

Modeling angularly resolved resonant phase jumps in fine-structure-split regions of heavy atoms

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In the current communication, we use the random phase approximation with exchange method to investigate the fine-structure split energy region between the first and second ionization thresholds of xenon and radon. Such regions can be found in all noble gases, save for helium, and contain a series of autoionizing resonances which strongly modulate the photoionization process. For both xenon and radon, we calculate the angularly integrated and resolved cross section and photoionization phases. We find that, near some resonances, the phase switches between a less than π and a 2π jump at given photoelectron emission angles. This holds for both the Wigner and atomic phase, although the angles may differ, causing sharp modulations in the continuum-continuum contribution. To explain this behavior, we present a model capable of capturing both the angularly integrated and resolved resonant variations of the atomic and Wigner phase. The angles at which the phase-jump switches occur are also predicted by the model and may be calculated analytically.

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I. INTRODUCTION

All rare gas atoms, except helium, show series of autoionizing resonances, i.e., localized states embedded in the continuum, between the first ($np_{3/2}$) and the second ($np_{1/2}$) ionization threshold. These resonances were first reported by Beutler in the 1930s [1], and a comprehensive review of the studies carried out since then can be found in Ref. [2]. For the lighter elements these resonances are of highly excited Rydberg type with a hole in $np_{1/2}$ and a particle in a truly high n state, but as the nuclear charge increases, and the fine-structure splitting grows, lower n values become possible. The series of odd parity resonances of $J = 1$ symmetry, i.e., reachable through one-photon absorption from the $J = 0$ ground state, begins with $2p_{1/2}^{-1}12\ell$ in Ne [3], $3p_{1/2}^{-1}9\ell$ in Ar [4], $4p_{1/2}^{-1}6\ell$ in Kr [5], and $5p_{1/2}^{-1}6\ell$ in Xe [6]. In radon, where experimental data are scarce, calculations indicate that the resonance series starts with $6p_{1/2}^{-1}7s$ and $6p_{1/2}^{-1}6d$, i.e., with the excitation to the lowest available orbitals.

The presence of a resonant state significantly affects the photoionization dynamics, which are encoded in the phase of the outgoing photoelectron wave. For example, pronounced phase modulations have been observed near the argon [Ne]3s3p⁶4p resonance [7–9], which lies between the 3p and 3s thresholds. Although the resonance is commonly labeled according to the leading configuration [Ne]3s3p⁶4p,

it is in fact strongly influenced by so-called shake-up configurations such as [Ne]3s²3p⁴3d4p. This originates from the importance of [Ne]3s²3p⁴nd configurations in explaining the 3s-ionization energy. These configurations also have a strong effect on the autoionization width and the Fano shape parameter [10] of the resonance, as discussed, for example, in Ref. [11].

The resonances found in noble gases between the outer $np_{3/2}$ and $np_{1/2}$ thresholds are less affected by shake-up configurations and therefore less cumbersome for theory. The effect of such resonances on the photoionization cross section has been studied both theoretically and experimentally [12,13]. However, to the best of our knowledge, their influence on the photoelectron phase, and hence the photoionization dynamics, has not yet been investigated. In the present work, we address this gap by theoretically studying the series of autoionizing resonances between $np_{3/2}$ and $np_{1/2}$ in xenon and radon, observing both their signature in the cross section and photoionization phase.

Using attosecond techniques, the influence of autoionizing resonances on the phase of the photoelectron wave packet [7,14–17], as well as on that of its angularly resolved components [15–18], can be investigated. In the nonresonant continuum, these phases can be interpreted in terms of the scattering delay experienced by the electron as it leaves the atomic potential. In the presence of a resonant state, however, such interpretation is lost, as discussed in Ref. [19].

In the present work, we focus on modeling the well-established RABITT technique [20], which is based on the interference between two-photon paths. It has previously been shown [7,21] that the complex transition amplitude near a resonance can be written on a Fano-like form, using a complex shape-parameter $\tilde{q}$. This allows for an analytical treatment of the angularly integrated atomic phase, as measured in RABITT, as well as its one-photon Wigner contribution. Here we

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further extend the model to the angularly resolved case, by showing that $\tilde{q}(\theta)$ can be calculated analytically for any given emission angle. We also derive an expression for the complex beta parameters $\tilde{\beta}_n$, which describe the angular dependence of the phase.

The communication is structured as follows: In Sec. II we provide a brief overview of the underlying theory, including photoionization phases and delays, the Fano formalism employed in the analytical models, and the angular distribution of photoelectrons expressed in terms of asymmetry parameters. Section III then describes the numerical approach. In Sec. IV we present an analytical framework for modeling resonant phase jumps and its extension to the angularly resolved case. Section V presents the results of the study, and Sec. VI summarizes our conclusions.

II. THEORETICAL BACKGROUND

A. Photoionization phases

Ultrafast electronic dynamics can be investigated using attosecond techniques such as the Reconstruction of Attosecond Beatings by Interference of Two-photon Transitions (RABITT) [20] and the attosecond streak camera [22]. In these approaches, modulations in the photoelectron spectra arise when ionization by extreme ultraviolet (XUV) attosecond pulses occurs in the presence of a laser field that is phase locked to the attosecond radiation. These modulations can be used to probe the phase of the emitted electron wave packet [7,23–29]. The derivative of this phase with respect to energy can then be interpreted as the photoionization delay.

In this work, the focus lies on modeling RABITT, an interferometric technique that uses an attosecond pulse train—i.e., an XUV comb in the frequency domain—to ionize the atom in the presence of a weak, superimposed infrared (IR) field. The spectral components of the XUV comb correspond to odd harmonics of the driving laser field. Through the absorption or stimulated emission of an IR photon, sidebands at the even harmonics can be reached. Each sideband can be accessed via two quantum pathways: from the lower harmonic through absorption of an IR photon, and from the upper harmonic through stimulated emission. The interference between these pathways produces an intensity

$$\begin{aligned} S &= |A_a + A_e|^2 = |A_a|^2 + |A_e|^2 + A_a^* A_e + A_a A_e^* \\ &= |A_a|^2 + |A_e|^2 + 2 \times |A_a| |A_e| \cos [\arg(A_a) - \arg(A_e)], \end{aligned} \quad (1)$$

where $A_{a/e}$ denotes the complex two-photon amplitude either for the absorption (a) or the emission (e) of an IR photon.

The last term in Eq. (1) generates oscillations in the sideband intensity and can be written as

$$\cos [\arg(A_a) - \arg(A_e)] = \cos [2\omega\tau - \phi_{\text{XUV}} - \phi_A]. \quad (2)$$

Here τ is the delay between the IR and XUV pulses which is manually controlled, ϕ_{XUV} is the XUV pump attochirp, and ϕ_A is known as the atomic phase. As neither pulse delay ($\tau = 0$) nor attochirp ($\phi_{\text{XUV}} = 0$) is included in the calculations, the atomic phase can be calculated as the argument

$$\phi_A = \arg(\mathcal{A}) \quad (3)$$

of the sideband interference term $\mathcal{A} = A_e A_a^*$.

In the traditional RABITT scheme, the energy of the sideband, as well as those of the intermediate harmonics, are determined by the frequency of the driving IR field. Using time-independent theoretical calculations, as will be discussed below, $A_{a/e}$ can instead be calculated directly for any intermediate (harmonic) and final (sideband) energy. Unless otherwise stated, phases reported herein will be given as a function of the sideband energy, with both harmonics being separated by 1.55 eV from the sideband. Thus, although S and $A_{a/e}$ are introduced without argument, Eq. (3) is applicable, after tracing over nonresolved variables, to the interference term $\mathcal{A}(E)$ at any sideband energy E , as well as, using the angularly resolved form of $A_{a/e}$ presented below, to the interference term $\mathcal{A}(E; \hat{\Omega})$ at any sideband energy and in any emission direction $\hat{\Omega}$.

Although both ϕ_{XUV} and ϕ_A correspond to a phase difference of the two quantum paths, ϕ_{XUV} is independent of the target system and can be accounted for through relative measurements. The phase ϕ_A corresponds to the atomic delay $\tau_A = \phi_A/2\omega$. A recent review of the experimental method can be found in [30]. The measured atomic phase (or delay) can, to a good approximation [31–33], be decomposed as $\phi_A \approx \phi_W + \phi_{cc}$. Here ϕ_W is a Eisenbud-Wigner-Smith-like phase [34–36], or simply Wigner phase, associated with the one-photon ionization process, and ϕ_{cc} is a contribution arising from the interaction with the IR laser field in the presence of the atomic potential, known as the continuum-continuum phase. For atoms, the contribution from the IR photon is to a large extent universal [31], in the sense that it depends primarily on the kinetic energy of the photoelectron, the photon energy of the laser field, and the charge of the remaining ion, but hardly at all on the atomic species. However, as will be discussed, deviations from this universal behavior can be seen in the presence of resonances.

B. Fano formalism

Autoionizing resonances are localized states that are embedded in the continuum and therefore have a finite lifetime. In photoionization spectra, resonances show up as prominent features where the ionization probability can vary between being strongly enhanced and suppressed. Resonances are characterized by their position E_{res} (here given relative to the ground state E_0), by their width Γ , and (in photoionization studies) by their shape parameter q introduced by Fano [10]. In the vicinity of a resonance the angularly integrated cross section takes the form

$$\sigma(\omega) = \sigma^{\text{res}} \frac{(\epsilon + q)^2}{\epsilon^2 + 1} + \sigma^{\text{bg}}, \quad \epsilon = \frac{\hbar\omega - (E_{\text{res}} - E_0)}{\Gamma/2}. \quad (4)$$

Here σ^{res} is a scaling factor, while σ^{bg} represents the background contribution, which in the simplest case is constant (or zero if only a single channel is open). The q parameter depends on the ratio between the matrix element from the ground state to the localized part of the resonance and that to the continuum in which it is embedded.

These parameters depend on not only the excited, localized state but also on the continuum into which it decays. Thus, they can be seen to differ when measuring photoelectrons associated with different parent ions [37,38]. Although we

here restrict our treatment to resonances below the second ionization threshold, the discussion in the present communication is readily applicable to measurements of partial decay channels.

In the context of complex scaling, where the resonance appears as an eigenstate to the non-Hermitian Hamiltonian matrix, this translates to a dependence on the ratio between the real and imaginary part of the matrix element from the ground state to this eigenstate [39].

C. Angular distributions

It has previously [40] been shown that, for linearly polarized light, the complex sideband interference term $\mathcal{A}$, as well as its Wigner contribution, can be written in the form

$$\begin{aligned}\mathcal{A}(\omega; \theta) &= \mathcal{A}_0(\omega) \sum_{n=0}^{\infty} \tilde{\beta}_{2n} P_{2n}(\cos \theta) \\ &= \mathcal{A}_0(\omega) \left(1 + \sum_{n=1}^{\infty} \tilde{\beta}_{2n} P_{2n}(\cos \theta) \right)\end{aligned}\quad (5)$$

in the dipole approximation, where θ is the angle against the external field polarization direction. Here $\mathcal{A}_0(\omega)$ is the angularly integrated interference term, the $\tilde{\beta}_{2n}$ parameters are given by the relative values between different symmetries of the dipole transition matrix elements $\tilde{M}_{\kappa, K}^{(\gamma)}$ (introduced in the following section), and P_n are Legendre polynomials. For the zeroth-order terms it holds that $P_0 = \tilde{\beta}_0 = 1$. For the one-photon amplitude, it holds that $\tilde{\beta}_{2n} = 0$ for $n > 1$. For the two-photon amplitude, the same holds for $n > 2$. Further, all terms of order $n > 0$ disappear during angular integration, leaving only $\mathcal{A}_0(\omega)$.

This is a generalization of the well-known formula [41] for the cross section

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_0}{4\pi} \left(1 + \sum_{n=1}^{\infty} \beta_{2n} P_{2n}(\cos \theta) \right), \quad (6)$$

which also terminates after β_2 for one-photon interaction and β_4 for two-photon interaction, and where σ_0 is the angularly integrated cross section.

The atomic phase of electrons emitted at an angle θ relative to the polarization direction of the linearly polarized XUV light can be written as

$$\phi_A(\theta) = \phi_{A,0} + \arg(1 + \tilde{\beta}_2^A P_2(\cos \theta) + \tilde{\beta}_4^A P_4(\cos \theta)), \quad (7)$$

where $\phi_{A,0}$ denotes the phase of the angularly integrated signal. The one-photon Wigner phase takes an analogous form,

$$\phi_W(\theta) = \phi_{W,0} + \arg(1 + \tilde{\beta}_2^W P_2(\cos \theta)). \quad (8)$$

Note the distinction between the second-order asymmetry parameter $\tilde{\beta}_2^A$ for the atomic phase and $\tilde{\beta}_2^W$ for the Wigner phase.

The asymmetry parameters β_{2n} for the cross section are real, while those for the amplitudes and phases, $\tilde{\beta}_{2n}$, are complex.

III. NUMERICAL METHODS

A. Random Phase Approximation with Exchange

The Random Phase Approximation with Exchange (RPAE) method since the 1970s [42–44] has been successful in calculating photoionization cross sections. It is quick and grasps the overall picture very well. The method accounts for the coupling of different ionization channels, and can further be described as *time-dependent Hartre-Fock* [45], since the change in the interaction between initially occupied orbitals due to the photon field is fully accounted for within the space of single excitations, i.e., by including all configurations that differ by one hole and one particle relative to the initial state Slater determinant. More recently the RPAE method has been used as starting point for the description of above threshold ionization in connection with attosecond measurement techniques [46–49].

