Two photon above threshold ionization in a relativistic framework

Attosecond delays in high Z elements

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Abstract

Recent advances in experimental physics opens up for improved time resolution on measurements of ionizing processes in atoms caused by an EM-field. There exist non-relativistic models that describe photo-ionization events involving two photons, for various atoms, where relativistic effects, e.g. spin-orbit interactions, are small. The ambition of this thesis project was to develop a computational software that includes relativistic effects by starting from the Dirac equation. Investigation of the photo-ionization events are done by calculating the two-photon matrix elements, taking into account essential many body effects using Random Phase Approximation with Exchange (RPAE) for the atomic response to the interaction with the first photon. During the development of the software it was discovered that the choice of dipole operator, length or velocity, had a large influence on the results when including the second photon, and it is concluded that the more straightforward calculations are done with the dipole operator in length gauge.

The examined results demonstrate a program that works as desired; it agrees well with the non-relativistic calculations for the lighter elements and provides data for more detailed analysis of heavier elements.
List of Papers

PAPER I: Fano’s propensity rule in angle-resolved attosecond pump-probe photoionization
David Busto, Jimmy Vinbladh, Shiyang Zhong, Marcus Isinger, Saikat Nandi, Mathieu Gisselbrecht, Anne L’Huillier, Eva Lindroth, Jan Marcus Dahlström
Submitted to Physical Review Letters

PAPER II: Many-body calculations of two-photon, two color matrix elements for attosecond delays
Jimmy Vinbladh, Jan Marcus Dahlström, and Eva Lindroth∗
In Manuscript
Author’s contribution

This thesis is based on the work I accomplished while developing a computational software that includes essential many body effects to investigate time delays in two-photon ionizing events from high $Z$ elements. The relativistic data presented in this thesis are calculated by utilizing this software which uses the Dirac equation as a starting point. Due to the use of the Dirac equation calculations are more time consuming, compared to non-relativistic calculations, however this issue was mitigated by parallelizing the code using OpenMP.

This thesis is a continuation of my Master Thesis (Numerical calculations of relativistic many-body interactions), which focused on single photon ionization, and contains reprocessed and in a few cases directly adapted material from the Master Thesis.
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>3</td>
</tr>
<tr>
<td>List of Papers</td>
<td>5</td>
</tr>
<tr>
<td>Author's contribution</td>
<td>7</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Overview</td>
<td>1</td>
</tr>
<tr>
<td>1.2. Properties of particular interest</td>
<td>1</td>
</tr>
<tr>
<td>1.3. Motivation and Purpose</td>
<td>2</td>
</tr>
<tr>
<td>2. Solving the Dirac Equations for an Atom</td>
<td>7</td>
</tr>
<tr>
<td>2.1. Overview of the Dirac equation</td>
<td>7</td>
</tr>
<tr>
<td>2.1.1. With Central potential</td>
<td>8</td>
</tr>
<tr>
<td>2.2. Numerical solution the the Radial Dirac equation using b-splines</td>
<td>11</td>
</tr>
<tr>
<td>2.2.1. Numerical calculations of Hydrogen-like atoms</td>
<td>11</td>
</tr>
<tr>
<td>2.2.2. Radial Dirac equation with Hartree-Fock potential</td>
<td>13</td>
</tr>
<tr>
<td>2.2.3. Projected potential</td>
<td>15</td>
</tr>
<tr>
<td>3. Photon Interactions</td>
<td>17</td>
</tr>
<tr>
<td>3.1. One photon interaction</td>
<td>17</td>
</tr>
<tr>
<td>3.1.1. The electromagnetic field</td>
<td>17</td>
</tr>
<tr>
<td>3.1.2. Calculation of the interaction element</td>
<td>18</td>
</tr>
<tr>
<td>3.1.3. Exterior complex scaling and the outgoing electron wave</td>
<td>19</td>
</tr>
<tr>
<td>3.1.4. Time Dependent Hartree-Fock or Random Phase Approximation with Exchange</td>
<td>20</td>
</tr>
<tr>
<td>3.2. Second photon</td>
<td>22</td>
</tr>
<tr>
<td>3.2.1. Constructing Coulomb functions</td>
<td>22</td>
</tr>
<tr>
<td>3.2.2. Final state</td>
<td>23</td>
</tr>
<tr>
<td>3.2.3. Two photon element</td>
<td>25</td>
</tr>
<tr>
<td>4. Results</td>
<td>27</td>
</tr>
<tr>
<td>4.1. Overview of photo-electron delays $\tau_{\text{atom}}$, $\tau_{\text{wigner}}$ and $\tau_{\text{cc}}$</td>
<td>27</td>
</tr>
<tr>
<td>4.2. Velocity or length gauge</td>
<td>29</td>
</tr>
<tr>
<td>4.3. Delays in the outer orbitals</td>
<td>30</td>
</tr>
<tr>
<td>4.4. Inner orbitals</td>
<td>33</td>
</tr>
</tbody>
</table>
5. Conclusion and Outlook 39
   5.1. Conclusion and Summary ........................................ 39
   5.2. Outlook ....................................................... 40

A. Appendix 41
   A.1. Spin-angular functions ......................................... 41
   A.2. B-Splines ...................................................... 41
   A.3. Details about eigenvalue $\kappa$ ............................... 42
   A.4. Radial Dirac equation with B-Splines ......................... 44
   A.5. The Hartree-Fock method with b-splines ...................... 46
   A.6. Photo-ionization from a noble gas ............................. 47
   A.7. Coulomb phase ................................................ 47
      A.7.1. Non-relativistic .......................................... 47
      A.7.2. Relativistic .............................................. 47
   A.8. Cross-section ................................................ 48
   A.9. RPAE elements ................................................ 51
   A.10. Relationship between regular and irregular Coulomb functions .... 52

Bibliography 55
1. Introduction

1.1. Overview

Until recently processes that involve electron dynamics, like photo-ionization, could for all practical purposes be considered as instantaneous as it take place on an atto-second time-scale and such a short time-scale could not be experimentally resolved. However, recent advances in experimental techniques have enabled an improved time-resolution, e.g. by using atto-second pulses of XUV-radiation phase-locked with longer pulses of IR-radiation. This has allowed processes such as photo-ionization to be studied in the time domain [1, 2]. Consequently, interest in the theoretical description of the temporal aspects of photo-ionization has increased, and a considerable amount of work has been done in this field in the frame-work of non-relativistic quantum mechanics [3, 4, 5]. For an in-depth description of the subject see the tutorial: Introduction to attosecond delays in photoionization by M. Dahlström et al.[6]. However, for heavier elements, as well as for ionization from inner orbitals, relativistic effects can play an increasingly important role. This is the motivation to use the Dirac equation as a starting-point when examining photo-ionization events and go beyond non-relativistic quantum mechanics.

1.2. Properties of particular interest

In the theoretical description, features of the ionization process can be evaluated by examining the properties of the outgoing electron wave. One aspect of the ionization process is the ionization cross-section for which there exists plenty of experimental data for several atoms. The cross-section is proportional to the square of the amplitude of the electron wave and consequently the validity of this aspect of the theoretical models is well studied. Another property of the outgoing electron wave, which is of special interest when trying to describe electron dynamics, is the phase of the wave function. The phase, or more exactly the part of the phase that depends on the electron energy, contains information about the delayed appearance of the photo-electron after the photon has been been absorbed [7]. By comparing the outgoing wave with functions originating from different atomic orbitals, the relative phase, where the shift arises from different interactions with the total atomic many-body potential, can be determined. Theoretically it is also possible to compare the outgoing wave function with pure Coulomb wave functions. Coulomb wave functions
are solutions to the Coulomb wave equation\(^1\) and describe the behavior of a charged particle \((E > 0)\) moving in a Coulomb potential. The phase difference between the outgoing electron wave and the Coulomb waves is due to potential differences, i.e. the outgoing electron is influenced by effects (e.g. EM-field, many-body effects) in addition to the Coulomb potential. Fig. 1.1 illustrates this in a simple yet informative manner.

![Figure 1.1. Illustration of a wave being influenced by an additional potential, resulting in a wave that in comparison with the original wave exhibits an altered phase.](image)

1.3. Motivation and Purpose

The motivation for this work comes to a considerable extent from the experimental advances described in sec. 1.1. What follows is a brief overview of one of the experimental methods used and it will also demonstrate what this work intends to accomplish to have comparable results.

Experimentally, a so called delay in photoionization can be obtained from the probability of creating a photoelectron, at a given energy, in the presence of the XUV and IR field. The probability is measured by recording a spectrogram of photoelectrons as function of kinetic energy and the delay, \(\tau\), between the XUV field and the IR field.

The XUV field is an attosecond pulse train that consists of odd high order harmonics of the IR field, \(\Omega = (2N + 1)\omega\), where \(\omega\) is the photon energy of the IR field. This means that energies equivalent to absorbing an even number of IR photons, \(2N\omega\), primarily can be reached by absorbing one XUV photon with energy

\(^1\)The Schrödinger equation with a Coulomb potential.
(2N - 1)\,\omega \text{ and then by absorbing one IR photon, or by absorbing one XUV photon with energy } (2N + 1)\,\omega \text{ and then by emitting one IR photon. This is illustrated in Fig. 1.2 together with a representation of an experimental signal. The interference}

Figure 1.2.: (a) Photoelectron spectrogram over absorbed energy and delay between IR field and the attosecond pulse train (XUV). The intensity of the modulated signals at energies equal to even harmonics can be expressed as 

\[ I = \alpha + \beta \cos (2\omega \tau - \Delta \phi - \Delta \delta) \]

and contains information about the ionizing process.

(b) A schematic energy diagram displaying different paths leading to the same final energy \(2N\omega\).

This is slightly modified version of Figure 5 in reference [6].

between these two different two-photon processes is what is creating the modulated signal of interest. The signal intensity is proportional to the probability, \(P\), that a photoelectron will reach the specific energy state, which can be expressed by the wave functions representing the photoelectrons, \(\Psi^a\) (absorbing an IR photon) and \(\Psi^e\) (emitting an IR photon).

\[ I \propto P = |\Psi^a + \Psi^e|^2 = |\Psi^a|^2 + |\Psi^e|^2 + 2 |\Psi^e| |\Psi^a| \cos (\arg[\Psi^a\Psi^e]) \]

The modulation depends on the cosine term and relevant information is given by

\[ \arg[\Psi^a\Psi^e] = 2\omega \tau - \Delta \phi - \Delta \delta \tag{1.1} \]

where the first two terms are parameters in the experimental setup, \(\tau\) being the time difference between the fields and \(\Delta \phi\) is connected to the group delay of the XUV
field and is unknown. The last term, $\Delta \delta$, is an intrinsic atomic quantity associated with the different quantum paths leading to the final state, and the intention of this work was to determine this quantity with theoretical calculations. Experimentally, information about $\Delta \delta$ can be extracted by simultaneously measuring photoelectrons originating from different subshells (and/or atoms), or photoelectrons at different angles, and analyzing the difference between the measurements. In theoretical calculations it is possible to directly obtain a value for $\Delta \delta$ and the delay connected to the atom

$$\tau_{\text{atom}} = \frac{\Delta \delta}{2\omega}.$$ 

In the non-relativistic picture the radial function for a free electron, with a specific energy and angular momentum, in the presence of a pure Coulomb potential can be expressed as combination of an irregular and a regular Coulomb function [8],

$$\Psi (r) = G(r) \pm IF(r)$$

$$\rightarrow \cos \left( kr - \eta \ln (2kr) - \frac{l\pi}{2} + \sigma_l \right) \pm i \sin \left( kr - \eta \ln (2kr) - \frac{l\pi}{2} + \sigma_l \right) \text{ when } r \rightarrow \infty$$

$$= \exp \left[ i \left( kr - \eta \ln (2kr) - \frac{l\pi}{2} + \sigma_l \right) \right] \text{ when } r \rightarrow \infty .$$

All the components of the argument of this function can be expressed analytically; the details can be found in the appendix sec. A.7. The photoelectrons in the experiment creating the signal can be described in a similar way but with a different amplitude, $M_2$, and an additional phase component, $\delta$, since the electron is interacting with more than just a pure Coulomb potential

$$\rightarrow \lim_{r \rightarrow \infty} \Psi (r) = M_2 \exp \left[ i \left( kr - \eta \ln (2kr) - \frac{l\pi}{2} + \sigma_l + \delta \right) \right].$$

Consequently, this thesis covers the steps leading up to the matrix element, $M_2$, and the phase component, $\delta$, associated with these interactions, where the bulk of the work necessary are in the steps taken to calculate the matrix element. In a one particle system it can be expressed as

$$M_2 = \sum_{p} \frac{\langle q | D | p \rangle \langle p | D | i \rangle}{\varepsilon_{i} + \Omega - \varepsilon_{p}},$$

with $i$ being the initial state, $q$ being the final state with energy $\varepsilon_q = \Omega \pm \omega$, $p$ runs over the whole spectrum (discrete and continuous) and $D$ is the dipole operator. However, in a many-body system many-body effects will modify the matrix element further. Primarily, the interest will be in electrons detected in the direction of the
polarization of the electromagnetic field and the left hand side of 1.1 can then be expressed as

\[
\int \arg \left[ \left( \sum_{l,l'} M^{l,l'}_{2a} e^{i(-l\pi/2 + \sigma_l + \delta)} Y_{l,0}(0, \phi) \right)^* \times \left( \sum_{l,l'} M^{l,l'}_{2e} e^{i(-l\pi/2 + \sigma_l + \delta)} Y_{l,0}(0, \phi) \right) \right] \, d\phi
\]

(1.2)

where the sum is over all possible \( l \) for both the final state \( q \) and for the intermediate state, with initial state \( i \). This is the non-relativistic expression; the relativistic expression is similar but with a wave function expressed as four components in a vector and the sums are over \( j \) and \( m_j = -\frac{1}{2}, \frac{1}{2} \). And for relativistic ab initio calculations the first step is to solve the Dirac equation for the atom of interest.
2. Solving the Dirac Equations for an Atom

2.1. Overview of The Dirac equation

Often when studying quantum mechanical system like an atom the Schrödinger equation is used,

\[ H\psi = i\hbar \frac{\partial}{\partial t}\psi \]

with a non-relativistic Hamiltonian

\[ H = -\frac{\hbar^2}{2m}\nabla^2 + V(r). \]

Numerous quantum mechanic effects can be understood with this approach but it is not always sufficient. Issues that arise include: it cannot account for the details in the hydrogen spectrum; the phenomenon of spin is not explained; and it is inconsistent with special relativity where time and space are differentially of the same order (the Schrödinger equation is first order in \( \partial/\partial t \) and second order in \( \partial/\partial x \)).

A solution to these issues is the Dirac equations which has a Hamiltonian operator that yield the relativistic energy eigenvalue for a free particle, \( E = \sqrt{p^2c^2 + m^2c^4} \).

\[ \rightarrow (-i\hbar c \alpha \cdot \nabla + \beta mc^2)\psi = i\hbar \frac{\partial}{\partial t}\psi \]

where

\[ \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}, \quad \alpha_1 = \begin{pmatrix} 0 & \sigma_{x_1} \\ \sigma_{x_1} & 0 \end{pmatrix} \]

\[ \alpha_2 = \begin{pmatrix} 0 & \sigma_{x_2} \\ \sigma_{x_2} & 0 \end{pmatrix}, \quad \alpha_3 = \begin{pmatrix} 0 & \sigma_{x_3} \\ \sigma_{x_3} & 0 \end{pmatrix} \]

where \( \sigma_{x_i} \) are the Pauli matrices, and \( I \) is a 2x2 identity matrix. As a result the states, \( \psi \), are now described as four component objects.
2.1.1. With Central potential

To be able to study the wave function of an electron in an atom the Hamiltonian of interest is

\[ H = c \alpha \cdot p + \beta mc^2 + V(r) \]  \hspace{1cm} (2.1)

where \( p \) is the momentum operator and \( V(r) \) is a spherically symmetric potential. For this Hamiltonian it can be shown that the total angular momentum operator \( J \) is a constant of the motion although that will not reveal information about the spin state, i.e. if it is parallel or anti-parallel to the total angular momentum. In non-relativistic quantum mechanics it is identified by the eigenvalues of

\[ \sigma \cdot J = \sigma \cdot \left( L + \frac{\hbar}{2} \right), \]

however, a \( 4 \times 4 \) generalization of this, \( \Sigma \cdot J \), will not commute nicely with \( H \). An operator that will commute with both \( H \) and \( J \) is the operator \( K \) which is defined by

\[ K = \beta \Sigma \cdot J - \beta \frac{\hbar}{2} = \beta (\Sigma \cdot L + \hbar) = \begin{pmatrix} \sigma \cdot L + \hbar & \hbar \\ 0 & - (\sigma \cdot L + \hbar) \end{pmatrix} \]

and the eigenvalue \( -\kappa \hbar \). It can be shown\(^1\) that the eigenvalues of \( K^2, J^2, K \) and \( J \) are related by

\[ \kappa^2 \hbar^2 = \left( j(j+1) + \frac{1}{4} \right) \hbar^2 = \left( j + \frac{1}{2} \right)^2 \hbar^2 \quad \text{and} \quad \kappa = \pm \left( j + \frac{1}{2} \right) \]  \hspace{1cm} (2.2)

Furthermore, by writing the four-component wave function as

\[ \Psi = \begin{pmatrix} \Psi_A \\ \Psi_B \end{pmatrix} \]

where \( \Psi_A \) and \( \Psi_B \) are two-component wave functions, and analyzing how \( K \) and \( J^2 \) act on these wave functions (and that \( (\sigma \cdot L + \hbar) = \frac{1}{2} \left( J^2 - L^2 \right) + \frac{\hbar}{2} \)), it is possible to obtain

\[ -\kappa = j(j+1) - l_A (l_A + 1) + \frac{1}{4}, \quad \kappa = j(j+1) - l_B (l_B + 1) + \frac{1}{4}. \]  \hspace{1cm} (2.3)

In other words, for a specific value of \( j \) there are two possible values of \( l \) corresponding to two possible values of \( \kappa \). By using Eq.(2.2) and Eq.(2.3) it is possible

\(^1\)More details are provided in Section sec.A.3
to determine the values of \( l \) for a specific \( \kappa \). As an example, for \( j = \frac{1}{2} \), \( \kappa \) can be –1 with \( l_A = 0 \) or \( \kappa \) can be 1 with \( l_A = 1 \). For \( j = \frac{3}{2} \) there is \( \kappa = -2 \), \( l_A = 1 \) and \( \kappa = 2 \), \( l_A = 2 \) and so on continuing with the same pattern for higher \( j \) values.

\[
\kappa = \begin{cases} 
  l & \text{if } j = l - \frac{1}{2} \\
  -(l + 1) & \text{if } j = l + \frac{1}{2}
\end{cases}
\]

This is basically confirming what is known from non-relativistic quantum mechanics, but with the new information that for a fixed \( \kappa \) the two-component eigenfunctions \( \Psi_A \) and \( \Psi_B \) must have opposite orbital parities. The requirements put on \( \Psi \) are met by writing it as

\[
\Psi = \begin{pmatrix} \Psi_A \\ \Psi_B \end{pmatrix} = \begin{pmatrix} f(r) \mathcal{Y}_{jl_A}^{m_j} \\ ig(r) \mathcal{Y}_{jl_B}^{n_j} \end{pmatrix}
\]

(2.4)

where \( \mathcal{Y}_{jl}^{m_j} \) are normalized \( r \)-independent spin-angular eigenfunctions of \( J^2, J_3, L^2 \) and \( S^2 \) formed by the combination of the Pauli spinor with the spherical harmonics.\(^2\)

The functions \( f \) and \( g \) are radial functions that evidently will depend on \( \kappa \). The factor \( i \) on \( g \) is inserted to make the solutions real for bound state solutions. With the two-component functions the Dirac equation can be rewritten:

\[
H \Psi = E \Psi \iff \left( c \alpha \cdot p + \beta mc^2 + V(r) \right) \Psi = E \Psi
\]

\[
\iff \left( \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \cdot p + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} mc^2 + V(r) \right) \begin{pmatrix} \Psi_A \\ \Psi_B \end{pmatrix} = E \begin{pmatrix} \Psi_A \\ \Psi_B \end{pmatrix}
\]

\[
\iff c \sigma \cdot p \Psi_B = \left( E - mc^2 - V(r) \right) \Psi_A, \quad c \sigma \cdot p \Psi_A = \left( E + mc^2 - V(r) \right) \Psi_B
\]

(2.5)

Instead of directly inserting Eq.(2.4) into Eq.(2.5) it is useful to notice that (using Eq.(A.1))

\[
\frac{(\sigma \cdot r)^2}{r^2} = 1
\]

\[
\rightarrow \sigma \cdot p = \frac{(\sigma \cdot r)}{r^2} (\sigma \cdot r) (\sigma \cdot p) \iff \frac{(\sigma \cdot r)}{r^2} \left( -ihr \frac{\partial}{\partial r} + i \sigma \cdot (r \times p) \right)
\]

\[
\iff \frac{(\sigma \cdot r)}{r^2} \left( -ihr \frac{\partial}{\partial r} + i \sigma \cdot L \right)
\]

When acting on \( \mathcal{Y}_{jl}^{m_j} \) the operator \( (\sigma \cdot r)/r \) must result in an eigenfunction of \( J^2, J_3 \) and \( L^2 \) with the same eigenvalues \( j \) and \( m_j \) but with opposite orbital parity. Hence \( [(\sigma \cdot r)/r] \mathcal{Y}_{jl}^{m_j} \) is equal to \( \mathcal{Y}_{jl}^{m_j} \) multiplied with a phase factor, that can be shown

\(^2\)See sec. A.1 for explicit expression of \( \mathcal{Y}_{jl}^{m_j} \).
to be $-1$, and similarly for $(\sigma \cdot r) / r$ acting on $\mathcal{Y}^{m_j}_{jl_B}$ the result is $-\mathcal{Y}^{m_j}_{jl_A}$.

