Interpretation of time delay in the ionization of two-center systems

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For the ionization of diatomic molecules the conditions and mechanisms giving rise to large positive and negative time delays of the ejected electrons are studied. It is shown that for H_2 and H_2^+ the singularities in the angular distribution of time delay occur when at a certain energy the amplitudes of all partial spheroidal waves, except one, turn into zero, i.e., they coincide with the so-called Cooper minimum. By analytical consideration of the emitted electron wave-packet evolution it is demonstrated that large negative values of the phase derivative with respect to energy do not violate the causality principle. We also analyze the dependence of time delay upon the electron energy for Coulomb spheroidal waves with different spheroidal quantum numbers.

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I. INTRODUCTION

Recently the appearance of laser systems that can generate superintense pulses as short as a few hundred attoseconds [1,2] gave rise to new capabilities in studying electron dynamics in atoms and molecules, which were not available earlier [3,4]. Among these, of particular interest are the methods of measuring the delay of electron ejection from the atom subject to photoionization [5–7]. At present the measurements of ionization delay are already being performed [8–10] in noble gas atoms using the methods of attosecond streaking [11,12] and reconstruction of attosecond beating by interference of two-photon transition (RABITT) [13]. Time delays in photoionization of molecules are a subject of growing theoretical and experimental interest [14–18].

In particular, the numerical study [18] of the time delay in the process of single-photon ionization of a hydrogen molecule H_2 revealed an interesting feature, namely, that at certain energies of the ejected electron the angular distribution of the molecular photoionization time delay possesses singularities. Figure 1(a) shows the Wigner time delay t_W vs the electron ejection angle θ_e for single ionization of an oriented H_2 molecule under the condition that the molecular axis is parallel to the polarization of radiation, $\mathbf{R} \parallel \mathbf{e}$. The dependence was calculated for different energies of the ejected electron using the *ab initio* exterior complex scaling method [19]. For the energy of ionizing radiation photon $\hbar\omega = 84$ eV there is a discontinuity at the angle $\theta_e = 39^\circ$, in the vicinity of which t_W tends to $\pm\infty$. From Fig. 1(b) one can see that this discontinuity coincides with the zeros of the ionization single-differential cross section. Although the probability of electron ejection in the directions close to this zero is small, it is still possible in principle to measure the time delay for the electron ejection in these directions. Large negative values of t_W contradict the causality principle [20], since formally they mean that the electron is ejected by the molecule long before the absorption of the photon.

The aim of the present paper is to clarify the origin of singularities in t_W and to resolve the paradox of large negative delay in two-center systems. We reconsider the physical meaning of Wigner time delay t_W in Coulomb systems; study the dependence of t_W upon the electron energy and ejection angle by the example of the molecular hydrogen ion H_2^+, a benchmark two-center system; and analyze the behavior of the ejected electron wave packet under the conditions of t_W singularities.

Throughout the present paper we use the approximation of fixed nuclei (the Born-Oppenheimer approximation). After ionization the nuclei begin to move from each other due to uncompensated Coulomb repulsion. However, the ejected electron usually moves away from the nuclei fast enough to reach a great distance long before the internuclear distance considerably changes. Experimentally this fact allows determination of internuclear distance before ionization by measuring the kinetic-energy release (KER) of the dissociating nuclei [21]. The exception is the case in which before the final release the electron appears in a long-living quasistationary state (QSS) [16,17]. However, H_2^+ has no QSS, and in H_2 the energies of all QSSs are lower than the threshold of double ionization, while the singularities, observed in Fig. 1(a), occur at the energy values above this threshold. Possible influence of nuclear motion on the time delay due to the presence of singularities themselves is separately discussed at the end of Sec. V.

The paper is organized as follows. In Sec. II the theory of Wigner's time delay is briefly recalled and the notion of ejection delay is introduced as a convenient tool for analyzing the delay features arising due to deviation of the potential from the Coulomb one. In Sec. III we study the energy dependence of the time delay for spheroidal Coulomb waves. Section IV is devoted to clarifying the origin of singularities in the angular distribution of the Wigner time delay in two-center targets, and Sec. V presents the physical interpretation of these singularities.

Below, we use the atomic units of measurement, unless otherwise noted.

II. COMMON THEORY OF THE IONIZATION TIME DELAY

In the framework of quantum mechanics the behavior of a system, ionized by an external laser field, is described by the wave function. After the finish of the external action it can be presented in the form

$$\psi(\mathbf{r},t) = \int f(\mathbf{k})\varphi_{\mathbf{k}}^{(-)}(\mathbf{r})e^{-i\frac{k^2}{2}t}d\mathbf{k}, \qquad (1)$$

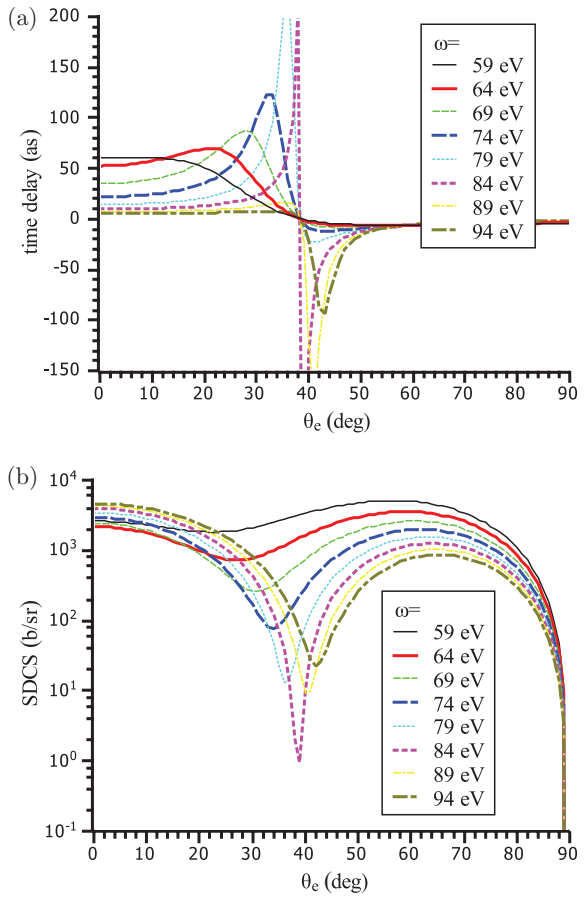

FIG. 1. (Color online) (a) Wigner time delay and (b) single differential cross section $\frac{d\sigma}{d\Omega_e}$ of the single ionization of molecular hydrogen H_2 vs the ejection angle θ_e at $\mathbf{R} \parallel \mathbf{e}$ for different values of the energy of ionizing radiation photon $\hbar\omega$.

where $f(\mathbf{k})$ is the ionization probability amplitude and $\varphi_{\mathbf{k}}^{(-)}(\mathbf{r})$ is the wave function of the continuous spectrum, describing the free particle with the momentum $\mathbf{k}$ at the infinitely large distance.

