Departamento de Física .UBAexactas

ATTOSECOND PHYSICS

UNIT X ATTOSECOND CHRONOSCOPY

Diego Arbó
diego.arbo@uba.ar

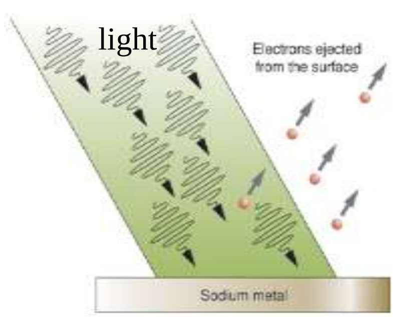
1st Semester 2024, Buenos Aires, Argentina

Departamento de Física .UBAexactas

ATTOSECOND CHRONNOSCOPY

Spectroscopy: Energy-domain information
Chronoscopy: Time-domain information

Fundamental question: Does Einstein's photoelectric effect happen instantaneously or is there a finite time the electronic wavepacket need to be formed?



1921

Antecedent: Femtosecond Chemistry (Ahmed Zewail)

1999

Departamento de Física .UBAexactas

ATTOSECOND CHRONNOSCOPY

IAFE CONICET UBA

Quantum Theory

Whereas time is a good physical magnitude accessible to measurement in classical mechanics, it is not in quantum mechanics.

In quantum mechanics for a classical observable there is an associated quantum mechanical operator, the expectation value thereof is connected to the classical observable.

$$\hat{x} = i\hbar \frac{\partial}{\partial p}; \quad \hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\hat{H} = i\hbar \frac{\partial}{\partial t}; \quad \hat{t} = \frac{\hbar}{i}\frac{\partial}{\partial E}$$

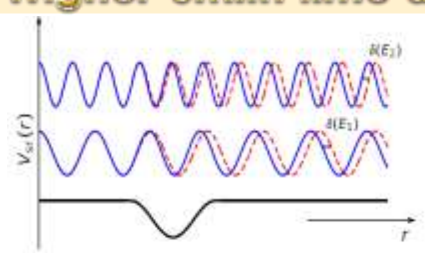
In contrast to space, momentum, and energy such a well-defined operator does not exist for time.

Departamento de Física .UBAexactas

Eisenbud-Wigner-Smith time delay

IAFE CONICET UBA

Scattering theory:



Schematics of one-dimensional potential scattering. An incoming plane wave from the left is scattered at a short-ranged potential $V_{st}(r)$ and gains an asymptotic phase shift $\delta(E)$. Considering a wavepacket consisting of different energy components (Eq. 2.2) this results in a time delay (group delay) $t_{EWS} = \hbar\frac{\partial}{\partial E}\delta(E)$ of the wavepacket.

Free propagation wavepacket: $\psi(r,t) = \int_0^\infty A(E)e^{i(kr-\omega t)}\mathrm{d}E$

Scattering propagation wavepacket: $\psi(r,t) = \int_0^\infty A(E)e^{i(kr-\omega t+\delta(E))}\mathrm{d}E$

Departamento de Física .UBA exactas

Eisenbud-Wigner-Smith time delay

Stationary phase: $\frac{\partial}{\partial\omega}[kr - \omega t + \delta(E)] = 0$

$$\frac{r}{(\partial\omega/\partial k)} - t + \frac{\partial\delta(E)}{\partial\omega} = 0$$

Eisenbud-Wigner-Smith arrival time of the wavepacket: $t = r/v_g + t_{\mathrm{EWS}}$

$$t_{\mathrm{EWS}} = \hbar\frac{\partial}{\partial E}\delta(E)$$

Exercise 17: Consider a rectangular potential of with *a* and height V_0, where V_0 may be positive (barrier) or negative (well). For $E > V_0$, calculate the transition amplitude and corresponding phase shift.

