How to study dynamics on the Quantum scale?

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Stockholm University

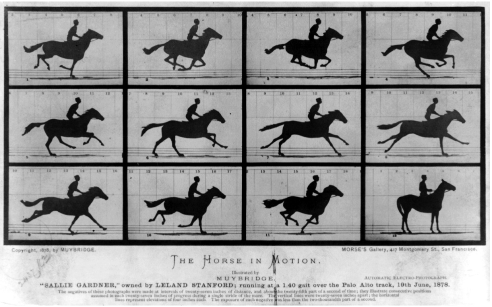
Quantum Connections, 14 June 2024

How can we see what happens very quickly?

High Speed Camera $\sim$ 1000 fps

- Take snap shots on the time scale of the movement
- what can we learn?

How can we see what happens very quickly?

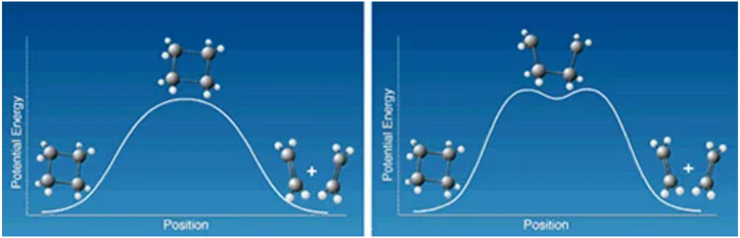


Are all four feet of a horse off the ground at the same time? In 1878 Muybridge settled it.

Method:

- 12 cameras photographing a galloping horse in a sequence of shots
- $\Delta t = 1/25$ s

How can we "see what" happens very quickly?



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

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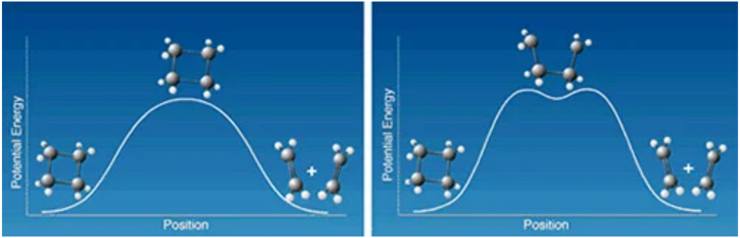

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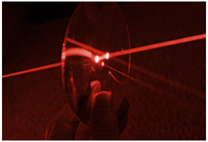
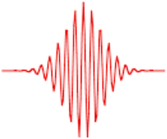
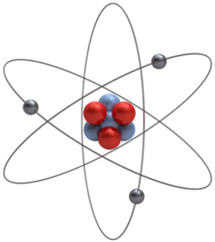




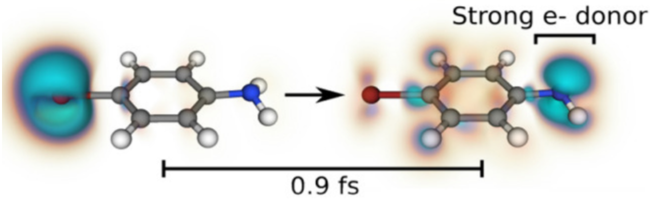
- Femtosecond (10^{-15} s) laser pulses. Infrared light.
- $\Delta t = 10 - 100$ fs

Nobel prize background material 1999

"Femtochemistry has fundamentally changed our view of chemical reactions. From a phenomenon described in relatively vague metaphors such as *activation* and *transition state*, we can now see the movements of individual atoms as we imagine them."



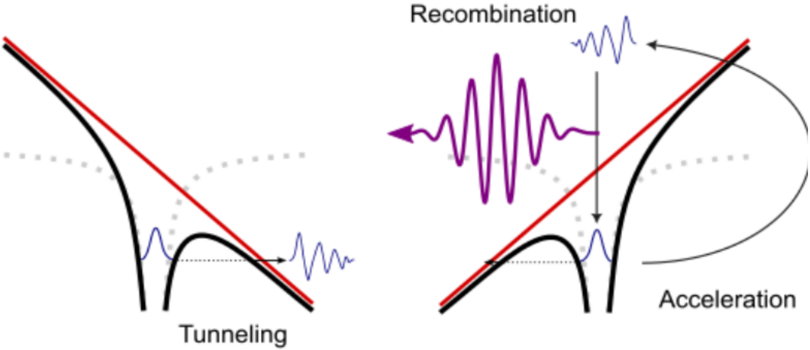
- The "orbit time" in the Bohr model is 150 as ($1\ \mathrm{as} = 10^{-18}$ s)



Simulation of charge migration in a bromobenzene molecule. From Folorunso et al.

