Propensity rules and interference effects in laser-assisted photoionization of helium and neon

Mattias Bertolino, David Busto, Felipe Zapata and Jan Marcus Dahlström

Department of Physics, Lund University, Box 118, SE-221 00 Lund, Sweden

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Abstract
We investigate the angle-resolved photoelectron spectra from laser-assisted photoionization for helium and neon atoms using an ab initio method based on time-dependent surface flux and configuration interaction singles. We find that the shape of the distributions can be interpreted using a propensity rule, an intrinsic difference in the absorption and the emission processes, as well as interference effects between multiple paths to the final angular momentum state. The difference between absorption and emission is hidden in the first sideband in neon due to the multiple competing channels, while in the second sideband a qualitative difference between absorption and emission is observed. In the \( m \)-resolved case, a clear difference is observed already in the first sideband, as exemplified in helium and \( m \)-resolved neon.

Keywords: electronic excitation and ionization, light–matter interaction, photoemission, single- and few-photon ionization and excitation, ultrafast phenomena

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

1. Introduction

Photoionization is a fundamental process in nature where absorption of a photon by an atom leads to the emission of a photoelectron and to the creation of a positive ion: \( A + \gamma \rightarrow A^+ + e^- \). The photoelectric effect is possible only when the energy of the photon, \( \hbar \omega \), is sufficiently large to overcome the electron binding energy of the atom, \( I_p \). Although the process is explained qualitatively as a one-electron transition from an occupied atomic orbital to a continuum of states, the quantitative photoionization rates are affected by electron–electron correlation effects in the atom, as evidenced in works based on many-body perturbation theory \([1–3]\). Given photons with a wavelength that is larger than the size of the atom, \( \lambda_0 = 5.29 \times 10^{-11} \text{ m} \), the electronic transitions can be simplified to follow the dipole selection rules, where the angular momentum of the electron must change by one unit: \( \Delta \ell = \pm 1 \). This reduces the complexity of the problem to a finite set of continua that can be reached by the photoelectron. As a complement to the dipole selection rules, Fano proposed a propensity rule, which states that absorption of light favours increasing the electron angular momentum, \( \ell \rightarrow \ell + 1 \), over decreasing the angular momentum, \( \ell \rightarrow \ell - 1 \) \([4]\). This simple rule explains why in neon the probability to reach the \( d \)-wave from the initial \( 2p \) orbital is larger than the probability to reach the \( s \)-wave. As with most simple rules, there are also some notable exceptions, e.g. in photoionization from the \( 3p \) orbital in argon in the vicinity of the Cooper minimum, where the \( d \)-wave contribution becomes very small due to a vanishing dipole element for the transition \([5]\).

In recent years, novel light sources have made it possible to study light–matter interactions in more extreme conditions where the atoms are subject to more intense short-wavelength fields \([6]\), multi-color fields \([7–11]\) and short pulses with duration on the femtosecond and attosecond time scale \([12]\). One class of problems that has attracted attention is laser-assisted photoionization, where an atom is photoionized using radiation of short-wavelength, typically extreme ultraviolet...
radiation (XUV), but with an additional long-wavelength laser field, typically in the infrared range (IR), which dresses the atom: $A + γ_{\text{XUV}} \pm qγ_{\text{IR}} \rightarrow A^+ + e^-$. In this case, the electron is emitted by the XUV-field and then subsequently interacts with the IR-field, leading to laser-driven continuum–continuum transitions. In the multi-cycle pulse limit, the resulting photoelectron spectrum includes a main peak at an energy given by the XUV photoelectric effect and a number of sideband peaks due to the increasing number of interactions with the IR-field: $E_{\text{kin}} = h\omega_{\text{XUV}} \pm q\hbar\omega_{\text{IR}} - I_p$. In the case where the IR-field is weak, the strength of the sidebands decreases with each order as expected from perturbation theory with a probability determined by the intensity power law in atomic units: $P_q \propto (I_p)^q$. In the opposite case, when the IR-field is strong, laser-assisted photoionization can be interpreted using semi-classical electron trajectories [13, 14].

Laser-assisted photoionization has been studied analytically using time-dependent Volkov states, which by their closed-form solution allow for efficient calculations of cross-sections for laser-assisted scattering and ionization [15–17]. More accurate numerical studies have been performed by perturbation theory within the single-active electron (SAE) approximation [18, 19] and by many-body perturbation theory at the level of one-photon random phase approximation with exchange (RPAE) with uncorrelated continuum–continuum transitions for closed shell atoms [20] and for photodetachment of negative ions [21]. Recently, a gauge-invariant two-photon RPAE approach has been demonstrated [22]. Numerical simulations have also been performed in the time domain within the SAE [23–26], for helium [27] and many-electron atoms, e.g. neon by R-matrix theory [28, 29] and argon by density functional theory (DFT) [30]. Many-electron correlations in non-linear photoionization has also been studied by time-dependent theories based on configuration interaction singles (CIS) [31] and multi-configuration self-consistent fields (MCSCF) [32].