Traditionally the RPAE equations are solved iteratively, but it is also possible to construct a matrix equation that can be solved either as a system of linear equations, or through diagonalization of the matrix. The popularity of the iterative procedure can be explained by its very limited use of memory and storage resources, but it is prone to have convergence problems both close to thresholds and close to resonances. The direct solution of the matrix equation is in contrast very robust: It requires more storage but has no built-in convergence problems. In addition the solution procedure that starts with diagonalization opens up for a better understanding of structures in the continuum. If it, for example, is combined with complex scaling, resonance properties such as positions, widths and Fano shape parameters are readily obtained.

Here a relativistic implementation of the RPAE method (RRPAE) is used, described in detail in Ref. [49], although now solved directly as a matrix equations instead of through the iterative approach from Ref. [49]. Our solution method will be described in future publications, but a short description is given below.

The starting point is the Dirac-Fock approximation

$$h_{\text{DF}} = c\boldsymbol{\alpha} \cdot \mathbf{p} + \left(u_{\text{DF}} - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r} \right) \mathbf{1}_4 + mc^2\beta, \quad (9)$$

where $\boldsymbol{\alpha}$ and β are the four-component Dirac matrices. When the Dirac-Fock potential u_{DF} is spherically symmetric, as it is for the rare gas atoms treated here, the two-component radial part of the wave function can be separated out and it is determined by the radial Hamiltonian

$$(h_{\kappa}^{\text{DF}}(r) - mc^2) \begin{pmatrix} f_{\kappa}(r) \\ g_{\kappa}(r) \end{pmatrix} = (E - mc^2) \begin{pmatrix} f_{\kappa}(r) \\ g_{\kappa}(r) \end{pmatrix}, \quad (10)$$

where $\epsilon = E - mc^2$ is the orbital energy and where

$$\begin{aligned}h_{\kappa}^{\text{DF}}(r) - mc^2 &= \begin{pmatrix} u_{\text{DF}}(r) - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r} & -c\hbar\left(\frac{d}{dr} - \frac{\kappa}{r}\right) \\ c\hbar\left(\frac{d}{dr} + \frac{\kappa}{r}\right) & u_{\text{DF}}(r) - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r} - 2mc^2 \end{pmatrix}. \quad (11)\end{aligned}$$

Here f_{κ} is the upper, typically larger, component, and g_{κ} the lower, typically smaller, component. The relativistic quantum number κ is determined by the ℓ and j -quantum numbers: $\kappa = \ell(\ell + 1) - j(j + 1) - 1/4$.

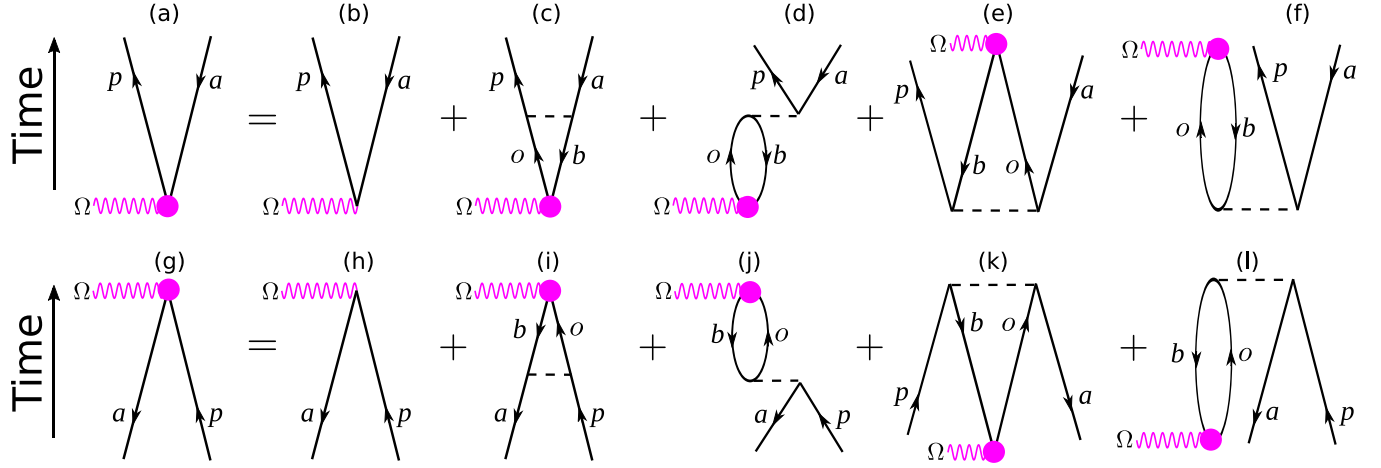


FIG. 1. Goldstone diagrams illustrating RPAE for the many-body screening of the photon interaction. Diagrams (a) and (g) correspond to forward and backward propagation, respectively, where the spheres indicate the correlated interactions to infinite order. The wavy lines indicate the photon interactions and the dashed lines the Coulomb interactions. Lines going down (labeled with a and b) represent holes created when electrons are removed from initially occupied orbitals, and lines going up (labeled with o and p) represent initially unoccupied states.

The perturbed wave function, i.e., the correction to the system due to the interaction with a photon of energy Ω , as obtained by the RPAE approximation is illustrated by the diagrams in Fig. 1, and given by

$$(\epsilon_a \pm \hbar\Omega - h_{\kappa}^{\text{DF}}) |\rho_{\Omega,a}^{\pm}\rangle = \sum_p^{\text{exc}} |p\rangle \langle p| (d_{\Omega_j} + \delta u_{\Omega}^{\pm}) |a\rangle, \quad (12)$$

where $\delta u_{\Omega}^{\pm}$ are the (linearized) corrections to the Dirac-Fock potential induced by the electromagnetic field; cf. Figs. 1(c)–1(f) and 1(i)–1(l). The $\pm$ signs correspond to the forward (+) and backward (−) propagating solution. A detailed derivation can be found in Ref. [48].

B. Matrix formulation

Figure 1 and Eq. (12) indicate an iterative solution. Here, however, the equation is expressed in a matrix form, as

$$\begin{pmatrix} \mathbb{A} - \hbar\Omega & \mathbb{B} \\ \mathbb{B} & \mathbb{A} + \hbar\Omega \end{pmatrix} \begin{pmatrix} \mathbf{X}_+ \\ \mathbf{X}_- \end{pmatrix} = - \begin{pmatrix} \mathbf{S}_+ \\ \mathbf{S}_- \end{pmatrix}, \quad (13)$$

for each photon energy Ω . When complex scaling is used (see Sec. III C), the matrix on the left-side is complex symmetric, and not Hermitian.

The upper half of the right-hand-side vector, $\mathbf{S}_+$, consists of the dipole matrix elements of the type

$$\langle p | d_{\Omega} | a \rangle, \quad (14)$$

and the lower half, $\mathbf{S}_-$, of the ones of the type

$$\langle a | d_{\Omega} | p \rangle. \quad (15)$$

The $\mathbb{A}$ matrix is built from the elements

$$(\epsilon_p - \epsilon_a) \delta(a, b) \delta(o, p) - \langle bp | \frac{1}{r_{12}} | ao \rangle + \langle pb | \frac{1}{r_{12}} | ao \rangle, \quad (16)$$

where $a^{-1}p$ and $b^{-1}o$ are single excitations. $\mathbb{A}$ can thus be identified as the Hamiltonian matrix within the space of single excitations, used, for example, in the time-dependent

configuration-interaction singles method [50], and the solution to

$$(\mathbb{A} - \hbar\Omega) \mathbf{X}_+^f = -\mathbf{S}_+ \quad (17)$$

gives the RPAE-forward solution. Here the vector $\mathbf{X}_+^f$ contains the coefficients for single excitations $|p\rangle$ in Eq. (12), with the contributions from only the forward diagrams, shown in Figs. 1(b)–1(d).

To also incorporate the reverse time-order effects, shown in the second row of Fig. 1, the matrix $\mathbb{B}$, corresponding to the mixed time-order terms [Figs. 1(e), 1(f), 1(k), and 1(l)], must be calculated. It is built from the elements

$$-\langle op | \frac{1}{r_{12}} | ab \rangle + \langle po | \frac{1}{r_{12}} | ab \rangle. \quad (18)$$

With these reverse-order effects included, $\mathbf{X}_+$ gives the full RPAE solution.

As described in Ref. [49] the calculations are performed with a basis set obtained through diagonalization of the radial one-particle Dirac-Fock Hamiltonians, Eq. (11), in a primitive basis of B-splines, defined on a knot sequence in a spherical box, and combined with complex scaling. The size of the matrix on the left-side of Eq. (13) will be determined by the number of considered holes (for example, $4d_{3/2}$, $4d_{5/2}$, $5s_{1/2}$, $5p_{1/2}$, and $5p_{3/2}$ for xenon), combined with the contributing angular momenta of the particle (for example $s_{1/2}$, $d_{3/2}$ and $d_{5/2}$ for single-photon excitation from $p_{3/2}$) times the number of particle states for each symmetry which is determined by the B-spline set. In the considered cases this gives matrices of around $10\,000 \times 10\,000$.

It is convenient to transform Eq. (13) as

$$\begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbb{A} - \hbar\Omega & \mathbb{B} \\ \mathbb{B} & \mathbb{A} + \hbar\Omega \end{pmatrix} \begin{pmatrix} \mathbf{X}_+ \\ \mathbf{X}_- \end{pmatrix} = - \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbf{S}_+ \\ \mathbf{S}_- \end{pmatrix}, \quad (19)$$

giving

$$\left[\begin{pmatrix} \mathbb{A} & \mathbb{B} \\ -\mathbb{B} & -\mathbb{A} \end{pmatrix} - \hbar\Omega \begin{pmatrix} \mathbb{I} & 0 \\ 0 & \mathbb{I} \end{pmatrix} \right] \begin{pmatrix} \mathbf{X}_+ \\ \mathbf{X}_- \end{pmatrix} = \begin{pmatrix} -\mathbf{S}_+ \\ \mathbf{S}_- \end{pmatrix}. \quad (20)$$

Here it is clear that the solution can be divided into two steps. First the Ω -independent part of the matrix on the left-hand side is diagonalized, after which the solution can be obtained by projection into the matrix' eigenbasis. This second step becomes very quick, allowing the equation to be efficiently solved for multiple values of Ω . The diagonalization will directly give the resonance parameters.

Although the left and right eigenvectors of the transformed matrix differ, they still have a simple relation as is shown in Appendix A.

C. Complex scaling

For partial cross sections in the different available channels, and for calculation of above threshold ionization, complex scaling is used, implemented through the transformation

$$r \rightarrow \begin{cases} r, & 0 < r < R_C \\ R_C + (r - R_C)e^{i\varphi}, & r > R_C, \end{cases} \quad (21)$$

of the radial position coordinate r . This has the effect of killing the wave function as it approaches the boundary, giving it a decaying shape for $r > R_C$, effectively enforcing Dirichlet boundary conditions, while preventing errors from propagating in towards the nucleus. Uniform complex scaling (where $R_C = 0$) is typically less numerically demanding, while still allowing for the calculation of resonance parameters, as well as the total photoabsorption cross section [39,51]. Here, however, exterior complex scaling (where $R_C > 0$) is used. This allows for a physical description of the outgoing electron in the continuum (at distances $r < R_C$), which is required when describing two-photon processes.

With complex scaling, the Hamiltonian matrix will become non-Hermitian and its eigenstates will consist of a discretized representation of the continuum where the argument of the energies will be determined by the rotation angle φ in Eq. (21), and of resonances that will stay put when this angle is varied. An imaginary eigenvalue corresponding to a resonance will take the form

$$\tilde{E} = (E_{\text{res}} - E_0) - i\frac{\Gamma}{2}, \quad (22)$$

where the resonance position E_{res} and width Γ were introduced in Eq. (4). As before, the resonance position is defined relative to the ground state energy E_0 .

D. Above threshold ionization

Regardless of whether one or two photons are exchanged, the photoelectron wave function approaches an outgoing Coulomb wave with a phase shift outside the atomic core. Asymptotically, it has radial upper and lower components of

the form [49,52]

$$\lim_{r \rightarrow \infty} u_{\kappa,K}^{(\gamma)}(r) = -\pi M_{\kappa,K}^{(\gamma)} \sqrt{\frac{1}{1+\zeta^2}} \sqrt{\frac{2m}{\pi k \hbar^2} \left(1 + \frac{\varepsilon}{mc^2}\right)} \times \begin{pmatrix} e^{i(kr+\eta \ln 2kr+\Delta_\kappa)} \\ i\zeta e^{i(kr+\eta \ln 2kr+\Delta_\kappa)} \end{pmatrix}, \quad (23)$$

where γ denotes the number of photons with which the electron has interacted, ε the kinetic energy, and $M_{\kappa,K}^{(\gamma)}$ is the complex transition matrix element connecting the initial electron state to the final state specified by the quantum number κ and the rank K of the effective photon interaction. Although not explicitly written in the expression above, the matrix element naturally depends on the energy of one photon (in the one-photon case) or the energies of two photons (in the two-photon case). Asymptotically, the quotient of the large (upper) and the small (lower) component converges towards

$$\zeta = \sqrt{\frac{E - mc^2}{E + mc^2}} = \frac{k\hbar}{2mc} \frac{1}{\left(1 + \frac{\varepsilon}{2mc^2}\right)}, \quad (24)$$

where $E = mc^2 + \varepsilon$ is the total electron energy (including the rest mass contribution mc^2), and the momentum k and the dimensionless parameter η are given by the relativistic generalizations

$$k = \frac{\sqrt{E^2 - m^2c^4}}{\hbar c} = \frac{\sqrt{2\varepsilon m}}{\hbar} \sqrt{1 + \frac{\varepsilon}{2mc^2}}, \quad (25)$$

$$\eta = Z\alpha E \sqrt{\frac{1}{E^2 - m^2c^4}} = \frac{Z}{a_0 k} \left(\frac{\varepsilon}{mc^2} + 1 \right) \quad (26)$$

of corresponding nonrelativistic expressions. The phase shift of the outgoing wave is given by

$$\Delta_\kappa = -\gamma\pi/2 + \sigma_\kappa + \nu + \delta, \quad (27)$$

where

$$\gamma^2 \equiv \kappa^2 - \alpha^2 Z^2, \quad (28)$$

σ_κ is the phase acquired due to the Coulomb interaction

$$\sigma_\kappa = \arg[\Gamma(\gamma - i\eta)], \quad (29)$$

ν is given by

$$e^{2i\nu} = \frac{(-\kappa + \frac{iZ}{ka_0})}{(\gamma + i\eta)}, \quad (30)$$

and δ is the phase shift induced by the short-range non-Coulombic potential.

