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## Comment

# Comment on ‘Time delays in molecular photoionization’

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### Abstract

In a recent article by Hockett *et al* (2016 *J. Phys. B: At. Mol. Opt. Phys.* **49** 095602), time delays arising in the context of molecular single-photon ionization are investigated from a theoretical point of view. We argue that one of the central equations given in this article is incorrect and present a reformulation that is consistent with the established treatment of angle-dependent scattering delays (Eisenbud 1948 *PhD Thesis* Princeton University; Wigner 1955 *Phys. Rev.* **98** 145–7; Smith 1960 *Phys. Rev.* **118** 349–6; Nussenzveig 1972 *Phys. Rev. D* **6** 1534–42).

In their recent article [1] investigating the spectral and angular dependence of time delays occurring during the process of molecular single-photon ionization, Hockett *et al* provide the following general expression (equation (4) in the original publication) for the time delay  $\tau_{\text{W}}^{\text{g}}(k, \theta, \phi)$  associated with the outgoing photoelectron with momentum  $k$  and emission direction described by the spherical angles  $\theta$  and  $\phi$ :

$$\tau_{\text{W}}^{\text{g}}(k, \theta, \phi) = \hbar \frac{\text{d arg} \left( \sum_{l,m} \psi_{lm}^*(k, \theta, \phi) \right)}{\text{d}\epsilon}. \quad (1)$$

In the above equation,  $\epsilon$  denotes the continuum electron energy,  $\hbar$  is the reduced Planck constant and the quantity  $\psi_{lm}$  denotes the partial waves in terms of which the continuum wave function  $\Psi_{\text{g}}$  is expanded:

$$\Psi_{\text{g}} = \sum_{lm} \psi_{lm}. \quad (2)$$

We argue that the definition given in (1), combined with the accompanying text (section 2 in the original publication) to describe the physical meaning of the quantities  $\Psi_{\text{g}}$  and  $\psi_{lm}$  (‘outgoing wavepacket’ and ‘partial wave(s)’/‘wavefunctions’, respectively) leads to a misinterpretation of the meaning of  $\tau_{\text{W}}^{\text{g}}$  that is not consistent, neither with the established interpretation of time delay phenomena [2–5] nor the recent theoretical work on photoionization delays of atomic systems (see, e.g. [6]). Following the derivation given by Wigner, the time delay  $\tau$  in molecular photoionization can be related to the group delay of the outgoing photoelectron wave

packet. This quantity is given by the energy derivative of the complex photoionization amplitude  $f(\epsilon)$ :

$$\tau = \frac{\text{d}}{\text{d}\epsilon} \arg(f(\epsilon)) = \text{Im} \left\{ \frac{1}{f(\epsilon)} \frac{\text{d}f}{\text{d}\epsilon} \right\}. \quad (3)$$

A convenient practical route towards calculating  $f(\epsilon)$  from first principles using the single-photon perturbation framework employed in [1] consists in performing a partial-wave expansion in spherical waves:

$$f(\epsilon) = \sqrt{\frac{4\pi}{3}} \sum_{l,m} \langle \psi_{lm} | r | \psi_0 \rangle Y_{lm}^*(\Omega_{\hat{k}}) Y_{1\nu}^*(\Omega_{\hat{\nu}}), \quad (4)$$

where the quantities  $Y_{lm}$  denote the spherical harmonic functions describing the orientation of the outgoing photoelectron vector ( $\Omega_{\hat{k}} = (\theta, \phi)$ ) and the photon polarization ( $\Omega_{\hat{\nu}}$ ) directions. The exact form of the above equation may vary depending on the normalization conditions imposed on the continuum wave functions or the gauge (length versus velocity). Differentiating the phase of  $f(\epsilon)$  with respect to  $\epsilon$ , we obtain for the time delay  $\tau$ :

$$\tau(k, \theta, \phi, \Omega_{\hat{\nu}}) = \hbar \frac{\text{d}}{\text{d}\epsilon} \arg \left( \sqrt{\frac{4\pi}{3}} \sum_{l,m} \langle \psi_{lm} | r | \psi_0 \rangle \times Y_{lm}^*(\Omega_{\hat{k}}) Y_{1\nu}^*(\Omega_{\hat{\nu}}) \right). \quad (5)$$

This definition of the photoionization delay has been given and illustrated in our recent publications [7–9]. We emphasize that

expression (5) contains two differences as compared to (1), namely the presence of dipole matrix elements  $\langle \psi_{lm} | r_{\hat{\nu}} | \psi_0 \rangle$  between the continuum waves and the initial state  $\psi_0$  and the angular factors.

Since Hockett *et al* limit their analysis to the cases of molecules aligned parallel and perpendicular to the polarization direction of the ionizing radiation, we assume in what follows a fixed value of  $\Omega_{\hat{\nu}}$  and suppress the dependence on the index  $\hat{\nu}$  in the remaining part of the text. Following the definition given in (1) (and simultaneously denoting the dependence on  $k$  explicitly), the quantity  $\tau_W^g(k, \theta, \phi)$  can be written as:

$$\begin{aligned} \tau_W^g(k, \theta, \phi) &= \hbar \frac{d}{d\epsilon} \arg \left\{ \sum_{lm} \psi_{lm}^*(r, \mathbf{k}) \right\} \\ &= \hbar \frac{d}{d\epsilon} \arg \left\{ \sum_{lm} \psi_{lm}^*(r, k) Y_{lm}^*(\theta, \phi) \right\}, \end{aligned} \quad (6)$$

while the time delay defined by equation (5) has the form:

$$\tau(k, \theta, \phi) = \hbar \frac{d}{d\epsilon} \arg \left( \sqrt{\frac{4\pi}{3}} \sum_{lm} \langle \psi_{lm}(k) | r | \psi_0 \rangle Y_{lm}^*(\theta, \phi) \right). \quad (7)$$

In the special case of a non-degenerate, real-valued initial-state function, one finds

$$\arg(\langle \psi_{lm}(k) | r | \psi_0 \rangle) = \arg(\psi_{lm}^*(r, k)). \quad (8)$$

Therefore, the delays defined in equations (6) and (7) only become equivalent in situations where a single partial wave (single value of  $l$ ) contributes to the photoionization process, which is practically never the case in molecular photoionization. In general, the definitions given in equations (6) and (7) involve taking the argument of a sum of complex terms,

which, albeit having equal phases, in general possess different amplitudes. Thus, the final results obtained from equations (6) and (7) will not be equivalent in general.

The discrepancy between equations (1) and (5) can however be resolved by replacing the definition of  $\psi_{lm}$  as continuum partial-wave *functions* with the definition of  $\psi_{lm}$  as partial-wave *matrix elements*. This is apparently what the authors of [1] have done in their numerical illustrations of equation (1).

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