From this follows

$$
(\sigma \cdot p) \Psi_B = \left( \frac{(\sigma \cdot r)}{r^2} \right) \left( -i\hbar \frac{\partial}{\partial r} + i \sigma \cdot \mathbf{L} \right) \Psi_B = \left( \frac{(\sigma \cdot r)}{r^2} \right) \left( -i\hbar \frac{\partial}{\partial r} + i \sigma \cdot \mathbf{L} \right) ig(r) \mathcal{Y}^{m_j}_{jl_B} 
$$

$$
= \left( \frac{(\sigma \cdot r)}{r^2} \right) \left( \hbar r \frac{\partial g(r)}{\partial r} - (\kappa - 1) hg(r) \right) \mathcal{Y}^{m_j}_{jl_B} = \left( -\hbar \frac{\partial g(r)}{\partial r} - \frac{(1 - \kappa)}{r} hg(r) \right) \mathcal{Y}^{m_j}_{jl_B} 
$$

(2.6)

and in a similar way

$$
(\sigma \cdot p) \Psi_A = \left( \frac{r}{\hbar} \frac{\partial f(r)}{\partial r} + \frac{(1 + \kappa)}{r} hf(r) \right) \mathcal{Y}^{m_j}_{jl_B}. 
$$

(2.7)

So evidently when inserting Eq.(2.4) into Eq.(2.5) the spin-angular functions can be canceled, leaving only the radial parts.

$$
\to c \hbar \left( -\frac{d}{dr} - \frac{(1 - \kappa)}{r} \right) g(r) = \left( E - mc^2 - V(r) \right) f(r) 
$$

(2.8)

$$
\to c \hbar \left( \frac{d}{dr} + \frac{(1 + \kappa)}{r} \right) f(r) = \left( E + mc^2 - V(r) \right) g(r) 
$$

(2.9)

As in the non-relativistic case the functions

$$
P(r) = rf(r) \quad \text{and} \quad Q(r) = rg(r)
$$

are introduced and inserted into Eq.(2.8) and Eq.(2.9), starting with the left hand side of the equations.

$$
\left( -\frac{d}{dr} - \frac{(1 - \kappa)}{r} \right) \frac{Q(r)}{r} = -\frac{r^2 \frac{dQ(r)}{dr}}{r^2} - \frac{(1 - \kappa)}{r^2} Q(r) = -\frac{1}{r} \frac{dQ(r)}{dr} + \frac{\kappa}{r^2} Q(r)
$$

$$
\Rightarrow c \hbar \left( -\frac{d}{dr} + \frac{\kappa}{r} \right) Q(r) = \left( E - mc^2 - V(r) \right) P(r) 
$$

(2.10)

$$
\left( \frac{d}{dr} + \frac{(1 + \kappa)}{r} \right) \frac{P(r)}{r} = \frac{dP(r)}{dr} + \frac{\kappa}{r^2} P(r)
$$

$$
\Rightarrow c \hbar \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P(r) = \left( E + mc^2 - V(r) \right) Q(r) 
$$

(2.11)
2.2 Numerical solution the the Radial Dirac equation using b-splines

The end result, Eq.(2.10) and Eq.(2.11), are two coupled first-order ordinary differential equations. Put on matrix form,

\[
\begin{pmatrix}
V(r) & -c\left(\frac{d}{dr} - \frac{\kappa}{r}\right)
\end{pmatrix}
\begin{pmatrix}
P(r) \\
Q(r)
\end{pmatrix}
= \left(E - mc^2\right)
\begin{pmatrix}
P(r) \\
Q(r)
\end{pmatrix},
\]

it is often referred to as the radial Dirac equation and when solved it will include both positive and negative energy solutions. \(E - mc^2\) can be redefined as \(E\) since when discussing the energy of an electron in an atom the rest mass energy is generally not considered. At non-relativistic energies \(P(r)\) is the function that will most resemble non-relativistic solutions while \(Q(r)\) will be considerably smaller. Therefore the functions are often labeled the large and small component of the Dirac wave function.

2.2. Numerical solution the the Radial Dirac equation using b-splines

Two programming languages were used for the purpose of this thesis. The primary program that performed the calculations was constructed in Fortran and made use of various LAPACK routines[9]. Further minor calculations, evaluation and visualization of the results was handled by scripts in Python and the open source libraries NumPy, SciPy and Matplotlib [10, 11, 12].

In the rest of this thesis (Hartree) atomic units will be used, which means that the following constants numerical value are defined as 1; the elementary charge, the reduced Planck’s constant, the mass of the electron and Coulomb’s constant.

\[
e = 1 \\
h = 1 \\
m_e = 1 \\
\frac{1}{4\pi\epsilon_0} = 1
\]

Derived units that will be used often are energy, that will be in units of Hartree \((\approx 27.211 \text{ eV})\), and length, which will be in units of Bohr \((\approx 5.2918 \cdot 10^{-11} \text{ m})\). The value of speed of light can in atomic units be expressed as \(1/\alpha\) where \(\alpha\) is the fine structure constant. But since the letter alpha already has a different meaning in the Dirac equation, and to avoid confusion, the fine structure constant will be denoted \(\alpha_{fsc}\). In the numerical calculations the value used was \(\alpha_{fsc}^{-1} = c = 137.035999074(44)\) [13].

2.2.1. Numerical calculations of Hydrogen-like atoms

With these units the radial Dirac equation to solve is then

\[
\begin{pmatrix}
V(r) & -c\left(\frac{d}{dr} - \frac{\kappa}{r}\right)
\end{pmatrix}
\begin{pmatrix}
P(r) \\
Q(r)
\end{pmatrix}
= \left(E - mc^2\right)
\begin{pmatrix}
P(r) \\
Q(r)
\end{pmatrix},
\]

(2.12)
where $E$ is the energy with the rest mass energy subtracted. For a hydrogen-like system, with $V(r) = -Z/r$, it is possible to find an analytical solution but for systems with additional electrons the solutions are found numerically. In this work the numerical calculations has been done using b-splines, which are piecewise polynomial functions designed for the purpose of approximating arbitrary functions. If $f(x)$ is the function of interest it can be represented as

$$f(x) = \sum_{i}^{N} c_i B_{i,k}$$

where $B_{i,k}$ is the $i$:th b-spline (on a grid) of order $k$, and $c_i$ are coefficients. In a numerical problem like this the goal will be to find the coefficients to represent the sought after function(s). Further details such as definition and properties can be found in the appendix, Section sec.A.2.

However, a well studied problem in numerical implementations of the Dirac equation is that in the discretized energy-spectrum so called spurious states might appear [14][15]. Several schemes have been suggested to avoid these states, and here we will follow Froese Fischer and Zatsarinny [16] who have shown that if the large and small components of the Dirac wave function are expressed in b-splines of different orders, stable solutions free of spurious states are obtained. Thus, with b-splines, the large and small components are expressed as

$$\rightarrow P(r) = \sum_{i}^{N} c_i B_{i,k}(r), \quad Q(r) = \sum_{i}^{N+1} d_i B_{i,k'}(r), \quad k' = k + 1.$$ 

Assuming that $V(r)$ is known, e.g. $V(r) = -Z/r$, exchanging the functions in Eq.(2.12) with the b-spline representation and multiplying with

$$\left( \sum_{j}^{N} B_{j,k}(r) \quad \sum_{j}^{N+1} B_{j,k'}(r) \right)$$
on both sides from the left

$$\left( \sum_{j}^{N} B_{j,k}(r) \quad \sum_{j}^{N+1} B_{j,k'}(r) \right) \begin{pmatrix} V(r) \\ -c \left( \frac{d}{dr} - \frac{\kappa}{r} \right) \end{pmatrix} \begin{pmatrix} \sum_{i}^{N} c_i B_{i,k}(r) \\ \sum_{i}^{N+1} d_i B_{i,k'}(r) \end{pmatrix} = E \begin{pmatrix} \sum_{j}^{N} B_{j,k}(r) \quad \sum_{j}^{N+1} B_{j,k'}(r) \end{pmatrix} \begin{pmatrix} \sum_{i}^{N} c_i B_{i,k}(r) \\ \sum_{i}^{N+1} d_i B_{i,k'}(r) \end{pmatrix}$$

and integrating over the grid, the result can be expressed as

$$\begin{pmatrix} V^1 \\ K^1 \end{pmatrix} \begin{pmatrix} c \\ d \end{pmatrix} = E \begin{pmatrix} B^1 \\ 0 \end{pmatrix} \begin{pmatrix} c \\ d \end{pmatrix}$$

where $V^i$, $K^i$ and $B^i$ are matrices with the elements

$$V_{ji} = \int B_{j,k}(r)V(r)B_{i,k}(r)dr, \quad K^2_{ji} = -c \int B_{j,k}(r) \left( \frac{d}{dr} - \frac{\kappa}{r} \right) B_{i,k'}(r)dr$$

12
2.2 Numerical solution the the Radial Dirac equation using b-splines

\[ K^1_{ji} = c \int B_{j,k'}(r) \left( \frac{d}{dr} + \frac{\kappa}{r} \right) B_{i,k}(r)dr, \quad V^2_{ji} = \int B_{j,k'}(r) \left( V(r) + 2\epsilon^2 \right) B_{i,k}(r)dr \]

\[ B^1_{ji} = \int B_{j,k}(r)B_{i,k}(r)dr, \quad B^2_{ji} = \int B_{j,k'}(r)B_{i,k}(r)dr, \quad c_i = c_i, \quad d_i = d_i \]

and the problem to solve is a generalized eigenvalue problem. The integrals are calculated using Gauss–Legendre quadrature and the eigenvalue problem is solved with the help of LAPACK routines. The solution will include both the positive and negative energy solutions but for the purpose of this work the negative energy solutions are considered to be of small significance and therefore not included in the following calculations. For hydrogen-like atoms it is possible to solve the Dirac equation analytically and the analytical expression for the positive energies is

\[ E_{\text{analytical}} = c^2 \left( \frac{1}{\sqrt{\frac{Z^2\alpha_f^2}{n - |\kappa| + \sqrt{\kappa^2 - Z^2\alpha_f^2}}} - 1} \right) \]

and a comparison with the numerical calculated energies can be seen in Tab.2.1. The numerical calculations were done in a spherical box with a radius of 150 bohr with b-spline parameters \( k = 7, k' = 8 \) on a mixed knot sequence, exponential around the origin and then linear, with 250 unique knot-values. Calculations where the same order b-splines has been used for both functions \( P(r) \) and \( Q(r) \) are also displayed in the table and for \( \kappa = 1 \) an example of the spurious solutions can be seen.

2.2.2. Radial Dirac equation with Hartree-Fock potential

To be able to calculate the energies and wave functions of electrons in non-hydrogen like atoms, the electrostatic repulsion between electrons must be taken into consideration. The method described below will use the central field approximation, which means assuming that the total potential is spherically symmetric and the same for all electrons, which is a satisfying approximation when considering atoms with closed sub-shells. For \( N \) electrons in an atom the Hamiltonian can be expressed as

\[ H = H_D + H_{ee} \]

where

\[ H_D = \sum_i^N h_i, \quad h_i = c \alpha \cdot p_i + \beta c^2 + \frac{Z}{r_i} \quad (2.15) \]

and

\[ H_{ee} = \sum_{i<j}^N \frac{1}{r_{ij}}, \quad r_{ij} = |r_i - r_j|. \quad (2.16) \]
Table 2.1.: Solutions to the Dirac equation for hydrogen. The numerical values are calculated as described in sec. 2.2.1 in a spherical box with radius 150 Bohr radii, \( k' = 8 \) and a mixed knot sequence with 250 unique knot-values. Examples of spurious solutions can be seen for \( \kappa = 1 \) and \( k' = k \) and are marked red.

\[ H_{ee} \text{ is the added potential that takes into account electron-electron interactions. For that to be possible the electrons' positions, or at least average positions, must be known, i.e. the wave functions must be known. This is a somewhat circular argument, to be able to calculate the wave functions the wave functions must be known, but leads to an iterative method known as the Hartree-Fock method. The Hartree-Fock equation is then derived with the variational method and can be expressed as } \]

\begin{equation}
N \text{ single electron equations}
\end{equation}

\[ h_i |\psi_s(q_i)\rangle + u_{HF} |\psi_s(q_i)\rangle = E_s |\psi_s(q_i)\rangle \]
new set of solutions. This new set of solutions is then used to calculate another set of solutions and this is repeated until the solutions converge to a desired approximation, i.e. are self-consistent. Details about the numerical implementation can be found in sec. A.5.

2.2.3. Projected potential

The bound state solutions returned by the Hartree-Fock method are the ground state solutions, and the remaining solutions returned are continuum solutions for an electron affected by an atom with closed sub-shells. Modifications need to be made to better describe an electron that has been excited from a ground state to an excited (bound or continuum) state. The modifications must meet certain criteria: keep the Hamiltonian hermitian; not affect the ground state solutions; and remove the effect of one electron in the electron-electron potential, i.e. creating an electron hole, for the excited states. The adjustments to achieve this is here referred to as the projected potential, $u_{pp}$, and with the electron hole denoted $h$, it can be expressed as [17]

$$
\begin{align*}
\sum_p |p\rangle \langle p| &= 1 - \sum_b |b\rangle \langle b|, \\
\sum_q |q\rangle \langle q| &= 1 - \sum_d |d\rangle \langle d|
\end{align*}
$$

$$
\Rightarrow \quad u_{pp} = -\langle h| \frac{1}{r_>^b} |h\rangle + \sum_b \left( \langle h| \frac{1}{r_>^b} |bh\rangle + |bh| \langle h| \frac{1}{r_>^b} |bh\rangle - \sum_d \sum_b |b\rangle \langle bh| \frac{1}{r_>^b} |dh\rangle \langle d| \right).
$$

(2.18)

The calculations of the brackets are similar to the calculations for Hartree-Fock and the resulting contributions to the potential are, as for Hartree-Fock, added to their respective matrix element (in Eq.2.14). This addition to the potential is performed after the Hartree-Fock calculations are done and it has the same convergence criteria as the Hartree-Fock solutions. In the calculations presented in this thesis the “electron hole” was primarily chosen to be the orbital with the lowest binding energy occupied in the ground state.
3. Photon Interactions

The following sections will go over the methods used to calculate the two photon matrix element, $M_2$, with primary focus on the expressions describing the interactions and not the numerical implementation. Although it is conceptually fairly straightforward to implement the methods described in sec. 2.2 (e.g. b-splines and Gauss–Legendre quadrature) in this chapter, in practice it becomes slightly more cumbersome and much less brief.

3.1. One photon interaction

3.1.1. The electromagnetic field

To describe a system where an atom interacts with an electromagnetic field, the often utilized semi-classical approach was used. This means that the atomic system is quantized and the electromagnetic field is described classically. Describing the EM field classically is a satisfactory approximation as long as the photon density in the field is sufficiently high, and for the assumed field in the calculations for this thesis this will hold true.

The classical EM-field is described by electrical, $E$, and magnetic, $B$, field vectors

$$E = -\nabla \phi - \frac{\partial A}{\partial t}$$

$$B = \nabla \times A$$

where $\phi$ is a scalar field and $A$ is a vector field. By using Coulomb gauge and setting $\phi = 0$ (source free field), both $E$ and $B$ can be expressed by the vector field $A$ alone and the vector field itself can be expressed as a monochromatic plane wave with angular frequency $\Omega$.

$$\rightarrow A(r, t) = A_0 \hat{\varepsilon} \left( e^{i(k \cdot r - \Omega t)} + e^{-i(k \cdot r - \Omega t)} \right) \quad (3.1)$$

In the plane wave expression $\hat{\varepsilon}$ and $k$ are perpendicular to each other and referred to as the polarization and propagation vector respectively. The goal is to calculate the EM-field’s effect on an atom and consequently the properties of the outgoing electron (when a photon is absorbed and the atom is ionized). Though there are
other effects, in the systems considered here, this is the dominating effect and as a result the second term in Eq.3.1, which corresponds to emission, can be omitted. Furthermore, for the systems examined here, the wavelength of the wave will be much larger than the extension of the atom and \( e^{i k r} \approx 1 \) can be assumed. This is commonly known as the dipole approximation.

The equation to solve is achieved by making the substitution \( p \rightarrow p - A \) in the Hamiltonian in Eq.2.1.

\[
\rightarrow i \frac{\partial}{\partial t} \Psi = (H_0 - c \alpha \cdot A) \Psi, \quad (H_0 = c \alpha \cdot p + \beta c^2 + V(r)) \quad (3.2)
\]

Since the term \( c \alpha \cdot A \) can here be considered small and the equation can be solved with time-dependent perturbation theory, this results in the wave-function \( \rho(r, t) \) and can be expressed as

\[
\rho(r, t) = \sum_k \frac{\langle \psi_k | H_p | \psi_1 \rangle}{E_1 + \Omega - E_k} e^{-i(E_1 + \Omega)t}, \quad \text{with } H_p = c \alpha \cdot A \quad (3.3)
\]

and the time-independent part is then

\[
\rho(r) = \sum_k \frac{\langle \psi_k | H_p | \psi_1 \rangle}{E_1 + \Omega - E_k}. \quad (3.4)
\]

### 3.1.2. Calculation of the interaction element

With the assumption that \( A \) is a vector potential in the \( z \)-direction, i.e. linearly polarized light, (together with the approximation that \( A \) is space independent \( (e^{i k r} \approx 1) \) ) the interaction elements in 3.4, \( \langle \psi_k | H_p | \psi_1 \rangle \), can be expressed as

\[
\langle s | c \alpha \cdot A | a \rangle = c \langle s | \alpha_z | a \rangle A_0 = c \langle s | \alpha | a \rangle (-1)^{j_s - m_s} \begin{pmatrix} j_s & 1 \\ -m_s & 0 & m_a \end{pmatrix} A_0 \quad (3.5)
\]

where the last step is achieved with the use of Wigner-Eckarts theorem. The explicit calculation of the reduced matrix element is given by

\[
\langle s || \alpha_z || a \rangle = \langle P_s || \sigma_z || Q_a \rangle + \langle Q_s || \sigma_z || P_a \rangle \quad (3.6)
\]

\[
= i (-1)^{j_s + j_a + 1} \sqrt{6} \sqrt{2j_a + 1} \sqrt{2j_s + 1} \cdot \left((-1)^{l_P + 1/2 - j_a} \int P_s(r)Q_a(r) dr \begin{pmatrix} j_a & 1 \\ l_P, l_a & 1/2 \end{pmatrix} \delta (l_P, l_a) \right)
\]

\[
- (-1)^{l_P + 1/2 - j_s} \int Q_s(r)P_a(r) dr \begin{pmatrix} j_a & 1 \\ l_P, l_a & 1/2 \end{pmatrix} \delta (l_Q, l_P) \right)
\]

18
3.1 One photon interaction

where the curly brackets, \( \{ \} \), are sums of products of four 3-j symbols and are known as 6-j symbols [18]. The reduced matrix element in Eq.3.6 is often called the dipole element and when calculating it in the way described above, it is often referred to as using velocity gauge. An alternative way to calculate the dipole element is to use \( \mathbf{r} \cdot \mathbf{E} \) (potential energy of a dipole), referred to as length gauge, which can be expressed as

\[
\mathbf{r} \cdot \mathbf{E} = \mathbf{r} \cdot \left( -\frac{\partial \mathbf{A}}{\partial t} \right) = \mathbf{r} \cdot i \Omega \mathbf{A}.
\]

The resulting reduced matrix element can then be expressed as

\[
i\Omega \langle s|\mathbf{r}|a \rangle = i\Omega \langle s|C^a|a \rangle \left( \int P_s r P_a dr + \int Q_s r Q_a dr \right)
\]

with \( C^a_q = \sqrt{\frac{4\pi}{2k+1}} Y^k_q (\theta, \phi) \) [18].

