Nondipole Effects in Time Delay of Photoelectrons from Atoms, Negative Ions, and Endohedrals

M. Ya. Amusia\textsuperscript{a, b, *} and L. V. Chernysheva\textsuperscript{b}

\textsuperscript{a} Racah Institute of Physics, the Hebrew University, Jerusalem, 91904 Israel
\textsuperscript{b} Ioffe Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia

*e-mail: amusia@vms.huji.ac.il

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We investigate the nondipole effects in time delay of photoelectrons emitted by many-electron atoms, negative ions, and respective endohedrals. We present the necessary general formulas in the frame of the random phase approximation with exchange (RPAE) applied to atoms, negative ions, and properly adjusted to endohedrals. We concentrate on low photon energy region, where nondipole effects are very small in the cross sections, but become observable in angular distributions. We not only derive the formulas for nondipole effects in time delay but also perform corresponding numeric calculations. We demonstrate how the nondipole corrections can be isolated in experiment. Concrete calculations are performed for noble gas atoms Ar and Xe, isoelectronic to them negative ions Cl– and I– and endohedrals Ar(Cl–)@C\textsubscript{60} and Xe(I–)@C\textsubscript{60}. We found that the forward–backward photoelectron time delay differences give direct information on nondipole effects. They proved to be quite measurable and prominently affected by the presence of the fullerenes shell.

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1. The aim of this work is to find the contribution of nondipole corrections to the time delay of electrons that due to low-energy photon absorption leave atoms A, negative ions A– and endohedrals A@C\textsubscript{N} or A–@C\textsubscript{N} that present A or A– stuffed inside the fullerenes shell C\textsubscript{N} constructed of N carbon atoms C. Ionization by a photon with low energy \( \omega \) is a process determined predominantly by dipole transition matrix elements. The nondipole contribution to the absolute photoionization cross section is much smaller than the dipole term, being different by additional factor \((\omega r_a/c)^2 \ll 1\), where \( r_a \) is the atomic radius and \( c \) is the speed of light. The smallness of the nondipole cross section is enhanced by a numeric small factor.

However, the role of nondipole term is much bigger in the angular distributions of photoelectrons that differ from the respective dipole terms by a factor \((\omega r_a/c)^2 \ll 1\), which is much bigger than \((\omega r_a/c)^2 \ll (\omega r_a/c) \ll 1\) (see, e.g., [1]). The investigation of nondipole transitions is stimulated by the interest to quadrupole transitions and quadrupole phase shifts of the outgoing electron wavefunctions. Apart from angular distribution, there exists another source of information on these quantities, namely, the time delay of electrons released from an atom, ion, or endohedral under the action of the incoming photon.

The theoretic approach to temporal description of processes in quantum objects has been developed long ago in a number of publications [2–5]. The construction of lasers with attosecond pulses permitted to measure the duration of atomic photoionization processes. As a result, pure theoretical development was relatively recently complemented by intensive experimental activity leading to temporal description of photoionization processes (see [6–10] and references therein). The corresponding times are called EWS time delays, thus referring to the family names of authors L. Eisenbud [2], E. Wigner [4], and F. Smith [5], respectively.

As is demonstrated in [2–5], the time delays are well-defined quantities that characterize a physical process only if the outgoing particles interact via short-range force. In course of photoionization, the outgoing electron interacts with the residual ion with infinite range Coulomb interaction, making it impossible to define accurately enough scattering phases at any outgoing electron energy \( \varepsilon > 0 \). This forced to calculate time delays in photoionization starting from not too low \( \varepsilon \) [7, 11]. This is why in this work we consider along with neutral targets, A and A@C\textsubscript{N}, also negative ions that have the same electronic configuration as A, A–, and A–@C\textsubscript{N}, for which the residual ion is neutral. In concrete calculations, our choice are pairs Ar, Cl– and Xe, I–. As C\textsubscript{N} we take an almost spherically sym-
metric well-studied and reasonably good modeled C$_{60}$ [12].

The time delay of a photoelectron emitted at a given angle at low $\omega$ is determined by the interference of electron waves emitted in a given direction due to absorption of a photon that include dipole and quadrupole terms. We will take into account the electron correlation in A(A$^-$) and the action of C$_{60}$ upon A(A$^-$) as well as the action of C$_{60}$ upon the outgoing electron. This will be done in the frame of the random phase approximation with exchange (RPAE), just as in [13, 14], substituting the C$_{60}$ by a static potential and adding approximation with exchange (RPAE), just as in [13, 14], substituting the C$_{60}$ by a static potential and adding to it the account of the polarization of C$_{60}$ electron shell by the incoming photon beam.

