Attosecond Physics and the Dream of an Electron Movie

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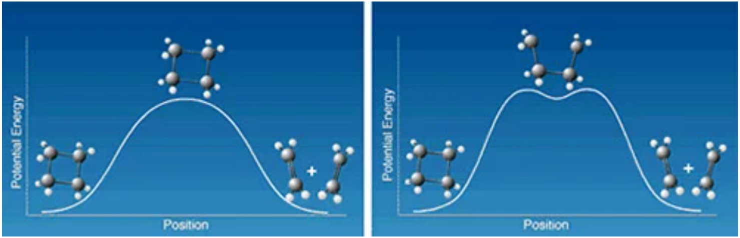
To resolve fast dynamics

High Speed Camera $\sim$ 1000 fps

We need a fast camera!

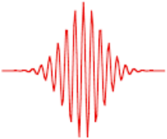
How to follow Chemical reactions in time

How does cyclobutane dissociate into ethylene?

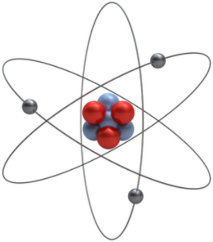


Direct Observation of **Transition States**. Once a Holy Grail of Chemistry

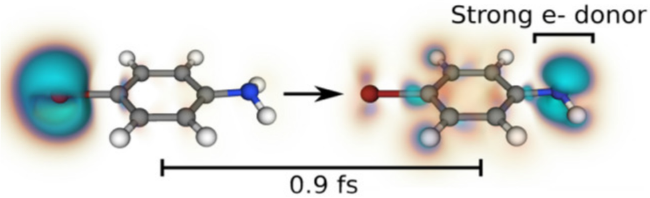
- Zeweil 1994
- Intermediate state
  $\tau \sim 700$ fs



- Femtosecond laser pulses. Infrared light.
- $\Delta t = 10 - 100$ fs

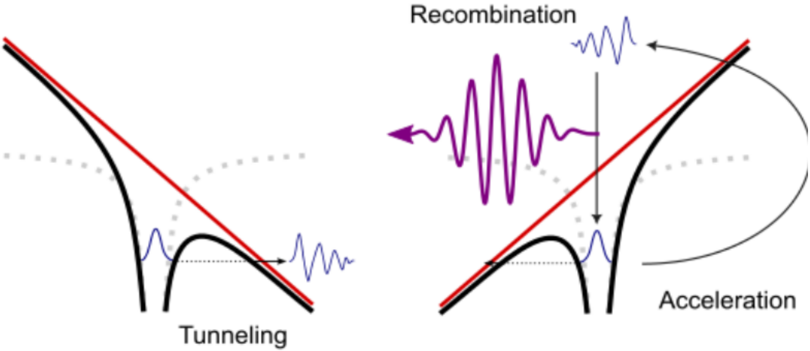


- The “orbit time” in the Bohr model is 150 as ($1\ \mathrm{as} = 10^{-18}$ s)



Simulation of charge migration in a bromobenzene molecule. From Folorunso et al. Phys Chem A. 2023

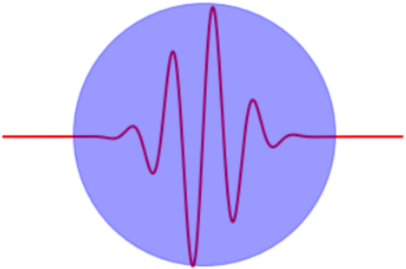
High Harmonic Generation



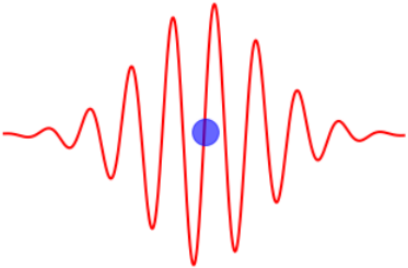
- M Ferray A L'Huillier et al
  J. Phys. B 21 L31 (1988)
- $\hbar\Omega_{XUV} = (2n+1)\hbar\omega_{IR}$
- train of XUV-pulses, ~ 100 as

To be both a particle and a wave

- All matter has both particle and wave properties



Atoms in chemical reactions are mostly particle-like



Electrons around atoms and molecules are mostly wave-like

Time in Quantum Mechanics?