If the interaction of the particle with the center is described by a short-range potential, then $\varphi_{\mathbf{k}}^{(-)}(\mathbf{r} \to \infty) = (2\pi)^{-3/2} \exp(i\mathbf{kr})$. In the limit case $t \to \infty$ the major contribution to the integral Eq. (1) comes from the vicinity of the stationary point $\mathbf{k}_0 = \mathbf{k}_0(\mathbf{r},t)$, in which the derivative of the integrand phase is zero:

$$\mathbf{r} + \frac{d\delta}{dk}(\mathbf{k}_0)\frac{\mathbf{r}}{r} - \mathbf{k}_0 t = 0, \tag{2}$$

where $\delta(\mathbf{k}) = \arg f(\mathbf{k})$ is the phase of the ionization complex amplitude. Therefore, at the point $\mathbf{r} = r\mathbf{n}$ at the moment of time

$$t(r) = \frac{r}{k} + \frac{1}{k}\frac{\partial\delta}{\partial k}(\mathbf{k}), \tag{3}$$

one can detect the particle having the momentum $\mathbf{k} = k\mathbf{n}$ with the maximal probability. Since the ratio r/k is the time required for the arrival at the point $\mathbf{r}$ of the particle that left the center $r = 0$ at the time $t = 0$ and moved with the uniform velocity k, the expression

$$t_W = \frac{1}{k}\frac{\partial\delta(\mathbf{k})}{\partial k} = \frac{\partial\delta}{\partial E}(\mathbf{k}) \tag{4}$$

has the physical meaning of the time delay of the particle arrival at the distance r from the center with respect to that in the case of the uniform rectilinear motion.

The interpretation of the energy derivative of the phase as the time delay was first proposed by Eisenbud [22] and Wigner [20] (see also [23,24]). In [20] Wigner has shown that if a particle is incident from the infinity then after passing the center of a short-range potential the delay with respect to the free space motion equals $2t_W$. In the same paper he has shown that if the potential is attractive then $t_W > 0$ only for near-resonance energy (i.e., when the particle is captured into a quasistationary state for a long time). For the rest of the energy values, $(-r_{\rm pot}/k) \leqslant t_W \leqslant 0$ (where $r_{\rm pot}$ is the potential action radius); i.e., t_W corresponds to the expected from the point of view of classical physics. For brevity, below we will refer to the energy derivative of the phase, t_W, as the Wigner time delay.

If the potential is not short range and at large distances behaves like the Coulomb one, Z/r, then the asymptotic form of the wave function becomes essentially different, since now the phase of the integrand in Eq. (1) contains the term that is logarithmic in r [25]. The stationary point is now determined by the solution of the equation

$$\mathbf{r} + \left[-\frac{Z}{k_0^2}\ln 2k_0 r + \frac{Z}{k_0^2} + \frac{d\delta}{dk}(\mathbf{k}_0)\right]\frac{\mathbf{r}}{r} - \mathbf{k}_0 t = 0. \tag{5}$$

So, it is apparent that for the electron, having the momentum k, the time of arrival at the point separated by r from the Coulomb center with the charge Z is

$$t(r) = \frac{r}{k} - \frac{Z}{k^3}\ln 2kr + \frac{Z}{k^3} + t_W. \tag{6}$$

As mentioned above, in systems with short-range potentials the Wigner time delay has a simple physical meaning; namely, it is the delay of the arrival of the particle, ejected from the force center, as compared to the case of rectilinear and uniform motion. It is desirable to introduce a quantity for which the physical interpretation in the case of a field with Coulomb asymptotic behavior is as clear as that of the Wigner time delay in the case of a short-range potential. For this aim the comparison should be made with a certain classical motion in the Coulomb field. The most rational choice is the motion of a particle with zero angular momentum, starting from the center $r = 0$ at the moment of time $t = 0$. Such motion is purely radial and one dimensional, so (see, e.g., [26])

$$t_C(r) = \int_0^r \frac{dr}{p(r)}, \tag{7}$$

where $p(r) = \sqrt{k^2 + 2Z/r}$ is the momentum of the particle at the distance r from the center. Performing the integration, we get

$$t_C(r) = \frac{p(r)r}{k^2} + \frac{Z}{k^3}\ln\frac{p(r)/k - 1}{p(r)/k + 1}. \tag{8}$$

The asymptotic form of this expression is

$$t_C(r \to \infty) = \frac{r}{k} - \frac{Z}{k^3} \ln \frac{2k^2 r}{Z} + \frac{Z}{k^3}. \tag{9}$$

Let us introduce the *ejection delay* as the delay between a "quantum" particle and a classical one with $\ell = 0$, ejected from the center at the time moment $t = 0$, both moving in the asymptotically Coulomb field, i.e.,

$$t_0 = \lim_{r\to\infty} [t(r) - t_C(r)]. \tag{10}$$

From Eqs. (6) and (9) it follows that the ejection delay t_0 and the Wigner time delay t_W are related as

$$t_0 = t_W + \frac{Z}{k^3} \ln \frac{k}{Z}. \tag{11}$$

Figure 2(a) shows the Wigner time delays for the ionization of a helium ion He^+ at different values of the final angular momentum ℓ. It is seen that at small energies $t_W \to -\frac{Z}{k^3} \ln \frac{k}{Z}$ for all values of ℓ. This fact complicates the detailed analysis of time delay as a function of ℓ and, generally, the delay features arising due to deviation of the potential from the Coulomb one. Moreover, at large E the Wigner time t_W for the s wave ($\ell = 0$) becomes negative. In Fig. 2(b) the delays t_0 are shown.

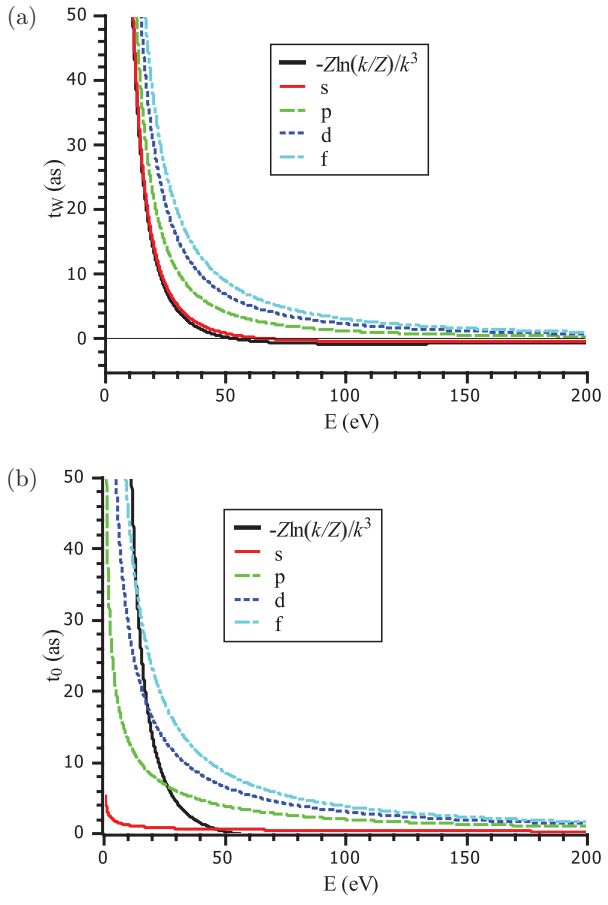

FIG. 2. (Color online) Dependence of the time delay upon the energy of the ejected electron for a helium ion He^+. (a) Wigner time delay. (b) Ejection delay, Eq. (11). The thick solid line is the common shift of t_W relatively to t_0. Time delays for $\ell = 0$ (solid line), $\ell = 1$ (dashed line), $\ell = 2$ (dotted line), and $\ell = 3$ (dashed-dotted line) are shown.

