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# Attosecond delays in photoionization:

## Time *and* quantum mechanics

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### Abstract

This article addresses topics regarding time measurements performed on quantum systems. The motivation is linked to the advent of “attophysics” which makes feasible to follow the motion of electrons in atoms and molecules, with time resolution at the attosecond ( $1 \text{ as} = 10^{-18} \text{ s}$ ) level, *i.e.* at the natural scale for electronic processes in these systems. In this context, attosecond “time-delays” have been recently measured in experiments on photoionization and the question arises if such advances could cast a new light on the still active discussion relative to the status of the time variable in quantum mechanics. One still debated issue is to decide whether one can define a quantum *time operator* with eigenvalues associated to measurable “time delays”, or time is a *parameter*, as it is implicit in Newtonian classical mechanics. One objective of the present paper is to investigate if the recent attophysics-based measurements could shed light on this *parameter-operator* conundrum. To this end, we present here the main features of the theory background, followed by an analysis of the experimental schemes that have been used to evidence attosecond “time-delays” in photoionization. Our conclusion is that these results reinforce the view that time is a *parameter* which cannot be defined without reference to classical mechanics.

## I. INTRODUCTION

The field of “attophysics” has emerged in the 2000s with the advent of a new generation of radiation sources delivering “attosecond” pulses of Extreme Ultra Violet (XUV) radiation via the High-order Harmonic Generation process.<sup>1-3</sup> The time resolution attainable with this new class of sources goes much beyond the realm of “femtochemistry” explored by Zewail *et al.*<sup>4</sup> The latter technique relies on using optical laser pulses with a few tens of femtosecond duration, thus making possible to follow the motion of *nuclei* inside molecules. The essential difference is that the new generation of “attosecond” XUV sources makes feasible to follow in real time the motion of *electrons* inside atoms or molecules. As explained below, experimentalists have been able to measure attosecond “time-delays”, that are associated to the photoionization process.<sup>5-8</sup>

The physical meaning of such measurements of “time” raises the question of the status of the time variable, *i.e.* whether it is a *parameter* or a quantum *operator*. This is a matter of discussion since the early days of the quantum theory in spite of the fact that, following a very brief footnote in 1933’s Pauli’s *General Principles of Quantum Mechanics*,<sup>9</sup> there is an (almost-)general consensus about the idea that there is no *time operator* with eigenvalues being associated to the measurement of “time-delays”. Were not the recent improvements in the time resolution of experiments, the subject would have rested in the quiet repository of academic topics, of interest only to a handful of scholars. However, since the 1980s, in parallel with the advent of Scanning Tunneling Microscopy and studies of the transport of electrons in semi-conductor devices, there has been a significant renewal of research activity regarding the related topic of “tunneling times”. The idea was to associate a characteristic timing to the quantum process of electron tunneling through potential barriers,<sup>10</sup> or to answer the bold question put forward by Steinberg: *How much time does a tunneling particle spend in the barrier region?*<sup>11</sup> This field of research has given rise to an abundant literature that is not exempt from controversies, see the review papers.<sup>12-16</sup> In parallel, there were many attempts to define *time operators*, with eigenvalues that could be associated to “tunneling time”, “time of arrival”, “dwell time”, “time of occurrence”, etc. See, for instance, a non-exhaustive list of papers in refs.<sup>17</sup> as well as the book edited by Muga.<sup>18</sup>

As regards to the performances of the new sources, recent advances in both generation schemes and attosecond metrology have evolved in two distinct directions: One has resulted

in the generation of single isolated XUV pulses with duration down to 80 as,<sup>19</sup> while the other resulted in the emission of attosecond pulse trains, the emitted bursts of XUV radiation having durations down to 63 as.<sup>20</sup> As explained below, when recombining such radiation fields with an infrared (IR) laser pulse, one can realize “two-color” pump-probe experiments with enough temporal resolution to monitor the motion of electrons on its natural time-scale (1 atomic unit of time  $\approx 24$  as).<sup>21</sup> A representative illustration of these advances is provided by the real-time imaging of the electron-hole dynamics in the dinitrogen  $N_2^+$  molecular ion in the presence of a strong IR laser pulse, with sub-femtosecond time resolution.<sup>22</sup> Another line of research has been opened by looking at the photoionization of atoms in the time domain. One major outcome has been to evidence intrinsic “time-delays” associated to the process.<sup>5-8,23</sup> We stress that this concept differs fundamentally from the well established notions of quantum dynamics related to the lifetime of excited states. Regarding the input of attophysics in this latter field, see refs.<sup>24-26</sup>

To address the theoretical aspects of the question, we have collected here several results that are relevant to expose the formal background required to address the *parameter-operator* conundrum. It turns out that most of the textbooks in advanced quantum mechanics report Pauli’s statement in favor of the *parameter* nature of time, without giving the hint of a proof.<sup>9</sup> This makes difficult for students (and even to confirmed researchers) to convince themselves of the validity of the assertion that there is no *time operator*, see for instance Sakurai’s *Modern Quantum Mechanics*.<sup>27</sup> In fact, the theoretical literature about this topic is scattered in books on the mathematical foundations of Quantum Mechanics that are not easily accessible, even on internet.<sup>28,29</sup> Another issue is that the topic is often treated in a rather abstract way, in mathematically oriented papers, not easy to decipher by non-specialists. We mention that the subject has been also discussed in a series of pedagogically-oriented papers, where the emphasis was focused on historical aspects, thus shedding light on the reasons why there is still a debate about the status of the time variable in quantum mechanics.<sup>30</sup> One purpose of the present paper is to expose the theoretical background, in a “user friendly” way. In the same spirit, we shall describe also the physical basis of the experimental techniques implemented to measure attosecond “time-delays” in photoionization. We stress that, given the rather “pedagogical” orientation of our paper, this latter part is not intended as a comprehensive account of the literature recently published on what is considered by now as a “hot-topic” in the field.

The organization of the paper is as follows: In the next section, we shall present the uncertainty relations as they were exposed by Heisenberg. The so-called “Stone-von Neumann theorem”, which provides the mathematical basis put forward to show that there is no quantum *time operator*, will be introduced in Section III. In Section IV we shall outline different approaches used to rationalize the transition from mathematical *inequalities* for the variances of hermitian operators and of Fourier Transform duals to Heisenberg’s *uncertainties*. The relation between the *phases* of quantum transition probabilities amplitudes and “time-delays”, will be introduced in Section V. In Section VI, we shall present the physical background of the “two-color” IR-XUV schemes that have been used to measure such attosecond “time-delays” in the photoionization processes. The Section VII will contain the conclusions and perspectives, while two Appendices will contain mathematical material supporting the reasoning.

## II. HEISENBERG’S UNCERTAINTY RELATIONS

In 1927, Heisenberg has published a highly-cited paper on the so-called “uncertainty relations” governing the precision of measurements performed simultaneously on couples of conjugated variables of classical mechanics.<sup>31</sup> The couples encompassed the momentum-position  $(p, q)$ , action-angle  $(J, \omega)$  and time-energy  $(t, E)$  pairs, all of them being Fourier Transform duals of each other. Heisenberg derived the uncertainty relations from the commutators of the operators associated to these variables, when transposed in the quantum mechanical formalism. The discussion was focused on two of them, related to the position-momentum and time-energy pairs:<sup>31</sup>

$$\Delta q \cdot \Delta p \sim h, \tag{1}$$

$$\Delta E \cdot \Delta t \sim h. \tag{2}$$

Here,  $\Delta q$  and  $\Delta p$  are the uncertainties on the position and momentum of the particle considered, defined for a 1-dimensional system and  $h \approx 6.63 \times 10^{-34}$  J s is the Planck constant. Similar definitions are implied for the time and energy uncertainties. The corresponding relation for the action  $J$  and angle  $\omega$  pair, was not discussed by Heisenberg, as it could be derived from the one for the position-momentum couple. At the time of publication of the paper, the question of the existence of a quantum *time operator* was not questioned.