High Harmonic Generation

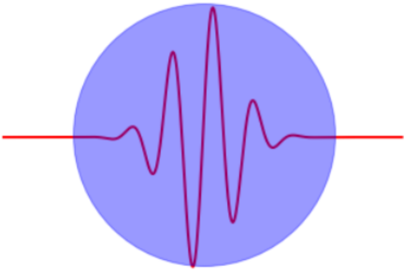
Compare David Busto's Monday lecture



- M Ferray A L'Huillier et al J. Phys. B 21, L31 (1988)
- XUV pulses with a duration of 100as

To be both a particle and a wave

- All matter has both particle and wave properties, $\lambda_B = h/p$



Atoms in chemical reactions are mostly particle-like.

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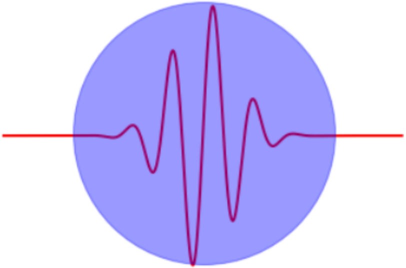
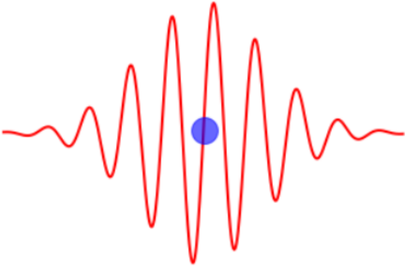


Atoms in chemical reactions are mostly particle-like. Activation Energy 100kJ/mol ~ 1 eV/particle. carbon atom $\lambda_B \sim 0.1$ Bohr radii



Electrons around atoms and molecules are mostly wave-like: $E = 1$ eV $\lambda_B \sim 23$ Bohr radii

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*

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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?

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- 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**

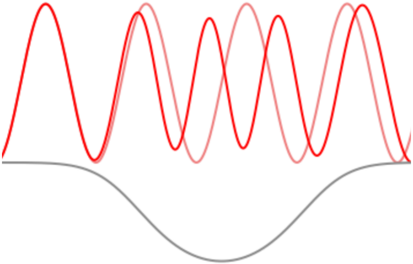
Use the wave properties

The relation between a phase shift and time

- Free particle in empty space

Use the wave properties

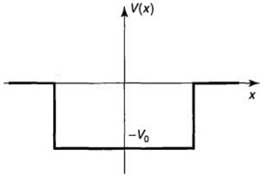
The relation between a phase shift and time



- Over attractive potential

A classical analogy

- A free particle passes over a potential well



Classically

- the particle speeds up over the well

$$v_I = \sqrt{2E/m}$$
$$v_{II} = \sqrt{2\left(E + V_0\right)/m}$$

- and arrives earlier

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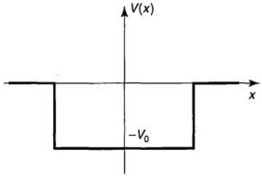

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Quantum Mechanically

- the wavelength gets shorter over the well

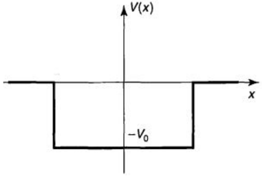
$$k_I = \sqrt{2Em}/\hbar$$
$$k_{II} = \sqrt{2(E+V_0)m}/\hbar$$

- and there is a phase shift

A classical analogy

Classically

- The particle arrives earlier/later



- For the square well

$$\Delta t = \Delta x \left(\frac{1}{v_{II}} - \frac{1}{v_I} \right)$$

Quantum Mechanically

- There is a phase shift η

$$\frac{d\eta}{dE} = \frac{d\eta}{dk} \frac{dk}{dE}$$

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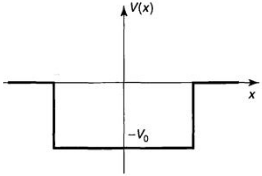

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- The group velocity

$$v_g = \frac{1}{\hbar}\frac{dE}{dk} = \frac{\hbar k}{m}$$

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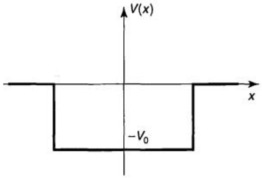

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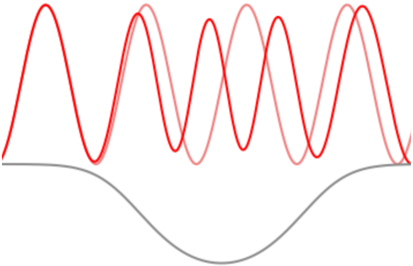
- For the square well ($\frac{\Delta\eta}{\Delta k} = \Delta x$)

$$\Delta t = \hbar\frac{d\eta}{dE} = \frac{m}{\hbar}\Delta x \left(\frac{1}{k_{II}} - \frac{1}{k_I} \right)$$