For one-photon interactions, the matrix elements with phase shifts $e^{i\Delta_\kappa} M_{\kappa,K}^{(1)}$ are computed within the RPAE framework by matching the perturbed wave function to a pure Coulomb wave. In contrast, to evaluate the matrix elements in the two-photon case [i.e., those determining the atomic phase ϕ_A in Eq. (2)], the perturbed wave function must interact with a second photon. Since these continuum-continuum transitions cannot be evaluated in a finite spatial domain, a combination of numerical integration in the region close to the ion and analytical integration along the imaginary axis extending to infinity is used. This approach is described in Refs. [46,49]. The phase shift in the two-photon case is extracted from the final continuum state obtained from

the Hamiltonian describing the coupled ion-photoelectron system. To a good approximation, this Hamiltonian can be expressed as the sum of the Dirac-Fock Hamiltonian h_{DF} from Eq. (9) and the so-called projected potential, as discussed in detail in Ref. [49].

As shown in Ref. [40], for linearly polarized light the complex transition amplitude for electrons ionized from orbital with total angular momentum j with projection m_j can be written in the concise form

$$A^{(\gamma)}(\omega; \hat{\Omega}) = \sum_{\kappa' m_j} \sum_K (-1)^{2j'+K+j-m_j} \begin{pmatrix} j' & K & j \\ -m_j & 0 & m_j \end{pmatrix} \times \left(\sum_{m_{\ell_f} m_s} \langle \ell_f m_{\ell_f} s m_s | j' m_j \rangle Y_{\ell_f}^{m_{\ell_f}}(\hat{\Omega}) \xi_{m_s} \right) \bar{M}_{\kappa', K}^{(\gamma)}(\omega), \quad (31)$$

where primed index indicates the final state, the matrix element after γ photons

$$\bar{M}_{\kappa, K}^{(\gamma)}(\omega) = e^{i\Delta_\kappa(\omega)} M_{\kappa, K}^{(\gamma)}(\omega) \quad (32)$$

includes the ionized electron phase shift Δ_κ , ξ_{m_s} (for $m_s = \pm 1/2$) denotes the spin function, and the angular momentum associated with the small component is $\ell_g = \ell_f \pm 1$, with ℓ_f referring to the angular momentum of the large component, $\ell_f = j' \mp 1/2$. Furthermore, the spin functions satisfy $\langle \xi_{m_s} | \xi_{m'_s} \rangle = \delta(m_s, m'_s)$. In the sum over the photon-interaction rank K , one-photon absorption in the dipole approximation corresponds to $K = 1$, whereas for two-photon interactions $K \in 0, 1, 2$, although $K = 1$ is forbidden for the linearly polarized light used in this study.

The formalism presented in Eq. (31) enables a clean separation between the radial and angular parts of the problem: the radial part is evaluated using the RPAE method, supplemented by additional integrations in the two-photon case, after which the angular dependence—determined by the m_j quantum number and the light polarization—can be incorporated independently. Using this form of the amplitude, one can also derive explicit expressions for the $\tilde{\beta}_{2n}$ parameters appearing in Eqs. (7) and (8), which further simplifies the description of the angular distribution.

IV. ANALYTICAL FRAMEWORK

A. Modeling resonant phase jumps

If the XUV photon hits a resonance in either the absorption or emission path, the sideband is also strongly modulated. In the vicinity of a lone resonance, located in the emission pathway, the angularly integrated sideband interference term can be modeled in a form

$$\mathcal{A}(\omega) = \mathcal{A}^{\text{res}} \frac{\epsilon + q}{\epsilon + i} + \mathcal{A}^{bg}, \quad (33)$$

assuming a smooth background, analogously to the cross section in Eq. (4). Here the coefficients $\mathcal{A}^{\text{res}}$ and $\mathcal{A}^{bg}$ can be calculated by fitting the formula to two points near the resonance. If the resonance occurs in the absorption pathway,

the complex conjugate of the expression in Eq. (33) must be used. Similar treatments have been made in Refs. [7, 21].

It is illustrative to rewrite Eq. (33) as

$$\mathcal{A}(\omega) = \frac{\epsilon + \tilde{q}}{\epsilon + i} (\mathcal{A}^{\text{res}} + \mathcal{A}^{bg}), \quad (34)$$

by defining a new, complex parameter

$$\tilde{q} = \frac{\mathcal{A}^{\text{res}} q + i \mathcal{A}^{bg}}{\mathcal{A}^{\text{res}} + \mathcal{A}^{bg}}. \quad (35)$$

As will be seen, an equivalent version of Eq. (34) is applicable in the angularly resolved case, which will be considered in Secs. IV B and IV C. The following discussion holds both in the integrated and resolved case.

From the form in Eq. (34) it is evident that the phase $\phi(\omega)$ can be separated into a variable component $\Delta\phi(\omega)$ determined by $\tilde{q}$ and a constant background shift ϕ_{bg} , as

$$\phi(\omega) = \arg[\mathcal{A}(\omega)] = \Delta\phi(\omega) + \phi_{bg}, \quad (36)$$

where

$$\begin{aligned} \Delta\phi(\omega) &= \arg \left[\frac{\epsilon + \tilde{q}}{\epsilon + i} \right] \\ &= \arg(\epsilon[\epsilon + \text{Re}(\tilde{q})] + \text{Im}(\tilde{q})) \\ &\quad + i\{\epsilon[\text{Im}(\tilde{q}) - 1] - \text{Re}(\tilde{q})\}, \end{aligned} \quad (37)$$

$$\phi_{bg} = \arg[\mathcal{A}^{\text{res}} + \mathcal{A}^{bg}]. \quad (38)$$

As was previously discussed in Ref. [21], the fraction in Eq. (37) behaves like a circle in the complex plane. The circle is centered at $\frac{1-i\tilde{q}}{2}$ and has a radius of

$$\left| \frac{\epsilon + \tilde{q}}{\epsilon + i} - \frac{1 - i\tilde{q}}{2} \right| = \frac{|1 + i\tilde{q}|}{2}. \quad (39)$$

At the limits $\epsilon \rightarrow \pm\infty$, the fraction takes the value

$$\forall \tilde{q} \in \mathbb{C}, \quad \lim_{\epsilon \rightarrow \pm\infty} \frac{\epsilon + \tilde{q}}{\epsilon + i} = 1, \quad (40)$$

as $\Delta\phi$ goes from 0 to 0 (or, equivalently, 2π).

The imaginary part of the ratio in Eq. (37) will be zero when

$$\epsilon_{\text{im}} = \frac{\text{Re}(\tilde{q})}{\text{Im}(\tilde{q}) - 1}, \quad \text{Im}(\tilde{q}) \neq 1, \quad (41)$$

while the real part will be zero when

$$\epsilon_{\text{re}}^{\pm} = \frac{-\text{Re}(\tilde{q}) \pm \sqrt{\text{Re}(\tilde{q})^2 - 4\text{Im}(\tilde{q})}}{2}, \quad \text{Im}(\tilde{q}) \leq \frac{\text{Re}(\tilde{q})^2}{4}. \quad (42)$$

The derivative of the phase can be calculated as

$$\begin{aligned} \frac{d\phi}{d\epsilon} &= \frac{d}{d\epsilon} \arg \left[\frac{\epsilon + \tilde{q}}{\epsilon + i} \right] \\ &= \frac{d}{d\epsilon} (\arg[\epsilon + \tilde{q}] - \arg[\epsilon + i]) \\ &= \frac{d}{d\epsilon} \left(\arctan \left[\frac{\text{Im}(\tilde{q})}{\epsilon + \text{Re}(\tilde{q})} \right] - \arctan \left[\frac{1}{\epsilon} \right] \right) \\ &= \frac{1}{1 + \epsilon^2} - \frac{\text{Im}(\tilde{q})}{\text{Im}(\tilde{q})^2 + [\epsilon + \text{Re}(\tilde{q})]^2}, \end{aligned} \quad (43)$$

with the limits

$$\lim_{\epsilon \rightarrow \pm\infty} \frac{d\phi}{d\epsilon} \rightarrow \begin{cases} \frac{1-\text{Im}(\tilde{q})}{\epsilon^2}, & \text{Im}(\tilde{q}) \neq 1 \\ 2\frac{\text{Re}(\tilde{q})}{\epsilon^3}, & \text{Im}(\tilde{q}) = 1 \end{cases}. \quad (44)$$

Further, by setting $\frac{d\phi}{d\epsilon} = 0$, the extrema of the phase are given as the real solutions to

$$\epsilon_{\text{ext}}^{\pm} = \frac{-\text{Re}(\tilde{q}) \pm \sqrt{\text{Im}(\tilde{q})[(\text{Im}(\tilde{q}) - 1)^2 + \text{Re}(\tilde{q})^2]}}{1 - \text{Im}(\tilde{q})}, \quad \text{Im}(\tilde{q}) \neq 1, \quad (45a)$$

$$\epsilon_{\text{ext}}^1 = -\frac{\text{Re}(\tilde{q})}{2}, \quad \text{Im}(\tilde{q}) = 1. \quad (45b)$$

From these, the separation in phase between the extrema can be calculated as

$$\Delta\phi_{\text{jump}} = 2 \arg \left[2 + \sqrt{\frac{(1 - \text{Im}(\tilde{q}))^2 + \text{Re}(\tilde{q})^2}{\text{Im}(\tilde{q})}} i \right], \quad \text{Im}(\tilde{q}) > 0. \quad (46)$$

This can be interpreted as the total magnitude of the phase jump.

With these equations in hand, it is possible to create a complete taxonomy of the different types of phase jumps. Below they are ordered by the $\text{Im}(\tilde{q})$ to which they correspond, since $\text{Im}(\tilde{q})$ is the main determinant of the phase behavior. The qualitatively different behaviours of the phase are illustrated in Fig. 2, assuming a resonance in the emission pathway. Similar logic holds, however, for absorption path resonances, by changing the sign of the phase $\Delta\phi \rightarrow -\Delta\phi$.

1. $\text{Im}(\tilde{q}) < 0$

The path $\frac{\epsilon + \tilde{q}}{\epsilon + i}$ starts and ends at 1, as $\epsilon \rightarrow \pm\infty$. If and only if it takes on a negative real value does it encircle the origin. Using Eq. (41), this condition can be written as

$$\text{Re}\left(\frac{\epsilon_{\text{im}} + \tilde{q}}{\epsilon_{\text{im}} + i}\right) = \text{Re}\left(\frac{\frac{\text{Re}(\tilde{q})}{\text{Im}(\tilde{q})-1} + \tilde{q}}{\frac{\text{Re}(\tilde{q})}{\text{Im}(\tilde{q})-1} + i}\right) = \text{Im}(\tilde{q}) < 0. \quad (47)$$

As the root in Eq. (42) is larger than $|\text{Re}(\tilde{q})|$ when $\text{Im}(\tilde{q}) < 0$, it can further be seen that $\epsilon_{\text{re}}^- < 0 < \epsilon_{\text{re}}^+$. Thus, the path crosses into all four quadrants, corresponding to a 2π phase jump. This case is illustrated in Fig. 2(a), where the phase and corresponding path in the complex plane is shown for $\tilde{q} = -1 - 0.3i$.

Also noteworthy is that the derivative $\frac{d\phi}{d\epsilon}$, given in Eq. (43), is strictly positive for $\text{Im}(\tilde{q}) \leq 0$. This shows that the 2π phase jumps caused by a resonance in the emission pathway always move in positive mathematical direction, from 0 to 2π with increasing energy. For resonances in the absorption pathway, the case is the inverse.

2. $\text{Im}(\tilde{q}) = 0$

For the edge case of $\text{Im}(\tilde{q}) = 0$, Eqs. (41) and (42) give

$$\epsilon_{\text{im}} = -\text{Re}(\tilde{q}) = \begin{cases} \epsilon_{\text{re}}^+, & \text{Re}(\tilde{q}) \leq 0 \\ \epsilon_{\text{re}}^-, & \text{Re}(\tilde{q}) \geq 0 \end{cases}, \quad (48)$$

and the complex amplitude takes the form

$$\mathcal{A}(\omega) = \frac{\epsilon + \text{Re}(\tilde{q})}{\epsilon + i} (\mathcal{A}^{\text{res}} + \mathcal{A}^{\text{bg}}), \quad (49)$$

corresponding to a pure, backgroundless Fano profile with amplitude $(\mathcal{A}^{\text{res}} + \mathcal{A}^{\text{bg}})$ and the Fano parameter $\text{Re}(\tilde{q})$. Although no background ($\mathcal{A}^{\text{bg}} = 0$) does imply a real $\tilde{q} = q$, the exact condition of $\text{Im}(\tilde{q}) = 0$,

$$|\mathcal{A}^{\text{bg}}|^2 + \text{Re}(\mathcal{A}^{\text{res}} \overline{\mathcal{A}^{\text{bg}}}) + \text{Im}(\mathcal{A}^{\text{res}} \overline{\mathcal{A}^{\text{bg}}})q = 0, \quad (50)$$

is less strict, allowing for nonzero values of $\mathcal{A}^{\text{bg}}$.

