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Excitation of helium Rydberg states and doubly excited resonances in strong extreme ultraviolet fields: Full-dimensional quantum dynamics using exponentially tempered Gaussian basis sets

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Recently optimized exponentially tempered Gaussian basis sets [P. R. Kapralova-Zdanska and J. Smydke, J. Chem. Phys. 138, 024105 (2013)] are employed in quantitative simulations of helium absorption cross-sections and two-photon excitation yields of doubly excited resonances. Linearly polarized half-infinite and Gaussian laser pulses at wavelengths 38–58 nm and large intensities up to 100 TW/cm² are considered. The emphasis is laid on convergence of the results with respect to the quality of the Gaussian basis sets (typically limited by a number of partial waves, density, and spatial extent of the basis functions) as well as to the quality of the basis set of field-free states (typically limited by the maximum rotational quantum number and maximum excitation of the lower electron). Particular attention is paid to stability of the results with respect to varying complex scaling parameter. Moreover, the study of the dynamics is preceded by a thorough check of helium energies and oscillator strengths as they are obtained with the exponentially tempered Gaussian basis sets, being also compared with yet unpublished emission wavelengths measured in electric discharge experiments. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4819495]

I. INTRODUCTION

Photoexcitation and ionization in gases exposed to intense short-wavelength radiation is a very important topic in astrophysics, planetology, thermonuclear fusion research, etc. For several decades, the photoexcitation and ionization of gases has been studied with sources emitting ionizing electromagnetic radiation at low peak brightness (e.g., Henkes tubes, helium resonance lamps, synchrotron radiation sources, etc.).1–3 The recent advent of extreme ultraviolet (XUV) and soft X-ray (SSXR) lasers (see, for example, Refs. 4–7) has made it possible to investigate the interaction of several energetic photons, i.e., a high-amplitude, high-frequency electromagnetic wave, with an isolated atom and/or molecule.

Theoretical methodology for simulation of atoms and molecules in strong electromagnetic fields is divided into studies of phenomena related directly to electronic dynamics such as absorption/transmission (A/T), high order harmonic generation (HHG), above-threshold ionization (ATI), superfluorescence, etc., on one hand, and effects involving nuclear dynamics such as the Coulomb explosion on the other. The methodology for laser-induced electronic phenomena (A/T, etc.) has to address the problem of very long paths of driven electrons, which reach up to a few nanometers, and operate in spectroscopic accuracy of atomic or molecular spectra. This is why, at the time being, literature on theoretical studies of the laser-induced electronic phenomena are more or less limited to atoms and diatomics. Due to high symmetry of atoms and diatomics it is possible to constrain the long-range motion into a single (radial) axis, where the Coulomb singularity is placed at its origin. This specific axis is then sampled. Below we indicate the most common methods for representation of the driven electrons in the radial axis. The laser induced electronic phenomena occur in attosecond time-scales and therefore the theoretical methods typically neglect the nuclear motion. Usually, electronic processes during attosecond pulses are simulated by a direct propagation of the electronic wavefunction, while problems involving more than few optical cycles are better solved using the Floquet formalism. The B-spline approach8, 9 was used quite early to calculate ionization and excitation of helium in XUV pulses10 and nowadays appears to be the most widespread approach, being used by several authors in combination with different methods. B-splines, generalized in terms of exterior complex scaling, a well-known approach to calculate resonances with the help of L2 basis sets, have been used to calculate ionization cross-sections of helium,11 and also applied to one-electron atomic and diatomic molecular ions both in conjunction with direct propagation12–15 and Floquet formalism.16, 17 Other authors have combined the B-spline and R-matrix methods and developed a full-dimensional approach for double-ionization of many-electron atoms in attosecond pulses18, 19 and yet others have used it to simulate helium in a pump-probe experiment by direct propagation in a femtosecond time-scale.20

Other methods employ various types of numerical lattices to represent the electronic phase-space. Among these is a generalized pseudospectral method, which has been combined with complex scaling and time-dependent density functional applications.
theory, formulated in conjunction with the Floquet formalism into a methodology that has been applied to problems involving many-electron atoms and diatomics. Also, discrete variable representation has been applied to simulate double ionization of helium and other atoms.

Analytical basis sets are used less frequently to represent the electronic motion. Apart from simulations of the hydrogen atom, where the natural basis set of Coulomb wavefunctions has been used, a similar long-range basis set of Coulomb-Sturmian functions has been used to simulate helium double ionization. Large sets of even tempered Gaussian basis sets have been used for calculation of HHG in helium and simulation of the He$_2$ cluster in very strong x-ray fields.

Thus far, discussed methods have specialized in atoms and diatomics. Some laser induced electronic phenomena may, however, be linked only to larger molecules. These include selection rules in molecular HHG induced by a circularly polarized laser field in molecules with discrete rotational symmetry. Although there have been attempts to simulate molecular HHG of benzene in a circularly polarized laser field based on a one-electron two-dimensional model and time-dependent density functional theory, as far as we know, highly accurate methodologies for the laser-induced electronic phenomena in larger molecules have not been developed yet. This is because the methodologically efficient separation of quasi-radial and angular motions of the driven electron is no longer possible for molecules with more than two nuclei. The present study is particularly motivated by this methodological issue.

We assume a possible future use of the quantum chemistry approach for simulations of the laser-induced electronic phenomena in molecules, where large, optimized Gaussian basis sets would be placed on each nucleus. The advantage in using Gaussians lies in the simple evaluation of the Hamiltonian matrix even if the basis functions are mutually shifted in space, being centered on individual nuclei, while being reasonably effective in expressing multiple cusps in the Coulomb-like wavefunctions. On the other hand, Gaussians are not traditionally used to represent spatially extent Rydberg states into a high degree of accuracy, which would be important in representation of driven electrons by strong laser fields. Nevertheless, our recent study shows that optimized Gaussian basis sets prove effective for Rydberg states as well. In the particular case of helium, 13 Gaussians are used to represent the ground state, while only one or two Gaussians must be added per each additional Rydberg state, where energies of all states are calculated with six significant figures.

It should be stressed that the standard quantum chemistry basis sets (such as the Dunning-Huzinaga or Lund Atomic Natural Orbital basis sets) are inadequate for the purpose of simulations of the electronic phenomena in strong laser fields for two reasons. First, they do not include basis functions which are broad enough, and second, they are optimized only up to chemical accuracy. The latter problem is reflected in rotations of bound states to the complex plane when using complex scaling (see Table IX in Ref. 38). These artifacts would derail dynamical simulation after a few attoseconds, which clearly shows in the course of the present paper. In our previous work, Ref. 38, we have suggested preferable exponentially tempered Gaussian (ExTG) basis sets with a higher density of Gaussians improving the stability with respect to complex rotation, and additional diffuse functions describing more Rydberg states. Two Gaussian basis sets, ExTG5G and ExTG7F, are now available for the helium atom. The ExTGnl basis sets are designed for calculations of helium states dominated by configurations with excitation numbers of the individual electrons up to $n$. The basis sets include a limited number of partial waves given by $l$. The absolute precision of the $S$-states is about 1 cm$^{-1}$ with the exception of low lying states, which have shifted energies due to the small numbers of partial waves. Energies of the $S$-states remain constant within 1 cm$^{-1}$ for a large interval of the complex scaling parameter.

The present study deals with the application of the ExTG5G and ExTG7F basis sets to the helium atom interacting with a strong linearly polarized XUV field for intensities in the order of tens of TW/cm$^2$. We assume half-infinite laser pulses with constant intensity as well as finite Gaussian-shaped laser pulses, and calculate the absorption cross-sections and two-photon excitation yields of doubly excited resonances. In the first part of the study, we perform a detailed precision test of all helium states that are involved in the laser excitation. The methods for the stationary calculations are described in Sec. II A. The errors of the calculated helium energies are discussed in Sec. III A. This part of the study is followed by the calculation and precision test of the coupling dipole elements and corresponding transition frequencies, which immediately enter or influence dynamical calculations. We use the fact that the transition dipole elements are directly connected with the oscillator strengths, as outlined in Sec. II B. We focus on the transitions in the UV range involving the ground state and the infrared transitions between the Rydberg states and resonances. In Sec. III B, we compare our calculations using the ExTGnl basis sets with exact theoretical and experimental benchmarks. Experimental data, which are partly available in the literature and partly obtained from the emission spectra measured in helium discharge, can be used as a benchmark for transition frequencies.

The main body of the paper concerns simulations of the laser-induced dynamics of the helium atom. The theoretical approach, which is formulated within the dipole approximation (Sec. II C), is based on the solution of the Floquet Hamiltonian in the basis set of the complex scaled field-free states. The Floquet problem is solved using the $(t, t')$-method (Sec. II D). The dynamical wavefunction for the half-infinite pulse is constructed as a linear combination of the Floquet states (Sec. II E) and is used to derive formulas for absorption cross-section and excitation yields of bound states and resonances (Sec. II F). The method for half-infinite pulses is easily generalized to finite pulses in Sec. II G.

In Sec. III C, we address three questions: which states must be put into interaction to obtain converged results; how sensitive the results are to the number of partial waves and diffuse basis functions in the Gaussian basis sets; and how sensitive the results are to the choice of the complex scaling parameter. First, we test a convergence of the Floquet state corresponding to the helium ground state. The converged complex quasi-energies for the wavelength of 47 nm obtained
for several laser intensities are further used to obtain the photoionization cross-section, which is compared with the experimental value and other theoretical predictions.

The next discussion, still involved in the basis set convergence, is focused on dynamical excitation yields in half-infinite laser pulses for the laser intensities ranging from about 2 to 100 TW/cm². Simulations of a single-photon absorption are performed for three different wavelengths, \( \lambda = 38.3783 \text{ nm}, 53.6938 \text{ nm}, \) and 58.0023 nm. The corresponding processes are dominated by a direct ionization, resonant absorption to the 3 \( \Pi \) state, and near-resonant absorption to the 2 \( \Pi \) state with the detuning given by \( \Delta = 1242.8 \text{ cm}^{-1} \), respectively. A two-photon absorption is studied for a single wavelength, \( \lambda = 38.3783 \text{ nm} \). This process leads to a population of the 4 \( \Pi \) state, 5 \( \Pi \) state, and 4 \( \Pi \) state, and 4 \( \Pi \) state doubly excited resonances.

Finally, we use the ExTGnl basis sets in calculations of absorption and excitation cross-sections for finite Gaussian-shaped pulses, Sec. III D. First, we demonstrate that Rabi oscillations observed in the half-infinite laser pulses leave their fingerprints on total absorption cross-sections. The effect depends on an integral field amplitude of a pulse, independently of whether the Gaussian or square pulse is used. Then, the fingerprints of Rabi oscillations are studied for a near resonance absorption, where we demonstrate that an oscillatory behavior of the cross-sections is related to a particular pulse shape. In the case of Gaussian pulses, the atom becomes transparent for longer pulses. Then, we calculate total ionization yields for the case of above-threshold ionization, where we confirm a sole dependence of the absorption cross-section on a total absorbed energy, with no effect of a particular pulse shape. Finally, two-photon excitation cross-sections of doubly excited resonances are predicted for the case of Gaussian pulses, where we determine optimal pulse lengths which maximize the excitation yields. All calculations for finite pulses are accompanied with discussions of their possible experimental realizations using free-electron lasers.

In Sec. IV, we summarize the paper and present our conclusions.

II. THEORETICAL METHOD

A. Representation of the field-free Hamiltonian based on complex scaling and exponentially tempered Gaussian basis sets

The stationary states of the helium atom are calculated using the complex scaled spin-free Hamiltonian given by

\[
\hat{H}_0^{(0)} = -\frac{\hbar^2 e^{-2i\theta}}{2m_e} \left( \hat{\Delta}_{r_1} + \hat{\Delta}_{r_2} \right) + e^{-i\theta} \left( \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1|} - \frac{1}{|\mathbf{r}_2|} \right),
\]

where \( m_e \) and \( e \) are the electron mass and charge, \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) are the Cartesian electronic coordinates, and \( \hat{\Delta}_{r_1}, \hat{\Delta}_{r_2} \) are the corresponding Laplace operators. \( \theta \) is the complex scaling parameter, where \( 0 \leq \theta < \pi/4 \). The complex scaling transformation is a widely used method to correctly represent ionization in the realm of finite spatial basis sets. Note without proof that it is equivalent to a representation of the usual Hamiltonian in terms of a nonhermitian basis set given by \( \sqrt{e^{-i\theta}/2\pi \hbar} \exp (i \mathbf{r} \cdot \mathbf{p} e^{-i\theta}) \).