(By using the commutator

\[
[H_0, \mathbf{r}] = -ic\alpha
\]

and evaluating the element

\[
\langle s||i[H_0, \mathbf{r}||a \rangle = i \langle s||[H_0 \mathbf{r} - \mathbf{r} H_0]|a \rangle = i\Omega_{sa} \langle s||r||a \rangle , \quad \text{where } \Omega_{sa} = E_s - E_a
\]

it is also possible to examine the connection between velocity and length gauge.)

### 3.1.3. Exterior complex scaling and the outgoing electron wave

The denominator in Eq.3.3 and 3.4 will be zero when \( E_k = E_1 + \Omega \), which means that the integral can be divided up into two parts, a principal value integral and a pole contribution, where the latter implies that the perturbed wave function, \( \rho \), must be complex. By rotating the radial dimension, \( r \), as follows

\[
r \rightarrow \begin{cases} 
  r & \text{for } r < R_0 \\
  R_0 + (r - R_0) e^{-i\eta} & \text{for } r \geq R_0
\end{cases}
\]

where \( R_0 \) defines where the rotated region begins and \( \eta \) is the rotation angle, the energies for the continuum states will take a detour in the complex plane, while leaving the bound states unaffected[19]. This will result in a is less cumbersome integral since the integrand is going towards zero when being sufficiently far out on the real axis (the line integral that connects the real axis with the segment in the complex plane is zero, Cauchy’s integral theorem, see, e.g., “Mathematical Methods for Physicists” by Arfken et al. [20]). The nature of the outgoing photo-electron wave is left unaffected in the unrotated region thus, for information that can only
be extracted from the asymptotic behavior of the outgoing wave function, it is necessary that \( R_0 \) is chosen at an appropriate distance from the origin. By using complex scaling the numerical calculations of \( \rho \) becomes very straightforward, since only the sum over the pseudo continuum is needed and no integral is required, the time-independent parts of the outgoing electron waves are given by

\[
\rho = \sum_s \frac{|s\rangle \langle s| \langle D| a\rangle}{\epsilon_a - \epsilon_s + \Omega}.
\]

(3.7)

where \( D \) is the dipole operator in either length or velocity gauge. Due to the selection rules for the dipole elements there are three possible outgoing waves (if \( j_a = 1/2 \) only two) for each orbital, e.g. \( np_{3/2} \rightarrow s_{1/2}, \, d_{3/2}, \) or \( d_{5/2} \).

### 3.1.4. Time Dependent Hartree-Fock or Random Phase Approximation with Exchange

The perturbed wave function, \( \rho \), as calculated in Eq.3.7, is an one particle function which works under the approximation that the remaining electrons are unaffected by the incident photon. As a result the outgoing electron is affected by a potential that is unaltered by the photon, e.g. the remaining electrons’ wave functions are not properly adjusted to the loss of an electron or to the effects of the EM-field. A substantial improvement would be achieved by taking a large amount of these many body effects (e.g. ground state correlation, multi-channel excitation, polarization of the atom due to the EM-field) into account by including a correction, \( \delta u_{HF} \), to the Hartree-Fock potential in the calculation of the dipole elements and hence the outgoing wave function.

\[
\rightarrow \langle s| D + \delta u_{HF} | a\rangle
\]

(3.8)

The method used here is sometimes referred to as time dependent Hartree-Fock and it is derived by adding time dependent one particle wave function as a perturbation, e.g.

\[
e^{\pm i\Omega t} \rho_0 (r),
\]

to the time dependent Schrödinger equation and solve it within the Hartree-Fock approximation scheme. The effects can consequently be expressed as

\[
\langle s| \delta u_{HF} | a\rangle
\]

\[
= \sum_b \left( - \langle bs| \frac{1}{r_{12}} | a\rho_{b \rightarrow r}^\dagger \rangle + \langle sb| \frac{1}{r_{12}} | a\rho_{b \rightarrow r}^\dagger \rangle + \langle s\rho_{b \rightarrow r} \frac{1}{r_{12}} | ab \rangle - \langle \rho_{b \rightarrow r}s \frac{1}{r_{12}} | ab \rangle \right)
\]

and as with the Hartree-Fock method it is an iterative calculation scheme and a solution is reached when a convergence criteria is met. A more common name for
3.1 One photon interaction

This method is Random Phase Approximation with Exchange, RPAE. The zeroth order of 3.8 is then expressed as

\[ M_0^{\pm} = \frac{\langle s | D | a \rangle}{\varepsilon_a - \varepsilon_s \pm \Omega} \]

with the corresponding wave function

\[ \rho_{a \rightarrow s}^{\pm} = \sum_s \frac{|s\rangle \langle s| D | a \rangle}{\varepsilon_a - \varepsilon_s \pm \Omega} = \sum_s |s\rangle M_0^{\pm} \]

Element of order \( i \) is expressed as

\[ M_i^{\pm} = \frac{\langle s | D | a \rangle + \langle s | \delta u_{HF} | a \rangle}{\varepsilon_a - \varepsilon_s \pm \Omega} \]

\[ = M_0^{\pm} + \sum_{b,r} \left[ \langle bs | \frac{1}{r_{12}} | ar \rangle + \langle sb | \frac{1}{r_{12}} | ar \rangle \right] M_i^{\pm} \]

\[ + \left( \langle sr | \frac{1}{r_{12}} | ab \rangle - \langle rs | \frac{1}{r_{12}} | ab \rangle \right) M_i^{\pm} \]

(A more detailed expression of the RPAE elements can be found in sec. A.9, also included is a representation of Eq. 3.8 using Goldstone diagrams.)

When the convergence criteria is met the final perturbed wave function is given by

\[ \rho_{a \rightarrow s}^{\pm} = \sum_s |s\rangle M_{final} \]

The method is invariant to the form of the dipole operator, velocity or length, if the sum over \( b \) includes all possible single electron ground states. However, it is not always necessary to include all single electron ground states, as some of the inner ground states might have a very small effect on the final result. Hence, to considerably reduce computation time, the sum often only includes the outer electrons that are believed to significantly contribute. By starting with results including the projected potential in the Hartree-Fock solutions, sec. 2.2.3, the convergence rate will be faster, but some of the integrals must be omitted in the calculations since they are equivalent to the effect of the projected potential (Eq.A.19 with \( K = 0 \)).

3.2. Second photon

When investigating the electrons two-photon interaction it is not unreasonable to assume that the dominant interaction is XUV+IR, i.e. the XUV-photon is absorbed first and that the electron is interacting with the IR-photon after leaving it’s bound state. With the calculation of the perturbed wave function after one photon completed (XUV), the matrix element after two photons (XUV+IR),

\[
M_2 = \sum_s \frac{\langle q | D | s \rangle \langle s | D | a \rangle}{\varepsilon_a + \Omega - \varepsilon_s}
\]

can be expressed as

\[
M_2 = \langle q | D | \rho \rangle \quad (3.9)
\]

where \( D \) is the dipole operator and

\[
\rho = \sum_s \frac{\langle s | D | a \rangle}{\varepsilon_a - \varepsilon_s + \Omega}
\]

with \( D = D + \delta u_{HF} \). The next step, to be able to calculate 3.9, is to find the radial function of the final state \( q \).

3.2.1. Constructing Coulomb functions

Before continuing it is necessary to discuss the Coulomb functions which here are used primarily in two ways; as reference points when evaluating phase shifts and to construct the phase shifted wave functions for an arbitrary \( r \). As already mentioned in sec.1.3, the radial wave function for a free electron in the presence of a pure Coulomb potential can be described as an irregular, \( G(r) \), and a regular, \( F(r) \), Coulomb function as

\[
\Psi_C (r) = G (r) \pm i F (r) \quad (3.10)
\]

and when \( r \to \infty \) the asymptotic form is

\[
\to \Psi_C (r) = \cos (\theta (r)) \pm i \sin (\theta (r)) = \exp (\pm i \theta (r))
\]

with \( \theta (r) = kr + \eta \ln (2kr) - l \frac{\pi}{2} + \sigma_\kappa \).

However, is also possible to express the irregular and the regular Coulomb functions for large but not necessarily infinite \( r \).

\[
F (r) = g \cos (\theta (r)) + f \sin (\theta (r))
\]

\[
G (r) = f \cos (\theta (r)) - g \sin (\theta (r))
\]
where \( f \) and \( g \) can be obtained through recursive sums \cite{25} and are slowly increasing and decreasing respectively and when \( r \rightarrow \infty \), \( f = 1, g = 0 \). \( \Psi_C \) in 3.10 in terms of \( f \) and \( g \) then becomes

\[
\rightarrow \Psi_C = f \cos (\theta (r)) - g \sin (\theta (r)) \pm i (g \cos (\theta (r)) + f \sin (\theta (r)))
\]

\[
= f (\cos (\theta) \pm i \sin (\theta (r))) \pm ig (\cos (\theta (r)) \pm i \sin (\theta (r)))
\]

\[
= (f \pm ig) \exp (\pm i \theta (r)) \tag{3.11}
\]

This makes it possible to compare photo-electron wave functions and find the phase shift, \( \delta \), that exists due to interactions with the photons and the atom, e.g. for \( \rho \), and also to create wave functions with the argument \( \theta + \delta \), at any \( r \). The latter will be of importance when calculating \( M_2 \) in Eq.3.9.

### 3.2.2. Final state

The final state, \( q \), will have a the specific energy \( \varepsilon_q = \varepsilon_i + \Omega \pm \omega \) and to find the radial function to such a state the original hamiltonian, with the hatree-Fock potential and the projected potential, can be used. Instead of solving an eigenvalue problem the system of equations is solved for the specific energy \( \varepsilon_q \).

\[
\rightarrow H \left| q \right\rangle = \varepsilon_q \left| q \right\rangle \quad \text{with} \quad \varepsilon_q = \varepsilon_i + \Omega \pm \omega
\]

The solutions will be on the form a phase shifted regular Coulomb function,

\[
q(r) = \begin{pmatrix}
P_q(r) \\
Q_q(r)
\end{pmatrix}
\]

\[
= A \left( \frac{1}{\varepsilon_q + 2c^2} \left( \frac{d}{dr} + \frac{c}{r} \right) \right) F(r, \delta_q)
\]

\[
= A \left( \frac{1}{\varepsilon_q + 2c^2} \frac{d}{dr} \right) \sin(\theta + \delta_q) \quad \text{when} \quad r \rightarrow \infty
\]

with an amplitude \( A \) and a phase shift \( \delta_q \). By knowing the function value of one of the Coulomb functions, e.g. \( AF(r, \delta_q) \), it is possible to calculate the function value of the second, e.g. \( AG(r, \delta_q) \) (see sec.A.10 for details). This is done to create the function

\[
A (G(r, \delta_q) + iF(r, \delta_q)) = A (f + ig) \exp (i (\theta (r) + \delta_q)) \tag{3.12}
\]

\(^1\text{Eq.14.5.8}\)
and to evaluate the argument and compare it to \((f + ig)\exp(i\theta(r))\) and obtain the phase shift \(\delta_q\).

\[ \rightarrow \delta_q = \arg [A(f + ig)\exp(i(\theta(r) + \delta))] - \arg [(f + ig)\exp(i\theta(r))] \]

The amplitude, \(A\), of \(q(r)\) will be arbitrary and the continuum solution is not normalizable in a traditional sense. To ensure that matrix elements, Eq.3.9, for different final states are comparable, the solutions \(q(r)\) are given amplitudes that assures equal rates/probability flux for outgoing waves, independent of energy. The rate/probability flux can be calculated by constructing the function

\[
q^+(r) = A\left(\frac{c}{\varepsilon_q + \frac{2c^2}{\pi}}\left(\frac{d}{dr} + \frac{\pi}{r}\right)\right) \exp(i(\theta(r) + \delta_q)) = \left(\frac{P_{q+}^+(r)}{Q_{q+}^+(r)}\right)
\]

to calculate the time derivative of the probability density, \(P\), of this outgoing wave,

\[
\frac{\partial}{\partial t} P = \frac{\partial}{\partial t} q^+ q^+ = i\left((Hq^+)q^+ - q^+HQ^+\right)
\]

inside a sphere

\[ \rightarrow \frac{\partial}{\partial t} \int PdV = \frac{\partial}{\partial t} \int i\left((Hq^+)q^+ - q^+HQ^+\right) dV. \tag{3.13} \]

This results in the expression

\[ ic[P_{q+}^+(r)^*Q_{q+}^+(r) - P_{q+}^+(r)Q_{q+}^+(r)^*]_{r=R} \]

which can be calculated for any \(R\) being sufficiently far out of the electron cloud. (The details of the steps between Eq. 3.13 and 3.14 can be found in sec.A.8.) Since the result will be the same for any \(R\) lets use \(r \rightarrow \infty\) to simplify the evaluation of 3.14 (and \(\varepsilon_q + 1/r + 2c^2 \approx 2c^2\)).

\[ \rightarrow ic[P_{q+}^+(r)^*Q_{q+}^+(r) - P_{q+}^+(r)Q_{q+}^+(r)^*]_{r=R} = \lim_{r \rightarrow \infty} ic(P_{q+}^+(r)^*Q_{q+}^+(r) - P_{q+}^+(r)Q_{q+}^+(r)^*) \]

\[
\begin{align*}
Q(r) &= \frac{1}{2c} \left(\frac{d}{dr} + \frac{\pi}{r}\right) P(r) = \frac{1}{2c} \frac{d}{dr} A e^{i(\theta(r) + \delta)} \text{when } r \rightarrow \infty \\
\text{using Eq. 2.10, 2.11 and } \varepsilon_q + 1/r + 2c^2 &\approx 2c^2 \\
&= ic \left(A e^{-i(\theta(r) + \delta_q)} \frac{d}{dr} A e^{i(\theta(r) + \delta_q)} - A e^{i(\theta(r) + \delta_q)} \frac{d}{dr} A e^{-i(\theta(r) + \delta_q)}\right) \\
&= ic \left(\frac{ikA^2}{2c} e^{-i(\theta(r) + \delta_q)} e^{i(\theta(r) + \delta_q)} + \frac{ikA^2}{2c} e^{i(\theta(r) + \delta_q)} e^{-i(\theta(r) + \delta_q)}\right) \\
&= -A^2 k
\end{align*}
\]
3.2 Second photon

By calculating this and dividing the function $q(r)$ with the square root of the result, $A\sqrt{k}$, gives the solution the amplitude $A_q = 1/\sqrt{k}$ and is often referred to as energy normalized. This ensures that the matrix elements, $\langle q | D | \rho \rangle$, with different final solutions, $q$, are comparable.

It should be noted that $\rho$ does not need to be normalized, however, Eq. 3.14 is used to determine the amplitude of $\rho$ (and when cross-section are calculated).

### 3.2.3. Two photon element

One major obstacle to solve when calculating the radial part in the reduced matrix element of Eq. 3.9 is that both functions are continuum functions and the radial part consequently needs to be integrated for $r \to \infty$ to achieve a result. Depending on if velocity or length gauge is being utilized the integrals will look slightly different, but for simplicity lets first only consider the length gauge integrals.

$$\rightarrow \int_{0}^{\infty} P_q(r)rP_\rho(r)dr + \int_{0}^{\infty} Q_q(r)rQ_\rho(r)dr$$

Either integral can be divided into two parts, e.g.

$$\int_{0}^{R_p} P_q(r)rP_\rho(r)dr + \int_{R_p}^{\infty} P_q(r)rP_\rho(r)dr$$

where the first integral is over an interval contained on the grid where the functions are properly represented and thus easily calculated. By knowing the amplitudes and the phase shifts, $A_q$, $A_\rho$, $\delta_q$ and $\delta_\rho$, it is possible to calculate the function values needed, using Eq. 3.11, to do the integration of the second integral along the imaginary axis. This is beneficial because by using Cauchy’s integral theorem and by choosing an appropriate integral path along the imaginary axis the integrand will converge. This becomes clear when examining the second integral and the asymptotic behaviors of the wave functions,

$$\rightarrow \int_{R_p}^{R_p+iB} A_q \sin (\theta_q(r) + \delta_q) r A_\rho e^{i(\theta_\rho(r)+\delta_\rho)}dr$$

$$= \frac{A_q A_\rho}{2i} \int_{R_p}^{R_p+iB} \left( e^{i(\theta_q(r)+\delta_q)} - e^{-i(\theta_q(r)+\delta_q)} \right) r e^{i(\theta_\rho(r)+\delta_\rho)}dr$$

The phase terms, $l^\pi_T$, $\sigma_\kappa$ and $\delta$, are not $r$-dependent and can be expressed as a constant, $C$, outside the integral, included in this is also the ln-term, $\eta \ln(2kr)$,
since at very large \( r \) its rate of change will be negligible compared to \( kr \).

\[
s → \frac{A_q A_p}{2i} C \int_{R_p}^{R_p+iB} (e^{ik_q r} e^{ik_p r} - e^{-ik_q r} e^{ik_p r}) \, dr
\]

\[
= \frac{A_q A_p}{2i} C \int_{R_p}^{R_p+iB} (r e^{i(k_q+k_p)r} - r e^{i(k_p-k_q)r}) \, dr
\]

\[
= \frac{A_q A_p}{2i} C \left( \int_{R_p}^{R_p+iB} r e^{i(k_q+k_p)r} \, dr - \int_{R_p}^{R_p+iB} r e^{i(k_p-k_q)r} \, dr \right)
\]

If integrating along the positive imaginary axis, \( B > 0 \), the argument \( i (k_q + k_p) r = -(k_q + k_p) r \) will go towards zero and subsequently it is possible to find a \( B \) where the integral has converged. In the second integral the integration path will depend on if \( k_q < k_p \) or \( k_q > k_p \), i.e. if an IR-photon was emitted or absorbed. In the latter case, \( k_p - k_q < 0 \), a path along the negative imaginary axis is needed to get a converging result, while for the first case a path along the positive imaginary axis will work. Since the result should be independent on the choice of \( R_p \), in the numerical calculations the full integrals are evaluated for several different \( R_p \) to assure that the result is correct. This method will work both for length gauge, as used in this example, and for velocity gauge.