2. The temporal description of photoionization concentrates on determining the time delay of an electron that leaves the target in a given direction after absorbing a photon. As demonstrated in [2–5], the time delay $\tau$ of a physical process as a function of its energy $\varepsilon$ is related to the phase of the amplitude $f$ of the process under consideration as

$$\tau(\varepsilon) = \frac{d}{d\varepsilon} \arg f(\varepsilon) = \frac{d}{d\varepsilon} \arctan \frac{\Im f(\varepsilon)}{\Re f(\varepsilon)} = \Im \frac{1}{f(\varepsilon)} \frac{df(\varepsilon)}{d\varepsilon}. \quad (1)$$

The photon–electron interaction operator with lowest order nondipole corrections is presented in the so-called “length” form by the expression [14]

$$\hat{M}_k = \hat{M}_k^0 + \xi_k \equiv \omega((\varepsilon r) + i(\varepsilon r)(\varepsilon r)). \quad (2)$$

Here, $\varepsilon$ is the photon polarization vector and $k$ is the photon momentum, $|k| = \omega/c$. For linearly polarized light, one has

$$\hat{M}_k = r \left[ P_z(\cos \theta) + i \frac{\omega}{c} r P_y(\cos \theta) \right]. \quad (3)$$

In the one-electron Hartree–Fock (HF) approximation, the photoionization amplitude $f^{HF}(k)$ is determined by the matrix element $\langle \psi^{HF}_i | \hat{M}_k^0 | \phi \rangle$, which describes the transition of an atomic electron from initial state $i$ with the wavefunction $\phi_i(r) = R_{nl}(r)Y_{lml}(\hat{r})$ to the continuous state of an electron with momentum $k$ after absorbing a linearly polarized photon, in which case the polarization vector is directed along the $z$ axis and $z = \sqrt{4\pi/3}\int Y_{l0}(\hat{r})^2 d\hat{r}[7, 15]$. Thus, $f(\omega) = f^{HF}_{nl}(\varepsilon, \theta, k)$ in the HF approximation is determined by the following formula that is similar to (2) in [11], but with addition of another reduced radial matrix element:

$$f^{HF}_{nl}(\varepsilon, \theta, k) = \left(\frac{2\pi}{k}\right)^{3/2} \frac{4\pi^2}{3k^{1/2}}$$

Here, $\varepsilon = k^2/2, l, l'$ denotes the angular momentum of the outgoing photoelectron and $n, l, l'$ are the principal quantum number and angular momentum of the ionized electron. The continuous spectrum radial wavefunction are normalized in the energy scale according to the relation $\langle \varepsilon | \varepsilon' l \rangle = \delta(\varepsilon - \varepsilon')$ and their asymptotic is given by the formula [16]

$$R_{\varepsilon}(r)_{r \to \infty} = \sqrt{\frac{2}{\pi\hbar r}} \sin \left[ kr - \frac{l\pi}{2} + \delta_{l} \right]. \quad (5)$$

Here, $\delta_{l} \equiv \delta_{l}(\varepsilon)$ is the continuous spectrum electron scattering phase in the HF approximation [13–15].

Usually, in attosecond time delay measurements the forward direction amplitude is of interest [7]. In this case, one has to substitute $Y_{lm}(k = 0)$ by $\sqrt{(2l + 1)/4\pi\hbar_0}$. In this work, in order to better separate the nondipole contribution from the dipole one, we will need also the backward direction amplitudes that can be obtained from (4) substituting there $Y_{lm}(k = \pi)$ by $(-1)^l \sqrt{(2l + 1)/4\pi\hbar_0}$. In order to investigate also angular dependence of the time delay at any $\theta$ in the simplest way, let us study only the case $m_l = 0$, so that $Y_{lm}(\theta, \phi, k)$ has to be substituted by $\sqrt{(2l + 1)/4\pi P_l(\cos \theta)}$. According to Eq. (1), common numeric factors in the total amplitude are inessential, since they do not affect the time delay. Therefore, we can define the photoionization amplitude neglecting common factors. Therefore, for the aims of time delay determination, we have in the HF approximation, omitting factor $2^{1/2}\pi/k^{1/2}$, instead of (4) the relation

