Capturing electron dynamics - the role of theory

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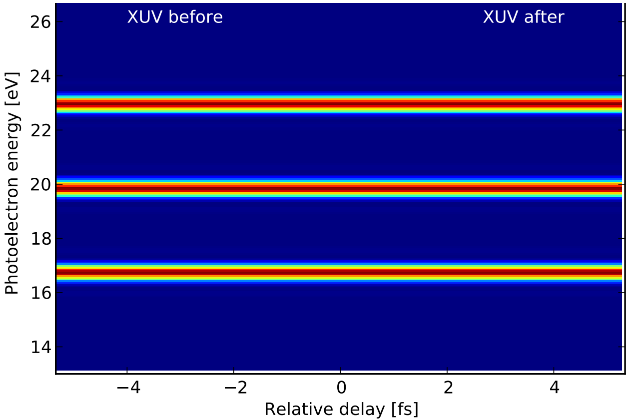
Stockholm University

Quantum Connections, 19 June 2024

PHOTOELECTRON SPECTROGRAMIN XUV + IR

One photon absorption from **XUV comb** + dressing by **laser field**



Redistribution of three harmonic peaks due to laser dressing: Formation of **sidebands***. (Courtesy Marcus Dahlström)*

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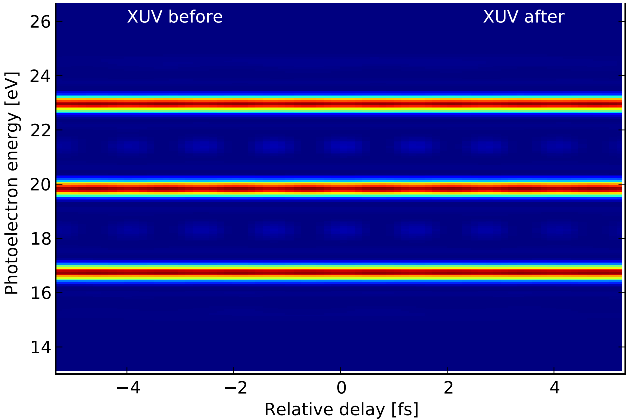

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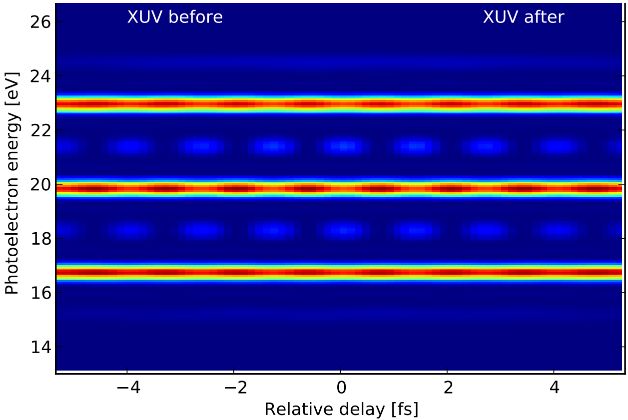

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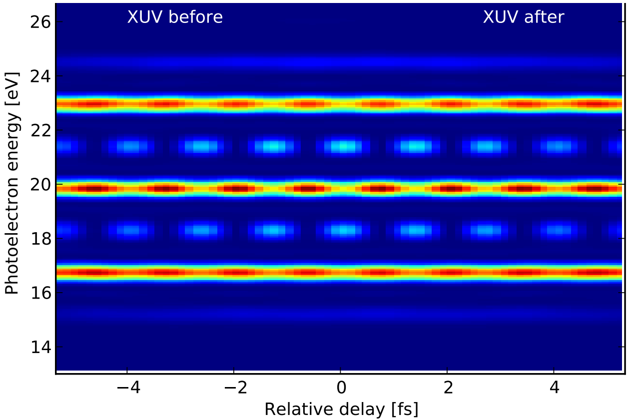
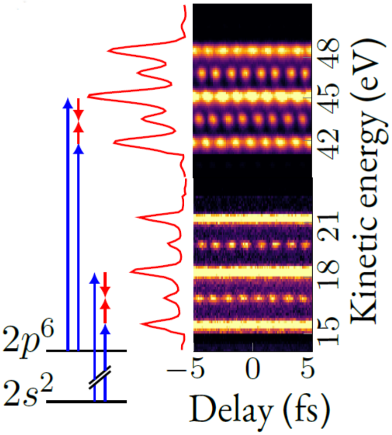


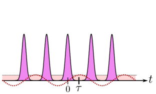
Redistribution of three harmonic peaks due to laser dressing: Formation of **sidebands***. (Courtesy Marcus Dahlström)*

How it looks in reality

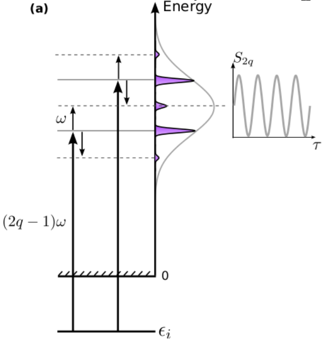


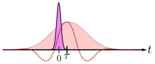
A. L'Huillier group Isinger et al. Science **358**, 893, 2017

What do we have to describe?

