

Response to *Comment on “Time delays in molecular photoionization”*: Extended Discussion & Technical Notes

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In a comment on our article *Time delays in molecular photoionization* [1], Baykusheva & Wörner reproduce canonical scattering theory, and assert that our results are inconsistent with this well-established theory [2]. We absolutely refute this assertion and the spirit of the comment, although we do agree with Baykusheva & Wörner that the textbook theory is correct. In a short response, *Response to Comment on “Time delays in molecular photoionization”* [3], we have already provided a clear rebuttal of the comment, but gave no technical details. In this fuller response we extend those brief comments in the spirit of completeness and clarity, and provide three clear rebuttals to Baykusheva & Wörner based on (1) logical fallacy (category error), (2) theoretical details of the original article, (3) textural content of the original article. In particular, rebuttal (1) clearly and trivially points to the fact that there is no issue here whatsoever, with recourse to theoretical details barely required to demonstrate this, as outlined in the short version of our response. Our numerical results are correct and reproduce known physical phenomena, as discussed in the original article hence, as careful readers will recognise, the formalism used is canonical scattering theory, and cannot be anything other. In fact, there is no new fundamental physics here to dispute whatsoever, and nor was this the *raison d’être* of the original article. Additionally, rebuttal (2) provides the opportunity to discuss, at length, some of these textbook aspects of photoionization theory, and we hope this discussion might be of service to new researchers entering this challenging field.

Preamble

In our article *Time delays in molecular photoionization* [1], we discussed Wigner time-delays within the context of canonical scattering theory. More specifically, we discussed the historic background and physical concepts (sect. 1), then sketched an outline of canonical theory in a wavepacket notation (sect. 2), with the aim of providing a physically-intuitive and pedagogical picture for the general reader; we then proceeded to illustrate the results of numerical methods making use of computational tools developed by the scattering and photoionization communities and, finally, to discuss recent experimental methods which have the potential to measure angle-resolved Wigner delays. Our aim, therefore, was to present and discuss our methodology and numerical results in very general terms to a general audience; to discuss the core scattering physics; and to demonstrate that Wigner delays can now be computed readily with modest computational resources using established and user-friendly tools, with only minimal post-processing of the results required.

In this case, we saw both the potential interest for a general audience in the methodology and paradigmatic results (particularly in the attosecond community, where there has been much recent interest in this topic), but were also aware of the possibility that an unbalanced presentation may be viewed as too technical – hence unsuitable for a general physics audience – or may be perceived to lack novelty due to the use of existing techniques from scattering theory, even though these techniques have never before been applied to the computation of Wigner delays (to the best of our knowledge). In this light, we sought to strike a balanced presentation between the well-known concepts, the application of numerical methods within this framework, and a discussion of the results so obtained. This is, of course, standard practice in writing a manuscript, in which one must always seek to balance the presentation of new results and developments with background/prerequisite fundamentals, in a manner which best serves the target reader. Textbook results were, therefore, not reproduced in detail, but the focus was placed on general concepts, and how results for Wigner delays in the case of molecular photoionization can now be obtained from well-established numerical methods, and illustrations of such results for paradigmatic cases. This does, of course, place the onus on the reader to follow-up with references if they wish to improve their background knowledge. To balance this somewhat, additional information was provided in supplementary documents and data files for the interested or expert reader (available online via Figshare at <http://dx.doi.org/10.6084/m9.figshare.2007486>), which more explicitly detailed the numerical methods used, and their specification within the usual photoionization theory formalism. The raw numerical results were also provided directly, for researchers wishing to work further with this material. The original referees of the article enjoyed this presentation, and saw the results as useful for the community.

However, it seems that, perhaps lacking this context, and perhaps unaware of the supplementary documentation, confusion has arisen, leading Baykusheva & Wörner to the conclusion that the standard fundamental theories underlying our numerical computations

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were somehow both non-standard and incorrect. Since we wish to clear-up any such confusion, we present here three categorical rebuttals to Baykusheva & Wörner's specific assertion that "... the definition given in (1) is not consistent, neither with the established interpretation of time delay phenomena [2, 3, 4, 5] nor the recent theoretical work on photoionization delays of atomic systems (see, e.g. [6])." [2].

Specifically, our rebuttals are categorised as follows:

1. **Logical fallacy (category error):** while we hope that Baykusheva & Wörner's technical argument is due purely to an issue of notation and presentation with our original manuscript, after careful reading of their comment it seems quite probable to us that the spirit of the challenge is, in fact, rooted in a category error (*vide infra*). This seems to be the case since it is trivial to demonstrate the logical fallacy in their assertion, which appeared to be made in earnest. Since this argument does not rely on any fundamental knowledge of scattering theory or photoionization physics, and is a simple application of logic, we present this first as a robust rebuttal to Baykusheva & Wörner's comment, and most readers will find this sufficient to dispense with the issue. The short "official" response to Baykusheva & Wörner's comment was based on this analysis [3].
2. **Formalism:** technical details of the original article, discussion of the formalism therein, and extensions providing explicit derivations for otherwise implicit definitions. In the sense of completeness and transparency, we include technical details (further discussion and derivations), as another clear rebuttal of Baykusheva & Wörner's technical argument, and in the hope of alleviating any possibility of notational confusion with the original manuscript.
3. **Textural content of the original article:** a range of quotes from the manuscript illustrating statements at odds with Baykusheva & Wörner's assertions. Again, we include this for completeness, although it will not be of interest to most readers.

Since it seems to us that (1) is a rather serious issue, we also take the opportunity to discuss, at length, some additional aspects of photoionization theory, including tutorial examples and paedagogy, and classic papers on the topics, which we hope will serve as additional, useful material for researchers struggling with the complex, and somewhat inaccessible, topic of molecular photoionization physics.