With \( \langle q | \mathcal{D} | \rho \rangle \) calculated it is possible to set up the relativistic version of Eq(1.2), with \( j \) and \( \lambda \) being the final and intermediate total angular momentum it can be expressed as

\[
→ \arg \left[ \sum_{j,\lambda,m=\pm \frac{1}{2}} M_{j\lambda m}^{2a} \left( \frac{A_q A_p}{2c} \right)^{j\lambda m} j^l a (t_{\sigma_n} + \delta) \right] (3.15)
\]

\[
= \Delta \delta = 2 \omega \tau_{\text{atom}}
\]

which was the ambition outlined in sec.1.3.
4. Results

The results from the Fortran program, which is performing the heavy calculations, can be produced without taking into account the quantum number $m_j$, this is something that conveniently can be included later. In experiments the photoelectrons are either detected at a specific angle, often then in the direction of the polarization, or collected with a magnetic-bottle spectrometer. The time delay results presented here are all for electrons emitted in the direction of the polarization of the electromagnetic field and the calculations has been done with $m_j = \pm 1/2$. However, calculations including a wider range of $m_j$ was performed for the data in Paper I [26]. It should also be noted that in all the calculations the energy of the IR-photon is 1.55 eV ($\omega = 1.55 \text{ eV}$)

4.1. Overview of photo-electron delays $\tau_{atom}$, $\tau_{wigner}$ and $\tau_{cc}$

The result from 3.15, $\Delta \delta$, can be formally expressed as a sum of two terms, where each term can be interpreted as connected to one of the exchanged photons.

$$2\omega \tau_{atom} = \Delta \delta = \Delta_{wigner} + \Delta_{cc} \quad \rightarrow \quad \frac{\Delta \delta}{2\omega} = \tau_{atom} = \tau_{wigner} + \tau_{cc}$$

The first term, $\tau_{wigner}$, is due to the phase-shift associated with the transition induced by the first photon, i.e. the Wigner delay [7], and the second term, $\tau_{cc}$, to the phase-shifts associated with the continuum-continuum transition. The final state can be reached by absorbing a XUV-photon with energy $(2N + 1)\omega$ and then emitting an IR-photon with energy $\omega$, or absorbing a XUV-photon with energy $(2N - 1)\omega$ and then absorbing an IR-photon with energy $\omega$. In the former case the phase-shift due to the XUV-photon is expressed as $\theta^+$ and the phase shift due to the IR-photon is expressed as $\varphi^-$, and similarly in the latter case the phase-shifts are $\theta^-$ and $\varphi^+$. Subsequently the two terms can then be expressed as

$$\rightarrow \quad \Delta_{wigner} = \theta^+ - \theta^- \quad \Delta_{cc} = \varphi^+ - \varphi^-.$$ 

where $\theta^\pm$ is information which can be extracted from the resulting wave functions of the RPAE calculations. The Wigner time delay is defined as the derivative of the phase with respect to energy,

$$\rightarrow \quad \tau_{wigner} = \frac{d\theta}{dE}$$
which can be approximated with
\[ \tau_{\text{wigner}} \approx \frac{\theta^+ - \theta^-}{2\omega}. \]

This makes it possible to examine the phase shift due to the interaction with the second photon by calculating the difference between \( \tau_{\text{atom}} \) and \( \tau_{\text{wigner}} \):
\[ \tau_{\text{cc}} = \tau_{\text{atom}} - \tau_{\text{wigner}}. \]

Non-relativistic calculations [27, 5] have shown that in different elements and sub-shells this difference is remarkably similar and can be well approximated with an analytical formula, which can be worked out by looking at continuum-continuum transitions in the presence of a Coulomb potential. With the results presented here it is possible to determine if this also holds for relativistic calculations.

These three properties, \( \tau_{\text{atom}} \), \( \tau_{\text{wigner}} \) and \( \tau_{\text{cc}} \), for different atoms and orbitals, are the results that primarily will be presented and compared to non-relativistic calculations and experimental measurements of \( \tau_{\text{atom}} \). The methods used for the non-relativistic calculations are the same as described in reference [5].

**Figure 4.1:** Atomic delay, \( \tau_{\text{atomic}} \), for argon 3p\(_{3/2}\) calculated with both length and velocity gauge. Also displayed is the Wigner delay, \( \tau_{\text{wigner}} \), which is gauge invariant as expected (all orbitals were included in the RPAE calculations).
4.2. Velocity or length gauge

When starting this work it was assumed that, with the methods used, the choice of gauge would only give negligible differences. The reasoning being that the result after the first photon is invariant to gauge (assuming enough orbitals are included in the RPAE calculations) and then for the second low energy photon the choice of gauge would not have a significant effect on the result. This turned out to be incorrect and the choice of gauge has a substantial effect on the result after the second photon. An example of the difference can be seen in Fig. 4.1 where the atomic delay in argon $3p_{3/2}$ has been calculated with both length and velocity gauge. The same figure also displays the Wigner delays and it is clear that the difference in the atomic delays originates from the calculations of the second photon interaction.

![Figure 4.2: Non-relativistic calculations of atomic delay for ionizing from Argon 3p along the polarization axis. The delays calculated using velocity gauge are the blue lines. The solid blue line is a regular calculation with XUV+IR, the dotted blue line has included IR+XUV, the dashed-dotted blue line also includes hole fluctuations and the dashed blue line includes, in addition to IR+XUV and hole fluctuations, full two-photon RPAE calculations. The red solid line is calculated using length gauge with only XUV+IR and the red dashed line is length gauge with all the mentioned interactions included. A more detailed description can be found Paper II.](image)

This discrepancy between the two choices was first noticed when comparing rela-
Chapter 4 Results

tivistic velocity gauge results with non-relativistic length gauge results (for lighter elements). It was not obviously clear at first, but after implementing length gauge calculations in the relativistic program and velocity gauge calculations in the non-relativistic program, it was possible to demonstrate that the discrepancy is due to choice of gauge. Inclusion of additional effects in the interaction with the second photon is needed to achieve invariant results. Though there has been some work to include the essential effects in the relativistic code this is still not fully accomplished. However, these inclusions seem to predominately effect the velocity gauge result and to only have minor effects on the calculations using length gauge.

This can be concluded since the same effects are observed in the non-relativistic calculation which is much further along in producing gauge independent result after two photons. In Fig. 4.2 the effects on velocity gauge calculations are shown when additional effects are added, while compared to a length gauge calculations. As can be seen these contributions have a significant effect on the velocity gauge results, but also that it is eventually possible to find good agreement between velocity and length gauge. In comparison, when these effects are included in length gauge calculations the correction to the results are very minor and the dominant interaction seems to be XUV+IR, which is also displayed in Fig. 4.2.

Initially the intention had been to use velocity gauge in the relativistic calculations but due to these findings, which strongly indicates that length gauge allows for a more straightforward calculation, all two photon data presented here are in length gauge unless stated otherwise.

4.3. Delays in the outer orbitals

Calculated results for $\tau_{atom}$, $\tau_{wigner}$ and $\tau_{cc}$ in argon, krypton, xenon and radon are presented in Fig. 4.3 to Fig. 4.6 and compared to non-relativistic calculations of $\tau_{atom}$. In argon the difference in delays between electrons originating from $3p_{3/2}$ and $3p_{1/2}$ is barely noticeable and are very similar to the non-relativistic calculations, which can be expected, but when the atoms are getting heavier the differences becomes more apparent. In the radon calculations there is an interval around the ionization energies for $5d_{5/2}$ and $5d_{3/2}$ where no data is presented and the reasons behind this includes convergence and resonance problems.

Non-relativistic calculations for lighter elements have been compared to experimental data and show overall good agreement. This includes measurement of delay differences between: electrons originating from $2p$ and $2s$ in neon [28]; valence electrons in Helium, Neon and Argon [29]; and different photoelectron angles in argon [30]. However, the delay between electrons originating from $3p$ relative to those from $3s$ [2] in argon in the region of the Cooper minimum\(^1\) has not yet been possible

\(^1\)Cooper minima are minima in the cross-sections which are caused by non-overlapping wave functions in the dipole element, and here it is due to the $3p \rightarrow d$ cross-sections.
4.3 Delays in the outer orbitals

Figure 4.3.: Calculated delays for argons 3p orbitals. The characteristics of the curve are due to a Cooper minima that also can be noticed when examining the cross-section. The difference between relativistic and non-relativistic calculations are small which is due to the lower nuclear charge of Argon.

to explain, and the reason for this is still an open question. Since the relativistic calculations agrees very well with the non-relativistic calculations for the these elements it will not have much to contribute; instead the focus is on the heaver elements. Delay differences between electrons originating from the outer \( p_{3/2} \) and \( p_{1/2} \) orbitals have been measured for both Krypton and Xenon [31]. In Fig. 4.7 and Fig. 4.8 these measurement are compared to differences that can be extracted from the atomic delays that are presented in Fig. 4.4 and Fig. 4.5. The Krypton measurements agrees fairly well with the calculations but in Xenon there are discrepancies in 3 out of 5 measurements. The region in the vicinity of the ionizing threshold for \( 5s_{1/2} \) is affected by resonances and might not be well represented in the RPAE calculations which could explain the disagreement in the second measurement point. In the region between 26-33 eV there is a high density of doubly excited states which are not included in the RPAE calculations and is likely the reason for the large discrepancies between the calculations and the measurements in this region.

The resulting \( \tau_{cc} \) is very similar for the different elements and agrees well with what has been observed in non-relativistic calculations. As it can be seen in Fig. 4.9 the analytical formula developed for non-relativistic calculations also seem to hold well for the heavier systems presented here and it appears to be a universal behavior. It should be noticed that close to threshold energies the analytical formula starts to deviate from the numerical calculations, this is displayed in Fig. 4.10, which is
Chapter 4

Figure 4.4.: Calculated delays for krypton $4p$ orbitals. Included is also two vertical lines indicating where the absorbed photon energy is equal to the binding energy (Hartree-Fock energy) for $4s_{1/2}$ with a solid line for $4p_{3/2}$ and a dashed for $4p_{1/2}$.

Figure 4.5.: Calculated delays for xenon $5p$ orbitals. Included is also two vertical lines indicating where the absorbed photon energy is equal to the binding energy (Hartree-Fock energy) for $5s_{1/2}$ with a solid line for $5p_{3/2}$ and a dashed for $5p_{1/2}$.
4.4 Inner orbitals

Figure 4.6.: Calculated delays for radon $6p$ orbitals. As in the earlier figures there are two vertical lines indicating where the absorbed photon energy is equal to the binding energy (Hartree-Fock energy) for $6s_{1/2}$ with a solid line for $6p_{3/2}$ and a dashed for $6p_{1/2}$, but also two dotted lines indicating the range where it reaches the energies of the $5d$ orbitals. The left line is at the energy difference between $6p_{3/2}$ and $5d_{5/2}$ while the right line is at the difference between $6p_{1/2}$ and $5d_{3/2}$.

observed in the non-relativistic calculations as well.

4.4. Inner orbitals

The difference between relativistic and non-relativistic calculations in the former section are noticeable, especially for the heavier atoms, and it can primarily be attributed to the differences in the bound state energies for the orbitals due to the fine structure. Though this is important, exploring areas where the difference is larger and not primarily caused by energy differences due to fine structure, can be of further interest. One such example is provided by the Xenon $4d$ orbitals, which is the focus of the calculations discussed below.

The primary motivation for this work was to investigate phase differences in photoelectrons after interacting with two photons. It is however possible to extract other interesting information from these numerical calculations and some of that information includes one photon interaction results such as cross-sections, branching ratios and phase-shifts. In addition to being interesting in itself, the results can also be used to validate some aspects of the calculated one photon interactions by com-
Figure 4.7.: The difference between the atomic delays for $4p_{3/2}$ and $4p_{1/2}$ in Krypton. The solid blue line is the calculations and the black filled circles are the experimental measurements\cite{31}. The dashed vertical line marks the experimental ionization threshold for $4s_{1/2}$ and the dot-dash line the Hartree-Fock energy for $4s_{1/2}$.

Figure 4.8.: The difference between the atomic delays for $5p_{3/2}$ and $5p_{1/2}$ in Xenon. The solid blue line is the calculations and the black filled circles are the experimental measurements\cite{31}. The dashed vertical line marks the experimental ionization threshold for $5s_{1/2}$ and the dot-dash line the Hartree-Fock energy for $5s_{1/2}$.
4.4 Inner orbitals

Figure 4.9.: $\tau_{cc}$ for argon, krypton, xenon and radon. As can be seen, the delay caused by the second photon is generally very similar for all elements, with small differences at the lower energies.

Figure 4.10.: $\tau_{cc}$ for argon, krypton, xenon and radon in the interval where the analytical formula start to deviate from the numerically calculated results.
paring with similar calculations. In Fig.4.11 the branching ratios for Xe 4d (ratio of cross-sections for 4d\(_{5/2}\) and 4d\(_{3/2}\)) are displayed together with experimental data \(^2\) and as can be seen the results agree well, but obviously differs significantly from what you would expect with a non-relativistic result (\(\frac{\sigma}{\sigma^0} = 1.5\)). In the same figure there is also a curve calculated from the non-relativistic cross-sections by shifting 6 of the electrons according to the 4d\(_{5/2}\) (Hartree-Fock) energy level, −71.60 eV, and 4 of the electrons according the 4d\(_{3/2}\) (Hartree-Fock) energy level, −73.73 eV, and then evaluating the branching ratio. This is just an approximation and is not expected to overlap well with the relativistic results, however, the large difference below 100 eV (photon energy) reveals that there are interesting effects to investigate in this region where the energy difference is not the primary reason behind this ratio. In Fig.4.12 the calculated delays from Xenon 4d orbitals are presented, however it

![Xenon 4d Branching ratios](image)

**Figure 4.11.** Branching ratio for Xenon 4d\(_{5/2}\)/4d\(_{3/2}\), calculated and experimental measurements[32]. Included as well is an approximation of the branching ratio calculated from the non-relativistic cross-sections but with shifted energies to 4d\(_{5/2}\) and 4d\(_{3/2}\). The horizontal line is the statistical ratio.

does not seem to reveal anything of great interest. The behavior of the Wigner delay at the lower energies, larger values with a higher rate of change, is similar to what is presented in the other figures, but here it is not as close to the threshold. This

---

\(^2\)This reference also displays additional experimental data and similar relativistic calculations which agrees very well with the calculations displayed in Fig. 4.11.
4.4 Inner orbitals

could be an indication of something interesting but to be certain the calculations need to extend down to lower energies. Unfortunately, in the energy interval of interest, there are a convergence problems in the RPAE calculations that need to be solved. However, it should be noted that $\tau_{cc}$ shows the same behavior as in the other calculations.

![Image of a graph showing calculated delays from Xenon 4d orbitals.](image)

**Figure 4.12.:** Calculated delays from Xenon 4d orbitals.
5. Conclusion and Outlook

5.1. Conclusion and Summary

For lighter elements the relativistic calculations agrees well with the non-relativistic calculations which could be seen in Fig. 4.3 where only a minor difference can be noticed. Elements even lighter were not displayed here since the differences are very small and not easily detected. In argon the shapes of the time delay curves, which are there due to the cooper minima, aides in the detection of the differences.

For Kryptons and Xenons outer $p$-orbitals it is possible to compare to experimental measurements, however in Xenon the calculations did not agree well with the measurements. This is most likely, as already mentioned, due to interactions that are not included in the RPAE calculations. The Hartree-Fock energies for the $p$-orbitals are very close to the experimentally measured ionization thresholds, but for the closest $s$-orbitals, which are indicated in Fig. 4.7 and Fig. 4.8, there is a significant difference. Taking this into account in the Xenon calculation will not improve the comparison, but in Krypton it might have a small effect.

For all the elements presented here, Fig. 4.9 shows that at energies well over the thresholds the delays caused by the second (IR) photon can be described with an analytical formula. This indicates that one-photon (numerical) calculations often can be sufficient when theoretically investigating delays caused by two-photon interactions, in the way it is described in this thesis, since the effects of the second photon can be well approximated and does not depend on the initial, intermediate or final state of the photoelectron.

The branching ratio for $4d$-orbitals agrees well with experimental measurements and very well with earlier calculations, however there are some convergence problems that needs to be solved and that is being worked on at the moment. With this accomplished, further investigation of the atomic delays in this region will be possible.

In conclusion, it is possible with the Fortran program created during this work to perform the numerical calculations needed to produce useful results. This was the initial goal, to be able to study photoelectrons after interacting with two photons, and it was expected to be fairly straightforward. However, the encounter of unexpected discrepancies between velocity and length gauge calculations made this into a bit more challenging task. These results and possible solutions were discussed in
sec. 4.2, but work is still ongoing in this area to better understand the underlaying mechanisms behind the gauge variance.

5.2. Outlook

Much of the focus in this thesis was on photoelectrons originating from the outer orbitals of noble gases. With the software working as intended, the efforts can be focused on thoroughly investigating problems of particular interest, e.g. specific elements, orbitals and energy intervals. For example, the initial analysis of ionizations from the $4d$ orbitals in Xenon performed this thesis. The numerical calculations can also extend to a wider range of elements than just noble gases, it is also possible to make these calculations on closed sub-shell ions.

Primarily the results presented here was the time delay of photoelectrons traveling in the direction of the polarization of the electromagnetic field, however, this not due to a limitation in the software. As already mentioned briefly, calculations can be done for any $m_j$ (and angles), and the program contributed with data for Paper I, *Fano’s propensity rule in angle-resolved attosecond pump-probe photoionization* [26]. The article primarily considered lighter elements, hence relativistic effects was not of importance, but it further demonstrates the abilities of the program, which opens up for a wide range of possible calculations.

Hopefully the results presented here and the program produced to perform these calculations, with further use and improvements, will contribute to the understanding of ionization processes.
A. Appendix

A.1. Spin-angular functions

These functions are normalized eigenfunctions of $J^2$, $J_3$, $L^2$ and $S^2$ and are constructed out of a combination of the Pauli spinor and spherical harmonics of order $l$ [33, 34].

For $j = l + \frac{1}{2}$

$$\Psi_{jl}^{m_j} = \sqrt{\frac{l + m_j + \frac{1}{2}}{2l + 1}} Y_{l}^{-m_j - \frac{1}{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sqrt{\frac{l - m_j + \frac{1}{2}}{2l + 1}} Y_{l}^{m_j + \frac{1}{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

For $j = l - \frac{1}{2}$

$$\Psi_{jl}^{m_j} = -\sqrt{\frac{l - m_j + \frac{1}{2}}{2l + 1}} Y_{l}^{-m_j - \frac{1}{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sqrt{\frac{l + m_j + \frac{1}{2}}{2l + 1}} Y_{l}^{m_j + \frac{1}{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

A.2. B-Splines

B-splines, or basis splines, are piecewise polynomial functions designed for the purpose of approximating arbitrary functions. The arbitrary function, $f(x)$, is approximated as a linear combination of b-splines, $B_{i,k}$,

$$f(x) = \sum_{i}^{N} c_i B_{i,k}$$

where $c_i$ are coefficients. The b-splines are defined on a grid with a certain number of points, $t_i$, usually referred to as a knot sequence where $t_i \leq t_{i+1}$. B-splines with a polynomial degree $k - 1$ are derived with a recursion formula

$$B_{i,1}(x) = \begin{cases} 1 & \text{if } t_i \leq x < t_{i+1} \\ 0 & \text{otherwise} \end{cases}$$

$$B_{i,k}(x) = \frac{x - t_i}{t_{i+k-1} - t_i} B_{i,k-1}(x) + \frac{t_{i+k} - x}{t_{i+k} - t_{i+1}} B_{i+1,k-1}(x)$$
where $k$ is called the order of the b-splines. In Fig. A.1 b-splines of different orders are displayed. B-splines defined as described above will have $k - 2$ continuous derivatives where the derivatives of b-splines of order $k'$ can be expressed as b-splines of order $k' - 1$.

$$\frac{dB_{i,k'}(x)}{dx} = (k' - 1) \left( \frac{B_{i,k'-1}(x)}{t_{i+k'-1} - t_i} - \frac{B_{i+1,k'-1}(x)}{t_{i+k'} - t_{i+1}} \right)$$

The properties of the b-splines make it possible to reach high accuracy in many numerical calculations and still have sensible computational times. [35, 36]

In the calculations performed for this thesis, the b-splines were generated by either the Fortran routine bsplvb [35] or a modified well-tested version of bsplvb that can handle complex grids.