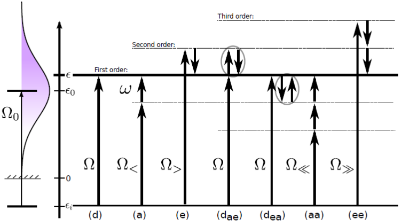


IR field weak: one-photon regime





Stronger IR-pulse, multi-photon regime



Streaking onset - dom. by one IR-photon

What are the challenges and options?

- Should we solve the time-dependent Schrödinger (Dirac) equation? Heavy!
- Or use perturbation theory (one, two, three ... photons) ? Complicated if many photons are needed!

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What are the challenges and options?

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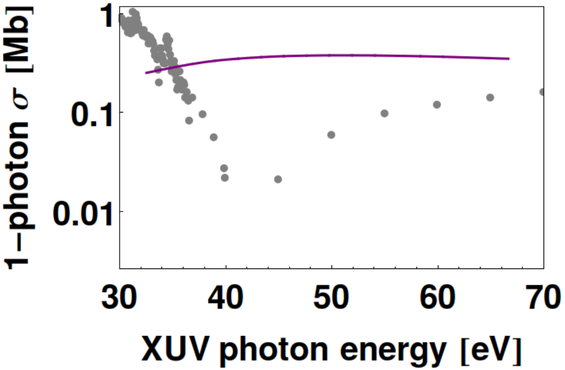
- We are interested in many-body system. What sophistication of the many-body treatment do we need?
- How to treat the coupling to the continuum?

Needed to describe one-photon interaction?

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!

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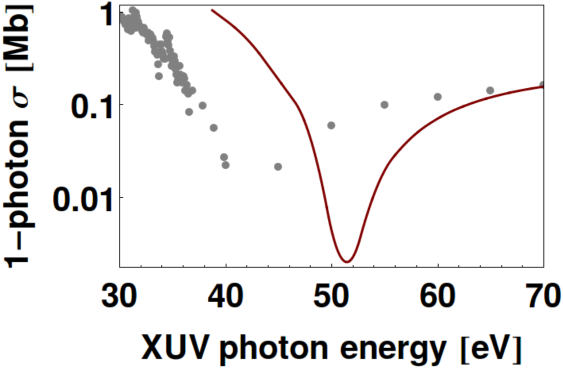

Argon 3*s* photoionization, Exp. Möbus *et al.* Phys. Rev. A 47, 3888 (1993)

.. adding single excitations, CI singles/RPAE forward, is often not enough. (RPAE=Random Phase Approximation with Exchange)

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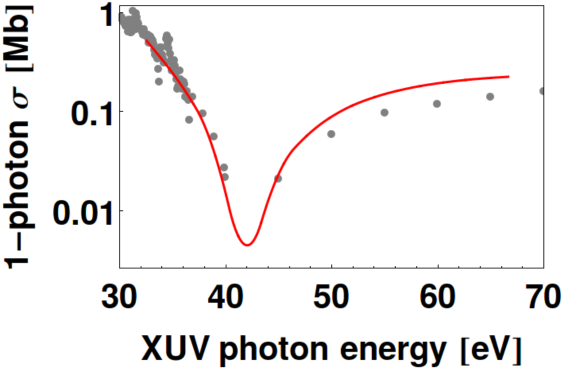
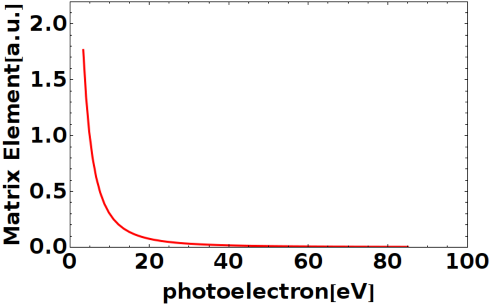


Argon 3*s* photoionization, Exp. Möbus *et al.* Phys. Rev. A 47, 3888 (1993)