Laser-assisted photoionization is an important process in attosecond science, where it is at the core of both pulse characterization techniques using the RABBIT technique [33] and for measurement of atomic delays in photoionization [34, 35]. Recently, atomic delay measurements have been performed with angular resolution [36–38]. This has evidenced that subtle differences in absorption and emission processes in the continuum–continuum transitions can lead to a strong dependency on the atomic delay with angle of emission, incomplete quantum interference in RABBIT measurements and to qualitatively different angular distributions of photoelectrons, as explained by Busto et al by extending Fano’s propensity rule to continuum–continuum transitions [37].

In this paper, we perform ab initio simulations of laser-assisted photoionization by propagating the time-dependent Schrödinger equation (TDSE) within the configuration interaction singles approximation (TDCIS) [39, 40] and resolving the photoelectron wave packet using the time-dependent surface flux method (t-SURFF) [41]. This allows us to examine the angular distributions and propensity rules in laser-assisted photoionization of helium and neon atoms for both the first sideband and higher-order sidebands generated by absorption or emission of multiple IR-photons. We find different angular distributions formed by absorption and emission processes in the continuum, and we are able to verify that the propensity rules can be extended to higher-order continuum–continuum transitions driven by the IR-field. The paper is structured as follows. In section 2, our method is described along the relevant laser parameters. In section 3, we present our results of the numerical simulations. The presented data is discussed in section 4 together with a discussion of potential topics for future studies. Finally, in section 5, we summarize our conclusions. Atomic units ($h = e = m_e = 4\pi\epsilon_0 = 1$) are used throughout this paper if not specifically stated.

2. Method

In this section we describe our method to compute laser-assisted photoionization from closed-shell atoms. In part A we describe the vector potential used to model the electromagnetic fields, in part B we review the TDCIS ansatz, in part C we present details of our t-SURFF implementation and in part D we give some more details on our numerical implementation.

2.1. Field description

The numerical experiments are carried out with Gaussian XUV- and IR-pulses, linearly polarized along the quantization axis $\hat{z}$, that are overlapped in time and defined by a vector potential given by

$$A = \left[ A^\text{XUV}_0 \sin(\omega\text{XUV}t) + A^\text{IR}_0 \sin(\omega\text{IR}t) \right] \times \exp \left[ -2 \ln(2) \frac{r^2}{\tau^2} \right],$$

(1)

where $A^\text{XUV}_0 = 0.005$ a.u. and $A^\text{IR}_0 = 0.003$ a.u. which yields a peak intensity of the IR pulse of $5.6 \times 10^9$ W cm$^{-2}$. This intensity implies only perturbative action by the IR-field. The duration of the pulses is given by $\tau = 410$ a.u. $\approx 10$ fs and the frequency of the IR-field is given by $\omega_{\text{IR}} \approx 1.55$ eV to match a Ti-Saph laser system. The fact that the XUV pulse duration is longer than the IR period, $\tau > 2\pi/\omega_{\text{IR}}$, implies that the photoelectron spectrum will consist of discrete peaks that correspond to interaction with $q$ photons in the continuum.

2.2. TDCIS ansatz

The TDCIS ansatz [39] for the many-electron wavefunction is

$$|\Psi(t)\rangle = \alpha_0(t) |\Phi_0\rangle + \sum_u \sum_p \alpha_p^u(t) |\Phi_p^u\rangle,$$

(2)

where $|\Phi_0\rangle$ is the Hartree–Fock ground state and the singly excited states $|\Phi_p^u\rangle$ are constructed using the framework of second quantization,

$$|\Phi_p^u\rangle = \frac{1}{\sqrt{2}} \left\{ \hat{c}_{p+} \hat{c}_{u+} + \hat{c}_{p-} \hat{c}_{u-} \right\} |\Phi_0\rangle,$$

