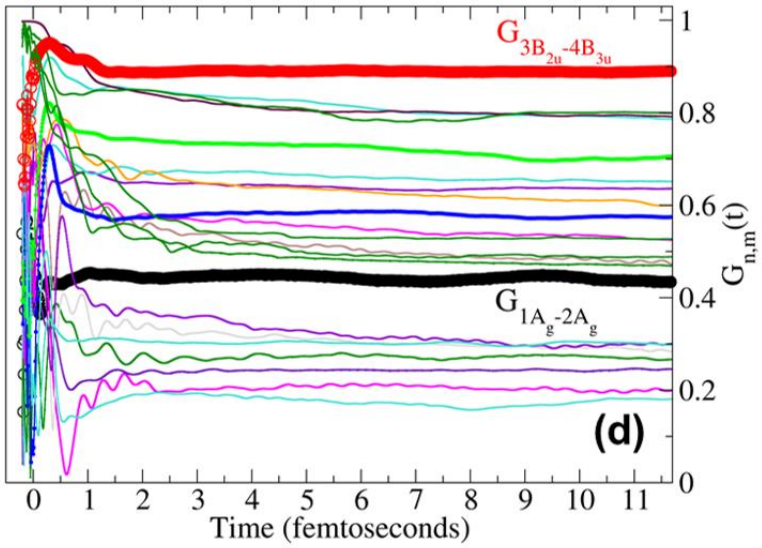


Central Pump
photon energy = 25 eV
Intensity = 6 x 10^{11} W/cm^2

Ionic decoherence due to coupling to the emitted photoelectron







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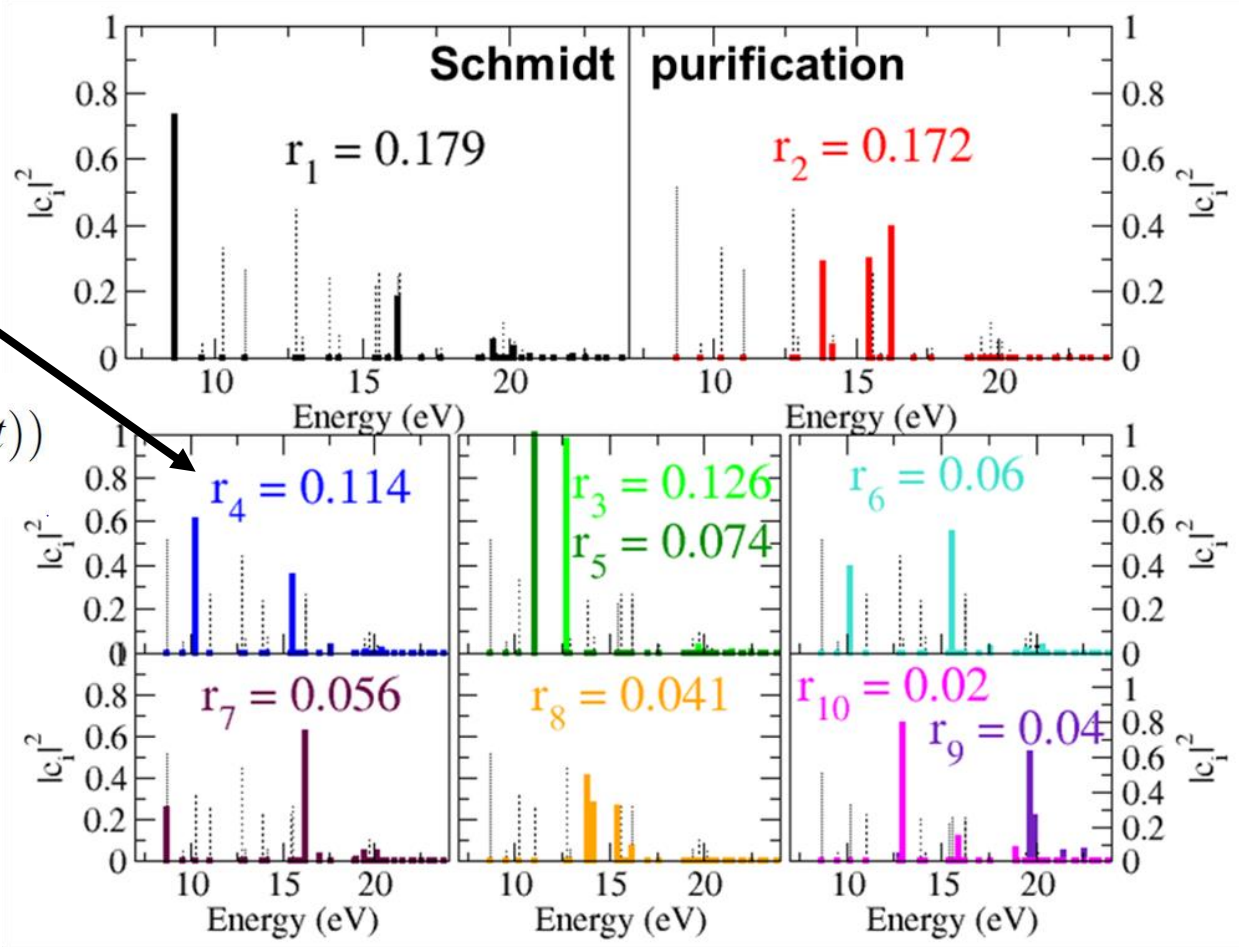
Faraday Discussions (2020)

Schmidt decomposition of ionic density matrix

Schmidt decomposition of ionic density matrix: incoherent sum of coherent ionic channels – each wavefunction has weight $\mathbf{r_i}$

$$\hat{\tilde{\rho}}(t) = \sum_{i=1,N} r_i(t)\hat{P}_i(t)$$

$$s^{\mathrm{Ion}}(t) = -\sum_{i=1,N} r_i(t) \times \ln(r_i(t))$$



M. Ruberti,
Faraday Discussions (2020)

PROBE-STEP

X-ray attosecond transient absorption spectra of XUV-ionized pyrazine

First-principles simulation of the **probe step:**

Time-Dependent von Neumann equations for the ionic density matrix interacting with the X-ray probe pulse

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\tilde{\rho}}(t) = -\frac{i}{\hbar}\left[\hat{H}^{\mathrm{Ion}}(t), \hat{\tilde{\rho}}(t)\right]$$

X-ray probe duration = 180 as; Intensity = 10^{14} W/cm^2

Photon energies:

N K-edge absorption window
photon energy = 393 eV

C K-edge absorption window
photon energy = 272 eV

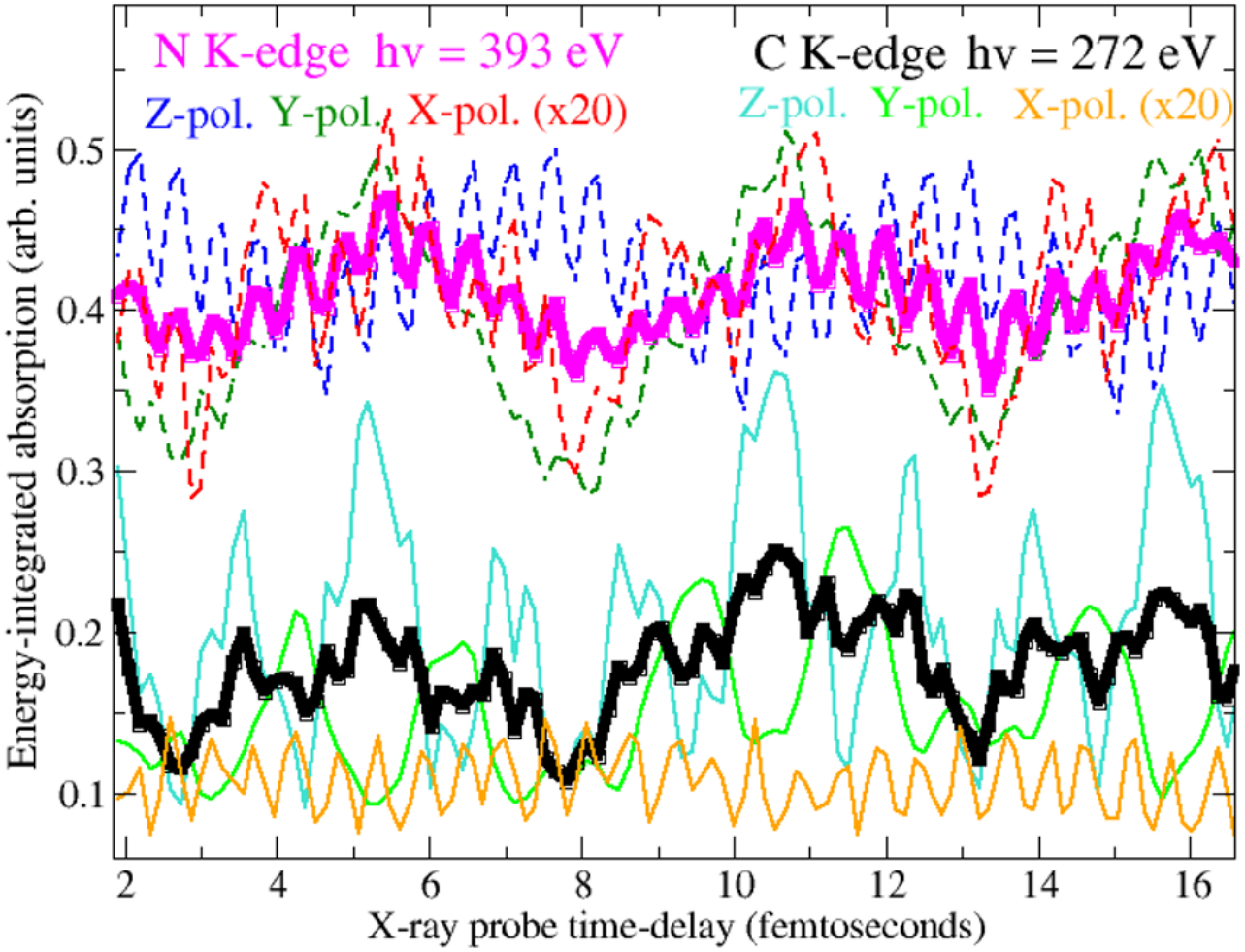
PROBE-STEP

X-ray energy-integrated transient absorption of XUV-ionized pyrazine

Attosecond (XUV) pump - (X-ray) probe spectroscopy of charge dynamics:

- high temporal resolution;
- chemical selectivity;
- spatial resolution.

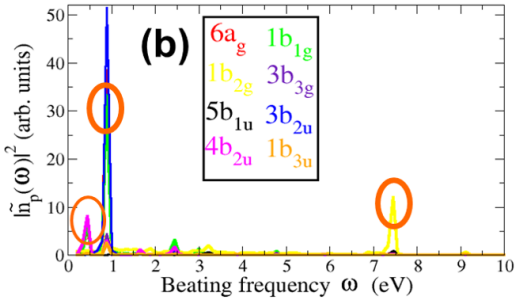
C-N charge oscillation period T ~ 0.54 fs



Quantum electronic coherences

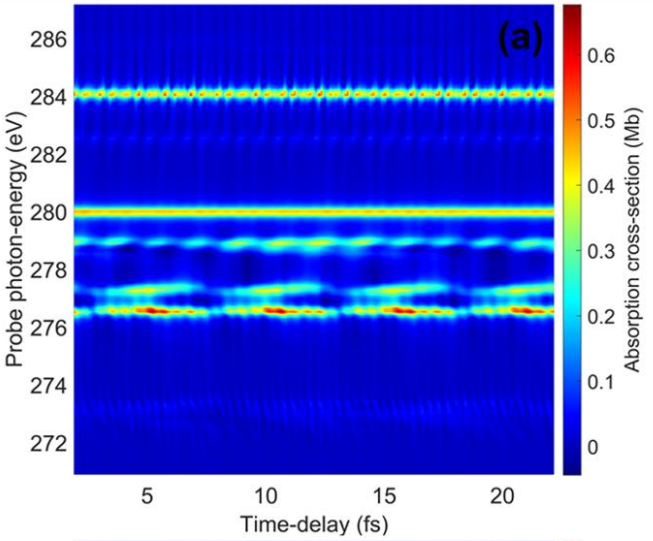
by attosecond transient absorption spectroscopy