The solution of the complex scaled Hamiltonian is based on the Full Configuration Interaction (FCI) expansion constructed from the exponentially tempered Gaussian basis sets, ExTG5G and ExTG7F. The ExTG5G and ExTG7F basis sets excel in their stability with respect to complex scaling of the Hamiltonian in the radial coordinate due to an ample sampling of the radial subspace. The basis sets are tailored for an accurate calculation of highly excited states up to \( n = 5 \) or 7 with the error of 1 cm⁻¹. The number of partial waves is given by \( l_{\text{max}} = 4 \) or 3.

The basis sets constitute of large series of Gaussian primitives \( \{x^{\alpha_1} y^{\alpha_2} z^{\alpha_3} \exp(-\xi^{(n_1+n_2+n_3)} r^2)\} \), which satisfy the relation for exponentially tempered Gaussians given by

\[
\log \xi^{(n)} = \log \xi^{(0)} + \frac{\exp(\beta^{(n)} n) - 1}{\beta^{(n)}} \log \alpha^{(0)}, \quad n = 0 \ldots N^{(0)}.
\]

The series of exponentially tempered Gaussians has been proposed in Ref. 38 as a generalization of the well-known even tempered Gaussians. The new series is better suited for Coulomb-like problems including highly excited states.

The parameters \( \xi^{(0)}, \alpha^{(0)}, \beta^{(0)} \), and \( N^{(0)} \) are first optimized based on a modified Restricted Hartree Fock (RHF) method, which ensures that the virtual orbitals form a Rydberg-like series with negative orbital energies and constitute leading configurations in the FCI expansions. The modified Fockian for helium is defined by dropping the redundant term \( (\hat{J}_\psi - \hat{K}_\psi) \) from the ordinary Fockian for helium \( (\hat{h} + 2\hat{J}_\psi - \hat{K}_\psi) \), such that

\[
\hat{f} = \hat{h} + \hat{J}_\psi,
\]

where \( \psi(r) \) is the 1s orbital and \( \hat{J}_\psi, \hat{K}_\psi \) are the Coulomb and exchange operators based on the 1s occupied orbital, respectively. In order to assure correlation consistency, the exponents and the number of the narrowest Gaussians in the ExTG5G and ExTG7F basis sets are corrected to provide the converged FCI ground state energy of helium.

B. Transition dipole moments and oscillator strengths

The oscillator strength \( f \) due to the radiative transition from the state \( |\psi^{(LM)}\rangle \) with the energy \( E \) to the set of degenerate states \( |\psi^{(LM')}\rangle \) with the energies \( E' \) is defined as

\[
f = \frac{2m_e |\mu_{\text{tot}}|^2}{\hbar^3},
\]

where \( \omega \) is the radiation frequency defined as \( (E - E')/\hbar \). The oscillator strength is related to the Einstein coefficient \( A \) such that

\[
A = \frac{\omega^2}{2\pi \varepsilon_0 m_e \hbar c_0^2} f,
\]

where \( \varepsilon_0 \) is the vacuum permittivity, and \( c_0 \) is the speed of light. \( |\mu_{\text{tot}}|^2 \) is defined by the corresponding transition dipole
moments such that

\[ |\mu_{tot}|^2 = \sum_{M'=-M}^{M+1} \int |d\mathbf{r}| \Psi(\mathbf{r}) e^{i\mathbf{r}} (x_1 + x_2 + y_1 + y_2 + z_1 + z_2)^2 |\Psi(\mathbf{r})|^2. \]  

(6)

We simplify the definition in Eq. (6) for the practical calculation (see the Appendix) such that

\[ |\mu_{tot}|^2 = \frac{2L' + 1}{\max(L, L')} |\mu_c|^2, \]  

(7)

where

\[ \mu_c = \int |d\mathbf{r}| \Psi(\mathbf{r}) e^{i\mathbf{r}} (z_1 + z_2). \]  

(8)

The wavefunctions \( \Psi(\theta) \) and \( \Psi(\mathbf{r}) \) are obtained using the complex scaled Hamiltonian, therefore the obtained transition dipole moments are generally \( \theta \)-dependent, unless \( |\Psi(\theta)| \) and \( |\Psi(\mathbf{r})| \) are bound states or resonances. In the latter case, \( |\mu_{tot}(\theta)|^2 \) is approximately constant in a large interval of \( \theta \), where the length of such an interval and the measure of stability of \( |\mu_{tot}(\theta)|^2 \) within such an interval strongly depends on the quality of the Gaussian basis set. The variational condition for \( |\mu_{tot}(\theta)|^2 \) is defined as \( \min(d|\mu_{tot}(\theta)|^2/d\theta) \).

### C. Interaction Hamiltonian for a linearly polarized half-infinite square pulse in a classical dipole approximation

The interaction of the helium atom with a linearly polarized strong electromagnetic pulse is represented in the classical dipole approximation,

\[ \hat{H}_I(t) = \hat{H}_0 + e e^{i\omega t} (z_1 + z_2) f_E(t) \sin \omega t, \]  

(9)

where \( \hat{H}_0 \) is the field-free Hamiltonian (Eq. (1)), \( z_1, z_2 \) represent electronic coordinates, \( \omega \) is the leading laser frequency, and \( f_E(t) \) represents the electric field that generally defines the envelope of the laser pulse. The electric field \( f_E \) is related to the field strength \( I \) via the relation \( f_E = \sqrt{2I/e\epsilon_0} \).

First, we assume the half-infinite square pulse, where

\[ f_E(t < 0) = 0, \quad f_E(t \geq 0) = f_{EO}. \]  

(10)

This model is addressed while investigating the suitability of the Gaussian basis sets and limited quasi-complete sets of the field-free states. It is reasonable to study the basis sets independently of the pulse shape, namely, for pulses with constant field strength. A strictly corresponding assumption, \( f_E(t) = \text{const.} \), leads to the Floquet model. In fact, the Floquet model has often been used to study electronic properties of laser driven systems, such as HHG; however, this idealization fails in describing Rabi oscillations for near resonance excitation frequencies. On the other hand, the half-infinite square pulse, still assuming a constant strength of the electromagnetic field, is able to reflect the Rabi oscillations correctly.

Then we study absorption cross-sections and two-photon excitation yields in Gaussian pulses,

\[ f_E(t) = f_{EO} \exp(-t^2/2\tau^2), \]  

(11)

where \( f_{EO} \) is the peak electric field, and \( \tau \) defines the pulse-length. \( f_{EO} \) typically corresponds to the field strengths of a few to a few tens of TW/cm² in both models. \( \tau \) is typically given by a few to a few tens of femtoseconds.

### D. Complex scaled Floquet Hamiltonian

Even though we assume the half-infinite and femtosecond Gaussian laser pulses, it is still useful to describe this dynamical system in the basis set of Floquet states \( \Phi_{k,n}(r, t) \).

The complex scaled Floquet Hamiltonian \( \hat{H}_\theta \) is defined as usual\(^{33-35} \)

\[ \hat{H}_\theta = \hat{H}_0(t) - i\hbar \frac{\partial}{\partial t}. \]  

(12)

The use of complex scaling brings about the need for calculating the left vectors \( \Phi_{k,n}^{(l)}(r, t) \), which are solutions of the left Floquet Hamiltonian given by

\[ \hat{H}_\theta^{(l)} = \hat{H}_0(t) + i\hbar \frac{\partial}{\partial t}. \]  

(13)

Note that the left Floquet Hamiltonian is defined as the sum of the transposed time-dependent Hamiltonian (Eq. (9)), which is not equal to its complex conjugate due to complex scaling, and the transposed photon number operator, which is equal to its complex conjugate as usual. This gives rise to non-trivial definitions of the left Floquet states, which are therefore carefully listed below.

We expand the Floquet states in the basis set of the dressed states, which are given as a direct product of the atomic states, \( \Phi_k^{(l)}(r, t) \) and the field states, \( \exp(in\omega t) \), such that

\[ \Phi_{k,n}^{(l)}(r, t) = \frac{1}{\sqrt{T}} \sum_{k', n'} c_{k', n'}^{(l)}(r) \Phi_k^{(l)}(r) e^{in\omega t}, \]  

(14)

where \( T \) is the optical cycle, \( T = 2\pi/\omega \). \( \Phi_k^{(l)}(r) \) and \( \Phi_k^{(l)}(r) \) are the right and left solutions of the field-free Hamiltonian of helium \( \hat{H}_0 \) (Eq. (1)). The number of Floquet channels \( n \) is generally infinite, while in practical calculations it is approximated in a finite interval \( n \in \{m_{\max}, \ldots, m_{\max}\} \), where \( m_{\max} \) is large enough. The corresponding Floquet matrices \( \hat{H}_\theta^{(l)}(r) \) and \( \hat{H}_\theta^{(l)}(r) \) are organized, as usual, in blocks coupling the Floquet channels, \( \hat{H}_0^{(l)}(r) \) and \( \hat{H}_0^{(l)}(r) \).

Floquet states in various Brillouin zones meet the trivial relationships \( \Phi_{k,n}^{(l)}(r, t) = \Phi_{k,n}^{(l)}(r, t)e^{i\omega nt} \) and \( \Phi_{k,n}^{(l)}(r, t) = \Phi_{k,0}^{(l)}(r, t)e^{i\omega nt} \). Consequently, it is sufficient to calculate the Floquet states in the zeroth Brillouin zone, \( \Phi_{k,0}^{(l)}(r, t) \) and \( \Phi_{k,0}^{(l)}(r, t) \), while the Floquet states of the other zones are defined as

\[ c_{k', n'}^{(l)}(r) = c_{k, n'}^{(l)}(r) e^{i\phi}, \quad c_{k', n'}^{(l)}(r) = c_{k, n'}^{(l)}(r) e^{i\phi}. \]  

(15)

The coefficients \( c_{k', n'}^{(l)}(r) \) are calculated with the help of the \( (t, t') \)-method developed by Peskin and Moiseyev.\(^{42-46} \)

First, the sections of Floquet states for the time point \( t = 0 \), \( \Phi_{k,n}(r, t = 0) \), and \( \Phi_{k,n}(r, t = 0) \) are calculated. They are...
defined in the basis set of the field-free atomic states such that

\[ \Phi_{k,n}^{(0)}(r,0) = \frac{1}{\sqrt{T}} \sum_{k'} c_{k',k}^{(0)} \phi_{k'}^{(0)}(r), \]

\[ \Phi_{k,n}^{(1)(0)}(r,0) = \frac{1}{\sqrt{T}} \sum_{k'} c_{k',k}^{(1)} \phi_{k'}^{(1)(0)}(r). \]  

(16)

The matrices of the expansion coefficients \( \tilde{c}^{(0)} \) and \( \tilde{c}^{(1)(0)} \) are obtained as eigenvectors of evolution matrices for one optical cycle \( T \), \( u_{T}^{(0)} \) and \( u_{T}^{(1)(0)} \), respectively. The eigenvalues of the evolution matrices \( \lambda_k, \lambda_k' \) define the corresponding Floquet energies \( \epsilon_k \) for the zeroth Brillouin zone such that

\[ \lambda_k = \exp\left(\frac{i}{\hbar} \epsilon_k T \right), \quad \lambda_k' = \exp\left(\frac{i}{\hbar} \epsilon_k T \right). \]  

(17)

The evolution matrices \( u_{T}^{(0)} \) and \( u_{T}^{(1)(0)} \) are calculated via the successive propagations

\[ u_{T}^{(0)} = \prod_{m=0}^{N-1} u_{\Delta t}^{(0)}(m \Delta t), \]

\[ u_{T}^{(1)(0)} = \prod_{m=0}^{N-1} u_{\Delta t}^{(1)(0)}(m \Delta t), \]  

(18)

using a short propagation time \( \Delta t \) that divides the optical cycle \( T \) into \( N \) parts, \( \Delta t = T/N \). The evolution matrices \( u_{\Delta t}^{(0)}(m \Delta t) \) and \( u_{\Delta t}^{(1)(0)}(m \Delta t) \) are related to the propagation from the time point \( m \Delta t \) to the next time point \( (m+1) \Delta t \). \( u_{\Delta t}^{(0)}(m \Delta t) \) and \( u_{\Delta t}^{(1)(0)}(m \Delta t) \) are defined based on the \( (t, t') \)-approach such that

\[ u_{\Delta t}^{(0)}(m \Delta t) = \sum_{n,m} \Delta t^m \epsilon^{n \Delta t(m+1) \Delta t} \]

\[ u_{\Delta t}^{(1)(0)}(m \Delta t) = \sum_{n,m} \Delta t^m \epsilon^{n \Delta t(m+1) \Delta t} \]  

(19)

\( H^{(0)} \) and \( H^{(1)(0)} \) represent the Floquet Hamiltonians in the basis sets of the dressed states, as defined in (Eq. (14)) and the text below. In Eq. (19), the index \( (n, 0) \) denotes a concrete block of the block matrix enclosed in the square brackets, that is, after operating with the \( m \)th power on the whole Floquet super-matrix.