For $k \to 0$ they tend to infinity, but much more slowly, as $1/k^2$, rather than as $-\frac{Z}{k^3} \ln \frac{k}{Z}$. Besides, t_0 is positive for all values E and grows with increasing ℓ. This is because t_0 is chosen such that the centrifugal potential [26] can be considered as a short-range repulsive one, giving rise to additional delay with respect to the pure Coulomb field. In free space the centrifugal potential itself produces no delay. The delay introduced by the centrifugal potential in the presence of the Coulomb potential is due to the fact that because of the trajectory bending the electron spends a longer time in the region of strong centrifugal potential action, as compared to the free space motion.

It should be noted that experimental measurements using the attosecond streaking or RABITT methods yield the time delays that differ from both t_W and t_0 because of the so-called Coulomb-laser coupling [27–31]. The detailed discussion of this issue will be presented elsewhere.

III. TIME DELAY FOR SPHEROIDAL TWO-CENTER COULOMB WAVES

Before proceeding to ionization of two-center targets let us dwell on a one-center centrosymmetric system. This will allow comparison of the two cases and better understanding of the two-center specificity.

Assuming the external impact on the system to be weak, one can calculate the ionization amplitude using the first-order perturbation theory:

$$f(\mathbf{k}) = \langle \mathbf{k}|\hat{w}|i\rangle, \tag{12}$$

where $|i\rangle$ is the wave function of the initial state of the system, $|\mathbf{k}\rangle \equiv \varphi_{\mathbf{k}}^{(-)}(\mathbf{r})$ is the wave function of the final state describing the free electron with the momentum $\mathbf{k}$ at infinity, and $\hat{w}$ is the operator of external perturbation.

For a centrosymmetric system the wave function can be expanded as [25]

$$\varphi_{\mathbf{k}}^{(-)}(\mathbf{r}) = 4\pi \sum_{\ell m} i^\ell e^{-i\delta_\ell(k)} Y^*_{\ell m}(\widehat{k}) Y_{\ell m}(\widehat{r}) R_{k\ell}(r), \tag{13}$$

where $R_{k\ell}(r \to \infty) = \frac{1}{kr} \sin(kr - \pi\ell/2 + \delta_\ell)$ is the radial wave function of the partial spherical wave and δ_ℓ is the phase of the spherical wave. In this case the amplitude is expressed as

$$f(\mathbf{k}) = \sum_{\ell m} A_{\ell m}(k) i^{-\ell} e^{i\delta_\ell(k)} Y_{\ell m}(\widehat{k}). \tag{14}$$

If the transition amplitude $A_{\ell m} = 4\pi \langle R_{k\ell} Y_{\ell m}|\hat{w}|i\rangle$ differs from zero only for the one value of ℓ, then, obviously, the Wigner time delay depends only on the corresponding partial phase:

$$t_W = \frac{d\delta_\ell}{dE}. \tag{15}$$

Therefore, if the final state has definite angular momentum, then the Wigner time delay is completely determined by the energy and the orbital quantum number and is independent of the initial state and the particular form of the perturbation potential.

Now let us proceed to the time delay in the ionization of two-center targets and dwell on specific phenomena that occur

in this case. As a benchmark object we choose the simplest molecule, the molecular hydrogen ion H_2^+, for which the separation of variables in the time-independent Schrödinger equation is possible using the spheroidal coordinates

$$\xi = \frac{\left|\mathbf{r}-\frac{\mathbf{R}}{2}\right| + \left|\mathbf{r}+\frac{\mathbf{R}}{2}\right|}{R} \in [1,\infty),$$
$$\eta = \frac{\left|\mathbf{r}-\frac{\mathbf{R}}{2}\right| - \left|\mathbf{r}+\frac{\mathbf{R}}{2}\right|}{R} \in [-1,1], \quad \phi \in [0,2\pi),$$

and the solutions (Coulomb spheroidal functions [32]) are known [33,34].

The two-center Coulomb continuum wave function may be presented as a sum of partial spheroidal waves [33]:

$$\varphi_{\mathbf{k}}^{(-)}(\mathbf{r}) = (2\pi)^{3/2} 4\pi \sum_{lm} \Upsilon_{lm}^{*}\left(\frac{kR}{2},\theta_e,\phi_e\right) i^l \times e^{-i\delta_{lm}} T_{ml}\left(\frac{kR}{2},\xi\right) \Upsilon\left(\frac{kR}{2},\arccos\eta,\phi\right). \quad (16)$$

Here the spheroidal harmonics are introduced as

$$\Upsilon_{lm}(c,\theta,\varphi) = \overline{S}_{ml}(c,\cos\theta)\frac{\exp(im\varphi)}{\sqrt{2\pi}},$$
$$\Upsilon_{lm}(0,\theta,\varphi) = Y_{lm}(\theta,\varphi), \quad (17)$$

where $\overline{S}_{ml}(c,\eta)$ is the normalized quasiangular spheroidal function [32], m is the quantum number of the angular momentum projection onto the molecular axis, l is the quasiazimuthal quantum number, and $c = kR/2$ is the dimensionless parameter. The quasiradial Coulomb spheroidal function $T_{ml}(c,\xi)$ has the asymptotic form

$$T_{ml}(c,\xi\to\infty) = \frac{1}{c\xi}\sin\left[c\xi + \frac{RZ_+}{2c}\ln(2c\xi) - \frac{l\pi}{2} + \delta_{lm}\right], \quad (18)$$

where Z_+ is the total charge of the nuclei and δ_{lm} is the partial wave phase, entering Eq. (16).

First let us consider the case in which after the ionization an electron appears in the state with the fixed angular spheroidal quantum numbers m and l. In analogy with the spherical case [i.e., Eq. (15)] one can introduce the Wigner time delay for a spheroidal partial wave:

$$t_W = \frac{d\delta_{lm}}{dE}. \quad (19)$$

The ejection delay t_0 for the given Wigner time delay is calculated using Eq. (11), assuming $Z = Z_+ = 2$; i.e., in this case t_0 is in fact the delay compared to the classical electron, ejected from the center of a helium ion He^+.

Figure 3 presents the energy dependence of the ejection time delay for different partial waves of the H_2^+ continuum with two values of the internuclear distance, $R = 2$ and 1.4 a.u. The distance $R = 2$ a.u. is the equilibrium internuclear distance for H_2^+. The distance $R = 1.4$ a.u. coincides with the equilibrium internuclear distance in the hydrogen molecule H_2, which makes it easier to compare the results for H_2^+ and H_2.