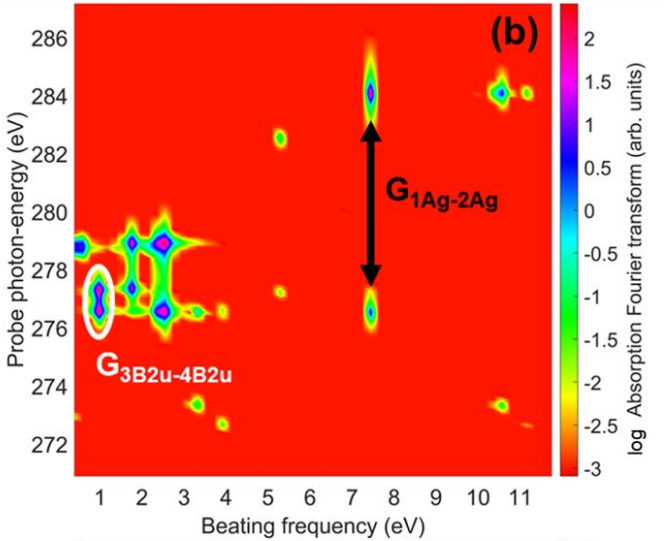
Carbon K-edge
photon energy = 272 eV

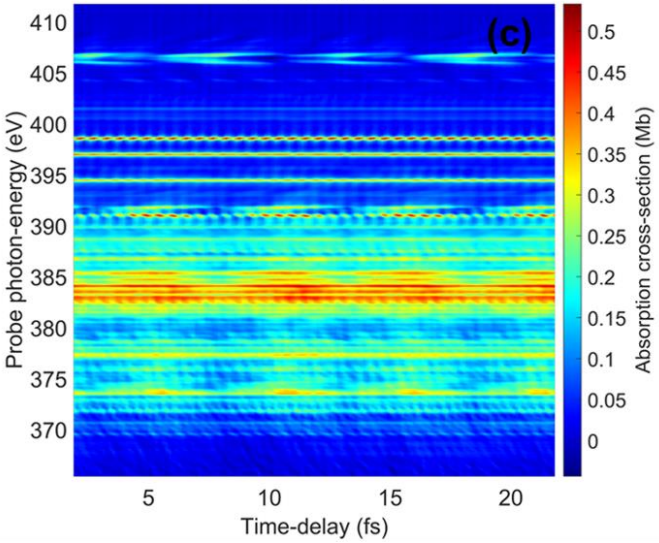


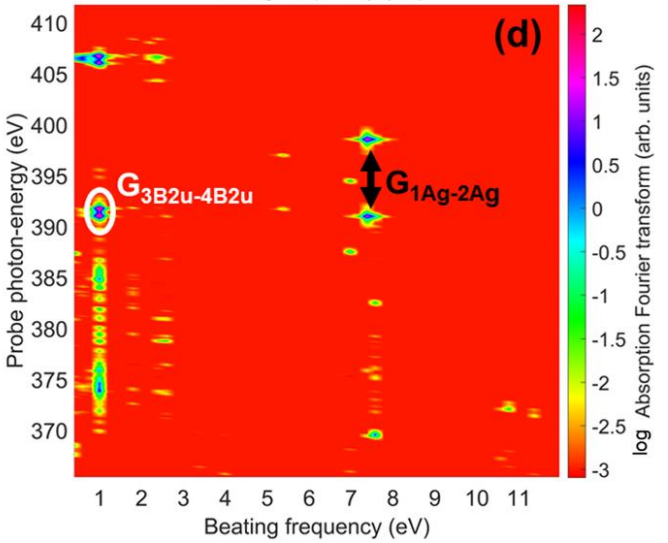
Nitrogen K-edge
photon energy = 393 eV

All (1h and 2h1p)
final core-ionised
states included







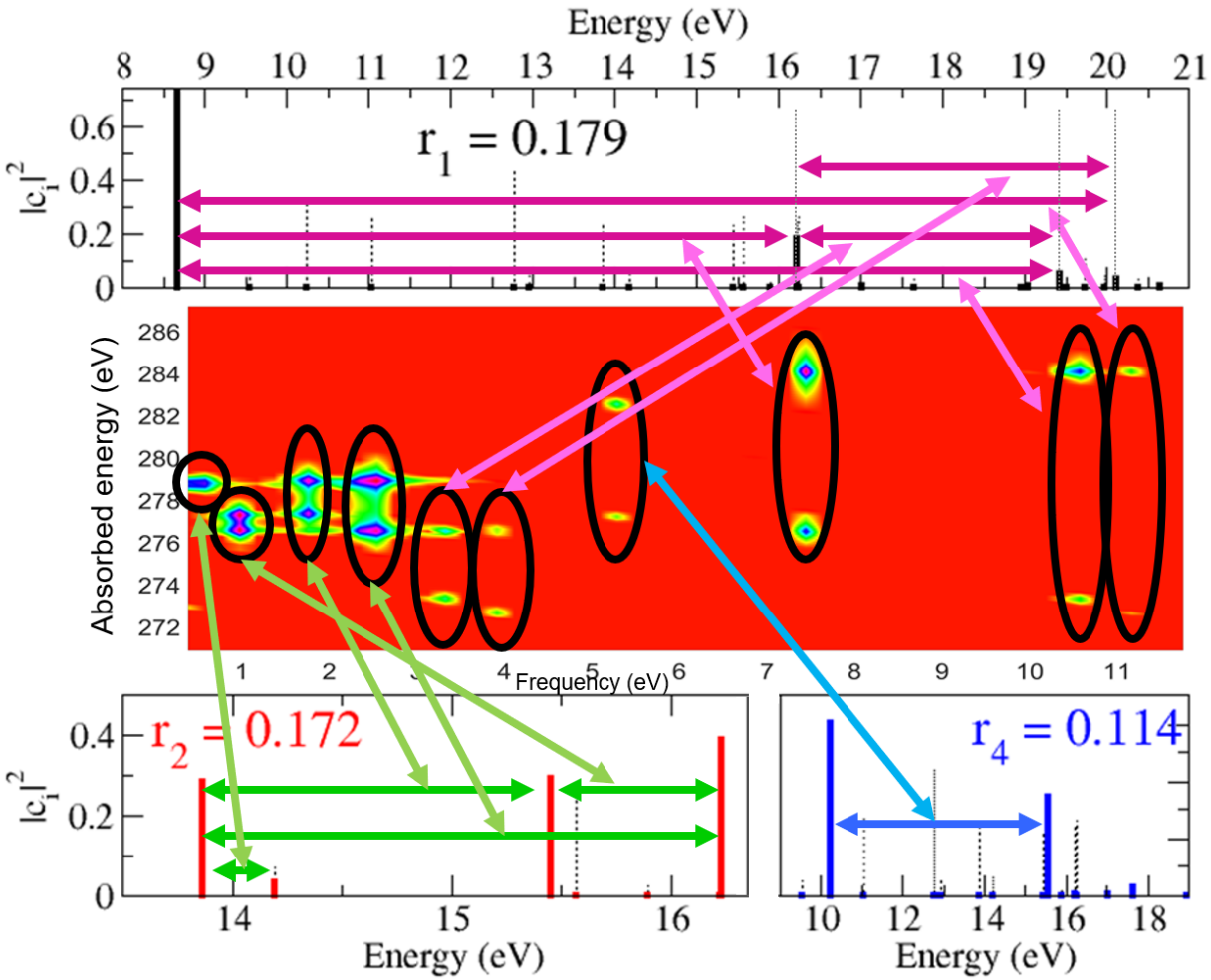


M. Ruberti,
Faraday Discussions (2020)

PROBE-STEP

Mapping ATAS observable onto ionic coherences

Quantum electronic coherences by attosecond transient absorption spectroscopy



Peaks in the Fourier-transformed ATAS

$$\hat{\tilde{\rho}}(t) = \sum_{i=1,N} r_i(t)\hat{P}_i(t)$$

Schmidt decomposition of ionic density matrix

M. Ruberti,
Faraday Discussions (2020)

B-spline ADC, RCS-ADC Publications

B-spline ADC theory

2014 -Atomic ***photoionization cross-section*** and ***high harmonic generation spectra***, J. Chem. Phys.

2016 -***XUV-IR transient absorption*** in helium New J. Phys.

2018 -Book chapter in "Attosecond Molecular Dynamics", RSC Theoretical and Computational Chemistry series.

2018 -Multi-channel dynamics in ***high harmonic generation*** of CO_2, Phys. Chem. Chem. Phys.

2018 -***IR-pump – XUV-probe attosecond experiment*** in CO_2, J. Chem. Theory Comput.

B-spline RCS-ADC theory

2019 -Total ***photoionization cross-sections*** of molecules, J. Chem. Theory Comput.

2019 -***Ionic coherence and charge dynamics*** in XUV attosecond ionization of C_2H_2 and C_2H_4, Phys. Chem. Chem. Phys.

2019 -***Coherent control*** of single-photon Laser Enabled Auger Decay in Neon, New J. Phys.

2020 -XUV pump – X-ray probe ***attosecond transient absorption spectroscopy*** in pyrazine, Faraday Discussions.

2021 -***Time-Resolved photoelectron spectroscopy***: Femtosecond X-ray pump – X-ray probe in glycine, arXiv:2012.04852**,** under review in Science.

First-principles simulation of XUV-pump X-ray probe attosecond spectroscopy of molecules: summary

- Time-dependent B-spline RCS-ADC a*b initio* method describes many-electron ionization dynamics in polyatomic molecules with inclusion of relaxation & correlation effects (shake-up) and full description of photoelectron.
- Quantum electronic coherence/entanglement formation can be calculated *ab initio*, in the molecular case, as a function of the ionizing pulse parameters.
- Going beyond the sudden approximation is necessary especially in the lower photoelectron energy regime.
- Fully *ab initio* simulations of complete attosecond pump - attosecond probe experiments possible in polyatomic molecules.
- X-ray ATAS set-up is a promising and powerful scheme to retrieve the many-electron quantum ionic coherences arising in attosecond photoionization and pre-determining the subsequent charge-directed reactivity.
- Quantum coherence decay mechanisms: residual interaction with slow photoelectrons, Auger decay, coupling to nuclear motion, vibrational ground-state spatial spread. Unravelling the interplay between these mechanisms is the next theoretical, computational and experimental challenge...

Research vision

Quantum State Tomography for Attosecond Ionization of Entangled Many-Electron Systems

- Fundamental understanding of the physics underlying photochemical & photophysical transformations of matter at attosecond to femtosecond timescales

- *Extend and apply concepts of Quantum Information to the field of attosecond dynamics*

Full characterisation
+
tomographic reconstruction
+
coherent quantum control
of
X-ray atto-ionised
quantum state

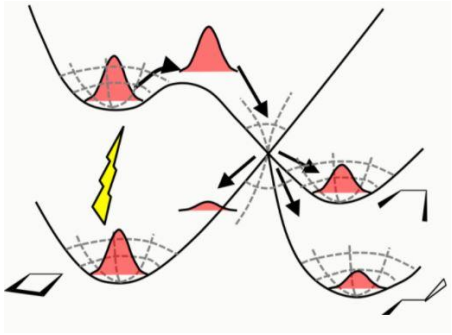
Research Vision-
Theoretical “ingredients”

