Time and Spin in Attosecond Spectroscopy

Olga Smirnova
Max-Born Institute, Berlin
The Roadmap

- Defining ionization time: from one to many photons
  - The Spin-Orbit Larmor clock for ionization
  - Connection to Larmor time for tunnelling
  - Connection to quantum orbits and WKB analysis

- Measuring strong-field ionization times
  - The atto-clock setup
  - The transient absorption setup: IR pump – XUV probe. Effects of electron-hole entanglement
  - The high harmonic spectroscopy setup
  - Connection between different measurement protocols
Goal:
Observe & control electron dynamics at its natural time-scale (1 asec = 10^{-3} fsec)

One of key challenges:
• Observe non-equilibrium many-electron dynamics
  • This dynamics can be created by photoionization
  • Electron removal by an ultrashort pulse creates coherent hole

Ionization by XUV

Ionization by IR

Coherent population of several ionic states
Attosecond spectroscopy: Questions

How long does it take to remove an electron with light and create a hole?

Experiment & Theory:


Wigner-Smith Time (group delay of the electron wave-packet)

For MPI unique definition of ionization time is missing

Ionization by XUV

Ionization by IR

Today: New questions

• How does this time depend on the number of absorbed photons (strong IR vs weak XUV)?

• What is the connection between different measurement protocols, e.g. atto-clock vs HHG vs IR pump-XUV-probe transient absorption?

• How does electron-hole entanglement affect electron rearrangement and its time-scale?

Can we find a clock to define this time?
The Roadmap

• Defining ionization time: from one to many photons
  • The Spin-Orbit Larmor clock for ionization
  • Connection to Larmor time for tunnelling
  • Connection to quantum orbits and WKB analysis

• Measuring strong-field ionization times
  • The atto-clock setup
  • The transient absorption setup: IR pump – XUV probe. Effects of electron-hole entanglement
  • The high harmonic spectroscopy setup
  • Connection between different measurement protocols
There is a built-in Larmor-like clock in atoms!

- Based on Spin-Orbit Interaction
- Good for any number of photons $N$
- We will use it to define ionization time
The Larmor clock for tunnelling

I. Baz’, 1966

For $e^-$, the core rotates around it
- Rotating charge creates current
- Current creates magnetic field
- Electron’s spin precesses in this field

- The clock must be calibrated
Gedanken experiment for Calibrating the clock

One-photon ionization of Cs by right circularly polarized pulse

No SO interaction in the ground state

Photon absorption turns on SO interaction

Detect electron spin
Gedanken experiment for Calibrating the clock

One-photon ionization of Cs by right circularly polarized pulse
Define angle of rotation of electron spin during ionization

\[ |s_{in}\rangle = \alpha |\downarrow\rangle + e^{i\varphi \beta} |\uparrow\rangle \]

\[ |s_f\rangle = a_\downarrow \alpha |\downarrow\rangle + a_\uparrow e^{i\varphi \beta} |\uparrow\rangle \]

No SO interaction in the ground state

\[ \phi_{Larm} = \text{arg}(a_\downarrow a_\uparrow^*) \]

ionization amplitude:
- \( a_\downarrow \) for spin-down component
- \( a_\uparrow \) for spin-up component
SO Larmor clock as Interferometer

Looks easy, but ... -- the initial and final states are not eigenstates, thanks to the spin-orbit interaction

- Record the phase between the spin-up and spin-down pathways
SO Larmor clock as Interferometer

\[ R_{1,3} = |R_{1,3}| e^{i\phi_{1,3}} \]

Radial photoionization matrix element

\[ a_\uparrow = R_3 \]

\[ a_\downarrow = \frac{1}{3} (R_3 + 2R_1) \]

U. Fano, 1969

Phys Rev 178,131

A crooked interferometer: arm + double arm
SO Larmor clock as Interferometer

\[ R_{1,3} = |R_{1,3}| e^{i\phi_{1,3}^R} \]
Radial photoionization matrix element

\[ a_{\uparrow} = R_3 \]

\[ a_{\downarrow} = \frac{1}{3} (R_3 + 2R_1) \]

A crooked interferometer: arm + double arm

Wigner-Smith time hides here

\[ \tan \phi_{LARM} = -\frac{\sin(\phi_1^R - \phi_3^R)}{0.5|R_3|/|R_1| + \cos(\phi_3^R - \phi_1^R)} \]

U. Fano, 1969
Phys Rev 178,131
The appearance of Wigner-Smith time

\[ \phi_1^R - \phi_3^R = ? \]

\[ \phi_1^R - \phi_3^R = \phi (E + \Delta E_{SO}) - \phi(E) = \tau_{WS} \Delta E_{SO} \]

\[ \tau_{WS} = \frac{\partial \phi(E)}{\partial E} \]

\[ \tan \phi_{LARM} = -\frac{\sin(\tau_{WS} \Delta E_{SO}^e)}{0.5|R_3|/|R_1| + \cos(\tau_{WS} \Delta E_{SO}^e)} \]