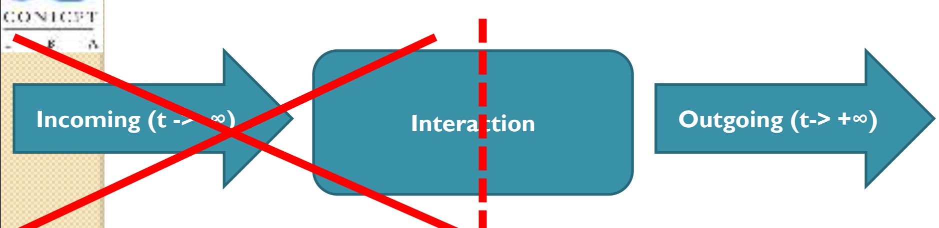
Lifetime operator: $\hat{t}_{\mathrm{EWS}} = -iS^\dagger(E)\frac{\partial}{\partial E}S(E)$

Spherical symmetry: $t_{\mathrm{EWS}}(E,\ell) = 2\frac{d}{dE}\delta_\ell(E)$ *S(E)*: scattering matrix

Departamento de Física .UBA exactas

Photoionization

No incoming electron



Ionization is a half-scattering problem

$$\hat{t}_{\mathrm{EWS}} = -iS^\dagger(E)\frac{\partial}{\partial E}S(E)$$ *S(E)*: scattering matrix

$$t_{\mathrm{EWS}}(E,\ell) = \cancel{2}\frac{d}{dE}\delta_\ell(E)$$

One-photon ionization

First Born Approximation: First order perturbative method. The final wave function is represented by the non-distorted solution of the free Hamiltonian H_0. Thus, the laser field is neglected in the final channel. This is a good approximation for **weak** external electric fields: $H_{int} << H_0$.

$$T_{if} = i\int_{-\infty}^{+\infty} dt \left\langle \Phi_f(t) \middle| \vec{r}\cdot\vec{E}(t) \middle| \Phi_i(t) \right\rangle$$

$$= i\int_{-\infty}^{+\infty} dt E(t) \left\langle \phi_f \middle| e^{iE_f t} z e^{iI_p t} \middle| \phi_i \right\rangle$$

$$= i\left\langle \phi_f \middle| z \middle| \phi_i \right\rangle \int_{-\infty}^{+\infty} dt E(t) e^{i(E_f+I_p)t}$$

$$= i\left\langle \phi_f \middle| z \middle| \phi_i \right\rangle \tilde{E}\left(E_f + I_p\right)$$

Departamento de Física
UBA exactas
IAFE CONICET UBA

One-photon ionization

Partial wave expansion of a plane wave:

$$e^{i\mathbf{kr}} = \sum_{\ell=0}^{\infty}(2\ell+1)i^{\ell} j_{\ell}(kr)P_{\ell}(\cos\theta)$$

Partial wave expansion of a scattering state:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\ell=0}^{\infty}(2\ell+1)i^{\ell} e^{i\delta_{\ell}}\phi_{\ell,k}(kr)P_{\ell}(\cos\theta)$$

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell(\ell+1)}{r^2} - 2V_{sr}(r) + k^2\right) r\phi_{\ell,k}(r) = 0$$

Short-range potential

Short-range potential: It falls off faster than r^{-1}

$$\phi_{\ell,k} \underset{r\to\infty}{\sim} \sin\left(kr - \frac{1}{2}l\pi + \delta_\ell\right)$$

Introducing the partial wave decomposition into the transition amplitude:

$$T_{if} = -i\langle\phi_f|z|\phi_i\rangle\tilde{E}\left(E_f + I_p\right)$$
$$= -i\sum_{l=0}^{\infty}(2l+1)i^l e^{i\delta_l(k)}\phi_{l,k}(kr)P_l(\cos\theta)\langle\phi_{l,k}|z|\phi_i\rangle\tilde{E}\left(\frac{k^2}{2}+I_p\right)$$