### A.3. Details about eigenvalue $\kappa$

Operator $K$ which is defined by

$$K = \beta \Sigma \cdot J - \beta \frac{\hbar}{2} = \beta (\Sigma \cdot L + \hbar) = \begin{pmatrix} \sigma \cdot L + \hbar & 0 \\ 0 & -(\sigma \cdot L + \hbar) \end{pmatrix}$$
and the eigenvalue \(-\kappa \hbar\). To provide further information about \(\kappa\) it is useful to look at the relation between \(\kappa\) and \(j\). First by looking at \(K^2\)

\[
K^2 = \beta (\Sigma \cdot L + \hbar) \beta (\Sigma \cdot L + \hbar) = (\Sigma \cdot L + \hbar)^2
\]

[using \((\sigma \cdot A) (\sigma \cdot B) = A \cdot B + i \sigma \cdot (A \times B)] \quad (A.1)

\[
= L^2 + i \Sigma \cdot (L \times L) + 2\hbar \Sigma \cdot L + \hbar^2
\]

[using \(L \times L = i\hbar L\)]

\[
= L^2 + \hbar \Sigma \cdot L + \hbar^2
\]

and then \(J^2\)

\[
J^2 = \left(L + \frac{\hbar}{2} \Sigma \right)^2 = L^2 + \hbar \Sigma \cdot L + 3\frac{\hbar^2}{4}
\]

it becomes clear that \(K^2\) can be expressed as

\[
K^2 = J^2 + \frac{\hbar^2}{4}.
\]

From this follows that the eigenvalues of \(K^2\) and \(J^2\) are related by

\[
\kappa^2 \hbar^2 = \left(j(j + 1) + \frac{1}{4}\right) \hbar^2 = \left(j^2 + j + \frac{1}{4}\right) \hbar^2 = \left(j + \frac{1}{2}\right)^2 \hbar^2
\]

and that

\[
\kappa = \pm \left(j + \frac{1}{2}\right). \quad (A.2)
\]

Further insight will be gained by writing the four-component wave function as

\[
\Psi = \begin{pmatrix} \Psi_A \\ \Psi_B \end{pmatrix}
\]

where \(\Psi_A\) and \(\Psi_B\) are two-component wave functions, and analyzing how \(K\) and \(J^2\) act on these wave functions.

\[
K \Psi = \begin{pmatrix} \sigma \cdot L + \hbar & 0 \\ 0 & -(\sigma \cdot L + \hbar) \end{pmatrix} \begin{pmatrix} \Psi_A \\ \Psi_B \end{pmatrix} = -\kappa \hbar \Psi
\]

\[
\rightarrow (\sigma \cdot L + \hbar) \Psi_A = -\kappa \hbar \Psi_A, \quad (\sigma \cdot L + \hbar) \Psi_B = \kappa \hbar \Psi_B \quad (A.3)
\]
\[ J^2 \Psi = J^2 \Psi_{A,B} = \left( L + \frac{\hbar}{2} \sigma \right)^2 \Psi_{A,B} \]
\[ = \left( L^2 + \hbar \sigma \cdot L + 3 \frac{\hbar^2}{4} \right) \Psi_{A,B} = j \left( j + 1 \right) \hbar^2 \Psi_{A,B} \tag{A.4} \]

When acting on the two-component wave functions \( \Psi_A \) and \( \Psi_B \), the operator \( L^2 \) can be expressed as
\[ L^2 = J^2 - \hbar \sigma \cdot L - 3 \frac{\hbar^2}{4} \]

and any two-component eigenfunction of \( J^2 \) and \( \sigma \cdot L + \hbar \) is also an eigenfunction of \( L^2 \). It is not a four-component eigenfunction, as \( L^2 \) does not commute with \( H \), but \( \Psi_A \) and \( \Psi_B \) separately are eigenfunctions of \( L^2 \) with eigenvalues \( l_A (l_A + 1) \hbar^2 \) and \( l_B (l_B + 1) \hbar^2 \). This makes it possible to rewrite Eq.(A.3) by using Eq.(A.4),
\[ (\sigma \cdot L + \hbar) = \frac{1}{\hbar} \left( J^2 - L^2 \right) + \frac{\hbar}{4} \]
and to obtain
\[ -\kappa = j \left( j + 1 \right) - l_A (l_A + 1) + \frac{1}{4}, \quad \kappa = j \left( j + 1 \right) - l_B (l_B + 1) + \frac{1}{4}. \tag{A.5} \]

As can be seen, for a specific value of \( j \) there are two possible values of \( l \) corresponding to two possible values of \( \kappa \). By using Eq.(A.2) and Eq.(A.5) it is possible to determine the values of \( l \) for a specific \( \kappa \).

\[ \rightarrow \kappa = \begin{cases} 
   l & \text{if } j = l - \frac{1}{2} \\
   - (l + 1) & \text{if } j = l + \frac{1}{2}
\end{cases} \]

**A.4. Radial Dirac equation with B-Splines**

\[
\begin{pmatrix}
-\frac{Z}{r} \\
c \left( \frac{d}{dr} + \frac{\kappa}{r} \right)
\end{pmatrix}
\begin{pmatrix}
F(r) \\
G(r)
\end{pmatrix}
= E
\begin{pmatrix}
F(r) \\
G(r)
\end{pmatrix}
\tag{A.6}
\]

Functions \( F \) and \( G \) are expressed as combinations of b-splines
\[ \rightarrow F(r) = \sum_i c_i B_{i,k}(r), \quad G(r) = \sum_i d_i B_{i,k'}(r), \quad k' = k + 1 \]

Expressing the functions in Eq.(A.6) with the b-spline representation and multiplying with
\[ \left( \sum_j^N B_{j,k}(r) \sum_j^{N+1} B_{j,k'}(r) \right) \]
on both sides from the left

\[
\left( \sum_j^N B_{j,k}(r) \sum_{j,+1}^{N+1} B_{j,k'}(r) \right) \left( \begin{array}{cc}
\frac{Z}{r} & -c \left( \frac{d}{dr} - \frac{\xi}{r} \right) \\
c \left( \frac{d}{dr} + \frac{\kappa}{r} \right) & -\frac{Z}{r} - 2c^2 \end{array} \right) \left( \begin{array}{c}
\sum_i^N c_i B_{i,k}(r) \\
\sum_i^{N+1} d_i B_{i,k'}(r) \end{array} \right)
\]

\[= E \left( \sum_j^N B_{j,k}(r) \sum_{j,+1}^{N+1} B_{j,k'}(r) \right) \left( \begin{array}{c}
\sum_i^N c_i B_{i,k}(r) \\
\sum_i^{N+1} d_i B_{i,k'}(r) \end{array} \right).\]

Integrating over the grid the results can be expressed as

\[
\left( \begin{array}{cc}
H_{11} & H_{12} \\
H_{21} & H_{22} \end{array} \right) = E \left( \begin{array}{c}
B_{11} \\
B_{22} \end{array} \right)
\]

with the matrix elements

\[H_{11} = -\sum_j^N \sum_i^N c_i \int B_{j,k}(r) \frac{Z}{r} B_{i,k}(r) dr \]

\[H_{12} = -c \sum_j^N \sum_{i,+1}^{N+1} d_i \int B_{j,k}(r) \left( \frac{d}{dr} - \frac{\kappa}{r} \right) B_{i,k'}(r) dr \]

\[H_{21} = c \sum_j^{N+1} \sum_i^N c_i \int B_{j,k'}(r) \left( \frac{d}{dr} + \frac{\kappa}{r} \right) B_{i,k}(r) dr \]

\[H_{22} = -\sum_j^{N+1} \sum_{i,+1}^{N+1} d_i \int B_{j,k'}(r) \left( \frac{Z}{r} + 2c^2 \right) B_{i,k'}(r) dr \]

\[B_{11} = \sum_j^N \sum_i^N c_i \int B_{j,k}(r) B_{i,k}(r) dr, \quad B_{22} = \sum_j^{N+1} \sum_{i,+1}^{N+1} d_i \int B_{j,k'}(r) B_{i,k'}(r) dr.\]

Expressing each of these elements as matrices yields

\[
\left( \begin{array}{cc}
V^1 & K^2 \\
K^1 & V^2 \end{array} \right) \left( \begin{array}{c}
c \\
d \end{array} \right) = E \left( \begin{array}{cc}
B^1 & 0 \\
0 & B^2 \end{array} \right) \left( \begin{array}{c}
c \\
d \end{array} \right)
\]

where

\[V^1_{ji} = -\int B_{j,k}(r) \frac{Z}{r} B_{i,k}(r) dr, \quad K^2_{ji} = -c \int B_{j,k}(r) \left( \frac{d}{dr} - \frac{\kappa}{r} \right) B_{i,k'}(r) dr \]

\[K^1_{ji} = c \int B_{j,k'}(r) \left( \frac{d}{dr} + \frac{\kappa}{r} \right) B_{i,k}(r) dr, \quad V^2_{ji} = -\int B_{j,k'}(r) \left( \frac{Z}{r} + 2c^2 \right) B_{i,k'}(r) dr \]

\[B^1_{ji} = \int B_{j,k}(r) B_{i,k}(r) dr, \quad B^2_{ji} = \int B_{j,k'}(r) B_{i,k'}(r) dr, \quad c_i = c_i, \quad d_i = d_i.\]
A.5. The Hartree-Fock method with b-splines

With each new iteration only the radial integrals need to be recalculated and for the numerical calculations it is possible to simplify the general expression

\[ \langle a | u_{HF} | c \rangle = \sum_b \langle ab \psi_{B'_b} | \frac{1}{r_{12}} | cb \psi_{B'_b} \rangle - \langle ab \psi_{B'_b} | \frac{1}{r_{12}} | bc \psi_{B'_b} \rangle \]

and express it in radial functions only. Each wave function has two components,

\[ |a\rangle = \begin{bmatrix} F_a \\ G_a \end{bmatrix}, \quad |b\rangle = \begin{bmatrix} F_b \\ G_b \end{bmatrix}, \quad |c\rangle = \begin{bmatrix} F_c \\ G_c \end{bmatrix}, \quad |\psi_{B'_b}\rangle = \sum_{j,k} B_{j,k} \]

where \(|a\rangle\) is the set of b-splines that are multiplied from the left (compare with Eq.2.13), \(|b\rangle\) is the solutions to the last iteration\(^1\) (or initial guess) and \(|c\rangle\) is the wave function where the coefficients \(c_i\) and \(d_i\) will be determined when the equations are solved, and this results in

\[ \langle a | u_{HF} | c \rangle \rightarrow \]

\[ \sum_b \left[ \langle F_a F_b | \frac{1}{r_{12}} | F_c F_b \rangle - \langle F_a F_b | \frac{1}{r_{12}} | F_b F_c \rangle \right. \]

\[ \left. + \langle F_a G_b | \frac{1}{r_{12}} | F_c G_b \rangle - \langle F_a G_b | \frac{1}{r_{12}} | F_b G_c \rangle \right. \]

\[ \left. + \langle G_a F_b | \frac{1}{r_{12}} | G_c F_b \rangle - \langle G_a F_b | \frac{1}{r_{12}} | G_b F_c \rangle \right. \]

\[ \left. + \langle G_a G_b | \frac{1}{r_{12}} | G_c G_b \rangle - \langle G_a G_b | \frac{1}{r_{12}} | G_b G_c \rangle \right. \]

\[ = \sum_b \left[ \sum_j \sum_i c_i \left( \langle B_{j,k} F_b | \frac{1}{r_{12}} | B_{i,k} F_b \rangle - \langle B_{j,k} F_b | \frac{1}{r_{12}} | B_{i,k} F_b \rangle \right) \right. \]

\[ \sum_j \sum_i c_i \langle B_{j,k} G_b | \frac{1}{r_{12}} | B_{i,k} G_b \rangle - \sum_j \sum_i d_i \langle B_{j,k} G_b | \frac{1}{r_{12}} | F_b B_{i,k} \rangle \]

\[ \sum_j \sum_i d_i \langle B_{j,k} F_b | \frac{1}{r_{12}} | B_{i,k} F_b \rangle - \sum_j \sum_i c_i \langle B_{j,k} F_b | \frac{1}{r_{12}} | G_b B_{i,k} \rangle \]

\[ \sum_j \sum_i d_i \langle B_{j,k} G_b | \frac{1}{r_{12}} | B_{i,k} G_b \rangle - \sum_j \sum_i c_i \langle B_{j,k} G_b | \frac{1}{r_{12}} | G_b B_{i,k} \rangle \]

Since the notation is the same as in sec. A.4 it is straightforward to add each of these double sums (of sums) to the respective double sums in Eq.A.9-A.12 (resulting in revised matrix elements \(V^1_{ji}, K^1_{ji}, V^2_{ji}\) and \(K^2_{ji}\)).

\(^1\)Both \(F_b\) and \(G_b\) are, of course, also sums of b-splines but expressing them as that will not serve any purpose and not doing it will make the equations appear a bit cleaner.
A.6. Photo-ionization from a noble gas

For an atom the ground-state wave function, $\Psi_g$, can be expressed as a Slater determinant, here denoted $\{abcd\ldots\}$. An atom in an excited state, $\Psi_e$, where the electron in orbital $a$ has been promoted to orbital $s$ is expressed with the Slater determinant $\{sabcd\ldots\}$. It is possible to write the time-independent perturbed part as

$$\partial \Psi = \sum_e \frac{|\Psi_e\rangle \langle \Psi_e| H_p |\Psi_g\rangle}{E_g - E_e + \omega} = \sum_s \frac{\langle\{sabcd\ldots\}| H_p |\{abcd\ldots\}\rangle}{E_g - E_e + \omega}$$

where $E_g = \varepsilon_a + \varepsilon_b + \varepsilon_c + \varepsilon_d + \ldots$ and $E_e = \varepsilon_s + \varepsilon_b + \varepsilon_c + \varepsilon_d + \ldots$. With the perturbation being a one particle operator, $H_p = c \alpha \cdot A$, it can be expressed as

$$\partial \Psi = \sum_s \frac{\langle\{sabcd\ldots\}| c \alpha \cdot A |a\rangle}{\varepsilon_a - \varepsilon_s + \omega}$$

By projecting this on the state of the ion, $\{bcd\ldots\}$, the result is the one particle function $\rho$

$$\rightarrow \rho = \sum_s \frac{\langle s| c \alpha \cdot A |a\rangle}{\varepsilon_a - \varepsilon_s + \omega}.$$  \hspace{1cm} (A.13)

A.7. Coulomb phase

A.7.1. Non-relativistic

Expression for $\eta$ and $\sigma_l$:

$$\eta = Z/k$$

$$\sigma_l = \arg \left[ \Gamma \left( l + 1 - i \left( Z/\sqrt{2E} \right) \right) \right]$$

$\Gamma$ is the gamma function.

A.7.2. Relativistic

Expressions for $E$, $k$ and $\eta$:

$$E = \sqrt{p^2c^2 + m^2c^4}$$

$$k = \frac{\sqrt{E^2 - m^2c^4}}{hc}$$

47
\[ \eta = Z\alpha_{\text{FSC}}E\sqrt{\frac{1}{E^2 - m^2c^4}} \]

Also introducing

\[ \eta' = Z\alpha_{\text{FSC}}mc^2\sqrt{\frac{1}{E^2 - m^2c^4}} \]

Relativistic Coulomb phase. For \( \kappa > 0 \)

\[ \sigma_{\kappa>0} = \frac{1}{2} \arg \left[ \left( \frac{l - i\eta'}{\gamma_i - i\eta} \right) \frac{\Gamma(\gamma_i + 1 - i\eta)}{\Gamma(\gamma_i + 1 + i\eta)} \right] + \frac{\pi}{2} (l - \gamma_i) \]

[using that \( \arg[\Gamma(z)] = -\arg[\Gamma(z^*)] \) and \( \arg\left[ \frac{z_1}{z_2} \right] = \arg[z_1 \cdot z_2] \)]

\[ = \arg[\Gamma(\gamma_i + 1 - i\eta)] + \frac{1}{2} \arg[(l - i\eta') (\gamma_i + i\eta)] + \frac{\pi}{2} (l - \gamma_i) \] (A.14)

and in a similar way, for \( \kappa < 0 \)

\[ \sigma_{\kappa<0} = \frac{1}{2} \arg \left[ \left( \frac{l + 1 + i\eta'}{\gamma_{i+1} + i\eta} \right) \frac{\Gamma(\gamma_{i+1} - i\eta)}{\Gamma(\gamma_{i+1} + i\eta)} \right] + \frac{\pi}{2} (l + 1 - \gamma_{i+1}) \]

\[ = \arg[\Gamma(\gamma_{i+1} - i\eta)] + \frac{1}{2} \arg[(l + 1 + i\eta') (\gamma_{i+1} - i\eta)] + \frac{\pi}{2} (l + 1 - \gamma_{i+1}) \]

\[ = \arg[\Gamma(\gamma_{i+1} - i\eta)] + \frac{1}{2} \arg[(l + 1) \gamma_{i+1} + \eta\eta' - i(\eta (l + 1) - \eta'\gamma_{i+1})] + \frac{\pi}{2} (l + 1 - \gamma_{i+1}) \] (A.15)

In both equations, the first term on the right hand side approaches the non-relativistic expression for low energies and low \( Z \). The two following terms are of purely relativistic origin. Also worth noting is that the last term in both A.14 and A.15 are energy independent and will not contribute to the time delay.

### A.8. Cross-section

The cross-section is defined as

\[ \sigma = \frac{(\text{Energy/unit time}) \text{ absorbed by the atom}}{\text{Energy flux of the em-field}}. \] (A.16)
An expression for the numerator in Eq.A.16 can be obtained by taking the time derivative of the probability density, $P$, for the outgoing electron. By using the general time-dependent Schrödinger equation (Eq.??) this can expressed as

$$\frac{\partial}{\partial t} P = \frac{\partial}{\partial t} \rho^* \rho = \left( \frac{\partial}{\partial t} \rho^* \right) \rho + \rho^* \left( \frac{\partial}{\partial t} \rho \right) = i (H \rho)^* \rho - \rho^* H \rho .$$

The time derivative of the probability density inside a volume is then given by

$$\frac{\partial}{\partial t} \int P dV = \int i (H \rho)^* \rho - \rho^* H \rho \ dV . \quad \text{(A.17)}$$

With $H = c \alpha \cdot p + \beta c^2 + V$ ($V$ being a spherical symmetric potential) only the first term in the Hamiltonian will contribute (the last two will cancel out). The calculated function $\rho$, Eq.3.7, is a relativistic two component wave function,

$$\rho = \begin{pmatrix} P_\rho(r)^{-1} \mathcal{G}^m_j & iQ_\rho(r)^{-1} \mathcal{G}^{-m}_j \\ iQ_\rho(r)^{-1} \mathcal{G}^m_j & P_\rho(r)^{-1} \mathcal{G}^{-m}_j \end{pmatrix} \quad \text{(A.18)}$$

and thus

$$H \rho = c \alpha \cdot p \rho = c \left( \begin{array}{cc} 0 & \sigma \cdot p \\ \sigma \cdot p & 0 \end{array} \right) \begin{pmatrix} P_\rho(r)^{-1} \mathcal{G}^m_j & iQ_\rho(r)^{-1} \mathcal{G}^{-m}_j \\ iQ_\rho(r)^{-1} \mathcal{G}^m_j & P_\rho(r)^{-1} \mathcal{G}^{-m}_j \end{pmatrix} .$$

As seen in ?? (Eq.2.6 and 2.7)

$$c \sigma \cdot p P_\rho(r)^{-1} \mathcal{G}^m_j = ic \left( \frac{1}{r} \frac{\partial}{\partial r} + \frac{\kappa}{r^2} \right) P_\rho(r) \mathcal{G}^m_j$$

$$c \sigma \cdot p iQ_\rho(r)^{-1} \mathcal{G}^{-m}_j = -ic \left( \frac{1}{r} \frac{\partial}{\partial r} - \frac{\kappa}{r^2} \right) Q_\rho(r) \mathcal{G}^{-m}_j$$

and the two terms on the RHS of Eq.A.17 are then

$$i \int (c \alpha \cdot p \rho)^* \rho \ dV = i \int \left( c \alpha \cdot p \rho \right)^* \rho r^2 \ dr \ d\Omega =$$

$$ic \int \left[ \frac{Q_\rho(r)}{r} \mathcal{G}^{-m}_j \left( \frac{1}{r} \frac{\partial}{\partial r} + \frac{\kappa}{r^2} \right) \left( P_\rho(r) \mathcal{G}^m_j \right)^* - \frac{P_\rho(r)}{r} \mathcal{G}^m_j \left( \frac{1}{r} \frac{\partial}{\partial r} - \frac{\kappa}{r^2} \right) \left( Q_\rho(r) \mathcal{G}^{-m}_j \right)^* \right] r^2 \ dr \ d\Omega$$

$$= ic \int \left[ \frac{Q_\rho(r)}{r} \left( \frac{1}{r} \frac{\partial}{\partial r} + \frac{\kappa}{r^2} \right) P_\rho(r)^* - \frac{P_\rho(r)}{r} \left( \frac{1}{r} \frac{\partial}{\partial r} - \frac{\kappa}{r^2} \right) Q_\rho(r)^* \right] r^2 \ dr$$

and

$$i \int \rho^* c \alpha \cdot p \rho \ dV = i \int \rho^* c \alpha \cdot p r^2 \ dr \ d\Omega =$$

$$ic \int \left[ \left( \frac{G_\rho(r)}{r} \mathcal{G}^m_j \right)^* \left( \frac{1}{r} \frac{\partial}{\partial r} + \frac{\kappa}{r^2} \right) F_\rho(r) \mathcal{G}^{-m}_j - \left( \frac{F_\rho(r)}{r} \mathcal{G}^m_j \right)^* \left( \frac{1}{r} \frac{\partial}{\partial r} - \frac{\kappa}{r^2} \right) G_\rho(r) \mathcal{G}^{-m}_j \right] r^2 \ dr \ d\Omega$$

49
\[
\frac{1}{r} \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} + \frac{\kappa}{r^2} \right) P_\rho(r) - \frac{\kappa}{r^2} \frac{1}{r} \frac{\partial}{\partial r} P_\rho(r)^* \right] Q_\rho(r) \right] r^2dr.
\]

In the last step, for both integrals, an integration over all angles was performed which disposed of the angular functions and left only the radial part. When inserting these two integrals into Eq. A.17 all the \( \kappa \)-terms will cancel and the result is
\[
= ic \int \frac{r^2}{2} \left( \frac{Q_\rho(r) dP_\rho(r)^*}{dr} - \frac{P_\rho(r) dQ_\rho(r)^*}{dr} - \frac{Q_\rho(r)^* dP_\rho(r)}{dr} + \frac{P_\rho(r)^* dQ_\rho(r)}{dr} \right) dr
\]
\[
= ic \int \frac{d}{dr} \left( (P_\rho(r)^* Q_\rho(r) - P_\rho(r) Q_\rho(r)^*) \right) dr.
\]

However, the correct value of the integral can only be achieved if the unconsidered factors from Eq.3.5 are reinserted. Summing over the allowed \( m \)-values in the 3-j symbol for the dipole element will result in \( 1/\sqrt{3} \). Thus the time derivative of the probability density inside a sphere with radius \( R \) is
\[
= \frac{i c A_0^2}{3} \left[ P_\rho(r)^* Q_\rho(r) - P_\rho(r) Q_\rho(r)^* \right]_{r=R},
\]
and multiplying this with the energy of a photon gives the numerator in Eq.A.16
(\( R \) being sufficiently large to be outside the electron cloud).