The delays t_0 presented in Fig. 3 for small energies and any spheroidal quantum number l tend to those of the helium ion He^+ [shown in Fig. 2(b)] with the same corresponding

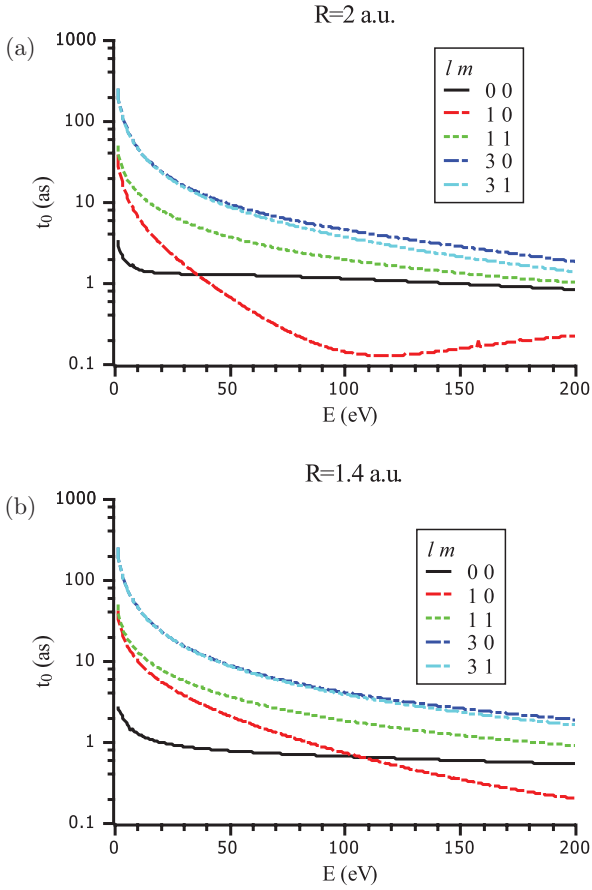

FIG. 3. (Color online) Ejection time delay vs the ejected electron energy for partial waves of the continuum in the hydrogen molecular ion. (a) $R = 2$ a.u. (b) $R = 1.4$ a.u. Time delays for $l = 0$ (solid line); $l = 1, m = 0$ (dashed line); $l = 1, m = 1$ (dotted line); $l = 3, m = 0$ (dashed-dotted line); and $l = 3, m = 1$ (dashed-dotted-dotted line) are shown.

spherical azimuthal quantum number $\ell = l$. The explanation is clear: at large wavelengths the particular form of the potential near the center becomes unimportant, and the main contribution comes from the region where the potential practically coincides with the one-center Coulomb one. At large energies essential differences from the one-center case arise. First, a growing difference appears between the curves with the same l but different m. For $m = 1$ the results are very close (they differ by less than 10% for $l = 1$ and 20% for $l = 3$ over the entire studied range of energies) to the corresponding results for the helium ion at $\ell = l$.

A spheroidal partial wave may be considered as a sum of converging and diverging spheroidal waves; i.e., it describes the process once considered by Wigner: the electron comes from infinity, passes near the nuclei, and leaves for infinity. Correspondingly, the quantity $2t_0$ in this case is the delay of the electron as compared to the classical one, passed through the Coulomb center with the charge $Z = 2$. The spheroidal functions with $m \neq 0$ are zero near the molecular axis; i.e., the probability of detecting the electron in such state near the molecular axis is extremely small. Hence, we can conclude that t_0 at $m \neq 0$ is close to t_0 for a hydrogenlike ion with $Z = 2$ and appropriate ℓ just because the electrons move far

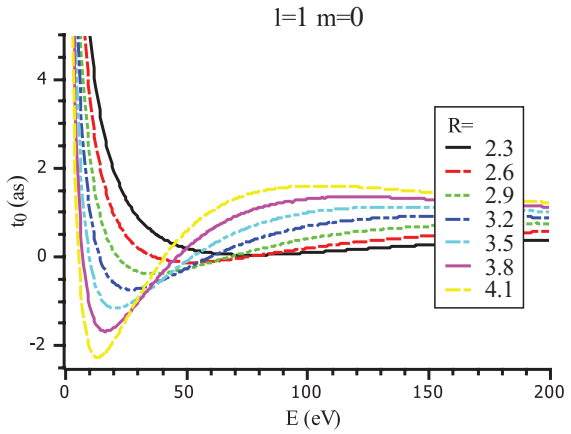

FIG. 4. (Color online) Dependence of the time delay for the partial wave with $l = 1$ and $m = 0$ of the H_2^+ continuous spectrum upon the energy of the ejected electron at different large values of R.

enough from the molecular axis, i.e., in the region where the acting potential is close to that of a single center with the charge $Z = 2$. Now it becomes clear why for $l = 3, m = 1$ the deviation from the single-center case is greater: the spheroidal harmonic $\Upsilon_{31}(\eta,\phi)$, although tending to zero [as $\Upsilon_{11}(\eta,\phi)$] at $\eta = \pm 1$, i.e., in the vicinity of the nuclei, possesses additional maxima near $\eta = \pm 1$, so that the electron more strongly feels the difference between the two-center and single-center potentials.

For $m = 0$ the value of t_0 is smaller than for the waves with $m \neq 0$ at the same l. Moreover, the curve for $l = 1, m = 0$ quickly descends with growing E, crosses the curve for $l = 0$, and appears below it. Note that for $R = 2$ a.u. the effect of "advance" of the partial wave with $l = 1, m = 0$ is more pronounced. Therefore, it seems interesting to trace the variation of the curve for $l = 1, m = 0$ under the increase of R. Figure 4 shows the dependences $t_0(E)$ for different values of R. It is seen that with the growth of R the dip in $t_0(E)$ is shifted toward smaller E and becomes deeper. At $R > 2.6$ a.u. the minimal $t_0(E)$ becomes negative; i.e., the electron in the field of two centers, each having the charge $Z = 1$ (only one of them approached close enough), arrives faster than in the field of a single center with the charge $Z = 2$.

Let us try to explain all these phenomena. The spheroidal partial wave with $l = 0$ has the maximal amplitude in the middle between the potential centers [see Fig. 5(a)], and the angular distribution is approximately uniform. In the wave with $l = 1, m = 0$ the maximal amplitude is achieved near the nuclei [see Fig. 5(b)]. As a result, the potential along the electron trajectories for $l = 1, m = 0$ is deeper than for $l = 0$, and, when the wavelength is small enough for the electron to feel the two-center character of the potential, t_0 for $l = 1, m = 0$ becomes smaller than for $l = 0$, since in the former case the electron upon the average moves somewhat faster. However, this effect itself is not sufficient to make t_0 negative, since this happens at large R and large wavelengths (see Fig. 4); indeed, the negative t_0 means that the electron arrives faster than that from a nucleus with the charge $Z = 2$, as if this charge was placed as a whole in the center of the molecule. The possible explanation is that the electron with $l = 1, m = 0$ and the wavelength comparable with R is