Once the matrices of coefficients \( \tilde{c}^{(0)} \), \( \tilde{c}^{(1)(0)} \), which define the Floquet wavefunctions at time point \( t = 0 \) (Eq. (16)), are calculated, the wavefunctions \( \Phi_{k,n}^{(0)}(r,0) \) and \( \Phi_{k,n}^{(1)(0)}(r,0) \) are propagated with the help of the evolution matrices \( u_{\Delta t}^{(0)}, u_{\Delta t}^{(1)(0)} \) in order to complete the calculation of the Floquet states along the whole time axis, \( 0 \leq t < T \). Thus calculated Floquet states are defined in the basis set of the field free atomic states such that

\[ \Phi_{k,n}^{(0)}(r,t) = \sum_{k'} c_{k',k}^{(0)}(t) \phi_{k'}^{(0)}(r), \]

\[ \Phi_{k,n}^{(1)(0)}(r,t) = \sum_{k'} c_{k',k}^{(1)(0)}(t) \phi_{k'}^{(1)(0)}(r). \]  

(20)

where

\[ \tilde{c}^{(0)}(M \Delta t) = e^{i M \Delta t} \prod_{m=0}^{M-1} c_{k,m}^{(0)}(m \Delta t) \tilde{c}^{(0)}(0), \]

\[ \tilde{c}^{(1)(0)}(M \Delta t) = e^{-i M \Delta t} \prod_{m=0}^{M-1} u_{k,m}^{(1)(0)}(m \Delta t) \tilde{c}^{(1)(0)}(0), \]  

(21)

where \( \epsilon \) is a diagonal matrix including the Floquet energies for the zeroth Brillouin zone, \( n = 0 \), obtained before (Eq. (17)). The time-dependent expansion coefficients \( \tilde{c}^{(0)}(t), \tilde{c}^{(1)(0)}(t) \) are transformed into the frequency domain such that,

\[ c_{k,n',k,0}^{(0)} = \frac{1}{\sqrt{T}} \sum_{M=0}^{N-1} c_{k,m}^{(0)}(M \Delta t) e^{-i 2 \pi n M/N}, \]

\[ c_{k,n',k,0}^{(1)(0)} = \frac{1}{\sqrt{T}} \sum_{M=0}^{N-1} c_{k,m}^{(1)(0)}(M \Delta t) e^{i 2 \pi n M/N}. \]  

(22)

E. Time-dependent wavefunction for the half-infinite square laser pulse

First, we define the initial wavefunction, given by the helium ground state \( \phi_{k}^{(0)}(r) \), \( k = 0 \), in the basis set of the Floquet states. We use the fact that the Floquet states are given in the basis set of the dressed states (Eq. (14)), and we perform the inverse transformation to define the dressed states as a combination of the Floquet states,

\[ \frac{1}{\sqrt{T}} \Phi_{k}^{(0)}(r) e^{i \omega t} = \sum_{k',n'} c_{k,n'}^{(0)} \Phi_{k',n'}^{(0)}(r,t). \]  

(23)

After a minor simplification using the symmetry of the Floquet vectors (Eq. (15)) and setting \( t = t_0 \), we obtain the formula for the initial helium state given by

\[ \phi_{k}^{(0)}(r) = \sqrt{T} \sum_{k',n'} c_{k,n'}^{(0)}(t_0) \Phi_{k',n'}^{(0)}(r,t_0) e^{-i \omega t_0}. \]  

(24)

The choice of \( n \) and \( t_0 \) is arbitrary.

In the next step, we let the initial helium state evolve in time according to the time-dependent complex scaled Schrödinger equation

\[ i \hbar \frac{\partial \phi_{k}^{(0)}(r,t)}{\partial t} = \hat{H}_{0} \phi_{k}^{(0)}(r,t). \]  

(25)

Due to the expansion of \( \phi_{k}^{(0)}(r) \) in terms of the Floquet states (Eq. (24)), the problem transforms to the evolution of the time-sections of the Floquet states \( \Phi_{k,n}^{(0)}(r,t) \), which evolve along the time interval \( 0 \rightarrow t \) to \( \Phi_{k,n}^{(1)}(r,t_0 + t) \exp\left(-i \epsilon_k t / \hbar - i n \omega t \right) \), such that

\[ \phi_{k}^{(0)}(r,t_0 + t) = \sqrt{T} \sum_{k',n'} c_{k,n'}^{(0)}(t_0) \Phi_{k',n'}^{(0)}(r,t_0 + t) \exp\left(-i \epsilon_k t - i n \omega t - i \omega t_0 \right). \]  

(26)

Finally, we substitute the Floquet wavefunctions \( \Phi_{k,n}^{(0)}(r,t) \) by their expansions in terms of the dressed states,
Eq. (14), such that
\[
\psi^{(1)}(r; t) = \sum_{k'} \psi_k^{(1)}(r) u_{k', k}(t), \tag{27}
\]
where
\[
u_{k', k}(t) = \sum_{k', n, n', \mu} c_{k,n-n', k', n'}^{(1)}(0) e^{i\epsilon_{k'} t} \exp\left(-\frac{i}{\hbar} \epsilon_{k,n} t\right) e^{i\omega t} e^{-i\omega t} u_{n', k, 0} e^{i\omega t},
\]
which after a few algebraic operations based on reorganized indices and the choice \(n = 0\), yields the symmetrical expression
\[
u_{k', k}(t) = \sum_{k} \sum_{n'} c_{k,n,n', k'}^{(1)}(0) \exp\left(-\frac{i}{\hbar} \epsilon_{k,n} t\right) c_{k', k'}^{(1)}(t_0), \tag{29}
\]
where \(c_{k,n,n', k'}^{(1)}(t_0)\) and \(c_{k,n,n', k'}^{(1)}(0)\) are defined as
\[
c_{k,n,n', k'}^{(1)}(t_0) = \sum_{n''} c_{k,n,n'', k}^{(1)} e^{-i\epsilon_{k,n} t_0}, \tag{30}
\]
These definitions correspond to the earlier definitions given in Eq. (20) explaining that the matrices \(c_{k,n,n', k'}^{(1)}(t_0)\) and \(c_{k,n,n', k'}^{(1)}(0)\) represent the sections \(\Phi_{k,n,n', k'}^{(1)}(r, t_0)\) in the basis set of \(\Phi_k^{(1)}(r)\) and \(\Phi_{k,n,n', k'}^{(1)}(r, t_0)\) in the basis set of \(\Phi_k^{(1)}(r)\), respectively.

### F. Time-dependent populations of ground and excited states

For the half-infinite pulse we assume that the propagation is started from the ground state, \(k = 0\). Now, we apply the inverse complex scaling transformation on both sides of Eq. (27). Note that the transformation acts only on the wavefunctions but leaves the amplitudes \(u_{k', 0}(t)\) untouched. The (unscaled) time-dependent wavefunction \(\psi_0^{(0)}(r; t)\) may be projected on any bound state of the system \(\psi^{(0)}_0(r)\). Clearly, \(|u_{k', 0}(t)|^2\) has the meaning of the time-dependent population of the bound state \(k'\) and thus should be independent of the complex scaling parameter \(\theta\).

A simplified expression for \(u_{k', 0}(t)\), obtained by setting \(t_0 = 0\) and \(k = 0\) in Eq. (29), reads,
\[
u_{k', 0}(t) = \sum_{k,n} \sum_{n'} c_{k,n,n', k}^{(1)}(0) \sum_{n''} c_{k,n,n'', k}^{(1)}(0) \exp\left(-\frac{i}{\hbar} \epsilon_{k,n} t\right) e^{i\omega t} e^{-i\omega t} \tag{31}
\]
The absorption \(\alpha(t)\) is defined as one minus the population of the ground state in the time-dependent wavefunction \(\psi_0^{(0)}(r; t)\),
\[
\alpha(t) = 1 - |u_{0, 0}(t)|^2. \tag{32}
\]
Note that the conjectures concerning populations of bound states cannot be rigorously applied to populations of resonances and a rotated continuum. However, we still apply them to approximately define time-dependent populations of doubly excited resonances of helium for the propagation times which are much shorter than the resonance life-times.

### G. The evolution matrix for general pulse shapes

The evolution matrix in the basis set of field free complex scaled states for finite pulses is constructed as follows. It is assumed that the pulse envelope can be approximated by a finite number of stairs, which the laser intensity remains constant. The number of stairs may be as large as needed to obtain a convergence for any pulse shape. Floquet states and evolution matrices \(u_{k', k}(t_{j+1} - t_j)\) are calculated for every laser intensity \(I_j\) occurring during the time interval \(t_j \rightarrow t_{j+1}\). We employ Eq. (29) in order to define \(u_{k', k}(t_{j+1} - t_j)\), where \(k\) is now referencing to any component of the initial state of the propagation within the given stair, and not only the ground state. The evolution matrix for the whole pulse is given by the product of the evolution matrices for the individual stairs,
\[
u = u^{(M)} \cdot \ldots \cdot u^{(1)}. \tag{33}
\]
It is important for reasons that seem rather numerical that the \(t_0\) parameter in Eq. (30), which should be arbitrary, is set precisely to \(t_0^{(j)} = t_j\) for every evolution matrix \(u^{(j)}\). The evolution matrices \(u^{(j)}\) are thus defined as
\[
u_{k', k}(t_{j+1} - t_j) e^{-i\epsilon_{k', k} i (t_{j+1} - t_j)} \Phi_{k', k}^{(j)}(t_j), \tag{34}
\]
where \(\Phi_{k', k}^{(j)}\) and \(\Phi_{k, k}^{(j)}\) are defined in Eq. (30), here based on the Floquet vectors for the corresponding laser intensity \(I_j\).

The components of the total evolution matrix \(u\) are used to define the populations of bound states and the instant populations of resonances at the moment right after the pulse ends, in the manner explained in Sec. II F.

### III. RESULTS

#### A. Precision and numerical stability of the helium spectrum calculated using the exponentially tempered Gaussian basis sets

We have calculated, classified, and tabulated all bound states and resonances below the first and second ionization thresholds (see Tables I–V including only the singlet states and the supplementary material56 for a full version of these tables also including the triplet states). The reason is that these states, in particular those with singlet spin symmetry, enter dynamical calculations and constitute the Floquet resonances, therefore it is important to be aware of numerical qualities of this part of the calculation. Triplet states are included for the sake of completeness.

#### 1. Series of bound states below the first ionization threshold

The classification of the bound states below the first ionization threshold is quite straightforward (Table I); \(n\) denotes the orbital excitation in the leading configurations \(1sns\) for the \(S^0\) states, \(1spn\) for the \(P^0\) states, etc. The numerical convergence error due to radial sampling is very small in the ExTGnl basis sets. An estimate based on stability of \(S^0\) resonances with the complex scaling parameter assumes the error of \(10^{-6} E_h\), i.e., 0.2 cm\(^{-1}\), see Ref. 38. Therefore, all numerical
In Table I of the supplementary material. All of the listed energies are converged with respect to the radial subspace and thus represent the individual s-, p-, and d-limits.

2. Series of S resonances below the second ionization threshold

The $1^S$ and $3^S$ resonances below the second ionization threshold (Table II and Table s-II in the supplementary material) split into two series, which differ according to the mutual angle of the two interacting electrons with respect to the nucleus, $(\cos \theta_{12})$. The $1^S(a)$-series starts from $n = 2$ with the energy $(-0.7779 - 0.002271i) E_h$. The value of $n$ indicates the orbital excitation within this resonance ($2\xi^2$). The $1^S(b)$-series starts from $n = 3$ for the lowest energy $(-0.622 - 0.000108i) E_h$. Here, $n$ is determined such that the energies of the Rydberg states with the same value of $n$ in the $(a)$ and $(b)$ series, respectively, approximately correspond to each other. Similarly, in the numbering of the triplet states, we try to reach the best energy correspondence of these states with respect to each other and with the $1^S$ states with the same values of $n$.

