Angle-resolved RABBITT: theory and numerics

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Abstract

Angle-resolved (AR) RABBITT measurements offer a high information content measurement scheme, due to the presence of multiple, interfering, ionization channels combined with a phase-sensitive observable in the form of angle and time-resolved photoelectron interferograms. In order to explore the characteristics and potentials of AR-RABBITT, a perturbative 2-photon model is developed; based on this model, example AR-RABBITT results are computed for model and real systems, for a range of RABBITT schemes. These results indicate some of the phenomena to be expected in AR-RABBITT measurements, and suggest various applications of the technique in photoionization metrology.

Keywords: photoionization, angle-resolved, photoelectron spectroscopy, ultrafast, atto

(Some figures may appear in colour only in the online journal)

1. Introduction

The RABBITT methodology—‘reconstruction of attosecond harmonic beating by interference of two-photon transitions’ [1]—essentially defines a scheme in which XUV pulses are combined with an IR field, and the two fields are applied to a target gas. The gas is ionized, and the photoelectrons detected. In the typical case, the IR field is at the same fundamental frequency ω as the field used to drive harmonic generation, and the XUV field generated is an atto-second pulse train with harmonic components nω, with odd-n only. In this case, if the intensity of the IR field is low to moderate, the resultant photoelectron spectrum will be comprised of discrete bands corresponding to direct 1-photon XUV ionization, and sidebands corresponding to 2-photon XUV+IR transitions [1]. (The energetics of this situation are illustrated in figure 1.) Temporally, if the XUV pulses are short relative to the IR field cycle, the sidebands will also show significant time-dependence, since they will be sensitive to the optical phase difference between the XUV and IR fields, with an oscillatory frequency of 2ω. In this case, a measurement which is angle-integrated, or made at a single detection geometry, can be viewed as a means to characterizing the properties of the XUV pulses (spectral content and optical phase), provided that the ionizing system is simple or otherwise well-characterized [1]; RABBITT can therefore be utilized as a pulse metrology technique [1, 2], and this is the typical usage.

Conversely, RABBITT can also be regarded as a photoelectron metrology technique, since it is sensitive to the magnitudes and phases of the various photoionization pathways accessed. In contrast to most traditional (energy-resolved) photoelectron spectroscopy techniques, RABBITT has the distinction of interfering pathways resulting from different 1-photon transition energies: it is thus sensitive to the energy-dependence of the photoionization dynamics, as well as to the partial-wave components within each pathway. An angle-resolved (AR) RABBITT measurement is particularly powerful in this regard, since the partial-wave phases are encoded in the angular part of the photoelectron interferogram. Although this is a potentially powerful technique, the underlying photoionization dynamics may be extremely complicated, hence quantitative analysis of experimental results is challenging.

In essence, AR-RABBITT can therefore be considered as a technique which combines traditional photoionization and scattering physics with an additional (time-dependent) perturbation in the form of the IR laser field. This field provides additional couplings between the 1-photon (XUV) channels. In the usual RABBITT intensity regime, these two steps can be decoupled, allowing for the XUV absorption to be treated as a weak-field bound-free transition (photoionization), followed by absorption of an IR photon—this latter step is a transition purely between different free electron states in the
continuum, often termed continuum–continuum coupling. This scheme is illustrated in the energy-domain in figure 1(left). Therefore, the problem becomes one of dealing with a two-photon matrix element, describing these two sequential light–matter interactions. Furthermore, if the continuum–continuum coupling is assumed to be at long-range (i.e. temporally and spatially distinct from the bound-continuum coupling of the first, bound-free, step, and at the asymptotic limit of the continuum wavefunction), then a simplified treatment can be developed for this second transition. In this vein, Dahlström, L’Hullier and coworkers have done significant work, including angle-integrated resonant cases and extensive theoretical treatments of the problem. See, for instance, Introduction to attosecond delays in photoionization [3] and Study of attosecond delays using perturbation diagrams and exterior complex scaling [4] for general background theory and perturbative treatments similar to those discussed herein, Phase measurement of resonant two-photon ionization in helium [5] for a specific example (angle-integrated), and On the angular dependence of the photoemission time delay in helium [6] for work on this specific AR case.

In this work, the same basic conceptual path to modelling RABBITT as a sequential two-photon process is followed, but the emphasis is placed on the role of the photoionization dynamics. This provides a route to the modelling and analysis of AR-RABBITT, based on canonical photoionization theory and employing a full partial-wave treatment of the continuum. Following the similar treatment of [7], which investigated sequential 3-photon ionization in a time-dependent IR field (conceptually similar to a RABBITT scheme), the electric fields are modelled in a circular basis to allow for arbitrary field polarization states. The treatment is general, and applicable to any atomic or molecular system, provided that the IR field can be neglected for the first step. Essentially, within this framework AR-RABBITT can be considered as an extension of traditional AR photoelectron measurements, and many of the same fundamental considerations and potential applications apply [8, 9]. As usual, in cases where the XUV and/or IR field is strong, only full numerical treatments are capable of correctly describing the coupled light-matter system (see, for instance, [10–12]), and this regime is not within the scope of the perturbative model discussed herein.

In the following, a framework for AR-RABBITT modelling is defined in terms of the general form of the required photoionization matrix elements, the final continuum wavefunctions and the resultant observables (section 2). This framework is then applied to simple model cases (section 3), in order to develop a phenomenological understanding of AR-RABBITT measurements. To explore the application of the framework to real systems (section 4), numerical treatments for the radial matrix elements are detailed (section 4.1), and the framework is applied to model a range of specific AR-RABBITT measurements of neon.

2. Theory

In this section, a basic theoretical framework for AR-RABBITT is defined. Further numerical details are discussed in section 4.