The denominator in Eq.A.16 (the energy flux of the EM-field) is, in SI-units,
\[
\frac{c \varepsilon_0 E^2 + \frac{c}{\mu_0} B^2}{2} = \frac{c \varepsilon_0}{2} \left( E^2 + c^2 B^2 \right) = \frac{c \varepsilon_0}{2} \left( E^2 + c^2 B^2 \right), \quad \text{(In vacuum } \varepsilon_0 \mu_0 = \frac{1}{c^2})
\]
and with \( E^2 = c^2 B^2 \) the flux can be expressed as
\[
\rightarrow c \varepsilon_0 E^2.
\]

The magnetic field can be described by the electric field through the relation
\[
E = -\frac{\partial A}{\partial t}, \quad (\phi = 0),
\]
and with \( \mathbf{k} \cdot \mathbf{r} \approx 1 \)
\[
\rightarrow A_0 \hat{\mathbf{e}} \left( e^{-i \omega t} + e^{i \omega t} \right) = 2 A_0 \hat{\mathbf{e}} \cos (\omega t),
\]
this implies
\[
\mathbf{E}^2 = \left( \frac{\partial A}{\partial t} \right)^2 = \left( \frac{\partial}{\partial t} 2 A_0 \hat{\mathbf{e}} \cos (\omega t) \right)^2 = \omega^2 4 A_0^2 \sin^2 (\omega t)
\]
and the flux can be written as
\[
c \varepsilon_0 \mathbf{E}^2 = c \varepsilon_0 \omega^2 4 A_0^2 \sin^2 (\omega t) = 2 c \varepsilon_0 \omega^2 A_0^2.
\]

Which means that in atomic units the cross-section is given by
\[
\sigma = 4 \pi c \frac{A_0^2}{3} \left[ P_\rho(r)^* Q_\rho(r) - P_\rho(r) Q_\rho(r)^* \right]_{r=R} = 2 \pi i \frac{P_\rho(r)^* Q_\rho(r) - P_\rho(r) Q_\rho(r)^*}{3 \omega}.
\]
A.9. RPAE elements

Through Wigner-Eckarts theorem [18] the elements in the expressions for $M_i^\pm$ can be expressed as

$$\langle bs | \frac{1}{r_{12}} | ar \rangle = \sum_K \langle bs | \frac{r^K}{r^{K+1}} | ar \rangle X_K (K, j_b, j_s, j_a, j_r) (-1)^{j_b+j_r+1} \left\{ j_a \ K \ j_s \ K \ j_b \ j_r \right\}$$

(A.19)

$$\langle sb | \frac{1}{r_{12}} | ar \rangle = \left[ \langle sb | \frac{r^K}{r^{K+1}} | ar \rangle X_K (K, j_s, j_b, j_a, j_r) \frac{(-1)^{j_b+j_r}}{3} \right]_{K=1}$$

(A.20)

$$\langle sr | \frac{1}{r_{12}} | ab \rangle = \left[ \langle sr | \frac{r^K}{r^{K+1}} | ab \rangle X_K (K, j_r, j_s, j_a, j_b) \frac{(-1)^{j_b+j_r}}{3} \right]_{K=1}$$

(A.21)

$$\langle rs | \frac{1}{r_{12}} | ab \rangle = \sum_K \langle rs | \frac{r^K}{r^{K+1}} | ab \rangle X_K (K, j_r, j_s, j_a, j_b) (-1)^{j_b+j_r+1} \left\{ j_a \ K \ j_s \ K \ j_b \ j_r \right\}$$

(A.22)

$X_K$ is the $m$-independent angular part of the integration and $\{ \}$ are 6-j symbols.

A representation of the elements using Goldstone diagrams can be found in Fig. A.2.

![Figure A.2.](image)

Figure A.2.: Diagrammatic representation of Eq. 3.8 where the last four diagrams are equivalent to the RPAE elements.
A.10. Relationship between regular and irregular Coulomb functions

With

\[ \theta(r) = kr + \eta \ln(2kr) - \frac{l\pi}{2} + \sigma_k \]

the Coulomb functions can be expressed as

\[
\rightarrow F(r) = g \cos(\theta(r)) + f \sin(\theta(r)) \quad (A.23)
\]

\[
\rightarrow G(r) = f \cos(\theta(r)) - g \sin(\theta(r)) \quad (A.24)
\]

where \(f\) and \(g\) are functions of \(r\) which are slowly increasing and decreasing respectively and when \(r \rightarrow \infty\), \(f = 1, g = 0\). They can be obtained through recursive sums \([25] 14.5.8\).

\[
\cos(\theta(r)) = \frac{gF(r) + fG(r)}{g^2 + f^2}
\]

\[
\sin(\theta(r)) = \frac{fF(r) - gG(r)}{g^2 + f^2}
\]

By knowing the function value and the derivative of one of the functions it is possible to calculate the other. Looking at the derivative of \(F(r)\)

\[
\rightarrow \frac{d}{dr} F(r) = \frac{dg}{dr} \cos(\theta(r)) + \frac{df}{dr} \sin(\theta(r)) - g \frac{d\theta}{dr} \sin(\theta(r)) + f \frac{d\theta}{dr} \cos(\theta(r))
\]

\[
= \frac{dg}{dr} \cos(\theta(r)) + \frac{df}{dr} \sin(\theta(r)) - g \left(k + \frac{\eta}{r}\right) \sin(\theta(r)) + f \left(k + \frac{\eta}{r}\right) \cos(\theta(r))
\]

\[
= \frac{dg}{dr} \left(gF(r) + fG(r)\right) + \frac{df}{dr} \left(fF(r) - gG(r)\right) - g \left(k + \frac{\eta}{r}\right) \sin(\theta(r)) + f \left(k + \frac{\eta}{r}\right) \cos(\theta(r))
\]

\[
= \frac{1}{g^2 + f^2} \left(\frac{dg}{dr} + \frac{df}{dr}\right) F(r) + \left(\frac{dg}{dr} f - \frac{df}{dr} g\right) G(r) + \left(k + \frac{\eta}{r}\right) G(r)
\]

\[
\Leftrightarrow \frac{d}{dr} F(r) = \frac{1}{g^2 + f^2} \left(\frac{dg}{dr} + \frac{df}{dr}\right) F(r) + \left(\frac{1}{g^2 + f^2} \left(\frac{dg}{dr} f - \frac{df}{dr} g\right) + \left(k + \frac{\eta}{r}\right)\right) G(r)
\]
A.10 Relationship between regular and irregular Coulomb functions

\[ G(r) = \frac{d}{dr}F(r) - F(r) \frac{1}{g^2 + f^2} \left( \frac{dg}{dr} f + \frac{df}{dr} g \right) \]

In the same way it is possible to get an expression for \( F(r) \),

\[ \frac{d}{dr}G(r) = \frac{df}{dr} \cos(\theta(r)) - \frac{dg}{dr} \sin(\theta(r)) - f \frac{d\theta}{dr} \sin(\theta(r)) - g \frac{d\theta}{dr} \cos(\theta(r)) \]

\[ = \frac{df}{dr} g F(r) + f G(r) \frac{g^2 + f^2}{g^2} - \frac{dg}{dr} f F(r) - g G(r) \frac{g^2 + f^2}{g^2} - \left( k + \frac{\eta}{r} \right) \left( g \cos(\theta(r)) + f \sin(\theta(r)) \right) \]

\[ = \frac{1}{g^2 + f^2} \left( G(r) \left( \frac{df}{dr} f + \frac{dg}{dr} g \right) + F(r) \left( \frac{dg}{dr} f - \frac{df}{dr} g \right) \right) - \left( k + \frac{\eta}{r} \right) F(r) \]

\[ F(r) = \frac{d}{dr} G(r) - \frac{1}{g^2 + f^2} G(r) \left( \frac{df}{dr} f + \frac{dg}{dr} g \right) \]

\[ \frac{1}{g^2 + f^2} \left( \frac{df}{dr} g - \frac{dg}{dr} f \right) - \left( k + \frac{\eta}{r} \right) \]
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[17] Private communication with Prof. Eva Lindroth.


Fano’s propensity rule in angle-resolved attosecond pump–probe photoionization

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Interferometric measurements based on combining extreme ultraviolet (XUV) attosecond pulse trains with a weak infrared field, have been successfully used to study time-resolved and recently angle-resolved photoionization in various systems. These measurements rely on quantum interferences between electron wavepackets created by absorption of XUV radiation, with further absorption or emission of laser photons. In this work, we extend Fano’s propensity rule to these above-threshold ionization processes and show that the asymmetry between absorption and emission results in incomplete quantum interference. This leads to periodic emission of photoelectrons perpendicular to the laser polarization at specific delays between the attosecond pulse train and the laser field.

In quantum mechanics, the possible transitions between different states are dictated by selection rules which are based on symmetry arguments. For example, the famous parity and angular momentum selection rules are at the core of our understanding of light-matter interactions. In contrast to these stringent selection rules, the concept of propensity rules, which was introduced by Berry [1], is based on the fact that all allowed transitions are not equally probable. Selection and propensity rules play a fundamental role in physics and chemistry to understand the possible outcomes and reaction rates. One of the most fundamental reactions is the photoionization of an atom following the absorption of a high energy photon, \( A + h\nu \rightarrow A^+ + \epsilon^- \), where an electron is promoted to a manifold of degenerate continuum states. The well-known electric dipole selection rules greatly simplify the problem, restricting the possible transitions to those where the electron angular momentum changes by one unit, \( \Delta l = \pm 1 \). Fano’s propensity rule states that out of the two possible transitions, the one increasing the electron angular momentum is favored, due to increase of the centrifugal potential with angular momentum [2]. Conversely, for the time-reversed process, decreasing angular momentum is favored as a photon is emitted.

This Letter deals with laser-assisted photoionization, \( A + h\nu_{\text{XUV}} \pm h\nu_{\text{IR}} \rightarrow A^+ + \epsilon^- \), where absorption of an XUV photon brings an electron to the continuum, followed by absorption or stimulated emission of laser radiation, often in the infrared (IR), between unbound states. A natural question is whether Fano’s propensity rule, originally stated between a bound and a continuum state, can be extended to this regime and how a possible asymmetry between absorption and emission affects the photoelectron distribution, both in probability and emission angle.

Laser-assisted photoionization is a cornerstone of attosecond science, used in the temporal characterization of XUV radiation, such as high-order harmonics [3–5], the measurement of attosecond pulses [6, 7] and in many applications, especially the investigation of photoionization dynamics in atoms [8–12], molecules [13–16] and solids [17–19]. Attosecond precision is obtained by laser-assisted photoionization with consecutive, phase-locked harmonics in the so-called RABBIT technique (Reconstruction of attosecond beating by interference of two-photon transitions) [7]. Initially used for the characterization of attosecond pulses, the RABBIT technique has been widely applied to measurements of photoionization time delays in a variety of systems. Recently, angle-resolved RABBIT studies have shown that atomic ionization delays depend on the direction of emission of the photoelectrons [20, 21] and that the photoelectron angular distributions (PAD) vary with the delay between the attosecond pulse train and the probe field [21]. Time- and angle-resolved electron wavepackets have also been studied using a variation of the RABBIT technique, which is based on both even and odd harmonics and leads to an up-down asymmetry in the PADs due to parity mixing of the final states [22, 23].

From a theoretical perspective, angle-resolved laser-assisted photoionization is a long-studied subject [24–27], and angle-resolved RABBIT has been investigated using lowest-order perturbation theory [28–30] as well as by solving numerically the time-dependent Schrödinger equation (TDSE) [20, 31, 32]. While a modification of PADs over delay has been predicted at moderate IR intensities \( (10^{11} - 10^{12}) \text{ W/cm}^2 \) [33], and the emission of photoelectrons perpendicular to the laser polarization has been discussed in the strong field regime \( (10^{13} - 10^{14}) \text{ W/cm}^2 \) [34], the underlying reason for delay-dependence of PADs in RABBIT experiments is still not understood.

Here, we show that the RABBIT scheme leads to incomplete quantum interference resulting in the periodic emission of photoelectrons perpendicular to the laser polarization. This result is a consequence of Fano’s propensity rule and it is observed both experimentally and in theoretical calculations based on many-body perturbation theory. Our findings are verified to be universal and Fano’s propensity rule is found to be satisfied in above-threshold transitions for all studied noble gases.

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FIG. 1: Delay-dependent PADs. (a) Angle-integrated signal measured in SB 14 (squares) and fitted oscillation (gray line). (b) Interpolated delay-dependent PAD measured in SB 14 normalized to the angle-integrated signal at each delay. (c) Delay-dependent $\beta_2$ extracted from the experimental angle-resolved RABBIT for SB 14 to SB 22. The insets in (a) show the PAD of SB 14 reconstructed from the measured $\beta$ parameters for delays indicated by the colored squares. The solid arrows indicate the polarization axis $\hat{e}$ and the dashed arrows correspond to the photoelectron momentum $\hat{k}$.

In our experiments, we focus an XUV attosecond pulse train, together with a fraction of the fundamental IR field ($\hbar \omega = 1.58\,\text{eV}$) used for the generation of the pulse train, with a variable delay, into a gas jet of argon atoms. Because the XUV pulse train is composed of coherent odd harmonics with frequency $(2n+1)\hbar \omega$, the combined XUV±IR interaction results in above-threshold ionization to photoelectron peaks, referred to as sidebands and denoted SB $2n$, if created from absorption of the $(2n+1)^{th}$ harmonic and emission of one laser photon. The photoelectrons are detected using a Velocity Map Imaging Spectrometer (VMIS) to resolve delay-dependent momentum distributions (see [21] for more details on the experimental setup and [35] for details on the VMIS). The interference of the two paths leading to a sideband results in an oscillation of the angle-integrated sideband signal as a function of the relative delay, $\tau$, between the XUV and IR pulses, as can be seen in Fig. 1(a). The sideband signal oscillates according to [7]:

$$P_{SB}(\tau) = A + B \cos (2\omega \tau + \Delta \phi) ,$$  \hfill (1)

where $A$, $B$ and $\Delta \phi$ are specific constants for each sideband.

The differential ionization cross-section $d\sigma^{(N)}/d\Omega$ after interaction (absorption or emission) with $N$ photons can be decomposed as a sum of Legendre polynomials $P_n$ weighted by the asymmetry parameters $\beta_n$ [36]

$$d\sigma^{(N)}/d\Omega = \frac{\sigma_0}{4\pi} \left[ 1 + \sum_{n=1}^{N} \beta_n P_n(\cos \theta) \right] ,$$  \hfill (2)

where $\sigma_0$ is the total ionization cross section and $\theta$ is the angle of emission with respect to the laser polarization. In the case of a two-photon transition, all the final states have the same parity such that the odd-order asymmetry parameters, $\beta_1$ and $\beta_3$, vanish, giving rise to an up-down symmetric PAD described by $\beta_2$ and $\beta_4$ [25].

Fig. 1(b) presents the delay-dependent PAD of SB 14. Since the signal oscillates as a function of the delay, we normalize the PAD by the angle-integrated signal in order to facilitate the comparison of the PADs at different delays. Around the maxima of the SB oscillations, electrons are mainly emitted along the polarization axis, close to the minimum of the SB signal. The two insets in Fig. 1(a) present the PADs at the maximum and minimum of the oscillations, showing clearly the emission of electrons perpendicularly to the polarization axis, close to the minimum of the SB signal. We quantify the modifications of the PAD by extracting the asymmetry parameters for SBs 14 to 22. Fig. 1(c) shows that the $\beta_2$ parameters oscillate as a function of $\tau$, and that the amplitude of these oscillations decreases with increasing sideband order. In our experimental conditions, the values of $\beta_2$ for SB 16 (shown by a dashed line) are affected by the presence of nearby autoionizing resonances and will not be considered in the following [21].

Figure 2 shows (a) the delay-dependent PAD for SB 14, calculated with the method presented below and (b) the extracted $\beta_2$ parameters for sidebands 14 to 22. The
delay dependence of the PADs and the sub-cycle variation of the $\beta_2$ parameter observed in the experiment is well reproduced by our theoretical results. The weaker oscillation amplitude observed in the experiment can be attributed to several factors such as delay sampling and jitter as well as limited angular resolution of the VMIS or too low signal close to the minima of the SB oscillations. Relative phase shifts between the $\beta_2$ oscillations of different sidebands can be observed in both experiment and theory. In the theory, this is solely attributed to the phase of the matrix elements, while in the experiment, part of these phase shifts can also be attributed to the positive chirp of the attosecond pulses [37], which was not included in our calculations for simplicity.

The angular distributions shown in Fig. 2(a) are calculated according to (we now use atomic units $[\hbar = m = e = 4\pi\varepsilon_0 = 1]$ unless stated otherwise)

$$P_{SB}(\phi, \tau) = \int d\phi \sum_m \sum_n Y_{Lm}(\phi, \tau) \exp[-iL\pi/2 + i\lambda L]\left(\lambda L_{\pm} e^{i\pi(\phi)} + \beta L_{\pm} e^{-i\pi(\phi)}\right)^2,$$

where

$$M_{Lm}^{(L\pm)} = \sum_p \frac{\langle q | z | p \rangle \langle p | z + \delta_{\text{RPAE}} | a \rangle}{\epsilon_a - \epsilon_p + \omega(2n + 1)},$$

are two-photon transition matrix elements within the dipole approximation from an initial state $\alpha$ (the $3p$ orbital of argon with energy $\epsilon_a = -15.76 \text{ eV}$) to a final electron continuum state $q$ with asymptotic phase, $\eta_L$, and angular momentum, $L = 1, 2, 3, 5$, via all virtual electron states $p$ with energy, $\epsilon_p$, and angular momentum, $\lambda = 0, 2$. The common linear polarization of XUV and IR fields ensures conservation of the magnetic quantum number, $m$, from the initial state. The amplitudes of XUV and IR fields are set to one for clarity. Our calculations are based on a one-electron Hamiltonian, with a Dirac-Fock potential plus a correction that ensures the correct long-range potential for ionized photoelectrons [28]. Electron correlation effects are included by self-consistent changes in the potential, $\delta_{\text{RPAE}}$, known as the Random Phase Approximation with Exchange (RPAE) for absorption in the singlet XUV photon [38].