Beyond the evident formal similarity between Eqs. (1) and (2), there is however a profound difference between them, based on the nature of the variables considered. Position and momentum are dynamical variables of classical mechanics, often referred to as canonical variables that are partial derivatives of the Lagrangian.<sup>32</sup> While energy is a function of positions and momenta, time is not a canonical variable and is considered as a parameter in Newtonian mechanics.<sup>32</sup>

The position-momentum  $(Q, P)$  operators commutation relation, written in matrix form for 1-D systems, had been established by Heisenberg as follows:

$$[Q, P] = QP - PQ = i\hbar\mathbf{1}, \quad (3)$$

where  $\mathbf{1}$  is the unit matrix. As we shall outline below, Eq. (1) can be recovered directly from this commutation relation. The question at stake is whether or not one could write a similar equation for a pair of time-energy  $(T, H)$  operators, where  $H$  is the hamiltonian operator and  $T$  would be a *time operator*. Then it would take the following form, as written by Heisenberg in his paper (see pages 177-178 in ref.<sup>31</sup>):

$$[T, H] = TH - HT = i\hbar\mathbf{1}. \quad (4)$$

If this latter equality were correct, then Eq. (2) would follow with the same reasoning as the one used to establish Eq. (1). However, as pointed out by Pauli,<sup>9</sup> Eq. (4) cannot hold, because the energy spectrum of the hamiltonian operator  $H$  for a real physical system is bounded from below and is possibly discontinuous with discrete eigenvalues. The mathematical argument used to address this point is based on the so-called Stone-von Neumann theorem which is presented in the next section.

### III. THE STONE-VON NEUMANN THEOREM

The self-adjoint operators  $P$  and  $Q$  act in an Hilbert space  $\mathcal{H}$  of complex-valued, square-integrable  $L^2$  functions. It turns out that Eq. (3) is verified only if  $P$  and  $Q$  are unbounded, *i.e.* if their spectral radius is infinite and if  $\mathcal{H}$  is infinite-dimensional. This can be verified with the help of the following general considerations, exposed here for two hermitian operators  $A$  and  $B$ :

i) If  $A$  and  $B$  are bounded, *i.e.* with finite spectral radius, then  $AB$  and  $BA$  are bounded. If one assumes that  $AB - BA = \alpha\mathbf{1}$ , with  $\alpha \neq 0$ , then the spectra of  $AB$  and  $BA$  are

translated by  $\alpha$ . However, this is inconsistent with  $AB = A(BA)A^{-1}$  which indicates that  $AB$  and  $BA$  have the same spectrum, since they are linked by a similarity transform.<sup>33</sup> Thus, if  $P$  and  $Q$  were bounded, Eq. (3) could be verified only in the limit  $\hbar = 0$ .

ii) If  $A$  and  $B$  act in a finite dimensional Hilbert space, their commutator cannot verify a relation like  $[A, B] = \alpha \mathbf{1}$  with  $\alpha \neq 0$ . This is because the trace of their commutator is identically zero while the trace of the identity matrix is equal to the dimension of  $\mathcal{H}$ . Again, if  $P$  and  $Q$  were defined on a finite Hilbert space, Eq. (3) could be verified only in the limit  $\hbar = 0$ .

These results are satisfying for physicists, who are not bothered with infinite Hilbert spaces and who assume safely that a particle position and momentum components are intrinsically unbounded. However, Weyl put forward a more formal approach,<sup>28</sup> which contributed to a deeper insight in the properties of this class of operators and has opened most interesting perspectives in group theory. In fact, his argument provided the background to establish the so-called Stone-von Neumann theorem,<sup>34,35</sup> which had a profound influence in Mathematical Physics, as testified by the abundant literature devoted to its consequences.<sup>36</sup> An account of the line of reasoning followed by Weyl can be summarized as follows:

Weyl's insight was that the self-adjoint operators of quantum mechanics can be exponentiated to one-parameter unitary groups – this has been formally demonstrated a few years later by Stone—.<sup>34</sup> He introduced the following unitary operators, here written for  $P$  and  $Q$ :

$$U_\tau = e^{i\tau P} \text{ and } V_\tau = e^{i\tau Q}; \text{ with } \tau \in \mathbb{R}. \quad (5)$$

The usefulness of these exponentiated forms can be outlined as follows:

First, the action of these operators on  $P$  and  $Q$  leads to the following kind of double-sided expansion:

$$\begin{aligned} U_\tau Q U_{-\tau} &= e^{i\tau P} Q e^{-i\tau P} = \left[ 1 + i\tau P + \frac{(i\tau)^2}{2!} P^2 + \frac{(i\tau)^3}{3!} P^3 + \dots \right] \\ &\times Q \left[ 1 - i\tau P + \frac{(-i\tau)^2}{2!} P^2 + \frac{(-i\tau)^3}{3!} P^3 + \dots \right] \end{aligned} \quad (6)$$

When rearranging the terms in powers of  $\tau$ , this product can be conveniently rewritten in terms of nested commutators, under the form of the so-called ‘‘Baker-Campbell-Hausdorff’’

formula:<sup>37</sup>

$$\begin{aligned}
U_\tau Q U_{-\tau} &= Q + i\tau(PQ - QP) + \frac{(i\tau)^2}{2!}(PPQ - 2PQP + QPP) + \dots \\
&= Q + i\tau[P, Q] + \frac{(i\tau)^2}{2!}[P, [P, Q]] + \frac{(i\tau)^3}{3!}[P, [P, [P, Q]]] + \dots
\end{aligned} \tag{7}$$

If the commutator of the involved operators obeys Eq. (3) so that  $[P, Q] = -i\hbar$ , all the terms in  $\tau^n$  with  $n > 1$  are identically zero and one ends with:

$$U_\tau Q U_{-\tau} = Q + \hbar\tau. \tag{8}$$

As  $Q$  and  $U_\tau Q U_{-\tau}$  are linked by a similarity transform, they have the same spectrum. Thus, Eq. (8) shows that the spectrum of  $Q$  is invariant under a finite translation  $\hbar\tau$  along the real axis or, in other words, it is located on the real line and is unbounded. Clearly, the same analysis holds for  $P$ . More formal developments relative to the Stone-von Neumann theorem are summarized in Appendix A.

#### IV. HEISENBERG'S INEQUALITIES

The above theorem, established for the conjugated operators  $(P, Q)$ , cannot be transposed to the pair  $(T, H)$ . Regarding the time variable  $t$ , it can be assumed to flow uniformly on the real line  $] -\infty, +\infty [$  and an associated *time operator*  $T$  would be unbounded. However, as pointed out by Pauli, the hamiltonian operator  $H$  with real eigenvalues associated to energies is always bounded from below in non-relativistic systems (or it has a discontinuous spectrum in the gap between  $[-mc^2, +mc^2]$  in a relativistic context).<sup>9</sup> This implies that its spectrum is not invariant under a finite translation along the real axis as in Eq. (8) and, accordingly, that Eq. (4) cannot be satisfied.

It remains to justify Heisenberg's time-energy uncertainty relation in Eq. (2). As we shall show below in Subsection A, it can be established by exploiting the properties of the Fourier transform, without any reference to quantum operators. It turns out that the same analysis holds also for the  $(P, Q)$  pair, once the operator relation  $P = -i\hbar\partial/\partial Q$  is admitted.<sup>28</sup> This implies that the uncertainty relation Eq. (1) can be established indifferently in two ways either using the Fourier Transform formalism exposed below in Subsection A, or using the commutation relation Eq. (3), as shown in Subsection B. Interestingly, the so-called Cauchy-Schwarz inequality plays a central role in both derivations: Heisenberg's



*uncertainties* relations derive directly from this central theorem of analysis which establishes the *inequalities* obeyed by the products of the *variances* attached to each variable.