Note added Jan. 17: Following this comment, and review by J. Phys. B, Baykusheva & Wörner issued a slightly updated comment. The original comment remains on the arXiv (1611.09352v1, <https://arxiv.org/abs/1611.09352v1>), as does our original response (1612.00481v1, <https://arxiv.org/abs/1612.00481v1>). Their final comment, and our brief all-author response, will be published in J. Phys. B [2, 3], the latter including reference to this longer reply for interested readers. We note that the choice of publication of the comment and response was down to the editors and reviewers at J. Phys. B, who decided that the comment and both responses formed "extremely valuable additions to the literature" and, in particular, "the second section [technical response] to the rebuttal is necessary, and more helpful to the general reader". However, due to the separate author list on this longer response, and J. Phys. B's 'single response per comment' publication policy, this longer response will not be published directly in J. Phys. B, and becomes (effectively) peer-reviewed online Supplementary Material to the official response, which will be hosted on the arXiv (1612.00481, <https://arxiv.org/abs/1612.00481v1>) and Figshare (DOI: 10.6084/m9.figshare.2007486, <http://dx.doi.org/10.6084/m9.figshare.2007486>).

I. LOGICAL FALLACY

The core scientific assertion of Baykusheva & Wörner's comment is that our formalism does not include the dipole matrix element and full angular dependence of the scattering wave, as defined in canonical energy-domain scattering theory. They provide a form of the standard partial wave expansion for photoionization (eqn. 4 in their comment, further technical details are provided in the following section), and the Wigner delay τ :

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

$$\tau = \frac{d}{d\epsilon} \arg(f(\epsilon)) \quad (2)$$

Baykusheva & Wörner conclude their comment with "Although the spatial contribution from the phase of the spherical harmonics is discussed in the original article, the dependence on the matrix elements has been neglected." In other words, following their canonical eqn. 4 (eqn. 1 herein), they believe our results to be based on continuum functions of the form:

$$f(\epsilon) = \sqrt{\frac{4\pi}{3}} \sum_{l,m} Y_{lm}(\Omega_{\hat{k}}) Y_{1\nu}(\Omega_{\hat{\nu}}) \quad (3)$$

or, possibly,

$$f(\epsilon) = \sqrt{\frac{4\pi}{3}} \sum_{l,m} Y_{lm}(\Omega_{\hat{k}}) \quad (4)$$

depending on whether one regards the photon angular momentum term to be part of the omitted dipole matrix element $\langle \psi_{lm} | r_{\nu} | \psi_0 \rangle$.

Without any detailed knowledge of fundamental scattering or photoionization physics, one can simply apply logic and physical intuition to see that this absolutely cannot be the case: without the requisite matrix elements there would be no energy dependence to our numerical results, as shown explicitly in eqn. 3, hence the Wigner delay would show no energy dependence. To be even clearer here: *the dipole matrix elements define the expansion coefficients for the partial waves*. If these expansion coefficients are ignored, one is simply left with an arbitrary sum over a set of states $\{l, m\}$ with unknown magnitudes and phases, thus selected, presumably, at random by the researcher, and with a fixed phase relationship defined purely as a function of angle by the form of the spherical harmonics, i.e.

$$\arg[f(\epsilon)] \rightarrow \arg\left[\sum_{l,m} Y_{l,m}(\theta, \phi)\right] \quad (5)$$

This is absolutely contrary to our results: in figures 1 & 2 clear angular and energy dependencies are seen in the results, which show both τ_w and the photoionization cross-sections, and this complex behaviour was the main focus of the original manuscript. Furthermore, the Supplementary Materials include full plots, and data, of the energy-dependent matrix elements used in the calculations.

Yet another form of this statement may be made in the framework of basic scattering theory: without a radial part to the solution, there can be no radial asymptote, hence no defined phase to the wavefunction in the asymptotic (free particle) limit. To restate again more generally: the well-known phenomena of scattering physics and photoionization physics (i.e. radial and angular dependence of the outgoing scattering wave, a defined asymptotic phase, and the energy dependence of the angular interference pattern of the partial waves etc. etc.), also observed in our results for the specific case of Wigner delays, *could not be observed without inclusion of the energy-dependent (radial) part of the problem*. Throughout our manuscript, we discuss our results within the expected phenomena of molecular photoionization physics, including polarization dependence, photoionization cross-sections (including the features of shape resonances and Cooper minima) and the underlying scattering physics. None of this physics would be present in results based on eqn. 3. Sections 3 and 4 of our manuscript would be entirely redundant in this case. With apologies to Baykusheva & Wörner, since we intend no embarrassment, we have to remark that, on reflection, we are therefore rather surprised by their assertion, which appears to be a severe, if earnest, category error rather than simple notational confusion.

In fairness to Baykusheva & Wörner, one could posit a hypothetical case where the scattering physics was correctly treated, and continuum wavefunctions computed, but no dipole integrals taken into account. In this case, there would be no logical fallacy in their argument: the calculations would correctly include the scattering physics, but omit the photoionization physics. Indeed, examples of such continuum wavefunctions were plotted in fig. 4 of the manuscript to provide physical insight, and the computation of the scattering solutions is a prerequisite for the calculation of the dipole matrix elements, since they are overlap integrals between the initial and final state wavefunctions. In this hypothetical case, there would be some energy and angular dependence of the continuum functions, but the photoionization physics would be missing, hence no coupling of the continuum and bound state wavefunctions incorporated, and no dipole overlap integrals between these states would be computed. More precisely, this case would yield correct continuum states for scattering, but not dipole-prepared continuum waves corresponding to photoionization, and there would be no difference to the continuum state as a function of electric-field polarization in the molecular frame, or ionizing orbital. This case, however, would not correspond to the to the case Baykusheva & Wörner posit, i.e. eqn. 3 above, which yields a purely angular expansion.