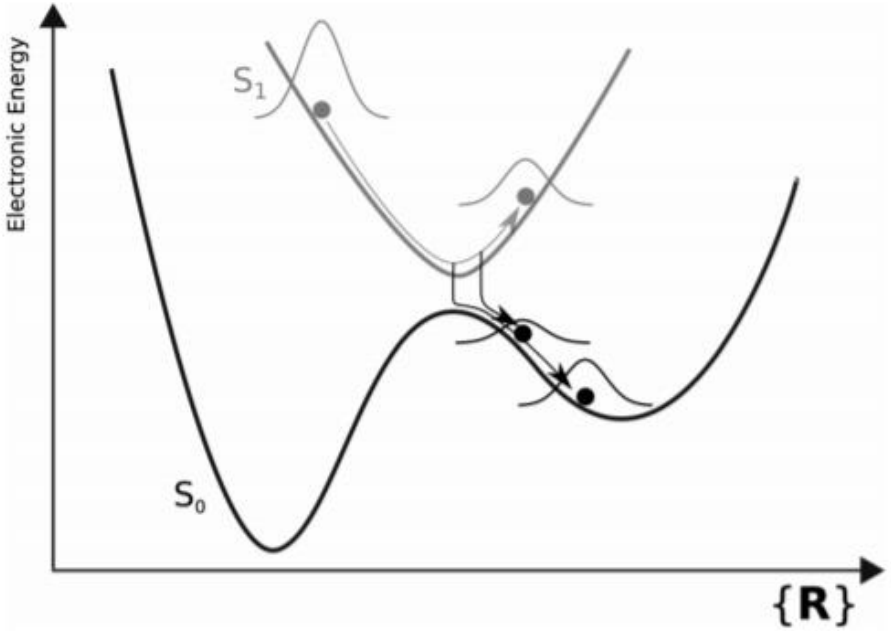
- ✓ Description of **electron correlation**: shakeup states, correlation satellite states.
- ✓ Description of **electronic relaxation**: relaxation satellite states.
- ✓ **Accurate partial cross-sections** for the many-electron ionic states of the system as a function of the ionising laser pulse parameters.
- ✓ **Time-dependent description** of the ionisation process: ultrafast formation and loss of coherence and effect of different laser field parameters.
- ✓ Description of the **N-electron wavefunction**, ion-photoelectron **entanglement**.
- ✓ Effect of the residual **inter-channel couplings** between the created ionic system and the **emitted photoelectron**. **Correlation effects in the continuum**.
- ❖ Description of **non-radiative relaxation processes**: Auger decay, Coster-Kronig. It can be done sequentially, or semi-empirically (introducing extra parameters). The model describes one electron in the continuum.

Research Vision - Theoretical “ingredients”

❑ **Coupling to nuclear motion**, multidimensional problem: electronic coherences among several electronic states –> non-adiabatic nuclear dynamics across several potential energy surfaces

❑ **Complete description of the QUANTUM many-body state of the molecular system**.





✓ *Ab initio* multiple spawning (**AIMS**) scheme for coupled electron-nuclear dynamics, developed by Prof. T. Martinez (PULSE Institute).

Fully quantum theory for ultrafast coupled electron-nuclear dynamics triggered by X-ray attosecond laser pulses

TD B-spline RCS-ADC theory

AIMS theory

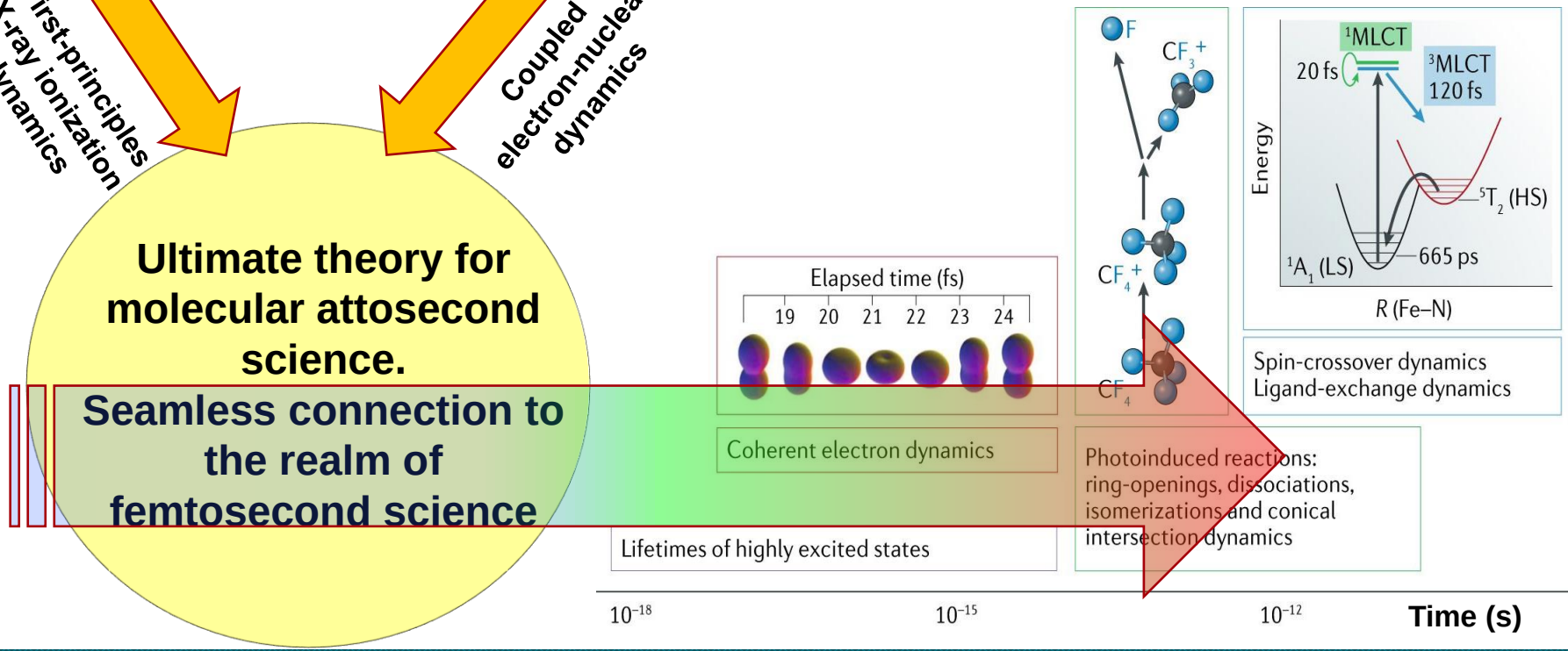
First-principles X-ray ionization dynamics

Coupled electron-nuclear dynamics

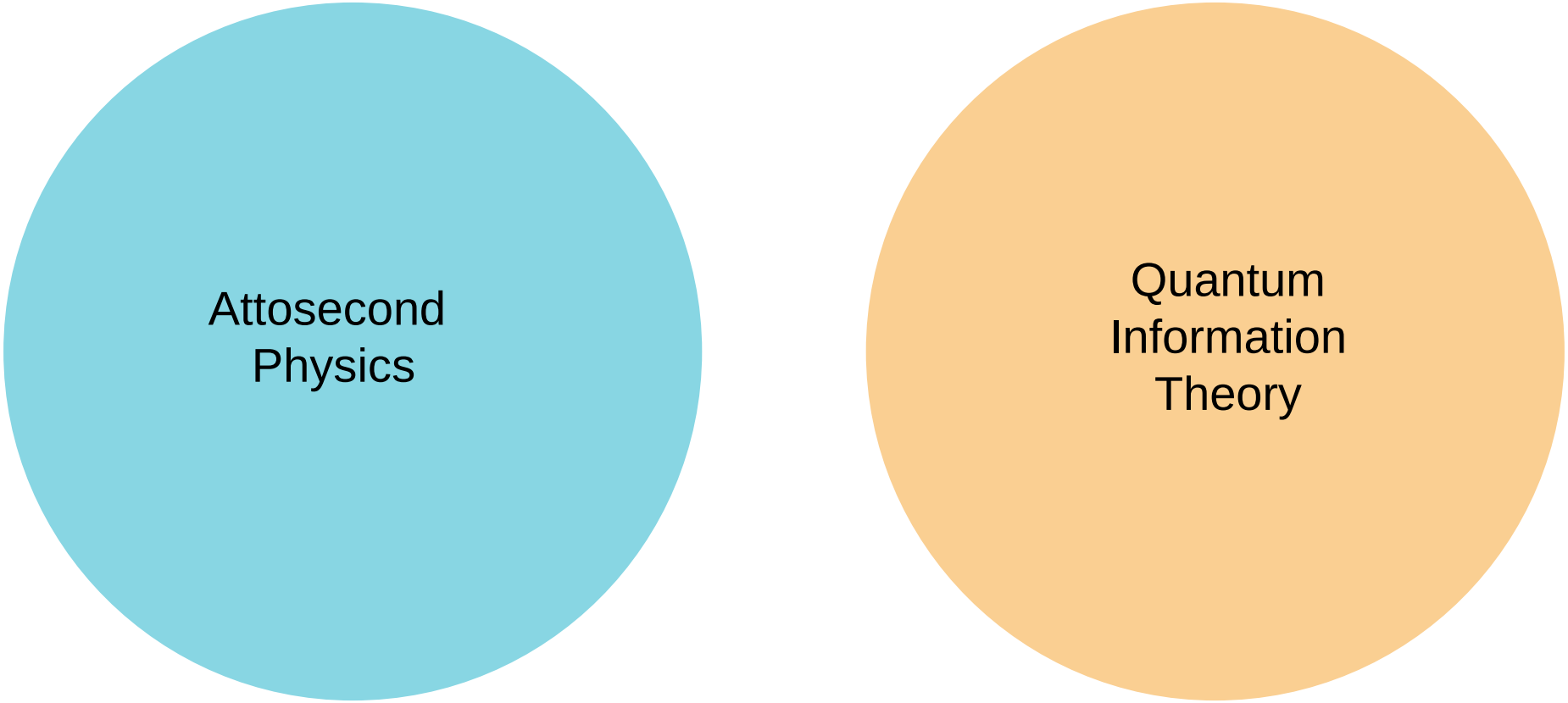
Ultimate theory for molecular attosecond science.