The precision of the calculated energies is again higher for triplets, while lower for singles. The smallest error of 0.006 cm$^{-1}$, which is reached for some triplet states, is already consistent with the sampling of the radial subspace and we can state that the number of partial waves is no longer the limiting factor for the precision of these states. There is also a remarkable difference between the precision of the $(a)$ and $(b)$ series, respectively. In the case of the less precise $(b)$ series, the two electrons orbit on the same side from the nucleus; therefore, they are strongly correlated. An extreme example is represented by the lowest state of the $1^S(b)$ resonances, which is obtained with the large error of 76 cm$^{-1}$ in the $g$-limit. The vital role of electron repulsion within this state is demonstrated also by a significant shift of the expectation value of $(\cos \theta_{12})$. The correlation effect is weakened as the mean radius of motion of the higher excited electron increases in Rydberg states. Thus the precision of excited states within the same series generally improves with the increase of the excitation number $n$.

Up to now, we have discussed the resonance positions (real parts of complex energies). As for the resonance widths, they are generally more accurate than the positions in the absolute scale. There is also a one order of magnitude improvement of the widths when moving from singlets to triplets, due to the weaker correlation effect. However, we shall note that the triplets are by two orders of magnitude narrower than the singles, again due to the weaker correlation; therefore, the relative precision is rather worse for the triplet than for singlet states, in the end.

A complete list of the results also including lower rotational limits obtained with the basis sets ExTG7S – ExTG7D for all states below the second ionization threshold can be found in the supplementary material.

3. Series of P, D, and F resonances below the second ionization threshold

$(1, 3) P^o$, $(1, 3) D^o$, and $(1, 3) F^o$ resonances below the second ionization threshold split into three series, see Tables III–V
and Tables s-III–s-V in the supplementary material, which differ according to the mutual angle of the electrons with respect to the nucleus, see Ref. 58. Each one of the series is characterized by different orders of magnitude of ionization decay rates. In the case of singlets, we find at least one of the long-lived series where the resonance widths are below the numerical precision of our calculations. The energies of the lowest $1^P(a)$ and $1^D(a)$ resonances include large errors of 32 cm$^{-1}$ and 27 cm$^{-1}$, respectively, due to the small number of partial waves. Note that the electrons are located on the same hemisphere in the similar radius with respect to the nucleus in these two cases.

TABLE III. The same as Table I but for doubly excited $S$-states below the second ionization threshold. The converged non-relativistic energies $E_\infty$ are borrowed from Ref. 75. A full version of this table including triplet resonances is available in Table s-II of the supplementary material.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l_{max}$</th>
<th>$E_1$</th>
<th>$E_\infty$</th>
<th>$(E - E_\infty)$</th>
<th>$E_1$</th>
<th>$E_\infty$</th>
<th>$(E - E_\infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4</td>
<td>-0.777859340</td>
<td>-0.777867636</td>
<td>1.821</td>
<td>-2.273407 × 10$^{-3}$</td>
<td>-2.270653 × 10$^{-3}$</td>
<td>-0.604</td>
</tr>
<tr>
<td>3</td>
<td>-0.589897917</td>
<td>-0.589894682</td>
<td>1.485</td>
<td>-6.810250 × 10$^{-4}$</td>
<td>-6.81239 × 10$^{-4}$</td>
<td>0.047</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>-0.544879752</td>
<td>-0.544881618</td>
<td>0.805</td>
<td>-2.454976 × 10$^{-4}$</td>
<td>-2.46030 × 10$^{-4}$</td>
<td>0.117</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-0.526684692</td>
<td>-0.526686857</td>
<td>0.475</td>
<td>-1.087186 × 10$^{-4}$</td>
<td>-1.09335 × 10$^{-4}$</td>
<td>0.135</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-0.517643032</td>
<td>-0.517641112</td>
<td>0.178</td>
<td>-5.604216 × 10$^{-5}$</td>
<td>-5.6795 × 10$^{-5}$</td>
<td>0.165</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>-0.512513168</td>
<td>-0.512514388</td>
<td>0.465</td>
<td>-3.239407 × 10$^{-5}$</td>
<td>-3.2992 × 10$^{-5}$</td>
<td>0.131</td>
</tr>
<tr>
<td>8</td>
<td>-0.509330841</td>
<td>-0.509332686</td>
<td>0.405</td>
<td>-5.528622 × 10$^{-5}$</td>
<td>-2.0795 × 10$^{-5}$</td>
<td>-7.570</td>
<td></td>
</tr>
</tbody>
</table>

and Tables s-III–s-V in the supplementary material, which differ according to the mutual angle of the electrons with respect to the nucleus, see Ref. 58. Each one of the series is characterized by different orders of magnitude of ionization decay rates. In the case of singlets, we find at least one of the long-lived series where the resonance widths are below the numerical precision of our calculations. The energies of the lowest $1^P(a)$ and $1^D(a)$ resonances include large errors of 32 cm$^{-1}$ and 27 cm$^{-1}$, respectively, due to the small number of partial waves. Note that the electrons are located on the same hemisphere in the similar radius with respect to the nucleus in these two cases.

TABLE III. The same as Table I but for doubly excited $P$-states below the second ionization threshold. The converged non-relativistic energies $E_\infty$ are borrowed from Ref. 75. A full version of this table including triplet resonances is available in Table s-III of the supplementary material, where the converged non-relativistic energies $E_\infty$ for triplets are borrowed from Ref. 76.
4. Discretized continuum

ExTG5G and ExTG7F are optimized just for the molecular orbitals of bound states; the representation of the continuum is left aside the optimization procedure. On average, six Gaussians per each RHF bound state are used to assure the high accuracy of the bound states’ energies. The excessive number of Gaussians creates a large orthogonal complement to the bound states, which provides an additional phase-space for the discretized continuum. The discretized continuum is rotated to the complex plane in complex scaling calculations as illustrated in Fig. 1. The highest density of the discretized continuum states is found near the ionization thresholds. This corresponds to decreasing spatial widths of the states with the increased kinetic energy of the free electron.

TABLE IV. The same as Table I but for doubly excited D-states below the second ionization threshold. The converged non-relativistic energies \( E_\infty \) are borrowed from Lindroth et al.\(^7\) and Madronero.\(^5,8\) A full version of this table including triplet resonances is available in Table s-IV of the supplementary material,\(^56\) where the converged non-relativistic energies \( E_\infty \) for triplets are borrowed from Argenti.\(^5,7\)

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l_{\text{max}} )</th>
<th>( \text{Re} \ E )</th>
<th>( \text{Re} \ E_\infty )</th>
<th>( \text{Re} (E - E_\infty) )</th>
<th>( \text{Im} E )</th>
<th>( \text{Im} E_\infty )</th>
<th>( \text{Im} (E - E_\infty) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4</td>
<td>-0.701822529</td>
<td>-0.701946(^a)</td>
<td>27.099</td>
<td>-1.187603 \times 10^{-3}</td>
<td>-1.181 \times 10^{-3}(^a)</td>
<td>-1.449</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>-0.569187994</td>
<td>-0.56922(^a)</td>
<td>7.025</td>
<td>-2.795587 \times 10^{-4}</td>
<td>-2.78 \times 10^{-4}(^a)</td>
<td>-0.342</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>-0.536712784</td>
<td>-0.5367246(^b)</td>
<td>2.593</td>
<td>-1.166786 \times 10^{-4}</td>
<td>-1.157 \times 10^{-4}(^b)</td>
<td>-0.215</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>-0.522735750</td>
<td>-0.5227417(^b)</td>
<td>1.306</td>
<td>-5.850929 \times 10^{-5}</td>
<td>-5.8 \times 10^{-5}(^b)</td>
<td>-0.112</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>-0.515444180</td>
<td>-0.5154540(^b)</td>
<td>2.155</td>
<td>-3.365285 \times 10^{-5}</td>
<td>-3.29 \times 10^{-5}(^b)</td>
<td>-0.165</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>-0.511174076</td>
<td>-0.5111802(^b)</td>
<td>1.344</td>
<td>-2.082212 \times 10^{-5}</td>
<td>-2.04 \times 10^{-5}(^b)</td>
<td>-0.093</td>
</tr>
</tbody>
</table>

\(^a\)Reference 77.
\(^b\)Reference 58.
\(^c\)References 56 and 76.

TABLE V. The same as Table I but for doubly excited F-states below the second ionization threshold. The converged non-relativistic energies \( E_\infty \) are borrowed from Ref. 58. A full version of this table including triplet resonances is available in Table s-V of the supplementary material.\(^56\)

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l_{\text{max}} )</th>
<th>( \text{Re} \ E )</th>
<th>( \text{Re} \ E_\infty )</th>
<th>( \text{Re} (E - E_\infty) )</th>
<th>( \text{Im} E )</th>
<th>( \text{Im} E_\infty )</th>
<th>( \text{Im} (E - E_\infty) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4</td>
<td>-0.556407954</td>
<td>-0.55643(^a)</td>
<td>4.839</td>
<td>-9.848421 \times 10^{-6}</td>
<td>-1 \times 10^{-5}(^a)</td>
<td>0.033</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>-0.531502114</td>
<td>-0.5315119(^b)</td>
<td>2.148</td>
<td>-5.474045 \times 10^{-5}</td>
<td>-5.4 \times 10^{-5}(^b)</td>
<td>-0.016</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>-0.520112196</td>
<td>-0.5201173(^b)</td>
<td>1.133</td>
<td>-3.103325 \times 10^{-6}</td>
<td>-3.10 \times 10^{-6}(^b)</td>
<td>-0.001</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>-0.513944180</td>
<td>-0.5139526(^b)</td>
<td>1.855</td>
<td>-1.841851 \times 10^{-6}</td>
<td>-1.89 \times 10^{-6}(^b)</td>
<td>0.011</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>-0.510237475</td>
<td>-0.5102428(^b)</td>
<td>1.180</td>
<td>-1.178764 \times 10^{-6}</td>
<td>-1.22 \times 10^{-6}(^b)</td>
<td>0.009</td>
</tr>
</tbody>
</table>

\(^a\)Reference 77.
\(^b\)Reference 58.
Due to the fact that the Gaussian basis sets are limited in space by the most diffuse Gaussians included (with the half-widths of 20 Å for ExTG5G and 30 Å for the ExTG7F, respectively), the thresholds are shifted to lower energies with respect to the exact values by 0.01 $E_h$ for ExTG5G and 0.004 $E_h$ for ExTG7F basis sets. The shift is approximately the same for all thresholds.

Between the well-optimized bound states and the discretized continuum lying higher above the ionization limit, artificial transient states are found. They bear the character of the continuum for lower values of the complex scaling parameter $\theta$. As $\theta$ increases, the transient states travel to the first quarter in the complex plane.

B. Precision and numerical stability of calculated quantities controlling radiative transitions

Radiative transitions are characterized by the transition wavelengths and the corresponding oscillator strengths (or Einstein coefficients). The precision of the calculation with respect to these quantities is related to the precision of dynamical cross-sections in strong laser fields, which is addressed in Sec. III C.

First, we check the quantities governing the one-photon excitation; therefore, we focus on transitions in the ultraviolet region involving the ground state, Table VI, and infrared transitions between Rydberg states, Tables VII and VIII. While the former transitions are related to the direct absorption of the XUV photons, the latter are influential in spreading of the excitation yields among several excited states, an effect that always takes place with strong laser intensities. The comparison of our calculations and the complete basis set limit shows that our errors are within 0.1 cm$^{-1}$, in the same order with relativistic, finite-nuclear-mass, and quantum electrodynamic effects, which are known due to state-of-the-art theoretical predictions by Drake that are also listed in the tables.

Infrared transitions within the region of 2000–4000 cm$^{-1}$ between singlet helium Rydberg states are listed in Table VII. Our experimental values are obtained from emission spectra measured in low pressure electric discharge with the resolution of 0.06 cm$^{-1}$. Experimental details can be found in Refs. 60–63. Experimental reference data for radiative transitions between singlet states within this region are rarely found in the literature. As far as we know, only the $5^1G^+ \rightarrow 4^1F^+$ transition has been previously measured indicating the transition frequency of 2469.75 cm$^{-1}$. According to the best theoretical values, this transition occurs at 2469.724 cm$^{-1}$, very close to its triplet counterpart $5^5G^+ \rightarrow 4^3P^+$ at 2469.731–2469.748 cm$^{-1}$. Our experimental value of 2469.738 cm$^{-1}$ probably mixes both singlet and triplet lines due to the given resolution (Table VII). The experimental benchmarks in the ultra-violet region are borrowed from Refs. 40, 65, and 66.

Next, we perform a preliminary check of the quantities governing two-photon processes in the case of the excitation wavelength $\lambda = 38.3783$ nm, simulated in Sec. III C. One-photon excitation is in resonance with the continuum, where the electron is detached from the ground state helium cation, He$^+$(1s) $+$ e$^−$. Two-photon absorption brings the system to the region of doubly excited resonances, $4^1P^0(\alpha)$, $5^1P^0(\alpha)$, $6^1P^0(\alpha)$, $7^1P^0(\alpha)$, and $8^1P^0(\alpha)$.