### A. Time-energy Heisenberg's uncertainty relation

The definition of the Fourier-transform for the time-frequency duals  $(t, \omega)$  is extended to the time-energy  $(t, E)$  pair via Planck's prescription  $E = \hbar\omega$ . This is the only place where quantum mechanics come into play in the line of reasoning. If  $f(t)$  is a square-integrable  $L^2$  function of the time variable, one can define its  $L^2$  Fourier transform  $g(E)$ , such as the two functions are linked via the relations (in physicist's notations):

$$\begin{aligned} f(t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbf{R}} dE e^{+iEt/\hbar} g(E), \\ g(E) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbf{R}} dt e^{-iEt/\hbar} f(t). \end{aligned} \quad (9)$$

They obey the Parseval's theorem:

$$\int_{\mathbf{R}} dt |f(t)|^2 = \int_{\mathbf{R}} dE |g(E)|^2, \quad (10)$$

and the average (or expectation) values  $t_0$  and  $E_0$ , related to each distribution are:

$$t_0 = \int_{\mathbf{R}} dt t |f(t)|^2; \quad E_0 = \int_{\mathbf{R}} dE E |g(E)|^2, \quad (11)$$

The uncertainties  $\Delta t$  ( $\Delta E$ ) defined by Heisenberg are linked to the variances  $\sigma_t$  ( $\sigma_E$ ) via:

$$\begin{aligned} (\Delta t)^2 &= \sigma_t^2 = \int_{\mathbf{R}} dt (t - t_0)^2 |f(t)|^2 = \int_{\mathbf{R}} dt (t^2 - t_0^2) |f(t)|^2, \\ (\Delta E)^2 &= \sigma_E^2 = \int_{\mathbf{R}} dE (E - E_0)^2 |g(E)|^2 = \int_{\mathbf{R}} dE (E^2 - E_0^2) |g(E)|^2, \end{aligned} \quad (12)$$

and, since the average values  $t_0$  and  $E_0$  can be removed from the integrands via variable changes such as  $t \rightarrow t + t_0$ , the squared uncertainties can be identified with the second moments of  $|f(t)|^2$  and  $|g(E)|^2$ :

$$(\Delta t)^2 = \int_{\mathbf{R}} dt t^2 |f(t)|^2, \quad (\Delta E)^2 = \int_{\mathbf{R}} dE E^2 |g(E)|^2. \quad (13)$$

From these definitions, one can show that the product of the squared uncertainties verifies the inequality:

$$\Delta E^2 \cdot \Delta t^2 \geq \left( \frac{\hbar^2}{4} \right) \int_{\mathbf{R}} dt |f(t)|^2 \cdot \int_{\mathbf{R}} dE |g(E)|^2, \quad (14)$$

which reduces to Heisenberg's inequality when  $|f(t)|^2$  (hence  $|g(E)|^2$ ) is normed to unity:

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}. \quad (15)$$

The details of the derivation, based on the Cauchy-Schwarz inequality, are summarized in the Appendix B.

When performing the change  $E \rightarrow \hbar\omega$ , Eq. (15), reduces to the well known inequality for the time-bandwidth product associated to the Fourier components of a signal  $f(t)$ , with finite support. The lower limit for the product  $\Delta\omega \cdot \Delta t = 1/2$  is attained only for Gaussian time-frequency distributions.

We mention also that a less formal derivation of Eq. (15) has been proposed by Mandelstam and Tamm in 1945.<sup>38</sup> It is based on the idea that  $\Delta t$  is a time interval that can be associated to the change  $\Delta E$  in the expectation value of the operator  $H$ . A clear exposition of the reasoning can be found in the book by Griffiths.<sup>39</sup>

We turn now to the direct connection which can be established between the commutator relation for the  $(P, Q)$  operators, Eq. (3), and Heisenberg uncertainty relation in Eq. (1). Here again, it can be derived from the Cauchy-Schwartz *inequality* verified by the product of the “expectation values” of these operators.

## B. Position-momentum Heisenberg's inequality

We consider first the general case of two hermitian operators  $A$  and  $B$ . Specialization to the  $(P, Q)$  couple will be presented at the end. The first step implies the definition of the variances of  $A$  and  $B$ , for a quantum system in a state  $|\Psi\rangle$ . The expectation values of these operators will be denoted  $\langle A \rangle = \langle \Psi | A | \Psi \rangle$  with the same definition for  $B$ . Then, it is convenient to define the auxiliary kets:

$$|f\rangle = (A - \langle A \rangle) |\Psi\rangle \text{ and } |g\rangle = (B - \langle B \rangle) |\Psi\rangle, \quad (16)$$

so that the variances attached to the observables  $A$  and  $B$  are expressed as:

$$\sigma_A^2 = \langle f | f \rangle, \quad \sigma_B^2 = \langle g | g \rangle, \quad (17)$$

which are directly linked to the uncertainties  $\Delta A = \sqrt{\sigma_A^2}$  and  $\Delta B = \sqrt{\sigma_B^2}$ , introduced by Heisenberg. The minimum value taken by the product of the variances is governed by the

Cauchy-Schwarz inequality which states that:

$$\sigma_A^2 \cdot \sigma_B^2 = \langle f|f \rangle \cdot \langle g|g \rangle \geq |\langle f|g \rangle|^2. \quad (18)$$

As the amplitudes  $\langle f|g \rangle$  are complex quantities with  $\langle g|f \rangle = \langle f|g \rangle^*$ , it remains to note that:

$$|\langle f|g \rangle|^2 = \left( \frac{\langle f|g \rangle + \langle g|f \rangle}{2} \right)^2 + \left( \frac{\langle f|g \rangle - \langle g|f \rangle}{2i} \right)^2, \quad (19)$$

with:

$$\langle f|g \rangle = \langle AB \rangle - \langle A \rangle \langle B \rangle, \text{ and } \langle g|f \rangle = \langle BA \rangle - \langle A \rangle \langle B \rangle, \quad (20)$$

so that:

$$\langle f|g \rangle + \langle g|f \rangle = \langle AB + BA \rangle - 2\langle A \rangle \langle B \rangle, \text{ and } \langle f|g \rangle - \langle g|f \rangle = \langle [A, B] \rangle. \quad (21)$$

When inserted in Eq. (19) and replacing in Eq. (18), one obtains the so-called ‘‘Robertson-Schrödinger’’ uncertainty inequality:<sup>40</sup>

$$\sigma_A^2 \cdot \sigma_B^2 \geq \left( \frac{1}{2} \langle AB + BA \rangle - \langle A \rangle \langle B \rangle \right)^2 + \left( \frac{1}{2i} \langle [A, B] \rangle \right)^2. \quad (22)$$

Being the sum of two squares, and specializing to the position-momentum couple in 1-D systems, with  $[Q, P] = i\hbar$ , see Eq. (3), one has clearly:

$$\sqrt{\sigma_P^2 \cdot \sigma_Q^2} = \Delta P \cdot \Delta Q \geq \frac{\hbar}{2}, \quad (23)$$

this relation establishing the minimum value attainable for the product of uncertainties for conjugated variables. The minimum is reached for the ground state of the harmonic oscillator system *i.e.* when the position probability density and the momentum distribution are Gaussian.

## V. FROM PHASE-SHIFTS TO ‘‘TIME-DELAYS’’

In view of the above, it appears clearly that there is a fundamental difference between:

i) the time-energy uncertainties product, directly linked to the classical time-bandwidth relation, as derived from a Fourier-transform analysis, where quantum physics comes into play when using Planck’s prescription  $E = \hbar\omega$ ;

ii) the position-momentum uncertainties relation that can be derived from *both* the Fourier-Transform analysis *and* from the quantum properties of matter, as described by self-adjoint operators.