$$I^{HF}_{nl}(\varepsilon, \theta, k) = I^{HF}_{nl}(\varepsilon, \theta, k) + I^{HF}_{nl}(\varepsilon, \theta, k)$$

$$= \sum_{l, l', \varphi} e^{i(\delta_{l} - \delta_{l'} + \pi/2)} P_l(\cos \theta) \sqrt{2l + 1} \left[ I^{HF}_{nl}(\varepsilon, \theta, k) \times \langle \varepsilon | \varepsilon | n, l \rangle + \sum_{l', \varphi} e^{i(\delta_{l'}) - \delta_{l'} + \pi/2/2} P_{l'}(\cos \theta) \sqrt{2l' + 1} \left[ I^{HF}_{nl}(\varepsilon, \theta, k) \right. \right.$$}

$$\left. \times \langle \varepsilon | \varepsilon | n, l \rangle \right]. \quad (6)$$

Here, $\varepsilon = \omega - \varepsilon_i = k^2/2$, while $\delta_{l}(\varepsilon), \delta_{l'}(\varepsilon)$ are photoelectron phases in the HF approximation. It is seen that at a given angle the dipole (first term) and quadrupole (the second term) amplitudes in (6) interfere leading to different time delays at different angles $\theta$. 
To obtain the photoionization amplitudes that take into account the interelectron correlation in RPAE, one has to substitute into (6) the matrix elements $\langle \ell' || D(\omega) || n_l, l \rangle$ and $\langle \ell' || Q(\omega) || n_l, l \rangle$ that are determined by the equations [13, 14]

\[
\langle \ell' || D(\omega) || n_l, l \rangle = \langle \ell' || r^2 || n_l, l \rangle 
+ \frac{1}{3} \sum_{n', l} \int d\epsilon \left[ \frac{\langle \epsilon' || D(\omega) || n_l, l \rangle \langle n_j, l || \epsilon' || U || n_{l'} \rangle}{\omega - \epsilon' + \epsilon_{n_j, l'} + i\eta} \right] 
+ \frac{\langle n_j, l || D(\omega) || \epsilon' || U || n_{l'} \rangle}{\omega + \epsilon' - \epsilon_{n_{l'}}}, \quad \eta \rightarrow +0
\]

and

\[
\langle \ell' || Q(\omega) || n_l, l \rangle = \langle \ell' || r^2 || n_l, l \rangle 
+ \frac{1}{3} \sum_{n', l} \int d\epsilon \left[ \frac{\langle \epsilon' || Q(\omega) || n_l, l \rangle \langle n_j, l || \epsilon' || U || n_{l'} \rangle}{\omega - \epsilon'' + \epsilon_{n_j, l'} + i\eta} \right] 
+ \frac{\langle n_j, l || Q(\omega) || \epsilon' || U || n_{l'} \rangle}{\omega + \epsilon'' - \epsilon_{n_{l'}}}, \quad \eta \rightarrow +0.
\]

In (7) and (8) summation over $n, l_j$ includes all occupied electron subshell of an atom, while summation over $n' l' (n'' l'')$ includes along with discrete vacant excited states also integration over continuous spectrum one-electron excitations. Here, matrix elements of $U$ are combinations of direct and exchange Coulomb interelectron interaction $V = 1/|r_1 - r_2|$. More details on solving (7), (8) and corresponding computing programs can be found in [14].

Thus, with the help of (7) and (8) the RPAE amplitude is given by the relation

\[
f_{n_{l'}}^{\text{RPAE}}(\epsilon, \theta_k) = f_{n_{l'}}^{\text{RPAE}}(\epsilon, \theta_k) + f_{n_{l'}}^{\text{RPAE}}(\epsilon, \theta_k)
= \sum_{l' = |l| + 1}^{\infty} \epsilon_{l' - 1/2} \epsilon_{l' + 1/2} P_l(\cos \theta_k) \sqrt{2l + 1} \left[ \begin{array}{ccc} l & 0 & 0 \\ 0 & 0 & 1 \end{array} \right] 
\times \langle \ell' || D(\omega) || n_l, l \rangle + \frac{\epsilon_{l' - 1/2} \epsilon_{l' + 1/2}}{2l + 1} \langle \ell' || Q(\omega) || n_l, l \rangle.
\]