Below we present a brief comparison of the experimental and theoretical benchmarks for the one-photon and two-photon processes. In the one-photon case, we performed a check for the following radiative transitions between singlet states within the region of 2000–4000 cm$^{-1}$. Experimental details can be found in Ref. 43. Table VI summarizes the theoretical predictions by Drake and our experimental results for the one-photon transitions. The agreement between experimental and theoretical data is very good. The maximal experimental deviation from the theoretical values is 0.49 cm$^{-1}$, which is well below the 0.5 cm$^{-1}$ threshold used in our work.

<table>
<thead>
<tr>
<th>$\lambda$ / nm</th>
<th>Theoretical benchmarks</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2^1P^0 \rightarrow 1S^0$</td>
<td>58.484</td>
<td>58.451</td>
</tr>
<tr>
<td>$3^1P^0 \rightarrow 1S^0$</td>
<td>53.752</td>
<td>53.719</td>
</tr>
<tr>
<td>$4^1P^0 \rightarrow 1S^0$</td>
<td>52.269</td>
<td>52.236</td>
</tr>
<tr>
<td>$5^1P^0 \rightarrow 1S^0$</td>
<td>51.608</td>
<td>51.577</td>
</tr>
<tr>
<td>$6^1P^0 \rightarrow 1S^0$</td>
<td>51.256</td>
<td>51.225</td>
</tr>
<tr>
<td>$7^1P^0 \rightarrow 1S^0$</td>
<td>51.046</td>
<td>51.014</td>
</tr>
</tbody>
</table>

$^a$Reference 65.
$^b$Reference 66.

Figure 1. Field free states of helium obtained with ExTG5G Gaussian basis set for the complex scaling parameter $\theta = 0.45$. The bound states and resonances are red and the discretized continuum is green. The blue dots show numerical transient states.
quantum electrodynamic effects. 

and lower states have been evaluated using the ExTG7F and ExTG5G basis sets, respectively. The remaining transitions have been obtained using the ExTG5G basis set for both states. A comparison with the complete basis set limit (\(l_{\text{max}} \to \infty\)) and the theoretical values including relativistic, finite nuclear mass, and quantum electrodynamic effects. 

<table>
<thead>
<tr>
<th>Gaussian basis sets</th>
<th>Theoretical benchmarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5^1 S^* \leftrightarrow 4^1 P^o)</td>
<td>2167.42</td>
</tr>
<tr>
<td>(6^1 S^* \leftrightarrow 4^1 P^o)</td>
<td>3618.65</td>
</tr>
<tr>
<td>(7^1 S^* \leftrightarrow 5^1 P^o)</td>
<td>2034.69</td>
</tr>
<tr>
<td>(5^1 P^o \leftrightarrow 4^1 S^*)</td>
<td>3003.44</td>
</tr>
<tr>
<td>(5^1 P^o \leftrightarrow 4^1 D^o)</td>
<td>2498.73</td>
</tr>
<tr>
<td>(6^1 P^o \leftrightarrow 4^1 D^o)</td>
<td>3826.4</td>
</tr>
<tr>
<td>(7^1 P^o \leftrightarrow 5^1 S^*)</td>
<td>2415.99</td>
</tr>
<tr>
<td>(7^1 P^o \leftrightarrow 5^1 D^o)</td>
<td>2159.86</td>
</tr>
<tr>
<td>(5^1 D^o \leftrightarrow 4^1 P^o)</td>
<td>2423.56</td>
</tr>
<tr>
<td>(5^1 D^o \leftrightarrow 4^1 F^o)</td>
<td>...</td>
</tr>
<tr>
<td>(6^1 D^o \leftrightarrow 4^1 P^o)</td>
<td>3765.37</td>
</tr>
<tr>
<td>(6^1 D^o \leftrightarrow 4^1 F^o)</td>
<td>...</td>
</tr>
<tr>
<td>(7^1 D^o \leftrightarrow 5^1 P^o)</td>
<td>2126.45</td>
</tr>
<tr>
<td>(7^1 D^o \leftrightarrow 5^1 F^o)</td>
<td>...</td>
</tr>
<tr>
<td>(5^1 F^o \leftrightarrow 4^1 D^o)</td>
<td>...</td>
</tr>
<tr>
<td>(6^1 F^o \leftrightarrow 4^1 D^o)</td>
<td>...</td>
</tr>
<tr>
<td>(7^1 F^o \leftrightarrow 5^1 D^o)</td>
<td>...</td>
</tr>
<tr>
<td>(5^1 G^o \leftrightarrow 4^1 F^o)</td>
<td>...</td>
</tr>
</tbody>
</table>

\(5^1 P^o(b), 5^1 P^o(c) 4^1 D^o(b), 4^1 D^o(c), 4^1 F^o(a), \) and \(4^1 F^o(b)\) with typical detunings of hundreds of cm\(^{-1}\). The most populated resonance is \(5^1 P^o(c)\) as follows from our simulations in Sec. III C. We give a list of the transitions involving the \(5^1 P^o(c)\) resonance in Table IX. The calculated frequencies converge much more slowly to the complete basis set limit as compared to the transitions below the first ionization threshold. The difference between the \(f\)- and \(g\)-limits (given by

\[f / \text{cm}^{-1}\]

<table>
<thead>
<tr>
<th>Gaussian basis sets</th>
<th>Theoretical benchmarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5^1 S^* \leftrightarrow 4^1 P^o)</td>
<td>0.47843</td>
</tr>
<tr>
<td>(6^1 S^* \leftrightarrow 4^1 P^o)</td>
<td>0.08651</td>
</tr>
<tr>
<td>(7^1 S^* \leftrightarrow 5^1 P^o)</td>
<td>0.11758</td>
</tr>
<tr>
<td>(5^1 P^o \leftrightarrow 4^1 S^*)</td>
<td>0.04821</td>
</tr>
<tr>
<td>(5^1 P^o \leftrightarrow 4^1 D^o)</td>
<td>0.03922</td>
</tr>
<tr>
<td>(6^1 P^o \leftrightarrow 4^1 D^o)</td>
<td>0.00836</td>
</tr>
<tr>
<td>(7^1 P^o \leftrightarrow 5^1 S^*)</td>
<td>0.01836</td>
</tr>
<tr>
<td>(7^1 P^o \leftrightarrow 5^1 D^o)</td>
<td>0.01498</td>
</tr>
<tr>
<td>(5^1 D^o \leftrightarrow 4^1 P^o)</td>
<td>0.38892</td>
</tr>
<tr>
<td>(5^1 D^o \leftrightarrow 4^1 F^o)</td>
<td>...</td>
</tr>
<tr>
<td>(6^1 D^o \leftrightarrow 4^1 P^o)</td>
<td>0.09173</td>
</tr>
<tr>
<td>(6^1 D^o \leftrightarrow 4^1 F^o)</td>
<td>...</td>
</tr>
<tr>
<td>(7^1 D^o \leftrightarrow 5^1 P^o)</td>
<td>0.09786</td>
</tr>
<tr>
<td>(7^1 D^o \leftrightarrow 5^1 F^o)</td>
<td>...</td>
</tr>
<tr>
<td>(5^1 F^o \leftrightarrow 4^1 D^o)</td>
<td>...</td>
</tr>
<tr>
<td>(6^1 F^o \leftrightarrow 4^1 D^o)</td>
<td>...</td>
</tr>
<tr>
<td>(7^1 F^o \leftrightarrow 5^1 D^o)</td>
<td>...</td>
</tr>
<tr>
<td>(5^1 G^o \leftrightarrow 4^1 F^o)</td>
<td>...</td>
</tr>
</tbody>
</table>
TABLE IX. Radiative transitions between helium doubly excited states lying above the first and below the second ionization thresholds, involving the $^1P^o(c)$ resonance. Note that the ionization and radiation are competitive except for the first transition, where the ionization process prevails (Tables II–IV). We used energy levels published in Refs. 58, 59, 75, 77 for a comparison with the complete basis set limit ($l_{\text{max}} \to \infty$).

<table>
<thead>
<tr>
<th>$\omega$ (cm$^{-1}$)</th>
<th>ExTG7D</th>
<th>ExTG7F</th>
<th>ExTG5G/F</th>
<th>ExTG5G</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6^1S^{(a)} \to 5^2P^o(c)$</td>
<td>18.4</td>
<td>100.3</td>
<td>104.7</td>
<td>103.3</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 5^2D^o(c)^a$</td>
<td>262.1</td>
<td>180.6</td>
<td>193.8</td>
<td>194.5</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 5^2D^o(b)$</td>
<td>262.1</td>
<td>440.7</td>
<td>438.8</td>
<td>439.2</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 5^2D^o(a)$</td>
<td>1043.6</td>
<td>1016.1</td>
<td>1014.7</td>
<td>1015.0</td>
</tr>
<tr>
<td>$6^1D^o(c) \to 5^2P^o(c)$</td>
<td>978.9</td>
<td>1061.3</td>
<td>1055.0</td>
<td>1064.7</td>
</tr>
<tr>
<td>$7^1D^o(c) \to 5^2P^o(c)$</td>
<td>1736.4</td>
<td>1819.1</td>
<td>1816.8</td>
<td>1822.6</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 5^2S^{(a)}$</td>
<td>1965.9</td>
<td>1884.7</td>
<td>1880.6</td>
<td>1881.7</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 5^2S^{(b)}$</td>
<td>2171.5</td>
<td>2104.1</td>
<td>2106.6</td>
<td>2104.6</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 4^1D^o(c)^a$</td>
<td>2506.4</td>
<td>2426.0</td>
<td>2452.6</td>
<td>2452.8</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 4^1D^o(b)$</td>
<td>2506.4</td>
<td>2938.6</td>
<td>2939.6</td>
<td>2939.0</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 4^1D^o(a)$</td>
<td>4059.9</td>
<td>4083.6</td>
<td>4082.6</td>
<td>4082.6</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 4^1S^{(a)}$</td>
<td>5957.2</td>
<td>5873.9</td>
<td>5874.7</td>
<td>5874.7</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 4^1S^{(b)}$</td>
<td>6608.0</td>
<td>6577.1</td>
<td>6570.0</td>
<td>6570.0</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 3^1D^o(b)$</td>
<td>7228.6</td>
<td>8400.2</td>
<td>8405.2</td>
<td>8405.2</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 3^1D^o(a)^a$</td>
<td>11070.7</td>
<td>11202.7</td>
<td>11215.5</td>
<td>11210.1</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 3^1S^{(a)}$</td>
<td>15831.6</td>
<td>15755.1</td>
<td>15753.1</td>
<td>15753.2</td>
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<tr>
<td>$5^1P^o(c) \to 3^1S^{(b)}$</td>
<td>22369.9</td>
<td>22624.5</td>
<td>22783.4</td>
<td>22709.1</td>
</tr>
<tr>
<td>$5^1P^o(c) \to 2^1D^o(a)^a$</td>
<td>40141.2</td>
<td>40283.8</td>
<td>40345.5</td>
<td>40320.0</td>
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<td>$5^1P^o(c) \to 2^1S^{(a)}$</td>
<td>57084.5</td>
<td>57009.7</td>
<td>57008.4</td>
<td>57008.2</td>
</tr>
</tbody>
</table>

$^a$Transitions converging very slowly with the number of partial waves.

ExTG7F and ExTG5G results) is typically a few cm$^{-1}$ but may reach up to 27 cm$^{-1}$; these errors are one order of magnitude larger compared to the transitions below the first ionization threshold, Table VII. The errors of the g-limit with respect to the non-relativistic theoretical benchmarks are of one to few cm$^{-1}$. The errors of the Einstein coefficients may be evaluated only from the difference of the f- and g-limits, typically of 20% (67% in the worst case). There errors are again significantly larger as compared to the transitions below the first ionization threshold, where the typical errors of the f- and g-limits are below one ppt. Results presented in this section suggest that simulations of two-photon processes will be more sensitive to the number of partial waves included in the basis sets than simulations of one-photon processes are. This hypothesis is confirmed in the simulations below.