Eisenbud -48 Wigner -55 Smith -60



$$\tau = \hbar \frac{d\eta}{dE}$$

- With a twist the concept is valid also for long range potentials

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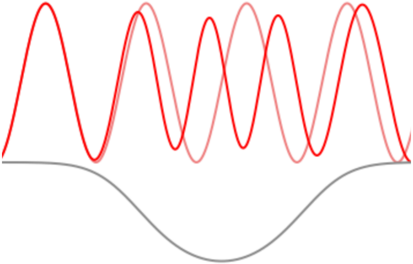
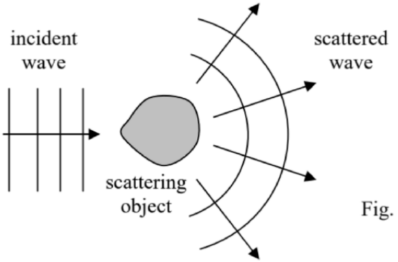


$$\tau = \hbar \frac{d\eta}{dE}$$

- With a twist the concept is valid also for long range potentials
- possible to define an hermitian delay **operator**

$$\hat{\tau} = -i\hbar S^{\dagger}(E) \frac{\partial}{\partial E} S(E)$$

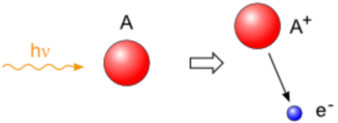


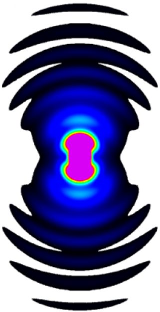
Classical scattering process

- Photoionization can be seen as **half scattering**

Photoionization

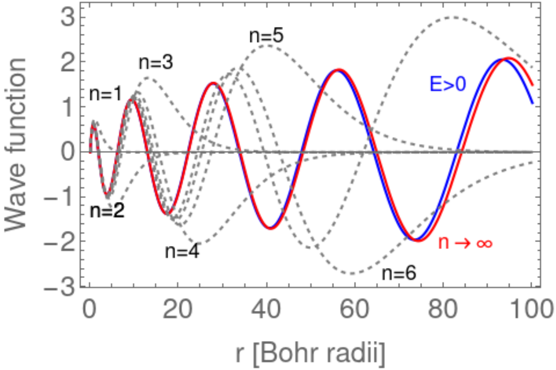
Electrons released by light from a quantum system





Outgoing wave packet

From Bound States to the Continuum



Radial Coulomb eigenfunctions, $\ell = 0$. Bound states renormalized $\sim 1/\Delta E$. Continuum state with energy normalization. *After H. Friedrich: Th. Atomic Physics.*

The outgoing wave packet

But a travelling wave has to be complex!

- The **perturbed wave function** concept

The outgoing wave packet

But a travelling wave has to be complex!

- The **perturbed wave function** concept (one or several ph:s)

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

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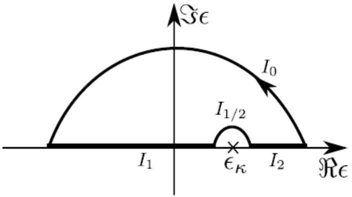
When the photon energy is high enough there will be a **pole**!



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

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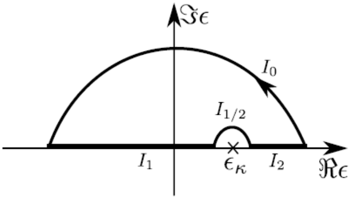
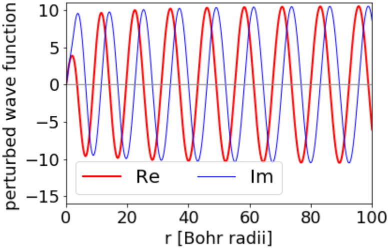
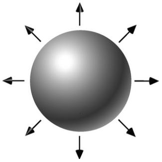


Pole-contribution ($\rightarrow i\sin(\ldots)$) +
Principal value part ($\rightarrow \cos(\ldots)$)

Example: Ar $3p \rightarrow d$



What can the perturbed wf tell us?



$\rightarrow Ae^{i(kr+\frac{Z}{k}\ln 2kr-\ell\frac{\pi}{2}+\sigma_\ell+\delta)}$

- Decreased probability density around the atom equals probability flux through spherical surface

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

- ionization rate (per unit time)
- energy absorbed: $\text{rate}\times\hbar\omega$

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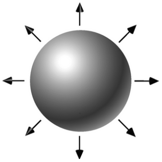

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- Photoabsorption cross section σ

$$\sigma=\frac{\text{Energy per unit time absorbed by the atom}}{\text{Energy flux of the radiation field}}.$$

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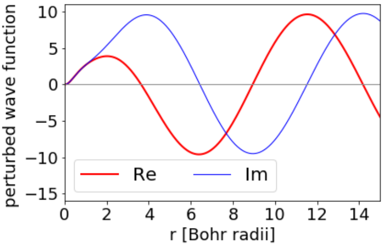
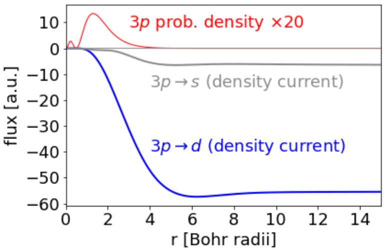
Example: Ar $3p \to d$, $E_{kin} \sim 3$ eV