2.1. 1-photon ionization by the XUV field

The dipole matrix element for 1-photon ionization by the XUV field, corresponding to direct ionization from an initial bound state \( |n_l l_m\rangle \) to a final continuum state \( |l_f m_f; k\rangle \), is given as:

\[
d_{\text{XUV}}(k, t) = \langle k; l_f m_f | \hat{\mu}_q | E(\Omega, t) q | n_l l_m \rangle
\]

\[
= R_{l_f l_m}(k) E_{\text{XUV}}(\Omega, t) \langle l_f m_f; 1q | l_m \rangle,
\]

where \( \hat{\mu}_q \) is the dipole operator. In the second line, the matrix element is decomposed in terms of radial and geometric parts. Here \( R_{l_f l_m}(k) \) denotes the radial integrals, which are dependent on the magnitude of the photoelectron wavevector \( k \); \( \langle l_f m_f; 1q | l_m \rangle \) is a Clebsch–Gordan coefficient which describes the angular momentum coupling for single photon absorption, where the field polarization (circular basis) is defined by \( q \), and the spectral \( (\Omega) \) and temporal \( (t) \) properties of each polarization component by \( E_{\text{XUV}}^{q}(\Omega, t) \).

This matrix element is essentially identical to canonical treatments for 1-photon ionization (e.g. Cooper and Zare [13, 14] for atomic photoionization, Dill [15] for fixed-molecule photoionization), apart from the inclusion of a time-dependent \( E \)-field. In this decomposition, the Clebsch–Gordan coefficients can be calculated analytically, the \( E \)-field can be defined analytically or numerically, and the \( R_{l_f l_m}(k) \) (complex) require numerical solution for a given ionizing system. Essentially, the analytical part of the solution encodes the angular momentum selection rules, while the \( R_{l_f l_m}(k) \) provide the amplitude and phase coefficients for each partial-wave
channel for a specific problem (ionizing system and energy). The notation used here implicitly assumes that the radial integrals \( R_{LJ}(k) \) are independent of \( m_r \) and \( m_p \). For atomic systems this is a good approximation, and allows for a simplified treatment of the photoionization dynamics, but for molecules this assumption does not hold (due to the loss of spherical symmetry in the core region) and all \( m \) components must be treated explicitly (see, e.g., [15, 16]).

2.2. Continuum–continuum coupling

The transition between two continuum states, \( i \) and \( f \), further labelled by energy and angular momentum, coupled by 1-photon absorption or emission from the IR field, can be similarly given as:

\[
d_{uv}(k_i, k_f, t) = \langle k_f; l_f m_f | \hat{\mu}_E | E(\Omega, t, q) | k_i; l_i m_i \rangle
\]

\[
= R_{LJ}(k_i, k_f) E^{\delta}_\Omega(\Omega, t) \langle l_f, m_f | 1q | l_i, m_i \rangle.
\]

(3)

(4)

Note that, as for bound-free ionization, the radial part of the matrix elements \( R_{LJ}(k_i, k_f) \) are here not defined explicitly, but must be considered specifically for the problem at hand.

2.3. Final state wavefunctions

The final continuum states populated are given by expansions in continuum partial-waves \( |l_f m_f; k_i \rangle \). The expansion parameters are defined by the matrix elements given above, for the various pathways of interest in a RABBITT scheme, as:

- One photon (XUV) final states

\[
\Psi_{XUV}(k, t) = \sum_{l_f m_f, l_i m_i} d_{uv}(k, t) |l_f m_f; k_i \rangle.
\]

(5)

- Two photon (XUV+IR) final states

\[
\Psi_{2}(k, t) = \sum_{l_f m_f, l_i m_i, l_m, m_m} d_{uv}(k, t) d_{uv}(k, t) |l_f m_f; k_i \rangle,
\]

(6)

where the \( \pm \) refers to absorption or emission of an IR photon, and \( \nu \) denotes the intermediate 1-photon continuum states.

- Generic channel summed and partial-wave resolved final states. This notation simply indicates a final state which is the resultant sum over various ionization channels \( c \), each decomposed into a set of final \( |l_f m_f \rangle \) waves, and serves as a general short-hand.

\[
\Psi(k, t) = \sum_c \Psi_c(k, t) = \sum_c \sum_{l_f m_f} \psi_{l_f m_f}(k, t).
\]

(7)

In this case, the number of angular momentum components \( (l, m) \) involved depends on the ionizing system. For centro-symmetric systems (e.g. hydrogen), \( l \) is a good quantum number and only bound-free transitions with \( \Delta l = \pm 1 \) are allowed; this is also usually a reasonable approximation for multi-electron atomic systems. However, as eluded to previously, for molecular systems many angular momentum components are typically expected, due to the loss in symmetry of the scattering potential at short range, and the problem becomes more complex; for discussion on this topic see, for instance, [15, 16].

In this treatment, \( t \) denotes the temporal dependence of the final states, due to both laser fields \( E(\Omega, t, q) \). This dependence can be simplified to a dependence upon only the relative XUV to IR field delay, \( \tau \), under the assumption that the XUV field is short relative to the rate of change of the IR field. In the limiting case, the time-dependence of the XUV field is a \( \delta \)-function, and only the instantaneous properties of the IR field at \( t = \tau \) are important, hence no temporal integration is required.

2.4. Observables

The energy and angle resolved photoelectron measurements, as a function of the XUV-IR delay \( \tau \), are then given by:

- One photon transitions, single path: direct ionization, the usual case for odd-harmonic bands in standard RABBITT experiments (odd-harmonics only in the XUV spectrum). Note this signal is effectively time-independent, since the signal does not depend on \( \tau \)

\[
I_1(\theta, \phi, \tau) = \langle \psi_{XUV}(k, t) \rangle \langle \psi_{IR}(k, t) \rangle \times c.c.
\]

(8)

- Two photon matrix elements, with two paths: usual RABBITT sidebands for an XUV spectrum with odd-harmonics only

\[
I_2(\theta, \phi, \tau) = (\langle \psi_{XUV}(k, \tau) \rangle + \langle \psi_{IR}(k, \tau) \rangle) \times c.c.
\]

(9)

- One and two photon paths: all photoelectron bands for ‘extended’ RABBITT experiments, when the XUV spectrum also contains even-harmonics

\[
I_3(\theta, \phi, \tau) = (\langle \psi_{XUV}(k, \tau) \rangle + \langle \psi_{IR}(k, \tau) \rangle) \times c.c.
\]