At $\epsilon = -\text{Re}(\tilde{q})$, the amplitude passes through the origin. This results in an abrupt phase jump of π , as is illustrated in Fig. 2(b) for $\tilde{q} = -1$. At this point, neither the phase nor its derivative are well defined, nor can the phase be said to complete a full 2π phase jump or not [Fig. 2(b) illustrates both a 2π and a π phase jump]. For a negative value of $\text{Re}(\tilde{q})$, this jump happens at energies above the resonance, for a positive value it happens below the resonance.

Even if this special case is not always present in the angularly integrated data, $\text{Im}(\tilde{q})$ may assume the value of zero for electrons emitted in certain critical angles. This will be further discussed in Sec. IV C.

3. $0 < \text{Im}(\tilde{q}) < 1$

When $0 < \text{Im}(\tilde{q}) < 1$, the phase is strictly increasing far from the resonance, as shown in Eq. (44). In between, it takes on two extrema $\epsilon_{\text{ext}}^{\pm}$ given by Eq. (45a)—first a maximum then a minimum. The separation in phase between these extrema is given by Eq. (46). This case is illustrated for $\tilde{q} = -1 + 0.3i$ in Fig. 2(c).

As $\text{Im}(\tilde{q})$ approaches one, either the maxima [for $\text{Re}(\tilde{q}) < 0$] or the minimum (for $\text{Re}(\tilde{q}) > 0$) will increase in approach of $-\frac{\text{Re}(\tilde{q})}{2}$. The other extremum will instead be dampened and move away from the resonance, approaching $\epsilon \rightarrow \pm\infty$.

4. $\text{Im}(\tilde{q}) = 1$

As $\text{Im}(\tilde{q})$ reaches one, only one extremum is present. Its position in energy is given by Eq. (45b) and its amplitude by Eq. (46). The sign of the jump is opposite to that of $\text{Re}(\tilde{q})$. This can be deduced from Eq. (44), where (far from the resonance) ϕ can be seen to increase when approaching the extremum for $\text{Re}(\tilde{q}) < 0$ and decrease for $\text{Re}(\tilde{q}) > 0$. The

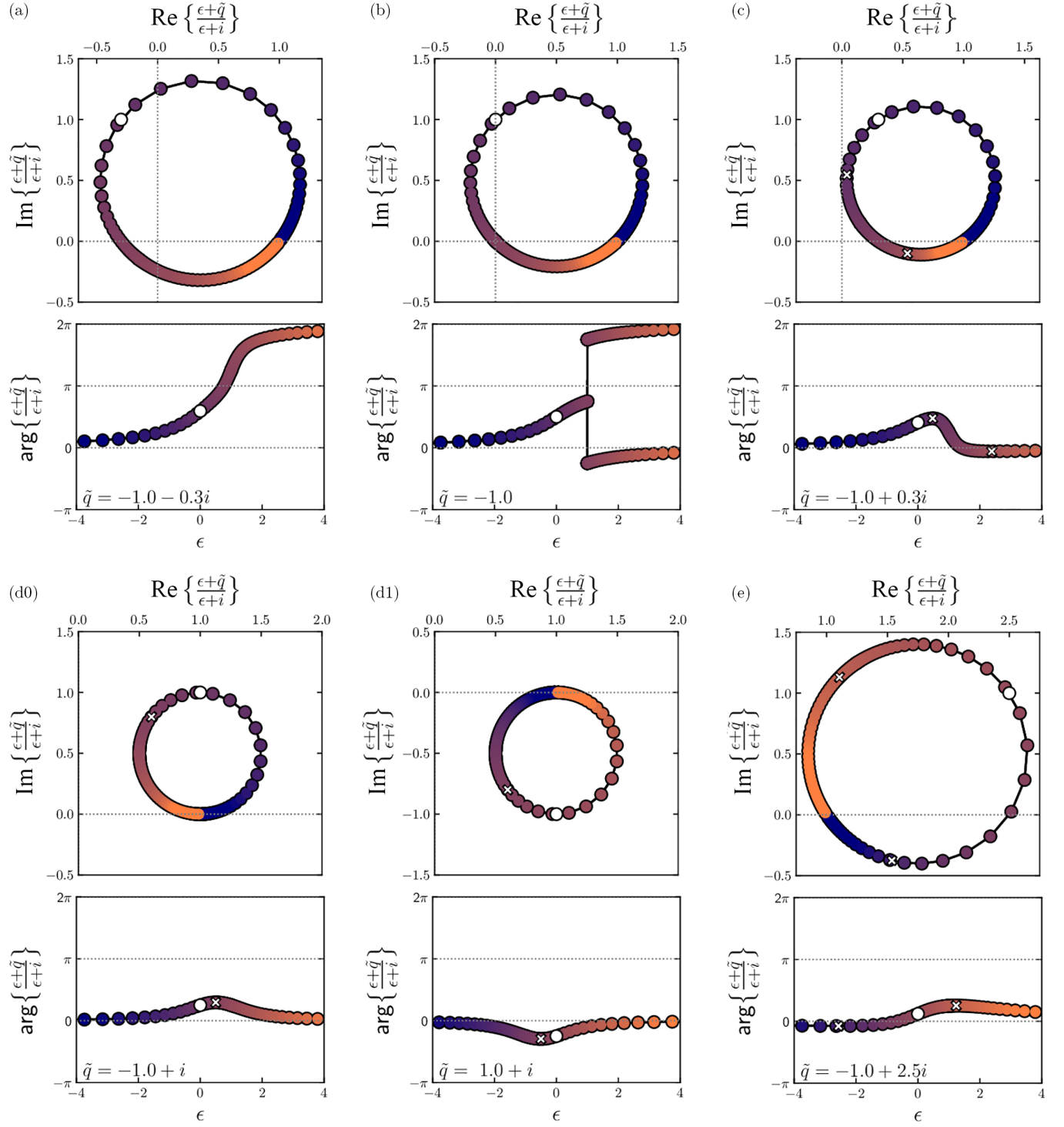


FIG. 2. The nonconstant part $\frac{\epsilon + \tilde{q}}{\epsilon + i}$ of the resonant transition amplitude (top panes) along with its phase (bottom pane), for different values of $\tilde{q}$. As ϵ goes from $-\infty$ (dark blue) to ∞ (orange), $\frac{\epsilon + \tilde{q}}{\epsilon + i}$ rotates around the complex plane, starting and ending at 1.0, which corresponds to an initial and final phase of 0 (or, equivalently, 2π). The qualitative behavior of the phase depends mainly on $\text{Im}(\tilde{q})$. The different behaviors are described in detail in Sec. IV A and are here given in the different panels: (a) when $\text{Im}(\tilde{q}) < 0$, (b) when $\text{Im}(\tilde{q}) = 0$, (c) when $0 < \text{Im}(\tilde{q}) < 1$, (d0) and (d1) when $\text{Im}(\tilde{q}) = 1$ with either (d0) $\text{Re}(\tilde{q}) < 0$ or (d1) $\text{Re}(\tilde{q}) > 0$ (the trivial case of $\tilde{q} = i \Rightarrow \frac{\epsilon + \tilde{q}}{\epsilon + i} = 1$ is not shown), and (e) when $\text{Im}(\tilde{q}) > 1$. The value at the resonance ($\epsilon = 0$) in each panel has been marked with a white circle. Points where the phase reaches either a minimum or maximum are marked with white crosses.

special case of $\text{Re}(\tilde{q}) = 0$ gives the trivial solution

$$\Delta\phi = \arg\left[\frac{\epsilon + \tilde{q}}{\epsilon + i}\right] = \arg\left[\frac{\epsilon + i}{\epsilon + i}\right] = \arg[1] = 0. \quad (51)$$

This case of $\text{Im}(\tilde{q}) = 1$ is illustrated in Fig. 2(d0) for $\text{Re}(\tilde{q}) < 0$ (with $\tilde{q} = -1 + i$) and in Fig. 2(d1) for $\text{Re}(\tilde{q}) > 0$ (with $\tilde{q} = 1 + i$).

5. $\text{Im}(\tilde{q}) > 1$

This case is qualitatively similar to the case of $0 < \text{Im}(\tilde{q}) < 1$, with two peaks at energies described by Eq. (45a) and a phase separation described by Eq. (46). The main qualitative difference comes from the order of the peaks. From the derivative of the phase given in Eq. (44), it can be seen that the minimum is located at lower energies than the maximum. This case is illustrated for $\tilde{q} = -1 + 2.5i$ in Fig. 2(e).

B. The analytical expression for $\tilde{\beta}$ parameters

In order to extend the model to the angularly resolved case, it becomes necessary to treat the complex asymmetry parameters $\tilde{\beta}_n(\omega)$, discussed in Sec. II C. These can be written as a linear combination

$$\tilde{\beta}_n(\omega) = \frac{\sum_{i,j} N_{ij}^n M_a^{i*}(\omega) M_e^j(\omega)}{A_0(\omega)} \quad (52)$$

of absorption and emission path matrix elements $M_a^i(\omega)$ and $M_e^j(\omega)$ to open ionization channels indexed i and j , divided by the angularly integrated term $A_0(\omega)$.

As noted above, the denominator can be expressed using Eq. (33) when a resonance is present in either the emission or absorption pathway. Since the numerator is also directly proportional to the matrix elements, the same reasoning can be applied to it, giving

$$\sum_{i,j} N_{ij}^n M_a^{i*}(\omega) M_e^j(\omega) = \mathcal{A}_n^{\text{res}} \frac{\epsilon + q}{\epsilon + i} + \mathcal{A}_n^{\text{bg}}, \quad (53)$$

with the constants $\mathcal{A}_n^{\text{res}}$ and $\mathcal{A}_n^{\text{bg}}$ depending on the mixing coefficients N_{ij}^n . Rewriting these on the form of Eq. (34) gives the expression

$$\tilde{\beta}_n(\omega) = \frac{\epsilon + \tilde{q}_n \mathcal{A}_n^{\text{res}} + \mathcal{A}_n^{\text{bg}}}{\epsilon + \tilde{q}_0 \mathcal{A}_0^{\text{res}} + \mathcal{A}_0^{\text{bg}}} \quad (54)$$

for the $\tilde{\beta}_n$ parameter near a resonance, where $\tilde{q}_0 = \tilde{q}$ from the angularly integrated case described above.

C. The angularly dependent $\tilde{q}(\theta)$

Using the expressions in Eq. (54) for the $\tilde{\beta}_n$ parameters, Eq. (5) simplifies to

$$\mathcal{A}(\omega; \theta) = \sum_{n=0}^{\infty} \frac{\epsilon + \tilde{q}_{2n}}{\epsilon + i} (\mathcal{A}_{2n}^{\text{res}} + \mathcal{A}_{2n}^{\text{bg}}) P_{2n}(\cos \theta). \quad (55)$$

This expression can be rearranged as

$$\mathcal{A}(\omega; \theta) = \frac{\epsilon + \tilde{q}(\theta)}{\epsilon + i} \sum_{n=0}^{\infty} (\mathcal{A}_{2n}^{\text{res}} + \mathcal{A}_{2n}^{\text{bg}}) P_{2n}(\cos \theta) \quad (56)$$

by introducing an angularly dependent complex q parameter

$$\tilde{q}(\theta) = \frac{\sum_{n=0}^{\infty} (\mathcal{A}_{2n}^{\text{res}} q + \mathcal{A}_{2n}^{\text{bg}} i) P_{2n}(\cos \theta)}{\sum_{n=0}^{\infty} (\mathcal{A}_{2n}^{\text{res}} + \mathcal{A}_{2n}^{\text{bg}}) P_{2n}(\cos \theta)}, \quad (57)$$

with the terms of the sum ending after $n = 1$ for one photon and $n = 2$ for two photons. This shows that Eq. (34), holds, not only for the angularly integrated case, but also for any emission angle. Thus, the angularly resolved phase $\phi(\omega; \theta)$ can, in a similar way, be decomposed into a variable component $\Delta\phi(\omega; \theta)$ and a background contribution $\phi_{bg}(\theta)$, which now acquire an explicit angular dependence:

$$\phi(\omega; \theta) = \arg[\mathcal{A}(\omega; \theta)] = \Delta\phi(\omega; \theta) + \phi_{bg}(\theta), \quad (58)$$

$$\Delta\phi(\omega; \theta) = \arg\left[\frac{\epsilon + \tilde{q}(\theta)}{\epsilon + i}\right], \quad (59)$$

$$\phi_{bg}(\theta) = \arg\left[\sum_{n=0}^{\infty} (\mathcal{A}_{2n}^{\text{res}} + \mathcal{A}_{2n}^{\text{bg}}) P_{2n}(\cos \theta)\right]. \quad (60)$$

As the emission angle θ changes, so does $\tilde{q}(\theta)$. Of special interest are the critical angles θ_{crit} at which $\text{Im}[\tilde{q}(\theta_{\text{crit}})] = 0$. These angles exhibit the case discussed in Sec. IV A 2 and illustrated in Fig. 2(b), where the phase makes an immediate π jump at $\epsilon = -\text{Re}(\tilde{q})$. The critical angles also serve as a boundary between those emission angles for which a less than π phase jump is present and those for which a 2π jump is present.