The Outgoing Wave



$\longrightarrow$

Probabblity density current



- Current constant $(k\hbar/2m)$ when the photoelectron has left the core region.
- Cross section determined by the square of the amplitude at ∞.

$$\frac{k\hbar}{2m}|A|^2$$

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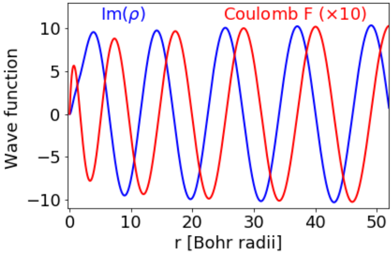
Phase shift (Ar $3p \to d$)



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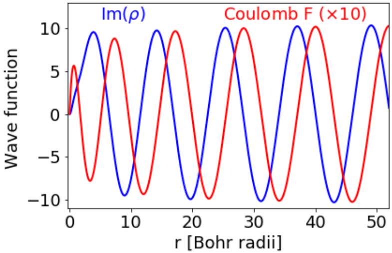

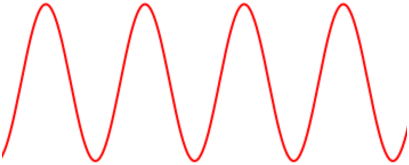

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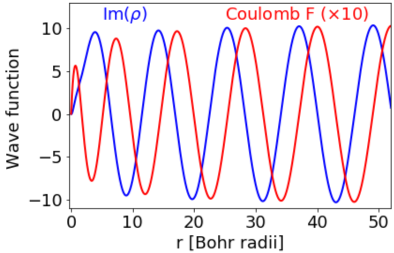

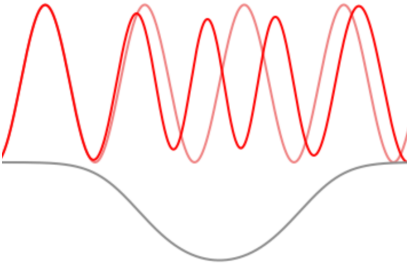

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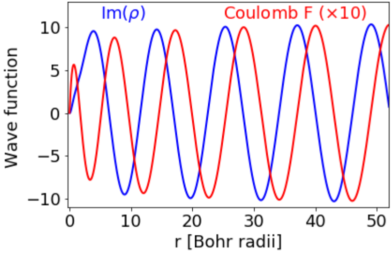

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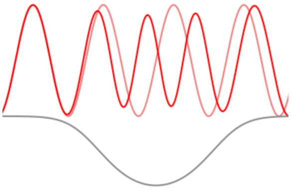
The "local wave number"

$$k(r) = \sqrt{2m(E - V(r))}$$

Accumulated phase.

$$\eta(r) = \int_0^r \sqrt{2m(E - V(r'))} dr'$$

$$\to \frac{d\eta}{dr} \text{ gives } V(r)$$



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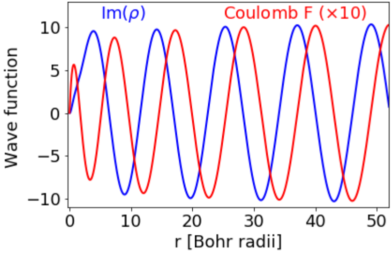

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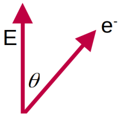
- Phase shift δ due to many-body potential at small distances.

$$e^{i(kr + \frac{Z}{k} \ln 2kr - \ell\frac{\pi}{2} + \sigma_\ell + \delta)}$$

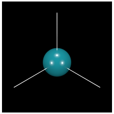
- After all: both amplitude and phase required to characterize the wave function!
- Did we never try to get hold of the phase before?

WHEN DOES THE PHASE COME INTO PLAY?

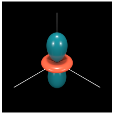
$$\Psi_{\epsilon_f}(r,\theta,0) \longrightarrow e^{i(kr+\frac{Z}{k}\ln 2kr)} \sum_{\ell_f,m} M_{\ell_0,m\to\ell_f,m}\, e^{i\Delta_{\ell_f}}\, Y_{\ell_f m}(\theta,0)$$



e.g. from p-orbital $\Longrightarrow$ $c_s \times$



$+$ $c_d \times$



s-wave

d-wave

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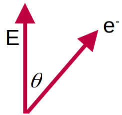
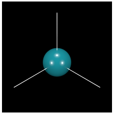
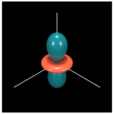


e.g. from p-orbital $\Longrightarrow$ $c_s \times$  $+$ $c_d \times$ 

s-wave d-wave

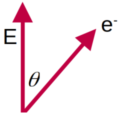
$$\sum_m |A(\theta,0)|^2 = \left| \sum_{\ell_f} Y_{\ell_f,m}(\theta,0)\, e^{i\Delta_{\ell_f}} \mathrm{M}_{\ell_f m} \right|^2$$