C. Precision and numerical stability of a time-dependent cross-section calculated for the helium atom interacting with strong XUV field

1. Problem of fast-decaying states in calculation of Floquet states via the $(t, t')$-method

As a matter of fact, if one includes very short-lived states of the rotated continuum in the basis set of the dressed states (Eq. (14)), the eigenvalues of the evolution operator exp($-i\hbar \epsilon_\ell \tau$) (Eq. (17)) become smaller than the floating point accuracy. For the laser frequencies in the interval of $0.78 \leq \omega \leq 1.2 E_h$, the limiting values of imaginary energies, where $\left|\exp(-i\hbar \epsilon_\ell \tau)\right| \leq 10^{-15}$, are given by $-4.3 \leq \min(\text{Im}E) \leq -6.6 E_h$. The only solution to this problem is omitting the most short-lived states (read states of the discretized rotated continuum, not the Feshbach resonances) decaying within less than 3 as from the calculation; but this may eventually lead to the results which are not fully converged.

Therefore, we perform a convergence test for the Floquet ground state energy for a reduced basis set of the dressed states consisting only of singly excited field-free states. The basis set is further truncated based on the criterion, Im$E_k > \min(\text{Im}E)$. The results obtained for the excitation wavelength of $\lambda = 47$ nm and complex scaling parameter $\theta = 0.4$ are given in Table X. They show that the convergence to the precision of $10^{-6} E_h$ is roughly obtained for the criterion $\min(\text{Im}E) = -2 E_h$. This corresponds to the lifetime of $\tau = 6$ as, which is about 4% of the optical cycle. To assure both convergence and stability, we employ $\min(\text{Im}E) = -3 E_h$ in all our calculations referred to below.

2. Dependence of the Floquet energies and widths on the complex scaling parameter

In Table XI, we demonstrate the stability of the complex Floquet energies corresponding to the ground state with the complex scaling parameter, $\theta$. Clearly, the values are stable in the whole tested interval of $0.2 \leq \theta \leq 0.55$ – the interval of $\theta$, where the complex energies vary in the interval of $10^{-6} E_h$ is given by $\Delta \theta \approx 0.1 – 0.2$. This result is comparable to the case of field-free doubly excited resonances calculated with the same type of Gaussian basis sets as discussed in detail in Ref. 38.
The complex scaling parameter $\theta$ is determined by the minimum imaginary component $\text{Im}(E)$ of the included states. The calculations are performed for the excitation wavelength of 47 nm and different laser strengths $I$ using the complex scaling parameter $\theta = 0.4$.

$$\text{min}(\text{Im}(E))$$

<table>
<thead>
<tr>
<th>$E_0$</th>
<th>1.6880</th>
<th>10.067</th>
<th>36.045</th>
<th>77.484</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re $\epsilon_0 (E_0)$</td>
<td>$-2.903350$</td>
<td>$-2.903369$</td>
<td>$-2.903375$</td>
<td>$-2.903224$</td>
<td>$-2.903142$</td>
</tr>
<tr>
<td>Im $\epsilon_0 (E_0)$</td>
<td>$-0.000024$</td>
<td>$-0.000168$</td>
<td>$-0.000614$</td>
<td>$-0.001327$</td>
<td>$-0.001716$</td>
</tr>
</tbody>
</table>

where $\omega$ is the laser frequency $\omega = 2\pi/\lambda$. The photoionization cross-section calculated using $\text{Im} \epsilon_0$ is given in Table XI. It is apparent that $\sigma$ diverges for the limit $f_E \to 0$, which indicates a somewhat larger relative numerical error at the lowest laser intensities; however, the experimental values of 6.64–6.649 Mb given in Refs. 47–49 are in complete agreement with our calculations for the largest laser intensities. We also evaluate correct values of $\text{Im} \epsilon_0$, which are based on the experimental photoionization cross-section, indicating that the precision of the present calculations are reasonably accurate (Table XI).

### 3. Numerical stability of calculated dynamical quantities controlled by one-photon processes

The calculated Floquet states are used for evaluation of the ground state population in the course of the laser excitation in the simplest but yet adequately representative case of the half-infinite laser pulse. Three representative wavelengths are studied, $\lambda = 38.3783$ nm, 53.6938 nm, and 58.0023 nm, where the single-photon absorption results in a direct ionization, resonant absorption to the $3^1P^0$ state, and near-resonant absorption to the $2^1P^0$ state with the detuning given by $\Delta = 1242.8$ cm$^{-1}$, respectively.

Fig. 2 demonstrates the time-dependent population of the ground state $|u_0(t)|^2$ (the complement of the total absorption, Eq. (32)), as it depends on the complex scaling parameter $\theta$. We observe Rabi oscillations for $\lambda = 53.6938$ nm and 58.0023 nm, which are only slightly perturbed by the absorption to the other states, and the exponential decay due to the direct ionization for $\lambda = 38.3783$ nm. The results demonstrated in Fig. 2 have been obtained using the ExTGSG basis set to generate the field-free states, out of which 734 (corresponding to the ground state, singly and doubly excited states

### Table XI. The $\theta$-trajectories of the Floquet resonance, which is dominated by the helium ground state. The first lines preceding the $\theta$-dependent values of Re $E$ and Im $E$ include the variational values, where $\mathrm{d}R \mathrm{e} E/\mathrm{d}t = 0$ or $\mathrm{d}\text{Im} E/\mathrm{d}t = 0$, respectively. The calculations are performed for the excitation wavelength of 47 nm and different laser strengths $I$. The basis set included helium bound states below the first ionization threshold and the corresponding discretized rotated continuum states down to the imaginary parts of complex energies given by $\min(\text{Im}(E)) = -3 E_0$. The experimental benchmarks for Im $E$ are based on an approximate calculation from the measured photoionization cross-section $\sigma = 6.64$. Více versa, the values for the photoionization cross-section $\sigma$ based on the calculated variational values of Im $E$ are given in the last line.

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>1.6880</th>
<th>10.067</th>
<th>36.045</th>
<th>77.484</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re $\epsilon_0 (E_0)$</td>
<td>$-2.903350$</td>
<td>$-2.903369$</td>
<td>$-2.903375$</td>
<td>$-2.903224$</td>
<td>$-2.903142$</td>
</tr>
<tr>
<td>Im $\epsilon_0 (E_0)$</td>
<td>$-0.000025$</td>
<td>$-0.000184$</td>
<td>$-0.000614$</td>
<td>$-0.001327$</td>
<td>$-0.001716$</td>
</tr>
<tr>
<td>Im $\epsilon_0 (E_0)$ (experimental benchmark)</td>
<td>$-0.000025$</td>
<td>$-0.000184$</td>
<td>$-0.000614$</td>
<td>$-0.001327$</td>
<td>$-0.001716$</td>
</tr>
<tr>
<td>$\sigma$ (Mb)</td>
<td>5.1772</td>
<td>6.3892</td>
<td>6.5850</td>
<td>6.6319</td>
<td>6.6418</td>
</tr>
</tbody>
</table>
Let us now compare the performance of the two basis sets ExTG5G and ExTG7F, where in both cases we include the excited states below the first three ionization thresholds, as in the case above. The main difference lies in the larger spatial extent of the ExTG7F basis set but also the lower number of included partial waves. The total number of helium states included in the dynamical simulation for the ExTG7F basis set extended to 1117. The two results do not differ essentially from each other, up to a 0.4% difference observed for the Rabi frequency in the case of $\lambda = 58.0023$ nm. The simulation remains stable with respect to the complex scaling parameter $\theta$ for about a one-third-longer laser pulse in the case of the ExTG7F basis set. This comparison provides evidence that absorption to the states well below and well above the ionization threshold is not influenced by the missing Rydberg states and other related artifacts such as the significant redshift of the threshold and the presence of the transient states in the basis set.

In the next step, we study the impact of different groups of excited states on single-photon absorption, with the goal to verify the convergence and suggest the minimum basis set for the dynamical simulation. Since both basis sets give stable results for $\theta = 0.2$, we restrict this particular discussion to the calculation for this single value of the complex scaling parameter and the ExTG5G basis set. First, we include only states up to a certain excitation number of the lower lying electron $n_1$ and search for the smallest value $n_1$ that allows for the convergence. Note that the ExTG5G basis set provides the excited states up to $n_1 = 5$. When decreasing $n_1$ from 5 down to 1, the number of corresponding helium states decreases rapidly, (1456, 1373, 734, 311, 84, respectively), leading to a significant gain in computational efforts. Fig. 3(a) demonstrates that even using only the singly excited states, $n_1 = 1$, is sufficient.

below the first to third thresholds, and the corresponding discretized continua have been used as a basis set in the dynamical simulation. The deviation of the results obtained for different values of $\theta$ is only apparent for the pulse length beyond 55 fs. However, the variational values of $\theta$, where $\partial |u_{00}(t)|^2/\partial \theta = 0$ can be well defined even up to the demonstrated pulse duration of 115 fs, as shown in the small panels in Fig. 2. Principal reasons for the described instability may lie in variations of complex Floquet energies (other than the ground state) with $\theta$ beyond $10^{-4} E_R$.
to obtain nearly converged results for the absorption cross-section. Next, Fig. 3(b) shows the convergence with the rotational symmetry of the interacting helium states. Lowering the maximum rotational number included from $L_{\text{max}} = 4$ down to 1 leads to the reduction of the number of states down to 84, 70, 54, 35, respectively, for $n_1 = 1$. Apparently, including only $S$, $P$, and $D$-states is sufficient. Finally, Fig. 3(c) gives the evidence of convergence with respect to $\min(\text{Im} \ E)$ showing the results obtained for $\min(\text{Im} \ E) = \{-3, -1, -0.5\} \ E_h$, where $n_1 = 1$ and $L_{\text{max}} = 2$.

Fig. 3(d) demonstrates how sensitive the absorption is with respect to the number of partial waves $l_{\text{max}}$ in the Gaussian basis sets. Only a slight difference is observed when downgrading the basis set from ExTG7F to ExTG7D, while $l_{\text{max}} = 3$ gives practically converged results.

In summary, the absorption cross-section is governed by one-electron processes, which allows for profound saving of computational efforts. The calculation of this quantity also has modest basis set requirements concerning the rotational and spatial extent of the electronic phase-space. On the other hand, the calculation shows high demands on stability of wavefunctions with the complex scaling parameter. This criterion is largely met by the ExTG5G and ExTG7F basis sets, which are optimized in this respect, but note that it would not be met by standard Gaussian basis sets.\textsuperscript{38}

4. Numerical stability of calculated dynamical quantities controlled by two-photon processes

We studied helium interacting with the radiation of $\lambda = 38.3783$ nm, where the one-photon excitation leads to the direct ionization, but the two-photon excitation uplifts helium to the energy $-0.5292929 \ E_h$, very close to the energies of the doubly excited resonances $4^1 P^\circ (a)$ (with the detuning $\Delta = 1113$ cm$^{-1}$), $5^1 P^\circ (b)$ ($\Delta = -438$ cm$^{-1}$), $5^1 P^\circ (c)$ ($\Delta = -368$ cm$^{-1}$), $4^1 D^\circ (b)$ ($\Delta = 487$ cm$^{-1}$), $4^1 D^\circ (c)$ ($\Delta = 0$), $4^1 F^\circ (a)$ ($\Delta = 650$ cm$^{-1}$), and $4^1 F^\circ (b)$ ($\Delta = 480$ cm$^{-1}$). Time-dependent populations of these resonances are calculated.