In calculating $\arg f_{n_{l'}}^{\text{RPAE}}(\epsilon, \theta_k)$ we have to include contributions that comes from singularity in the first terms in square brackets in (7), (8), determined by $\eta \rightarrow +0$. Since $\text{Re} \langle \ell' || D(\omega) || n_l, l \rangle$ and $\text{Re} \langle \ell' || Q(\omega) || n_l, l \rangle$ as functions of $\omega$ change sign thus going via zero, the phases $\arg f_{n_{l'}}^{\text{RPAE}}(\epsilon, \theta_k)$ jump from $\pi/2$ to $-\pi/2$ at respective points in $\omega$ and $\epsilon$. These jumps make numeric calculations considerably more complex. However, at these points the derivative $d[\arg f(\epsilon)]/d\epsilon$ that enters the time delay definition (1) is a smooth function. Therefore, instead of (1) we employ in RPAE an equivalent formula:

\[
\tau_{n_{l'}}^{\text{RPAE}}(\epsilon, \theta_k) = \frac{d\text{Im}f_{n_{l'}}^{\text{RPAE}}(\epsilon, \theta_k) / d\epsilon}{\text{Re}f_{n_{l'}}^{\text{RPAE}}(\epsilon, \theta_k)^2 + \text{Im}f_{n_{l'}}^{\text{RPAE}}(\epsilon, \theta_k)^2}.
\]

3. To investigate time-delays in endohedrals $A@C_{60}$, we substitute $C_{60}$ by a static potential $W(r)$ that corresponds to reasonable distribution of electric charges and satisfactorily reproduces the experimental value of the $s$-electron affinity of $C_{60}$, just as it was done recently in [17]. The potential $W(r)$ is added to the HF atomic A potential. We denote the corresponding approaches HF$_C$ and RPAE$_C$. It affects HF$_C$ and RPAE$_C$ matrix elements and phases. The chosen $C_{60}$ potential is the same as in [18]

\[
W(r) = -W_{\text{max}} d^2 / (r - R)^2 + d^2.
\]

In addition to the static potential $W(r)$ it is essential to take into account the polarization of the fullerene shell that prominently modifies the action of the incoming light beam upon the ionized inner atom A. Assuming for simplicity that the atomic radius $r_a$ is much smaller than $R$, one can in RPAE frame express the effect of dipole and quadrupole polarization by factors $G^d_{\text{C}_{60}}(\omega)$ and $G^q_{\text{C}_{60}}(\omega)$ that connects the endohedral photoionization amplitude in “atomic” RPAE $f_{n_{l'}}^{\text{RPAE}}(\epsilon)$ with the endohedral RPAE photoionization amplitude $f_{n_{l'}}^{\text{C}_{60}}(\epsilon)$ by a simple relation

\[
f_{n_{l'}}^{\text{C}_{60}}(\epsilon, \theta_k) = G^d_{\text{C}_{60}}(\omega) f_{n_{l'}}^{\text{RPAE}_{C_{60}}}(\epsilon, \theta_k)
+ G^q_{\text{C}_{60}}(\omega) f_{n_{l'}}^{\text{RPAE}_{C_{60}}}(\epsilon, \theta_k).
\]

The dipole $G^d_{\text{C}_{60}}(\omega)$ and quadrupole $G^q_{\text{C}_{60}}(\omega)$ polarization factors are expressed via dipole $\alpha^d(\omega)$ and quadrupole $\alpha^q(\omega)$ dynamic polarizabilities of $C_{60}$ [13, 14]:

\[
G^d_{\text{C}_{60}}(\omega) = [1 - \alpha^d(\omega)/R^3]
\]
\[
G^q_{\text{C}_{60}}(\omega) = [1 - \alpha^q(\omega)/4R^5].
\]
\[ \sigma(\omega) \] of \( C_N \) (see, e.g., [13]) that is measurable and limited by the so-called dipole sum-rule. As to \( \sigma_c^2(\omega) \), there is no experimental data that could help to determine this quantity. Therefore, only estimations are possible. Using Eqs. (9), (12), and (13), we obtain the following expression for the endohedral amplitude with nondipole corrections \( f_{n_0}^{ABC}(\theta, k) \):