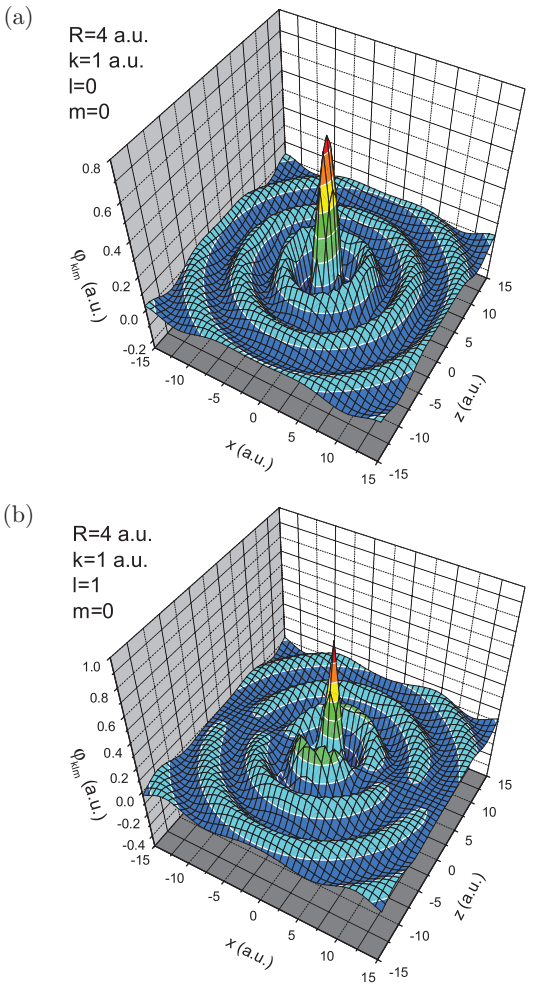

FIG. 5. (Color online) Spheroidal partial wave functions in the xOz plane ($Oz||\mathbf{R}$) for $R = 4$ a.u. and $k_e = 1$ a.u. (a) $l = 0$, $m = 0$. (b) $l = 1$, $m = 0$.

presumably scattered by only one nucleus and leaves in the opposite z direction. Due to the shift of the scattering center toward the detection point, t_0 acquires a negative contribution. This effect is clearly evident from the behavior of a classical electron originally moving along the molecular axis, i.e., along Oz at $x = 0, y = 0$. Such an electron will be scattered by the nearest nucleus and will fly exactly back. Since the scattering center is closer to the detector by $R/2$ than the center of the molecule, the backscattered electron will reach the detector earlier than that, scattered by a nucleus with the charge $Z = 2$, located at the center of the molecule. At large energies, because of the dependence of the angular spheroidal harmonic upon the energy (the harmonic appears to be "pushed off" the points with $\eta = \pm 1$), the maximal amplitude of the wave becomes shifted from the nuclei toward the molecule center, so that due to the decrease of the depth of the potential along the electron trajectories, as well as because of the shift of the turning point toward the center, the delay t_0 at sufficiently large energies begins to grow.

Thus, the parameter t_0 carries information about the potential in the region which the electron has traveled through. Since the angular distribution of the differential cross section at infinity represents a picture of the angular distribution of

these regions, the comparison of t_0 for different partial waves can provide information on the target structure. However, in contrast to the spherical case, in which the ejection of an electron with fixed angular momentum ℓ obeys the angular momentum selection rules, in the spheroidal case only the parity selection rule holds. Due to this fact the experimental measurement of time delays of partial waves is a nontrivial problem.

IV. TIME DELAY OF H_2^+ IONIZATION

Since in the process of the single-photon ionization of a two-center target, e.g., H_2^+, the dipole transition generally brings the system to a state containing more than one partial spheroidal wave, the time delay is expected to depend upon the ejection angle. To avoid the problem with possible jumps of the calculated phase of the ionization amplitude f, entering the time delay definition Eq. (4) and, therefore, the ejection delay Eq. (11), by 2π (due to the phase uncertainty of a periodic function) and by π (near the resonances), it is convenient to calculate the phase derivative as the imaginary part of the logarithmic derivative of the ionization amplitude itself, i.e.,

$$t_W = \mathrm{Im}\left(\frac{1}{f}\frac{\partial f}{\partial E}\right). \tag{20}$$

Figure 6 presents the angular distributions of the ejection delay t_0 for different values of energy and internuclear distance, when H_2^+ is ionized from the initial ground state with the molecular axis parallel to the polarization direction of the ionizing field. It is seen that, similar to the case of H_2 considered earlier [18] (see Fig. 1), the behavior of $t_0(\theta_e)$ demonstrates characteristic "zigzags." At the same positions the plots of the differential cross section demonstrate dips [18]. At certain energies ($E \sim 0$ eV for $R = 2$ a.u. and $E \approx 40$ eV for $R = 1.4$ a.u.) the range of $t_0(\theta_e)$ variation becomes huge. Since for each separate partial wave the delay (Fig. 3) has no singularities, it is apparent that singularities arise from superposition of several partial waves. Let us elucidate their origin. Equation (16) yields the following expression of the ionization amplitude angular dependence:

$$f(\mathbf{k}_e) = \sum_{lm} A_{lm} i^{-l} e^{i\delta_{lm}} \Upsilon_{lm}(c,\theta_e,\phi_e), \tag{21}$$

where A_{lm} is the amplitude of the transition to the spheroidal partial wave with the quantum numbers l,m. Figure 7 shows the amplitudes A_{l0} of the dipole transition from the ground state of H_2^+ to the partial waves of the continuum depending on the final energy. In the considered case the direction of the field polarization is parallel to the molecular axis, and the initial m value is conserved in the process of ionization. It is seen that for all energies only the partial waves with $l = 1$ and 3 are essential.

Consider the ionization amplitude as a sum of contributions from two dominating partial waves:

$$f = A_{10} e^{i\delta_1 - i\pi/2} \Upsilon_{10} + A_{30} e^{i\delta_3 - i3\pi/2} \Upsilon_{30}. \tag{22}$$

In correspondence with Eq. (20), t_W tends to infinity near the nodes $f(\theta_{e0},\phi_{e0}) = 0$, provided that $\frac{\partial}{\partial E} f(\theta_{e0},\phi_{e0}) \neq 0$. Obviously, the linear combination of two functions with

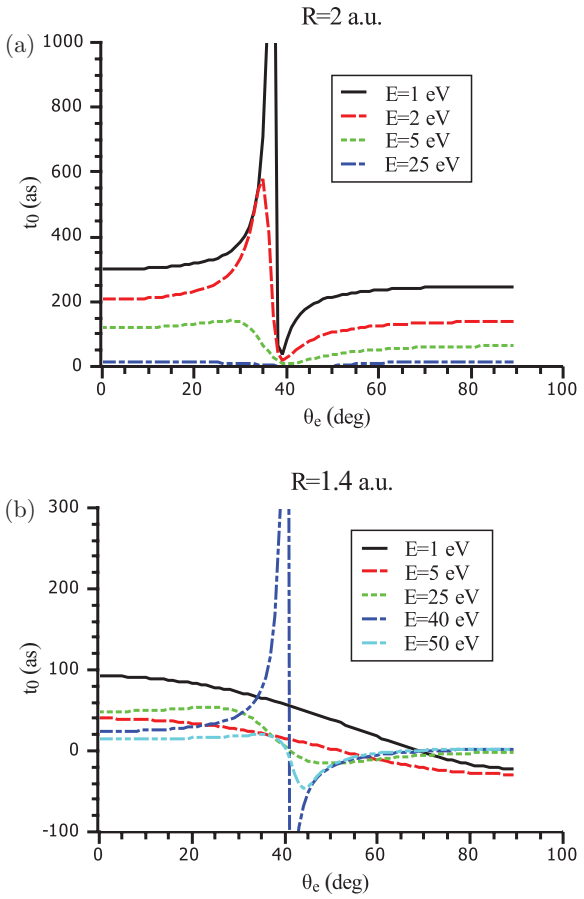

FIG. 6. (Color online) Ejection delay vs the ejection angle for the photoionization of H_2^+ in the ground state in the case of the ionizing radiation linear polarization direction $\mathbf{e} \parallel \mathbf{R}$. (a) $R = 2$ a.u.. (b) $R = 1.4$ a.u.

different positions of nodes equals zero only in two cases: (i) the phases of partial waves satisfy the condition $\delta_{30} - \delta_{10} = N\pi$, where N is an integer, and (ii) one of the expansion coefficients for the given energy turns into zero, so that the sum actually contains a single spheroidal harmonic. Figure 7 shows that the second statement is valid, i.e., that there are such values of energy ($E \sim 0$ eV at $R = 2$ a.u. and $E = 39$ eV at $R = 1.4$ a.u.) at which the amplitude for $l = 1$ turns into zero. At these energies only, Fig. 6 demonstrates the singularity of $t_0(\theta_e)$.