For one-photon absorption from the 1s state ➔ $\ell = 1$

$$\Rightarrow \quad t_{EWS} = \frac{\partial\delta_l(E)}{\partial E}$$

Short-range potential

Non-perturbative analysis:

$$i\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{\mathrm{H}}|\psi(t)\rangle$$

$$\hat{\mathrm{H}} = \frac{\hat{\mathrm{p}}^2}{2} + V_{sr}(r) + \hat{\mathrm{H}}_{el}$$

Asymptotically, $H = p^2/2$, with solutions $\langle\mathbf{r}|\mathbf{k}\rangle = e^{i\mathbf{kr}}$

$$\langle\mathbf{r}|\psi(t_f)\rangle = \langle\mathbf{r}|\int d^3k|\mathbf{k}\rangle\langle\mathbf{k}|\psi(t_f)\rangle$$
$$= \int d^3k e^{i(\mathbf{kr}+\arg(\langle\mathbf{k}|\psi(t_f)\rangle))}|\langle\mathbf{k}|\psi(t_f)\rangle|$$

Departamento de Física
UBA exactas

Short-range potential

Analogously for a 1D scattering freely propagating wave packet $e^{i(\mathbf{k}.\mathbf{r}-Et)}$

$$\mathbf{kr} - Et \quad \longrightarrow \quad \mathbf{kr} - Et + \delta = \mathbf{kr} + \arg\langle \mathbf{k}|\psi(t_f)\rangle$$

$$t_{\mathrm{EWS}}(\mathbf{k}) = \frac{\partial}{\partial E}\left[\arg\langle \mathbf{k}|\psi(t_f)\rangle + Et_f\right]$$

we have to subtract the free propagation phase e^{-iEt_f}

From $$T_{if} = i\langle \phi_f | z | \phi_i \rangle \tilde{E}\left(E_f + I_p\right)$$

$$t_{\mathrm{EWS}}(\mathbf{k}) = \frac{\partial}{\partial E}\left[\arg\langle \mathbf{k}|\hat{z}|\psi_0\rangle\right]$$

Departamento de Física
UBA exactas

Short-range potential

W. Brenig and R. Haag. *Allgemeine Quantentheorie der Stoßprozesse* Fortschr. Phys. **7**, 183 (1959).
C. A. A. de Carvalho and H. M. Nussenzveig. *Time delay.* Physics Reports **364**, 83 (2002).

proved that the expectation value of the position of a wave packet

$$\langle r\rangle = \langle v\rangle t + c + O(t^{-1}), \quad t \to \infty$$

$$\langle v\rangle = \frac{1}{m}\int \left|\tilde{\psi}(\hat{\mathbf{k}})\right|^2 \left|\hat{\mathbf{k}}\right| d^3k = \frac{\langle k\rangle}{m}$$

$$c = -\hbar \int \left|\tilde{\psi}(\hat{\mathbf{k}})\right|^2 \frac{\partial}{\partial k}\arg\tilde{\psi}(\hat{\mathbf{k}}) d^3k$$

$$= -\hbar\left\langle \frac{\partial}{\partial k}\arg\tilde{\psi}(\hat{\mathbf{k}})\right\rangle = -\hbar\left\langle v\frac{\partial}{\partial E}\arg\tilde{\psi}(\hat{\mathbf{k}})\right\rangle$$

$$t_{\mathrm{BH}} = \hbar\left\langle \frac{\partial}{\partial E}\arg\tilde{\psi}(\hat{\mathbf{k}})\right\rangle = \langle t_{\mathrm{EWS}}\rangle$$

Departamento de Física
UBA exactas

Short-range potential

Average dwell time

Definition: The time a particle spends inside a sphere of radius r centered at the origin

$$\langle \mathcal{T}(r) \rangle = \int_{-\infty}^{\infty} P(r,t)\mathrm{d}t\,,$$

$$P(r,t) = 1 - 4\pi \int_{r}^{\infty} |\psi(r',t)|^2 r'^2 \mathrm{d}r'$$

The difference between this average dwell time and the corresponding dwell time $\langle \mathcal{T}_0(r) \rangle$ in the absence of the scatterer, evaluated at large enough r for the potential to be negligible, is the average **dwell time delay**. Carvallo and Nussenzveig demonstrated that the average dwell time is equal to $\langle t_{EWS} \rangle$.