\[
\begin{align*}
\tau_{n_0}^{RPAE}(\epsilon, \theta, k) & = \tau_{n_0}^{RPAE}(\epsilon, \theta, k) + f_{n_0}^{ABC}(\epsilon, \theta, k) \\
& = \left[ G^d_{C_n}(\omega) \sum_{l=\pm 1} e^{i \delta_l(\epsilon) - l n/2} P_l(\cos \theta_k) \right] \\
& \times \sqrt{2l+1} \left[ \left( \begin{array}{ccc} 1 & 1 & l \\
0 & 0 & 0 \end{array} \right) \right] \left( ||D(\omega)|| n/1 \right) + \frac{\Omega G^d_{C_n}(\omega)}{c} \\
& \times \sum_{l=\pm 2, 0} e^{i \delta_l(\epsilon) - l n/2} P_l(\cos \theta_k) \\
& \times \sqrt{2l+1} \left[ \left( \begin{array}{ccc} 1 & 2 & l \\
0 & 0 & 0 \end{array} \right) \right] \left( ||Q(\omega)|| n/1 \right). 
\end{align*}
\]

Note that phases \( \delta_l^c(\epsilon) \) are determined in the HF approximation. The time delays for endohedrals \( \tau^{ABC}(\epsilon, \theta, k) \) are given by a formula similar to (10) where \( f_{n_0}^{RPAE}(\epsilon, \theta, k) \) is substituted by \( f_{n_0}^{ABC}(\epsilon, \theta, k) \).

In low-energy photoionization studies the parameter that characterizes the contribution of the quadrupole term as compared to the dipole one \( \omega r_A/c \) is small, particularly if at \( \omega r_A/c \leq 1 \). However, the nondipole terms are observed relatively easy at Cooper or interference minima in the dipole amplitude [13] or in cases when due to, e.g., resonance phenomena the quadrupole terms are unusually big.

For subvalent subshells \( n_s \) of noble gas atoms the dipole matrix elements are abnormally suppressed while the quadrupole terms are enhanced [13]. The same is valid to large extent for subvalent subshells in noble gas endohedrals. This is why \( s \)-subshells are of special interest for time delay investigation. For \( s \)-ionizing electrons, i.e., for \( l = 0 \), one has from (9) and (14), omitting a common in both terms an inessential for time delay factor \( i \), the formulas

\[
\begin{align*}
f_{n_0}^{RPAE}(\epsilon, \theta, k) &= e^{i \delta} \cos \theta_k \tilde{D}_1 - \sqrt{\frac{\omega}{c}} e^{i \delta} P_1(\cos \theta_k)\tilde{Q}_2, \\
f_{n_0}^{ABC}(\epsilon, \theta, k) &= G^d e^{i \delta} \cos \theta_k \tilde{D}_1 \\
& - \sqrt{\frac{\omega}{c}} G^d e^{i \delta} P_2(\cos \theta_k)\tilde{Q}_2. 
\end{align*}
\]

Here, \( \langle ||D(\omega)|| n/1 \rangle \equiv \tilde{D}_1 \exp[i \Delta_l(\epsilon)] \), \( \delta_l \equiv \delta_l(\epsilon) + \Delta(\epsilon) \), \( \langle ||Q(\omega)|| n/1 \rangle \equiv \tilde{Q}_2 \exp[i \Delta_2(\epsilon)] \) and \( \delta_l \equiv \delta_l(\epsilon) + \Delta(\epsilon) \).

The time delay for \( s \)-subshells in RPAE is particularly simple for \( \omega/c \ll \cos \theta_k \) where it is given by the formula

\[
\tau_{n_0}^{RPAE}(\epsilon, \theta, k) = \delta_l^c - \sqrt{\frac{\omega}{c}} P_2(\cos \theta_k) \left[ \frac{\tilde{Q}_2}{\tilde{D}_1} + \omega \left( \frac{\tilde{Q}_2}{\til{D}_1} \right)^* \right] \times \sin(\tilde{\delta}_2 - \tilde{\delta}_1) + \frac{\til{Q}_2}{\til{D}_1} (\til{\delta}_2 - \til{\delta}_1) (\cos(\til{\delta}_2 - \til{\delta}_1)).
\]

To compare the nondipole terms for \( \tau_{n_0}^{RPAE}(\epsilon, \theta, k) \) with that for the cross section \( \sigma_{n_0}(\omega) \), let us present the corresponding formula [13]

\[
\frac{d\sigma_{n_0}(\omega, \theta, k)}{d\Omega} = \frac{3\sigma_{n_0}(\omega)}{8\pi} \sin^2 \theta_k \left[ 1 + 4 \frac{\omega}{c} \frac{\til{Q}_2}{\til{D}_1} (\cos(\til{\delta}_2 - \til{\delta}_1)) \cos \theta_k \right].
\]