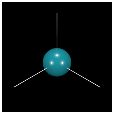
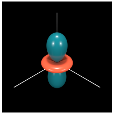
$$= \ldots \mathrm{M}^*_{\ell_i m} \mathrm{M}_{\ell_j m} e^{i\left(\Delta_{\ell_j}-\Delta_{\ell_i}\right)} Y^*_{\ell_i,m} Y_{\ell_j,m} + c.c$$

- Non-diagonal terms depend on the scattering phase

WHEN DOES THE PHASE COME INTO PLAY?

$$\Psi_{\epsilon_f}(r,\theta,0) \longrightarrow e^{i\left(kr+\frac{Z}{k}\ln 2kr\right)} \sum_{\ell_f,m} M_{\ell_0,m\rightarrow\ell_f,m} e^{i\Delta_{\ell_f}} Y_{\ell_f m}(\theta,0)$$



e.g. from p-orbital $\Longrightarrow$ $c_s \times$  $+$ $c_d \times$ 

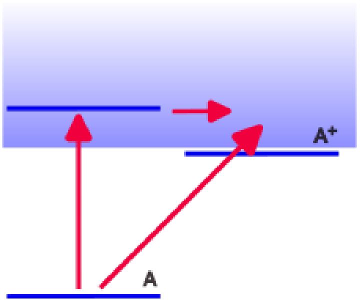
s-wave d-wave

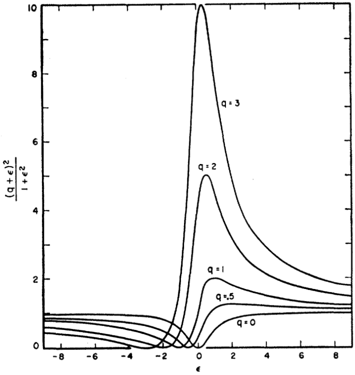
$$\sum_m |A(\theta,0)|^2 = \frac{\int |A(\theta,0)|^2 \, d\Omega}{4\pi} \left(1 + \sum_{n=1}^{\infty} \beta_n P_n(\cos\theta)\right)$$

- Cooper & Zare 1968
- valid both for atoms and molecules (when averaged over molecular orientation)

WHEN DOES THE PHASE COME INTO PLAY?

RESONANCES: TWO PATH INTERFERENCE



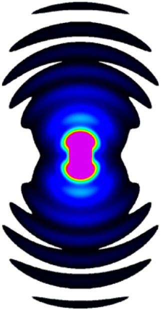


- direct photoionization AND via resonance

- Fano 1961
- Asymmetric line profiles quantified by q

Complete characterization of the e^- WP

- Amplitude **& Phase**

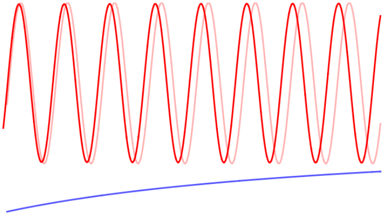


Traditional methods

- Angular dependence (β)
- Resonances (q)

New possibilities

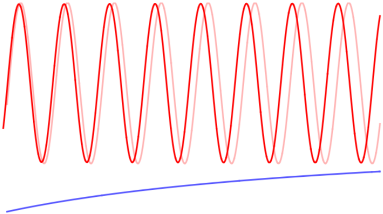
- to get hold of the phase with attosecond techniques...



- When $r \to \infty$

$$\rho(r) \to e^{i\left(kr + \frac{1}{ka_0} ln 2kr - \ell\frac{\pi}{2} + \sigma_\ell(E)\right)}$$

$$\sigma_\ell(E) = \arg\left[\Gamma\left(\ell + 1 - i\frac{Z}{ka_0}\right)\right]$$



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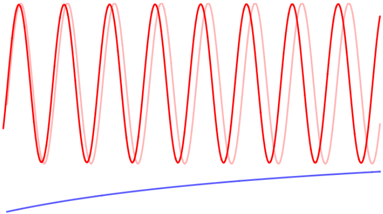
- The logarithmic term:

$$\hbar\frac{\partial}{\partial E}\left(\frac{1}{ka_0}\log 2kr\right) \to \frac{m}{\hbar k^3 a_0}(1 - \log 2kr)$$

- We cannot compare with a plane wave
- But we can compare different systems with the same long-range Coulombic potential

Coulomb field
Hydrogen



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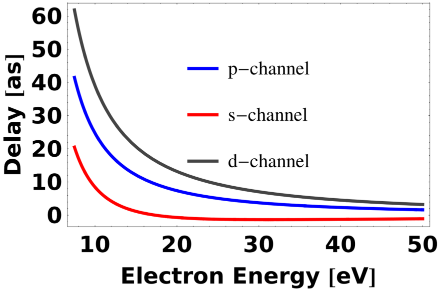
- Pure Coulomb field

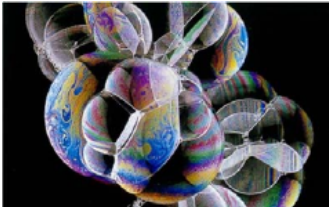
$$\Delta\tau = \hbar\frac{d\sigma_\ell(E)}{dE}$$

- Additional phase shift in many-electron systems!