The critical angles can be found analytically by setting $\text{Im}[\tilde{q}(\theta)] = 0$. This involves solving a second-order polynomial equation for the Wigner term and a fourth-order equation for the atomic term, as discussed in Appendix B, indicating a theoretical maximum of two critical angles in the Wigner phase and four in the atomic phase—one for each real solution.

V. RESULTS AND DISCUSSION

A. The one-photon cross section

There are three open angular momentum channels for one-photon ionization from a $np_{3/2}$ orbital: $\epsilon s_{1/2}$, $\epsilon d_{3/2}$, and $\epsilon d_{5/2}$. The integrated photoionization cross section for these three channels, along with the total cross section, is shown in Fig. 3 for both xenon and radon. The figure demonstrates the first few members of a series of $5p_{1/2}n\ell$ resonances in xenon and $6p_{1/2}n\ell$ resonances in radon that continues all the way up to the $np_{1/2}$ thresholds.

The radon cross section starts with one distinct, low energy resonance, labeled $6p_{1/2}^{-1}7s$, followed by a series of resonance pairs converging to the $6p_{1/2}$ threshold. Xenon contains resonance pairs very similar to those in radon, converging to the $5p_{1/2}$ threshold. Each resonance pair consists of two distinct types: one broad $5p_{1/2}^{-1}nd$ resonance ($6p_{1/2}^{-1}nd$ in radon) decaying mainly into the $d_{5/2}$ channel, and one narrow $5p_{1/2}^{-1}ns$ resonance ($6p_{1/2}^{-1}ns$ in radon) decaying into both $s_{1/2}$ and $d_{3/2}$. For brevity, only the n and ℓ quantum numbers of the excited electron resonances are specified below.

The experimentally measured xenon cross section from [13] is indicated by the purple dots in Fig. 3. At lower energies, a slight shift in the position of the peaks, gradually

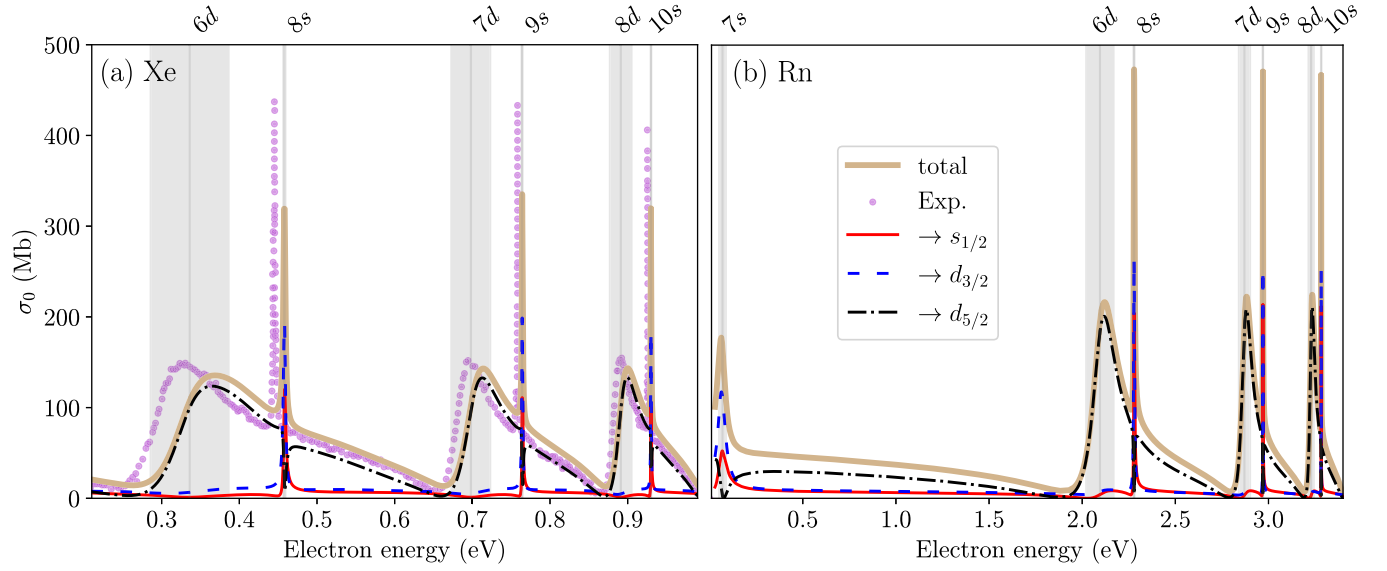


FIG. 3. The angularly integrated one-photon cross section (a) below the $5p_{1/2}$ ionization threshold in xenon and (b) below the $6p_{1/2}$ ionization threshold in radon. The thick beige line shows the total cross section, with purple dots indicating experimental values for xenon [13], while the thin lines represent the partial cross sections for each channel open for ionization from $np_{3/2}$ ($\epsilon s_{1/2}$, $\epsilon d_{3/2}$, and $\epsilon d_{5/2}$). The calculated resonance positions and widths are indicated in gray.

decreasing with as the energy rises, can be seen. The difference between the maxima associated with the $6d$ resonance is approximately 0.05 eV, while that for the $8s$ resonance is around 0.01 eV. The qualitative behavior of the cross section is captured and the overall agreement remains good.

Figure 4 displays the eigenvalues of the matrix in Eq. (20) for both systems, with the real value on the abscissa and the imaginary value on the ordinate. The region between the first and second ionization threshold is shown. As discussed in Sec. III C, the discretized continua are appearing as lines with a particular inclination, starting close to the corresponding threshold, while the resonances each have an individual

relation between the real and imaginary part of the energy eigenvalue. The presence of two series of resonances, marked with red crosses, is clear.

Tables I and II list the parameters of the first few resonance shown in Fig. 4. For xenon, the experimental resonance positions (E_{exp}) [3] and Fano parameters (q_{exp}) [13] are included in Table I for comparison.

The calculated q values of the nd resonances in xenon are similar to literature data, with the latter being slightly smaller. In contrast, the calculated q values of the ns resonances deviate from the experimental ones. However, the exact value and sign of the the q parameter does not significantly affect

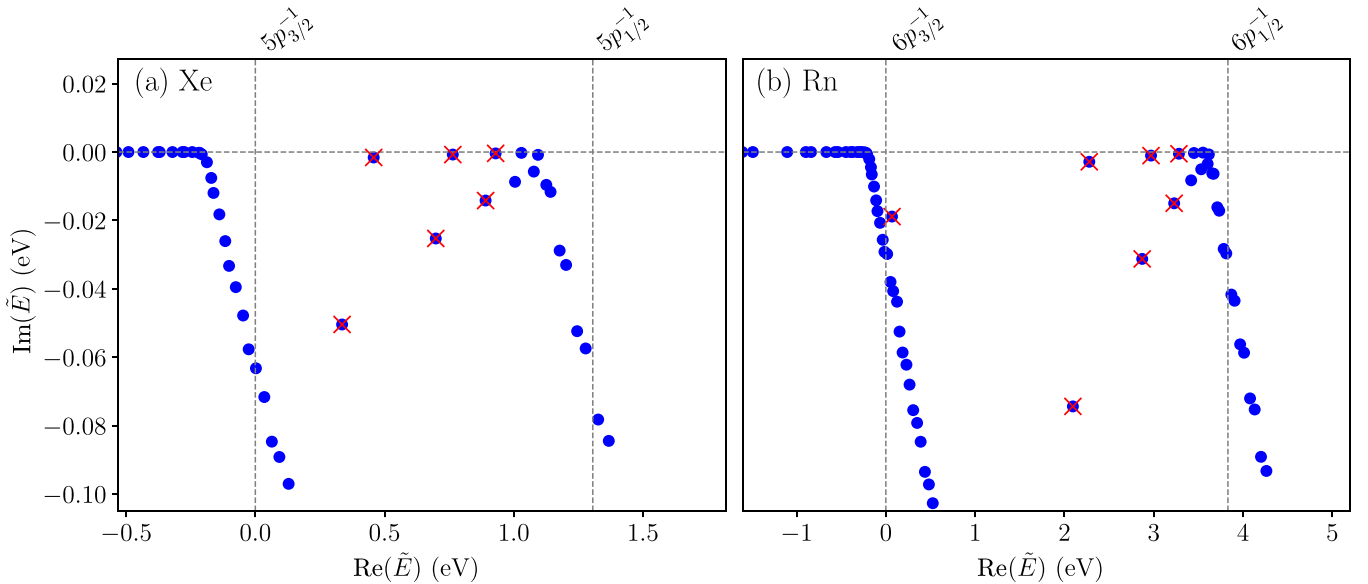


FIG. 4. The complex eigenenergies for (a) xenon near the $5p_{3/2}$ and $5p_{1/2}$ ionization thresholds, and (b) radon near the $6p_{3/2}$ and $6p_{1/2}$ thresholds. The thresholds are shown by dashed vertical lines. The energy scales are relative to $5p_{3/2}^{-1}$ for Xe and $6p_{3/2}^{-1}$ for Rn. The red crosses mark the resonances listed in Tables I and II.

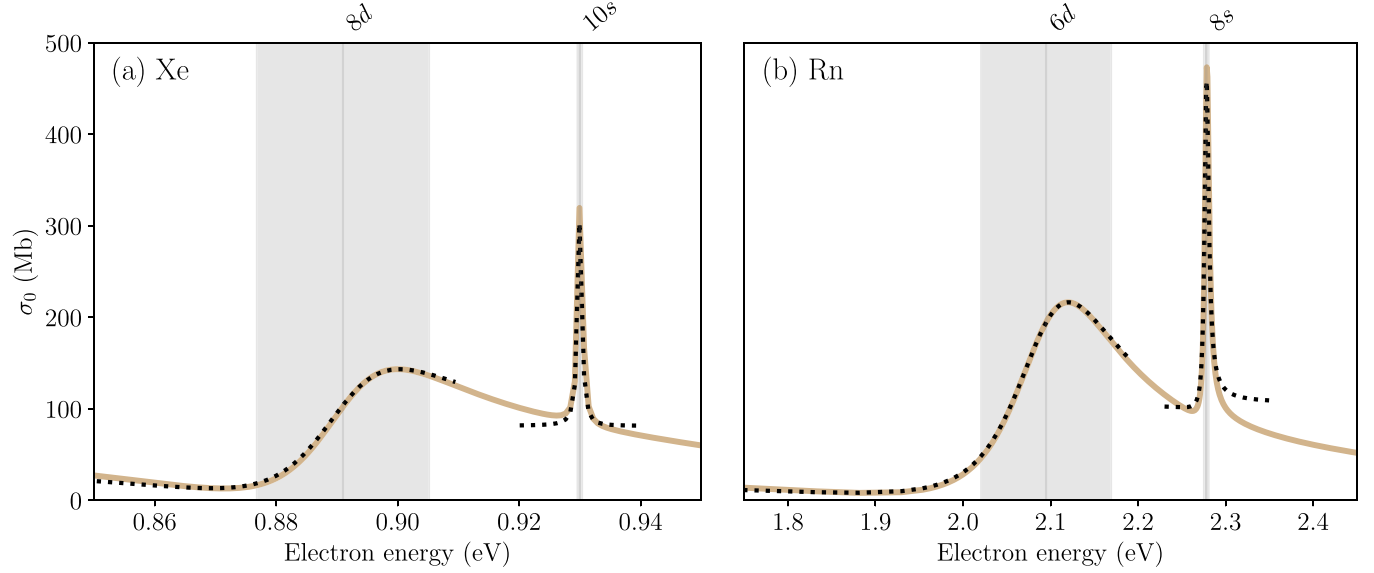


FIG. 5. The angularly integrated one-photon cross section in the vicinity of (a) the $5p_{1/2}^{-1}8d$ and $5p_{1/2}^{-1}10s$ resonances in xenon and (b) the $6p_{1/2}^{-1}6d$ and $6p_{1/2}^{-1}8s$ resonances in radon. The black dotted curves represent individual contributions from the nd and ns resonances, as predicted by the model in Eq. (4).

TABLE I. Parameters of selected xenon resonances. The energy positions (E_{res}) are given relative to Xe^+ ($5p_{3/2}^{-1}$). The experimental positions (E_{exp}) are obtained from [6], while the experimental Fano parameters (q_{exp}) are taken from [13].

Label	E_{res} [eV]	E_{exp} [eV]	Γ [eV]	q	q_{exp}
$5p_{1/2}^{-1}6d$	0.336	0.328	0.1009	1.61	1.49
$5p_{1/2}^{-1}8s$	0.458	0.447	0.0032	-28.69	22.70
$5p_{1/2}^{-1}7d$	0.698	0.696	0.0506	1.56	1.47
$5p_{1/2}^{-1}9s$	0.764	0.758	0.0015	-61.64	15.80
$5p_{1/2}^{-1}8d$	0.891	0.890	0.0284	1.52	1.45
$5p_{1/2}^{-1}10s$	0.930	0.926	0.0008	-136.62	13.90

the resonance shape if $|q|$ is large. This can be understood from Eq. (4), where the numerator is approximately constant near the resonance for $|q| \gg 1$. For the xenon ns resonances, both $|q| > 10$ and $|q_{\text{exp}}| > 10$ holds. Thus, as shown in Fig. 3, the ns -resonance profile is not sensitive to these deviations in q . The widths of the $6d$ and $8s$ xenon resonances were also measured experimentally in Ref. [53] and are reported

TABLE II. Parameters of selected radon resonances. The energy positions (E_{res}) are given relative to Rn^+ ($6p_{3/2}^{-1}$).