There is no time operator. Wolfgang Pauli 1933: *We conclude that the introduction of an operator T must fundamentally be abandoned and that the time in quantum mechanics has to be regarded as an ordinary number*

Time in Quantum Mechanics?

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- canonical commutation relation

$$[\hat{x}, \hat{p}_x] = i\hbar \rightarrow \Delta x \Delta p_x \geq \hbar/2$$

- $\hat{x}$ and $\hat{p}_x$ have both spectra $-\infty \rightarrow \infty$

- similar for time and energy?

$$\Delta t \Delta E \geq \hbar/2 \rightarrow \left[\hat{t}, \hat{H}\right] = i\hbar??$$

- But what would then $\hat{t}$ be?
- a physically realistic Hamiltonian must be bounded from below!

Time in Quantum Mechanics?

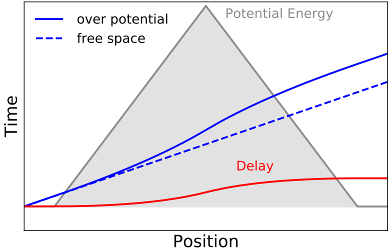
There is no time operator. Wolfgang Pauli 1933: *We conclude that the introduction of an operator T must fundamentally be abandoned and that the time in quantum mechanics has to be regarded as an ordinary number*

- no self-adjoint time operator conjugate to a general H
- $t \neq -i\hbar \frac{\partial}{\partial E}$

Still we want to talk about time!

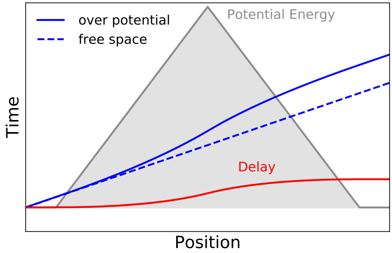
- life time $\Delta E \Delta t \geq \hbar/2$
- tunneling time?
- arrivial time
- **delay time**

Classical Picture



$$\tau = \int \left(\frac{1}{v\,(x)} - \frac{1}{v_0} \right) dx$$

Classical Picture



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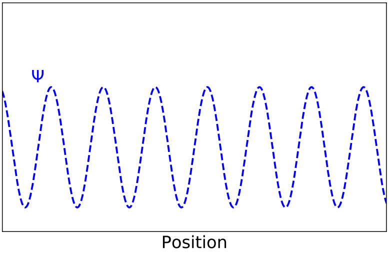
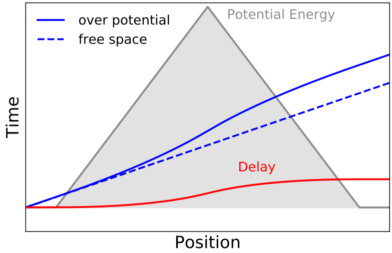
Quantum Picture



Classical Picture



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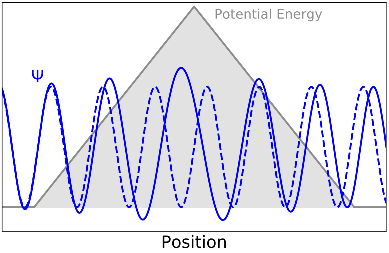
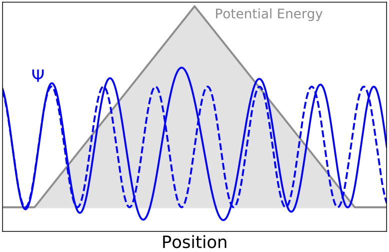
Quantum Picture



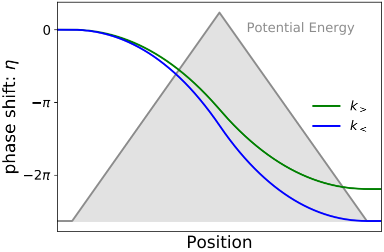
$$\eta = \int \left(k(x) - k_0 \right) dx$$

Quantum Picture



$$\eta = \int (k(x) - k_0)\, dx$$

Accumulated Phase Diff.