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

(RPAE=Random Phase Approximation with Exchange)

Cooper minima?
The regular situation

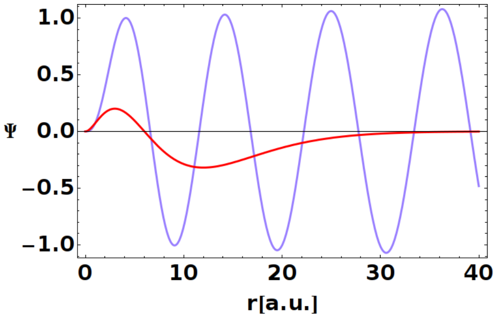


Leads to a monotonically decreasing one-photon matrix element

$$M^1(\vec{k}) = \langle\, \vec{k} \mid z \mid 3p \,\rangle$$

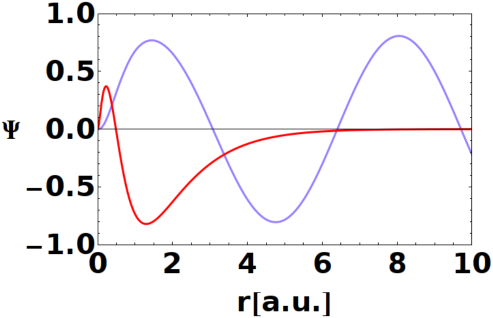
Cooper minima?

The regular situation



Bound state versus Continuum. Here $3p$ in H and photoelectron $\sim$ 4 eV.

$$M^1(\vec{k}) = \langle\, \vec{k} \mid z \mid 3p \,\rangle$$

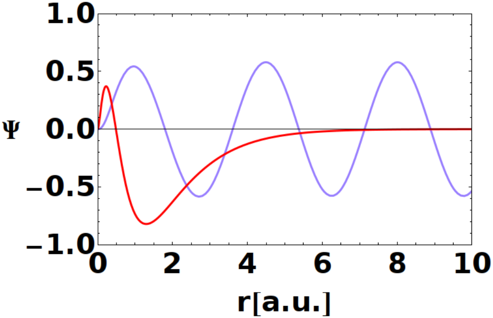


Bound state versus continuum. Here $3p$ in Ar and photoelectron $\sim$ 10 eV

$$M^1(\vec{k}) = \langle\, \vec{k} \mid z \mid 3p \,\rangle$$

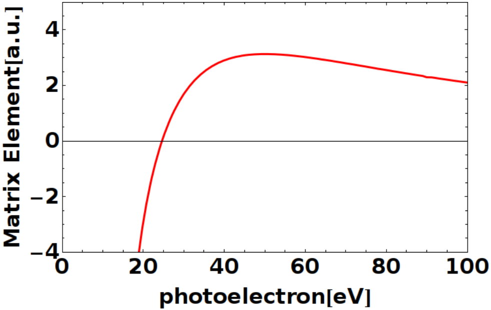
Cooper minima

Very different situation for Ar



Bound state versus continuum. Here 3*p* in Ar and photoelectron ∼ 40 eV

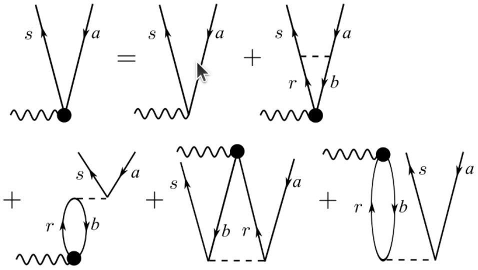
$$M^1(\vec{k}) = \langle\, \vec{k} \mid z \mid 3p \,\rangle$$



Leads to a vanishing one-photon matrix element for certain photoelectron energy

$$M^1(\vec{k}) = \langle\, \vec{k} \mid z \mid 3p \,\rangle$$

THE DIAGRAMMATIC PICTURE



- Goes under the name Random Phase Approximation with Exchange
- Alternatively (and better!) Time-dependent Hartree-Fock.
- What physics is included: Channel coupling, ground state correlation.
- equivalence between $\mathbf{r} \cdot \mathbf{E}$ & $\mathbf{p} \cdot \mathbf{A}$

The coupling to the continuum

- The **perturbed wave function**

The coupling to the continuum

- The **perturbed wave function**

$$\rho(r) \sim \lim_{\varepsilon \to 0^+} \sum\!\!\!\!\!\!\int_p \frac{| \, p \rangle \langle p \mid e \, \mathbf{E}_\omega \cdot \mathbf{r} \mid a \rangle}{\epsilon_a + \hbar\omega - \epsilon_p + i\varepsilon}$$

The coupling to the continuum

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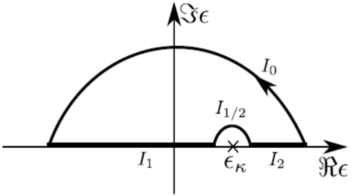
When the photon energy is high enough there will be a **pole**!