This leads to the idea that time is in fact a classical parameter, not amenable to a quantum description. This point is advocated by Briggs and Rost,<sup>41,42</sup> who have convincingly shown that time appears in the quantum mechanical description of microscopic systems, as the result of the coupling with the environment that is intrinsically macroscopic and classical. In this picture, the environment encompasses the time measurement device itself.<sup>43</sup>

Regarding the quantum mechanical description of an energy-conservative system, *time* enter the expression of the wave function through a *phase*-dependent term. This implies that *time-delays* are directly linked to *phase-shifts*. As shown next, in the the context of scattering theory, the formal relation existing between *time-delays* and the *phase-shifts* induced by the scattering event, has been established by Wigner.<sup>44</sup>

### A. Wigner-like “time-delays”

Wigner has introduced the concept of “time-delay” in the context of the scattering of a particle by a short-rang potential.<sup>44</sup> In the course of the process, the scattered particle experiences a delay, *as compared to the classical free motion*, this latter point being of importance in what follows. In a quantum context, the projectile, so long as it is in free motion, can be described by a wave-packet with constant group velocity. In the initial state, *i.e.* far from the scattering centre, the radial component of an incoming wave packet (here specialized to the case of an *s*-wave component) is of the general form:

$$\Psi_{\text{in}}(r, t) \propto \int_0^{+\infty} dE |A(E)| e^{-i(Et/\hbar + kr + \delta)}. \quad (24)$$

where  $|A(E)|$  is the amplitude of the energy distribution,  $k = mv/\hbar$  is the wave number and  $\delta$  is a phase fixed by the time when the maximum of the wave packet amplitude would be located at the origin  $r = 0$ . In a similar way, the asymptotic form of the outgoing wave packet is:

$$\Psi_{\text{out}}(r, t) \propto \int_0^{+\infty} dE |A(E)| e^{-i(Et/\hbar - kr + \delta - \eta(E))}, \quad (25)$$

where the new term  $\eta(E)$  is the energy-dependent *phase-shift* induced by the scattering potential.

The connection between this quantum description and classical “time-delays” can be found via a stationary phase argument: The dominant contribution to the above integrals comes from the energy range where the argument of the oscillatory exponential is stationary.

This range is located in the vicinity of the zero of its energy derivative. With  $\partial k/\partial E = m/(\hbar^2 k)$ , one establishes that the classical time-position relation for the incoming wave-packet,  $t = -r/v$ , is recovered via:

$$\frac{\partial}{\partial E}(Et/\hbar + kr + \delta) = \frac{t}{\hbar} + \frac{m}{\hbar^2 k}r = 0, \iff t = -\frac{m r}{\hbar k} = -r/v. \quad (26)$$

For the outgoing wave, the same reasoning leads to to the modified relation:

$$\frac{t}{\hbar} - \frac{m}{\hbar^2 k}r - \frac{\delta\eta(E)}{\partial E} = 0, \iff t = \frac{r}{v} + \tau_W, \quad (27)$$

where:

$$\tau_W = \hbar \frac{\partial\eta(E)}{\partial E}, \quad (28)$$

is the so-called Eisenbud-Wigner “time delay”.<sup>14,44</sup> The reference to classical mechanics is implicit in this derivation.<sup>45</sup>

We note that, in the context of collision theory, the measurement of such “time-delays” belongs to the realm of so-called *Gedanken* (*i.e.* thought-)experiments, which would imply distinguishing between the arrival times of particles having experienced or not the forces induced by a spatially localized potential.<sup>46</sup> As noted by several authors, such a scenario is not realizable in actual measurements and, for years, the concept of “time-delays” remained as a rather abstract topic, with however the exception of resonant scattering, *i.e.* when delays could be related to the lifetimes of decaying states in atoms, molecules or nuclei.<sup>14,46</sup>

## B. Quantum Tunneling

As mentioned in the introduction, the question of the link between phase-shifts and “time-delays” has been explored in more detail in the 1980s, in relation with the quantum phenomenon of tunneling. Again, energy derivatives of phase-shifts were invoked, the rationale being that, *as compared to free motion in the absence of the barrier*, the transmitted wave acquires a phase that depends on both the energy of the projectile and on the shape of the barrier. This can be schematized as shown in Fig. (1), which represents an incoming particle with kinetic energy lower than the top of the barrier, with its reflected and transmitted wave components. For a given barrier shape, the latter are represented as complex amplitudes  $R(E)$  and  $T(E)$  with general form:

$$R(E) = |R(E)|e^{i\phi(E)} ; T(E) = |T(E)|e^{i\eta(E)} \text{ with : } |R(E)|^2 + |T(E)|^2 = 1. \quad (29)$$

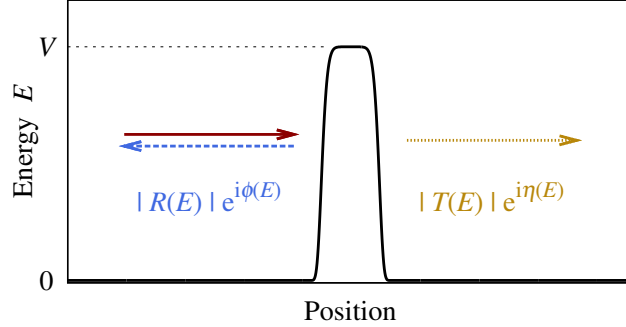


FIG. 1. Schematic representation of the tunneling of a particle with kinetic energy  $E$ , incoming from the left of a barrier with height  $V$ , with  $E < V$ . The transmitted and reflected wave components are complex quantities with modulus denoted  $|T(E)|$  and  $|R(E)|$ , with respective phases  $\eta(E)$  and  $\phi(E)$ , see Eq. (29).

It was tempting to define a Wigner-like “tunneling time” from the energy derivative of the phase of the transmission probability amplitude  $\tau_W = \hbar \partial\eta(E)/\partial E$ . However, it soon appeared that this approach was oversimplified and could not encompass the great variety of physical situations. For a barrier with height  $V$ , the following definitions have been proposed, in addition to the original Wigner definition for  $\tau_W$ :

$$\begin{aligned}
 \tau_L &= -\hbar \frac{\partial\eta}{\partial V} \\
 \tau_{BL} &= -\hbar \frac{\partial \ln |T|}{\partial V} \\
 \tau_{PM} &= \Im \left[ -\hbar \frac{\partial T}{T \partial E} \right].
 \end{aligned} \tag{30}$$

Here  $\tau_L$  stands for the dominant contribution to the Larmor time as defined for a region of space where a magnetic field makes the spin of the projectile to precess.<sup>13,14</sup> We mention that a more general definition had been proposed earlier by Baz’ *et al.*<sup>47</sup> It establishes the relation existing between a “time delay” and the deflection angle  $\theta$  of a charged projectile traveling through a finite region of space where a (weak-)magnetic field is present. Here the magnetic field plays the role of a “clock” device, so that a meaningful “time-delay” associated to the scattering event can be measured, via the determination of the deflection  $\theta$ .<sup>47</sup> On the other hand,  $\tau_{BL}$  stands for the Büttiker-Landauer time defined for a time-modulated barrier.<sup>10,13</sup> The last definition of  $\tau_{PM}$  stands for the Pollack-Miller imaginary time.<sup>48</sup> The latter originates from the fact that both a Feynman path-integral approach and the concept of time-averaged correlation functions lead to complex tunneling times,

with no clearcut physical interpretation of the real and imaginary components.<sup>14</sup> A common framework for these different definitions is presented in Yamada’s paper.<sup>49</sup>

One major reason for the lack of consensus is that the high-energy components of the incoming wave-packet are propagating faster, thus reaching the barrier first and having higher transmission probability. This entails that the spatio-temporal distribution of the transmitted wave-packet is changed with respect to the incoming one and that the stationary-phase derivation loses its relevance. Other criteria have been proposed to remedy to this difficulty, such as choosing the motion of the average value of the position operator, but all of them suffer from some inconsistencies.