Label	E_{res} [eV]	Γ [eV]	q
$6p_{1/2}^{-1}7s$	0.069	0.0377	23.65
$6p_{1/2}^{-1}6d$	2.095	0.1488	2.91
$6p_{1/2}^{-1}8s$	2.278	0.0057	9.44
$6p_{1/2}^{-1}7d$	2.871	0.0625	2.70
$6p_{1/2}^{-1}9s$	2.970	0.0021	9.55
$6p_{1/2}^{-1}8d$	3.229	0.0300	2.62
$6p_{1/2}^{-1}10s$	3.283	0.0010	9.64

as 0.0808 eV and 0.0023 eV, respectively. These values align well with those obtained in the present calculations.

The cross section is accurately described by the contributions from these resonances, as demonstrated in Fig. 5. The figure illustrates how two xenon resonances ($8d$ and $10s$) and two radon resonance ($6d$ and $8s$), govern the modulation of the cross section in the displayed energy regions. It also shows that the calculated q values, provides a good description of the resonant behavior.

The different energy dependencies of the three channels give rise to an angular dependence of the cross section that itself varies with energy, as illustrated for radon in Fig. 6. At $\theta = 0$, the Legendre polynomial in Eq. (6) is equal to one, and therefore $\frac{d\sigma}{d\Omega}/\frac{\sigma_0}{4\pi} = 1 + \beta_2$. At the peaks of the broad resonances, the cross section is dominated by a single channel, $6p_{3/2} \rightarrow \epsilon d_{5/2}$. As a result, the angular dependence remains approximately constant across the resonance, and the β_2 parameter varies only gradually. In contrast, near the cross-section minima and the ns resonances, the contributing channels are of comparable strength, leading to a pronounced energy dependence of the β_2 parameter.

B. Angularly integrated phases

We now consider the two-photon RABITT protocol, capable of measuring the phase. RABITT experiments typically employ a laser wavelength of 800 nm, corresponding to an IR photon energy of 1.55 eV, which is also used in the present calculations. It is important to note that the resonances studied here correspond to intermediate states, i.e., states reached after absorption of a single XUV photon, and their signatures appear in the RABITT sidebands whose energies are determined by the combination of XUV and IR photons. In the present calculations, the resonances are encountered in the absorption pathway. Consequently, positions of the resonances shown in

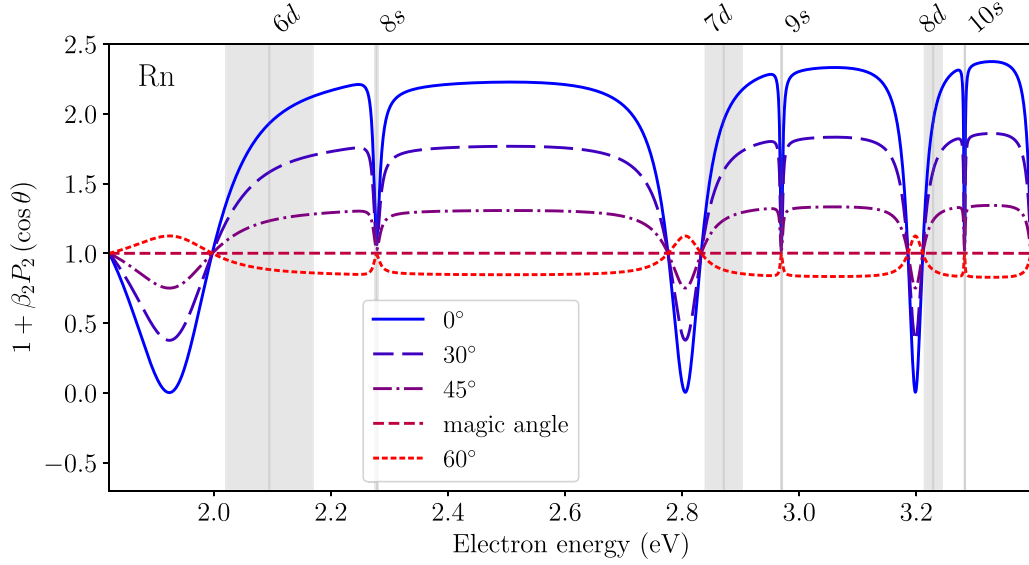


FIG. 6. The angular part of the cross section below the $6p_{1/2}$ ionization threshold in radon. The y axis represents the quantity $1 + \beta_2 P_2(\cos \theta)$, which corresponds to the differential cross section $\frac{d\sigma}{d\Omega}$ normalized by the integrated cross section over 4π , i.e. $\frac{d\sigma}{d\Omega} / \frac{\sigma_0}{4\pi}$. For $\theta = 0$, the Legendre polynomial equals one, and the plot therefore shows the value of the β_2 parameter shifted upward by one. At the magic angle ($\theta \approx 54.7^\circ$), the Legendre polynomial vanishes, such that the angular contribution is exactly equal to one and exhibits no energy dependence.

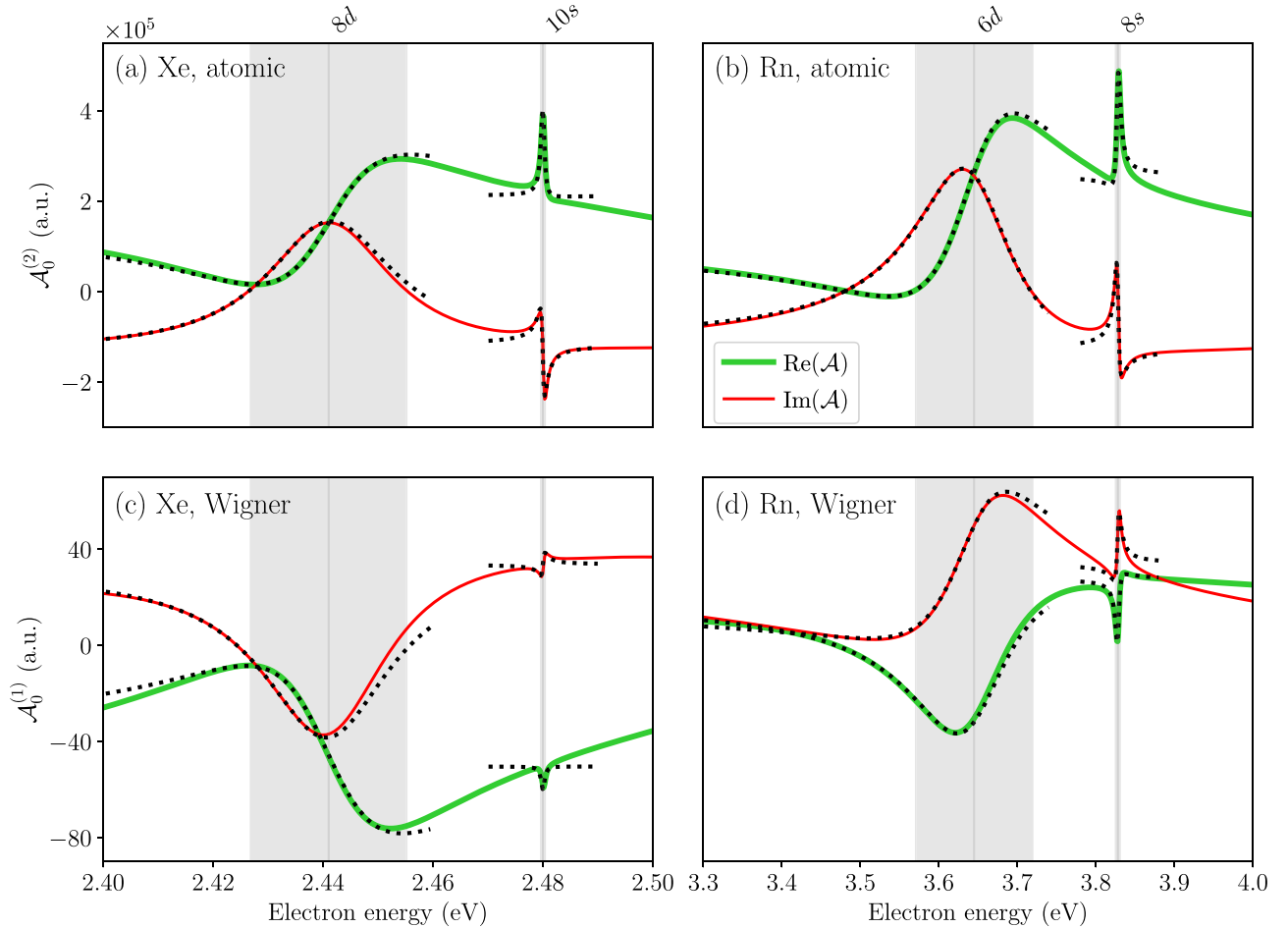


FIG. 7. Modulations in the angularly integrated sideband interference term (top row) and its Wigner contribution (bottom row) in the vicinity of $5p_{1/2}^{-1}8d$ and $5p_{1/2}^{-1}10s$ resonances in xenon (left column) and $6p_{1/2}^{-1}6d$ and $6p_{1/2}^{-1}8s$ resonances in radon (right column). The black dotted curves represent individual contributions from the nd and ns resonances, as predicted by the model in Eq. (34).

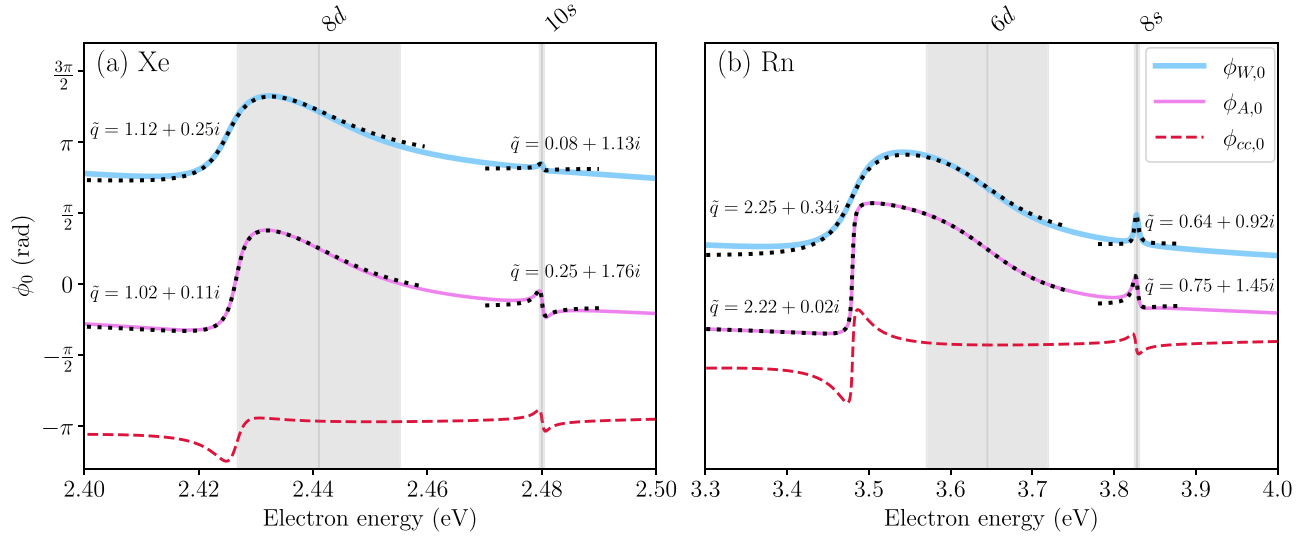


FIG. 8. The angularly integrated Wigner (top curve), atomic (middle curve), and continuum-continuum (bottom curve) phases in the vicinity of (a) $5p_{1/2}^{-1}8d$ and $5p_{1/2}^{-1}10s$ resonances in xenon and (b) $6p_{1/2}^{-1}6d$ and $6p_{1/2}^{-1}8s$ resonances in radon. The black dotted curves represent individual contributions from the nd and ns resonances, as predicted by the model in Eq. (36). The complex values indicated near each resonance in the atomic and Wigner phases correspond to the complex shape parameter $\tilde{q}_0$.

the figures below are shifted by +1.55 eV to align with the sideband energy.

The phases are extracted from the complex sideband interference term $\mathcal{A}^{(2)}$ (atomic phase) and its one-photon contribution $\mathcal{A}^{(1)}$ (Wigner phase), shown in Fig. 7. The model prediction from Eq. (34) is shown in black and captures the behavior in the resonant regions well.

From these terms, the phase is calculated and shown in Fig. 8. Here as well, the model is seen to reproduce the phase behavior accurately. In both atoms, the atomic phase associated with the nd resonances is sharper than the Wigner phase. This is particularly evident for radon, where the atomic phase exhibits a sharp jump below the $6d$ resonance. This behavior can be traced to the small, positive value of the imaginary part of $\tilde{q}$, $\text{Im}(\tilde{q}) \approx 0.02$, which lies close to the critical value $\text{Im}(\tilde{q}) = 0$. As a result, a near- π jump occurs at $\epsilon = -\text{Re}(\tilde{q}) \Rightarrow E \approx 3.48$ eV. Consequently, the continuum-continuum delay undergoes a pronounced modulation, deviating from the universal behavior of the CC delay discussed in Ref. [46].