II. FORMALISM

Let us return to the core scientific assertion of Baykusheva & Wörner's comment: that our formalism does not include the dipole matrix element and full angular dependence of the scattering wave, as defined in canonical energy-domain scattering theory. As per the above, they provide a form of the standard partial wave expansion for photoionization as (eqn. 4 in their comment):

$$f(\epsilon) = \sqrt{\frac{4\pi}{3}} \sum_{l,m} \langle \psi_{lm} | r_{\nu} | \psi_0 \rangle Y_{lm}(\Omega_{\hat{k}}) Y_{1\nu}(\Omega_{\hat{\nu}}) \quad (6)$$

Here, their notation indicates that the scattering wave $f(\epsilon)$ is defined by the matrix element $\langle \psi_{lm} | r_{\nu} | \psi_0 \rangle$, and the product of two spherical harmonics $Y_{lm}(\Omega_{\hat{k}})$ and $Y_{1\nu}(\Omega_{\hat{\nu}})$. In this form, the matrix element is, strictly speaking the generic dipole matrix element,

of the form $\langle \psi_f | \mathbf{r} \cdot \mathbf{E} | \psi_i \rangle$, written specifically for an initial state ψ_0 , and with both the dipole operator and the final state expanded in spherical harmonics, to allow separation of the radial and angular (geometric) parts of the scattering state, i.e.

$$\langle \psi_f | \mathbf{r} \cdot \mathbf{E} | \psi_i \rangle = \langle \psi_f | r_\nu | \psi_0 \rangle Y_{1\nu}(\Omega_{\hat{\nu}}) = \sum_{lm} \langle \psi_{lm} | r_\nu | \psi_0 \rangle Y_{1\nu}(\Omega_{\hat{\nu}}) Y_{lm}(\Omega_{\hat{k}}) \quad (7)$$

Here the matrix element defines a purely radial integral over the initial and final state wavefunction, coupled by the radial part of the dipole operator - as such this is often termed the *radial integral* or *radial matrix element* in the literature or, more generically, the *dipole or photoionization matrix element* (although this may refer to the full matrix element or the radial matrix element). If one is to be precise, this expansion assumes a single electron system (there is no residual ion included in the final state) or, equivalently, a single active electron. There is also an assumption of a single polarization geometry, defined by the coordinates $\Omega_{\hat{\nu}}$, resulting in an absorption of a single photon with one unit of angular momentum, and projection ν into the reference frame, implicitly assumed to be the molecular axis here. To be pedantic, since no angular integrations are defined, this wavefunction is more completely labelled as $f(\epsilon, \Omega_{\hat{k}}; \Omega_{\hat{\nu}})$, fully labelling the functional dependence on energy and angle, for a specific polarization geometry. With these stipulations, this equation indeed defines a valid scattering solution resulting from a dipole interaction.

It is of note that this type of solution is absolutely standard, has long been in textbooks [4] and in the literature, and has been written for many different sets of assumptions and with different notations. Particularly notable and clear derivations, for the specific cases of atomic and molecular photoionization, have been presented by Zare and colleagues [5–7], and Dill [8]; more recent works have also provided clear derivations in cases including molecular dynamics [9, 10], aligned molecular distributions [10, 11] and for a computationally-tractable simple model [12]. For clarity, we note that the core photoionization physics here is identical to the case of photoelectron angular distributions (PADs), in which the partial wave interferences are manifested in the angle and energy-dependent photoelectron yields. One of the current authors has been working in this field for almost a decade and has built significant expertise in this area; see, for example, refs. [13–18].

Throughout our manuscript we are clear on the use of exactly this standard formalism for our work but, since our aim was not to reproduce textbook materials, the notation was simplified to an effective partial wave expansion, vis.:

$$\Psi_g = \sum_{lm} \psi_{lm} \quad (8)$$

as given at the beginning of sect. 2. In this case, the notation is suppressed to a simple set of partial wavefunctions ψ , with l, m labels, to emphasize the core fundamentals of the scattering state - namely that it is comprised of a set of partial waves, and different angular momentum states will contribute and interfere (further discussion of this notational choice is provided below). Later in the article, in defining the Wigner delays, the same generic partial wavefunction is more explicitly labeled as $\psi_{lm}^*(k, \theta, \phi)$. In the main article we did not, however, explicitly define this wavefunction with a full partial wave expansion showing the constituent parts of the photoionization solution, although the contributing factors were discussed, including scattering phases, dipole integrals and so forth (again, see below for further discussion), as well as references to various articles on photoionization and scattering theory.

However, recognising that the interested or expert reader may wish to confirm the formalism used, or their general understanding of the physics, we did include further discussion in the Supplementary Material (included here as an appendix for completeness), in particular the following equations:

$$\Psi(\mathbf{r}) = \sum_{lm} A_l \chi_l(r) Y_{lm}(\theta, \phi) = \sum_{lm} \psi_{lm}(\mathbf{r}) \quad (9)$$

which defines a generic scattering wave expansion, with partial waves given as $\psi_{lm}(\mathbf{r})$; and for the specific case of photoionization:

$$d(E) = \langle \Phi_f(\mathbf{r}); \Psi(\mathbf{r}) | \hat{\mu} \cdot \mathbf{E} | \Phi_i(\mathbf{r}) \rangle \quad (10)$$

$$\Psi(E, \theta, \phi) = \sum_{lm} d_{l,m}(E) Y_{lm}(\theta, \phi) \quad (11)$$

which defines a general dipole matrix element $d(E)$, and the photoionization wavefunction $\Psi(E, \theta, \phi)$ as an expansion in spherical harmonics, with coefficients defined by the dipole matrix elements $d_{l,m}(E)$. We did not provide a full derivation here, but plugging $\Psi(\mathbf{r})$ into the form of $d(E)$, and solving analytically for a specific polarization geometry (with the dipole operator expanded as angular momentum coupling terms - see, for example, [5, 8]), will provide a full photoionization solution. In this case, one can still write a generic partial wave expansion, as per 8, e.g.

$$\Psi(E, \theta, \phi) = \sum_{lm} d_{l,m}(E) Y_{lm}(\theta, \phi) = \sum_{lm} \psi_{lm}(E, \theta, \phi) \quad (12)$$

where the partial wavefunction is explicitly a function of energy and angle, but the dependence on the dipole integrals is implicit. Again, this is perfectly standard notation.