(10)

In all cases the resultant observable, for each photoelectron band observed in a RABBITT scheme, centred at photoelectron energy \( E \), can be described by an expansion in spherical harmonics \( Y_{LM} \) with time-dependent expansion parameters \( \beta_{L,M,E}(\tau) \), and a Gaussian radial function:

\[
I(\theta, \phi, \tau) = \sum_{L,M} \beta_{L,M,E}(\tau) Y_{L,M}(\theta, \phi) G(E, \sigma).
\]

(11)

In practice, the Gaussian features centred at energies \( E \), of width \( \sigma \), are defined from the experimental harmonic spectrum. In principle, the energy dependence of the matrix elements across each photoelectron band, and the effect of this dependence on the radial spectrum, should be considered; however, in many cases it is reasonable to assume that the matrix elements are smoothly varying as a function of energy, and may be approximated as constant for each discrete photoelectron band (typically spanning a few 100 meV)—hence a single energy point at the peak of the band is assumed to be representative of the band. This is essentially the ‘smoothly
varying continuum’ approximation, but will clearly break- 
down in the presence of any sharp features such as auto-
ionizing resonances. For more general discussion, in the 
context of photoionization and the energy-dependence of 
PADs, see [16, 17].

3. Model systems

While general, the preceding treatment does not offer much 
direct insight since many details remain to be defined—spe-
cifically the angular momentum states which play a role, and 
the radial integrals. In order to proceed, one must model 
specific cases, thus select appropriate initial states and com-
pute the relevant integrals—for example, Dahlström et al 
have presented specific results for a hydrogenic treatment, 
including different levels of approximation [3]. Herein, the 
cases of ‘standard’ and ‘extended’ RABBITT are explored, 
starting with a basic model system to provide physical insight, 
while section 4 details specific real cases.

3.1. Sidebands in standard AR-RABBITT

The ‘usual’ RABBITT sidebands result from two interfering 
pathways, corresponding to 2 photon transitions via 
\( H(n) + \text{IR} \) and \( H(n + 2) - \text{IR} \), where \( H(n) \) denotes a 
harmonic of order \( n \). The corresponding wavefunctions were 
denoted by \( \Psi_+ \) and \( \Psi_- \) above. To model this, and explore 
paradigmatic behaviours, the dipole matrix elements required 
can be set as model parameters, and the energy dependence of 
the pathways neglected. This provides a model in which the 
angular interferograms, and temporal behaviour, can be 
probed.

Figure 1 illustrates a basic RABBITT scheme, for the 
simplest model system. Ionization is from a pure \( s \)-state, 
resulting in ionization pathways \( s \rightarrow p \rightarrow s + d \). To 
model this case, identical radial matrix elements were set for 
each 2-photon channel (denoted \( c \)), with variable phases:

\[
R_{i\rightarrow p} = 1 e^{i\phi_{i\rightarrow ps}}, \quad (12) \\
R_{p\rightarrow d} = 1 e^{i\phi_{p\rightarrow ps}}, \quad (13) \\
R_{c} = 0.3 e^{i\phi_{c}}. \quad (14)
\]

Figure 2 shows the results for these case, in which the 
laser fields are set to \( q = 0 \) only (linear polarization), and the 
XUV phases are set to zero. The phases of the dipole matrix 
elements were varied to probe the behaviour of the sidebands, 
and the three example cases have the following phases set:

(a): All phases set to 0.
(b): \( \phi_{s,p} = \pi/2 \)—an overall phase-shift in the second path.
(c): \( \phi_{s,p} = \pi/2 \) and \( \phi_{p,d} = \pi/4 \)—an overall phase-shift in 
the second path, plus a phase-shift of the \( d \)-wave for 
channel 1.

Physically, intra- and inter-channel magnitude and phase 
differences of the partial-wave components are expected 
purely from the energy-dependence of the ionization 
dynamics. Contributions from the harmonic phase, or from 
other physical processes such as resonances at the 1-photon 
level in specific channels, can also play a role. Depending on 
the physical origin, such phase effects might shift all partial 
waves in a given channel (the simplest case of an optical 
phase shift in the XUV), or affect the photoionization 
dynamics in more complex and subtle ways. For further 
discussion on and around this point see, for example: [18, 19] 
for a general discussion and observation of resonant phase 
effects in photoionization, [5] for a similar observation in 
RABBITT measurements, and [20] for the case of auto-
ionizing resonances in RABBITT-type measurements.
Figure 3. Partial-wave resolved RABBITT traces for (a), (b) elliptically and (c) circularly polarized E-fields. Each column shows, from top to bottom, the IR laser field $E_{fi}^c$, the two paths to the side-band and the resultant sum over paths. The plots for each path show the real part of the final-state wavefunction $\text{Re}[\psi_{fi}^c]$ as a function of partial-wave and time, and the sum over paths $\text{Re}[\sum_c \psi_{fi}^c]$, where $c$ is a channel index for path 1 and path 2. The legends show the various $l, m$ partial-waves plotted, and the final (angle-integrated) photoelectron yields $I_f(\tau)$. Insets show the (time-invariant) angular interferograms, $I_i(\theta, \phi)$ summed over all channels. The reference geometry is illustrated in the first panel; the laser pulses propagate along the $z$-axis, and the ellipticity is defined in the $(x, y)$ plane. The fields are defined by ellipticity $\xi$, and (equivalently) the phase-shift of the $y$-component, $\phi_y$ (radians).

(recently demonstrated experimentally [21]; [22] for the related case of control over multi-path ionization schemes, specifically with 1-wave parity breaking due to interfering 1 and 2-photon pathways, and [23] for application in an AR-RABBITT type experiment (see also sections 3.3 and 4.4 herein); [24] discusses conceptually similar cases of time-domain control schemes in photoionization, including temporal and polarization control in multi-photon ionization schemes.