How can the phase be measured?

- Waves interfere
- When there is a phase difference new patterns emerge



Early Example

Photoelectron emission from single-crystal tungsten

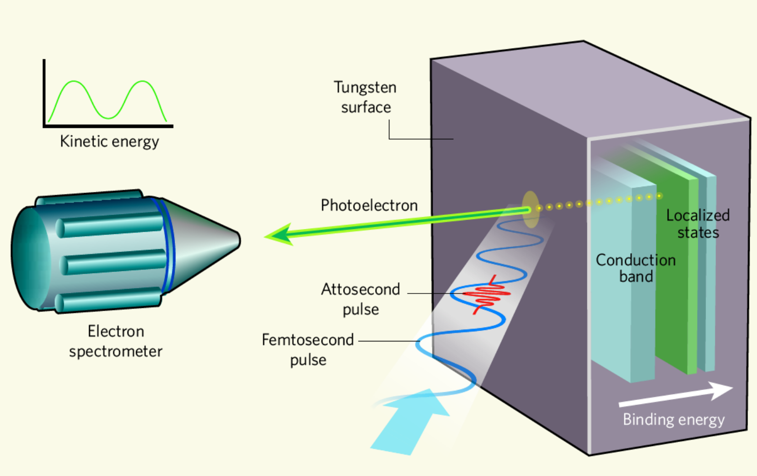
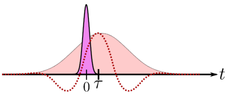
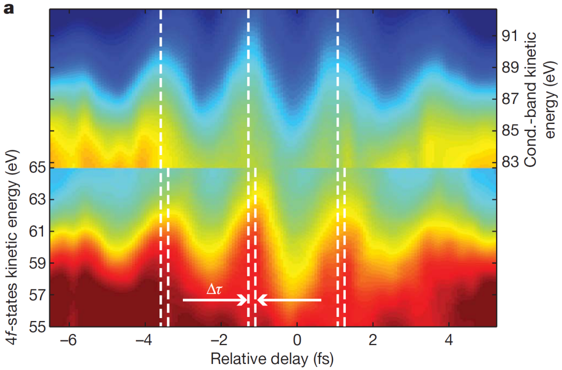


Illustration from Attophysics: At a glance Villeneuve Nature 449, 997,-07

Interferometric measurement - Streaking

- Photoelectron versus delay between the pulses
- $\Delta\tau = 110 \pm 70$ as

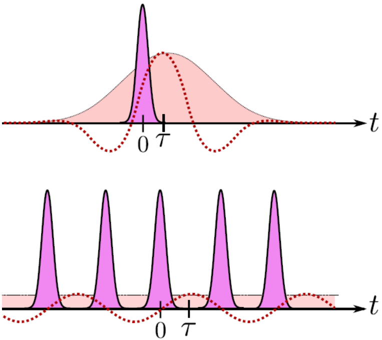




Cavalieri *et al.* Nature 449,1029. Pulse: $\tau \sim 300$ as, $\hbar\omega \sim 91 \pm 3$ eV

Pump & Probe

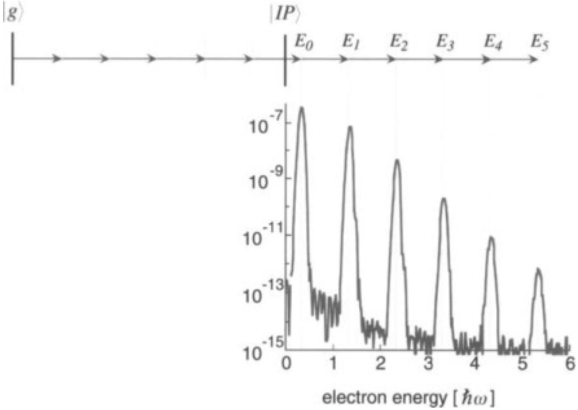
- Short (attosecond duration) bursts of short wave-length light



- Short IR-pulse → isolated atto - second pulse. Broad pulse in the energy domain. Simultaneous pump and probe. (Streaking)
- Train of attosecond pulses (RABBIT). Simultaneous pump and probe. Comb of XUV frequencies in the energy domain.