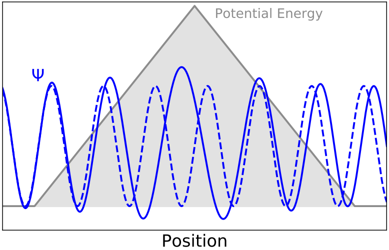


$$\tau = \hbar \frac{\partial \eta}{\partial E}$$

Eisenbud -48 Wigner -55 Smith -60

Delay: Classic and Quantum

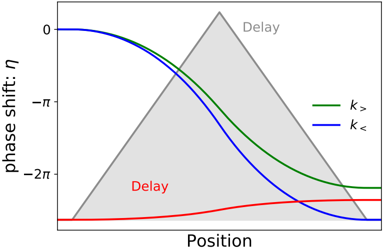
Quantum Picture



$$\eta = \int \left(k\left(x\right) - k_0\right) dx$$

$$= \frac{1}{\hbar} \int \left(\sqrt{2mE - V(x)} - \sqrt{2mE}\right) dx$$

Phase shift derivative

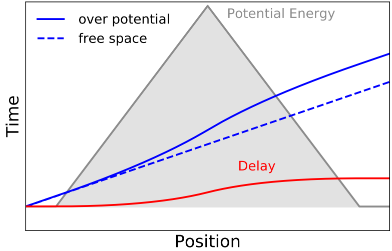


$$\tau = \hbar \frac{\partial \eta}{\partial E}$$

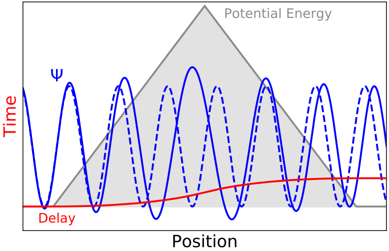
$$= \frac{m}{\hbar} \int \left(\frac{1}{k\left(x\right)} - \frac{1}{k_0}\right) dx$$

Delay: Classic and Quantum

Classical Picture



Quantum Picture



$$\tau = \int \left(\frac{1}{v(x)} - \frac{1}{v_0} \right) dx$$

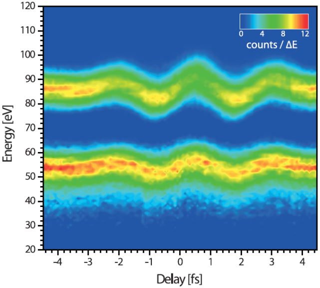
$$\tau = \hbar \frac{\partial \eta}{\partial E} = \frac{m}{\hbar} \int \left(\frac{1}{k(x)} - \frac{1}{k_0} \right) dx$$

- Photoionization is scattering from within!

Delay in Photoionization- first experiments

Photoelectron Energy [eV]

Ne 2s - 2p

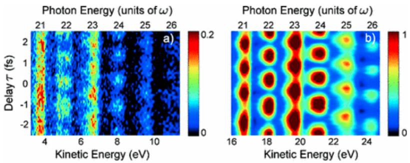


Delay IR/XUV [fs]

- Schultze et al. Science 328 , 1658, (2010)
- one point: $\hbar\omega = 106$ eV.
- e^- from 2s, 21 ± 5 as ahead

Ar 3s - 3p

Delay[as]



Photoelectron Energy[eV]

- Klünder et al PRL 106, 143002 (2011)

Delay in Photoionization- first experiments

Photoelectron Energy [eV]

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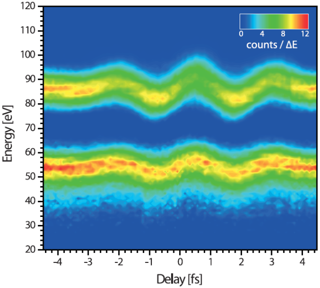
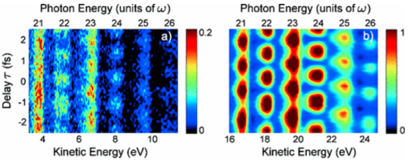