For the usual sidebands, the amplitude of the resultant wavefunction will oscillate at $2\omega_p$, with a total phase defined by the interfering partial-waves for each channel (including any contribution from the XUV optical phase). Within the approximations described above, the angular form of the sidebands will not show any time-dependence, since this requires a change in the relative phases of the contributing paths as a function of time. In this simple case, there are no dynamics which affect these quantities, and it is only the absolute amplitudes which vary as the IR-laser field oscillates. Hence, the AR interferograms will appear to simply breathe (in intensity) as a function of time. However, the presence of any time-dependence to the dipole matrix elements—e.g. Stark shifts affecting the ionizing states as the IR field cycles—would create additional time-dependence in the angular content, and might be expected in the strong-field regime.

Thus, in the usual regime, although the shape of the angular distribution is sensitive to the relative phases of the matrix elements, it is time-invariant; the total photoelectron yields are, however, sensitive to both the phases of the matrix elements and the instantaneous laser field. In particular, the phase shift of the yields relative to the laser field is sensitive to both the relative phases of the channels (hence may be used to probe the effect of resonances in one channel, as per [5]), and the partial-wave phases within each channel. In this manner, the angular information provides a phase-sensitivity which is otherwise lost in an angle-integrated measurement.

3.2. Sidebands in AR-RABBITT with nonlinearily polarized light

As illustrated in figure 1, the use of polarization states other than linear (and a parallel polarization geometry), will result in population of different $m$ states. In the most general case, where the XUV and IR fields have different polarization states, many additional pathways may play a role. Here a simplified case is illustrated, in which the XUV and IR fields are assumed to have the same ellipticity $\xi$, in order to illustrate the general concepts and trends with polarization state.

The results are shown in figure 3. In these calculations, the model system detailed above is utilized, incorporating the set of phase shifts (c) (section 3.1). The three columns in the figure show the results for different ellipticities, defined mathematically by the phase shift between the two Cartesian components of the E-fields ($\phi_y$) (see [7] for details), and illustrated by the two spherical components of the IR field ($q = \pm 1$). The effect of the polarization state is quite clear here: as the polarization state moves from linear (equal magnitudes for the $q = \pm 1$ components) towards pure circular polarization ($q = +1$ in this example) the continuum wavefunction becomes increasingly dominated by the $|d, m = 2\rangle$ component. In this (relatively) simple example, this is a direct consequence of the selection of pathway by the polarization state of the light: the handedness of the light is approximately mapped onto the $m = \pm 2$ final states. The most interesting case is, therefore, shown in figure 3(b), where the presence of both $q = \pm 1$ breaks the cylindrical symmetry of the distribution. In contrast, figure 3(c), pure $q = +1$ light, produces a much simpler angular distribution, with only the $|d, m = 2\rangle$ continuum state contributing. The symmetry breaking is also present in figure 3(a), but is not yet
pronounced with only a slight difference in the magnitudes of the $m = \pm 2$ states.

In this simple case, the additional pathways accessible with $q = \pm 1$ allow for breaking of the cylindrical symmetry of the angular distribution when the $E$-fields are elliptical, thus providing additional interferences, hence information content, in such measurements. Generally, the mapping between $q$ and the final observable is less direct, since many more states typically play a role. Examples for a more realistic case are given in section 4.3. In traditional ionization studies, the use of polarization state and geometry is a powerful tool, and has been used in a variety of methodologies, for example in photoelectron metrology [25–27] and control problems, including time-domain polarization-multiplexed schemes [28, 29]. Recently, the related case of XUV field polarization effects on photoionization in the strong field regime has been investigated by Yuan, Bandrauk and co-workers [30, 31]; of particular note in that case is the presence of a strong radial (energy) dependence of the angular interferogram within a single photoelectron energy band, and asymmetries in the molecular frame. Polarization geometry in XUV-XUV 2-photon transitions have been investigated theoretically by the same authors [32], and XUV-IR schemes with polarization control have also recently been investigated experimentally [33].

3.3. Sidebands in extended AR-RABBITT with even harmonics

Additional interferences in the final state wavefunction can be created by adding ionization channels. In a RABBITT experiment the addition of even-harmonics is the simplest scheme which achieves this, and is illustrated in figure 1. Adding an interfering 1-photon channels has two effects: (1) time-dependence of the angular interferograms is now present, since the 1-photon channel is not coupled to the IR field, hence remains an invariant reference throughout the measurement; (2) the mixing of channels with odd and even photon order provides a route to parity breaking via the mixing of odd- and even waves.

In more detail, (1) implies that this scheme can be considered as a heterodyne measurement, in which the 1-photon channel acts as a local reference for the 2-photon channels. This implies that additional information may be gained on the photoionization dynamics, since the usual sidebands are now additionally referenced to this 1-photon channel. In the usual case, the phase of the photoelectron yield provides relative phase information on the interfering 2-photon paths, referenced to the IR field. In this extended case, the overall phase remains referenced to the IR field, but the individual partial-wave phases play a more significant role in the time-dependence of the observed angular interferogram. In essence, one expects to see different features of the angular interferogram at different delays, and a much more complex time-dependence than the basic breathing mode of the usual RABBITT sidebands.

Generally, (2) applies to any scheme which mixes channels of odd and even photon order. While this type of final state control can be achieved in a number of ways (see, for example, [22, 34, 35]), in a RABBITT experiment the addition of even-harmonics is the simplest and most appropriate route [23]. In this specific case, one can view the temporal dependence of the resulting interferograms as a form of control, since this is nothing but a shift of the relative phase of the pathways defined by $\tau$; however, it is a relatively weak form of control, since the amplitudes of the 2-photon pathways are also dependent on the IR field. The use of additional $E$-fields, different polarization states, or shaped pulses, could all potentially provide more powerful means of interferogram control.

The basic concept of phase control is illustrated in figure 4, which shows the concept for a simplified two channel model. In this case, path 1 has only odd-$l$ components (as per the previous example, outlined in section 3.1), and path 2 has only even-$l$ components. The phases of all components are set to zero, but a relative phase between the paths is varied in the model. The resultant wavefunction therefore takes the form $\psi = \psi_1 + \psi_2 e^{i \phi}$. In this case, the change in the relative phase of the paths ($\phi^2$) results in different regions of constructive and destructive interference, with lobes in the final interferogram shifting as a function of phase. Again, this phase could be the result of the time-dependence of one path, as for (1) above, but could also be the result of another form of phase-control, or result from other dynamic effects. The full time-dependence of the angular interferograms in this class of scheme is discuss further in section 4.