(3)
where \( \hat{c}^\dagger_{\sigma p} \) creates an electron in the virtual (exc) orbital \( p \) with spin \( \sigma \), \( |\phi_{\sigma p}\rangle \), while \( \hat{c}_{\sigma p} \) creates a hole in the initially occupied (occ) orbital \( a \) with spin \( \sigma \), \( |\varphi_{\sigma a}\rangle \). The ansatz in equation (3) assures that the spin singlet state character of the closed-shell initial state is maintained also for excited states. Similarly, we assure that the spin \( J \) in accordance with Koopmans’ theorem, the photoelectron depends on the binding energy of orbital \( a \) with Coulomb interactions are neglected. The energy of ions of the time-dependent orbital in the region far from the XUV-photon. In addition, both helium and neon are well-described in the accessible continuum-state after the absorption of one initial angular momentum state and hence their difference of helium and neon is done on the basis of their different field-induced dynamics of the photoelectron beyond the \( \chi \) function, \( \chi^a(r,t) = \frac{1}{r} \sum_{\ell_p} \psi^a_{\ell_p\mu_a}(r,t) Y_{\ell_p\mu_a}(\Omega_r) \),

\[ \chi^a(r,t) = \frac{1}{r} \sum_{\ell_p} \psi^a_{\ell_p\mu_a}(r,t) Y_{\ell_p\mu_a}(\Omega_r) \times \exp \left[ -i \int_{t_0}^t dt' \left\{ \frac{k^2}{2} + A_c(t') k_z - \varepsilon_a \right\} \right], \]  

which are plane waves with a time-dependent phase.

The spectral amplitudes for laser-assisted photoionization are found using a complex amplitude for the overlap of time-dependent orbitals in the outer region, \( r > r_e \), using a radial Heaviside operator acting at \( r_e \), \( \Theta(r_e) \), defined as

\[ b_{ka}(t) = \left( \chi^{(v)}_{ka}(t) \Theta(r_e) \right) \chi(a)(t) \]  

The complex amplitude in equation (8) becomes the scattering amplitude after a sufficiently long time, \( t = T \), when all external fields have ended and when the photoelectron wave packet has propagated far away from the ion [41]. We obtain a final expression for the scattering coefficients in t-SURFF given by

\[ b_{ka}(T) = i \int_{-\infty}^{\infty} \frac{d\tau}{\pi} \exp \left[ i \int_{t_0}^T d\tau \left\{ \frac{k^2}{2} + A_c(\tau) k_z - \varepsilon_a \right\} \right] \times \sum_{\ell_p} \left\{ (-i)^\ell \left( \frac{1}{2} r_e j_\ell(k_{\ell_p}) + j_{\ell'}(k_{\ell_p}) \right) \right\} \psi^a_{\ell_p\mu_a}(r_e,t) \times Y_{\ell_p\mu_a}(\Omega_k) + \frac{4\pi}{3} r_e j_\ell(k_{\ell_p}) \psi^a_{\ell_p\mu_a}(r_e,t) \sum_{l=\ell+1} Y_{l\mu_a}(\Omega_k) \times \int d\Omega_r Y_{\ell_r\mu_r}(\Omega_r) Y_{\ell_0\mu_0}(\Omega_r) \times \psi^a_{\ell_0\mu_0}(\Omega_r), \]

where \( j_\ell(kr) \) is the spherical bessel function of order \( \ell \) and \( j_{\ell'}(kr) \) is its derivative, both evaluated at kr. Further, the integral over the spatial angles (\( \Omega_r \)) of the three spherical harmonics can be evaluated by using the relation

\[ \int d\Omega_r Y_{\ell_r\mu_r}(\Omega_r) Y_{\ell_0\mu_0}(\Omega_r) \times \psi^a_{\ell_0\mu_0}(\Omega_r) = \sqrt{\frac{3}{4\pi}} (-i)^{\ell_0} \psi^a_{\ell_0\mu_0}(\Omega_r) \times \left( \ell \begin{pmatrix} 1 & 0 & 0 \\ -m_\ell & m_\ell & 0 \\ m_\ell & 0 & 0 \end{pmatrix} \ell \begin{pmatrix} 1 \\ \ell_p \end{pmatrix} \right), \]

where the last two factors are Wigner 3–j symbols coupling the particle angular momenta to the adjacent angular momenta under the dipole approximation. We note that the t-SURFF method is an approximate method for analysis of photoelectrons when applied to this problem with a long-range potential from the remaining ion [41]. Single or multi-photon transitions that populate Rydberg states can also be expected to cause some problems in special cases due to their large radial extent, \( \sim a^2 \).

The angular distribution of the photoelectron can be described by a coherent superposition of partial waves with...
the corresponding angular momenta determined by dipole selection rules. As an example, the case of two final angular momenta, which is expressed by two spherical harmonics: $Y_{l_q,m}$ and $Y_{l_q,-m}$, with $l_q = l_q + 1$ and $l_q = l_q - 1$, has a complex amplitude with an angle-dependence given by

$$f(\theta) = \tilde{a}_{l_q,m} Y_{l_q,m}(\theta, \varphi) + \tilde{a}_{l_q,-m} Y_{l_q,-m}(\theta, \varphi),$$

(11)