The situation of a partial amplitude turning into zero at a certain value of energy is commonly referred to as Cooper's minimum, in honor of J. W. Cooper, who theoretically predicted this phenomenon for the photoionization of noble gases [35]. Such a situation takes place for the molecular case. It was shown [36] that for H_2 photoionization the square modulus of the spherical p wave has a minimum at $\omega \approx 82$ eV (i.e., the energy $E \approx 66$ eV), so that in the vicinity of this energy value the contribution of the f wave is dominant.

In the case of H_2^+ ionization, considered in this section, the contribution that turns into zero comes from the spheroidal wave with the quantum number $l = 1$, rather than from the spherical p wave. The remaining wave is the spheroidal wave with $l = 3$, so it is more consistent to refer to the phenomenon as the "spheroidal Cooper's minimum."

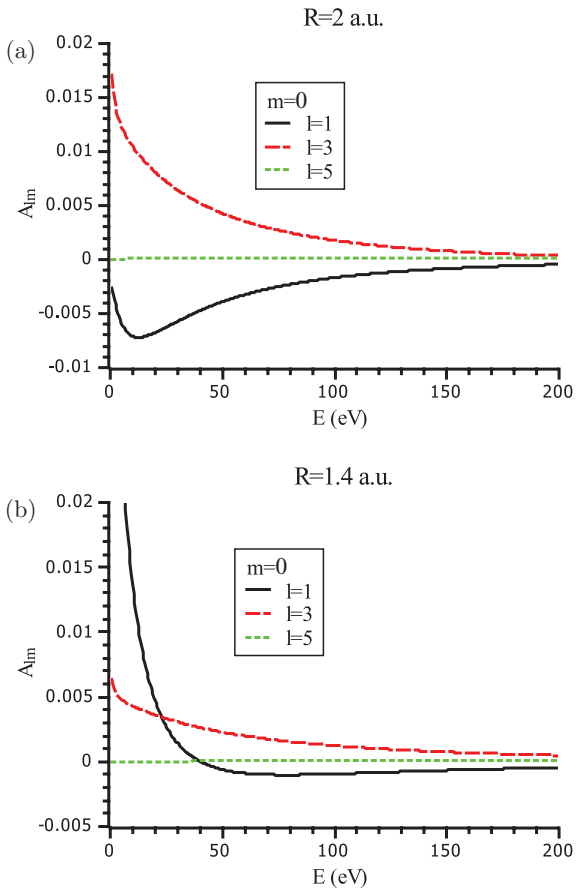

FIG. 7. (Color online) Energy dependence of partial components of the photoionization amplitude for the hydrogen molecular for $\mathbf{e} \parallel \mathbf{R}$. (a) $R = 2$ a.u. (b) $R = 1.4$ a.u. Partial amplitudes for $l = 1$ (solid line), $l = 3$ (dashed line), and $l = 5$ (dotted line) are shown.

A spheroidal harmonic can be expanded over the spherical ones [32]:

$$\Upsilon_{lm}(c,\theta,\phi) = \sum_{\ell} d_{\ell}^{lm}(c) Y_{\ell m}(\theta,\phi), \tag{23}$$

and correspondingly, the expansion Eq. (21) over spheroidal harmonics can be transformed into the expansion over the spherical ones. If $c = kR/2$ is not very large, the spheroidal harmonic Υ_{30} is rather close to the spherical one, Y_{30}; however, Υ_{30} contains also the contribution from Y_{10}, so that in the spheroidal Cooper's minimum the amplitude of the spherical p wave does not turn into zero. Moreover, since in the vicinity of Cooper's minimum the phase difference of spheroidal waves is $\delta_{30} - \delta_{10} \sim \pi/2$, the amplitude of the p wave does not turn into zero exactly at any energy, although its square modulus has a minimum near the energy of the spheroidal Cooper's minimum. This is the difference between Cooper's minima in two-center systems and in one-center ones, like noble gas atoms [10,35]. However, since Cooper's minimum for H_2^+ with the equilibrium internuclear distance $R = 2$ a.u. occurs at a very small energy of the ejected electron, and $\Upsilon_{30}(c \to 0,\theta,\phi) = Y_{30}(\theta,\phi)$, the photoionization of H_2^+ at small energies yields purely "octupole" electrons, i.e., those with $\ell = 3$.

Substitution of the expansion Eq. (22) into Eq. (20) in the vicinity of Cooper's minimum energy $E \approx E_C$, for which by definition $A_{10}(E_C) = 0$, yields

$$t_W = \frac{d\delta_{30}}{dE} + \frac{\Upsilon_{10}}{\Upsilon_{30}} \frac{A'_{10}(E_C)}{A_{30}(E_C)} \sin(\delta_{30} - \delta_{10}), \tag{24}$$

where $A'_{10}(E_C) = \frac{dA_{10}}{dE}|_{E=E_C}$. From Eq. (24) it is evident that Wigner time delay variation with the ejection angle at the energy E_C has no relation to the phase derivatives of the partial waves but depends on the the difference $\delta_{30} - \delta_{10}$ of phases themselves. As for the singularities, they arise at the ejection angles θ_e, for which the function $\Upsilon_{30}(c,\theta_e,\phi)$ possesses nodes that do not coincide with the node $\theta_e = 90^\circ$ of the function $\Upsilon_{10}(c,\theta_e,\phi)$.

In order to study the angle-independent part of t_W, let us average it over the directions of ejection:

$$\bar{t}_W = \frac{\oint t_W \sigma^{(1)} d\Omega}{\oint \sigma^{(1)} d\Omega} = \left[\sum_{lm} |f_{lm}|^2\right]^{-1} \sum_{lm} \mathrm{Im}\left(f_{lm}^* \frac{df_{lm}}{dE}\right), \tag{25}$$

where $\sigma^{(1)} = \frac{d\sigma}{d\Omega_e}$ is the ionization differential cross section and the partial amplitude is expressed as $f_{lm} = A_{lm} i^{-l} e^{i\delta_{lm}}$. In Cooper's minimum Eq. (25) yields $\bar{t}_W = \frac{d\delta_{30}}{dE}$. This apparently agrees with Fig. 8(b), demonstrating that near E_C the quantity $\bar{t}_0(E)$ has a maximum and coincides with the delay of the partial wave with $l = 3$.