Departamento de Física
UBA exactas

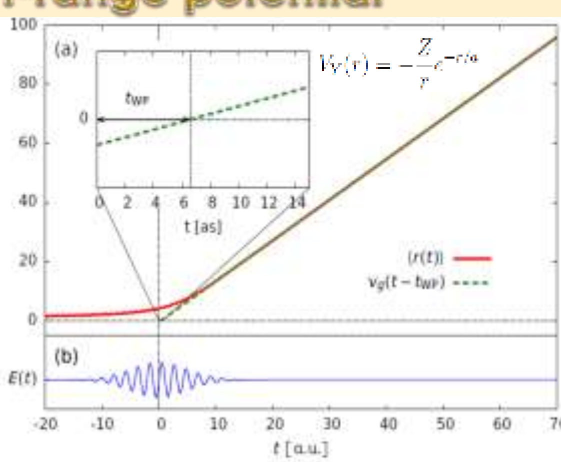
Short-range potential

Asymptotic behavior of the radial expectation value

Let's suppose an outgoing wavepacket formed by a coherent superposition of a band of continuum states around a central energy E_0.
The average of the radial position is:

$$\langle r(t) \rangle = v_g(t - t_{\mathrm{WP}}),$$

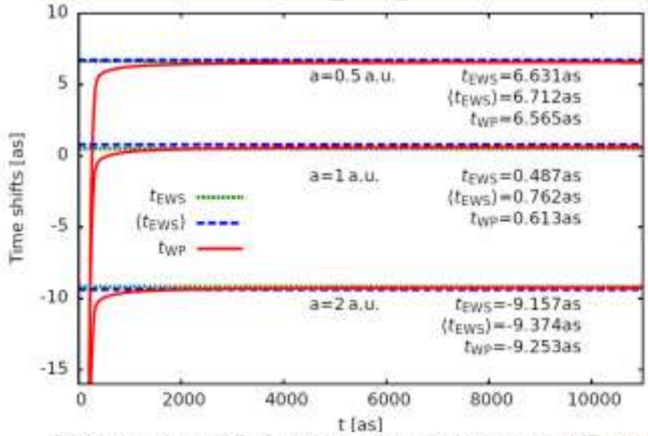
$$v_g = \left(\frac{\partial E}{\partial k}\right)_{E=E_0}$$



(a) Radial expectation value $\langle r(t) \rangle$ as a function of propagation time t after ionization from the ground state ($1s$) of a Yukawa potential (Eq. 2.37) with screening length $a = 0.5$ a.u. and $Z = 3.8166$, which results in a binding energy of -2 a.u.. The ionizing pulse has a FWHM duration of 200 as, $\hbar\omega = 80$ eV, and $I = 10^{13}$ W/cm^2. $\langle r(t) \rangle$ (red solid line) is for large times fitted to the free particle motion Eq. 2.35 (green dashed line). The intercept with the t axis (inset) gives t_{WP} in excellent agreement with $\langle t_{EWS} \rangle$ from the direct calculation for the scattering phase (Eq. 2.7). (b) The temporal variation of the XUV pulse.