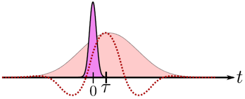
Delay IR/XUV [fs]

Ar 3s - 3p

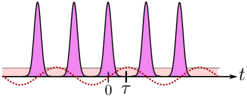
Delay[as]



Photoelectron Energy[eV]

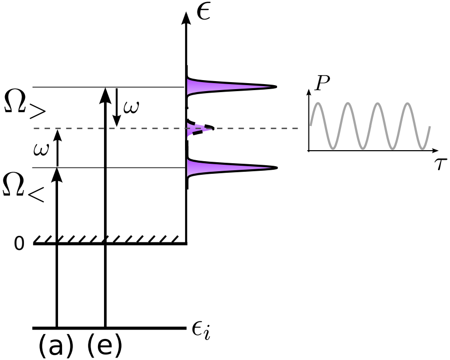


Streaking



Rabbit

Resolution of Attosecond Beating By Interference of Two-photon Transitions



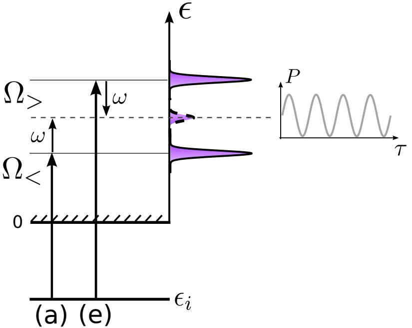
- Wigner delay - theoretical concept
- Atomic delay - measurable quantity

Laser-induced sideband signal:

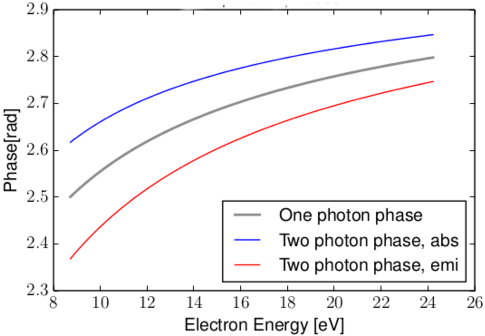
$$P \sim \mid M_{abs\,\omega} + M_{emi\,\omega} \mid^2 \sim A + B \cos[2\omega(\tau - \tau_{\rm GD}) - \eta_{\rm Atom}],$$

where $\tau_{\rm GD} \approx (\phi_> - \phi_<)/2\omega$ is group delay of attopulse

RABBIT - Phase

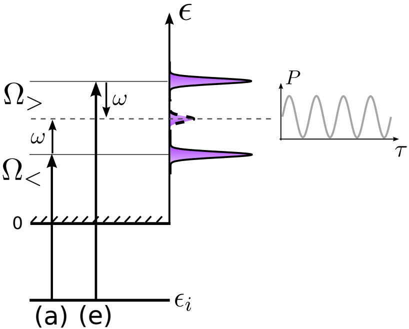


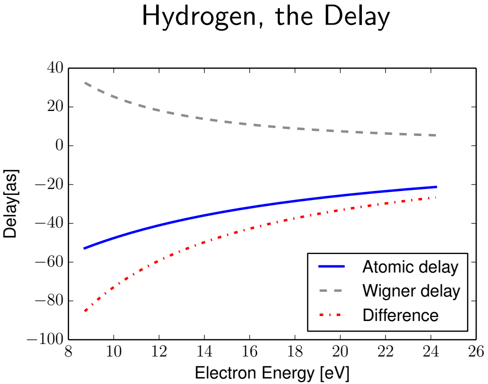
Hydrogen, outgoing wave-packet phase



- The experiments **do not measure the Wigner phase**
- they measure the difference between the **emission** and **absorption** path.