Seamless connection to the realm of femtosecond science

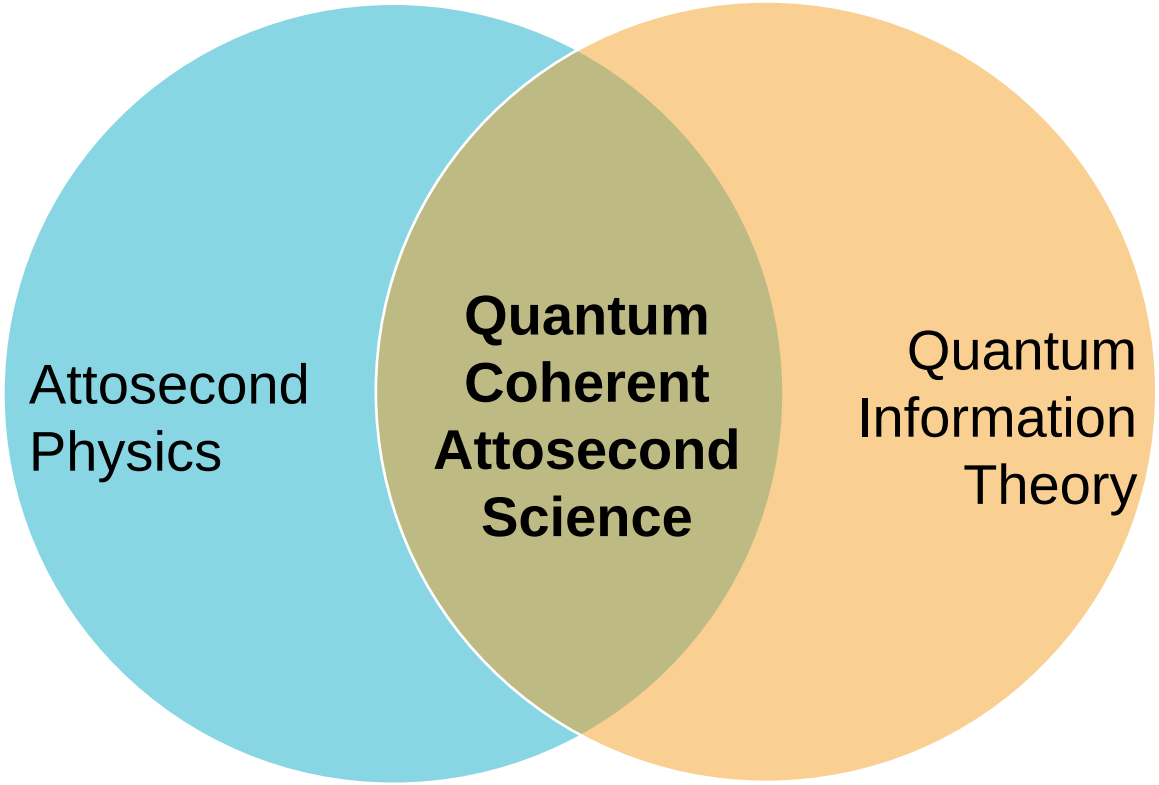
Collaboration with the **Ultrafast Theory and Simulation Group** of the Chemical Science Division at PULSE Institute (Prof. Todd Martinez)



Research Vision



Research Vision



My goal is to lay the foundations of a new field of study at the intersection of Attosecond Physics and Quantum Information

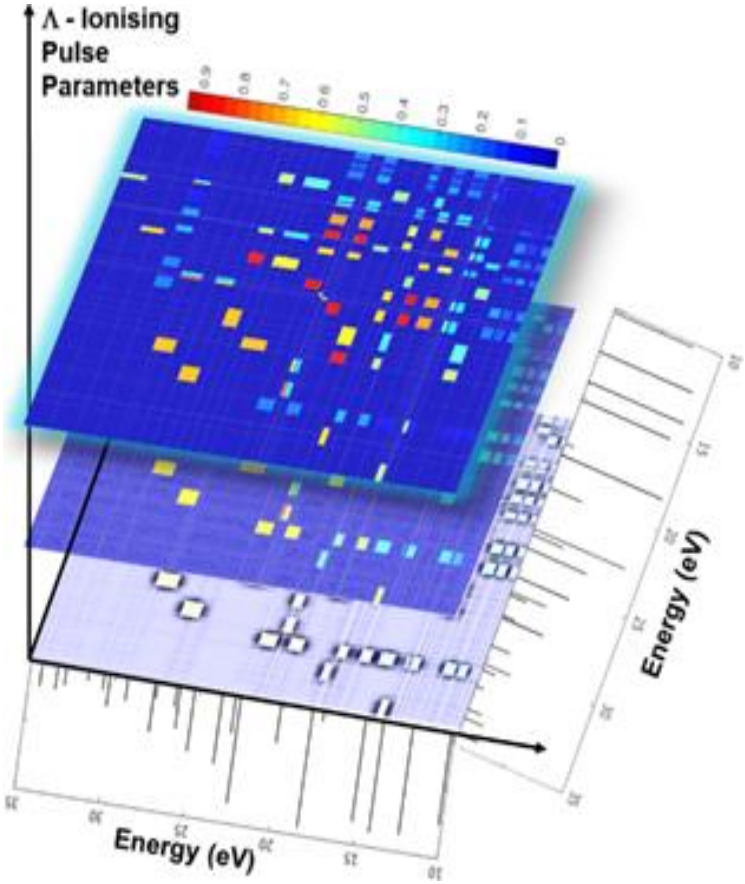
Research Vision

Quantum characterization of the *X-ray ionized state* ***in different light-matter interaction regimes***

Research goals:

- ***Physical mechanisms of coherence formation*** *upon X-ray attosecond ionization*
- *Coherent many-electron dynamics on time scales down to the attosecond regime.*
- *Competition between nuclear motion and Auger decay.*

Laser parameters: frequency, intensity, polarization, stochasticity, etc…



Collaboration with the **strong-field AMO Science Group** of the Chemical Science Division at PULSE Institute
(Prof. Philip Bucksbaum)