Departamento de Física
.UBAexactas

Short-range potential



Comparison of time shifts for ionization from a Yukawa potential (Eq. 2.37) for different screening lengths ($a = 0.5$ a.u., $a = 1$ a.u. and $a = 2$ a.u.) with the same laser parameters as in Fig. 2.2. The wavepacket time shifts t_{WP} (red solid lines) are shown as a function of the position (time) when the fit to Eq. 2.35 is performed. The intervals for the fits are 50 as ($[t - 25\,\text{as}, t + 25\,\text{as}]$). In comparison we also show the EWS time delays t_{EWS} (green dotted lines) extracted from the scattering phase $\delta_{\ell=1}(k)$ and the averaged EWS delays $\langle t_{EWS}\rangle$ (blue dashed lines) which agree perfectly with the asymptotic t_{WP}.

Departamento de Física
.UBAexactas

Long-range potential: classical

So far, we have considered short range potentials.

Let's consider now a classical Coulomb (Kepler) trajectory.
The effective potential energy is given by

$$U_{\text{eff}}(r) = -\frac{Z}{r} + \frac{L^2}{2r^2}$$

For an energy $E < 0$ the particle has a finite motion in an elliptical orbit ($e <$ 1) and for $E \geq 0$ the motion is infinite, either on a parabola ($E = 0$) or a hyperbola ($E > 0$) with $e > 1$.

The hyperbolic orbit can be expressed via the dependence of r and t on the parameter ξ, the "mean anomaly" of the Kepler orbit,

$$r = a(e\cosh\xi - 1), \quad t = \sqrt{a^3/Z}(e\sinh\xi - \xi)$$

the "semi-axis" of the hyperbola $a = Z/2E$

$$e = \sqrt{1 + 2EL^2/Z^2}$$

Departamento de Física .UBAexactas

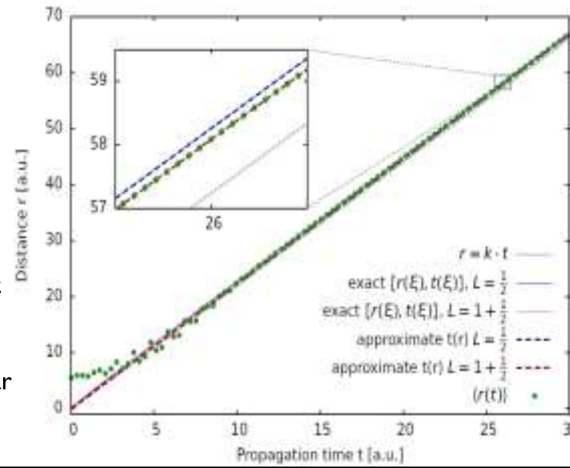
Long-range potential: classical

IAFE CONICET UBA

A closed solution for $r(t)$ does not exist. However, the inverse function $t(r)$ can be written down.

$$t(r) \underset{r\to\infty}{=} \frac{1}{k^3}\left[Z + k^2 r - Z\ln\left(\frac{2k^2 r}{\sqrt{Z^2+k^2L^2}}\right)\right] + \mathcal{O}\left(\frac{1}{r}\right)$$

Radial expectation value $\langle r(t)\rangle$ for ionization from the hydrogen ground state with a laser pulse of 200 as FWHM duration, $\hbar\omega$ = *80* eV and I = 10^{10}W/cm^2.
The wiggles in the beginning are due to the laser oscillations but as soon as the laser field is over, excellent agreement is found with the analytical solution of the exact classical equation of motion, and the approximation for $L = \ell + 1/2$ which is the (semi-)classical angular momentum for a quantum wave with $\ell = 1$.