Laser Assisted Photoionization

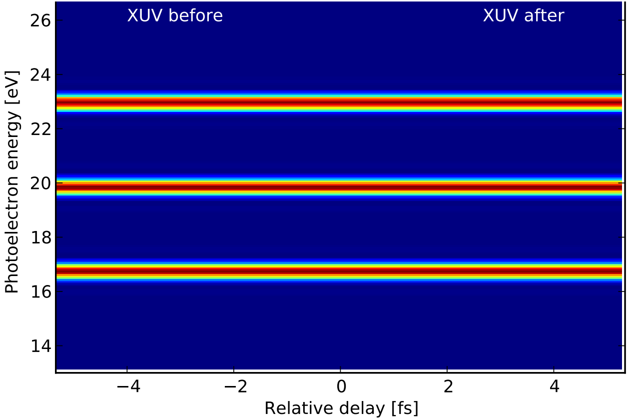
Above Threshold Ionization



- the electron absorbs or emits extra photons when it is already in the continuum
- Strong field phenomena
- First seen by P. Agostini et al. Phys. Rev. Lett. 42, 1127, -79 with 10^{13} W/cm^2 $\hbar\omega = 1.17$ EV

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)*

Photoelectron spectrogramin XUV + IR

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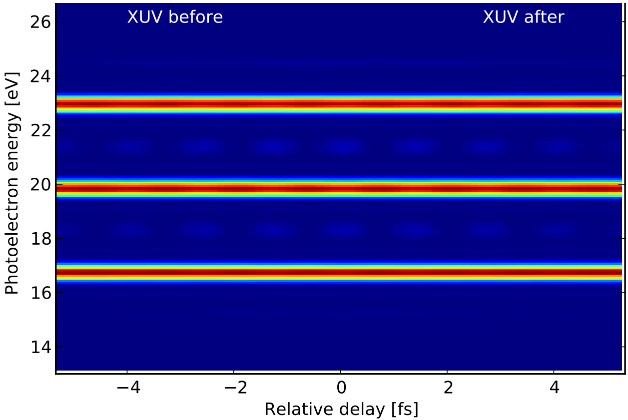

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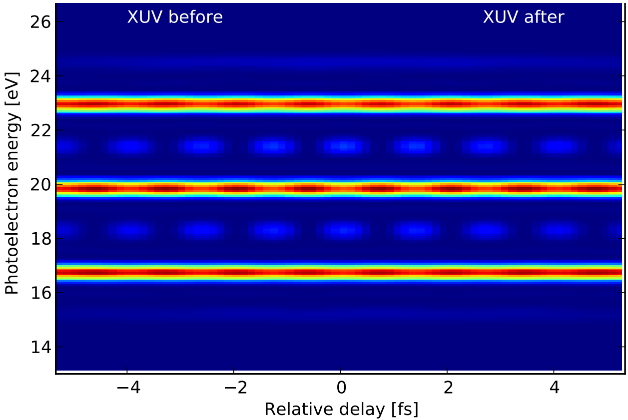

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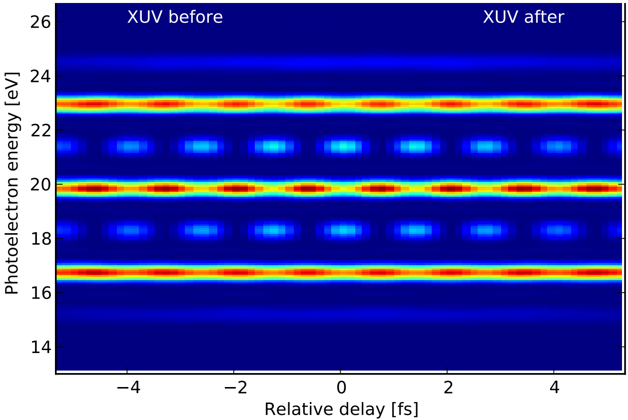
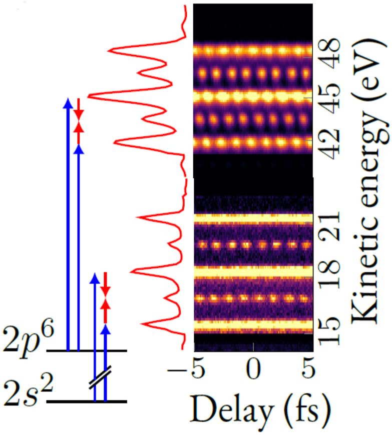


Redistribution of three harmonic peaks due to laser dressing: Formation of **sidebands**. *(Courtesy Marcus Dahlström)*