To obtain expressions similar to (15)–(17) but for endohedrals, one has to substitute \( \til{Q}_2, \til{D}_1, \til{\delta}_2, \) and \( \til{\delta}_1 \) by \( \til{G} = G^d \til{Q}_2, \til{D}_1 = G^d \til{D}_1, \til{\delta}_2 = \til{\delta}_1^c + \Delta', \) and \( \til{\delta}_1^c = \til{\delta}_1^c + \Delta^c \), where the following notations \( \til{G} = G^d \exp(i\Delta^d, \omega) = G^d(\omega) \) are employed.

According to (15), by measuring the time-delay at \( \theta_k = \pi/2 \) one can find directly the nondipole contribution since the dipole term in (15) is equal to zero. However, according to (17) the photoionization cross section at this angle is also zero. It is essential that the quadrupole term enters time delay and photoionization cross section in different combinations.

It is important to note that by going from observation angle \( \theta_k \to \theta_k + \pi \), from forward to backward directions, e.g., the dipole contribution to time delay does not change its sign, while the quadrupole contribution changes its signs. Thus, by measuring the differences \( \Delta \tau_{n_0}^{RPAE}(\epsilon, \theta, k) \equiv \tau_{n_0}^{RPAE}(\epsilon, \theta, k) - \tau_{n_0}^{RPAE}(\epsilon, \theta, k + \pi) \) or \( \Delta \tau_{n_0}^{ABC}(\epsilon, \theta, k) \equiv \tau_{n_0}^{ABC}(\epsilon, \theta, k) - \tau_{n_0}^{ABC}(\epsilon, \theta, k + \pi) \) one can obtain quantities that are directly proportional to \( \omega/c \).

The concrete analytic expressions for time delays for \( l > 0 \) are too cumbersome to be exposed here. Instead, we will present directly the numeric results of calculations of time delays. Note that the difference between \( d\sigma_{n_0}(\epsilon, \theta, k)/d\Omega \) at \( \theta_k \) and \( \theta_k + \pi \) is also proportional to \( 1/c \) that is illustrated for \( s \)-subshell by (17).

It is seen from (9), (14), (15), and (17) that the quadrupole term adds new information about the photoionization process, since it includes another photoionization amplitude and polarization factor and other scattering phase differences. It is essential that these characteristics appear in combinations dif-

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different from that in nondipole corrections to the angular distribution of photoelectrons (see (17)) [13]. Therefore, the results that could be obtained from studies of the nondipole corrections to the time delay are complimentary to that obtained from the angular distributions.

4. We have performed concrete calculations for many-electron atoms Ar, Xe, isoelectronic to them negative ions Cl\(^{-}\), I\(^{-}\) and respective endohedrals, consisting of C\(_{60}\) fullerene shell with one of atoms/ions inside: Ar, Cl\(^{-}\), Xe, I\(^{-}\@C\(_{60}\)\). We considered outer \(p\)- and subvalent \(s\)-subshells in all studied objects along with \(4d\) in Xe and I\(^{-}\), as well as in their endohedrals. We concentrate here on obtaining data on nondipole contributions. Calculations are performed in RPAE\(_C\). The parameters of the potential (11) are the same as in our recent papers, e.g., in [11]. Inclusion of fullerenes shell polarization in the RPAE frame is achieved by using \(G\)-factors (13), the parameters of which are the same as in [11]. The results for endohedrals are marked by upper indexes \(A@C\).

In calculations, we determine only HF scattering phases \(\delta_\rho(\varepsilon)\) (9) and (14). These phases are well defined only for short–range potentials. Such is the case for photoionization of negative ions and respective endohedrals. For neutral atoms and their endohedrals, the outgoing electron feels the single charged ion’s field. As a result, the very notion of a phase shift loses its sense. Trial calculations demonstrate that for considered objects it took place for \(\varepsilon < 0.1\) Ry. For negative ions the time-delay is well defined at any energy.