Figure 3 shows the ratio between the transition matrix elements [Eq. (4)] with absorption and emission of an IR photon from the same intermediate energy and angular momentum in various noble gas atoms, reached from the outer shell of helium (1s), neon (2p) and argon (3p), or an inner-shell of krypton (3d). The absorption/emission ratio is larger than one when angular momentum is increased, $L = \lambda + 1$ [Fig. 3(a)]. Conversely, the emission/absorption ratio is larger than one when angular momentum is decreased, $L = \lambda - 1$ [Fig. 3(b)]. This behaviour agrees with Fano’s propensity rule and extends it to the case of laser-assisted photoionization. As illustrated in Fig. 3(c), the transitions indicated by bold arrows are favored compared to those represented by dashed arrows. In all studied atoms, the ratios show an universal decreasing trend with energy that depends on the final angular momentum of the electron. As in the original case of a one-photon transition between a bound and a continuum state [2], the physical origin of the propensity rule comes from the increase of the centrifugal potential with angular momentum.

It is interesting to compare our results with that of the soft-photon approximation (SPA), which is a commonly used approximation to model laser-assisted photoionization [26]. Within the SPA, all interactions of the emitted photoelectron with the parent ion are neglected, which prevents photoemission perpendicular to the polarization of the fields. According to Eq. (2), this implies that the SPA asymmetry parameters, $\beta_2^{\text{SPA}}$ and $\beta_4^{\text{SPA}}$, are simply linked via the relation [27, 32]

$$\beta_4^{\text{SPA}} = \frac{4}{3} \left(\beta_2^{\text{SPA}} - 2\right).$$

In order to test the validity of this approximation we calculate $\beta_4^{\text{SPA}}$ using the value of $\beta_2$ from our simulations. The resulting value of $\beta_4^{\text{SPA}}$ does not correspond to that of real SPA calculation but rather provides an insight on the validity of this approximation when compared to...
our more advanced calculations. Fig. 4(a) presents the asymmetry parameters $\beta_2$, $\beta_4$ extracted from the simulated PADs for SB 18, as well as $\beta_4^{\text{SPA}}$ as a function of the relative delay. For most delays, the different angular channels interfere destructively perpendicularly to the laser polarization and we find good agreement between our calculations and the SPA. However, as the delay approaches half of the sideband oscillation period, the deformation of the PAD is weaker as the SB order increases (see supplemental material). It is clear that the delay dependence of the PAD indicates a breakdown of the SPA.

We observe a similar breakdown of the SPA around the minimum of the sideband oscillations in simulations performed for helium as well as in our experiment in argon (see supplemental material). While a lobe at 90° in helium has been previously predicted by TDSE calculations in [33], no physical interpretation of this surprising effect has yet been presented.

The origin of the delay-dependent PAD can be understood by constructing the delay-dependent final-state-resolved sideband probability that we define as

$$P_{Lm}(\theta, \tau) = \int d\phi |A_{Lm}(\tau)|^2 |Y_{Lm}(\theta, \phi)|^2,$$

where $A_{Lm}(\tau)$ is given by

$$A_{Lm}(\tau) = \sum_{\lambda} \left[ M_{\lambda Lm}^{(\uparrow)} e^{i\omega \tau} + M_{\lambda Lm}^{(\downarrow)} e^{-i\omega \tau} \right].$$

Fig. 4(b) presents the variations of $|A_{Lm}(\tau)|^2$ for the different final states as a function of delay. Around the maximum, the contribution of the different final states is similar, with the channel with lowest angular momentum being slightly dominant. The fact that the final states have similar contribution is due to Fano’s propensity rule since, for each final state with angular momentum $L$ reached from intermediate states with angular momentum $\lambda$, there is one path with an enhanced transition amplitude and one path with a reduced transition amplitude, as sketched in Fig. 4(c). However, as the delay approaches half of the sideband oscillation period, the contribution of the states with lowest angular momentum drops significantly and the higher angular momentum states become dominant, resulting in a strong modification of the angular distribution. As we will show, this behavior is also a consequence of Fano’s propensity rule.

To address this point, we now investigate why the contribution of the states with highest angular momentum does not cancel at the minimum of the sideband. In the case of a single intermediate channel, we can express $|A_{Lm}(\tau)|^2$ as:

$$|A_{Lm}(\tau)|^2 = |M_{\lambda Lm}^{(\uparrow)}|^2 + |M_{\lambda Lm}^{(\downarrow)}|^2 + 2 |M_{\lambda Lm}^{(\uparrow)}| |M_{\lambda Lm}^{(\downarrow)}| \cos(2\omega \tau + \Delta \varphi_{Lm})$$

where $\Delta \varphi_{Lm} = \arg(M_{\lambda Lm}^{(\uparrow)} M_{\lambda Lm}^{(\downarrow)})^*$. This can be easily extended to the case where there are multiple intermediate channels by summing them coherently. We now introduce the oscillation contrast,

$$R_{Lm} = \frac{2 |M_{\lambda Lm}^{(\uparrow)}| |M_{\lambda Lm}^{(\downarrow)}|}{|M_{\lambda Lm}^{(\uparrow)}|^2 + |M_{\lambda Lm}^{(\downarrow)}|^2},$$

which takes values between 0 and 1 and represents the ratio between the amplitude of the oscillations and their mean value. When $R_{Lm} = 1$, the amplitude of the oscillations is as large as the mean value and thus the minima of $|A_{Lm}(\tau)|^2$ are zero. This condition is fulfilled only if $|M_{\lambda Lm}^{(\uparrow)}|^2 = |M_{\lambda Lm}^{(\downarrow)}|^2$, which is the case in the SPA (see supplemental material). However, if $|M_{\lambda Lm}^{(\uparrow)}|^2 \neq |M_{\lambda Lm}^{(\downarrow)}|^2$, the ratio $R_{Lm}$ becomes smaller than 1, which means that $|A_{Lm}(\tau)|^2$ will never completely cancel. Figs. 3(a) and (b) show that the asymmetry between absorption and emission increases with the angular momentum of the final state. This results in the fact that $R_{Lm}$ is always smaller for states with higher angular momentum, which means that the sideband minima are shallower (deeper) at higher (lower) angular momentum. In this way, the modification of the PAD around the minima of the sideband oscillations is a direct consequence of Fano’s propensity rule. Because the SPA does not include Fano’s propensity rule, it works well at the maximum of the sidebands, where all allowed final angular momentum momentum states have comparable contributions, but not at the minimum of the sidebands, where
the high angular momentum states dominate over the low angular momentum states.

In conclusion, we have studied the angle-resolved quantum interference of photoelectrons created by an XUV attosecond pulse train combined with an IR field. When the relative delay of the fields is such that the interference is destructive, the cancellation of the two paths is incomplete, and leads to a strong deformation of the photoelectron angular distribution. The effect is universal and can be interpreted by extending Fano’s propensity rule to above-threshold ionization processes. Increased understanding of above-threshold ionization processes is of great importance for the development of attosecond physics, but also of general interest in other areas of physics where continuum-continuum transitions are present.

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I. SUPPLEMENTAL MATERIAL

In the main text we have shown the break-down of the soft-photon approximation (SPA) relation between the asymmetry parameters $\beta_2$ and $\beta_4$ in argon in Fig. 4. Here, we show in Fig. 5 that we observe a similar break-down of the SPA in our experimental data. In addition, in Fig. 6 we show that our calculations also predict a break-down of the SPA in helium, with an even larger deviation of $\beta_4^{SPA}$ from the value of $\beta_4$ extracted from our simulated PADs. Furthermore, we observe the apparition of lobes at 90° at the minimum, in agreement the predictions in [33] based on solving the time-dependent Schrödinger equation in the single active electron approximation.

In the following we show that SPA is inconsistent with Fano’s propensity rule, which states that absorption (emission) of a photon favors increasing (decreasing) the angular momentum of the electron.

The complex amplitude for laser-assisted photoionization...
tion within the SPA is given by [39]
\[ T_{fa}(n) = \frac{1}{2} \mathbf{A}_\gamma \cdot \mathbf{k}_f J_n \left( \frac{A_0/\omega \cdot \mathbf{k}_f - A_2^2/8\omega^2}{\omega} \right) \phi_\alpha(k_f), \] (10)
where \( \mathbf{A}_\gamma \) is the vector potential amplitude of the XUV (photoionizing) field and \( \mathbf{A}_0 \) is that of the laser (assisting) field, \( \mathbf{k}_f \) is the final momentum of the photoelectron described by a plane wave,
\[ \phi_{k_f}(r) = (r | k_f) = \frac{1}{(2\pi)^{3/2}} \exp(i \mathbf{k}_f \cdot \mathbf{r}) \] (11)
with energy, \( \epsilon_f = k_f^2/2 \), and momentum normalization. The final state is reached after exchange of \( n \) laser photons, \( \omega \), with an interaction amplitude given by the generalized Bessel function, \( J_n(u,v) \), and one XUV photon, \( \omega_\gamma \), from the initial state, \( \epsilon_a \), with energy, \( \epsilon_a \), and Fourier transform, \( \phi_\alpha(k_f) \). In Eq. (10) the scalar product, \( \mathbf{A}_\gamma \cdot \mathbf{k}_f = A_\gamma k_f \cos \theta_f \), shows that no photoelectrons will be emitted perpendicular to the laser field polarization, \( \theta_f = \pi/2 \), regardless of the number \( n \) of laser photons exchanged within the SPA. In the limit of a weak assisting field, the generalized Bessel function with one photon exchange reduces to
\[ J_n(A_0/\omega \cdot \mathbf{k}_f, 0) \approx \frac{1}{2} \frac{A_0 \cdot \mathbf{k}_f}{\omega} = \frac{A_0}{2\omega} k_f \cos \theta_f, \] (12)
which gives the two-photon perturbation amplitude
\[ T_{fa}(\pm 1) = \pm \frac{A_\gamma A_0}{4\omega} k_f^2 \cos^2 \theta_f \phi_\alpha(k_f), \] (13)
where \( + \) (\( - \)) corresponds to absorption (emission) of a laser photon with energy conservation,
\[ \epsilon_f - \epsilon_a = \omega_\gamma \mp \omega. \] (14)
The fact that Eq. (13) only differs by a sign between absorption and emission implies that absorption and emission processes have the same strength within the SPA to a given final momentum, \( \mathbf{k}_f \). As a sidenote, Eq. (13) can be easily obtained by evaluating the two photon (XUV±IR ) matrix element with all intermediate and final states replaced by plane waves in Eq. (4) in velocity gauge (\( z \rightarrow p_z \)). The final plane wave state in Eq. (11) can be expanded on partial waves,
\[ \phi_{k_f}(r) = \frac{4\pi}{(2\pi)^{3/2}} \sum_{l,m} i^l j_l(k_f \ell) Y_{\ell m}(\hat{r}) Y^*_{\ell m}(\hat{k}_f), \] (15)
where \( j_l(k_f \ell) \) are spherical Bessel functions and \( Y_{\ell m} \) are spherical harmonics, which implies that the contribution of a given angular momentum \( L \) and \( M \) is given by
\[ (Y_{LM} | \mathbf{k}) = \frac{4\pi}{(2\pi)^{3/2}} i^L j_L(kr) Y^*_{LM}(\hat{k}). \] (16)

By combining Eqs. (13) and (16), we see that absorption and emission processes to a given partial wave have the same strength from any final momentum, \( \mathbf{k}_f \). Adding up coherently all the contributions from all possible final directions of the photoelectron, \( \mathbf{k}_f \), will also result in equal strength of absorption and emission processes,
\[ c_{fLM}^{(a)} = \int d\Omega_{k_f} \langle Y_{LM} | \hat{k} \rangle T_{fa}(\pm 1) \]
\[ = \pm \frac{4\pi}{(2\pi)^{3/2}} i^L j_L(kr) \frac{A_\gamma A_0}{4\omega} k_f^2 \phi_\alpha(k_f) \]
\[ \times \frac{4\pi}{3} \int d\Omega_{k_f} Y^*_{LM}(\hat{k}_f) Y^*_{LM}(\hat{k}), \] (17)
where we further assumed the initial state to be an \( s \)-wave, so that it can be pulled out from the angular integration of the final momentum. The remaining angular integral is simply a Clebsch-Gordan coefficient equal to \(-1/\sqrt{3}\) for \( L = 0 \) and \( \sqrt{2}/3 \) for \( L = 2 \), respectively. This shows that Fano’s propensity rule is not recovered within the SPA.

Since the SPA does not predict different strengths between absorption and emission depending on the angular momentum of the final state, \( L \), the oscillation contrast is maximal and the same for all the angular channels, \( R_{Lm}^{SPA} = 1 \). This implies that within SPA there will be no delay-dependent modifications of the PAD. SPA works well around the maxima of the sidebands, where the perpendicular photoionization is relatively small, because the contributions to different \( L \) are similar. In contrast, SPA fails to explain the drastic modification of the PAD close to the sideband minima. However, as the photoelectron energy increases, \( R_{Lm} \) tends towards 1, and, therefore, to the delay-independent value predicted by the SPA. This is particularly clear in the case of helium [Fig. 7(a)]. The energy dependence of \( R_{Lm} \) for Ar [Fig. 7(b)] is complex due to the Cooper minimum but also converges towards 1 at high enough kinetic energy.


Many-body calculations of two-photon, two color matrix elements for attosecond delays

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We present full two-photon RPAE calculations for the atomic delays of atoms exposed to two-color fields, in both length and velocity gauge. The results are used to investigate the validity of the common assumption that measured atomic delays can be interpreted as the one-photon Wigner delay and a universal continuum-continuum contribution that depends only on the kinetic energy and angular momentum of the photoelectron, the laser frequency and the charge of the remaining ion, but not on the specific atom.

PACS numbers:

I. INTRODUCTION

Techniques for probing ultrafast electronic dynamics such as the Reconstruction of Attosecond Beating By Interference of Two-photon Transitions (RABBITT) [1] or the attosecond streak-camera [2], use phase modulations in photo-electron spectra to quantify the time it takes for an electron to escape an atomic potential [3–11]. These modulations arise since the interaction with the ionizing attosecond pulse (or pulse train) takes place in the presence of a laser field phase-locked to the attosecond light field. For weak enough light fields these modulations can be understood from two-photon processes. It has further been established [12–14] that the additional approximation of separating the measured atomic delay, $\tau_A$, into a Wigner-like delay, $\tau_W$, from the one-photon XUV ionization process, and a contribution from the interaction with the laser-field (typically of IR wavelengths), called the continuum-continuum delay ($\tau_{cc}$) or Coulomb-laser coupling delay is meaningful. In this context $\tau_{cc}$ denotes the contribution from a single unbound electron in a Coulomb field that absorbs or emits a photon, as detailed in [12, 13]. The Wigner delay is known to be strongly dependent on the atomic origin of the electron. In contrast the contribution from the second photon must, if this picture is to hold, be “universal” in the sense that it depends only on the kinetic energy and the angular momentum of the photoelectron, the photon energy of the laser field and the charge of the remaining ion.

The validity of the $\tau_{cc}$ correction has been studied through many-body calculations of the two-photon process both for angular integrated measurements and for detection along the polarization axis [15, 16]. Although there are exceptions, in particular close to resonances [7, 8, 16], the universality of the contribution from the laser photon has hitherto proved to be a good approximation, with important practical consequences when Wigner delays are to be extracted from measured atomic delays. The many-body calculations themselves have been benchmarked for example against the difference between 2$s$ and 2$p$ time delays in neon [10], over a wide energy range, and against time delay differences between the outermost shells of rare atoms [6]. Still, the procedure used so far have employed significant approximations. First, only the dominating time-order of the XUV photon being absorbed first, and the IR photon being exchanged subsequently in a continuum-continuum transition, was generally accounted for. Second a more careful account for many-body effects has only been done for the XUV photoionization process, while the interaction with the second photon has been calculated in the lowest order approximation. Although these approximations are reasonable they have important consequences: the result on this level is for example expected to be different if light matter interaction is expressed in the so called length or velocity gauge. In addition experimental results on the difference between 3$s$ and 3$p$ time delays in argon [4, 5] show a marked disagreement with theory in the region around the so called 3$s$ Cooper minimum (at photon energies of $\sim 40$ eV). It is thus important to push the study of photoionization delays one step further.

Here we have performed Random-Phase Approximation with Exchange (RPAE) type calculations for the full two-photon process. The RPAE approximation [17] is known to account for the dominating many-body effects in one-photon ionization. While the length and velocity form of the electric dipole interaction gives the same result for electrons in any local potential, the use of the Hartree-Fock exchange potential destroys this invariance. As was shown more than forty years ago [18], RPAE, which accounts fully for hole-particle excitations (including the effects usually called ground-state correlation, see below) is able to restore the gauge invariance. For two-photon processes [19, 20] and beyond [21] pioneering studies of many-body effects on the RPAE-level were done already in the nineteen eighties and nineties. The target at the time was absorption of equal energy photons, where one alone could not induce ionization. In contrast, our interest is in the interaction with two photons of very different energies, with important contributions from above

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threshold ionization. We will demonstrate that just as for one-photon ionization, gauge invariance is obtained when hole-particle excitations are fully accounted for, i.e. in a two-photon RPAE calculation. We further show that the size of individual contributions is vastly different in the two gauges and that the common approximation to neglect the time-order where the IR photon is absorbed first leads to wrong results in velocity gauge.

In Sec. II below we will briefly revisit the theory for atomic delays. The calculational method will be outlined in Sec. III and the results are presented in Sec. IV

II. THEORY

Here we will briefly discuss the calculation of delays in laser-assisted photoionization. A more detailed account can be found in Ref. [16]. We consider first an N-electron atom that absorbs one photon and subsequently ejects a photoelectron. The radial photoelectron wavefunction will asymptotically be described by an outgoing phase-shifted Coulomb wave

\[ u_{k,\ell}^{(1)}(r) \approx -\pi M^{(1)}(k, \ell, \Omega, a) \sqrt{\frac{2m}{\pi \hbar^2}} \times e^{i(kr + \frac{2\pi}{\Omega} \ln kr - \ell \frac{\pi}{2} + \sigma_{\ell, z}(k) + \delta_{\ell}(k))}, \]

(1)

where \( M^{(1)} \) is the electric dipole transition matrix element, which when correlation effects are accounted for can contribute to the phase shift, (see below), and \( \sigma_{\ell, z} \) is the Coulomb phase for a photoelectron with wave number \( k \) and angular momentum quantum number \( \ell \) in the field from a charge of \( Z e \):

\[ \sigma_{\ell, Z}(k) = \arg \left[ \Gamma \left( \ell + 1 - i \frac{Z}{k a_0} \right) \right]. \]

(2)

The phase \( \delta_{\ell}(k) \) in Eq. (1) denotes the shift induced by the short-range many-body atomic potential. In the following we label the full perturbed wave function associated with absorption of one photon with angular frequency \( \Omega \) and a hole in orbital \( a \), \( |p_{\Omega, a}\rangle \), including both radial, angular and spin parts implicitly.

We will consider measurements that employ Reconstruction of Attosecond Beating By Interference of Two-photon Transitions (RABBITT) [1], where an XUV comb of odd-order harmonics of a fundamental laser field, \( \Omega = (2n + 1)\omega \), is combined with a synchronized, weak \( \omega \) laser field. In the RABBITT setting the one-photon ionization process is assisted by an IR photon that is either absorbed or emitted. This gives rise to quantum beating of sidebands in the photoelectron spectrum at energies corresponding to the absorption of an even number of IR photons. The outgoing radial wave function after interaction with two photons will asymptotically have the form

\[ u_{k,\ell}^{(2)}(r) \approx -\pi M^{(2)}(k, \omega, \Omega, a) \sqrt{\frac{2m}{\pi \hbar^2}} \times e^{i(kr + \frac{2\pi}{\omega} \ln kr - \ell \frac{\pi}{2} + \sigma_{\ell, z}(k) + \delta_{\ell}(k))}, \]

(3)

where the important difference compared to the one-photon case lies in the presence of the two-photon transition element \( M^{(2)} \), which connects the initial state \( a \) to the continuum state \( k_{\ell} \) through all dipole-allowed intermediate states.