RABBIT -Delay, $\sim d\eta/dE$





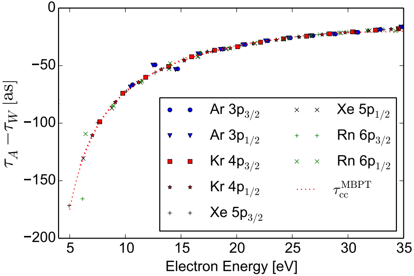
Finite Difference Approximation:

$$\tau_{atomic} = \frac{\arg\left[M_{emi\,\omega}\right] - \arg\left[M_{abs\,\omega}\right]}{2\omega}$$

- **Measured delay** different from fundamental **Wigner delay**!

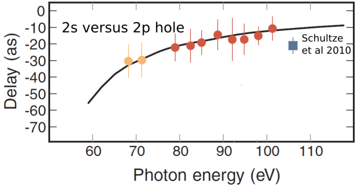
- Continuum-Continuum transitions

Rather Universal Contribution



Vinbladh et al. Atoms **2022**, 10, 80

Agrees with (new) Neon Experiment

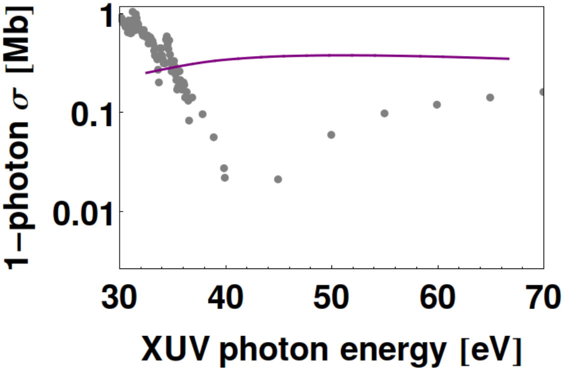


Isinger et al Science **358** 893 2017 (Spectral resolution giving by the sharpness of the comb teeth)

- but of course more complicated when you go into details

What was needed from theory?

After 50+ years with photoionization we know that ...



Argon 3*s* photoionization, Exp. Möbus *et al.* Phys. Rev. A 47, 3888 (1993)

... one particle models, as Hartree Fock, are insufficient!

What was needed from theory?

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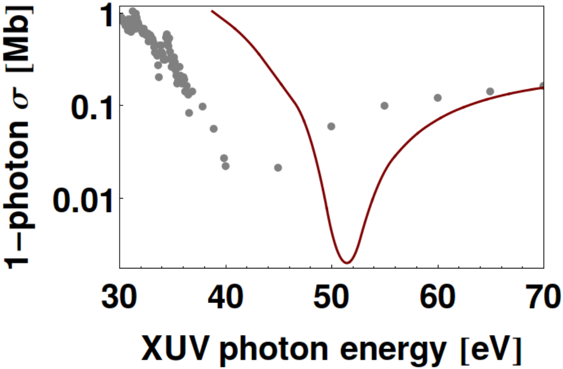

Argon 3*s* photoionization, Exp. Möbus *et al.* Phys. Rev. A 47, 3888 (1993)

.. adding single excitations, CI singles/RPAE forward, is often not enough.

What was needed from theory?

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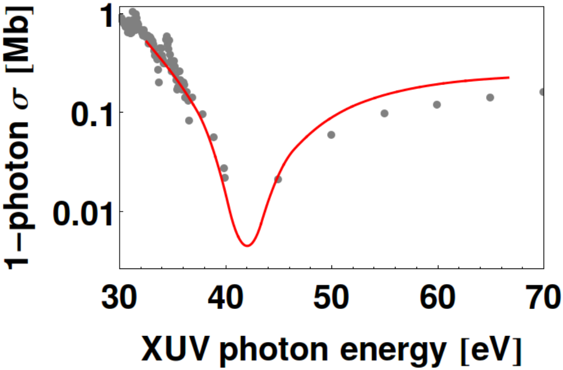

Argon 3*s* photoionization, Exp. Möbus *et al.* Phys. Rev. A 47, 3888 (1993)

.. RPAE, however, gets the cross section more or less right!

Next Step

- Neon well understood
- What about something slightly more complicated - like Argon?