Although $\bar{t}_0(E)$ is convenient for theoretical analysis, its experimental determination is a difficult problem. Using the method of attosecond streaking [11,12], one should repeat the measurement procedure many times, varying the direction of the probing radiation polarization with respect to that of ionizing radiation.

V. INTERPRETATION OF SINGULARITIES IN THE ANGULAR DISTRIBUTION OF TIME DELAY

In the previous section we determined the conditions that give rise to singularities in the angular distribution of the time delay. Now we focus our attention on their physical interpretation. Although huge values of the time delay appear in the vicinity of differential cross-section zeros, it is still possible in principle to measure the time delay. However, these large negative delays are in apparent contradiction with the causality principle, since from the formal classical viewpoint the electron seems to be ejected before the ionizing impact [20].

It is common to assume that if the molecule is affected by a laser pulse with a Gaussian envelope, and the pulse is long enough, then the momentum distribution of the electrons, ejected as a result of ionization, is also Gaussian [18]. At large distances from the center the Gaussian momentum distribution gives rise to a Gaussian wave packet in space. Following the Ehrenfest theorem, the behavior of the wave-packet center (even for non-Gaussian packets) coincides with the motion of the classical particle. But the packet center position itself depends on the shape distortions, caused by quantum effects. Therefore, it is necessary to consider the problem in terms of the wave-packet shape evolution.

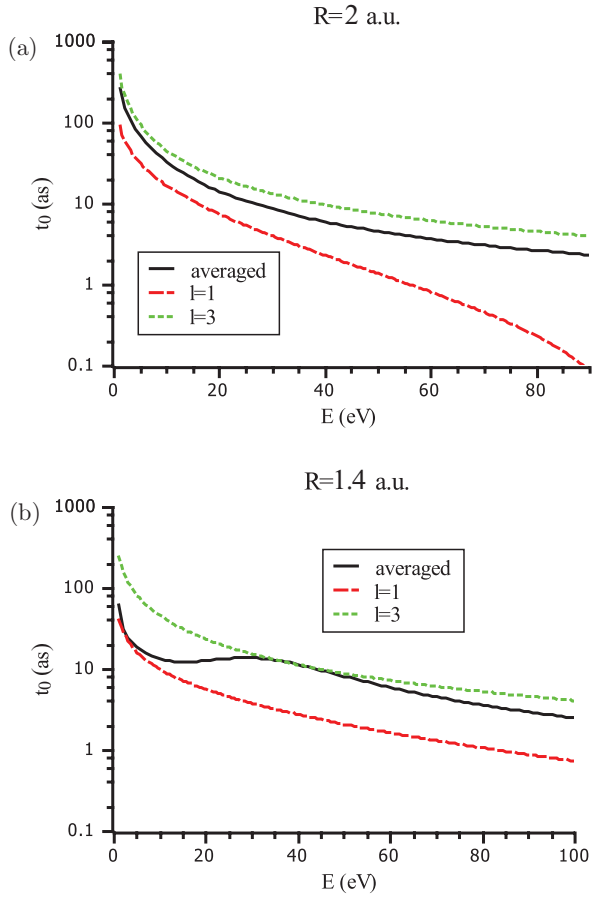

FIG. 8. (Color online) Energy dependence of the averaged delay $\bar{t}_0$ for the photoionization of H_2^+ (solid line) and the delay t_0 for partial waves with $l = 1$ (dashed line) and $l = 3$ (dotted line). (a) $R = 2$ a.u. (b) $R = 1.4$ a.u.

Let the ionizing extreme UV pulse have the Gaussian envelope function, the carrier frequency ω_0, and the duration T, so that the field strength is expressed as

$$\mathcal{E}(t) = \mathcal{E}_0 \exp\left(-\frac{t^2}{2T^2}\right)\sin\omega_0 t. \tag{26}$$

In the case of a weak ionizing field the first-order perturbation theory yields the following expression for the wave function, describing the ejected electron wave packet:

$$\psi(\mathbf{r},t) \sim \int f(k\mathbf{n})\exp\left[-\frac{w_0^2(k-k_0)^2}{2}\right]e^{ikr-iEt}dk. \tag{27}$$

Here $w_0 = k_0 T$ is the initial spatial width of the packet, $k_0 = \sqrt{2(\omega_0 - I_1)}$ is the central momentum (I_1 being the ionization potential), and $f(\mathbf{k}) = \langle \mathbf{k}|z|1\sigma_g\rangle$ is the amplitude Eq. (12) of ionization by a continuous wave having the frequency $\omega = k^2/2 + I_1$ in the first Born approximation.

Consider the dipole matrix element Eq. (22) for the energy near Cooper's minimum. From Eq. (24) it is obvious that the partial time delay determines only the general angle-independent time shift. Since we are interested in the interpretation of the second term in Eq. (24), we will assume for simplicity that the derivative of the phase is zero. Near Cooper's minimum $A_{10}(E) \simeq A'_{10}(E_C)(E - E_C) \approx A'_{10}(E_C)(k - k_C)k_C$; therefore, from Eq. (22) it follows that

$$f(\mathbf{k}) \approx -(k-k_C)k_C A'_{10}(E_C) i e^{i\delta_{10}}\Upsilon_{10}(\theta_e,\phi_e) + A_{30}(E_C) i e^{i\delta_{30}}\Upsilon_{30}(\theta_e,\phi_e). \tag{28}$$

Apparently, at the angles corresponding to zeros of the function $\Upsilon_{30}(\theta_e,\phi_e)$, the electron wave packet becomes essentially non-Gaussian. Hence, the case of Cooper's minimum requires special consideration.

The electron wave function after ionization in the k representation has the form

$$\psi(\mathbf{k}) = f(\mathbf{k})\sqrt{\frac{w_0}{\sqrt{\pi}}}\exp\left[-\frac{w_0^2(k-k_0)^2}{2}\right]. \tag{29}$$

Let us introduce the coefficients of its expansion

$$C_n = \int \varphi_n(k-k_0)\psi(\mathbf{k})dk \tag{30}$$

over the basis of functions

$$\varphi_n(k) = \sqrt{\frac{w_0}{2^n n!\sqrt{\pi}}}H_n(w_0 k)\exp\left[-\frac{w_0^2 k^2}{2}\right], \tag{31}$$

where $H_n(x)$ is the Hermite polynomial. In coordinate representation the functions in Eq. (31) describe expanding wave packets:

$$\psi_n(x,t) = \sqrt{\frac{1}{2^n n!\sqrt{\pi}w}}H_n(x/w) \times \exp\left[-\frac{x^2}{2w^2}\left(1 - it/w_0^2\right) - i\beta_n(t)\right], \tag{32}$$

where $w(t) = w_0\sqrt{1+(t/w_0^2)^2}$ is the packet width growing in time and the phase is expressed as $\beta_n(t) = (n + 1/2)\arctan(t/w_0^2) - n\pi/2$. The functions $\varphi_n(k-k_0)$ in the coordinate representation correspond to $\psi_n(x,t)\exp(ik_0 r - i\frac{k_0^2}{2}t)$. Here and below, $x = r - k_0 t$.