Again, we discuss the influence of the maximum value of the lower excitation number $n_1$, the number of partial waves $l_{\text{max}}$, the maximum total rotational number $L$, and the number of the states representing the continuum. The calculations are based on the complex scaling parameter $\theta = 0.2$. The influence of the excitation number of the lower electron $n_1$ is illustrated in Fig. 4 (left column). It is apparent that for quantitatively converged results, $n_1$ must exceed or equal four. On the other hand, the restricted calculations do not change the qualitative results. The similar rule applies for restriction of the total rotational number of the interacting states, as shown in Fig. 4 (middle column). Including

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{Populations of the $4^1 P^\circ (a)$, $5^1 P^\circ (b)$, and $5^1 P^\circ (c)$ doubly excited resonances below the second ionization threshold when helium is excited with the field of the wavelength $\lambda = 38.3783$ nm and the strength $100 \text{ TW/cm}^2$. The left column illustrates convergence of the calculation with respect to the maximum allowed excitation of the lower lying electron $n_1$, where the results for $n_1 = 5, 4, 3, 2$ are displayed in black, red, green, and blue colors, respectively. The other parameters of the basis set are given by $L_{\text{max}} = 4, \min(\text{Im} \ E) = -3 \ E_h$. The calculation of the helium states is based on the ExTG5G basis set. Middle column: the same as the left column, but here the effect of the maximum rotation included within the set of interacting states is displayed. The results for $L_{\text{max}} = 4$ are displayed in black, $L_{\text{max}} = 3$ in red, and $L_{\text{max}} = 2$ in green. The other basis set parameters are given by $n_1 = 5, \min(\text{Im} \ E) = -3 \ E_h$, and the ExTG5G basis set is used. Right column: the same as previous columns, but here the effect of the number of partial waves in Gaussian basis sets is displayed. The results obtained using the ExTG5G basis set, where $l_{\text{max}} = 4$, are displayed in black, ExTG7F ($l_{\text{max}} = 3$) in red, and ExTG7D ($l_{\text{max}} = 2$), in green. The other basis set parameters are given by $n_1 = 5, \min(\text{Im} \ E) = -3 \ E_h$, and $L = L_{\text{max}}$.}
\end{figure}
the $F$-states is sufficient to obtain quantitatively converged results. The restriction of the number of partial waves (rotational number of individual electrons) is much more influential. We compare the results obtained using the ExTG7D, ExTG7F, and ExTG5G basis sets in Fig. 4 (right column). Clearly, the ExTG7D basis set provides not even a qualitative agreement with the more extensive basis sets. An approximate convergence is found only for the ExTG7F basis set and still only for two of the examined resonances, $51P_a^{(a)}$, and $51P_b^{(b)}$ resonances for the laser parameters $\lambda = 38.3783$ nm and $I = 100$ TW/cm$^2$ when different values of the complex scaling parameter $\theta$ are used. Results for $\theta = \{0.2, 0.25, 0.3, 0.35\}$ are shown as the solid curves, while results for the higher values, $\theta = \{0.4, 0.45, 0.5, 0.55\}$, as the dashed curves. Dependence of the cross-sections on $\theta$ is displayed in the small panels for the selected time points, $t = \{10, 30, 50, 70, 90\}$ fs.

D. Prediction of one- and two-photon excitation cross-sections in finite XUV laser pulses

1. Resonance absorption to $31P^{(1s3p)}$ excited state with finite pulses

Now, as we have determined the basis set parameters that are required for calculations of time-dependent populations of ground and excited states in half-infinite pulses, we are able to apply the same basis sets in calculations of the corresponding cross-sections in finite pulses of different shapes. In the following illustration, we compare absorption using Gaussian-shaped pulses, Eq. (11), where $I_0 \leq 100$ TW/cm$^2$ and $\tau \leq 20$ fs and square pulses for $I = 52.36$ TW/cm$^2$ with different lengths.

First, let us comment on a numerical convergence of the calculations for the finite Gaussian pulses. The pulse has been divided into $M = 31$ stairs with constant laser field strengths, allowing for convergence of the results. Let us compare the computational effort using the present method based on Floquet calculations at several laser intensities with a possible direct propagation throughout the duration of the pulse. The propagation needs to cover the time interval of 5 $\tau$ for Gaussian pulses. The calculation of Floquet states based on the $(t, t')$-method requires two subsequent propagations with the lengths of one optical cycle; therefore, by dividing the pulse into $M$ steps, we need to propagate for the overall time-period $2MT$. When comparing the propagation times required by the two competitive methods we obtain the ratio of

$$\frac{5\tau \omega}{4M\pi}$$

in favor of the method based on subsequent Floquet calculations. For $\tau = 20$ fs, $M = 31$, and $\omega \approx 1$ a.u. a gain of 140-times is obtained. (Yet the actual gain is twice as large due to the symmetry of the Gaussian pulse, which reduces the number of Floquet calculations.)

Most of the basis set parameters have been copied from the converged calculations for the half-infinite pulses, namely, $n_1 = 1$, $l_{\text{max}} = 2$, $\min(\text{Im} E) = -3 E_h$, and $l_{\text{max}} = 4$, without a further specific convergence test. We have still performed a convergence test with respect to the complex scaling parameter $\theta$, showing that all values of $\theta$ in the interval $0.2 \leq \theta \leq 0.55$ provide stable results for pulses up to $\tau = 10$ fs, after which a huge instability occurs in the cases of higher values of $\theta$, while lower values of $\theta$ still converge. The variational limit generally occurs for the lowest values of $\theta$, exactly as it was for the half-infinite pulse, Fig. 2.

The resonance absorption at the wavelength of 53.6938 nm has been studied for different pulse lengths $\tau$ and peak intensities $I_0$. We have found that the absorption oscillates with the pulse length $\tau$, reminiscent of Rabi oscillations. Rabi-like oscillations also occur as a function of the square root of the peak intensity $\sqrt{I_0}$, supposing that the pulse length $\tau$ is constant. We have found empirically that the population of the ground state $|u_{00}|^2$ after a Gaussian or square pulse follows a simple formula given by

$$|u_{00}|^2 \approx \cos^2 \frac{f E}{2\hbar}$$

where $f = \frac{100}{E_h}$.
FIG. 6. (a) Resonance absorption to the excited state $3^1P^o (1s3p)$ using finite pulses of different types with the leading wavelength $\lambda = 53.6938$ nm. The final population of the ground state $|u_{00}|^2$ depends solely on an integral field amplitude $f_{Etot}$ (Eq. (38)). Red triangles, green squares, and blue crosses denote 25 fs, 10 fs, and 3.5 fs Gaussian pulses with variable intensities, respectively, while the magenta solid line denotes a $I_0 = 100$ TW/cm$^2$ Gaussian pulse with variable length, and the cyan dashed line denotes a $I_0 = 52.36$ TW/cm$^2$ square pulse with variable length. (b) The same as (a) but for the above threshold ionization ($\lambda = 38.3783$ nm), where the population depends solely on the total accepted energy $E_{tot}$ (Eq. (39)). (c) Near resonance absorption to the excited state $2^1Po (1s2p)$ for different detunings $\Delta_1 = 1242.8$ cm$^{-1}$ (solid lines) and $\Delta_1 = 621.4$ cm$^{-1}$ (dashed lines) using strong Gaussian pulses with the peak intensities of 50 TW/cm$^2$ (red) and 100 TW/cm$^2$ (green) as a function of the pulse length $\tau$ (Eq. (11)). Off-resonance absorption of Gaussian pulses ceases with the pulse length exponentially as indicated by the black lines. (d) Two-photon excitation yields of doubly excited resonances for Gaussian pulses with the peak intensity $I_0 = 100$ TW/cm$^2$, leading wavelength $\lambda = 38.3783$ nm, and varied pulse-lengths $\tau$. The results have been obtained in calculations, where the pulses have been approximated by either 31 stairs (dotted lines), 61 stairs (dashed lines), or 121 stairs (solid lines).

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where $f_{Etot}$ is a total electric field amplitude throughout the pulse defined as

$$f_{Etot}^{\mu z} = \int_{-\infty}^{\infty} f_E(t) dt,$$

and $\mu_\mu$ is the dipole coupling element between the ground and excited states as defined in Eq. (8) (here $|\mu_{\mu}| = 0.207985$ a.u. corresponding to the Einstein coefficient $A = 565.76$ $\mu$s$^{-1}$ given in Table VI). The observation summarized in Eq. (37) is illustrated in Fig. 6(a) for different Gaussian and square pulses. Equation (37) suggests that the fingerprints of Rabi oscillations can be observed independently on the pulse shape, depending only on the integral quantity $f_{Etot}$, although this claim has yet to be confirmed for more complicated pulses. (Following the two-level Rabi model for half-infinite pulses, the population of the ground state oscillates with $|u_{00}(t)|^2 = \cos^2 \Omega t/2$, where $\Omega$ is the Rabi frequency given by $\Omega = \mu_\mu f_E/\hbar$.)

It is expected that the fingerprints of Rabi oscillations after absorption of finite laser pulses will be observable in different free-electron laser experiments. A measurement of laser-induced collective spontaneous emission (superradiance)$^{68}$ might be a most sensitive probe, as, according to our expectations, the superradiance should occur as an oscillatory function of $f_{Etot}$. The fingerprints of Rabi oscillations after absorbing the whole pulse might also be observable in A/T experiments such as the one in Ref. 69. Yet, the present conjecture proposing the simple dependence of the fingerprints of the Rabi oscillations solely on the $f_{Etot}$ quantity should be further confirmed for complicated pulses generated by free-electron lasers.$^{70,71}$

2. Near resonance absorption to the $2^1Po (1s2p)$ excited state with Gaussian pulses

The fingerprints of the Rabi oscillations after absorbing the whole pulse are clearly observable when the leading frequency of the Gaussian or the square pulses coincides with the resonance frequency. Now we shall explore the near resonance absorption where the leading frequency is shifted from resonance by detuning $\Delta$. Absorption of four Gaussian pulses with different detunings of $\Delta = 1242.8$ cm$^{-1}$ and 621.4 cm$^{-1}$ from the resonance wavelength of $\lambda = 58.433$ nm, and the peak intensities $I_0 = 50$ TW/cm$^2$ and 100 TW/cm$^2$ is displayed in Fig. 6(c). Dependence of $|u_{00}|^2$ on the pulse shape is
apparent. The fingerprints of the Rabi oscillations, which are found in the half-infinite pulse, Fig. 2, are observable only for short Gaussian pulses with the length limited by $\tau_{\text{max}} = \hbar/\Delta$.

3. Above-threshold ionization cross-sections after finite pulses

The absorption cross-section for the above-threshold ionization at $\lambda = 38.3783$ nm depends exponentially on the total absorbed energy throughout the laser pulse $E_{\text{tot}}$:

$$E_{\text{tot}} = \int_{-\infty}^{\infty} I(t)dt,$$

(39)

where $I(t)$ is the laser intensity related to the field $f(t)$, see Sec. II C. This empirical conclusion, which is illustrated in Fig. 6(b), can be derived based on an assumption that within every stair of the divided pulse, the population of the ground state decreases according to $\exp[-\Gamma(t) dt]$. After applying this assumption sequentially for all stairs, and turning to infinitesimal lengths of the stairs, we get

$$|u_{00}|^2 \approx e^{-\int_{-\infty}^{\infty} \Gamma[I(t)] dt}.$$  

(40)

This expression can be evaluated assuming the approximate validity of Eq. (35) for the involved intensities $I(t)$ such that

$$|u_{00}|^2 \approx \exp\left[-\frac{\sigma(\omega)E_{\text{tot}}}{4\pi\omega E_0}\right].$$  

(41)

The approximation given by Eq. (41) holds almost exactly as demonstrated in Fig. 6(b).

4. Excitation yields of long-lived doubly excited resonances for a Gaussian-shaped laser pulse

Total two-photon excitation yields of the doubly excited resonances $4^1P^0(a)$, $5^1P^0(b)$, and $5^1P^0(c)$ for the Gaussian pulses have been calculated. The pulse duration $\tau$ varied from 0 to 20 fs, the leading frequency has been given by the wavelength $\lambda = 38.3783$ nm, and the peak intensity by 100 TW/cm$^2$; see Fig. 6(d). As for the numerical details of the simulations, values of numerical parameters have been copied from the corresponding best converged calculations for the half-infinite pulse, while the Gaussian pulse has been approximated using 31, 61, or 121 stairs. The finite number of stairs approximating the Gaussian pulses is reflected in a number of spikes on the curves of the total excitation yields in Fig. 6(d).

The total excitation yields correspond to the varied populations of these resonances $|\langle h_0 | t \rangle|^2$ in half-infinite pulses just in scale. The $5^1P^0(b)$ resonance is populated using the pulse lengths of $\tau = (4 \pm 2)$ fs, the $5^1P^0(c)$ resonance is populated when $\tau = (3 \pm 2)$ fs, while the $4^1P^0(a)$ resonance is preferentially populated in longer Gaussian pulses $\tau > 20$ fs. More definitive answers need to be found for complicated pulses generated by free electron lasers, due to the apparent dependence of the resonance populations on the square vs. Gaussian pulse shapes.

The relative excitation yields of the resonances are rather tiny, ranging from $2.4 \times 10^{-6}$ up to $3.2 \times 10^{-4}$. The $4^1P^0(a)$ and $5^1P^0(b)$ undergo spontaneous ionization within their lifetimes of 0.2 ps and 25 ps, Table III; therefore, their direct experimental observation is perhaps feasible only based on pump-probe experiments.\cite{72} As for the $5^1P^0(c)$ resonance, its ionization decay rate is as small as 5.8 $\mu$s$^{-1}$, (Table III), competing with the radiative spontaneous emission at the wavelengths of 175.4 nm, 438.9 nm, and 247.9 nm with the decay rates 8.54 $\mu$s$^{-1}$, 7.6 $\mu$s$^{-1}$, and 3.53 $\mu$s$^{-1}$, respectively, see Table IX. Therefore, this resonance might possibly be detectable using a time-resolved fluorescence spectroscopy.