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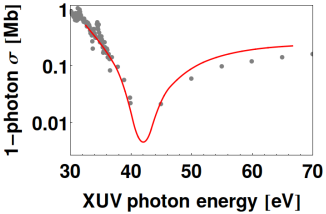
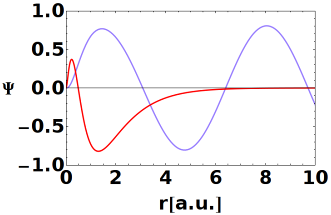


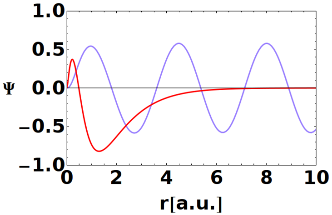
- Channels coupling induced Cross Section minimum in Ar 3s ionization

Cooper minimum in Argon 3p ionization

when the matrix element $\langle k \mid \mathbf{r} \mid a \rangle$ change sign:

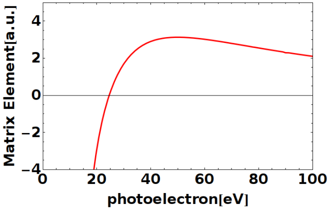


Ar 3*p* and photoelectron $\sim$ 10 eV

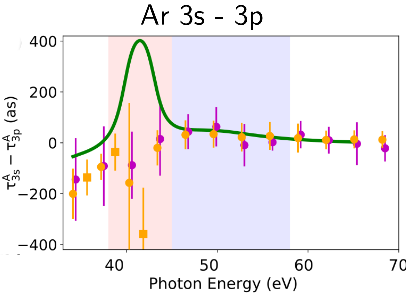


Ar 3*p* and photoelectron $\sim$ 40 eV

- vanishing matrix element for certain photoelectron energy
- Strong 3s/3p channel coupling



The Argon problem



Experiment from **Lund** & **Saclay**.
Theory (**RPAE**)

- Alexandridi et al Phys. Rev. Res. 3, L012012 (2021)

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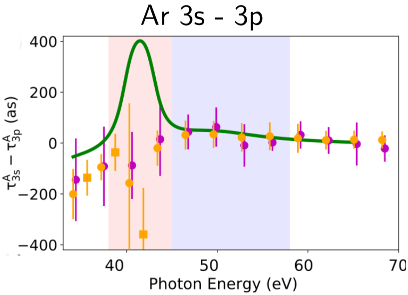

Experiment from **Lund** & **Saclay**.
Theory (**RPAE**)

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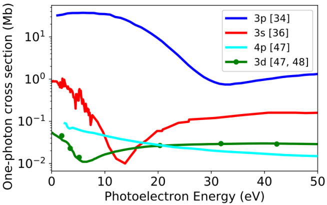
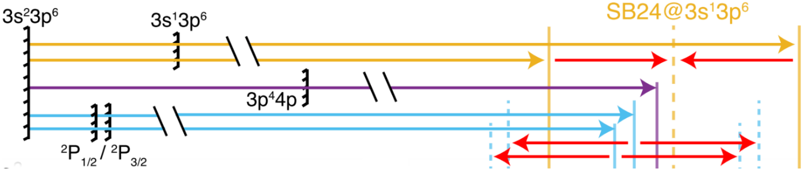
- Theory: enormous delay where there are hardly any electrons.
- Shake-up channels, e.g. $\left(\{3p^{-2}\}^1 D\, 3d\right)\ ^2S$, are also open. Is it these that are measured?



Is the delay positive or negative?