In contrast, the phase near the ns resonances exhibits smaller variations, yet it remains well described by the taxonomy shown in Fig. 2. For example, the Wigner phase near the $8s$ resonance in radon displays an almost single-peak profile, which can be attributed to the value of $\text{Im}(\tilde{q})$ being close to 1 [$\text{Im}(\tilde{q}) = 0.92$]. The real part of $\tilde{q}$ for this resonance is positive, corresponding to the case shown in Fig. 2(d1). However, in our calculations the resonance is encountered in the absorption pathway, and due to the resulting sign change of the phase ($\phi \rightarrow -\phi$), the minimum in Fig. 2(d1) is transformed into a maximum in the calculated phase.

Similarly, as is shown in Fig. 8(a), $\text{Im}(\tilde{q})$ is close to 1 for the Wigner phase near the $10s$ resonance in xenon. In this case, however, the real part of $\tilde{q}$ is nearly vanishing [$\text{Re}(\tilde{q}) = 0.08$], resulting in only weak phase variation.

C. Angularly resolved phases

To obtain the angular dependence of the phase, the $\tilde{\beta}_{2n}$ parameters may be calculated. As an illustration, the second-order parameters for the Wigner phase, $\tilde{\beta}_2^W$, and the atomic phase, $\tilde{\beta}_2^A$, are shown for xenon and radon in Fig. 9, together with the corresponding model predictions from Eq. (54). The model reproduces the calculated parameters accurately, with only slight deviations visible and even then only far from the resonances [most clearly visible below 3.5 eV in Fig. 9(c)]. The fourth-order atomic parameters, $\tilde{\beta}_4^A$, are not shown; however, they exhibit behavior similar to $\tilde{\beta}_2^A$ for both atoms and are equally well described by the model. Notably, the radon $\tilde{\beta}_{2n}$ parameters display a significantly stronger energy dependence than those of xenon near the considered nd resonances, indicating a clear difference in the angularly resolved energy dependence of the phase between the two systems.

This prediction is supported by Fig. 10, where the phase is shown for several emission angles (from 0° to 60°) for xenon and radon. In the case of xenon, both the atomic and Wigner phases near the $8d$ and $10s$ resonances exhibit phase jumps smaller than π , with the variation being significantly weaker near the $10s$ resonance. The figure also shows an increasing contribution from the IR photon with emission angle, as the continuum-continuum—and consequently the atomic—phases shift downward. This is congruent with previous research [40], which already has shown an increase of the continuum-continuum contribution with emission angle.

Despite these variations, the phases for xenon remain qualitatively the same irrespective of emission angle. This is not the case for radon, where the phases near the $6d$ resonance shift from exhibiting a 2π jump at 0° to a jump smaller than π at 60° . In between, a critical angle, discussed in Sec. IV C, can be predicted for both the atomic and the Wigner phase. Particularly notable is the behavior at 30° , where the Wigner and atomic phases display qualitatively different features. This

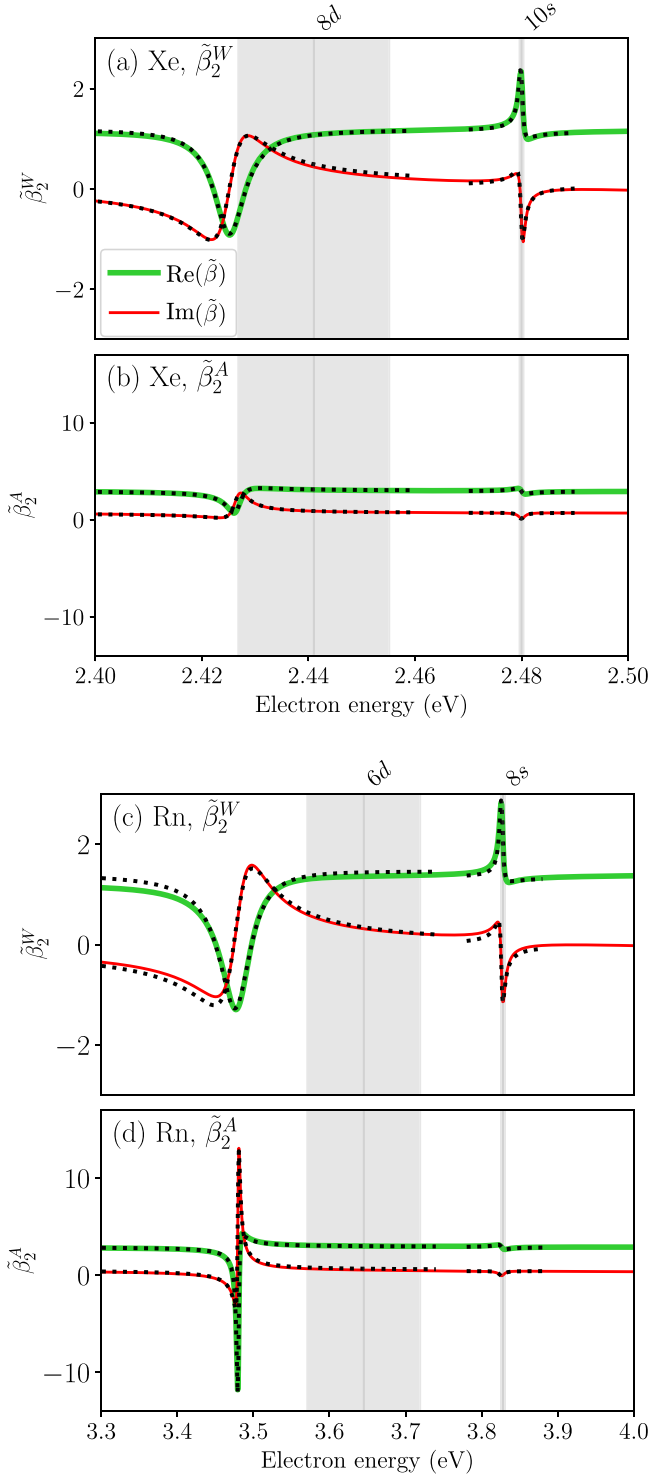


FIG. 9. The complex asymmetry parameters $\tilde{\beta}_2^W$ and $\tilde{\beta}_2^A$ in the vicinity of the $5p_{1/2}^{-1}8d$ and $5p_{1/2}^{-1}10s$ resonances in xenon (top panels) and the $6p_{1/2}^{-1}6d$ and $6p_{1/2}^{-1}8s$ resonances in radon (bottom panels). The black dotted curves represent individual contributions from the nd and ns resonances, as predicted by the model in Eq. (54).

results in a strong modulation of the continuum-continuum phase around 3.48 eV [shown in Fig. 10(f)], and indicates different values of the atomic and Wigner critical angles.

The transition between the two types of phase jumps in radon is illustrated in greater detail in Fig. 11. The atomic and

TABLE III. All critical angles of the Wigner and atomic phase for the $5p_{1/2}^{-1}8d$ and $5p_{1/2}^{-1}10s$ resonances in xenon and the $6p_{1/2}^{-1}6d$ and $6p_{1/2}^{-1}8s$ resonances in radon. Both the directly computed values $\theta_{\text{crit}}^{\text{true}}$ and those values $\theta_{\text{crit}}^{\text{pred}}$ predicted by the model in Sec. IV and calculated as described in Appendix B are given.

	Wigner		Atomic	
	$\theta_{\text{crit}}^{\text{pred}}$	$\theta_{\text{crit}}^{\text{true}}$	$\theta_{\text{crit}}^{\text{pred}}$	$\theta_{\text{crit}}^{\text{true}}$
Xe, 8d				
Xe, 10s	77.8°	79.4°		
Rn, 6d	21.9°	22.0°	38.5°	38.2°
			84.8°	84.4°
Rn, 8s	72.0°	72.6°	70.2°	70.5°
			76.1°	75.7°

Wigner phases near the $6d$ resonance are shown at angles 1° below and 1° above the corresponding critical angles, at which the transition occurs and the phase exhibits a discontinuous π jump. The predictions of the model in Eq. (58) are overlaid on the phase curves, showing that the model accurately captures the transition and reproduces it through a change in the sign of $\text{Im}[\tilde{q}(\theta)]$.

The imaginary part of $\tilde{q}(\theta)$, which determines the type of phase jump, is shown in Fig. 12 as a function of the emission angle for the considered resonances in xenon and radon. The difference between $\text{Im}[\tilde{q}(\theta)]$ for the Wigner and atomic cases increases with θ . As was mentioned above, this behavior can be attributed to the increasing influence of the IR photon at larger emission angles.

The condition $\text{Im}[\tilde{q}(\theta)] = 0$ can be used to predict the critical angles and is indicated in Fig. 12 by black dots. The predicted values, $\theta_{\text{crit}}^{\text{pred}}$, calculated as described in Appendix B, are compared with the ones extracted from the computed phases, $\theta_{\text{crit}}^{\text{true}}$, in Table III. It can be seen that, even under the strict assumption of a flat nonresonant path, the model provides accurate predictions. The largest deviation, 1.6° , occurs for the Wigner phase near the xenon $10s$ resonance, which may also be attributed to the highly energy-dependent background, caused by the $8d$ resonance. In no other case does the discrepancy exceed 0.6° .

VI. CONCLUSION

This work has investigated the autoionizing resonances between the lowest ($np_{3/2}$ and $np_{1/2}$) ionization thresholds of xenon and radon. The resonance parameters were calculated using the RRPAE method, and for xenon (where experimental data are available) were found to be in good agreement with literature values. Xenon displays a series of resonance pairs, each consisting of one $5p_{1/2}^{-1}nd$ - and one $5p_{1/2}^{-1}ns$ dominated resonance, starting with $5p_{1/2}^{-1}6d$ and $5p_{1/2}^{-1}8s$. The overall resonance structure in radon is found to be very similar to that of xenon, with the exception of the presence of the additional, low-lying $6p_{1/2}^{-1}7s$ dominated resonance.

The resonances strongly modulate the photoionization process, as reflected in the cross section as well as in the atomic phase and its Wigner contribution. The resonant phase modulation was found to vary strongly, shifting between a less than

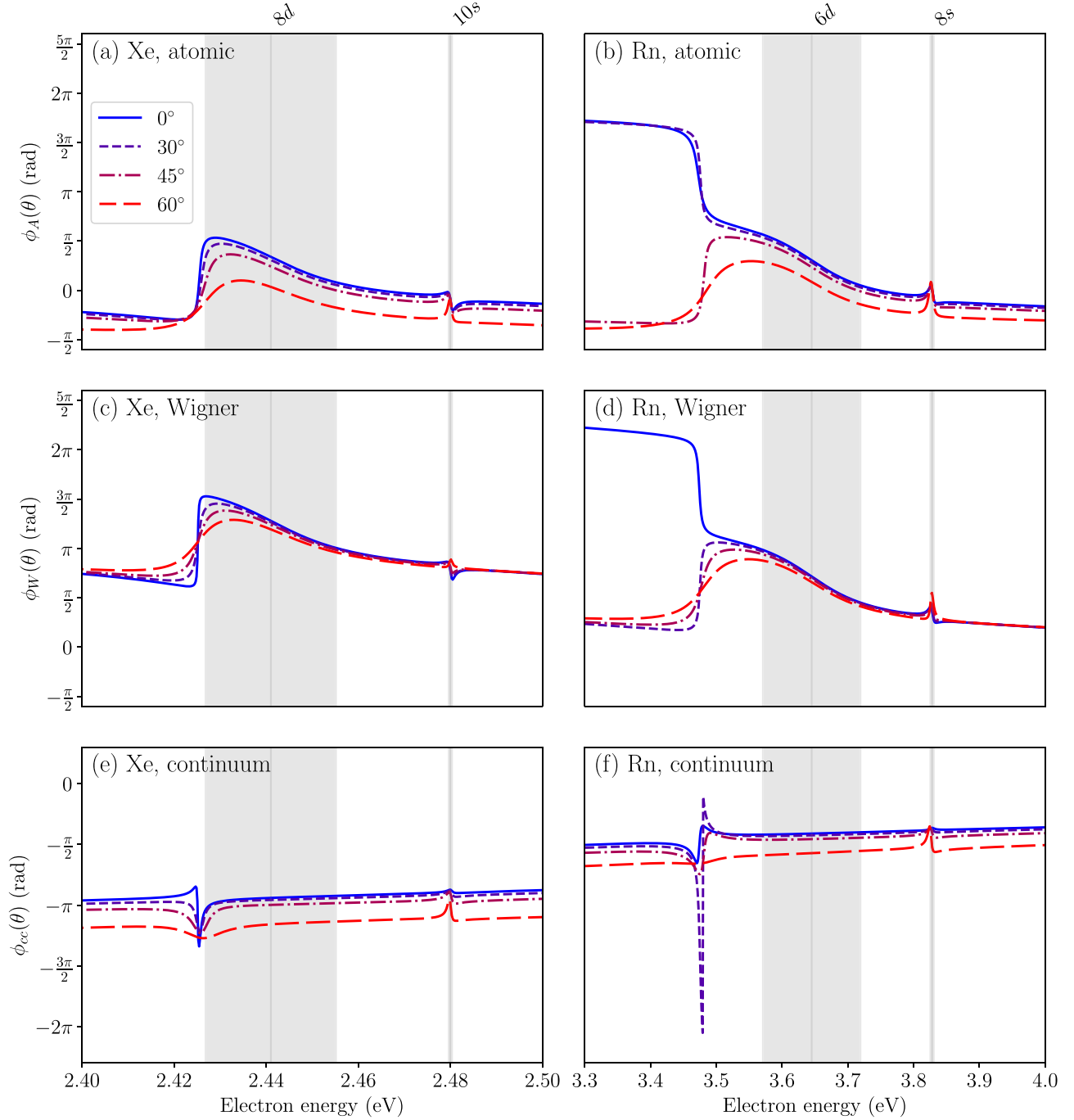


FIG. 10. The angularly resolved atomic (top row), Wigner (middle row), and continuum-continuum (bottom row) phases in the vicinity of $5p_{1/2}^{-1}8d$ and $5p_{1/2}^{-1}10s$ resonances in xenon (left panel) and $6p_{1/2}^{-1}6d$ and $6p_{1/2}^{-1}8s$ resonances in radon (right panel). The phases are shown for selected emission angles in the range of 0° to 60° .