Besides, the time-energy Heisenberg inequality implies that a temporal profile is associated to any complex dynamical phenomenon taking place in a quantum system. A single “time” can be associated to the process if the profile is relatively unstructured and localized in both time and energy, *i.e.* when the wave-packet motion remains dominantly classical. This is explicit in Wigner’s derivation of the relation existing between the energy derivative of a scattering phase-shift and a group delay. The correspondence is meaningful only via a reference to classical mechanics and it is *a priori* excluded for the purely quantum process of tunneling. This leads to the conclusion that a single “time” is not enough to fully characterize the spatio-temporal distribution of the transmitted wave-packet in tunneling. We note that this applies also to the reflected wave packet as well as to the notion of “dwell time” associated to the time spent by a scattered particle in a potential well.<sup>14</sup>

We mention that a very active field of related research has opened, in relation with the process of atomic (or molecular) strong field ionization taking place in the presence of an intense IR or mid-IR laser pulse. In such conditions, the dominant mechanism for ionization is tunneling through the barrier created by the superposition of the atomic binding potential and of the oscillating electric field associated to the IR laser. In the presence of the latter, with cycle duration in the femtosecond range, the oscillations of the barrier can be considered as being slow, as compared to the attosecond scale that characterizes the electronic motion in atoms.<sup>50</sup> Then, it is valid to develop a “quasi-static” approximation which exploits the results of calculations performed within the framework of the semi-classical WKB – time-independent – approximation for tunneling.<sup>51</sup> A natural consequence is that the question of “tunneling times” has arisen also in this context, the most recent experimental results reported being the ones obtained with the help of the so-called “attoclock”

scheme;<sup>52-54</sup> See also the reports of recent experiments,<sup>55,56</sup> as well as theory papers and references therein.<sup>57-59</sup>

We turn now to the study of the photoionization process, as seen in the time domain, in an attophysics context.

## VI. TIME-DELAYS IN ATTOSECOND XUV PHOTOIONIZATION

The main idea is that photoionization of atoms or molecules by a pulse of XUV radiation can be considered as a *half-collision* since the photoelectron, initially in a bound state, is ejected in a scattering state. Then, the energy-derivative of the scattering phase-shift of the ejected electron wave function can be related, as above, to a characteristic time associated to photoionization. We stress that the transfer of energy that leads to the ejection of the electron results from the annihilation of one photon, a process which can be considered as instantaneous.<sup>60</sup>

However, as above, the definition of a “time delay” requires to choose a “reference” system. Delays in “Gedanken” experiments or in numerical simulations can refer in principle to any arbitrarily chosen reference. By contrast, in real experiments, delays can be measured when two processes associated to distinct quantum transition amplitudes are launched simultaneously. Such conditions are met when ionizing atoms from two distinct sub-shells with the same radiation pulse. The general principle underlying these measurements is schematized in Fig. 2 for atoms, when irradiated by a attosecond pulse of XUV light. The frequency is chosen high enough so that electrons pertaining either to the valence or to the inner-valence sub-shells can be photoionized. For example, in the representative case of Ne submitted to an attosecond XUV pulse with central energy  $\hbar\omega_{XUV} \approx 100$  eV, a proportion of atoms are ionized from the inner-valence state  $2s$  while another part of them are ionized from the  $2p$  valence states. The ratio between the ionization yields is given by quantum mechanical rules determining ionization probabilities.<sup>6</sup> The photoelectron spectrum displays two distinct peaks, with widths governed by the combined bandwidths of the attosecond XUV pulse and of the electron spectrometer response.<sup>61</sup>

When generated in the sole presence of an XUV pulse, the experimentally recorded photoelectron spectra do not permit to measure characteristic photoionization delays in the absence of a time-discrimination device. A convenient way to realize such a time-discrimination



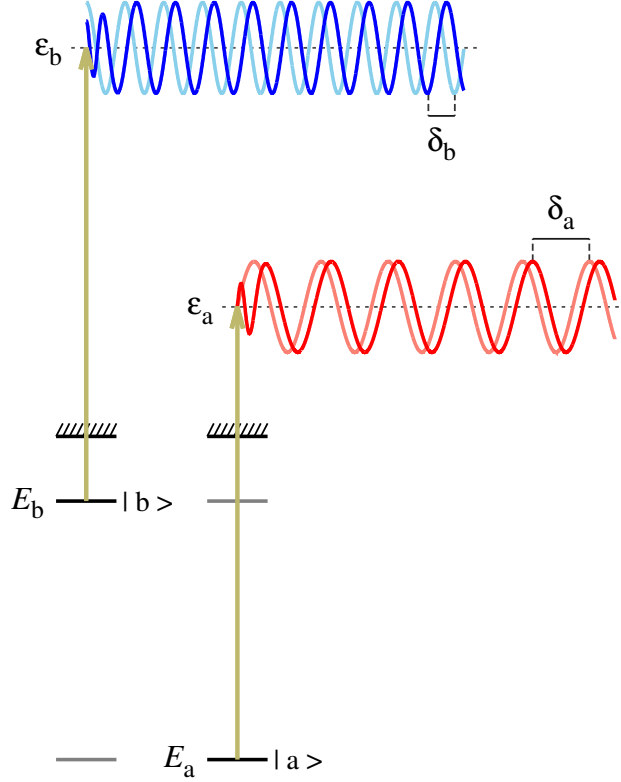


FIG. 2. Schematic representation of single-photon photoionization of atoms by XUV radiation with frequency high enough to extract an electron from either states  $|a\rangle$  or  $|b\rangle$ . In the asymptotic region, the phase-shifts  $\delta_a$  and  $\delta_b$  of each electron wave-packets differ, as compared to a free wave (light-color) with the same kinetic energy. When “clocked” by an auxiliary IR laser, one can evidence a “time-delay” between the wave-packets originating from either state  $|a\rangle$  or  $|b\rangle$ , (see text).

is to “clock” the process in the presence of an auxiliary IR field.<sup>62</sup> In such conditions, the emitted photoelectrons can exchange energy and momentum with the IR “dressing” field, through stimulated transitions (either absorption or stimulated emission).<sup>63–67</sup> Then, while the XUV pulse “pumps” electrons in the continuum, the coherent IR laser field plays the role of a “dressing” field used as a “probe”. As we shall show below, the difference in the timing of ionization of each atomic state can be determined from the analysis of the photoelectron spectra recorded when scanning the delay  $\tau$  between the XUV “pump” and the IR “probe”.<sup>55,56,63,64,73,74</sup>

Depending on the type of attosecond XUV pulse used, two distinct techniques have been implemented: i) “Streaking” relies on an isolated XUV pulse, combined with a few-cycle IR pulse;<sup>65–67</sup> ii) the so-called RABBIT technique uses XUV harmonics of the fundamental IR,

when they are produced as an Attosecond Pulse Train (APT).<sup>63,64,73,74</sup> The first technique makes feasible a direct measurement of delays,<sup>5,6,8</sup> while the latter gives access to the intrinsic *phases* of quantum transition amplitudes.<sup>63,64,73,74</sup>

We mention that a most interesting outcome of these investigations has been to evidence the role of the IR probe field: The “dressing” of the photoelectrons by the IR field changes the *phases* of the wave-packets created in the course of the primary photoionization process. In short, the outcome of the experiment is modified by the measurement device itself, such a situation illustrating one of the peculiarities of Quantum Mechanics. We turn now to a brief presentation of the theoretical background governing this class of experiments.