Pole-contribution ($\rightarrow i \sin(\ldots)$) +
Principal value part ($\rightarrow \cos(\ldots)$)

The coupling to the continuum

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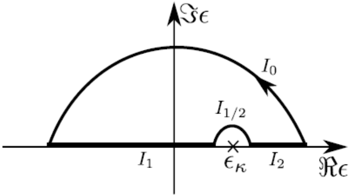
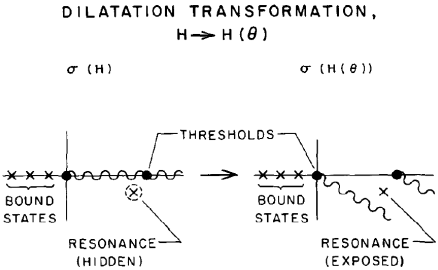


Pole-contribution ($\rightarrow i\sin(\ldots)$) +
Principal value part ($\rightarrow \cos(\ldots)$)

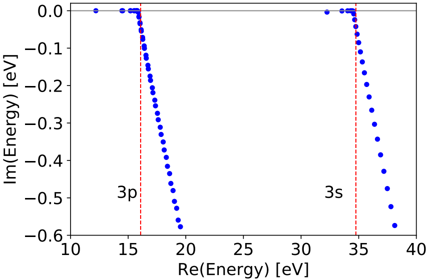
- But the Cauchy formalism is not easy to combine with a numerical many-body formalism.

Complex rotation

- Impose outgoing boundary conditions:
  $r \to R_0 + (r - R_0)e^{i\theta}$, for $r > R_0, (R_0 \geq 0)$
  Balslev & Combes 1971, Simon 1973, Doolen, Nuttal, & Stagat, 1974 ...
- $e^{ikr} \to e^{ikre^{i\theta}} \to 0$ for $r \to \infty$
- $H \to H^\theta$ Non-Hermitian with $H^\theta \Psi = E^\theta \Psi$, E^θ complex

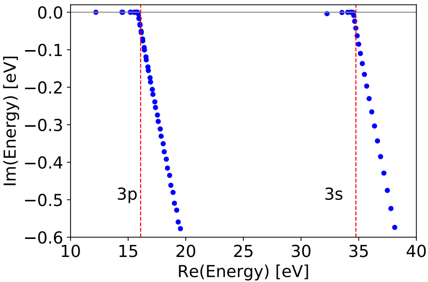


From Reinhardt, Ann. Rev. Phys. Chem. 1982



- Complex rotated spectrum of singly excited/ionized Argon (^1P)

Complex rotation



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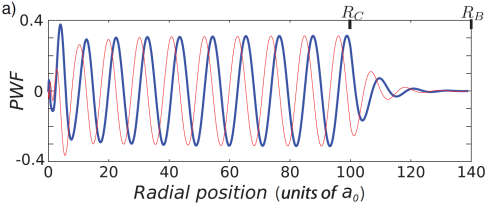
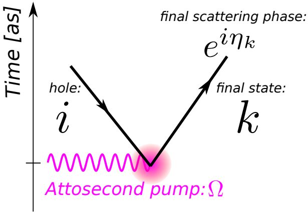


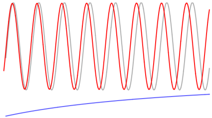
Outgoing wave function: Re [ρ], Im [ρ]

Laser-assisted photoionization

The effect of the laser field

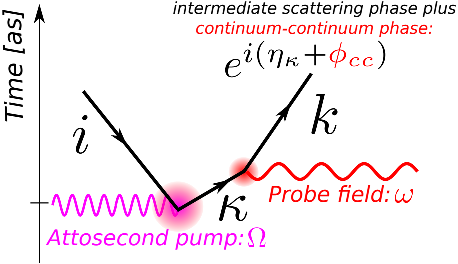


- One photon



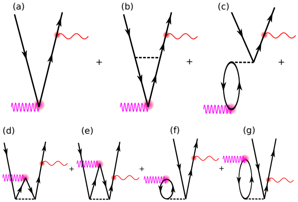
$$\rightarrow e^{i(kr + \frac{Z}{ka_0} \ln 2kr + \eta_k)},$$
$$\tau = \hbar d\eta/dE$$

- Two (or more) photons: Additional phase!