To find these partial wave amplitudes from the general scattering amplitudes, $a_{k_a}(T)$, we solve a minimization problem,

$$\tilde{a} = \arg \min_{a} \sum_q \left| F_q(\theta_q) - \sum_{m} \left| a_{m}(T)\right|^2 \right|^2,$$

(12)

for the general complex amplitudes $\tilde{a} = \{ \tilde{a}_m \}$ using the SciPy optimize.minimize function. The magnetic quantum number of the photoelectron is linked to that of the hole, $m_p = m_a = m$, which is typically unresolved in experiments and, therefore, is summed over incoherently. In equation (12) the angular probability distribution of a given peak $q$ is computed by integrating over energy, that is

$$F_q(\theta_q) = \frac{1}{2} \int_{E_{k_a} - \epsilon}^{E_{k_a}} dE |a_{k_a}(T)|^2,$$

(13)

where $E_q$ is the energy at the center of the peak $q$, using equation (8) for a given final momentum of the photoelectron, $k = |k|$, evaluated at a set of polar angles $\theta_i$. This procedure allows us to extract partial wave amplitudes for all photoelectron peaks, $\pm q$, which we label by $\tilde{a}_{m,q}$, where the reference to $m$ is sometimes omitted for brevity.

2.4. Numerical implementation

Our method is similar to that of Karamatskou et al [31] and Pabst et al [43], as it combines TDCIS for closed-shell atoms [40] with the time-dependent surface flux (t-SURFF) method [41], but our method differs in a number of ways: (i) our numerical implementation is based on B-splines [44], (ii) we use hard exterior complex scaling (ECS) to handle the boundary conditions of the outgoing photoelectrons [45], (iii) our final expression of t-SURFF, equation (9), differs from that of Karamatskou et al [31], as discussed in appendix .

In this work we restrict the active space configuration in energy, $E_{k_a}^p = \epsilon_p - \epsilon_a < 30$ a.u. = 816.33 eV, and use an electron angular momentum of at least $\ell = 6$. We also restrict the TDCIS calculation to the outermost valence orbital in the sum over occupied orbitals in equation (2) and, therefore, do not consider XUV-stimulated hole–hole transitions that can lead to further excitation of the ion within TDCIS [46]. The latter restriction implies that we consider the 1s orbital in helium, but only excitation from the 2p orbital in neon. The binding energies used are the Hartree–Fock binding energies $I_p = 0.918$ a.u. for helium and $I_p = 0.850$ a.u. for the 2p orbital in neon.

For the B-spline interpolation, we use 165 and 320 knot points in the inner region for helium and neon respectively and 30 knot points in the ECS region for both atoms. The polynomials used are chosen to be of order 6. We use a knot point spacing of 0.4 a.u. and an ECS-angle of 25 degrees. The use of ECS leads to a non-Hermitian Hamiltonian, where the virtual states are exponentially damped in time by complex eigenvalues. In space the electron wavefunctions remain physical within the radius $r_{ecs} = 64$ a.u. for helium and $r_{ecs} = 120$ a.u. for neon, while inside the ECS region, $r > r_{ecs}$, the photoelectron wavefunctions are damped radially, which helps to remove nonphysical reflections from the end point of the radial knot point sequence. The use of ECS restricts the propagation of TDCIS to the velocity gauge.

3. Results

In this section we present our results from laser-assisted photoionization simulations. We present the numerically obtained photoelectron angular distributions (PAD) for helium in part A and for neon in part B. The frequency of the XUV-photon, $\omega_{XUV}$, is varied in order to study how the PAD depends on different final kinetic energies of the photoelectron.

In figure 1, the laser-assisted photoionization paths are shown for helium and neon respectively. The main peak in the photoelectron spectrum is originating from absorption of one XUV-photon and it is denoted $q = 0$. The sidebands corresponding to additional absorption (+) and emission (–) of $q$ IR-photons are denoted by $\pm q$. The photoelectron alters its orbital angular momentum by plus or minus one for each interaction event with the dressing IR-field. The PAD results from different spherical harmonics in superposition, as shown for each value of $q$ in figure 1.

3.1. Helium

In figure 2(a) we present our simulation of the angle-resolved photoelectron spectrum in helium on a logarithmic scale. The main central line corresponds to absorption of one XUV-photon and the sidebands correspond to absorption or emission of $q$ IR-photons. Alongside the spectrum, the PADs for sidebands, retrieved by equation (13), are shown in figure 2(a) for the first absorption and emission peaks: $q = \pm 1$, and in figure 2(c) for the second absorption and emission peaks: $q = \pm 2$. The main peak, $q = 0$, is included for reference. The maxima of the angular distributions are normalized to unity in order to make the comparison between the PADs of the different peaks easier. The partial wave fitting, where only dipole-allowed spherical harmonics are included in the sum of equation (12), is in excellent agreement with the simulated PAD for all peaks, $q$. The PAD shows an asymmetry between absorption and emission of IR-photons in the continuum which is expressed by the different number of minima in the sideband peaks. For example, in the first absorption and emission peaks, $q = 1$ and $q = -1$, we observe two minima and one maximum, respectively.