### A. Isolated Attosecond XUV Pulses: Streaking

“Streaking” of photoelectron spectra consists in recording the kinetic energy variations of angle- and time-resolved signals, when combining an attosecond XUV pulse with a rather intense few-cycle IR pulse, with controlled delay  $\tau$ .<sup>65-67</sup> The physical background can be schematized as follows: When ejected in the presence of the “dressing” IR field with vector potential  $\vec{A}(\omega_{IR}, t)$ , the photoelectrons (with charge  $-e$  and velocity  $\vec{v}$ ), acquire a conserved “canonical” momentum:

$$\vec{p} = m\vec{v} - e\vec{A}(\omega_{IR}, t), \quad (31)$$

As shown in Figs. (3), the corresponding “streaked” spectrogram, *i.e.* the time-resolved photoelectron energy spectrum, follows in time the oscillations of the vector potential:

$$\begin{aligned} E_{\text{Kin}}(\omega_{IR}, t) &= \frac{1}{2}mv^2 = \frac{1}{2m}[\vec{p} + e\vec{A}(\omega_{IR}, t)]^2 \\ &\approx \frac{1}{2m}[p_0 + eA_0(\omega_{IR}, t)]^2, \end{aligned} \quad (32)$$

where the second line corresponds to an experimental configuration with detection aperture aligned with the polarization direction  $\parallel \vec{A}(\omega_{IR}, t)$ .<sup>6,67</sup> Here,

$$\frac{p_0^2}{2m} = \hbar\omega_{XUV} - I_p, \quad (33)$$

is the initial kinetic energy of the photoelectron born from a bound state with ionization energy  $I_p$ , upon absorption of one XUV photon  $\omega_{XUV}$ , in the absence of the IR field. In Fig. 3(a), we present the time-dependence of the vector potentials of a few-cycle IR field, and of an isolated attosecond XUV pulse with controlled delay  $\tau$ . A typical shape of a

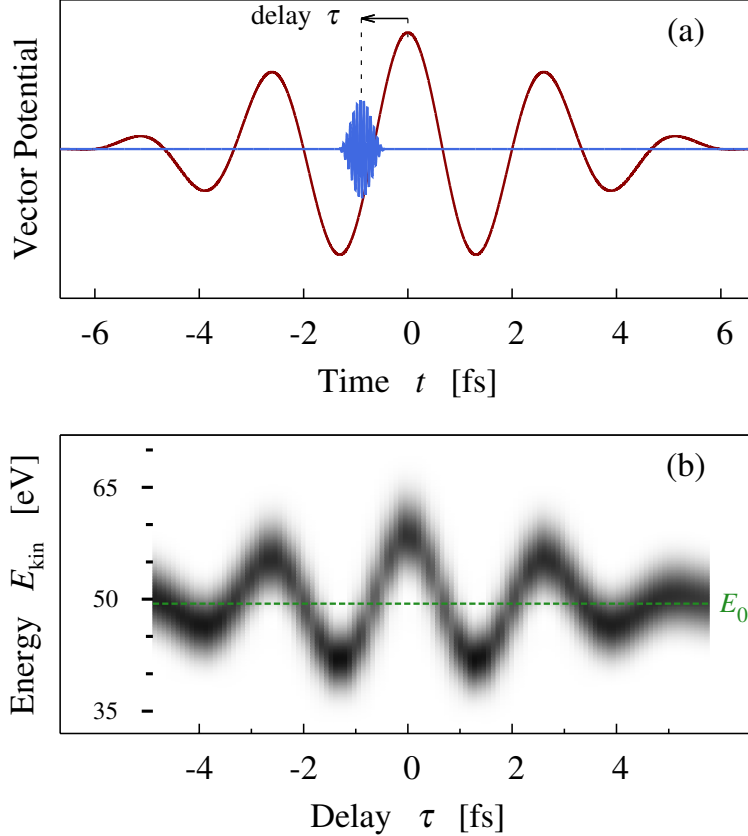


FIG. 3. (a) Schematic representation of the time dependence of the vector potentials of a few-cycle IR laser pulse ( $T \approx 2.6$  fs) and of an isolated “attosecond” XUV pulse. There is a delay  $\tau$  between the maxima of the envelopes of the vector potentials. (b) Numerical simulation of a streaking photoelectron spectrogram. The photoelectron kinetic energy variations are reported, as a function of  $\tau$ . This simulation has been realized by solving the Time-Dependent Schrödinger Equation for a 1-dimensional model potential with ionization energy  $I_P \approx 13.6$  eV, in the presence of the IR pulse and of an XUV pulse with central energy  $\hbar\omega_{XUV} \approx 63.6$  eV and a duration  $\approx 400$  as. Here, the width of the energy distribution of the photoelectrons is governed by the time-energy relation Eq. (15).

streaking photoelectron spectrogram, as a function of  $\tau$ , is displayed in Fig. 3(b). The photoelectron trace has an energy width that is governed by the attosecond XUV pulse duration, through Heisenberg uncertainty relation Eq. (15). In actual experiments, one has to include also the response of the electron spectrometer.<sup>6,61,67</sup> We mention that sophisticated iterative techniques, such as the one dubbed FROG-CRAB, have been developed to achieve a temporal resolution at the attosecond level, *i.e.* significantly more accurate than the limit

imposed by the duration of the pump XUV pulse.<sup>68</sup>

One of the major findings from this class of experiments was to observe that the streaking traces for the electrons originating from either the  $2s$  or  $2p$  states in Neon were off by an amount  $\Delta t_{2s,2p} \approx 21$  as which, although small, is significant given the time resolution of the experiment.<sup>6</sup> Together with other streaking experiments, this was the signature of the existence of different “time-delays” in the photoionization process, depending on which initial states the photoelectron were originating.<sup>5,8</sup>

As mentioned in the introduction, the theoretical interpretation of these results has given rise to several difficult questions. *A priori*, the only difference regarding the timing of ionization, lays in the different phase-shifts experienced by photoelectrons originating from distinct atomic states. In the cases considered here, the dipole approximation holds, with selection rule  $\Delta\ell = \ell \pm 1$ . As an example, the photoelectrons originating from an  $s$  states have a  $p$ -wave character, while those originating from a  $p$ -state are in a superposition of  $s$ - and  $d$ -waves. These photoelectron waves experience different effective radial potentials and their associated phase-shifts  $\eta_\ell(E)$ , as well as their energy derivatives  $\partial\eta_\ell(E)/\partial(E)$ , are different. This leads to the idea to derive corresponding  $\ell$ -dependent Wigner-like “time-delays”:

$$\tau_{\ell,W} = \hbar \partial\eta_\ell(E)/\partial E. \quad (34)$$

It turns out that, in the representative case of the  $2s$  and  $2p$  states in neon, there is no satisfactory agreement between the experimental value  $\approx 21 \pm 5$  as and the results derived from this Wigner-like model.<sup>6</sup> Indeed, the results of the simulations cluster around  $\tau \approx 10$  as, *i.e.* they are off from the experiment by  $\approx 10$  as. One open question is related to the intra-shell electron correlations that are expected to play an important role, when comparing ionization from different sub-shells in rare gases.<sup>69–72</sup> Also, the discrepancy might be ascribed to the difficulty to estimate the delay resulting from the “dressing” induced by the rather intense IR probe. The role of this latter effect has been addressed in detail in the context of the RABBIT spectroscopies which are implemented at lower IR intensities, see next.