Using (10) we calculate the RPAE\(_C\) and, after proper substitution of amplitudes, \(A@C\), forward and backward time delays at the photoelectron emission angle \(\theta_0 = 0\) and \(\theta_0 = \pi\), denoted in Figs. 1–4 as \(fw\) and \(bw\), respectively. The main finding here are time differences that are proportional to \(\omega/c\). They are presented in insets of these figures. The photon energy is in Rydbergs (\(\text{Ry} = 13.6\) eV) and time delay is in attoseconds (\(1\) as = \(10^{-18}\) s). We are not presenting here results of HF calculations since it is known that for the considered objects the role of RPAE corrections is big [13].

Each figure includes for a given subshell results for an atom, isoelectronic negative ion and respective endohedrals. Big negative values of time delay contradict the causality principle and as such has to be discarded. However, not too big negative values are compatible with causality due to quantum nature of the photoionization process (see [4]). The forward and backward time delays are quite big reaching hundreds attoseconds. The respective forward–backward time difference is characterized in Ar by a strong maximum that is quite noticeable for \(3p\)-subshell (see Fig. 1) and particularly big for \(3s\)-subshell in Ar and Ar\(^{-}\@C\(_{60}\) (see Fig. 2). The influence of the endohedral shell upon time delays and corresponding nondipole corrections is prominent, but only for Cl\(^{-}\) a deep minimum transforms into a high maximum for Cl\(^{-}\@C\(_{60}\) in \(\Delta \tau_{3p}(\varepsilon)\) (see Fig. 2, inset). The strong variation in \(\Delta \tau_{3p}(\varepsilon)\) is a consequence of smallness of dipole photoionization amplitudes and big influence upon them of quadrupole transition [1, 13]. The behavior of time delay for \(3p\) electrons follows the dependence of \(3p\) dipole amplitude upon \(\omega\) and results from its complete domination over the contribution of quadrupole transition.

We do not present results for \(5p\) in Xe and I\(^{-}\), as well as respective endohedrals, since the situation there is qualitatively similar to \(3p\) in Fig. 1 and due to lack of space. Figure 3 depicts the results for \(5s\)-photoelectrons. The \(5s\) photoionization amplitude for considered objects is strongly affected not only by outer \(5p\) electrons but by the intermediate \(4d\)-subshell also. The well-known feature of \(4d\) is its dipole Giant resonance that dominates the cross section in a broad
The time delay important is only the maximum that reflects the influence upon. Surprisingly enough, only small traces of the Giant resonance exist. The maxima in insets of Fig. 3 reflect the influence of the fact that the dipole photoionization cross section at about 11 Ry has a Cooper minimum [13]. Figure 4 demonstrates results for the subshell. As for the near threshold behavior is of interest, presenting quite different results for Xe and I\textsuperscript{–}. No essential traces of the Giant resonance is observed. However, in the region of Cooper minimum in the photoionization cross section we see a prominent minimum in time delays. The time differences for Xe and I\textsuperscript{–} has a remarkable variation of Fano profile shape that does not correspond, however, to a discrete level. Instead, it is a trace of dipole cross section variation. The polarization factor affects mainly the outer subshell, and leads to rather smooth addition to the time delay near thresholds of outer and subvalent subshells in respective endohedrals of Ar, Cl\textsuperscript{–}, Xe, and I\textsuperscript{–}. Naturally, the 4d subshell is deep enough, so the role of C\textsubscript{60} shell is negligible everywhere except near threshold region for all time delays.

5. We investigated here the photoionization amplitude at low photon energies that includes along with the main dipole also the small quadrupole contribution. Having this amplitude, we demonstrate for the first time, that quadrupole corrections to the times delay are quite noticeable and under concrete conditions can be isolated from the dipole ones, and measured. Of particular interest is the situation for the subshell in Ar, where the determined by quadrupole contribution time delay difference reaches 400 as.

To use attosecond lasers in studies of time delays is not a simple task since extraction from experiment the EWS time delays require to get rid of the additions introduced by the properties of the laser beam includ-
In spite of difficulties, the theoretical investigation of time delay differences and their experimental measurement is of interest as a source of unique information about ionized targets.

Fig. 4. (Color online) Time delays of photoelectrons from the 4d subshell of Xe, $\Gamma^-$ and endohedrals Xe@C$_{60}$ and $\Gamma^-$@C$_{60}$, emitted forward (fw) and backward (bw) and their differences $\Delta \tau_{\text{4d}}(\varepsilon) = \tau_{\text{4d}}(\varepsilon, 0) - \tau_{\text{4d}}(\varepsilon, \pi)$ (insets), determined by nondipole contributions.

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