How it looks in reality

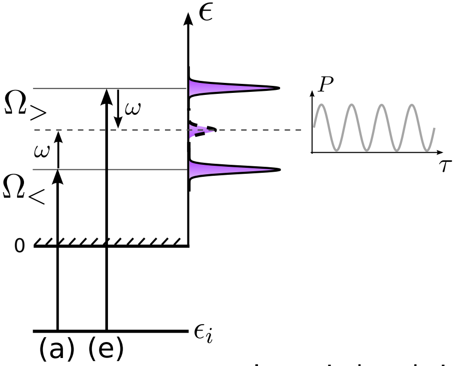


A. L'Huillier group Isinger et al. Science**358**, 893, 2017

Laser-assisted photoionization - RABBIT

Compare David Busto's Monday Lecture

Resolution of Attosecond Beating By Interference of Two-photon Transitions



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

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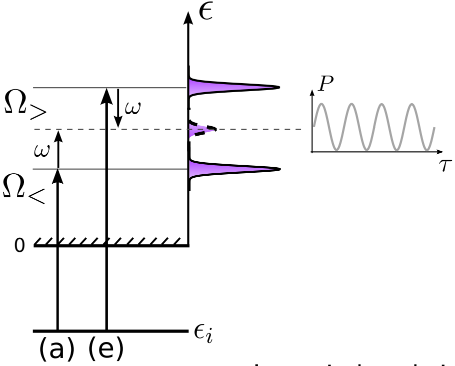

- initial idea: phase contribution from ω negligible
  $\rightarrow \eta_{\mathrm{Atom}} \approx \eta_{\mathrm{Wigner}}$
- But is that true?

Laser-induced sideband signal:

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

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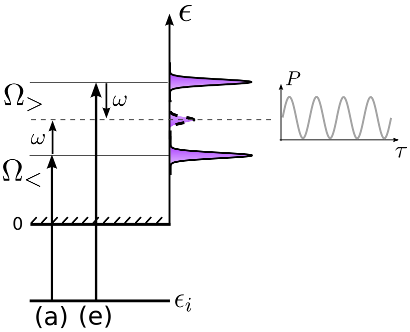
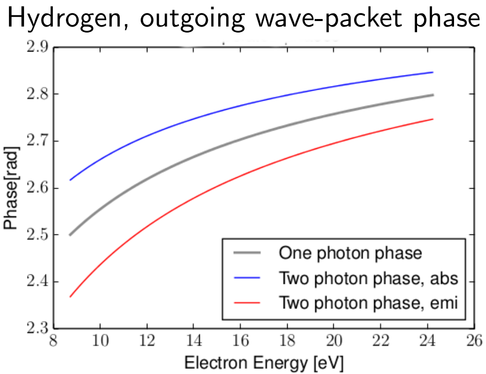
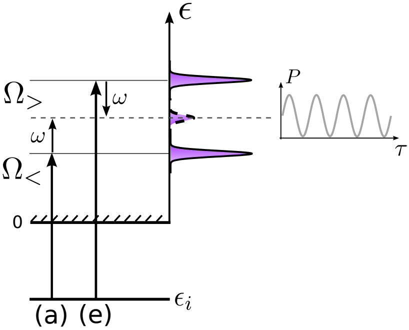
Back to Hydrogen - Phase

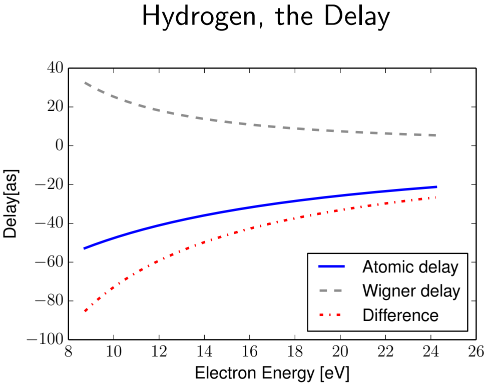




- The experiments **do not measure the Wigner phase**
- they measure the difference between the **emission** and **absorption** path.

Back to Hydrogen -Delay





Finite Difference Approximation:

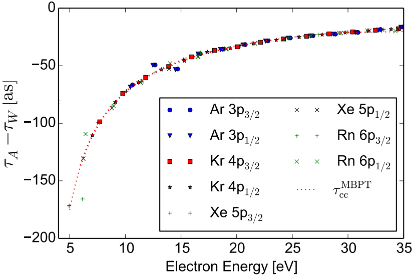
$$\tau_{atomic} = \frac{\arg\left[M_{emi\,\omega}\right] - \arg\left[M_{abs\,\omega}\right]}{2\omega}$$

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

The difference: Above threshold Ionization

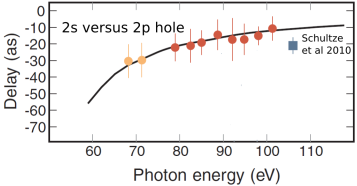
- Continuum-Continuum transitions

Rather Universal Contribution



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

Agrees with Experiment



Isinger et al Science **358** 893 2017

Summary

- There is time information in the scattering phase shift
- Photoionization is “half scattering”
- Interferometric techniques measure relative phases
- The measurement technique itself contribute with an extra phase that we have to understand and account for.