In figure 3, we present the normalized PAD as a function of XUV-photon energy for $q = 1$ and $q = 2$ peaks in helium. A uniform filter is applied to smooth spurious oscillations (that are inherent to the t-SURFF method for Coulomb-like problems). Each figure corresponds to multiple laser-assisted photoionization simulations with all parameters fixed except
the frequency of the ionizing XUV-field. In the high kinetic energy limit, the multiple minima of the absorption peaks, \( q = 1, 2 \), tend towards a polar angle of 90 degrees. On the contrary, in the case of emission, the position of the single minimum is independent of the kinetic energy and located at 90 degrees (not shown).

3.2. Neon

In figure 4, the obtained angle-resolved photoelectron spectrum in neon (a) is shown alongside the normalized PADs of the first (b) and second (c) absorption and emission peaks. The fitted spherical harmonics match well with the angular distribution of the peaks of the sidebands. Contrary to helium, we now have two possible intermediate cases after absorption of an XUV-photon with \( \ell = 0 \) and \( \ell = 2 \). In neon we do not observe any qualitative difference in the PAD, comparing the first absorption and emission peaks, \( q = \pm 1 \). Both peaks show one single minimum with a qualitatively similar angular distribution. However, in the second absorption and emission peaks, \( q = \pm 2 \), there is a clear difference between \( q = 2 \), which shows two distinct minima, and \( q = -2 \), which shows a single minimum.

Unlike helium, the angular distribution in neon results from an incoherent superposition of magnetic quantum numbers of the hole, \( m = m_e \). Therefore, we complement our neon studies with \( m \)-resolved PADs. Since we deal with systems of spherical symmetry, the positive \( m = +1 \) channel and the negative \( m = -1 \) channel will yield the same photoelectron angular distribution, and without loss of generality we can consider it one effective channel. We denote this channel as the gerade \( m = \pm 1 \) channel \([42]\). In figure 5, the angle-resolved photoelectron spectra are presented in neon on a logarithmic scale for \( m = 0 \) and \( m = \pm 1 \), respectively, alongside the normalized PAD of the absorption and emission peaks. For the \( m = 0 \) channel isolated, the PADs of \( q = \pm 1 \) show small differences. In absorption we find two shallow minima, while in emission there are instead two shoulders. Both absorption and emission have a deep minimum at 90 degrees. In total the \( m = 0 \) case has three minima for \( q = 1 \), and one minimum for \( q = -1 \). In the \( m = \pm 1 \) channel, the difference between one-photon absorption and emission, \( q = \pm 1 \), is more distinct because the PAD shows four and three clear minima, respectively (including the minima at 0 and 180 degrees). In \( q = \pm 2 \), there is a clear difference between absorption and emission of two IR-photons for both \( m = 0 \) and \( m = \pm 1 \). In the \( m = 0 \) channel, we identify two minima and two outer shoulders in the case of absorption, \( q = 2 \), and a flat region with a single shallow minimum in the case of emission, \( q = -2 \). Likewise, in \( m = \pm 1 \), we identify a clear difference between \( q = 2 \) and \( q = -2 \). The \( q = 2 \) peak has five minima, while the \( q = -2 \) peak has three minima (including the minima at the polar angle of 0 and 180 degrees).

In figure 6, we present the normalized PAD of peaks \( q = 1 \) and \( q = 2 \) as a function of the XUV-photon energy for neon in the non-resolved \( m \) case, and the two resolved \( m = 0 \) and \( m = \pm 1 \) cases. While the PADs change in shape with increasing XUV-photon energy, they maintain their qualitative attributes. We note that the neon \( m = \pm 1 \) cases, shown in figures 6(c) and (f), are qualitatively similar to the helium \( m = 0 \) case, shown in figures 3(a) and (b), with the exception of two stationary minima in neon at 0 and 180 degrees.

4. Discussion

In the previous section we have shown that the PADs of sidebands due to absorption and emission of IR-photons exhibit qualitative differences. In order to understand this difference we turn to a partial wave analysis that allows us to study the relative strength of different laser-assisted photoionization paths (see figure 1). A similar approach was recently used by Busto et al to study the first-order sidebands, \( q = \pm 1 \) \([37]\). Each transition between partial waves in the continuum is determined by a radial dipole integral as well as an angular dipole integral. According to Fano’s propensity rule for photoionization \([4]\), the radial integral favours transitions to higher angular momentum. In the continuum the photoelectron can both absorb and emit IR-photons, which respectively favours increasing and decreasing angular momentum \([37]\). This is a direct consequence of time-reversal symmetry for the two continuum processes. In the high-energy limit, this radial effect vanishes, while the angular effects remain constant. This
implies that the branching ratio of different partial waves will be determined by the angular integrals for both absorption and emission sidebands in the high-energy limit.