π and 2π phase jump, depending on the emission angle. The emission angles at which this shift takes place were identified. These critical angles were found to differ between the atomic and Wigner phase, indicating strong modulations in the continuum-continuum contribution.

We have further presented a model capable of describing the energy and angular dependence of the phase, as well as the complex asymmetry parameters $\tilde{\beta}_n$, in the vicinity of a resonance. The model was validated against the RRPAAE data, and successfully reproduced both the phase and the $\tilde{\beta}_n$ parameters,

while also predicting the critical angles with good accuracy. Within this framework we found a theoretical maximum of two critical angles for the Wigner phase and four for the atomic phase.

DATA AVAILABILITY

There are no publicly available research data or software supporting this article. Requests for further information or data should be sent to the authors.

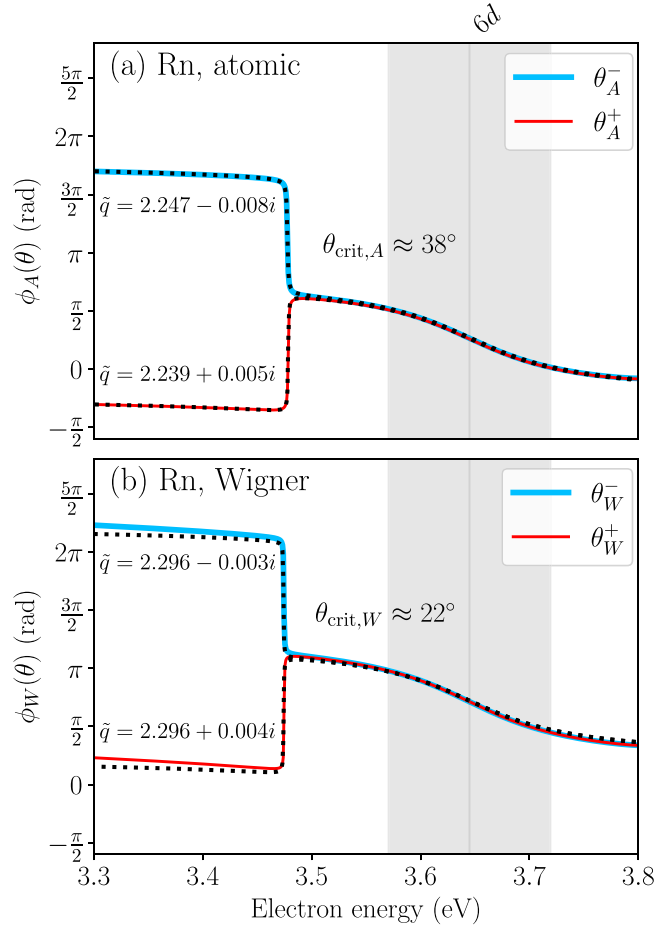


FIG. 11. The angularly resolved (a) atomic and (b) Wigner phases in the vicinity of the $6p_{1/2}^{-1}6d$ resonance in radon. The figure shows the atomic phase near the critical angle of $\theta_{\text{crit}}^A \approx 38^\circ$ and the Wigner phase near the corresponding critical angle of $\theta_{\text{crit}}^W \approx 22^\circ$. The phases are shown 1° below ($\theta_{A/W}^-$, in teal) and 1° above ($\theta_{A/W}^+$, in red) of the specified θ_{crit} . The black dotted curves represent the phase predicted by the model in Eq. (58). The corresponding complex shape parameters $\tilde{q}(\theta_{A/W}^\pm)$ are also marked in the figure.

APPENDIX A: LEFT VERSUS RIGHT EIGENVECTORS

Consider the matrix in Eq. (20):

$$\begin{pmatrix} \mathbb{A} & \mathbb{B} \\ -\mathbb{B} & -\mathbb{A} \end{pmatrix}. \quad (\text{A1})$$

It is illustrative to look at one of its right eigenvectors $\mathbb{R}_n$ with eigenvalue λ_n :

$$\begin{pmatrix} \mathbb{A} & \mathbb{B} \\ -\mathbb{B} & -\mathbb{A} \end{pmatrix} \mathbb{R}_n = \lambda_n \mathbb{R}_n. \quad (\text{A2})$$

It is possible to make a unitary transformation as

$$\begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbb{A} & \mathbb{B} \\ -\mathbb{B} & -\mathbb{A} \end{pmatrix} \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbf{X}_+^n \\ \mathbf{X}_-^n \end{pmatrix} = \lambda_n \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbf{X}_+^n \\ \mathbf{X}_-^n \end{pmatrix}, \quad (\text{A3})$$

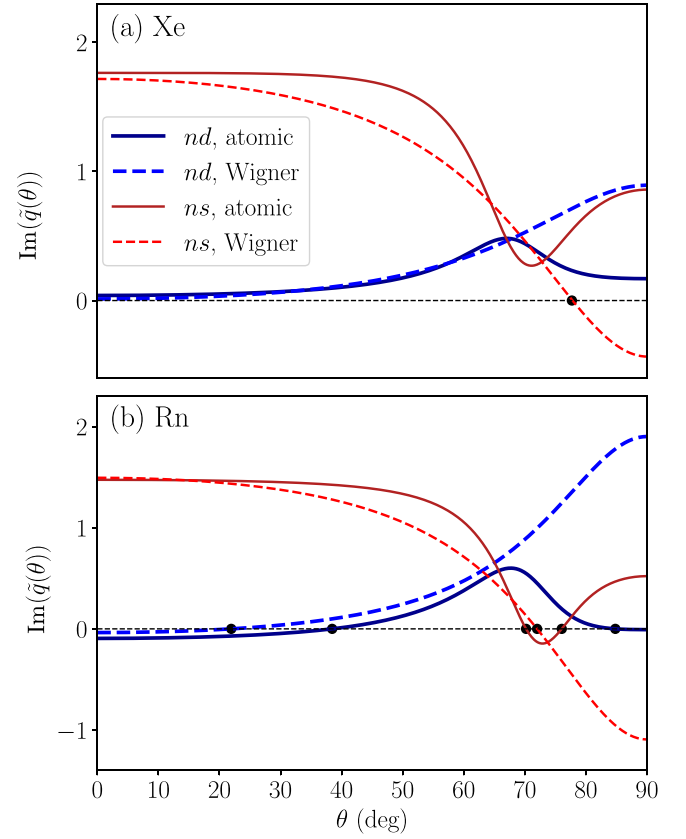


FIG. 12. The imaginary part of $\tilde{q}(\theta)$ as a function of the photoelectron emission angle θ for the $5p_{1/2}^{-1}8d$ and $5p_{1/2}^{-1}10s$ resonances in xenon (a) and the $6p_{1/2}^{-1}6d$ and $6p_{1/2}^{-1}8s$ resonances in radon (b). The black dots indicate the critical condition $\text{Im}[\tilde{q}(\theta)] = 0$, calculated as described in Appendix B.

giving

$$\begin{pmatrix} \mathbb{A} & -\mathbb{B} \\ \mathbb{B} & -\mathbb{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}_+^n \\ -\mathbf{X}_-^n \end{pmatrix} = \lambda_n \begin{pmatrix} \mathbf{X}_+^n \\ -\mathbf{X}_-^n \end{pmatrix}. \quad (\text{A4})$$

Taking the transpose of both the left- and the right-hand side gives

$$(\mathbf{X}_+^n, -\mathbf{X}_-^n) \begin{pmatrix} \mathbb{A} & -\mathbb{B} \\ \mathbb{B} & -\mathbb{A} \end{pmatrix}^T = \lambda_n (\mathbf{X}_+^n, -\mathbf{X}_-^n). \quad (\text{A5})$$

Since the submatrices $\mathbb{A}$, $\mathbb{B}$ are symmetric,

$$(\mathbf{X}_+^n, -\mathbf{X}_-^n) \begin{pmatrix} \mathbb{A} & \mathbb{B} \\ -\mathbb{B} & -\mathbb{A} \end{pmatrix} = \lambda_n (\mathbf{X}_+^n, -\mathbf{X}_-^n), \quad (\text{A6})$$

which gives the left eigenvector $\mathbb{L}_n = (\mathbf{X}_+^n, -\mathbf{X}_-^n)$ with eigenvalue λ_n , and it is related to the right eigenvector as

$$\mathbb{L}_n = (\mathbf{X}_+^n, -\mathbf{X}_-^n) = \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbf{X}_+^n \\ \mathbf{X}_-^n \end{pmatrix} = \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix} \mathbb{R}_n. \quad (\text{A7})$$

APPENDIX B: THE ANALYTICAL VALUES OF THE CRITICAL ANGLES

As noted in Sec. VC, the critical angles can be found by solving the equation

$$\text{Im}\{\tilde{q}(\theta)\} = \text{Im}\left\{\frac{\sum_{n=0}^N (\mathcal{A}_{2n}^{\text{res}} q + \mathcal{A}_{2n}^{bg} i) P_{2n}(x)}{\sum_{n=0}^N (\mathcal{A}_{2n}^{\text{res}} + \mathcal{A}_{2n}^{bg}) P_{2n}(x)}\right\} = 0, \quad (\text{B1})$$

where $x = \cos(\theta)$ is the cosine of the emission angle, $\mathcal{A}_n^{bg}$ and $\mathcal{A}_n^{\text{res}}$ are fitted parameters, $P_n(x)$ is the n th Legendre polynomial, and $N = 1$ for the Wigner phase and $N = 2$ for the atomic phase.

This can be simplified by multiplying both the denominator and numerator with the complex conjugate of the divisor. This gives a real denominator, simplifying the problem to

$$\text{Im}\left\{\sum_{n=0}^N (\mathcal{A}_{2n}^{\text{res}} q + \mathcal{A}_{2n}^{bg} i) P_{2n}(x) \times \sum_{n=0}^N (\mathcal{A}_{2n}^{\text{res}} + \mathcal{A}_{2n}^{bg})^* P_{2n}(x)\right\} = 0. \quad (\text{B2})$$

Although this multiplication increases the polynomial order from $2N$ to $4N$ of the numerator, it does not necessarily give any false roots, as the Im operator is nonlinear. However, the case where

$$\sum_{n=0}^N (\mathcal{A}_{2n}^{\text{res}} + \mathcal{A}_{2n}^{bg}) P_{2n}(x) = 0 \quad (\text{B3})$$

still gives false roots (and an undefined $\tilde{q}(\theta)$), and should be guarded against.

By defining

$$A_{n,m} = \text{Im}\{(\mathcal{A}_n^{\text{res}} q + \mathcal{A}_n^{bg} i) \times (\mathcal{A}_n^{\text{res}} + \mathcal{A}_n^{bg})^*\}, \quad (\text{B4})$$

the equation can be further simplified to

$$\sum_{n=0}^N \sum_{m=0}^N A_{2n,2m} P_{2n}(x) P_{2m}(x) = 0, \quad (\text{B5})$$

where the explicit expressions

$$P_0(x) = 1, \quad (\text{B6a})$$

$$P_2(x) = \frac{1}{2}(3x^2 - 1), \quad (\text{B6b})$$

$$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3) \quad (\text{B6c})$$

of the Legendre polynomials may be inserted. Noting that all terms in Eq. (B6) are even and that only positive real roots (corresponding to real values of $\theta \leq \pi/2$) are of interest, Eq. (B5) can be solved for $y = x^2 = \cos^2 \theta \in [0, 1]$, as a polynomial equation

$$\sum_{i=0}^{2N} C_i y^i = 0 \quad (\text{B7})$$

of second order for the Wigner phase and a fourth-order one for the atomic phase. Here only real values $y \in [0, 1]$ need to be considered, as these correspond to real values of $\theta = \arccos \sqrt{y}$.

1. Wigner

The explicit form of the coefficients in the Wigner case is solved through the second-order polynomial equation with coefficients

$$C_0 = 64A_{0,0} + 16A_{2,2} - 32B_{0,2}, \quad (\text{B8a})$$

$$C_1 = -96A_{2,2} + 96B_{0,2}, \quad (\text{B8b})$$

$$C_2 = 144A_{2,2}, \quad (\text{B8c})$$

where $B_{n,m} = A_{n,m} + A_{m,n}$.

2. Atomic

For the atomic phase, the critical angles can similarly be calculated from the coefficients

$$C_0 = 64A_{0,0} + 16A_{2,2} + 9A_{4,4} - 32B_{0,2} + 24B_{0,4} - 12B_{2,4}, \quad (\text{B9a})$$

$$C_1 = -96A_{2,2} - 180A_{4,4} + 96B_{0,2} - 240B_{0,4} + 156B_{2,4}, \quad (\text{B9b})$$

$$C_2 = 144A_{2,2} + 1110A_{4,4} + 280B_{0,4} - 500B_{2,4}, \quad (\text{B9c})$$

$$C_3 = -2100A_{4,4} + 420B_{2,4}, \quad (\text{B9d})$$

$$C_4 = 1225A_{4,4}, \quad (\text{B9e})$$

giving a fourth-order polynomial equation.

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