Research Vision

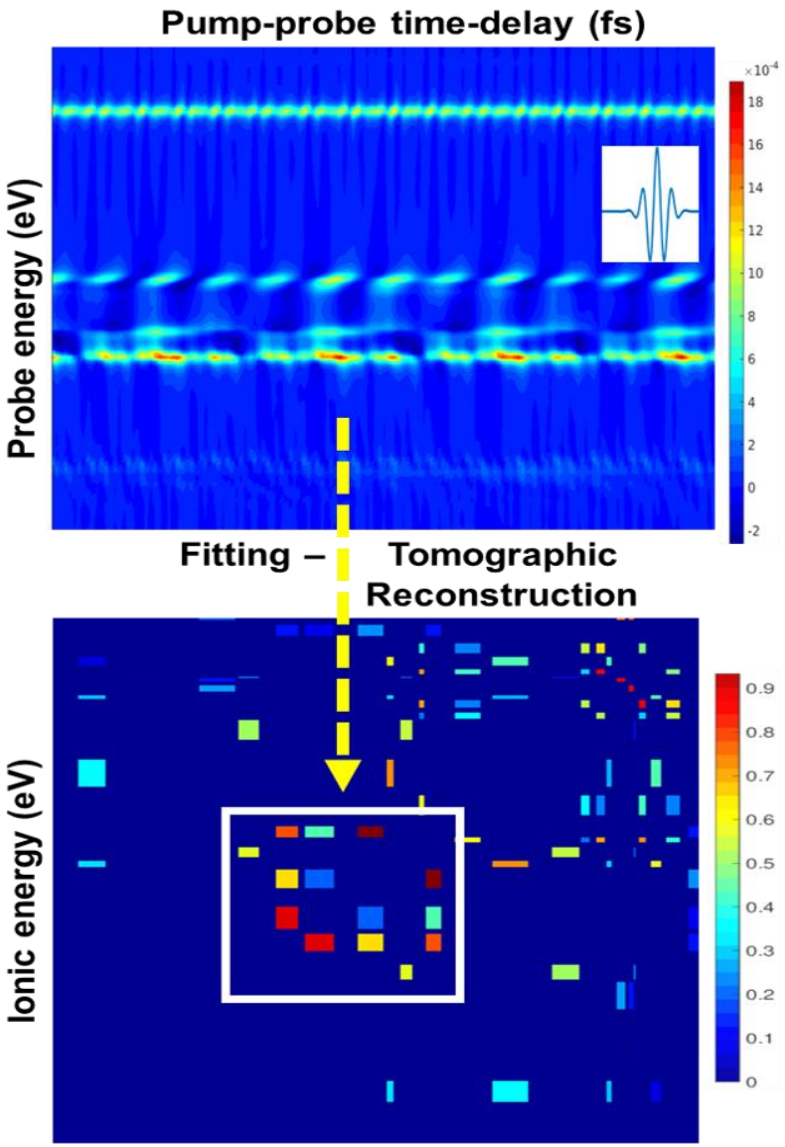
Quantum state tomography of *mixed ionic state* prepared by attosecond photoionization ***beyond the qubit case***

Research goal:

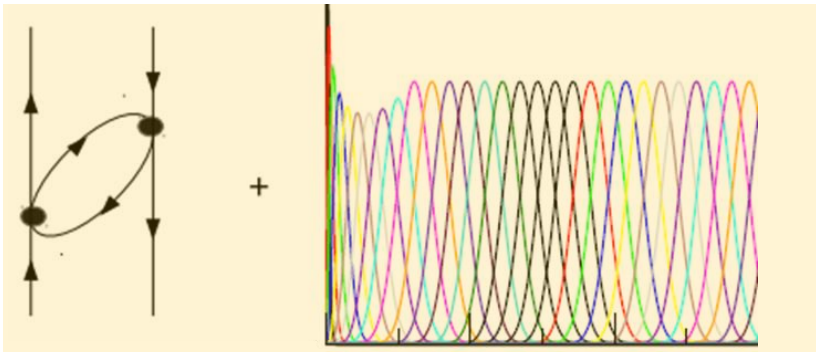
- *Develop theoretically quantum protocols for the* ***tomographic reconstruction of the attosecond ionized quantum states***

Extend spectroscopic technique to

- Time-Resolved Photoelectron Spectroscopy
- Auger Spectroscopy
- Stimulated X-ray Raman
- Multidimensional X-ray Spectroscopy



Research Vision

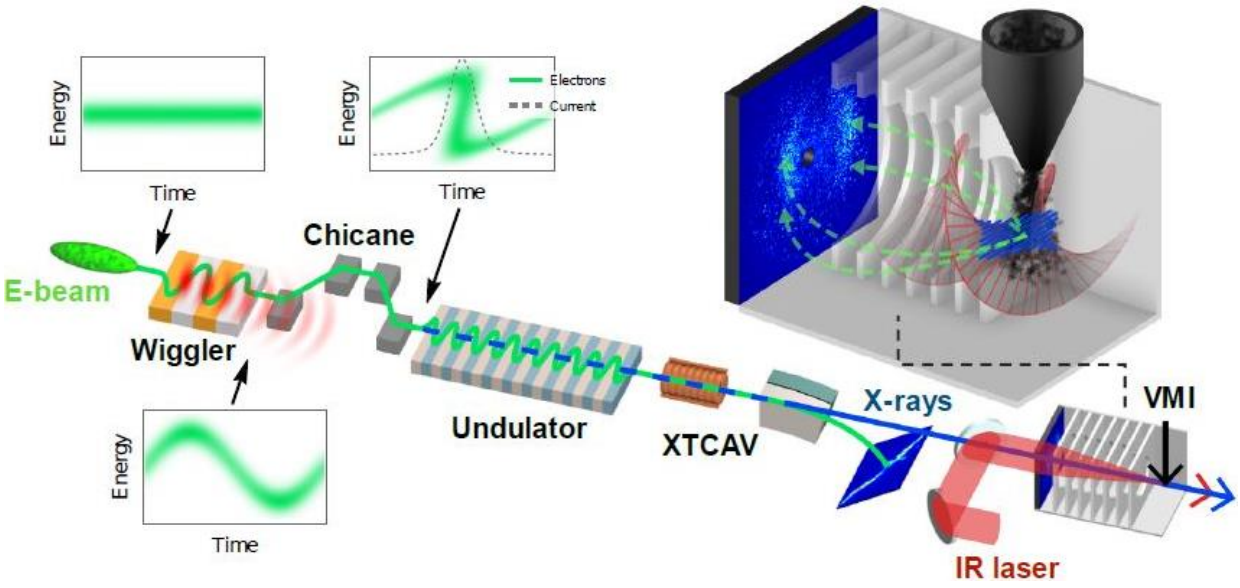


Unique technical expertise, pioneering numerical tool

Collaboration with the SLAC **Attosecond Science group** of the Chemical Science Division at PULSE Institute:
(James Cryan, Ago Marinelli, Peter Walter)

*Guide experimental efforts at **LCLS** towards the observation and characterization of new attosecond physical phenomena*

"Real-time Observation of Ultrafast Electron Motion using Attosecond XFEL Pulses" **Attosecond Campaign** at LCLS II using **XLEAP**



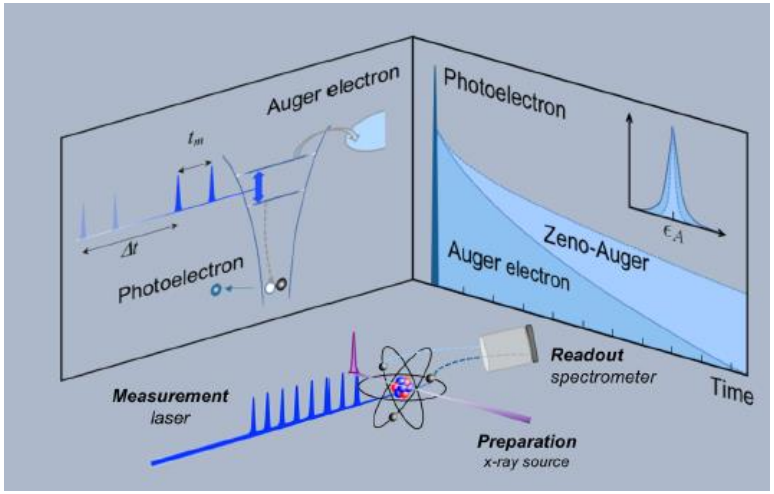
Research Vision

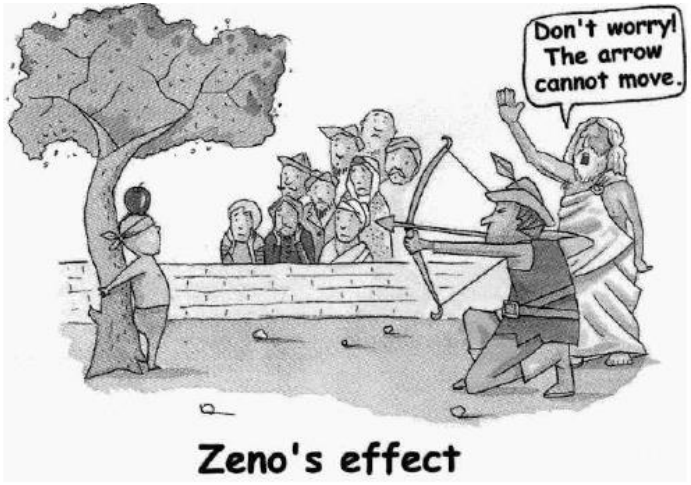
Quantum control of *X-ray triggered ultrafast electron-nuclear dynamics*