Finally, and more specifically, we included the formalism provided by the authors of ePolyScat, which defines the numerical computations reported in the manuscript (ref. [19]):

$$I_{l,m,\mu}^{p_i \mu_i, p_f \mu_f}(E) = \langle \Psi_i^{p_i, \mu_i} | \hat{d}_\mu | \Psi_f^{p_f, \mu_f} \varphi_{klm}^{(-)} \rangle \quad (13)$$

$$T_{\mu_0}^{p_i \mu_i, p_f \mu_f}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}}) = \sum_{l,m,\mu} I_{l,m,\mu}^{p_i \mu_i, p_f \mu_f}(E) Y_{lm}^*(\theta_{\hat{k}}, \phi_{\hat{k}}) D_{\mu, -\mu_0}^1(R_{\hat{n}}) \quad (14)$$

Full details of the notation are given in the original Supplementary Material, but suffice to note here that, structurally, this formalism is again - fundamentally - canonical scattering theory, with a partial wave expansion applied to the case of photoionization. In the ePolyScat case, the equations are further defined by point group symmetries (with the matrix elements symmetrized over sets of spherical harmonics as appropriate), and include a Wigner rotation matrix element for the polarization geometry, thus allowing any set of Euler angles to define this physical parameter. The radial matrix elements denoted $I_{l,m,\mu}^{p_i \mu_i, p_f \mu_f}(E)$ are output by the ePolyScat calculations, and post-processed according to eqn. 14, the Wigner delay is then calculated in the standard manner (see below).

To belabour the point - all of these formalisms are effectively identical, as far as the fundamental physics is concerned, and within a given set of approximations. There is no new physics here, and fundamental results of this type have been well-established since the 1950s in general, and since the 1960s and early 1970s for some of the specific photoionization cases. Baykusheva & Wörner comment that “We argue that the denition given in (1) [our original manuscript] is not consistent, neither with the established interpretation of time delay phenomena [2, 3, 4, 5] nor the recent theoretical work on photoionization delays of atomic systems (see, e.g. [6]).” In fact, notational differences aside, these various forms of the photoionization matrix element, the resultant scattered wave, and the total (asymptotic) phase, are essentially identical. Therefore, the phase content of the final wavefunction is the same, and will provide the same results for the Wigner delay. These results are absolutely canonical, and absolutely consistent with both the established interpretations of time delay phenomena and the recent work cited by Baykusheva & Wörner. For a more thorough touchstone review, which includes time delays for a range of types of scattering problem, including wavepackets, we refer the reader to ref. [20]. For a more thorough review of scattering theory, including various distinct energy and time-domain (wavepacket) frameworks, and the equivalence of the phase information of same, see ref. [21].

In practice, it was effectively the final flavour of these formalisms that was applied in the numerical calculations, which made use of ePolyScat results, as described in sect. 3.A. of the original manuscript (emphasis added):

“Continuum wavefunctions and *dipole matrix elements* were computed with ePolyScat, for the highest-lying σ -orbitals in both cases, for linearly polarized ionizing radiation in both parallel and perpendicular geometries, and for photoelectron energies from 1 to 45 eV. The *phase information from the raw matrix elements*, expressed in terms of angular momentum channels, provides the full scattering phase-shift, and application of eqn. 3 provides τ_w for each channel. Similarly, eqn. 4 provides the group, or photoelectron wavepacket, delay. In the calculations, *radial integrals* are evaluated for $r_{max} = 10 \text{ \AA}$, defining an effective range to the interaction at which the total phase (hence delay) is defined. By calculating the *photoionization matrix elements* for a range of photoelectron energies, the energy dependence of the process can be mapped out, and the complete dependence of the Wigner delay $\tau_w(k, \theta, \phi)$ obtained.”

Again, although no formalism is given explicitly here, we believe that most readers will follow the clear content and logic of the text.

To be yet more explicit, one can write the Wigner delay for this formalism, starting from the final simplified form given in the original manuscript and substituting in the full expression for the final state, as follows:

$$\tau_w^g(k, \theta, \phi) = \hbar \frac{d \arg(\sum_{l,m} \psi_{lm}^*(k, \theta, \phi))}{d\epsilon} \quad (15)$$

$$\rightarrow \tau_{w, \mu_0}^{g, p_i \mu_i, p_f \mu_f}(\epsilon, \theta_{\hat{k}}, \phi_{\hat{k}}; R_{\hat{n}}) = \hbar \frac{d}{d\epsilon} \arg \left(\sum_{l,m,\mu} I_{l,m,\mu}^{p_i \mu_i, p_f \mu_f}(\epsilon) Y_{lm}^*(\theta_{\hat{k}}, \phi_{\hat{k}}) D_{\mu, -\mu_0}^1(R_{\hat{n}}) \right) \quad (16)$$

In this form, the unsummed indicies from the ePolyScat results (which pertain to the specific ionization channel(s) present) remain explicit, the results are further labelled to correspond to a specific polarization geometry, as defined by the set of Euler angles $R_{\hat{n}}$,

and incident photon projection in the lab. frame (μ_0). For clarity, the energy dependence has been labelled with ϵ , instead of denoted by the photoelectron momentum k . Additional normalization factors are included within $I_{l,m,\mu}^{P_i\mu_i, P_f\mu_f}(\epsilon)$. Although this form appears complicated, we note that we have significant experience with the use of ePolyScat and post-processing of the results, and recently released the first version of a software suite, ePSproc, for such purposes. This software evolved from codes developed over a number of years, and carefully tested both in multiple applications. For the ePSproc release, the code was further tested against benchmark results provided by the authors of ePolyScat, for the computation of molecular frame photoelectron angular distributions - an almost identical problem to that discussed herein; further details, including the software, examples and documentation, may be found in refs. [22, 23].

The Wigner delays given here can be compared with eqns. (3) & (5) of Baykusheva & Wörner - again, canonical results - given in their notation as:

$$\tau = \frac{d}{d\epsilon} \arg(f(\epsilon)) \quad (17)$$

$$\tau(k, \theta, \phi, \Omega_{\hat{\nu}}) = \hbar \frac{d}{d\epsilon} \arg \left(\sqrt{\frac{4\pi}{3}} \sum_{l,m} \langle \psi_{lm} | r_{\nu} | \psi_0 \rangle Y_{lm}(\Omega_{\hat{k}}) Y_{1\nu}(\Omega_{\hat{\nu}}) \right) \quad (18)$$

where $f(\epsilon)$, as defined in eqn. 6, has been explicitly expanded in the full form. Again, this is seen to be functionally identical (apart from some assumptions and notational differences) to our formalism. It is, again, an absolutely standard result.