Departamento de Física .UBAexactas

Long-range potential: classical

IAFE CONICET UBA

The time delay of the classical Kepler trajectory with respect to a free-particle trajectory can be obtained directly from our asymptotic expression for $t(r)$

$$t(r) \overset{!}{=} \frac{r}{k} + \Delta t \quad \longleftrightarrow \quad \Delta t(r) \underset{r\to\infty}{=} \frac{Z}{k^3}\left[1 - \ln\left(\frac{2k^2 r}{\sqrt{Z^2+k^2L^2}}\right)\right]$$

The time delay as a function of the propagation time is obtained when we express *r* as a function of *t*.
To first order we take the free particle limit $r(t) = kt$.

$$t^{\text{cl.}}_{\text{Coul}}(E, L, r = kt) \approx \frac{Z}{k^3}\left[1 - \ln\left(\frac{2k^2 t}{\sqrt{\eta^2+L^2}}\right)\right]$$

when we introduce the Coulomb-Sommerfeld parameter $\eta = Z/k$

$$t^{\text{cl.}}_{\text{Coul}}(E, L, r = kt) = \frac{Z}{k^3}\ln(\sqrt{\eta^2+L^2}) + \Delta t_{\text{Coul}}(E, r = kt)$$

$$\Delta t_{\text{Coul}}(E, r) = \frac{Z}{k^3}\left(1 - \ln(2kr)\right)$$

Departamento de Física .UBAexactas
IAFE CONICET - UBA

Long-range potential: quantum

For the case of a hydrogenic atom, the quantum Coulomb scattering wave is:

$$\begin{cases} \Phi_f(t) = \Phi_{\vec{k}}(\vec{r},t) = e^{-i\varepsilon t} \dfrac{e^{i\vec{k}.\vec{r}}}{(2\pi)^{3/2}} D_c(Z,\vec{k},t) \\ D_c(Z,\vec{k},t) = N_T(k)\,{}_1F_1\left(-i\tfrac{Z}{k},1,-ikr-i\vec{k}.\vec{r}\right) \\ N_T(k) = e^{\frac{\pi Z}{2k}}\Gamma(1+i\tfrac{Z}{k}); \quad Z \text{ is the ion charge} \end{cases}$$

The asymptotic behavior of the Coulomb wave is given by

$$F_\ell(Z,k) \to \sin\left(kr + \frac{Z}{k}\ln(2kr) - \frac{\ell\pi}{2} + \sigma_\ell(k)\right)$$

The asymptotic behavior of Coulomb dwell time or the EWS time delay applied to the (divergent) phase of the Coulomb wave is known to be infinite with the typical logarithmic divergence.

$$\sigma_\ell(k) = \arg\Gamma\left(1+\ell-i\frac{Z}{k}\right) = \mathrm{Im}\ln\Gamma\left(1+\ell-i\frac{Z}{k}\right)$$

σ_ℓ is the Coulomb analogue to the phase shift δ_ℓ in standard scattering theory for short-ranged potentials.

Departamento de Física .UBAexactas
IAFE CONICET - UBA

Long-range potential: quantum

$$\begin{aligned} t_{\mathrm{Coul}}(E,\ell,r) &= \frac{\partial}{\partial E}\left(\frac{Z}{k}\ln(2kr) + \sigma_\ell(E)\right) \\ &= \Delta t_{\mathrm{Coul}}(E,r) + t^{C}_{\mathrm{EWS}}(E,\ell) \end{aligned}$$

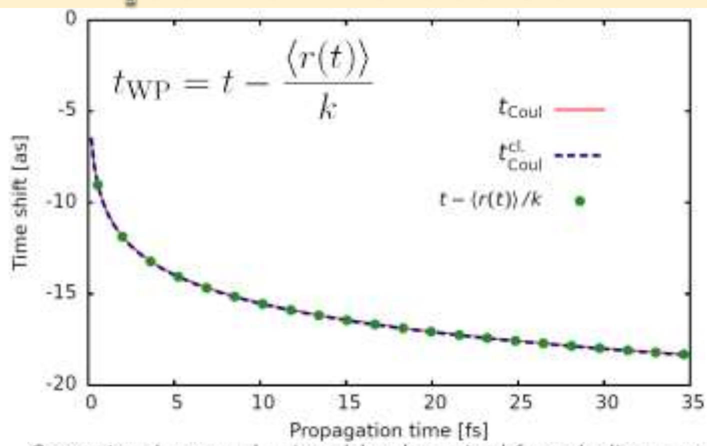
$$\Delta t_{\mathrm{Coul}}(E,r) = \frac{Z}{k^3}\left(1-\ln(2kr)\right)$$