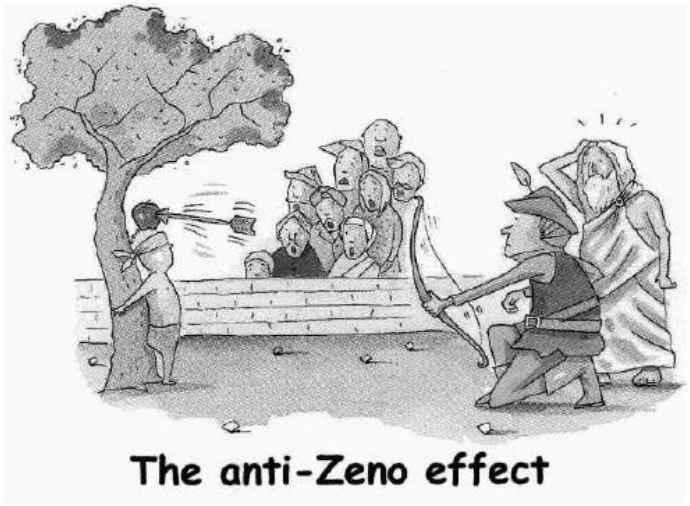
Research goals:

- ***Coherent quantum optimal control schemes*** *for the manipulation of the electronic coherence and attosecond hole migration*

- ***Quantum-Zeno based control schemes for Auger-decay*** *using trains of attosecond pulses*



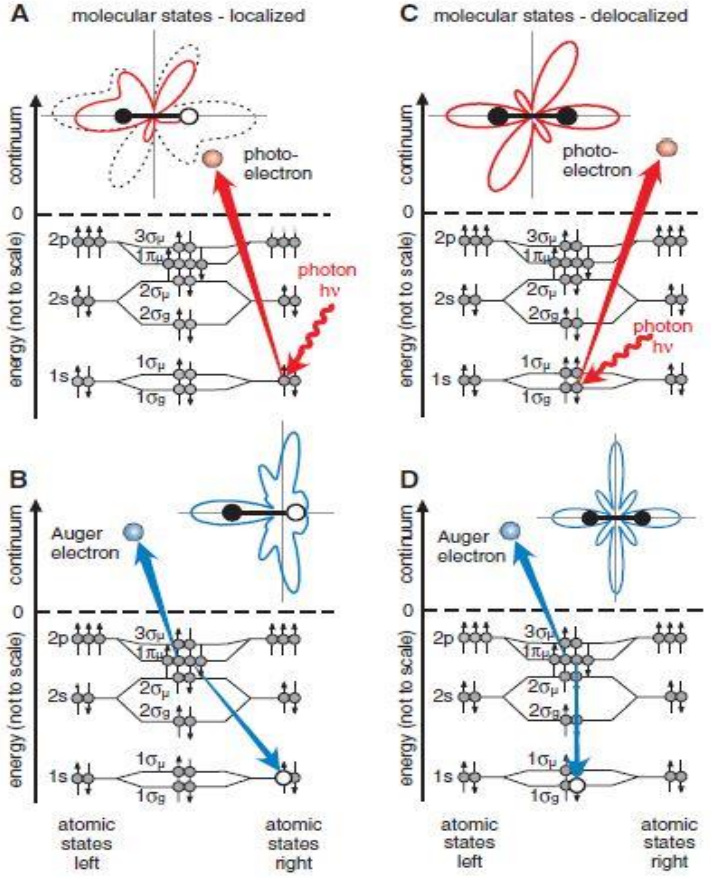




Investigating electronic entanglement via coincidence measurements

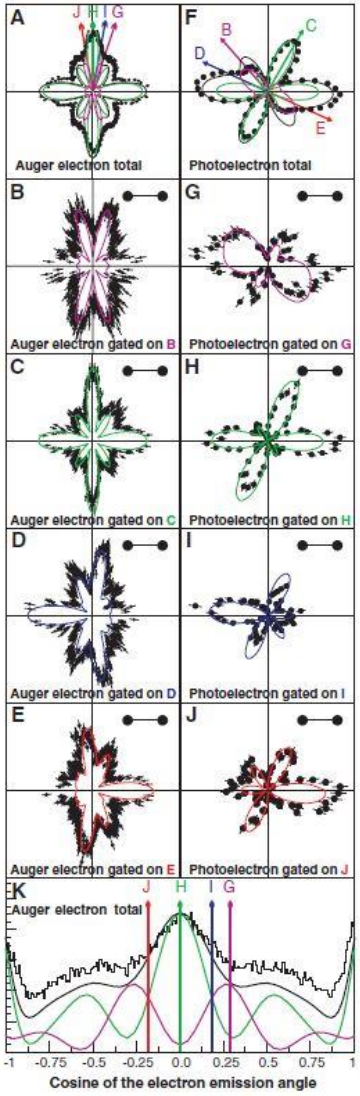
Pioneering experiment [Schöffler *et al., Ultrafast Probing of Core Hole Localization in N_2*, Science **320**, 920 (2008)]:

Localization of the core vacancy upon N_2 X-ray photoionization

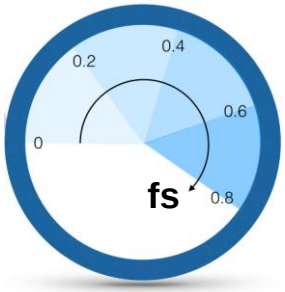


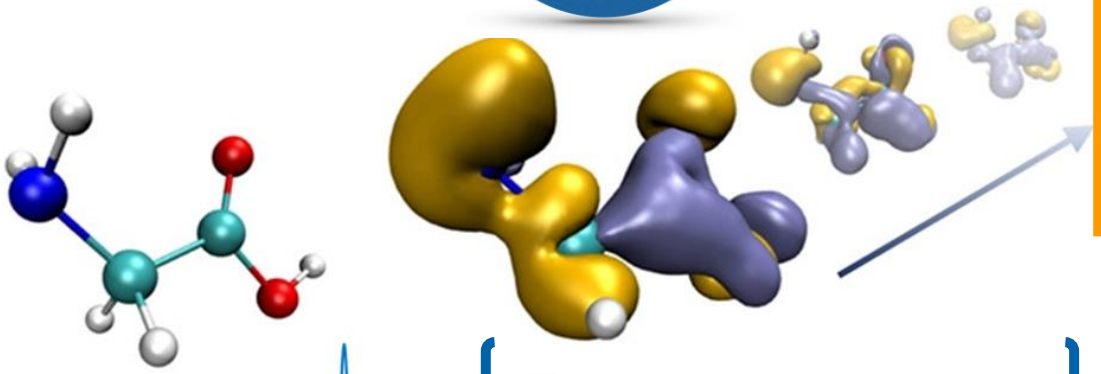
Auger electron angular emission patterns after inner-shell ionization as an ultrafast probe of hole localization:

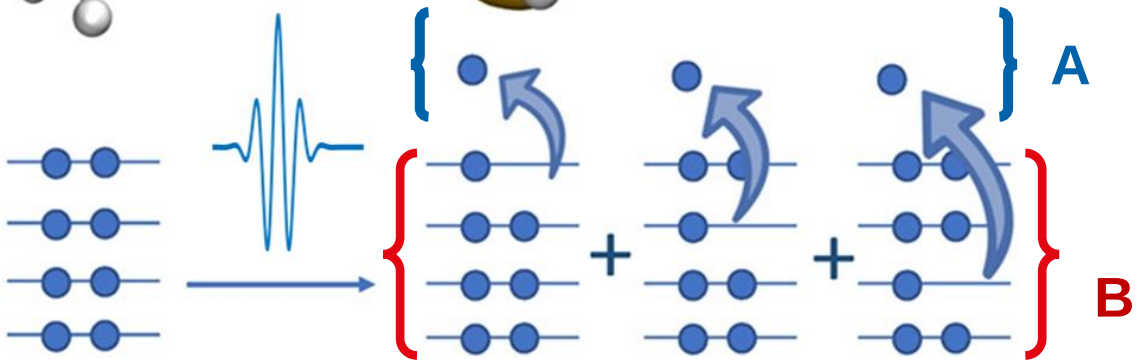
"Observation of symmetry breaking (localization) or preservation (delocalization) depends on how the quantum entangled Bell state created by Auger decay is detected by the measurement."