Note added Jan. 2017: Following this response, Baykusheva & Wörner provided a slightly updated comment, with additional eqns. 6 - 8. Specifically, they provide forms of eqn. 15 and 18 herein, effectively asserting again, but more categorically, that:

$$f(\epsilon) \neq \Psi_g \quad (19)$$

where $f(\epsilon)$ is the general scattering function in their notation, while Ψ_g is the generic continuum wavefunction in our notation. This is a more specific version of their original argument, but the core thrust is unchanged and again, as detailed above, we stress that these quantities are essentially identical. This notational misunderstanding is further obfuscated by their new discussion around their eqn. 8:

“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 Eqs. (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 eq. (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 eq. (6) and (7) will not be equivalent in general.”

Again, this, effectively, just another statement of eqn. 19, apparently resulting from basic notational misunderstanding. However, rather than addressing the original fallacy of the comment, this additional material merely serves to create further knots and confusion, since it posits some special case where the formalisms are identical, thus implying they are otherwise distinct, and the use of an apparently technical argument in this manner serves to provide the patina of physical legitimacy to the comment, despite a complete lack of physical foundation. Finally, Baykusheva & Wörner state:

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

This is again a statement founded on profound misunderstanding, namely that the dipole-prepared continuum wavefunction does not result from photoionization. The dipole-prepared continuum wavefunction absolutely contains the dipole matrix elements (as defined in, e.g. eqns. 9 - 11 herein), as it must since these provide the amplitudes and phases for the dipole coupling of the initial state and the continuum state(s); see discussion in Sect. 1. (However, Baykusheva & Wörner are correct on one point - this is indeed what was done in our numerical calculations, since it is the correct approach.)

Indeed, it seems to us, that the driving force here is simply to publish and claim originality. Again, we can clarify - as detailed above - that all of these notations are equivalent, and there is no issue here whatsoever, or at least nothing beyond basic physical misunderstandings. Again, we refer the interested reader who wishes to delve into the full textbook level of detail on this topic, to ref. [21] for a thorough and careful discussion of scattering physics in both stationary state (energy domain) and wavepacket (time domain) forms. Again, we remark that there is no new physics here, only new misunderstandings, wilful or otherwise.

III. TEXTURAL SPECIFICS

Although the above discussions are more than sufficient to dispense with Baykusheva & Wörner's contention, in the spirit of completeness and transparent discussion, we note here some additional points from our manuscript which also attest to the aims and content of the work. As noted above, throughout our manuscript we are clear on the use of a standard photoionization formalism for our work, and discussed this in a time-domain (wavepacket) picture, which is formally equivalent to the more usual energy-domain formalism. In particular:

- As stated in the introduction, in reference to scattering phases: "These results are most simply derived in a stationary state (energy-domain) picture of scattering, but a wavepacket (time-domain) treatment yields the same essential features [21]. Hence, in a time-domain picture of photoionization, the scattering phase-shift and associated time delay can be viewed as a group delay of the outgoing photoelectron wavepacket, born at a time t_0 within the ionizing laser pulse."
- Also from the introduction: "More traditional scattering theory approaches are usually time-independent and most suited to the weak field regime, hence are appropriate for the consideration of the intrinsic Wigner delay of the scattering system. Such approaches often use a *partial-wave* formalism, which allows separation into "geometric" and "dynamical" parts. In this case much progress can be made analytically, and a deep physical insight into the characteristics of the scattering can be gained (see, for example, ref. [8]). However, to obtain a complete solution to a complex scattering problem numerical methods are still ultimately needed for the dynamical part, and a specific formalism for the scattering system of interest is usually constructed in order to yield tractable equations (see, for example, refs. [24, 25]); solving molecular scattering problems is therefore non-trivial for even the simplest cases. This problem can, however, be addressed via the use of variational techniques to solve the numerical part of the problem [26], allowing for a methodology which retains the full physical insights of scattering theory and the generality of fully-numerical approaches, but at a significantly lower computational cost. In this work, we investigate Wigner delays from molecular ionization based on this general approach."

- The use of a time-domain formalism allows for a physically intuitive picture of the problem (see discussion in ref. [27] for example) and, as detailed in the canonical textbook by Rodberg and Taylor (ref. [21] as above), is formally identical. Rodberg and Taylor discuss this at length, and present numerous energy and time-domain derivations of canonical scattering theory, and the interested reader is referred to that seminal text for details.

- Many other authors have used a similar formalism, as pointed out at the start of sect. 2: "As discussed by Wigner [28], Smith [29] and, more recently, in some depth by various authors [20, 30, 31], the phase of the scattering wavefunction can be associated with a time delay of the outgoing wavepacket, Ψ_g . In a partial-wave decomposition, Ψ_g is expressed as a coherent sum over partial-waves, $\Psi_g = \sum_{lm} \psi_{lm}$. Here each component is defined by the quantum numbers (l, m) , the electronic orbital angular momentum and its projection onto a given quantization axis respectively, and each (l, m) pair defines a partial-wave scattering channel."

"Here η_g represents the total (group) scattering phase, determined from Ψ_g , hence from the coherent summation over the partial-wave channels."

- The dipole matrix elements (radial integrals) can be determined numerically from ePolyScat, as discussed in sect. 3.1: "The phase information from the raw matrix elements, expressed in terms of angular momentum channels, provides the full scattering phase-shift, and application of eqn. 3 provides τ_w for each channel. Similarly, eqn. 4 provides the group, or photoelectron wavepacket, delay. In the calculations, radial integrals are evaluated for $r_{max} = 10 \text{ \AA}$, defining an effective range to the interaction at which the total phase (hence delay) is defined. By calculating the photoionization matrix elements for a range of photoelectron energies, the energy dependence of the process can be mapped out, and the complete dependence of the Wigner delay $\tau_w(k, \theta, \phi)$ obtained.