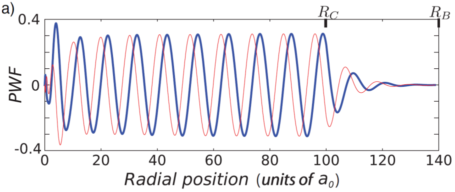


Now RPAE with Two Photons

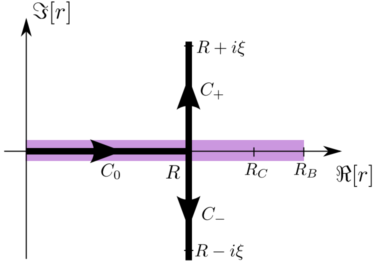
The dominating contribution



Dahlström *et al.* **Phys. Rev. A 86, 061402 (2012)**



Outgoing wave function: Re $[\rho]$, Im $[\rho]$



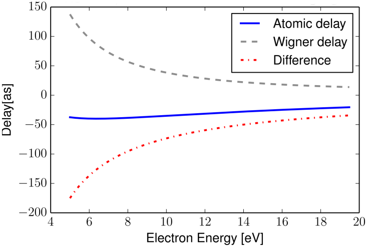
- We need:

$$M^{(2)} \sim \langle\, \vec{k} \mid \mathbf{E}_\omega \cdot \mathbf{r} \mid \rho\,(\Omega)\,\rangle$$

- Exterior complex scaling
- 2nd photon: Inner region numerically
- & Analytical calculation from R along imaginary axis

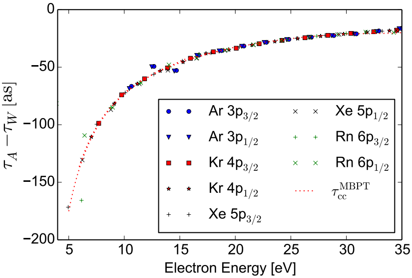
Continuum-Continuum transitions

separate the contributions



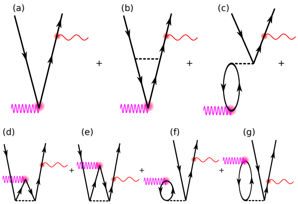
Example from Ne 2p

≈ universal Continuum-Continuum



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

Now RPAE with Two Photons



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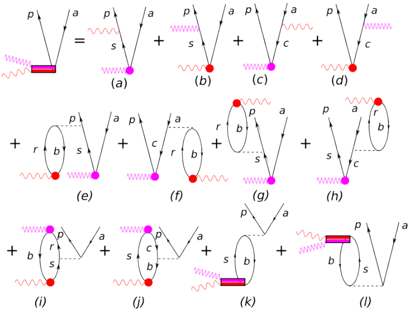
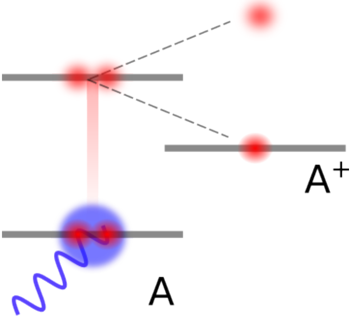


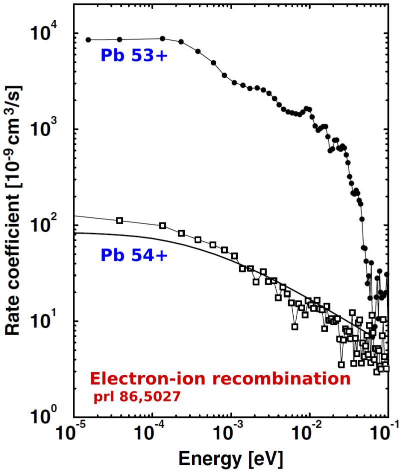
Vinbladh *et al.* Phys. Rev. A 100, 043424 (2019)

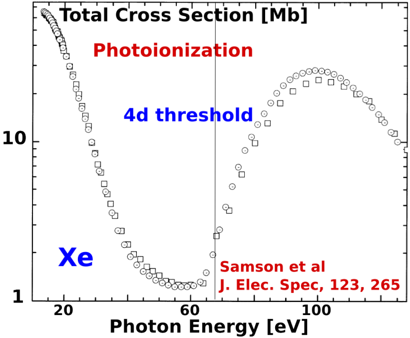
- Refined experimental studies - finer details play a role

Resonances



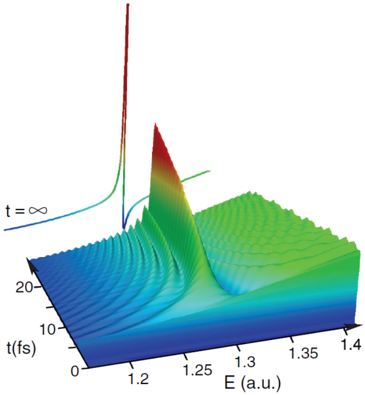
Resonances make a difference!