## B. Attosecond Pulse Trains: RABBIT photoelectron spectroscopy

The principle of the technique has been described first by Vénier *et al.*<sup>73</sup> while the RABBIT acronym stands for the title of Muller’s paper: “Reconstruction of Attosecond

harmonic Beating By Interference of Two-photon transitions".<sup>74</sup> A pedagogical description of the technique has been already published.<sup>75</sup>

Here, the IR field used to generate the XUV harmonics is multicycle, with durations of the IR pulse lying in the range of a few tens of fs, for 800 nm lasers with cycle duration of  $\approx 2.6$  fs. The XUV spectrum emitted by centrosymmetric systems (*e.g.* rare gas atoms) is constituted of a comb of equidistant harmonic frequencies labelled  $\dots\omega_{2N-1}, \omega_{2N+1}, \dots$ , that are odd multiples of the pump IR laser with  $\omega_{2N\pm 1} = (2N \pm 1)\omega_{IR}$ . Accordingly, when ionizing a test atom with such an harmonic pulse, the photoelectron energy spectrum is constituted of equally spaced lines, separated by  $2\hbar\omega_{IR}$  and located at energies  $\varepsilon_{2N\pm 1} \approx \hbar\omega_{2N\pm 1} - I_p$ . In the following, they will be labelled  $H_{2N\pm 1}$ . On the other hand, when seen in the time domain, see Fig. (4a), the harmonic radiation is emitted under the form of an APT, *i.e.* a train of equally spaced attosecond XUV pulses.<sup>63</sup>

As it is the case for "streaking", RABBIT is based on the fact that, in the presence of two different "colors", *e.g.* XUV + IR, the system can exchange energy (photons) from the two fields. The IR field intensity is kept low enough so that multiphoton ionization is negligible while, regarding the interaction with the harmonic XUV radiation, one-photon absorption is by far dominant.<sup>76</sup> By contrast, the probability for the two-photon processes associated to the joint absorption of one XUV photon and the exchange of one IR photon is not negligible. In fact, for suitably chosen IR intensities and delays, the cross sections of the two-color, two-photon IR-XUV processes become comparable to the one for the absorption of a single XUV photon.<sup>73</sup> This property is exploited in RABBIT spectroscopies where, in a suitably chosen regime, the corresponding transition amplitudes can be conveniently computed from second-order perturbation theory.<sup>63,73,74</sup>

As shown in Fig. (4b), in the simultaneous presence of the two fields, one observes sidebands, labelled  $S_{2N}$ , that are equidistant from the consecutive harmonic lines  $H_{2N\pm 1}$ .<sup>7,63,73</sup> Their magnitudes vary periodically with the delay  $\tau$  between the two fields. Such periodic variations result from the interferences between the amplitudes associated to the different quantum paths leading to a given sideband. Their  $\tau$ -dependence is given by the simple law:<sup>7,63,73-75</sup>

$$S_{2N} \approx \alpha + \beta \cos[2\omega_{IR}(\tau - \tau_{2N} - \tau_\theta)], \quad (35)$$

In this expression, derived from a lowest-order perturbation theory approach,  $\alpha$  and  $\beta$  are real parameters that characterize the atomic target and the fields amplitudes. They differ

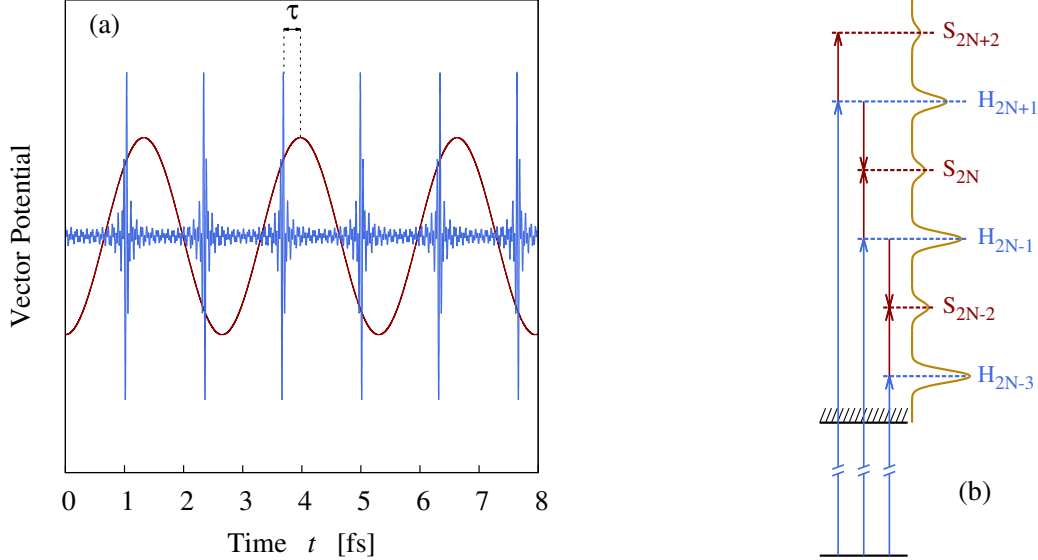


FIG. 4. (a) Schematic time-domain representation of the “two-color” configuration for RABBIT-like time-resolved measurements. Shown are the time dependence of the vector potentials of a many-cycle IR laser pulse ( $T \approx 2.6$  fs) with moderate intensity and of train of “attosecond” XUV pulse built from a set of harmonics of the IR. By controlling the delay  $\tau$  between the IR cycle and the peaks of the XUV pulse train, one “clocks” the time when ionization takes place. (b) Schematic frequency-domain representation of a photoelectron spectrum as obtained in a “multi-color” configuration, typical of a RABBIT experiment. Photoelectron peaks associated to the absorption of odd harmonics are denoted  $H_{2N\pm 1}$  and sidebands resulting from the exchange of one additional IR photon are denoted  $S_{2N}$ . The magnitudes of the sidebands change periodically, as shown in Eq. (35), when varying the delay  $\tau$  between the IR cycle and the peaks of the XUV pulse train.<sup>75</sup>

also, depending on the initial state ionized in the process.  $\tau_{2N}$  can be defined as a “group delay” associated to the difference in the emission times of consecutive harmonics.<sup>64</sup> On the other hand,  $\tau_\theta$  is an intrinsic “atomic time” associated to the two-photon ionization process. It is this latter quantity that is of interest here since it contains the channel-dependent ionization “time-delay” itself. Indeed, one can identify two dominant contributions to  $\tau_\theta$  which, to a very good approximation, can be expressed as:<sup>7,77</sup>

$$\tau_\theta \approx \tau_{W,\ell} - \tau_{cc}, \quad (36)$$

i) the first term  $\tau_{W,\ell}$  is the atomic, state-dependent Wigner-like delay as defined in Eq.

(34);

ii) the second term, denoted  $\tau_{cc}$ , is associated to the stimulated continuum-continuum transitions that result of the “dressing” of the photoelectron by the probe IR field.<sup>7,77</sup>

The validation of this important feature of RABBIT spectroscopy has been established, in parallel with a numerical comparison with the phase measurements performed for the  $3s$  and  $3p$  states of Argon.<sup>7,71,77</sup> From the measured values of these phases for a sequence of sidebands  $\cdots S_{2N-2}, S_{2N}, S_{2N+2}, \cdots$ , one can infer their energy dependence as well as their derivatives and deduce the corresponding ionization delays, according to Eqs. (34) and (36). Regarding theory, a detailed derivation of a closed form expression of  $\tau_{cc}$ , which accounts for the contribution of the “dressing” phenomenon, can be found in ref.<sup>78</sup> Performing the same measurements for two distinct atomic states, one can recover the difference between the characteristic ionization times of each atomic state. In the above mentioned case of the  $3s$  and  $3p$  states of Argon, the “time-delays” found  $\Delta t_{3s,3p} = \tau_{3s} - \tau_{3p}$  vary from  $-100$  to  $+10$  as, depending on the photoelectron energy.<sup>7,77</sup>

Before to leave the section dealing with the RABBIT technique, we mention that a very promising concept has been recently implemented in experiments. It exploits the fact that this type of measurements is interferometric by essence, since it involves interferences between different quantum paths leading to the same final state. Such measurements can be viewed also as double-slit experiments in the time domain. Recent developments deal with the case where one of the two “arms” of the “RABBIT interferometer” is transiting via a resonance, while the other explores a smooth continuum. Here, the two “arms” are the two distinct quantum paths leading to the same sideband. In such a case, the measured phases can be converted into delays which contain also the “dwell time” inherent to the time actually spent by the photoelectron in the resonant state. These topics have been addressed in recent papers dealing with excited bound states in He,<sup>79</sup> as well as with He autoionizing states,<sup>25,26</sup>. The case of molecular autoionizing state in  $N_2$  has been also investigated.<sup>80,81</sup>