We have calibrated the clock

Strong Field Ionization in IR fields

Multiphoton Ionization: $N \gg 1$

Adiabatic (tunnelling) perspective ($\omega/l_p \ll 1$)

Find time it takes to create a hole in general case for arbitrary Keldysh parameter

Keldysh, 1965
Strong-field Ionization in IR fields: Circular polarization

N>>1 ionization preferentially removes p^- (counter-rotating) electron

- Theoretical prediction: Barth, Smirnova, PRA, 2011
- Experimental verification: Herath et al, PRL, 2012

Closed shell, no Spin-Orbit interaction

Open shell, Spin-Orbit interaction is on

Ionization turns on the clock in Kr+
Clock operates on core states: $P_{3/2}$ ($4p^5, J=3/2$) and $P_{1/2}$ ($4p^5, J=1/2$)
SO Larmor clock operating on the core

$m_l = -1$
$M_l = 1$

$m_s = -1/2$
$M_s = 1/2$

$m_s = 1/2$
$M_s = -1/2$

At the moment of separation

$T_{1,3} = |T_{1,3}|e^{i\phi_{T_{1,3}}}$
Ionization amplitude

$\tan \phi_{LARM} = \frac{\sin(\Delta E_{SO}^h t - \phi_{13})}{0.5|T_3|/|T_1| + \cos(\Delta E_{SO}^h t - \phi_{13})}$
The SFI Time

- One photon, weak field

\[
\tan \phi_{LARM} = -\frac{\sin(\tau_{WS} \Delta E^{e}_{SO})}{0.5|R_3|/|R_1| + \cos(\tau_{WS} \Delta E^{e}_{SO})}
\]

- Many photons, strong field

\[
\tan \phi_{LARM} = \frac{\sin(\Delta E^{h}_{SO} t - \phi_{13})}{0.5|T_3|/|T_1| + \cos(\Delta E^{h}_{SO} t - \phi_{13})}
\]

\[
\phi_{13} = \phi^T_1 - \phi^T_3
\]

- Looks like a direct analogue of \( \tau_{WS} \Delta E_{SO} \)

- Does \( \phi_{13}/\Delta E_{SO} \) correspond to time?
The appearance of SFI time

\[ \phi_3 = \phi_c(I_p) + \phi_{3,SR} \]

\[ \phi_1 = \phi_c(I_p + \Delta E_{SO}) + \phi_{1,SR} \]

\[ \phi_{13} = \phi_c(I_p + \Delta E_{SO}) - \phi_c(I_p) + \Delta \phi_{13,SR} \]

- Part of \( \phi_{13} \) due to the common \( U \) yields Strong Field Ionization time
- Part of \( \phi_{13} \) due to the different \( U_{SR} \) is a trace of e-h entanglement
• Defining ionization time: from one to many photons
  • The Spin-Orbit Larmor clock for ionization
  • **Connection to Larmor time for tunnelling**
  • Connection to quantum orbits and WKB analysis

• Measuring strong-field ionization times
  • The atto-clock setup
  • The transient absorption setup: IR pump – XUV probe. Effects of electron-hole entanglement
  • The high harmonic spectroscopy setup
  • Connection between different measurement protocols
Strong-field ionization time & tunnelling time

Larmor tunneling time :

\[ \tau_L = \frac{\partial \phi_c}{\partial V} \]


SFI time:

\[ \tau_{SFI} = \frac{\partial \phi_c}{\partial I_p} \]

- \( x_F \cos \omega t \)

\( l_p \)

- Derivation has never relied on the tunnelling picture
- SFI time is consistent with the Larmor time for tunnelling through a static barrier of height \( V = l_p \)
• Defining ionization time: from one to many photons
  • The Spin-Orbit Larmor clock for ionization
  • Connection to Larmor tunnelling time
  • Connection to quantum orbits and WKB analysis

• Measuring strong-field ionization times
  • The atto-clock setup
  • The transient absorption setup: IR pump – XUV probe. Effects of electron-hole entanglement
  • The high harmonic spectroscopy setup
  • Connection between different measurement protocols
Strong-field ionization time & semiclassical time

Can we measure the SFI time $\tau_{\text{SFI}}$?