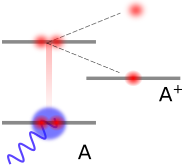


What are we missing

when we just look at the cross section (i.e. the amplitude)?

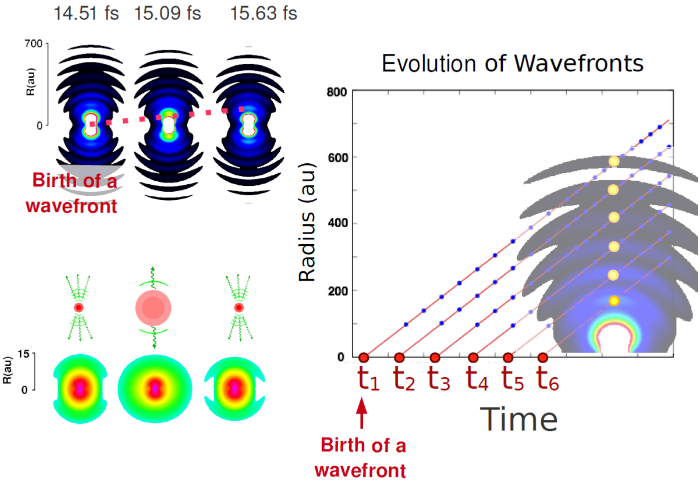


He: $2s2p\,^1P$. Argenti et al.
PRA 87 05340



- As soon as the resonance is populated it starts to decay
- The picture of a time-isolated excitation process and then a decay is a simplification

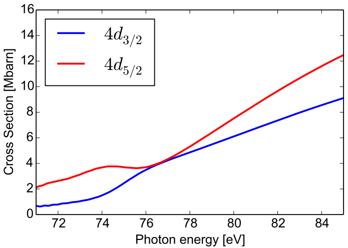
Time-dep. Sch. Eq. Simulations: Autoionization



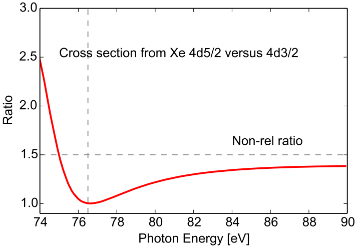
- But how can such dynamics be measured?
- Let's look at another system!

Unusual partial cross section close to Xenon 4d threshold

Partial Cross section



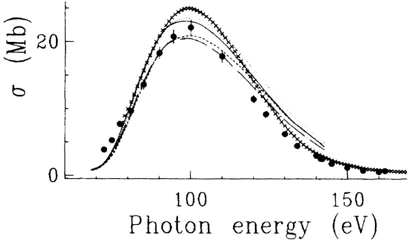
Ratio



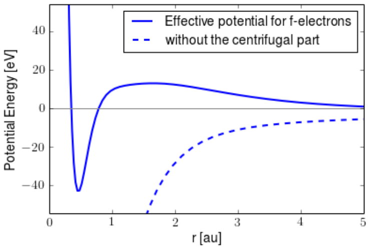
Threshold 67.5/69.5 eV $4d_{5,2,3/2}$

Seen also in Exp:Ausmees et al PRA51 855 1995

Photoionization from Xe 4d - the Giant resonance



Becker et al PRA39 3902 (1989).

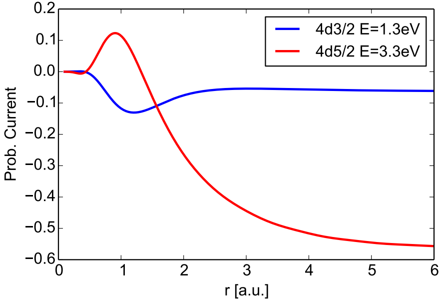


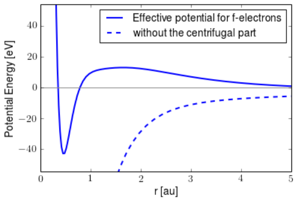
$\sim$ Effective potential

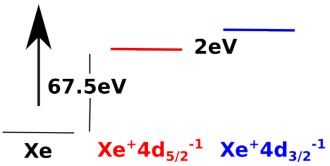
Low energy electrons "collide"