where we use the asymptotic momentum $k = \sqrt{2E}$

$$t^{C}_{\mathrm{EWS}}(E,\ell) = \frac{\partial}{\partial E}\sigma_\ell(E)$$

We want to compare the different extraction methods for the EWS time delay using the scattering phase $t_{EWS} = \partial\delta_l(E)/\partial E$, or the radial wave packet $\langle r(t)\rangle = v_g(t - t_{\mathrm{WP}}), \quad t\to\infty$, which are equivalent for short range potentials

Long-range potential: quantum-classical



Comparison between the time delay determined from the linear extrapolation with the slope taken at increasing propagation times (Eq. 2.43, points) with the Coulomb time $t_{\mathrm{Coul}}(E, \ell = 1, r = kt)$ (Eq. 2.32, solid line) and $t^{\mathrm{cl.}}_{\mathrm{Coul}}(E, L = 1.5, r = kt)$ (Eq. 2.45, dashed line) for ionization from the H(1s) state with an XUV pulse with $\hbar\omega = 80\,\mathrm{eV}$.

Long-range potential: quantum-classical

Comparing quantum and classical time delays for long-range potentials:

$$t_{\mathrm{Coul}}(E,\ell,r) = \frac{\partial}{\partial E}\left(\frac{Z}{k}\ln(2kr) + \sigma_\ell(E)\right) = \Delta t_{\mathrm{Coul}}(E,r) + t^{C}_{\mathrm{EWS}}(E,\ell)$$

$$t^{\mathrm{cl.}}_{\mathrm{Coul}}(E,L,r=kt) = \frac{Z}{k^3}\ln(\sqrt{\eta^2+L^2}) + \Delta t_{\mathrm{Coul}}(E,r=kt)$$

suggest to identify the classical analogue of the intrinsic EWS delay

$$t^{\mathrm{C,\,cl.}}_{\mathrm{EWS}}(E,L) = \frac{Z}{k^3}\ln\left(\sqrt{\eta^2+L^2}\right)$$

Long-range potential: quantum-classical

From quantum mechanics we saw that

$$\sigma_\ell(k) = \arg\Gamma\left(1+\ell-i\frac{Z}{k}\right) = \mathrm{Im}\ln\Gamma\left(1+\ell-i\frac{Z}{k}\right)$$

Then $\quad t^{\mathrm{C}}_{\mathrm{EWS}}(E,\ell) = \dfrac{Z}{k^3}\mathrm{Re}\left[\Psi(1+\ell-i\eta)\right]$

where Ψ is the digamma function.

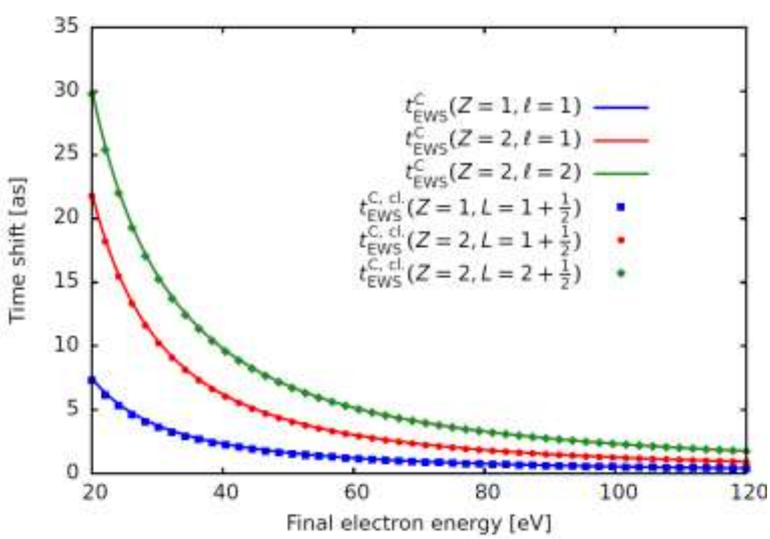
In the (semi) classical limit of large arguments