## VII. CONCLUSIONS

After the introduction in Section I and a brief exposition of Heisenberg’s inequalities in Section II, the sections III-IV of the present paper have dealt with a simplified presentation of the mathematical background serving as a basis to show that there is no hermitian *time*

*operator* in Quantum Mechanics. In short, this orthodox mathematical analysis leads to the conclusion that it is not possible to measure an absolute value of time, as an eigenvalue of an hermitian operator associated to a quantum system. However, this conclusion is still debated in the Mathematical Physics literature, most of the arguments being related to the quantum process of tunneling. An interesting feature of this analysis is to evidence the fact that the time-energy uncertainty relation in Eq. (2) – and the inequality in Eq. (15) – are derived only on the ground of Fourier analysis. By contrast, the momentum-position uncertainty relation in Eq. (1) – and the inequality in Eq. (23) – can be derived *either* by using the commutation relation of the associated hermitian operators, Eq. (3), *or* by using a Fourier analysis applied to the  $(P, Q)$  pair. This represents the main difference between the two types of inequalities.

In Section V, we have addressed the question of defining unambiguously characteristic “times” associated to collisions or to quantum tunneling. The theoretical framework is given by Wigner’s definition of a “time-delay” as the energy derivative of a phase-shift. From the experimental side, the difficulty is to determine the energy dependence of the “scattering phase” of the outgoing waves, as compared to free motion. The first investigations were focused on tunneling, but the advent of attophysics has shifted the discussion on the photoionization process. Given the “attosecond” duration of a pump XUV pulse, it is in principle possible to measure differences between the timing of ionization from distinct atomic or molecular states. However, defining absolute “time-delays” remain elusive since one needs always to compare to free motion.

The input of two-color attosecond spectroscopies, either “streaking” or RABBIT, has been described in Section VI. The advances achieved have been to measure the emission times of photoelectron wave packets originating from different initial atomic states. These “time delays” are the quantities that have been determined in the experiments performed on isolated atoms such as Ne,<sup>6</sup> and Ar.<sup>7</sup> However, the relation between phases and delays, as proposed by Wigner, is based on a stationary phase argument, the explicit relation between the energy derivative of the phase and time being established with reference to classical motion. This supports the idea that time is a parameter, as in classical dynamics.

More generally, there is no doubt that the advent of “attophysics” opens new perspectives in the study of time-resolved phenomena in atomic and molecular physics. This goes one step beyond Zewail’s “femtochemistry”,<sup>4</sup> as it permits in principle to follow in real time the



changes of the electron probability density within a reactive system. The concepts and the techniques described here will be of interest to follow the future developments of this new field of research.

### Appendix A: Formal developments relative to the Stone-von Neumann theorem

For the sake of completeness, we mention that the relation Eq. (8):  $U_\tau Q U_{-\tau} = Q + \hbar\tau$ , is valid also for any power  $Q^n$  and, consequently, for any function  $f(Q)$  expressible as a power series, so that:

$$U_\tau f(Q) U_{-\tau} = f(Q + \hbar\tau). \quad (\text{A1})$$

Clearly, this applies to  $V_\sigma = e^{i\sigma Q}$  with  $\sigma \in \mathbb{R}$  and one has:

$$U_\tau V_\sigma U_{-\tau} = e^{i\sigma(Q+\hbar\tau)} = e^{i\hbar\sigma\tau} V_\sigma, \quad (\text{A2})$$

the same applying to  $U_\tau$ :

$$V_\sigma U_\tau V_{-\sigma} = e^{i\hbar\sigma\tau} U_\tau. \quad (\text{A3})$$

This kind of relations constitutes the so-called *multiplicative form* of Heisenberg's commutation relation Eq. (3).

The Stone-von Neumann theorem establishes a formal proof of the above results, valid for infinite-dimensional Hilbert space  $\mathcal{H}$  and demonstrates the irreducibility of the system of unitary operators  $U_\tau$  and  $V_\sigma$ , which form Abelian (commutative) groups. In a simplified form, the theorem states that there exists always a norm-preserving transformation  $S$  of  $\mathcal{H}$  such as:<sup>82</sup>

$$SPS^{-1}f(q) = -i\hbar\frac{\partial}{\partial q}f(q), \text{ and } :SQS^{-1}f(q) = qf(q), \quad (\text{A4})$$

These equations are written in a 1-dimensional space, but the generalization to a finite-dimension euclidean space is straightforward, the analysis starting from the well known commutation relations:

$$[P_i, P_j] = 0, [Q_i, Q_j] = 0, [Q_i, P_j] = i\hbar\delta_{i,j}, \quad (\text{A5})$$

the irreducible representations of these operators being unitarily equivalent to each other. Starting from the Lie algebra generated by this set of relations, mathematicians have built a most active research area in Group Theory and related topics.<sup>36</sup> We mention also that the Eq. (A4), which provides the expressions of the operators  $P$  and  $Q$  in the  $q$ -representation, implies that  $p$  and  $q$  are Fourier-transform duals. This property is being used in Section IV.

## Appendix B: Cauchy-Schwarz inequality verified by the product of the variances of Fourier Transform duals

To establish the inequality verified by the product of the squared variances, one can start from Weyl's remark:<sup>28</sup>

$$|f(t)|^2 = \frac{d}{dt} [t f(t)] f^*(t) - \left( t \frac{df(t)}{dt} f^*(t) \right). \quad (\text{B1})$$

Replacing in the integral over  $|f(t)|^2$ , and integrating the first term by parts, one gets:

$$\begin{aligned} \int_{\mathbf{R}} dt |f(t)|^2 &= [t |f(t)|^2]_{-\infty}^{+\infty} - \int_{\mathbf{R}} dt t f(t) \left( \frac{df^*(t)}{dt} \right) - \int_{\mathbf{R}} dt t \left( \frac{df(t)}{dt} \right) f^*(t) \\ &= -2 \Re \left[ \int_{\mathbf{R}} dt t f(t) \left( \frac{df^*(t)}{dt} \right) \right] \leq 2 \left| \int_{\mathbf{R}} dt t f(t) \left( \frac{df^*(t)}{dt} \right) \right|. \end{aligned} \quad (\text{B2})$$

This result derives from the fact that, in the first line, the first term is zero, as a consequence of the  $L^2$  property of  $f(t)$ , while the remaining two terms are complex conjugate of each other, the absolute value of the real part being smaller or equal to the modulus of the integral. Then the Cauchy-Schwarz inequality can be invoked again, to establish that:

$$\left| \int_{\mathbf{R}} dt t f(t) \left( \frac{df^*(t)}{dt} \right) \right|^2 \leq \int_{\mathbf{R}} dt t^2 |f(t)|^2 \cdot \int_{\mathbf{R}} dt \left| \frac{df^*(t)}{dt} \right|^2. \quad (\text{B3})$$

In the left-hand side, the first factor is identified to  $(\Delta t)^2$  while the second one can be further transformed by using the derivation rule for Fourier transforms:

$$\frac{df^*(t)}{dt} \leftrightarrow - \left( \frac{i}{\hbar} \right) E g^*(E), \quad (\text{B4})$$

which, when using Parseval's identity, leads to:

$$\int_{\mathbf{R}} dt \left| \frac{df^*(t)}{dt} \right|^2 = \left( \frac{1}{\hbar^2} \right) \int_{\mathbf{R}} dE E^2 |g(E)|^2 = \frac{\Delta E^2}{\hbar^2}. \quad (\text{B5})$$

Thus, combining the results given in Eqs. (B2), (B3) and (B5), one obtains the inequality providing the minimum value for the product of variances (squares of uncertainties).

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