In order to study unique partial wave paths in the continuum to the first sidebands, $q = \pm 1$, we consider helium with $m = 0$ and neon with $m = \pm 1$. These are special transitions because they only have one intermediate angular momentum that is reached after absorption of the XUV-photon. Therefore, it is easy to compare absorption and emission of one IR-photon directly using the complex amplitudes of partial waves, $a_{\ell_{+1}/\ell_{-1}}$, extracted by equation (12) for $q = \pm 1$. The notation, $\ell_{+1/\ell_{-1}}$, refers to increasing and decreasing angular momentum, respectively, as defined above equation (11).

In Figure 7 we present the absolute ratio of the complex amplitudes, $|a_{\ell_{+1}}^{\pm}/a_{\ell_{-1}}^{\pm}|$. In the high-energy limit, we find that the ratios for $q = \pm 1$ approach a value determined by the angular part of the dipole matrix element, shown in Figure 7 as a gray dotted line. In helium, for $q = 1$, the limit of the ratio is given by

$$\left| \frac{a_{\ell_{+1}}^{+}}{a_{\ell_{-1}}^{+}} \right| \rightarrow \left| \frac{\langle Y_{20} | Y_{10} | Y_{10} \rangle}{\langle Y_{00} | Y_{10} | Y_{10} \rangle} \right| = \frac{2}{\sqrt{5}},$$

which means that it is more probable to decrease angular momentum. At low kinetic energies we find that the absorption process, $q = 1$, favours increasing angular momentum due to an enhancement from the radial dipole contribution. In neon, for $m = \pm 1$ and $q = \pm 1$, the limit is

$$\left| \frac{a_{\ell_{+1}}^{\pm}}{a_{\ell_{-1}}^{\pm}} \right| \rightarrow \left| \frac{\langle Y_{31} | Y_{10} | Y_{21} \rangle}{\langle Y_{11} | Y_{10} | Y_{21} \rangle} \right| = \sqrt{\frac{8}{7}}.$$

which means that it is more probable to increase angular momentum. At low kinetic energies we find that the emission process, $q = -1$, favours decreasing angular momentum due to an enhancement from the radial dipole contribution. Qualitatively, we understand that the $q = \pm 1$ ratios are close to one because there is one unique path to reach each final partial wave. This is related to the comparable magnitude of dipole matrix elements from $\ell_{0}$ to $\ell_{0} \pm 1$.

In the case of $q = \pm 2$ the physics is more complicated because there are two interfering paths leading to the lower angular momentum, while there is one unique path to the higher angular momentum for helium with $m = 0$ and neon with $m = \pm 1$. The two interfering paths leading to the lower angular momentum is coined a "diamond" due to its diagrammatically convincing shape. In Figure 7 we show the ratios of absolute complex amplitudes between higher and lower final angular momentum for $q = \pm 2$. For helium the limit of the ratio is

$$\left| \frac{a_{\ell_{+1}}^{+2}}{a_{\ell_{-1}}^{+2}} \right| \rightarrow \left| \frac{\langle Y_{30} | Y_{10} | Y_{20} \rangle \langle Y_{20} | Y_{10} | Y_{10} \rangle}{\langle Y_{10} | Y_{10} | Y_{20} \rangle ^2 + \langle Y_{10} | Y_{10} | Y_{00} \rangle ^2} \right| = \frac{2}{\sqrt{21}},$$

while for neon the limit is

$$\left| \frac{a_{\ell_{+1}}^{+2}}{a_{\ell_{-1}}^{+2}} \right| \rightarrow \left| \frac{\langle Y_{41} | Y_{10} | Y_{31} \rangle \langle Y_{31} | Y_{10} | Y_{21} \rangle}{\langle Y_{21} | Y_{10} | Y_{31} \rangle ^2 + \langle Y_{21} | Y_{10} | Y_{11} \rangle ^2} \right| = \frac{\sqrt{8}}{3\sqrt{3}}.$$
favoured over the higher angular momentum in the $q = \pm 2$ peaks. Although the matrix elements in the denominator of equations (16) and (17) are taken in absolute-square, one should not misunderstand this as an incoherent summation over paths in the diamond. Instead, this indicates that the two coherent paths to the lower angular momentum add up constructively. The fact that the two paths in the diamond add up in phase with each other can be understood by considering the continuum–continuum phases acquired in laser-stimulated transitions, which only weakly depend on the angular momentum transitions, cf reference [47].