with the potential bump

$\hbar\Omega \approx 71$ eV







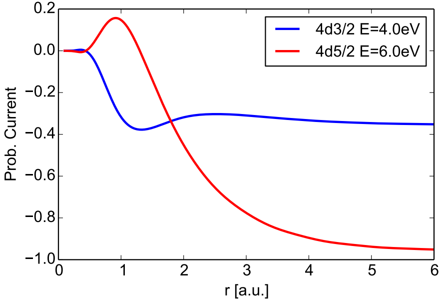
$$\frac{i\hbar}{2m}\left(\rho^*\frac{\partial\rho}{\partial r} - \rho\frac{\partial\rho^*}{\partial r}\right)$$

- Negative Prob. Current = Outwards
- and the $4d_{5/2}$ current goes first inwards..

Low energy electrons "collide"

with the potential bump

$\hbar\Omega \approx 73.5$ eV



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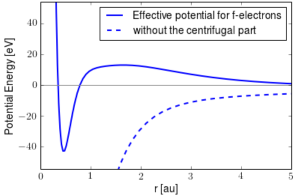

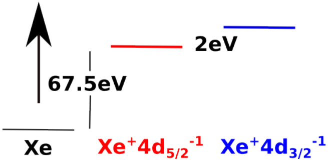

- Negative Prob. Current = Outwards
- and the $4d_{5/2}$ current goes first inwards..

Low energy electrons "collide"

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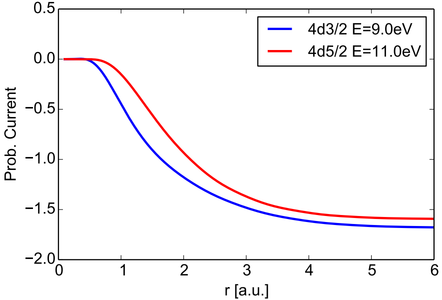
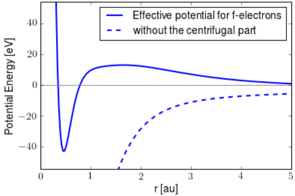
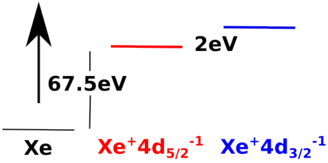
$\hbar\Omega \approx 78.5$ eV



$$\frac{i\hbar}{2m}\left(\rho^*\frac{\partial\rho}{\partial r} - \rho\frac{\partial\rho^*}{\partial r}\right)$$



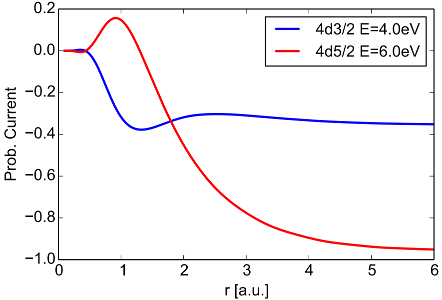


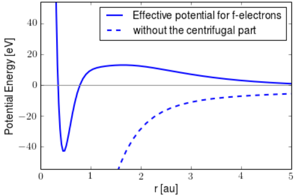
- Negative Prob. Current = Outwards
- When over the bump the situation is normal

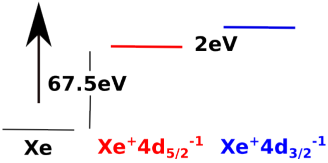
Not just energy

Higher energy wave packet reflected - the lower gets through

$\hbar\Omega \approx 73.5$ eV



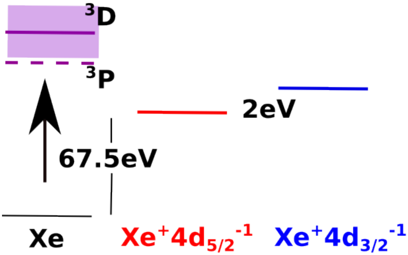


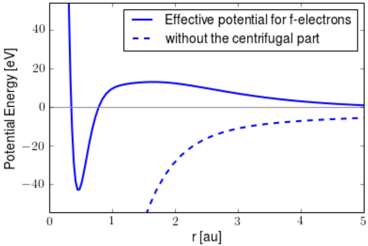


$$\frac{i\hbar}{2m}\left(\rho^*\frac{\partial\rho}{\partial r} - \rho\frac{\partial\rho^*}{\partial r}\right)$$

- Negative Prob. Current = Outwards
- and the $4d_{5/2}$ current goes first inwards..