4. Real systems

In order to treat real systems within the framework defined herein, a numerical treatment for the photoionization matrix elements (specifically, the radial integrals) for a given ionizing system is required. In this work, the bound-free matrix elements are computed using the ePolyScat (ePS) suite [36–38], and the continuum–continuum matrix elements treated as hydrogenic (similar to the treatment of [3]). This specific choice of numerical treatment is general, since ePS is capable of accurate calculations for both atomic and
molecular scattering systems, but is expected to be poor at low energies where the assumption of hydrogenic continuum–continuum transitions does not hold.

4.1. Numerical details

As discussed above, in order to model real systems numerical methods must be employed in order to determine the radial matrix elements (as distinct from the model cases above, in which the radial matrix elements are set as model parameters). In order to achieve this, a combination of numerical treatments was used:

- **Bound-free matrix elements.** For a given ionizing system and ionizing orbital, ePS can be used to compute dipole matrix elements. ePS takes electronic structure input from standard quantum chemistry codes, solves the continuum wavefunctions variationally with a Lipmann–Schwinger approach, and computes dipole integrals based on these wavefunctions; for further details, see [36–38].

- **Continuum–continuum matrix elements.** Absorption of an IR photon in the continuum is modelled using Coulomb wavefunctions, in a similar manner to [3], see section 4.1.1 for details.

- **Velocity map image (VMI) measurements.** To model the experimental VMI measurements, the input harmonic spectrum (800 nm driving field) was calculated as a series of Gaussians. Photoelectron energies then follow from the photon energies so defined, and the ionization potential (IP) of the ionizing system. This procedure also provided specific photoelectron energy points for the ePS and continuum–continuum calculations, and the matrix elements were assumed to be constant over the width of the spectral features and as a function of the laser field intensity. See section 4.1.3 for details.

In this manner, ionization of any given system, at a given photon energy, can be accurately computed (ePS), while the continuum–continuum coupling is approximated assuming Coulombic (asymptotic) continuum wavefunctions.

4.1.1. Continuum–continuum coupling with Coulomb wavefunctions. The continuum wavefunctions in this case are, as previously (equation (7)), given by a general expansion, which can be written in radial and angular functions. For the Coulombic case this is usually given as

\[
\psi_{lm}(k, r) = \phi_l(k, r) Y_{lm}(\theta, \phi) = A_l(k, r) F_l(r) Y_{lm}(\theta, \phi),
\]

(15)

where,

\[
A_l = \frac{2l + 1}{kr} e^{i\sigma_l},
\]

(16)

\[
\sigma_l = \arcsin \left[ l + 1 - \frac{Z_1 Z_2}{k} \right]
\]

(17)

Here \( F_l \) is a regular Coulomb function [40], \( \sigma_l \) is the (Coulomb) scattering phase, \( Z_1 \) and \( Z_2 \) are the charges on the scattering centre and scattered particle, and \( \Gamma \) is the gamma function. Solutions of these equations can be computed numerically, as herein; analytical approximations have also been derived [3].

The explicit form of the continuum–continuum radial matrix element, for specific initial and final states defined by \( |k, l, m\rangle \) is then given by:

\[
R_{li, j}(k_i, k_j) = \frac{\int dr \; \phi_{i,j}(k_f, r) r \phi_{i,j}(k_i, r)}{\int dr \; r^2 \phi_{i,j}(k_f, r) r \phi_{i,j}(k_i, r)}. \tag{18}
\]

Of note in this case is the assumption of an \( m \)-independence to the scattering problem, which is correct over all \( r \) for a Coulombic scatterer (point charge), but only correct asymptotically in general: hence this continuum–continuum form is appropriate only for overlap integrals at long-range from the ion core in general. (Further discussion on this point is presented in the following section.)

Finally, it is interesting to note that Dahlström et al [3] analyse these matrix elements analytically, and derive some approximate forms. Of particular interest is that the phase contribution from the continuum–continuum transition can be approximated as:

\[
\phi_{i,j}(k_i, k_j) \approx \arg \left\{ \frac{(2k_f)^{iZ/k_f}}{iZ/k_f} \Gamma [2 + iZ(1/k_f - 1/k_i)] + \gamma(k_i, k_j) \right\}, \tag{19}
\]

\[
\gamma(k_i, k_f) = \frac{iZ(k_f - k_i)(k_i^2 - k_f^2)}{2k_f^2 k_i^2} \Gamma [1 + iZ(1/k_f - 1/k_i)]. \tag{20}
\]

Here \( Z \) is the nuclear charge, and the term \( \gamma(k_i, k_f) \) is a long-range amplitude correction. This form, according to [3], ‘leads to an excellent agreement with the exact calculation at high energies’. However, this comparison with exact results also indicated that it is not expected to work well at low energies, <8 eV. Also of note in this approximation is that the continuum–continuum transition simply defines an energy-dependent phase-shift, with no \( l \)-dependence.

4.1.2. Approximations and regimes of applicability. At this point, a number of approximations have been introduced, in both the fundamental theory (section 2), and the specific numerical treatment detailed above. To clarify the treatment, and expected limitations (many of which remain implicit in the discussion so far), further explicit discussion is presented here.

Firstly, as stated previously, the fundamental treatment presented herein assumes a perturbative treatment in the dipole regime. For weak fields (<10¹⁰ W/cm⁻²) this is expected to be an excellent approximation, while for strong fields (>10¹² W/cm⁻²) it is expected to fail; for moderate fields, the approximation may hold, but will depend on the details of the system (the polarizability of the system may be taken as a proxy here, indicative of the susceptibility to the laser field). In cases where field-mediated effects play a role, a numerical treatment which fully incorporates the effect of the
time-dependent electric-field on the scattering system is required (i.e. non-perturbative or strong-field treatment).