In the high-energy limit, the value of the $q = \pm 2$ ratio between final angular momenta ($>/<$) is explained by a constructive interference effect between different intermediate partial waves, while it is the radial integrals that explain the difference between the PADs in absorption (+) and emission (−) at low energies. The $q = 2$ peak in neon $m = \pm 1$ is a good example of the importance of this interplay between angular and radial integral effects. The paths leading to the final lower angular momentum goes through increasing–decreasing or decreasing–increasing angular momentum pathways in the continuum that are (radially) weaker than the path of two times increasing the orbital angular momentum to the larger final angular momentum. Yet, the constructive interference to the lower angular momentum $\ell = 2$, results in a probability ratio strongly favouring the transition that lowers the angular momentum. In other words: two average paths tend to overtake the one enhanced path. However, in the low-energy limit the radial effect can dominate over the interference effect, as evidenced in figure 7(a) for $q = 2$, where the larger angular momentum amplitude is marginally greater than the smaller angular momentum amplitude.

We now turn to the question how the weak radial effects can change the number of minima in the PADs? The condition of a node in the angular distribution that consists of two partial waves, is found by setting $f(\theta)$ from equation (11) to zero. This leads to the following relation:

Figure 4. (a) Angle-resolved photoelectron spectrum in neon 2p using an XUV-photon energy of 38 eV. (b) PAD using $q = \pm 1$ and (c) PAD using $q = \pm 2$. The dots in (b, c) are fits to the data using equation (12).

Figure 5. Angle-resolved photoelectron spectrum and PADs in neon 2p with $m = 0$ (a–c) and $m = \pm 1$ (d–f). The XUV-photon energy is 38 eV. The dots in (b, c) and (e, f) are fits to the data using equation (12).
Figure 6. PAD of neon as a function of XUV-photon energy for peaks (a) $q = 1$ unresolved in $m$, (b) $q = 1$ with $m = 0$, (c) $q = 1$ with $m = \pm 1$, (d) $q = 2$ unresolved in $m$, (e) $q = 2$ with $m = 0$ and (f) $q = 2$ with $m = \pm 1$.

Figure 7. Ratio of the magnitude of the coefficients of fitted spherical harmonics of the peaks of the angle-resolved photoelectron angular distribution as a function of XUV-photon energy in (a) helium and (b) neon, $m = \pm 1$.

$$\tilde{a}_{1,0}^q = \frac{Y_{1,0}(\theta, \varphi)}{Y_{1,0}(\theta, \varphi)}$$

where $\tilde{a}_{1,0}^q$ are different for both absorption (+) and emission (−). Interestingly, we have found that the ratios on the right hand side of equation (18) are equal to

$$\lim_{\theta \to \pi/2} \frac{Y_{11}(\theta, \varphi)}{Y_{31}(\theta, \varphi)} = \frac{\sqrt{8}}{7} \quad (20)$$

$$\lim_{\theta \to \pi/2} \frac{Y_{10}(\theta, \varphi)}{Y_{30}(\theta, \varphi)} = \frac{2}{\sqrt{21}} \quad (21)$$

$$\lim_{\theta \to \pi/2} \frac{Y_{21}(\theta, \varphi)}{Y_{41}(\theta, \varphi)} = \frac{\sqrt{8}}{3\sqrt{3}} \quad (22)$$

In the limit of a polar angle equal to 90 degrees, which is equal to the corresponding ratios in equations (14)–(17). This implies that the condition for a node in equation (18) is just at the limit for 90 degrees and, therefore, sensitive to small changes in the magnitude of the partial wave amplitudes. In the case of absorption, the radial effect allows for nodes at angles close to 90 degrees due to increasing contribution of the higher angular momentum, while in emission this condition will not be satisfied. For PADs in helium, shown in figures 2(a) and (c), this effect explains the two sharp minima on either side of 90 degrees for both $q = 1$ and $q = 2$. The third sharp minimum at 90 degrees for $q = 2$ arises due to the odd parity of the photoelectron after absorption of an odd number of photons from the helium ground state. In contrast, there is no sharp minima for $q = -1$ and only a single sharp minimum for $q = -2$ due to odd parity in helium. This is because the condition for additional minima of equation (18) are not met due to an increased contribution of the lower angular momentum. In $q = -1$ in helium we do observe a local minimum at 90 degrees, which is not fulfilling the condition in equation (18).