If the width $1/w_0$ of the packet momentum distribution is small and $f(\mathbf{k})$ has no singularities or zeros higher than the first order; thus, only the first two coefficients of the expansion, C_0 and C_1, are not small. It is easy to show that in this case the shift of the packet center of mass $\langle x\rangle = \langle r\rangle - k_0 t$ with respect to the case of uniform motion with the velocity k_0 is

$$\langle x\rangle = 2\frac{\mathrm{Re}[C_1^* C_0\langle\psi_1|x|\psi_0\rangle]}{|C_0|^2 + |C_1|^2}. \tag{33}$$

Here the dipole matrix element is expressed as

$$\langle\psi_1|x|\psi_0\rangle = \frac{w}{\sqrt{2}}e^{i(\beta_1-\beta_0)}. \tag{34}$$

Using the asymptotic expression $e^{i(\beta_1-\beta_0)} = 1 - i w_0^2/t + O(t^{-2})$, we get

$$\langle x\rangle \simeq \sqrt{2}\frac{\mathrm{Re}[C_1^* C_0]}{|C_0|^2+|C_1|^2}\frac{t}{w_0} + \sqrt{2}\frac{\mathrm{Im}[C_1^* C_0]}{|C_0|^2+|C_1|^2}w_0. \tag{35}$$

The first term in this expression grows linearly in time, thus describing the velocity shift:

$$\Delta k = \frac{d\langle x\rangle}{dt} = \frac{\sqrt{2}}{w_0}\frac{\mathrm{Re}[C_1^* C_0]}{|C_0|^2+|C_1|^2}. \tag{36}$$

This correction arises as the momentum distribution is different from Gaussian centered at $k = k_0$. Indeed, Δk turns into zero if $C_1 = 0$, the coefficient C_1 describing the deviation from the Gaussian shape.

The second term in Eq. (35) describes the delay of the packet center arrival at the point r compared with the arrival time $r/(k_0 + \Delta k)$ corresponding to the case of uniform rectilinear motion:

$$t_{\mathrm{WP}} = \frac{\langle x\rangle - \Delta k t}{k_0} = \frac{\sqrt{2}w_0}{k_0}\frac{\mathrm{Im}[C_1^* C_0]}{|C_0|^2 + |C_1|^2}. \tag{37}$$

The delay t_{WP} of the packet center of mass arises due to the temporal variation of the packet shape, i.e., actually, because of the fact that the common phases of the wave packet without a node, $\beta_0(t)$, and the packet with a node, $\beta_1(t)$, have different time dependences. The functions in Eq. (32) are solutions of the time-dependent Schrödinger equation with the Hamiltonian of a harmonic oscillator with variable frequency $\varpi(t) = 1/\sqrt{w(t)}$, obtained from the free particle equation by transformation to the time-scaled coordinate system [37,38] $x/w(t)$. The phases $\beta_n(t) = -n\pi/2 + \int_0^t \epsilon_n(t)dt$ are time integrals of the eigenenergies $\epsilon_n = (n + 1/2)\varpi$ of the harmonic oscillator with variable frequency $\varpi(t)$. We can conclude that the delay t_{WP} is a consequence of the specific quantization that arises when the free particle motion is considered in the time-scaled coordinate system.

Consider the case in which the central frequency of the ionizing laser pulse coincides with Cooper's minimum, i.e., when $k_0 = k_C$. Then,

$$C_0 = -A_{30}(E_C) i e^{i\delta_{30}} \Upsilon_{30}, \tag{38}$$

$$C_1 = \frac{1}{\sqrt{2}w_0} k_C A'_{10}(E_C) i e^{i\delta_{10}} \Upsilon_{10}. \tag{39}$$

Equation (37) at $w_0 \to \infty$ yields the expression that does not depend upon w_0 and completely coincides with the second term in Eq. (24). The shift of the central momentum at $w_0 \to \infty$:

$$\Delta k = \frac{1}{w_0^2}\frac{\Upsilon_{10}}{\Upsilon_{30}}\frac{A'_{10}(E_C)}{A_{30}(E_C)}\cos(\delta_{30} - \delta_{10}); \tag{40}$$

i.e., for $w_0 = \infty$ the velocity shift turns into zero. Near the node θ_{e0} of the angular distribution, i.e., at $\Upsilon_{30}(\theta_e \to \theta_{e0}, \phi_e) \to 0$, the wave-packet center time delay takes the form

$$t_{\mathrm{WP}} = \frac{2w_0^2}{k_C^2}\frac{A_{30}(E_C)}{A'_{10}(E_C)}\sin(\delta_{30} - \delta_{10})\frac{\Upsilon_{30}}{\Upsilon_{10}}.$$

Thus, actually, in the vicinity of the node of the cross section the time delay does not tend to infinity. On the contrary, for any final w_0 its value tends to zero or, more rigorously, to the delay of the partial spheroidal wave with $l = 1$, neglected for simplicity in the above consideration. In fact, in the vicinity of the direction $\theta_e = \theta_{e0}$ the energy spectrum of ejected electrons is double humped, which causes problems with determination of time delay, considered in [39] for Cooper's minimum of an atom.

The maxima of $|t_{\mathrm{WP}}|$ are attained at $|C_0| = |C_1|$. The maximal possible delay or advance is

$$\max_{\Omega_e} |t_{\mathrm{WP}}| = \frac{w_0}{k_0}\frac{\sin(\delta_{30} - \delta_{10})}{\sqrt{2}} = T\frac{\sin(\delta_{30} - \delta_{10})}{\sqrt{2}}; \tag{41}$$

i.e., it apparently does not exceed the uncertainty of the ionizing laser pulse arrival time. This uncertainty is equal to the pulse duration T. Thus, there is no contradiction with the causality principle.

If the laser pulse is long enough to allow manifestation of large t_{WP}, the nuclear motion cannot be neglected. This is clear not only from general considerations but also from the fact that $t_{\mathrm{WP}}(\theta_e)$ can be large only in a very close vicinity of the node θ_{e0} of the angular distribution, and the position of angular distribution nodes depends upon the internuclear distance [40]. Hence, even a minor shift of the nuclei, accumulated by the time when the ejected electron appears far enough from the residual molecular ion not to feel the variation of potential, is expected to cause a shift of the node position, sufficient to provide a considerable change of t_{WP}. Obviously, in this case the assumption of classical nuclear motion, used to determine the initial internuclear distance from KER [21], also becomes invalid.

VI. CONCLUSION

To provide a better understanding of certain features in the angular dependence of the time delay observed earlier in numerical simulations of photoionization of H_2, we reconsider the theory of ionization time delay in terms of spheroidal Coulomb wave functions. The energy dependence of the time delay is studied for partial two-center spheroidal Coulomb waves. It is shown that for the energies, coincident with those of Cooper's minimum (in which the amplitude of one of the partial waves of the ejected electron turns into zero), at angles coinciding with the nodes of the angular spheroidal function having the quantum number $l = 3$ the angular distribution of the Wigner time delay for two-center targets has singularities, in the vicinity of which the time delay takes large positive and negative values. By analyzing the dynamics of the wave packet of the ejected electron, it is shown that these singularities do not lead to violation of the causality principle, since in the process of ionizing the molecule by an external laser pulse with finite duration the real delay or advance does not exceed the duration of the laser pulse.

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