Research Vision





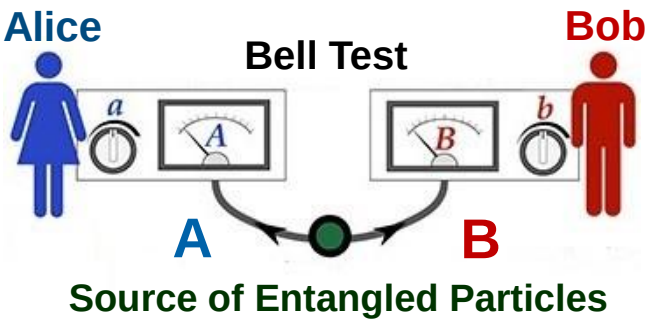


- Quantum electronic coherence & entanglement in molecular photo-ionisation

- Attosecond quantum control of physical & chemical change of matter

- New attosecond quantum phenomena

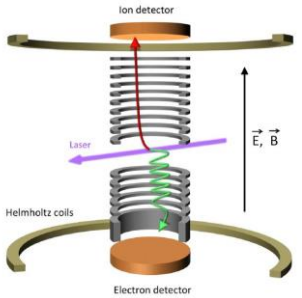
- Quantum information theory of photo-chemistry & radiation damage



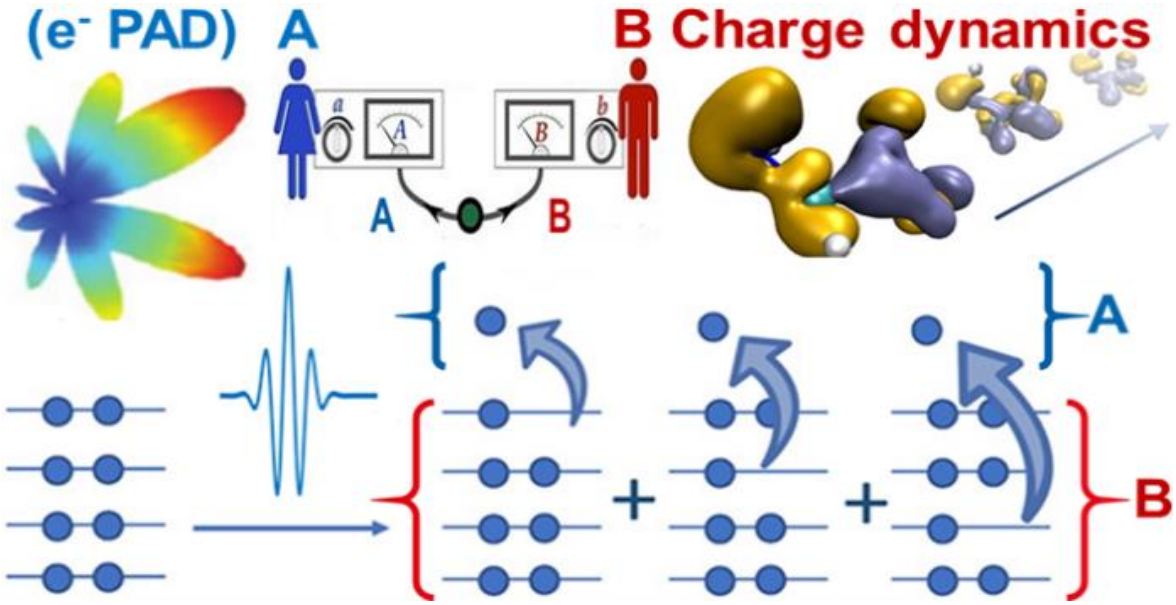
Research Vision

Research goals:

- ***Unravel the role of entanglement in ultrafast charge dynamics***
- ***Design Bell tests*** and ***entanglement witnesses*** in attosecond photoionization by ***coincidence techniques***



High (>100 kHz) rep. rate attosecond experiment with controlled time-delay and COLTRIMS detection.



Measuring entanglement between photoelectrons and ions: measure in coincidence photoelectrons & photoproducts from the partner ion fragments (by further ionising the system with a second pulse), i.e. examine in coincidence the two consecutively emitted photoelectrons.

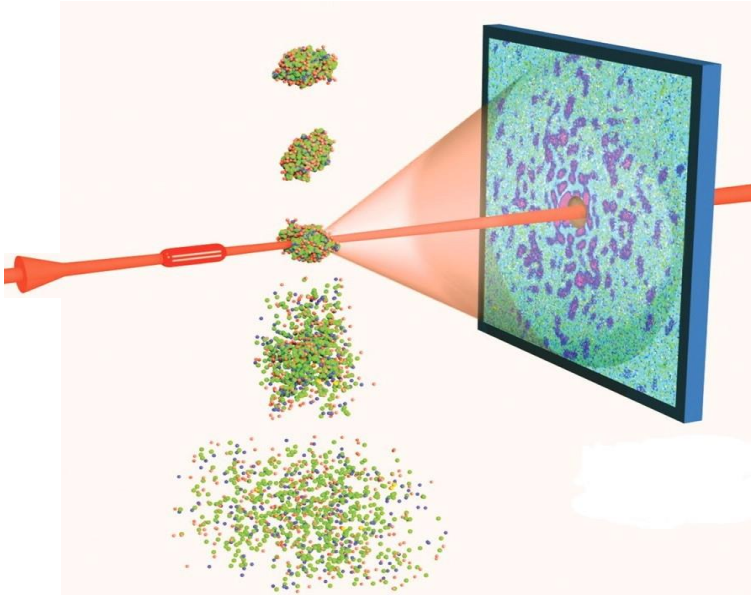
New physics for the DREAM end-station at LCLS-II

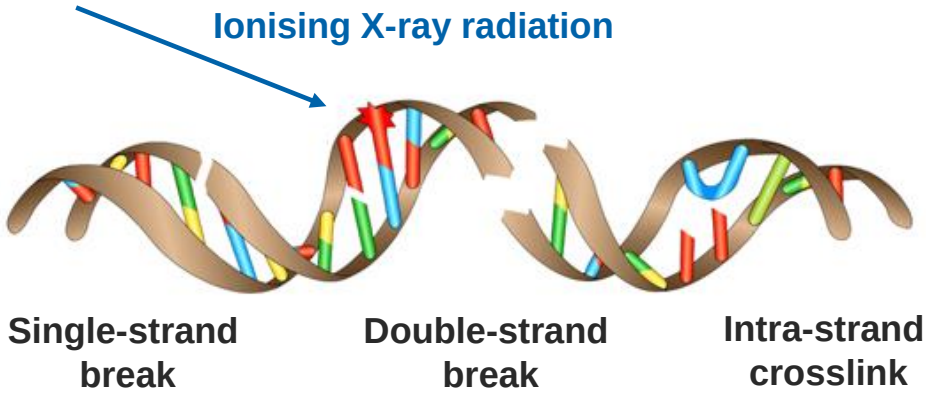
- Better statistics - higher rep rate with LCLS II and higher collection efficiency of electrons and ions with DREAM
- Increased temporal resolution (XLEAP)
- Probing several atomic sites to track charge migration using different probe energies using two-color XLEAP
- Suppression of unwanted background by coincidence measurement allows higher fidelity measurement
- Entanglement measurements correlating the emitted electrons with DREAM.

Research vision: longer-term impacts

On enabling drug discovery by single-biomolecule X-ray "diffract before destroy" measurement

On more efficient radiotherapy techniques for cancer treatment by understanding & control of radiation damage to DNA





Research Vision: summary

With my fundamental quantum attoscience program, I will:

- Equip SLAC with the world leading core capability in the many-body attosecond quantum theory

- Harness the power of LCLS-II, DREAM, XLEAP to obtain seminal quantum information insights into X-ray photoionization

Thank you for your attention

Quantum State Tomography for Attosecond Ionisation of Entangled Many-Electron Systems

Dr. Marco Ruberti

Imperial College London