For PADs in neon with $m = 0$, shown in figure 5(a) and (c), the condition for nodes is not satisfied for either $q = \pm 1$. The $q = 1$ case shows two shallow minima, while the $q = -1$ case shows two shoulders, which indicates that emission is further from the additional node condition in equation (18). There is a sharp minimum at 90 degrees in both $q = \pm 1$ in neon with $m = 0$ due to odd parity after exchange of two photon. For $q = 2$ we have three spherical harmonics that interfere.
this case we see two sharp minima, where the condition of a node is fulfilled, and two additional outer shoulders, where the node condition is not fully satisfied. For \( q = -2 \) the flat region comes from the fact that the condition for nodes is not fully met at either of these four instances. For neon with \( m = \pm 1 \), shown in figures 5(e) and (f), there are again two partial waves that interfere. The condition for additional nodes is found in both \( q = 1 \) and \( q = -2 \), while it is not found for \( q = -1 \) or \( q = -2 \). The nodes at 0, 90 and 180 degrees are related to the static symmetry properties of spherical harmonics with \( m = \pm 1 \).

Finally, the absence of a qualitative difference between \( q = 1 \) and \( q = -1 \) for neon with incoherent addition of both \( m = 0 \) and \( m = \pm 1 \), can be understood by the fact that \( m = 0 \) has two small maxima at approximately the same angles where \( m = \pm 1 \) have nodes, as seen in figure 5(a) and (e), respectively. This effect covers up the difference between absorption and emission processes in the first sideband of neon. This motivates precision experiments with resolution in the magnetic quantum number when using laser-assisted photoionization to study the propensity rules in atoms. Alternatively, the consequence of additional nodes that come from propensity rule effects can be studied by angle-resolved atomic delay measurements, as shown by Busto et al [37]. The good agreement between our partial wave analysis in figures 7 and 1(a) in reference [31] suggests that correlation effects in the continuum within the truncated TDCIS theory do not strongly alter the PAD. Further, the importance of including both \( m = 0 \) and \( m = \pm 1 \) contributions incoherently for atomic delay simulations in neon was shown by Ivanov and Kheifets [25]. Physically, this is due to the fact that only the absorption paths obtain additional nodes, a criterion formulated in equation (18). Each additional node is associated with a \( \pi \)-shift in the absorption paths. This suggests strong angle-dependence of atomic delays in experiments with higher-order sidebands, similar to the two-IR RABBIT experiment proposed by Harth et al [48] and the multi-photon sideband generation demonstrated by Maroju et al [11] in a free-electron laser setting.

5. Conclusions

With our combined TDCIS and t-SURFF approach, we are able to simulate angle-resolved photoelectron spectra and identify qualitative differences between sidebands formed by laser-driven absorption and emission processes in the continuum. First, we confirm the generalization of Fano’s propensity rule to continuum–continuum absorption and emission processes to the first sideband peaks, then we show that the propensity rule also has consequences for the second-order sideband peaks. In addition to the propensity rule, we identify that interference effects of different intermediate partial waves plays an important role, which is a stronger effect than the propensity rule at high kinetic energies. While Fano’s propensity rule for absorption of photons states that an increase of the angular momentum is favoured over a decrease of angular momentum, the interference effect from multi-photon processes can strongly favour a decrease of the angular momentum for both laser absorption and emission processes in the continuum. Finally, we find that the propensity rule can be used to explain the appearance of additional deep minima (nodes) in the angular distributions found in multi-photon absorption processes in the continuum in both the first and the second sidebands.

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Appendix. Comparison of the final expression

Here we compare in detail our final expression for TDCIS with t-SURFF given in equation (9) with that of the final expression in equation (22) of reference [31]. The final expressions differ in several places. The exponential factor should have a positive sign from the complex conjugated Volkov phase and there should be an energy shift of \( L_\nu = -\varepsilon_a \) which is missing in the earlier work, provided that the zero-point energy is at the Hartree–Fock ground state. Further, on the second line of equation (9), we have a factor

\[
\frac{1}{2} \left( \mathbf{k}_r \mathbf{j}_p(\mathbf{k}_r) + \mathbf{j}_p(\mathbf{k}_r) \right),
\]

whereas the earlier work has (given in our notation)

\[
\left( -\mathbf{j}_p(\mathbf{k}_r) + \mathbf{k}_r \frac{1}{2} \mathbf{j}_p(\mathbf{k}_r) - \frac{1}{2} \mathbf{j}_p(\mathbf{k}_r) \right).
\]

The last line of equation (22) of [31] includes also a factor \( (2\sqrt{\pi})^{-1} \) which should not be present and misses a square-root over the scaling-factor including adjacent particle angular momenta \( (2\ell + 1) \), both of which follow from the unnumbered equation right above equation (22). Finally, on the third line, there is an \( \mathbf{r}_\nu \) missing in reference [31].

ORCID IDs

Mattias Bertolino https://orcid.org/0000-0002-7430-7748
David Busto https://orcid.org/0000-0003-4311-3315
Jan Marcus Dahlström https://orcid.org/0000-0002-5274-1009

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