In the following, we present and discuss these results for the general reader. Supplementary materials, including additional technical details of the results, e.g. channel-resolved dipole matrix elements, which may be of interest to some readers, are available online via Figshare at <http://dx.doi.org/10.6084/m9.figshare.2007486>."

- The formalism for the ePolyScat results and photoionization matrix elements referred to above was given more explicitly in the Supp. Mat., wherein the details of the scattering calculations and results obtained from ePolyScat are discussed. The details of this discussion have already been sketched out above, and are also reproduced below for completeness. In this case, the dipole matrix element - equivalent to the term $\langle \psi_{lm} | r | \psi_0 \rangle Y_{1\nu}(\Omega_\nu)$ given by Baykusheva & Wörner - is defined as $d(E)$, and the full asymptotic wavefunction is then given by $\Psi(E, \theta, \phi) = \sum_{lm} d_{l,m}(E) Y_{lm}(\theta, \phi)$. Note that the matrix element includes integration over the radial coordinate r . The equivalent equation for the numerical results, as defined by the authors of ePolyScat [19], is given as $T_{\mu_0}^{p_i \mu_i, p_f \mu_f}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}}) = \sum_{l,m,\mu} I_{l,m,\mu}^{p_i \mu_i, p_f \mu_f}(E) Y_{lm}^*(\theta_{\hat{k}}, \phi_{\hat{k}}) D_{\mu, -\mu_0}^1(R_{\hat{n}})$, where $I_{l,m,\mu}^{p_i \mu_i, p_f \mu_f}(E)$ are, again, the radial dipole integrals defined as $I_{l,m,\mu}^{p_i \mu_i, p_f \mu_f}(E) = \langle \Psi_i^{p_i \mu_i} | \hat{d}_\mu | \Psi_f^{p_f \mu_f} \rangle$.
- Regardless of an energy or time-domain picture, the asymptotic phase of the photoelectron wavefunction is given by the scattering phase. In other words, $\arg(\Psi_g)$ is given by the scattering phase η_g , which is determined by the scattering of the electron from

the molecule (see ref. [7] for detailed discussion). In the case of photoionization - a “half-collision” - in the weak field limit, the composition of the outgoing scattering wave is described by a dipole matrix element, which couples the ionizing orbital to the continuum wavefunction. This matrix element defines the scattering phases. As discussed above, without this matrix element there would be no energy dependence to the scattering state, nor any dependence on the ionization dynamics, since the continuum wave would not be coupled to an ionizing orbital - ionization physics could not be modelled. This physical concept, and consequent details, are stressed multiple times throughout the manuscript, vis. [emphasis added]:

- “In atomic ionization, the relatively simple nature of the scattering potential results in a continuum wavepacket with little spatial structure, which can often be described by just two partial-wave channels. In molecular ionization, the anisotropic nature of the potential means that many more partial-waves are required to describe the photoelectron wavepacket, and significant spatial and energy structure is expected. In essence, the angular structure of the photoelectron wavepacket is the result of the angular interferences between the partial-waves at a given energy, while the difference in the dependence of the *phase-shift of any given l-wave on the photoelectron kinetic energy results in the strong energy-dependence of the photoionization cross-section and τ_w* .” (Sect. 2)
- “ In these plots the surface topography follows the magnitude of the dipole matrix element (proportional to the square-root of the photoionization cross-section), while the colour-map shows the energy and angle-resolved Wigner time.” (Sect. 3.B)
- “In both cases, the ionizing orbital is the valence σ -bonding orbital, with lobes oriented along the molecular axis. The choice of polarization of *the ionizing radiation* - either parallel or perpendicular to the molecular axis - defines the symmetry of the ionization continuum accessed, hence the symmetry of the continuum photoelectron wavefunction.” (Sect. 3.B)
- “Physically, the peaks in the cross-section correspond *to maxima in the dipole integrals which define the coupling between initial orbital and final continuum wavefunctions induced by ionizing radiation, with an angular dependence given by the partial-wave interferences*. For $N_2(\Sigma_u)$ this peak is the well-known shape-resonance [26, 32, 33], corresponding to an enhancement of the $l = 3$ partial-wave, which can be considered as a trapping of this part of the outgoing wavepacket due to the form of the molecular potential energy surface.” (Sect. 4, telling entitled “Scattering Dynamics”)
- “In the case of CO the picture is quite different. Here the Wigner delays are predominantly negative, indicating a slight net repulsive effect from the molecular potential, and the results are highly asymmetric, consistent with the loss of inversion symmetry and the form of the ionizing orbital for a polar diatomic. The repulsive nature of the potential is most significant at the oxygen end of the molecule, where the extent of the ionizing orbital is much reduced relative to the carbon end.” (Sect. 4)
- “This can be understood by consideration of the radial part of the continuum wavefunction: at higher energies the photoelectron wavelength becomes shorter, and the continuum function will become more penetrating relative to the core wavefunction. Consequently, *the spatial overlap integral* will incorporate more bound-state density closer to the core, which is effectively more strongly bound...” (Sect. 4)
- “Visualization of the scattering wavefunctions provides additional physical insight into the dynamics of the process. Figure ?? shows a selection of continuum wavefunctions at different photoelectron energies, chosen to represent the evolution of the scattering wavefunctions towards the peak in the cross-sections (shape-resonance), with symmetries concomitant with ionization parallel to the molecular frame ($N_2(\Sigma_u)$ and $CO(\Sigma)$).” (Sect. 4)
- “with the observed continuum structure corresponding to the rise and fall of the $l = 3$ partial-wave component over this energy range, including a significant change in the magnitude of the wavefunction in the core region which has a strong effect on the overall ionization yield” (Sect. 4)
- “In all cases, the asymptotic phase-shift of the waves is approximately established at the length-scales shown ($r_{max} = 10 \text{ \AA}$), and phase differences can be observed in the plots.” (Sect. 4)
- “The scattering phases of individual partial waves, at a single energy, can be determined by measurements of photoelectron angular distributions. These are usually termed “complete” photoionization experiments, and have been successfully demonstrated for a range of atomic and molecular ionization process (see refs. [6, 34] for example, for more comprehensive reviews see refs. [35, 36]), and most recently for multi-photon ionization with femto-second pulses, including electronic dynamics [16].” (Sect. 5)
- “The reconstructed phases agreed reasonably well with theoretical results, which were based on ePolyScat calculations similar to those employed herein.” (Sect. 5, in discussion of the results of ref. [37], with ePolyScat calculations and post-processing performed by some of the current authors)
- “...calculations based on a modified 3-step model using time-dependent ionization and propagation calculations, combined with accurate recombination matrix elements (hence scattering phases) were able to recreate the intensity envelope of the harmonic spectrum and spectral phase differences between opposites end of the molecule” (Sect. 5, in discussion of the results of ref. [38] - again, ePolyScat calculations and post-processing performed by some of the current authors)
- “Molecular ionization is a complex phenomenon, with the outgoing photoelectron wavepacket experiencing a highly anisotropic scattering potential. In the time-domain, this results in a highly-structured Wigner delay, as a function of energy and