Key result:

$$\tau_{\text{SFI}} = \frac{\partial \phi_c}{\partial I_p}$$

Coincides with the semiclassical ‘exit time’, if the semiclassical approximation is used for $\phi_c$.
The Roadmap

• Defining ionization time: from one to many photons
  • The Spin-Orbit Larmor clock for ionization
  • Connection to Larmor time for tunnelling
  • Connection to quantum orbits and WKB analysis

• Measuring strong-field ionization times
  • The atto-clock setup
  • The transient absorption setup: IR pump – XUV probe. Effects of electron-hole entanglement
  • The high harmonic spectroscopy setup
  • Connection between different measurement protocols
Ionization time measurements with Atto-clock

**Atto-clock principle**: ionization in strong circular IR fields maps ionization time \( t_{ion} \) on the electron detection angle. (U. Keller et al)

**Example**: Short-range potential

\[ \alpha = \pi/2 \]

- Electron is detected with final \( \mathbf{p} \perp \mathbf{E} \) at the ionization time \( t_{ion} \).
- Observable: angle between \( \mathbf{p} \) and \( E_{max} \) for a ‘single-cycle’ pulse.
SFI time and Atto-clock measurements

Ionization from a long-range potential: $\Delta \alpha$

$\Delta \alpha$ can be converted into time

$$\Delta t_{AC} = \frac{\Delta \alpha}{\omega}$$

Key result:

$$\frac{\Delta \alpha}{\omega} = \frac{\partial \phi}{\partial I_p}$$

- Attoclock measures the SFI time that we have introduced.
  - $\phi$ is the total phase.

- Is there a phase accumulated under the barrier? Our analytical theory says ‘no’
  - Let us compare with numerical experiment
Atto-clock ‘measurements’: TDSE

H-atom,
\( \lambda = 800 \text{ nm} \),
Circular polarization
FWHM = 2.8 fsec (just over one cycle)
ARM vs TDSE (long pulse)

H-atom, 
\( \lambda = 800 \) nm, 
Circular polarization 
(6 cycles flat top)
Atto-clock measurement of SFI time

Our results do not show tunnelling delays for this case.

How does ionization time depend on N photons?

H-atom, 800 nm, Circular polarization
Sin² pulse envelope, 4 cycles base to base
• Phase and delays are accumulated after exiting the barrier
• Larger $N$ – more adiabatic, exit further out
The Roadmap

- Defining ionization time: from one to many photons
  - The Spin-Orbit Larmor clock for ionization
  - Connection to Larmor time for tunnelling
  - Connection to quantum orbits and WKB analysis

- Measuring strong-field ionization times
  - The atto-clock setup
  - The transient absorption setup: IR pump – XUV probe. Effects of electron-hole entanglement
  - The high harmonic spectroscopy setup
  - Connection between different measurement protocols
Ionization times in transient absorption

Experiment: use a few cycle circularly polarized IR pulse as a pump

Closed shell, no Spin-Orbit interaction

Open shell, Spin-Orbit interaction is on

Ionization turns on the clock in Kr⁺
Clock operates on core states: $P_{3/2}$ (4p⁵, J=3/2) and $P_{1/2}$ (4p⁵, J=1/2)
Measuring ionization times with transient absorption

- **Pump:** Few fs IR creates p-hole and starts the clock
- **Probe:** Asec XUV pulse fills the p-hole and stops the clock
- **Observe:** Read the attosecond clock using transient absorption measurement
Transient absorption measurements

TA Signal $\propto \cos(\Delta \phi - \tau \Delta E_{SO})$

TA signal shows the phase difference $\Delta \phi$ due to ionization into $J=3/2$ and $J=1/2$

Kr atom: $I_p=14$ eV

$\Delta E_{SO}=0.67$ eV

$2.5 \times 10^{14}$ W/cm$^2$

Phase, rad

$\phi_{13} = \phi_1^T - \phi_3^T$

Total relative phase

WS-like phase delay

$-\Delta E_{SO}/I_p^{3/2}$

$e-h$ entanglement

$-0.4 F^2/I_p^{5/2}$

Number of photons
The Roadmap

- Defining ionization time: from one to many photons
  - The Spin-Orbit Larmor clock for ionization
  - Connection to Larmor time for tunnelling
  - Connection to quantum orbits and WKB analysis

- Measuring strong-field ionization times
  - The atto-clock setup
  - The transient absorption setup: IR pump – XUV probe.
    Effects of electron-hole entanglement
  - The high harmonic spectroscopy setup
  - Connection between measurement protocols
Delays: pump-probe vs Atto-clock

\[ \tau_0 = \frac{\Delta \phi}{\Delta E_{SO}} = \frac{\Delta \phi}{\Delta I_p} \]

Kr atom:
Ip=14 eV

Kr\(^+\)
\[ \Delta E_{SO} = 0.67 \text{ eV} \]

Circular field:
2.5\( \times 10^{14} \) W/cm\(^2\)

- ‘Apparent delay’ shows up in Transient Absorption measurement
- ‘Apparent delay’ is due to electron–hole entanglement
- ‘Apparent delay’ is not present in Attoclock measurement