IV. CONCLUSIONS

ExTGn (ExTG5G and ExTG7F) basis sets, developed with the intent of using them for quantum dynamical simulations of the dynamics of the helium atom in strong XUV fields, showed all prerequisites for this purpose.\cite{38} They provided accurate energies for helium $S$-states, both singly and doubly excited, including states up to the highest possible excitation numbers $n = 5$ and $n = 7$, respectively. They also proved an excellent stability of the results with the complex scaling parameter. So far, however, we also had some doubts about how existing limitations of the basis sets would influence quantities obtained in the dynamical simulations. In particular, the finite box, which is determined by the most diffuse Gaussians, causes an artificial redshift of the ionization energy by hundreds or even thousands of cm$^{-1}$ and the relatively small number of partial waves, $l_{\text{max}} = 3$ or $l_{\text{max}} = 4$, causes quite a large error in the ground state energy, of tens of cm$^{-1}$. Potential negative effects of these factors could have been clarified only by the present convergence numerical study.

We have chosen such excitation frequencies where we have suspected a considerable negative impact by the known, most pronounced spectral imprecisions. So, the resonance and near resonance excitation wavelengths of 53.6938 nm and 58.0023 nm provide a test of the influence of the shift of the ground state energy. The third excitation wavelength, 38.3783 nm, resulting in direct photo-ionization, has been chosen to reveal the effect of the shifted first ionization threshold. Our study clearly shows that specifically these suspected artifacts have a negligible influence on the dynamics. On the other hand, the study also reveals that the small number of partial waves causes variations of the excitation yields of some doubly excited resonances, which is not, however, related to the above mentioned pronounced spectral artifacts.

First, we have monitored the decaying population of the ground state in a half-infinite laser pulse of a few different strengths amounting up to 100 TW/cm$^2$. This quantity, controlled by one-photon processes, proved to be surprisingly insensitive to the quality of the Gaussian basis set as to the number of partial waves, where even $l_{\text{max}} = 2$ is sufficient, and the spatial extent of the diffuse functions where no difference for $n = 5$ and $n = 7$ is observed. Moreover, even the basis set of field-free helium states that enter the dynamical simulation can be truncated to only singly excited states and the discretized continuum of He$^+(1s) + e^-$.

Second, we have monitored the occupations of several doubly excited resonances below the second ionization
threshold for the excitation wavelengths given by 38.3783 nm. The population of these resonances is of about $10^{-4}$–$10^{-2}\%$, being controlled by the two-photon absorption, while the one-photon absorption leads to direct ionization. Again, we do not observe any influence of the redshift of the first ionization threshold on the excitation yields. Rather, we observe the enhanced sensitivity to the number of partial waves as mentioned above, where populations of some resonances still display considerable variations of the Rabi frequency for upgrades from the f- to g-limit. The probable cause is a somewhat higher sensitivity of the helium energies and oscillator strengths to the number of partial waves in the case of these resonances in comparison with Rydberg states. Also in contrast to the previous case, the basis set of field-free helium states that enter the dynamical calculation can be only very truncated; the convergence is achieved only for the lower excitation number $n_1 \geq 4$ and total rotational number $L \geq 3$.

Third, we paid special attention to the compatibility of the ExTGnl basis set with the complex scaling method. The complex scaling transformation is inevitable due to ionization – all Floquet states represent either resonances or the discretized continuum. From the numerical point of view, however, complex scaling may derail the dynamical calculation due to the different variations of every energy and oscillator strength with the complex scaling parameter. Moreover, complex scaling in conjunction with Gaussian basis sets may generate energies with positive imaginary parts near ionization thresholds, as is also the case of the ExTGnl basis sets. (This is probably caused by the insufficiency of the basis sets in the momentum phase-space at remote distances.) Therefore, we focused on testing the stability of the dynamical decay of the ground state population as well as dynamical excitation yields of doubly excited resonances with respect to the complex scaling parameter. We have verified that the proposed ExTGnl basis sets can be used in conjunction with the complex scaling method for quantitative simulations of helium in femtosecond pulses.

Finally, we have applied the ExTGnl basis sets to simulate the impact of finite Gaussian pulses on helium. We have discussed fingerprints of Rabi oscillations in absorption cross-sections for resonance and near-resonance leading frequencies, the total ionization cross-section for the above threshold ionization, and two-photon excitation cross-sections of doubly excited resonances. Possible experiments to verify the present calculations are also discussed.

This study confirms that special Gaussian basis sets of the ExTGnl type are applicable in quantitative simulations of multiphoton processes in the helium atom. Prospectively, the ExTGnl type of basis set should be useful for quantitative simulations of larger atoms and molecules interacting with strong fields, where the calculations would be based on the quantum chemical approach combined with complex transformations.

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APPENDIX: RELATION FOR TRANSITION DIPOLE ELEMENTS

$|\mu_{tot}|^2$ is defined in Eq. (6). We will express it as

$$|\mu_{tot}|^2 = |\mu_{M,1} + \mu_{M,2}|^2,$$

(A1)

where

$$\mu_M = \sum_{M' = M-1}^{M+1} \int dr \psi_{M'}^*(r) e^{i\theta} (r_1 + r_2) \psi_{M}(r).$$

(A2)

The two-electron wavefunction of the helium atom can be formally written as

$$\psi_{M}(r) = \sum_{l_1,l_2} F_{l_1,l_2}(r_1, r_2) |l_1, l_2, LM >,$$

(A3)

thus the integral can be formally expressed as

$$\mu_M = e^{i\theta} \sum_{l_1,l_2} \int dr \sum_{l_1'} \delta_{l_1,l_1'} \int dr F_{l_1'}^*(r_1, r_2) F_{l_1,l_2}(r_1, r_2) \times I_{l_1,l_2,l_1',l_2,LM}(r_1, r_2).$$

(A4)

where

$$I_{l_1,l_2,l_1',l_2,LM}(r_1, r_2) = \sum_{M' = M-1}^{M+1} \langle l_1', l_2' | L' M' | r_1 + r_2 | l_1, l_2, LM >.$$

(A5)

Let us now simplify the integral $I$. First, the two-electron spherical harmonics are expressed in terms of one-electron spherical harmonics,

$$I_{l_1,l_2,l_1',l_2,LM}(r_1, r_2) = \sum_{M' = M-1}^{M+1} \sum_{m_1', m_2', m_1, m_2} \langle l_1', l_2' | L' M' | r_1 + r_2 | l_1, l_2, LM > \times \delta_{m_1', m_1} \delta_{m_2', m_2}.$$  

(A6)

This expression is further simplified such that $I = I_{12} + I_{21}$, where

$$I_{12} = \delta_{l_1,l_2} \sum_{m_1', m_1} \langle l_1', m_1' | l_1, m_1 > \sum_{m_2', m_2} \langle l_1', m_1', m_2' | L' M' > \times \delta_{m_2', m_2},$$

(A7)

$$I_{21} = \delta_{l_1,l_2} \sum_{m_1', m_2} \langle l_1', m_2' | l_2, m_2 > \sum_{m_1', m_1} \langle l_1', m_1', m_2' | L' M' > \times \delta_{m_1', m_1}.$$  

(A8)

Further, we will simplify only $I_{12}$ since the two expressions are equivalent for the exchange of electrons $1 \leftrightarrow 2$. We
simplify \((l'_1m'_1|r_1|l_1m_1)\) such that
\[
(l'_1m'_1|x_1|l_1m_1) = \frac{1}{\sqrt{2}} \frac{r_1}{N} (l'_1m'_1)|Y^{-1}_1 - Y^+_1|l_1m_1),
\]
\[
(l'_1m'_1|y_1|l_1m_1) = \frac{i}{\sqrt{2}} \frac{r_1}{N} (l'_1m'_1)|Y^{-1}_1 + Y^+_1|l_1m_1),
\]
\[
(l'_1m'_1|z_1|l_1m_1) = \frac{r_1}{N} (l'_1m'_1)Y^0_1|l_1m_1), \tag{A9}
\]
where \(N = \sqrt{3}/4\pi\). Due to the Wigner-Eckart theorem,
\[
\langle l'_1m'_1|x_1|l_1m_1\rangle = \frac{f(r_1,l_1,l'_1)}{\sqrt{2}} ((l_1m_1|(-1)l'_1m'_1) \\
- (l_1m_1|11l'_1m'_1)),
\]
\[
\langle l'_1m'_1|y_1|l_1m_1\rangle = \frac{i f(r_1,l_1,l'_1)}{\sqrt{2}} ((l_1m_1|(-1)l'_1m'_1) \\
+ (l_1m_1|11l'_1m'_1)),
\]
\[
\langle l'_1m'_1|z_1|l_1m_1\rangle = f(r_1,l_1,l'_1)(l_1m_1 10l'_1m'_1).
\]
Now we define \(I_q\),
\[
I_q = \sum_{M=-M-1}^{M+1} \sum_{m_2} \sum_{1}^{M+1} \langle l_1m_1 1q | l'_1m'_1 \rangle
\times (l'_1m'_1|l_2m_2|L'M') (l_1m_1|l_2m_2|LM), \tag{A11}
\]
which relates to the components of \(I_{12}\) such that \(I_{12,x} = (I_{12} - I_{12}^y)/\sqrt{2}, I_{12,y} = (I_{12} + I_{12}^y)/\sqrt{2}\), and \(I_{12,z} = I_{12}\). The sum over \(m_1\) in Eq. (A11) can be solved\(^{13}\) such that
\[
I_q = \sum_{M=-M-1}^{M+1} \langle 1qLM|L'M' \rangle
\times \langle 1qLM|L'M' \rangle (M+q), \tag{A12}
\]
where
\[
\begin{align*}
&g_{l_1,l'_1,l_2,l'_2,L,L'}(r_1) = \delta_{l_1,l'_1} \delta_{l_2,l'_2} (r_1)(-1)^{l_1+l_2+L'} (2l'_1 + 1) \\
&\times (2l_1+1) \sqrt{2(l'_1+1)(2L+1)} \left\{ \begin{array}{ccc}
1 & l_1 & l'_1 \\
2l_1 & L' & L 
\end{array} \right\}.
\end{align*}
\] \tag{A13}

We obtain components of \(I\) immediately,
\[
I_x = \frac{a_{l_1,l'_1,l_2,l'_2,L,L'}(r_1,r_2)}{\sqrt{2}} ((1-1)LM|L'(M-1))
- (11LM|L'(M+1)),
\]
\[
I_y = \frac{a_{l_1,l'_1,l_2,l'_2,L,L'}(r_1,r_2)}{-i\sqrt{2}} ((1-1)LM|L'(M-1))
+ (11LM|L'(M+1)),
\]
\[
I_z = \frac{a_{l_1,l'_1,l_2,l'_2,L,L'}(r_1,r_2)}{10LM|LM'},
\]
where \(a_{l_1,l'_1,l_2,l'_2,L,L'}(r_1,r_2) = g_{l_1,l'_1,l_2,l'_2,L,L'}(r_1) + g_{l_1,l'_1,l_2,l'_2,L,L'}(r_2)\). We substitute the components of \(I\) into Eq. (A4) and obtain
\[
\mu_{M,x} = b_{L,LM} \frac{(1-1)LM|L'(M-1)) - (11LM|L'(M+1))}{\sqrt{2}},
\]
\[
\mu_{M,y} = b_{L,LM} \frac{(1-1)LM|L'(M-1)) + (11LM|L'(M+1))}{-i\sqrt{2}},
\]
\[
\mu_{M,z} = b_{L,LM} \langle 10LM|LM' \rangle, \tag{A15}
\]
where
\[
b_{L,LM} = e^{\iota \theta} \sum_{l_1,l'_1} \sum_{l_2,l'_2} \int dr F_{l_1l'_1l_2l'_2}^{(r_1)}(r_1, r_2)
\times F_{l_1l'_1l_2l'_2}^{(r_1)}(r_1, r_2). \tag{A16}
\]

The absolute value of the sum of all components defining the total transition dipole \(|\mu_M|^2\) (Eq. (A1)) is given by
\[
|\mu_{\text{tot}}|^2 = |b_{L,LM}|^2 \sum_{q=-1}^{1} \langle 1qLM|L'(M+q) \rangle^2
= |b_{L,LM}|^2 \frac{2L' + 1}{2L + 1}. \tag{A17}
\]
Clearly \(|\mu_{\text{tot}}|^2\) can be calculated from \(|\mu_{M=0,z}|^2\) such that
\[
|\mu_{\text{tot}}|^2 = \frac{1}{\max(L',L)} |\mu_{M=0,z}|^2. \tag{A18}
\]