angle in the molecular frame. With the use of scattering calculations, the angle-dependent Wigner delay $\tau_w^g(k, \theta, \phi)$ was examined for two simple diatomics, and these results illustrate the magnitudes of the delays, and types of structures, which might generally be expected in molecular photoionization. The deep link between the Wigner delay and the photoionization matrix elements is also revealed in the correlation of energy-domain photoionization phenomena - in this case the shape resonance in N_2 - with features in the Wigner delay." (Sect. 6)

Summary

In conclusion, we hope our response to Baykusheva & Wörner's contention is quite clear and robust: there is no issue here, either conceptually, in the technical details of the formalism used, or numerically. We further hope that our lengthy and detailed response serves as useful material for researchers interested in the fascinating and challenging topics of molecular photoionization and Wigner delays, and provides a suitable reading list of canonical works.

Appendix - Notes on Scattering Theory & ePolyScat for Photoionization, reproduced from the Supp. Mat.

The following notes, originally included in the Supplementary Materials for our article (available online via Figshare at <http://dx.doi.org/10.6084/m9.figshare.2007486>), are reproduced here for the interested reader.

General framework

Within scattering theory the free particle wavefunction can be expressed as a partial wave expansion in radial and angular functions:

$$\Psi(\mathbf{r}) = \sum_{lm} A_l \chi_l(r) Y_{lm}(\theta, \phi) = \sum_{lm} \psi_{lm}(\mathbf{r}) \quad (20)$$

The exact form of $\chi_l(r)$ and A_l will depend on the potential $V(r)$. For a Coulombic potential, $V(r) \propto Z_1 Z_2 / r$, where Z_1 and Z_2 are the charges on the scattering centre and scattered particle, solutions are given by (using incoming wave normalization):

$$\chi_l(r) = F_l(r) \xrightarrow{r \rightarrow \infty} \sin \left[kr - \frac{\pi l}{2} - \frac{Z_1 Z_2}{k} \ln(2kr) + \sigma_l \right] \quad (21)$$

$$A_l = \frac{2l+1}{kr} i^l e^{-i\sigma_l} \quad (22)$$

$$\sigma_l = \arg \Gamma \left[l + 1 - i \frac{Z_1 Z_2}{k} \right] \quad (23)$$

Here the solution to the radial wavefunction, $\chi_l(r)$, is given by the (regular) *Coulomb function* $F_l(r)$. This has a complicated functional form near the scattering centre, but asymptotically goes to a sinusoidal form. Both F_l and A_l contain terms involving σ_l , this is the *Coulomb phase*, and is given by equation 23. Γ is the gamma function.

While the Coulomb potential is the exact form for a point charge, more generally a scattering system may have an additional short-range contribution to the potential (one which scales as $1/r^n$, where $n > 1$), and this contribution may be non-centrally symmetric (i.e. anisotropic). However, the strength of these short-range interactions and multi-polar contributions to the potential will fall to zero much faster than the Coulombic term, and we can define a boundary, r_c , beyond which the potential is purely Coulombic. We now have a potential defined by $V'(r < r_c)$ and $V(r \geq r_c)$. We do not know the exact (analytic) form of the wavefunction in the region $r < r_c$. However, in the Coulombic region the radial wavefunction still has an analytic form, and is now described by:

$$\chi_l(r \geq r_c) = \cos(\delta_{lm}) F_l(r) + \sin(\delta_{lm}) G_l(r) \quad (24)$$

$$G_l(r) \xrightarrow{r \rightarrow \infty} \cos \left[kr - \frac{\pi l}{2} - \frac{Z_1 Z_2}{k} \ln(2kr) + \sigma_l \right] \quad (25)$$

$$A_l = \frac{2l+1}{kr} i^l e^{-i(\sigma_l + \delta_{lm})} \quad (26)$$

Here $F_l(r)$ is the regular Coulomb function as before, while $G_l(r)$ is the *irregular Coulomb function*. δ_{lm} is an additional *scattering phase shift*, which arises from the non-Coulombic part of the scattering potential. This phase shift defines the mixing of the regular and irregular Coulomb functions, and this mixing also determines the asymptotic phase shift:

$$\chi_l \xrightarrow{r \rightarrow \infty} \sin \left[kr - \frac{\pi l}{2} - \frac{Z_1 Z_2}{k} \ln(2kr) + \sigma_l + \delta_{lm} \right] \quad (27)$$

Hence the scattering phase δ_{lm} describes the effect of the non-Coulombic part of the potential, $V'(r)$, and is labelled with m to show that this may affect different components of each l -wave differently in an anisotropic scattering system. Note that the short-range part of the potential may still be centrally-symmetric, in which case only $m = 0$ components will be present. Although the form of the wavefunction is not generally known for $r < r_c$ (but could be found numerically for a given $V'(r)$), the scattering phase carries all of the information on the strength of the short range potential.