Secondly, for the specific numerical treatment introduced in this section, some additional approximation are implicit. The numerical methods reduce the scattering problem to a single active electron (SAE), and the scattering system is assumed to be static (no electronic or nuclear motion or relaxation). In this case, the ionizing system is described as a set of one-electron atomic or molecular orbitals in ePS (frozen core Hartree–Fock treatment), and photoionization instantaneously removes an electron from one of these bound states. (Further details regarding ePs can be found in [36, 37].)

For the continuum–continuum coupling, the numerics also assume SAE, and furthermore that the scattering occurs spatially in the region where the Coulombic part of the potential dominates—this is implicit in the choice of hydrogenic continuum waves, and mentioned in passing in the previous section. In more detail, this is the reason for the mention of overlap integrals at ‘long-range’ above. In this context, ‘long’ is a relative term, which is more properly defined as the onset of the Coulombic (or even asymptotic free-particle) form of the continuum wavefunction; equivalently, this is defined (as above) as the region where the potential is dominated by the Coulombic part, hence the multi-polar parts of the potential become negligible. For general discussion on short and long-range scattering, see [16]; for discussion of far-field onset in multi-polar systems see [41]; for discussion in the context of RABBITT see [3]; for specific diatomic examples see [42] (figure 4 and related discussion). Physically, these characteristics depend on the scattering system and the details of the potential (which may additionally be affected by the IR field in cases of moderate to strong fields); theoretically they may also depend on any additional approximations made beyond the assumption of hydrogenic continuum solutions. However, these approximations are expected to be reasonable for atomic and (small) poly-atoms, although are not expected to be good at low energies (<5 eV, see also the <8 eV limit suggested for the analytical phase approximation), where the photoelectron remains localized in the core region for longer interaction time-scales.

Also implicit in the numerical treatment is a neglect of multi-channel electronic effects (e.g. electron correlation, autoionizing resonances) and, for molecules, any other initial and final state dependent effects are also neglected (e.g. vibrational state effects, vibronic couplings). In general, for molecular photoionization, all of these types of effect might be expected. All of these effects will result in sharp changes in the photoionization dynamics with energy, and can be generically defined in this manner. These types of effect are not incorporated in the numerical treatment herein; however, with effort, these effects can be incorporated in numerical treatments, and investigated experimentally—see, for instance, [43–45]. In cases utilizing broad-bandwidth laser pulses, such as the AR-RABBITT experiments discussed herein, it might be expected that energy-averaging over the pulse bandwidth will mitigate the effects of any sharp behaviours, and that the simplified numerical treatment explored herein will therefore remain a reasonable approximation for a range of systems; nonetheless, the investigation of such effects remains a potentially fruitful area for research (although beyond the scope of the current study), since the interference between 1-photon pathways of different energies is somewhat unique to RABBITT measurements. The investigation of a bound-state resonance via RABBITT measurements in [5] is one example of this; [12] provides an interesting computational example, in which more advanced numerical treatments are employed to investigate intensity dependent effects, and autoionizing states, in RABBITT type situations. For more general extended discussions on various levels of approximation for related cases, which may also apply to the discussion herein, the reader is referred to [17] for discussion in the context of time-dependent pump-probe photoionization problems, and section 5 of [7] for discussion in the context of multi-path photoionization schemes, including more detail of types of effect in molecular photoionization, and other regimes of light–matter interaction.

Finally, it is worth considering these various approximations pragmatically. They are only expected to be valid within certain regimes, and may additionally fail for other reasons as detailed above. However, by treating the ionization and subsequent continuum—continuum interaction in a simplified one-electron picture, the numerical treatment becomes quite tractable, computational cheap, and within reach of many researchers using the available tools of the photoionization community (specifically, ePs). This type of numerical treatment therefore provides a basic foundation from which one can work and, indeed, proceed to specifically look for the particularly interesting experimental cases which indicate the breakdown of these approximations (see, e.g., discussion in section 3.1 above).

4.1.3. VMI simulation. In order to provide visceral results, and provide a more direct comparison with experimental measurements, the calculated photoelectron interferograms can be used to simulate VMI measurements of photoelectron interferograms. Numerically, this involves calculating a volumetric (3D) space, simulating the photoelectron distribution and summing to form 2D image planes: full details of the approach can be found in [7]. In the current model the radial (energy) spectrum is not calculated directly, so measured or estimated harmonic spectra are used to determine a set of Gaussian radial functions G(k), as discussed above, which are then mapped to velocity space and used to describe each band in the measured photoelectron spectrum. An example is given in figure 5, where the main features correspond to direct 1-photon ionization (labelled as ‘DB’) by the input harmonic spectrum (odd-harmonics from an 800 nm driving field), and the minor bands correspond to the position of the 2-photon RABBITT sidebands (labelled as ‘SB’) and even-harmonics (if present). These radial distributions are combined with the modelled angular distributions to determine the final photoelectron distribution on a 200 × 200 × 200 voxel
array, and consequent 2D projections on a 200 × 200 pixel grid.

4.2. AR-RABBITT results

Following the prescription of section 4.1, model results for photoionization of neon, and RABBITT measurements, were calculated. In modelling this case, ionization from a single initial state \( |pm,0 \rangle \) was assumed for simplicity, corresponding to one component of the \( p^2 \) valence orbital. Experimentally, one would assume that all degenerate \( m \) states contribute equally, however the general phenomenology and form of the results is unchanged by incorporating the degenerate \( m = \pm 1 \) initial states. Physically, the choice of a single \( m \) state corresponds to a choice of reference frame and, potentially, a form of alignment: in the atomic case this can be considered as orbital polarization, while in the molecular case may correspond to an aligned molecular ensemble, or to the molecular frame [15]. The calculated photoionization matrix elements for the 1 and 2 photon transitions are given in the appendix.

The position of the direct and sidebands calculated follow those shown in figure 5, which assumes an 800 nm driving field and the 1st ionization energy of neon (21.56 eV [46, 47]). The lowest energy feature, SB1, is not accurately modelled in this case, since the \( \Psi_0 \) pathway corresponds to direct (and possibly resonant) 2-photon ionization, which is not defined by the simple 2-step model. (For discussion of the similar case of RABBITT measurements in He, which also involved a resonant channel, see [5].) However, this pathway was approximated by using the lowest energy bound-free matrix elements, and is included here to emphasize the velocity mapping effect, which causes this central feature to perceptually dominate the final image, while high-energy features will be compressed, and appear as sharp outer rings in the image.