$$\Psi(1+\ell-i\eta) \sim \ln(1+\ell-i\eta)$$

$$t^{\mathrm{C}}_{\mathrm{EWS}}(E,\ell) \overset{|x|\gg 1}{=} \frac{Z}{k^3}\ln\left(\sqrt{(1+\ell)^2+\eta^2}\right)$$

$$\simeq \frac{Z}{k^3}\ln\left(\sqrt{L^2+\eta^2}\right) = t^{\mathrm{C,\,cl.}}_{\mathrm{EWS}}(E,L)$$

Long-range potential: quantum-classical



Coulomb EWS times for photoionization from H (Z =1) or He^{+} (Z =2) as function of the kinetic energy E

Departamento de Física .UBAexactas

Long-range potential: quantum-classical

IAFE CONICET UBA

The Coulomb singularity prohibits electrons at r=0, however, the expectation for an initial state with well-defined parity is still centered around zero (although the radial expectation value $\langle r(t)\rangle \neq 0$). This implies that the time delay is nearly independent of the principal quantum number as long as the initial states have the same angular momentum quantum number.

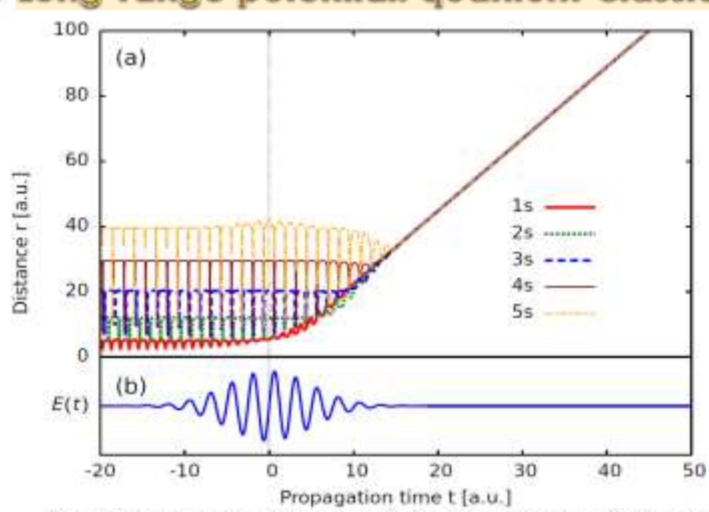
Since bound states can be chosen to be real, only the phase information of the final state enters in the definition of the EWS delay. As long as only one partial wave contributes, which is the case for initial s-states, the EWS time delay is independent of the principal quantum number n.

No matter where the electron initially was, it ends on the same trajectory as long as it has the same final kinetic energy (by choosing appropriate photon energies). The reason is that as long as the initial orbital has a well-defined parity, no matter how large the extension is, the mean position of departure is always at the origin. The radial expectation value $\langle r(t)\rangle$ of the continuum part with E > 0 depends on the main quantum number only as long as the ionization process is not finished (for the duration of the laser pulse).

Departamento de Física .UBAexactas

Long-range potential: quantum-classical

IAFE CONICET UBA



(a) Radial expectation value $\langle r(t)\rangle$ of the continuum parts of the wave function ($E > 0$) as a function of propagation time t after ionization from different initial states in hydrogen with $\ell = 0$ (spherically symmetric). The photon energy of the ionizing pulse was adjusted so that the final momentum is the same for all electrons ($k = 2.202$ a.u.). (b) The temporal variation of the XUV pulse.