Most generally, the overall phase of each partial-wave channel is denoted $\eta_{lm} = \sigma_l + \delta_{lm}$. The total phase (including angle-dependence) can be most cleanly written as, simply, $\eta_t(\mathbf{r}) = \text{arg}(\Psi(\mathbf{r}))$, which incorporates the scattering phases η_{lm} , as well as any additional channel-dependent phase contributions (e.g. phase contributions from Y_{lm} terms etc.).

Photoionization

The asymptotic wavefunction defines the final state of the system, thus any experimental observations. The solution above defines the continuum wavefunction in the presence of the scattering potential. In the case of photoionization, the amplitudes of the various partial-waves in the asymptotic limit must thus be found from some overlap from the initial state. Typically we work within the dipole regime, and the light-matter coupling at an energy E can be written:

$$d(E) = \langle \Phi_f(\mathbf{r}); \Psi(\mathbf{r}) | \hat{\mu} \cdot \mathbf{E} | \Phi_i(\mathbf{r}) \rangle \quad (28)$$

Here $\Psi(\mathbf{r})$ is the continuum (photoelectron) wavefunction of eqn. 20; $\Phi_i(\mathbf{r})$ is the initial N -electron state and $\Phi_f(\mathbf{r})$ the $N-1$ electron final state of the ionizing molecule; $\hat{\mu}$ is the dipole operator and \mathbf{E} the incident electric field.

In terms of the observable asymptotic wavefunction (or photoelectron wavepacket), which is defined as a function of energy and angle, these matrix elements will determine the overall amplitudes and phases of the continuum wavefunction prepared via photoabsorption. Hence we can write the final asymptotic wavefunction/wavepacket as:

$$\Psi(E, \theta, \phi) = \sum_{lm} d_{l,m}(E) Y_{lm}(\theta, \phi) \quad (29)$$

where $d_{l,m}(E)$ is the dipole matrix element expanded in partial-waves. Here, the dipole matrix elements include radial integration over the continuum wavefunction of eqn. 20, and incorporates the asymptotic phases η_{lm} . The final observable is the square of this wavefunction, and (for an angle-sensitive measurement) will retain phase sensitivity over the partial-wave channels:

$$I(E, \theta, \phi) = \Psi(E, \theta, \phi) \cdot \Psi^*(E, \theta, \phi) \quad (30)$$

ePolyScat

The dipole matrix elements are defined in ePolyScat [39–41] by, e.g., the definition of the MF-PADs as per eqns. 1-3 of ref. [19]:

$$I_{\mu_0}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}}) = \frac{4\pi^2 E}{c g_{p_i}} \sum_{\mu_i, \mu_f} |T_{\mu_0}^{p_i \mu_i, p_f \mu_f}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}})|^2 \quad (31)$$

$$T_{\mu_0}^{p_i \mu_i, p_f \mu_f}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}}) = \sum_{l, m, \mu} I_{l, m, \mu}^{p_i \mu_i, p_f \mu_f}(E) Y_{lm}^*(\theta_{\hat{k}}, \phi_{\hat{k}}) D_{\mu, -\mu_0}^1(R_{\hat{n}}) \quad (32)$$

$$I_{l,m,\mu}^{p_i\mu_i,p_f\mu_f}(E) = \langle \Psi_i^{p_i,\mu_i} | \hat{d}_\mu | \Psi_f^{p_f,\mu_f} \varphi_{klm}^{(-)} \rangle \quad (33)$$

In this formalism:

- $I_{l,m,\mu}^{p_i\mu_i,p_f\mu_f}(E)$ is the radial part of the dipole matrix element, determined from the initial and final state electronic wavefunctions $\Psi_i^{p_i,\mu_i}$ and $\Psi_f^{p_f,\mu_f}$, photoelectron wavefunction $\varphi_{klm}^{(-)}$ and dipole operator \hat{d}_μ . Here the wavefunctions are indexed by irreducible representation (i.e. symmetry) by the labels p_i and p_f , with components μ_i and μ_f respectively; l, m are angular momentum components, μ is the projection of the polarization into the MF (from a value μ_0 in the LF). Each energy and irreducible representation corresponds to a calculation in ePolyScat.
- $T_{\mu_0}^{p_i\mu_i,p_f\mu_f}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}})$ is the full matrix element (expanded in polar coordinates) in the MF, where \hat{k} denotes the direction of the photoelectron \mathbf{k} -vector, and \hat{n} the direction of the polarization vector \mathbf{n} of the ionizing light. Note that the summation over components $\{l, m, \mu\}$ is coherent, and hence phase sensitive.
- $Y_{lm}^*(\theta_{\hat{k}}, \phi_{\hat{k}})$ is a spherical harmonic.
- $D_{\mu,-\mu_0}^1(R_{\hat{n}})$ is a Wigner rotation matrix element, with a set of Euler angles $R_{\hat{n}} = (\phi_{\hat{n}}, \theta_{\hat{n}}, \chi_{\hat{n}})$, which rotates/projects the polarization into the MF.
- $I_{\mu_0}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}})$ is the final (observable) MFPAD, for a polarization μ_0 and summed over all symmetry components of the initial and final states, μ_i and μ_f . Note that this sum can be expressed as an incoherent summation, since these components are (by definition) orthogonal.
- g_{p_i} is the degeneracy of the state p_i .

The dipole matrix element of eqn. 33 - the radial part of the dipole matrix element - effectively defines the final state amplitude and phase. Hence, is equivalent to the general form of eqn. 28, but here expanded in terms of symmetries of the light-matter system.

In practice, the initial N -electron and final $(N-1)$ -electron wavefunctions are defined by standard computational chemistry methods (as implemented in Gaussian, Gamess, etc.). The scattering state is solved numerically by ePS via a Schwinger variational procedure [26], and the radial dipole integrals solved based on this scattering state. Numerically, an effective range for the interaction (r_{max}) is defined by the spatial grid used in the calculation; other calculation parameters may also affect the numerical results, see ref. [26]. Matrix elements $I_{l,m,\mu}^{p_i\mu_i,p_f\mu_f}(E)$ are output for further processing, e.g. for MF-PADs or calculation of Wigner delays.

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