![Figure 5: Example of energy to velocity space conversion in VMI, based on an approximate photoelectron spectrum. The main features correspond to direct ionization (direct bands, ‘DB’), reflecting the spectrum of the incident (odd) harmonics (Hn), while the minor features indicate sideband positions (‘SB’) in ‘usual’ RABBITT schemes, and also correspond to the position of even-harmonic orders. In this case, an 800 nm driving field was assumed, and an IP of 21.56 eV (1st IP of neon). Note that low-energy features are spread out in velocity space, hence appear as large central features in the final image, while high-energy features will be compressed, and appear as sharp outer rings in the image.](image)

![Figure 6: Photoelectron yields (angle-integrated) for the RABBITT sidebands, \( I_2(\tau) \), based on neon photoionization calculations. Each sideband is normalized to unity at the maxima.](image)

Figures 6–8 provide a summary of the results. Figure 6 provides the (angle-integrated) photoelectron yields, \( I_2(\tau) \) for the four sidebands, and the corresponding, time-invariant, angular interferograms are shown in figure 7 for both contributing channels, and the resultant (channel-summed) observable. Figure 8 illustrates a set of iso-velocity (Newton) spheres from the full 3D photoelectron distribution, with each sphere corresponding to one band in the photoelectron spectrum, and the 2D projection of the full distribution.
A number of features are of note from these results:

1. As expected, the sideband phases vary according to the ionization dynamics (as a function of energy), incorporating both the direct ionization phase and the continuum–continuum phase.

2. The angular interferograms reflect the changing magnitude and phases of the \( \Psi_{+} \) and \( \Psi_{-} \) channels, and this is particularly apparent for SB3 and SB4. In these cases, it is primarily the relative phase of the SBs which contributes to the change in the final observable. The PADs change form significantly, and the temporal traces show a phase difference of approximately \( \pi/2 \).

3. The resultant PADs indicate structures with \( L \) higher than the usual symmetry-imposed laboratory frame limit (for an isotropic initial state distribution) of \( L \leq 2N \), where \( N \) is the photon-order of the process \( [8, 15, 48, 49] \). However, these structures only follow from the assumption of polarized orbitals \( (m = 0 \) selection), which allow a specific definition of the frame of reference. Additional \( m \)-state averaging over all initial \( |pm\) components would reinstate the usual symmetry restriction; conversely, the presence of these structures in experimental measurements would provide evidence for orbital polarization, and this effect has recently been observed in AR-RABBITT measurements \([50, 51]\). As mentioned above, it is of note that these considerations are analogous to those for laboratory versus molecular frame measurements \([15]\) and angular distributions from aligned molecules \([52]\).

4. As discussed above, the simulated VMI measurements show a perceptual dominance of the lowest order bands due to the nonlinear mapping from energy to velocity space, despite the fact that all bands are modelled in an identical fashion. Essentially, the energy resolution of VMI is non-uniform over the image, with the central region magnified relative to the outer region. This feature of VMI has previously been utilized to enable high-resolution spectroscopy \([53, 54]\) and combined with field ionization for ‘photoionization microscopy’ experiments \([55]\).

Overall, these model results indicate some of the expected features of AR-RABBITT, as measured using VMI. Of particular note in this case is the fact that this modelling was motivated by recent work on neon AR-RABBITT measurements \([50, 51]\), in which aspects of the key features shown here were observed. In particular, the experimental measurements, performed at IR field intensities of \( \sim 10^{13} \) W cm\(^{-2}\), revealed a 6-fold central structure, suggesting orbital polarization and selection in the strong laser field. It is, however, of note that this observation may also indicate higher-order photon processes than those expected \( (N > 2) \) contribute to the observable: in general careful
intensity-dependence studies are required to determine which effect plays the key role [12].

4.3. Elliptically polarized light

Following from the above, example AR-RABBITT results were also computed for an elliptically polarized IR field ($\xi = 0.4$, as shown in figure 3(b)), and a circularly polarized IR field. In these cases the XUV field was assumed to be linearly polarized, and a crossed polarization geometry was also assumed. In this geometry, again assuming a single initial $|p, m = 0\rangle$ state, the XUV ionization accesses only $m = 0$ states, while the IR field additionally accesses $m = \pm 1$ states. Essentially, this case allows for some, but limited, $m$-state mixing in the continuum–continuum transition.

Results are shown in figure 9 for four sidebands. In the observables for the elliptically polarized case, the frame rotation between the XUV and IR field polarization vectors, and subsequent $m$-mixing in the continuum–continuum transition, results in ‘twisted’ structures (with specific handedness) appearing in the resultant distributions in most cases. It is of note that 2D VMI projections (figure 8) will usually obscure such symmetry breaking, see e.g. [56] and references therein for discussion; furthermore, other experimental factors which break spatial symmetry (e.g. a strong laser field) may also lift the $m$ state degeneracy in practice, and may thus constitute other mechanisms of spatial symmetry breaking. For the circularly polarized case, the lack of $m$-state interferences—since only $m = \pm 1$ states are accessed—results in distinct, but cylindrical symmetric, distributions. Experiments utilizing this geometry are therefore particularly sensitive to any effects which break the $m$-state symmetry, such as a slight ellipticity in the XUV field or $m$-state mixing in a strong IR field.

4.4. Extended AR-RABBITT

Extended AR-RABBITT, in which even harmonics also contribute, presents the most information rich measurement. In this case, the interference between the time-dependent and time-independent channels provides an additional phase reference, creates interferences between channels with different photon orders, and results in a time-dependent angular interferogram. This provides the potential for control and metrology schemes analogous to many explored in previous energy-domain studies, such as odd–even parity mixing [22] and bound state resonance measurements [18, 19]; indeed, related concepts have already been explored in the time-domain [5, 23, 57]. In principle, it may also be possible to obtain a full set of partial wave magnitudes and phases using this technique (see ‘complete’ photoionization studies, e.g. [8, 26, 28, 58]) for a large number of partial waves, and the concept has recently been demonstrated for the atomic case [51]; equivalently, one can consider the technique as a means of obtaining full AR Wigner delays [3, 42].