Approaches WS delay as N \( -> 1 \)

Approaches Larmor time for N \( \gg 1 \)

0.4\( F^2 / \Delta E_{SO} I_p^{5/2} \)
The Roadmap

- Defining ionization time: from one to many photons
  - The Spin-Orbit Larmor clock for ionization
  - Connection to Larmor time for tunnelling
  - Connection to quantum orbits and WKB analysis

- Measuring strong-field ionization times
  - The atto-clock setup
  - The transient absorption setup: IR pump – XUV probe.
    Effects of electron-hole entanglement
  - The high harmonic spectroscopy setup
  - Connection between different measurement protocols
High harmonic spectroscopy of ionization times

Oscillating field brings the electron back
Electron-ion recombination produces emission: high harmonics of IR
Measuring ionization times: Key idea

Strong $F_\omega \cos \omega t$

Weak probe $F_{2\omega} \cos (2\omega t + \phi)$

Strong $\omega$ field drives tunnelling
Weak $2\omega$ tags the electron
Dependence of $\Delta v$ and $\Delta r$ on $\phi$ encodes ionization times

How can we measure $\Delta v$ and $\Delta r$? – where to find two independent observables?

\[
\Delta v_{\perp} (t, t_i) = -\int_{t_i}^{t} F_{2\omega} (t') dt' = A_{2\omega} (t) - A_{2\omega} (t_i)
\]

\[
\Delta r_{\perp} (t, t_i) = \int_{t_i}^{t} \Delta v_{\perp} (t', t_i) dt'
\]
Measuring position shifts: 2D High harmonic spectroscopy

Oscillating field brings the electron back – harmonic emission
Parent ion is a perfect measurement device

Odd harmonic intensities maximize for minimal $\Delta r (\phi)$
Odd harmonics measure $\Delta r (\phi)$
Measuring velocity shifts: 2D High harmonic spectroscopy

Presence of $2\omega$ leads to even harmonics

Harmonic emission means that electron has returned

Even harmonic intensity maximizes for maximal asymmetry between two subsequent half-cycles

Maximal asymmetry means maximal $\Delta v (\phi)$

Even harmonics measure $\Delta v (\phi)$
Measurements in Helium

Helium, 40 fsec pulse, 800 nm at $4 \times 10^{14} \text{ W/cm}^2$, 400 nm at 1-2% intensity level

Odd harmonics

Even harmonics

Results of reconstruction in Helium

Helium, 40 fsec pulse, 800 nm at 4 \(10^{14}\) W/cm\(^2\), 400 nm at 1-2% intensity level

Results are:
• in agreement with the ‘exit times’
• consistent with the theory predicting no tunnelling delay, within < 30 asec accuracy
The Roadmap

• Defining ionization time: from one to many photons
  • The Spin-Orbit Larmor clock for ionization
  • Connection to Larmor time for tunnelling
  • Connection to quantum orbits and WKB analysis

• Measuring strong-field ionization times
  • The atto-clock setup
  • The transient absorption setup: IR pump – XUV probe. Effects of electron-hole entanglement
  • The high harmonic spectroscopy setup
  • Connection between measurement protocols
Ionization time measurements: Attoclock vs HHG

Photoelectron spectroscopy - PES (Attoclock in circular fields)

HHG spectroscopy

Do they measure same ionization times?
Ionization time measurements with HHG

**Example:** Short-range potential

- Below threshold harmonics: \( N\omega < I_p \)
- \#130 asec

For long trajectories ionization times are the same in HHG and PES

**Graph:**
- **Photo**
- **HHG**
- **Attoclock measurement**
- Ionization window ~250 asec
- 670 asec
- Real time of return, units of laser cycle
- 0 0.2 0.4 0.6 0.8 1
- Ionization time, units of laser cycle
- 0 0.05 0.1 0.15 0.2 0.25

For long trajectories ionization times are the same in HHG and PES.
Conclusions

• Using SO Larmor clock we defined delays in hole formation:
  • Actual delay in formation of hole wave-packet
    • Larmor- and Wigner-Smith – like,
    • Applicable for any number of photons, any strong-field ionization regime
  • Apparent ‘delay’ – trace of electron-hole entanglement:
    • Clock-imparted ‘delay’ (encodes electron – hole interaction )
    • Analogous to spread of an optical pulse due to group velocity dispersion
    • does not depend on clock period
  • Absorbing many photons takes less time than absorbing few photons, but not zero

• The SO interaction has been used to derive $\tau_{SFI}$ but is not needed to measure it!

• Directly related to times measured in IR-pump-XUV-probe scheme
  (e.g. Transient absorption, tiny difference due to entanglement)
• Directly related to ionization times in HHG (tiny difference)
• Directly measured by Atto-clock