- Recent results from Sizuo Luo et al, Jilin University
- Improved spectral accuracy (100 meV) resolve shake-up channels
- The delay is indeed negative.
- **What has theory missed?**

Back to the cross section

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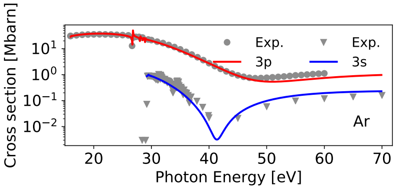

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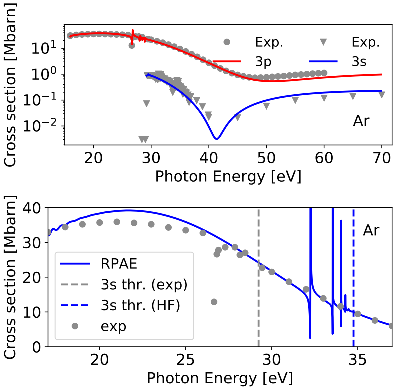

Back to the cross section

- Recent results from <u>Sizuo Luo</u>,
- Improved spectral accuracy (100 meV) resolve shake-up channels
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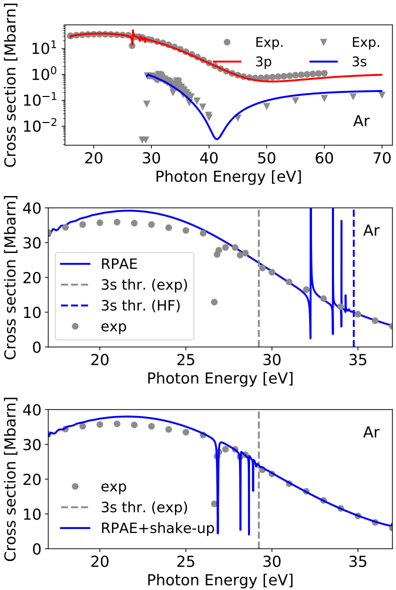
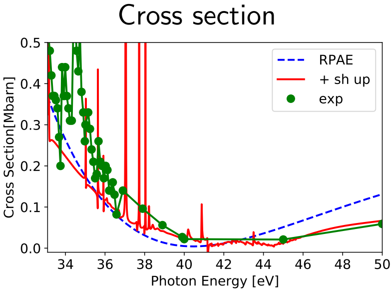
- **What has theory missed?**
- **Shake-up type correlation?**
- q-value a phase-dependent property!



Back to the Cooper minimum

- now including shake-up type correlation

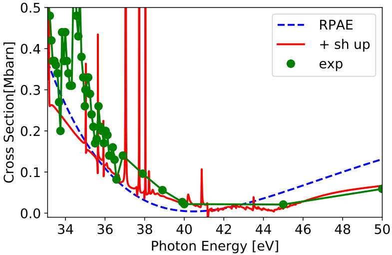


- just slightly affected

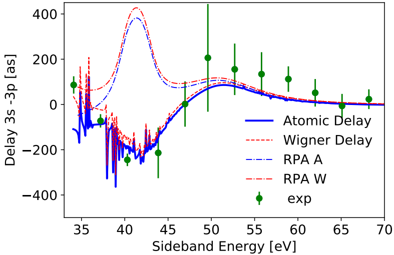
Back to the Cooper minimum

- now including shake-up type correlation

Cross section



Delay



- just slightly affected
- Phase (Delay) sometimes a very sensitive probe!
- drastically affected
  - Experiment led by Sizuo Luo, Jilin University et al

Why is the phase more sensitive?

$$z = z_0 + \delta z$$

$z_0 : 3s \to \epsilon p$ δz through correlation with $3p$

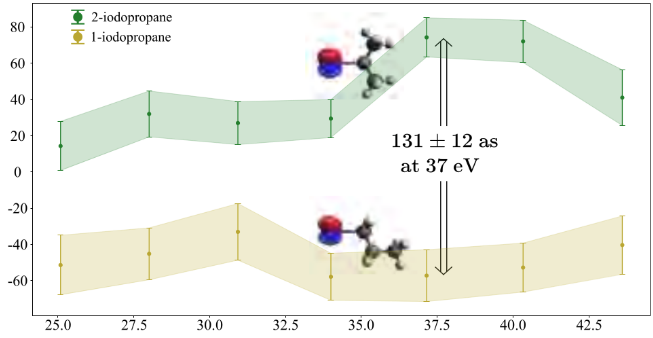
$$z = \mid z_0 \mid e^{i\phi} \left(1 + \frac{\mid \delta z \mid}{\mid z_0 \mid} e^{i\Delta\phi}\right)$$