The same model methodology as outlined above was employed, but with the addition of even harmonics in the XUV spectrum. Example results are shown in figure 10, which shows the resultant observables $I(\theta, \tau; E)$ and associated $\beta_{LM}(t; E)$ for three different photoelectron bands. In all cases complex behaviours can be observed, with multiple $l$-waves and phase contributions in the 3-path photoionization interferometer leading to highly structured observables. Across all of the bands, a similar structural motif is observed in the $I(\theta, \tau)$ plots, with the lobes along the laser polarization axis ($\theta = 90^\circ$, $270^\circ$) dominant, and weaker higher-order lobes. This structure is particularly clear in the polar plots given at discrete time-steps, and the corresponding $\beta_{LM}(t)$ parameters, which contain both even and odd $L$ terms.

The time-dependence of the observables now contains two frequency components: even $L$ terms which oscillate at $2\omega$, and odd $L$ terms which oscillate at $\omega$. This basic behaviour has previously been observed and modelled by Laurent et al [59]. However, the oscillation of the even terms corresponds to the same ‘breathing’ mode as described in the 1-colour case (since no additional cross-terms between the 1 and 2-photon pathways contribute), in which the photoelectron yield oscillated, but the angular distribution shows no time-dependence. Hence, normalization of the angular interferograms by the total yield removes the time-dependence, and reveals time-invariant even $L$ terms. For this reason, no oscillations are observed in the even $L$ terms shown in figure 10 (right column), and this part of the angular interferogram is time-invariant as for the ‘usual’ RABBITT case. The odd $L$ terms are more interesting, and result from the interferences between even and odd $l$-waves, correlated with the 1 and 2 photon transitions respectively. The effect of these interferences is, as noted above, to create up-down asymmetries in the observables. Clearly, the resultant interferograms are complicated, and the exact form of the observables are sensitive to the relative contributions and phases of the $l$-waves contributing to each of the three pathways. The relative phases observed in the $\beta_{LM}(t)$ can be considered as a probe of this behaviour, since different $l$-waves contribute to different $L$ terms [7, 60]; AR-RABBITT thus suggests a route to disentangling different phase contributions, related to the contributing ionization paths and $l$-waves, for use in phase-sensitive metrology scenarios. Of particular interest in this vein are ‘complete’ photoionization experiments, and AR Wigner delays, as noted previously.
Also noteworthy is the apparent temporal asymmetry of the observable in some cases: this is particularly apparent in the higher energy bands (e.g. band at 7.9 eV, figure 10(c)), with arrow-like structures spreading from the central lobes. This characteristic of the observable is a result of distinct temporal dependencies to the phases of the $l$-waves from different channels, leading to a skew in the temporal behaviour in some cases. Similar behaviour has previously been predicted based on a 2-path interferometer mediated by a vibronic wavepacket \[61\], which resulted in analogous $l$-wave interferences; however, in that case the asymmetry was not cleanly observed experimentally due the the temporal resolution of the measurement, although the results did strongly suggest such asymmetry was present. The presence of this type of temporal asymmetry in experimental measurements can therefore be regarded as a (relatively) direct phenomenological signature of significant phase-shifts between different $l$-waves. This characteristic is potentially useful as a means to observe experimentally-mediated changes in $l$-wave phases (e.g. due to laser intensity or wavelength) without the necessity of a full theoretical analysis of the results.

Figure 10. Time-dependent observables for three photoelectron bands for extended AR-RABBITT. Left column shows full $I(\theta, t; E)$ surfaces, with insets showing 1D cuts $I(\theta)$ in polar form at specific times. Right column shows the associated $\beta_{LM}(t; E)$ values, normalized by the total yields $\beta_{00}(t, E)$. 

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5. Summary and conclusions

In this work, some general properties of AR-RABBITT measurements have been investigated via a multi-channel, 2-photon ionization model in the perturbative regime. A range of interesting phenomena are observed in this case, due to the range of interferences contributing to the final observable. Of particular note is the fact that RABBITT type schemes mix bound-free matrix elements of different energies, which cannot be interfered in usual (energy-resolved) photoionization studies; furthermore, AR-RABBITT provides observables which are also highly sensitive to the ionization matrix elements as a function of angular-momentum and energy. Studies of photoionization dynamics in the energy and time-domain (Wigner delays) both come under this category, as does polarization-sensitive XUV pulse metrology. Experiments investigating the effects of bound-state or continuum resonances are one clear application of AR-RABBITT, and such effects can also be investigated as a function of the IR field intensity. The capabilities of ‘extended’ AR-RABBITT schemes, utilizing even harmonics, are most interesting here, since 1 and 2-photon channels are interfered in this case, providing a heterodyne phase reference. This scheme also allows for control over the resultant photoelectron interferogram, since up-down asymmetry can be broken as a function of IR field phase (i.e. XUV-IR time-delay).

Some of these concepts have already been investigated using RABBITT or AR-RABBITT techniques, but much work is open to fruitful exploration in this vein. Since VMI apparatus, along with other AR charged particle techniques (e.g. COLTRIMS), have proliferated in recent years, AR photoelectron measurements are now routine for many experimenters. This has lead to a range of novel studies utilizing the related high-information content observable of photoelectron angular distributions [9], and the outlook and utility of AR-RABBITT is similarly promising.

Appendix. Matrix elements

The full set of matrix elements for the neon calculations are shown in figure 11. As detailed in section 4.1, the 1-photon bound-free matrix elements were computed using ePs, while the continuum–continuum elements assume Coulomb wavefunctions. In all cases the matrix elements are shown as a function of the final photoelectron energy. For the 2-photon bands the calculations assume an 800 nm IR field, hence $h\nu = 1.55$ eV, and this is the energy difference assumed between the final and intermediate (1-photon) states in the calculation.

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