Spin flip resonance acts as a switch
QM Interference feeds one channel and depletes the other



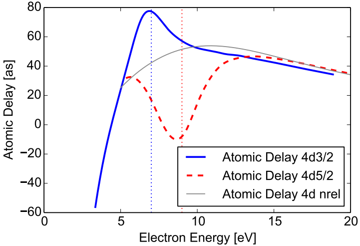


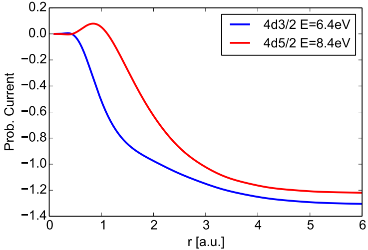
- The potential supports the Giant Resonance (two of ^{1}P -symmetry)
- but also two "cousins" of ^{3}P and ^{3}D symmetry
- populated through spin-orbit interaction
- ^{3}D equal composition of $4d_{5/2}^{-1}$ and $4d_{3/2}^{-1}$

- Can it be seen in the time domain?

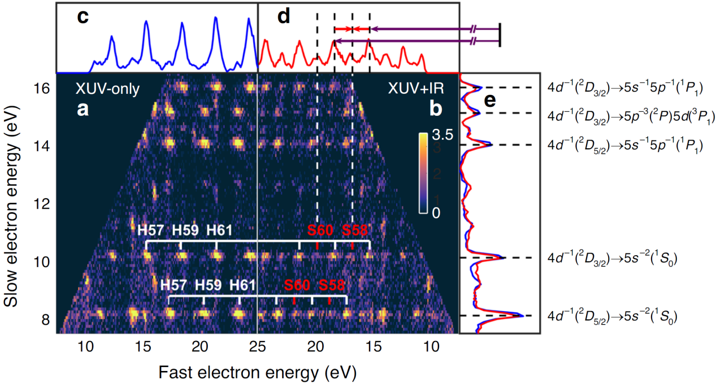
Large atomic delay difference $4d_{3/2}$ vs $4d_{5/2}$

Strong modulation of the delay at the position of the ^{3}D -resonance





- $4_{3/2}$ and $4_{5/2}$ channels:
- The resonance redistribute the prob. current
- And also the delay!



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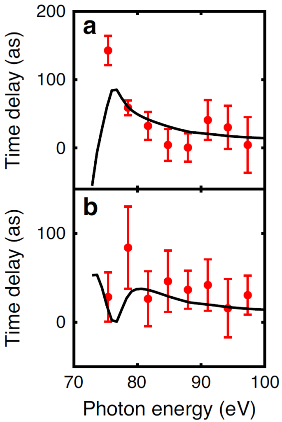
Fast electron in coincidence with specific Auger line - possible to disentangle $^2D_{3/2}$ and $^2D_{5/2}$

Xe 4d

different Atomic delays for different fine structure components



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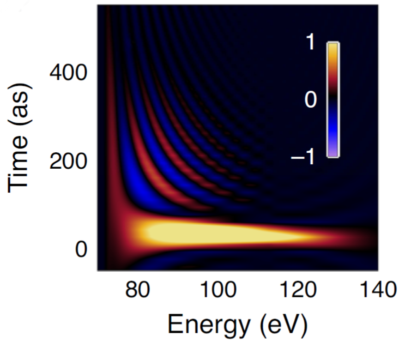
- from $4d_{3/2}$ (upper)
- from $4d_{5/2}$ (lower)

- Exp: Xe($4d_j$) delay measured relative Ne($2p$)
- 100 as differences between $4d_{3/2}$ and $4d_{5/2}$ close to threshold

Wigner representation



$4d_{5/2} \rightarrow \epsilon f_{5/2}$ channel

$$W(E,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\epsilon D_i\left(E+\frac{\epsilon}{2}\right)D_i^*\left(E-\frac{\epsilon}{2}\right)e^{-\frac{i\epsilon t}{\hbar}}$$

- Sharp feature with long decay time (200-300 as) at low energy
- Extended feature over the whole interval with short life time (10-30 as))

- Is the contribution from the “2nd photon” still universal?

Summary

- Non-Hermitian formalism for calculations of ionization
- The continuum-continuum contributions to the phase and the delay is substantial, but often universal: depend only on long-range potential, energy and photon wave length
- ... but more accurate experiments on resonances challenges this view
- resonances in both atoms and molecules interesting to study in the time-domain