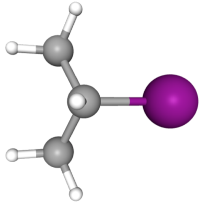
$$\mid z \mid^2 = \mid z_0 \mid^2 \left(1 + \frac{\mid \delta z \mid^2}{\mid z_0 \mid^2} + 2\frac{\mid \delta z \mid}{\mid z_0 \mid} \cos(\Delta\phi)\right)$$

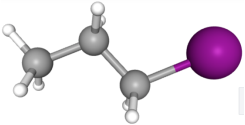
Amplitude (cross section) insensitive to the sign of $\Delta\phi$!

Sensitive probe of molecular environment

Ionization delay relative Ne [as]





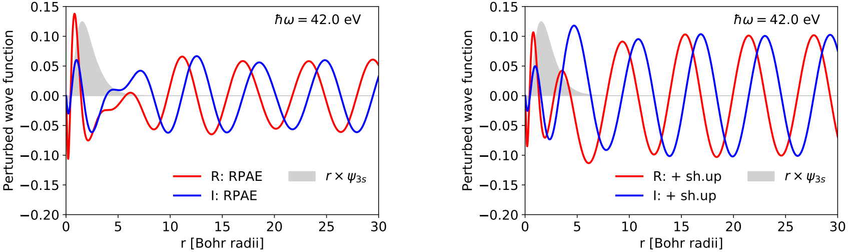


Electron kinetic energy[eV]

- Delay of I 4d-electron ionization of C_3H_7I, from Menezes Ferreira et al Abstract to Atto X 2025

Phase and potential

Outgoing wave: $r \to \infty$. $\rho(r) \sim e^{ikr}$



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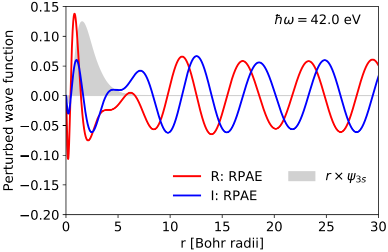
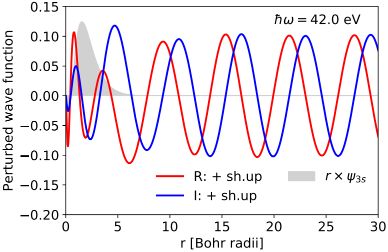
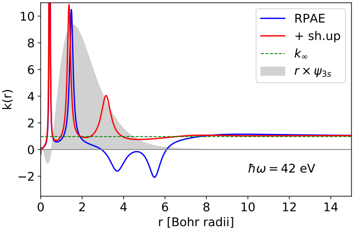
$$\frac{d}{dr} \arg(\rho) = k(r)$$





$$E = \frac{k^2(r)}{2m} + V(r)$$



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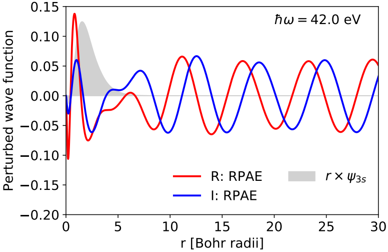

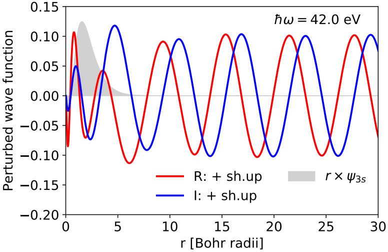

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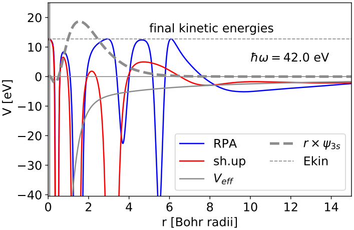

Final Remarks

- Ionization delay is a sensitive tool to study the potential landscape
- Today used on a variety of system: molecules, surfaces, nanostructures...
- Both streaking and RABBIT are used.
- Recently also with X-ray pulses e.g. oxygen K-shell electrons in NO.

Thank you for listening!

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Sizuo Luo