A. The form of the light-matter interaction

The standard expression for light-matter interaction comes from minimal coupling ( \( p \to p + eA \) ). If the spatial dependence of \( A \) can be neglected the surviving interaction term is

\[ H^{vel}_l = \frac{e}{m} p \cdot A, \]

(4)

usually referred to as the velocity gauge form. A unitary transformation of the wave function can be employed to find the alternative length gauge form

\[ H^{length}_l = e r \cdot E, \]

(5)

for details see e.g. Ref. [22]. The equivalence of the two forms is readily shown by application of the unitary operator \( U = \exp(i e r \cdot A / \hbar) \) on the time-dependent Schrödinger equation in the usual way, i.e.:

\[ U (H_0 + H^{vel}_l) U^\dagger U \Psi = i\hbar U \frac{\partial U^\dagger U \Psi}{\partial t}. \]

(6)

Here it is worth noting that in order to arrive at Eq. 5 from Eq. 6 it is necessary to assume that the potential term in \( H_0 \) commutes with \( U \). This is obviously true for the Coulomb interaction with the nucleus, as well as between the electrons. However, due to the non-local nature of the Hartree-Fock exchange potential this is not the case within the Hartree-Fock approximation. Only by adding the RPAE class of many-body effects can the invariance between the two forms be restored [18]. Close agreement between the two forms is often considered a quality mark for more elaborate calculations. Since the agreement is trivial for any local potential it has though to be considered a necessary, albeit not sufficient property.

With linearly polarized light we may now write the transition matrix elements from Eq. (1) as

\[ M^{(1)}(k_{\ell}, \Omega, a) = \langle k_{\ell} | e z | a \rangle E_{\Omega}, \]

(7)

in length gauge or

\[ M^{(1)}(k_{\ell}, \Omega, a) = \langle k_{\ell} | e Z | a \rangle A_{\Omega}, \]

(8)
in velocity gauge. These non-correlated transition matrix elements can be chosen to be real in Eq. 7 and imaginary in Eq. 8.

Similarly the two-photon matrix element in Eq. (3) can be written as
\[
M^{(2)}(q', \omega, \Omega, \alpha) = \lim_{\varepsilon \rightarrow 0^+} \sum_{p} \frac{\langle q' | \sum_{n} \epsilon_n \gamma_n | p \rangle \langle p | \sum_{n} \epsilon_n \gamma_n^{*} | a \rangle}{E_n + \hbar \Omega - E_p + i \varepsilon} E_{\omega} E_{\Omega}. \tag{9}
\]
in length gauge and similarly with the \( p_z \) operator in velocity gauge. An important difference compared to one-photon absorption is that the two-photon matrix element is intrinsically complex for above threshold ionization, i.e. when \( h\Omega \) exceeds the binding energy, even if correlation effects are neglected.

The atomic contribution to the quantum beating of the side band at energy \( 2\hbar \omega \) in a RABBITT experiment is the phase difference between the quantum path where the XUV harmonic \( n \hbar \Omega = (2n + 1) \hbar \omega \) is absorbed and an IR-photon is emitted and that where both an XUV harmonic, now of energy \( n \hbar \Omega = (2n - 1) \hbar \omega \), and an IR-photon is absorbed. Eq. (9) shows the most important path, but contributions will also come from the reversed time-order where the IR photons are exchanged before absorption of any XUV photon. For this latter path there is in the general case no on-shell intermediate state that can contribute. It is thus assumed to be of less importance and is consequently often neglected. While this is a justified approximation for calculations in length gauge the situation is very different in velocity gauge as we will see below.

B. The time delay

Following the usual RABBITT formalism [16], we construct the phase differences for the two quantum paths leading to emission of a photoelectron along the common polarization axis of the fields,
\[
\Delta \phi^{(2)}_{\theta=0} = \arg \left[ \sum_{\ell'} M^{(2)}(2e) e^{(\ell' \eta_{Z,\kappa,\ell})} Y_{\ell',0}(\theta,0) \right] \\
\times \left( \sum_{\ell} M^{(2a)}(2e) e^{(\ell \eta_{Z,\kappa,\ell})} Y_{\ell,0}(\theta,0) \right) \tag{10}
\]
where we use the following short-hand notation
\[
M^{(2e)} = M^{(2)}(k_{\ell'}, -\omega, \Omega_{\ell'}, \alpha) \\
M^{(2a)} = M^{(2)}(k_{\ell}, \omega, \Omega_{\ell}, \alpha), \\
\eta_{Z,\kappa,\ell'} = \sigma_{Z,\kappa,\ell} + \delta_{k,k'},
\]
so that the atomic delay can be calculated for sideband \( 2n \) as
\[
\tau_{a} = \frac{\Delta \phi^{(2)}_{\theta=0}}{2\omega}. \tag{11}
\]
Similarly the one-photon dipole phases in the \( \theta = 0 \) direction
\[
\phi^{(1,\kappa>)}_{\theta=0} = \arg \left( \sum_{\ell} M^{(1)}(1e) e^{(\ell \eta_{Z,\kappa,\ell})} Y_{\ell,0}(\theta,0) \right), \\
\phi^{(1,\kappa<)}_{\theta=0} = \arg \left( \sum_{\ell} M^{(1)}(1e) e^{(\ell \eta_{Z,\kappa,\ell})} Y_{\ell,0}(\theta,0) \right), \tag{12}
\]
where \( \kappa \) is the photoelectron wave number after the first photon, can be used to compute the Wigner-like delay at sideband \( 2n \) as
\[
\tau_{W} = \frac{\phi^{(1,\kappa>)}_{\theta=0} - \phi^{(1,\kappa<)}_{\theta=0}}{2\omega}. \tag{13}
\]
We will refer to the quantity \( \tau_{a} - \tau_{W} \) as the delay difference introduced by the second photon.

III. METHOD

In earlier studies [16, 23, 24] some of us used the RPAE-approximation for the interaction with the ionizing XUV photon and treated the above threshold interaction with the IR photon in lowest order. Here this last approximation is lifted and we will discuss the procedure in some detail.

The calculations are performed with a basis set obtained through diagonalization of effective one-particle Hamiltonians in a radial primitive basis of B-splines [25] in a spherical box. For each angular momentum \( \ell \) this one-particle Hamiltonian reads:
\[
h_{0}^{\ell}(r) = -\frac{\hbar^{2}}{2m} \frac{\partial^{2}}{\partial r^{2}} + \frac{\hbar^{2}}{2m} \frac{\ell(\ell + 1)}{r^{2}} - \frac{e^{2}}{4\pi \epsilon_{0} r} + u_{HF} + u_{proj}. \tag{14}
\]
It includes the (non-local) Hartree-Fock potential (HF), \( u_{HF} \), for the closed shell with \( N \) electrons and a correction, \( u_{proj} \) (also non-local), which ensures that any excited electron feels an approximate long-range potential with \( N - 1 \) electrons remaining on the target. The latter potential is projected on virtual states and thus it does not affect the occupied HF orbitals. The projected potential allows us to include some effects already in the basis set, that would otherwise be treated perturbatively through the RPAE-iterations. The eigenstates to \( h_{0} \) form an orthonormal basis with eigenenergies \( \epsilon_{i} \) that is used for the description of the occupied orbitals, but it is also used to span the virtual space of the photoelectron. We use external complex scaling (ECS)
\[
r \rightarrow \begin{cases} r, & 0 < r < R_C \\ R_C + (r - R_C) e^{i\theta}, & r > R_C \end{cases}, \tag{15}
\]
and thus the eigenenergies of the virtual orbitals are complex in general.

We start with writing the interaction between one electron and the electromagnetic field as

$$ h_I = d_{\Omega} \left( e^{i \Omega t} + e^{-i \Omega t} \right), $$

with $d_{\Omega}$ being time-independent. In length gauge and with linearly polarized light $d_{\Omega} = e z E_{\Omega}$. Consider now an electron in occupied orbital $| a \rangle$, i.e. in an eigenstate of the one-particle Hamiltonian in Eq. (14). When it absorbs $(+)$, or emits $(-)$ one or several photons of energy $\Omega_1$ and $\Omega_2$, it will acquire corrections to its wave function:

$$ \Psi_a(r,t) = | a \rangle e^{-i \epsilon_a t/\hbar} + \sum_{i=1}^2 \rho_{\Omega_1,a}^{(1)\pm} e^{-i(\epsilon_a \pm \hbar \Omega_1) t/\hbar} + \sum_{i,j=1}^2 \rho_{\Omega_1,\Omega_2}^{(2)\pm} e^{-i(\epsilon_a \pm \hbar \Omega_1 \pm \hbar \Omega_2) t/\hbar} + \ldots, $$

where the superscripts, $(1)$ or $(2)$, refer to the number of photons being absorbed or emitted. Expressions for $\rho^{(n)\pm}$ can be found through the time-dependent Schrödinger equation

$$ (h + h_I) \Psi(r,t) = i \hbar \frac{\partial \Psi(r,t)}{\partial t}. $$

Collecting the contributions that scale linearly with the electric field $E_{\Omega}$, we find

$$ (\epsilon_a + \hbar \Omega_1 - h) \rho_{\Omega_1,a}^{(1)\pm} = d_{\Omega_1} | a \rangle, $$

and similarly the terms proportional to $E_{\Omega_1} E_{\Omega_2}$ can be collected. For a single particle system the desired one-photon correction to the wave function is now readily obtained from Eq. (19). For a many-electron system, however, there is one more effect to consider. Since the interaction with the other electrons is accounted for by the Hartree-Fock potential the possible changes in it due to the interaction with the electromagnetic field have to be considered. We will return to this question below. For the time being we just note that Eq. (19) gives the lowest order correction and label it $\rho_{0,\Omega,a}^{(1)\pm}$ with the solution:

$$ | \rho_{0,\Omega,a}^{(1)\pm} \rangle = \sum_p \frac{\langle p | d_{\Omega} | a \rangle}{\epsilon_{\pm} - h \Omega}, $$

The sum over $p$ is here restricted to unoccupied states, but that is not really necessary since the $(+)$ excitation of orbital $a$ into $b$ will cancel the $(-)$ excitation of orbital $b$ into $a$. If $\epsilon_p = \epsilon_a + h \Omega > 0$ there is a pole in the denominator of Eq. (20). An advantage with ECS is that the integration over the continuum is effectively performed along a path in the complex energy plane that avoids the poles and it is possible to replace the original integration over continuum states with a sum over a discretized representation of the excited states, $p$, as in Eq. (20).

A. One-photon RPAE

The many-body response to the interaction with the photon is neglected in Eq. (20), but the bulk of these effects can be added through the RPAE method [17], where certain sub-classes of many-body effects are included through the iterative solution of the equations for the coupled channels. Another name for RPAE is time-dependent Hartree-Fock [26], and we will here use that point of view to derive the expression we need. With the HF-approximation each orbital is described as moving in an average potential from the other orbitals, and its matrix element between an occupied and an unoccupied

\[
\begin{align*}
\text{(a) and (g) are forward and backward propagation, respectively, where the sphere indicates the correlated interaction to infinite order.}
\end{align*}
\]
orbital is:

\[ \langle p | u_{HF} | a \rangle = \sum_b \langle \{ pb \} | V_{12} | \{ ab \} \rangle \]

where curly brackets denote anti-symmetrization and the Coulomb interaction is given by

\[ V_{12} = \frac{e^2}{4\pi\varepsilon_0} \sum_{i<j} \frac{1}{r_{ij}} = \frac{e^2}{4\pi\varepsilon_0} \sum_{i<j} \sum_{K} \frac{r^{K}_{i}}{r^{K+1}} C^K (i) \cdot C^K (j). \]

(22)

When the electrons interact with the field and acquire perturbations according to Eq. (17) the potential itself will change, \( u_{HF} \rightarrow u_{HF} + \delta u_{HF}^{\pm(1)} + \delta u_{HF}^{\pm(2)} + \ldots \). This gives rise to additional paths for orbital \( a \) to absorb or emit one photon. Letting \( b \rightarrow b + \rho_{\Omega,b}^{\pm(1)} \) in Eq. (21) and collecting the terms scaling linearly with the electromagnetic field, we find:

\[ \langle p | \delta u_{HF,\Omega}^{\pm(1)} | a \rangle = \sum_b \langle \{ pb \} | V_{12} | \{ a \rho_{\Omega,b}^{\pm(1)} \} \rangle + \langle \{ pb \} | V_{12} | \{ ab \} \rangle \]

(23)

and a new equation is subsequently obtained for \( \rho^{\pm(1)} \):

\[ (\epsilon_a - \hbar \Omega) | \rho^{\pm(1)}_{\Omega,a} \rangle = \sum_{p \in \text{exc}} \langle p | \delta u_{HF}^{\pm(1)} | a \rangle. \]

(24)

When the projected potential, cf. Eq. (14), is taken to be the monopole interaction with the considered hole, \( h \),

\[ u_{proj} = -\sum_{r,s} | r \rangle \langle r | \left\{ \frac{1}{\sqrt{r.s}} - \left( \Omega - \tilde{\Omega} \right) s | r \rangle \langle s | \right\}, \]

(25)

the corresponding part of the the \( \delta u_{HF} \), are accounted for already in the basis sets and must be removed from the equation. This brings us to the final expression:

\[ | \rho^{\pm(1)}_{\Omega,a} \rangle = | \rho^{\pm(1)}_{\Omega,a} \rangle - | \rho^{\pm(1)}_{\Omega,a} \rangle - \sum_{p \in \text{exc}} \langle p | \epsilon_a - \epsilon_p \pm \Omega \rangle \]

\[ \times \left\{ \sum_b \left\{ \langle p | V_{12} | a \rho^{\pm(1)}_{\Omega,b} \rangle - \langle p | V_{12} | \rho^{\pm(1)}_{\Omega,b} \rangle \right\} \right\}

\[ + \langle \rho^{\pm(1)}_{\Omega,b} | V_{12} | ab \rangle - \langle p | \rho^{\pm(1)}_{\Omega,b} | V_{12} | ab \rangle \right\}

\[ - \langle p | u_{proj} (r) | \rho^{\pm(1)}_{\Omega,a} \rangle \}. \]

(26)

where the curly brackets have been dropped. The converged RPAE result gives the same functions \( \rho^{\pm(1)}_{\Omega,a} \) regardless if the projected potential is used or not, but the convergence is often much improved in the latter case, especially close to ionization thresholds. It is also possible to include a in-plane dipole contribution to the potential in Eq. (25) to further improve the convergence properties. The upper part of Fig. 1 shows the Goldstone diagrams for \( \rho^{\pm(1)}_{\Omega,a} \), where Fig. 1 (b) is the uncorrelated absorption of a photon \( \Omega \), as given in Eq. (20). Fig. 1 (c) and (d) account for the electron–hole interaction in forward propagation, while Fig. 1 (e) and (f) account for ground-state correlation effects.

B. Two-photon RPAE

We now want to consider interaction with two, possibly different, photons. Collecting the terms proportional to \( E_\Omega, E_\Omega \) from Eq. 18 we get,

\[ \langle \epsilon_a - \hbar \Omega_1 \pm \hbar \Omega_2 | \rho^{\pm(2)}_{\Omega,a} \rangle = \sum_{i,j=1,i \neq j}^{\text{exc}} \left( \sum_p \langle p | \rho^{\pm(1)} \rangle \langle p | \rho^{\pm(1)} \rangle | d_{\Omega_1} | d_{\Omega_2} | a \rangle \right), \]

(27)

The first term on the second line allows for the last photon to interact with the outgoing electron, Fig. 2a-b, while the second term accounts for the possibility that it causes the hole to be transferred to another orbital, Fig. 2c-d). The next step is to consider the full many-body response. First order corrections to the Hartree-Fock potential can generate terms proportional to \( E_\Omega, E_\Omega \) when working on \( \rho^{\pm(1)} \), and second order corrections to \( u_{HF} \) can generate them directly from the initial orbital. This latter corrections are found by again letting \( b \rightarrow b + \rho_{\Omega,b}^{\pm(1)} \) in Eq. (21), but now collecting the terms scaling as \( E_\Omega, E_\Omega \):

\[ \langle p | \delta u_{HF}^{\pm(2)} | a \rangle = \sum_b \langle \{ pb \} | V_{12} | \{ a \rho^{\pm(2)}_{\Omega,b} \} \rangle + \langle \{ pb \} | V_{12} | \{ ab \} \rangle \]

\[ + \sum_{i,j=1,i \neq j}^{\text{exc}} \left( \sum_p \langle p | \rho^{\pm(1)}_{\Omega,b} \rangle \langle p | \rho^{\pm(1)}_{\Omega,b} \rangle | d_{\Omega_1} | d_{\Omega_2} | a \rangle \right) \]

\[ - \sum_{b,c} \langle \rho^{\pm(1)}_{\Omega,b} | \rho^{\pm(1)}_{\Omega,c} \rangle \langle \{ pb \} | V_{12} | \{ ab \} \rangle \}

(28)

The expression for Eq. (17) uses intermediate normalization. That is, orbital | a ⟩ is normalized and orthogonal to the corrections \( \rho^{\pm(1)}_{a,\Omega} \), but \( \Psi_a (r,t) \) is not itself normalized. The last term on the right-hand side of Eq. (28) compensate precisely for this.

The many-body equation for the second order response have contributions both from \( \delta u_{HF}^{\pm(2)} \) and from \( \delta u_{HF}^{\pm(1)} \),
and it can now be written as:

\[
\rho_a^{(2)} = \left(\rho_a - h \pm \hbar \Omega_i \pm \hbar \Omega_j\right) |\rho_{\pm}^{(2)} a\rangle \langle \rho_{\pm}^{(2)} a|
\]

\[
= \sum_{i,j=1,i \neq j}^{\text{exc}} \left( \sum_{p} |p\rangle \langle p| \left( d_{i\Omega_i} + \delta u_{HF,i\Omega_i}^{(1)} \right) |\rho_{\pm}^{(1)} a\rangle \langle \rho_{\pm}^{(1)} a| \right) \\
- \sum_{c} \left( \sum_{p} |p\rangle \langle p| \left( d_{c\Omega_c} + \delta u_{HF,c\Omega_c}^{(1)} \right) |\rho_{\pm}^{(1)} a\rangle \langle \rho_{\pm}^{(1)} a| \right) \\
+ \sum_{p} \left( |p\rangle \langle p| \delta u_{HF}^{(2)} |a\rangle \langle a| - |p\rangle \langle p| u_{\text{proj}}(r) |\rho_{\pm}^{(2)} a\rangle \langle \rho_{\pm}^{(2)} a| \right).
\]

(29)

The \(\delta u_{HF}^{(2)}\) term on the second line gives rise to Fig. 2 e) and g), while the \(\delta u_{HF}^{(1)}\) term on the third line is depicted in Fig. 2 f) and h). Only the direct diagrams are shown. The Goldstone diagrams in Fig. 2 i-l), are all accounted for by the \(\delta u_{HF}^{(2)}\) term on the last line of Eq. (29). Note that two of them, Fig. 2 k-l), are just the usual RPAE diagrams but now due to the two-photon interaction. The very last term on the right-hand side of Eq. (29) is again compensating for the use of a projected potential in the basis set. It presence is important for convergence.

**C. Calculation of two-photon matrix elements**

If equipped with \(\rho^{(2)}\) from Eq. (29), one may directly extract the two-photon matrix elements needed for the calculation of the atomic delay, cf. Sec.II.B. However, due to the on-shell above threshold contributions to the diagram in Fig. 2 a), the construction of \(\rho^{(2)}\) involves the integration over a double pole and is not trivial. To circumvent this we calculate the two-photon matrix element separately for the diagrams in Fig. 2 a-d) and iterate only the additional corrections to \(\rho^{(2)}\). The different steps are detailed below.

The contributions from Fig. 2 a-d) are calculated directly from the first order corrections \(\rho^{(1)}_{\Omega_j}\). In length gauge it amounts to:

\[
M^{(2,a/c)}_{\text{TO1}} = \left( f | \text{ez} | \rho^{(1)}_{(2n+1)\omega,a} \right) \langle \text{ez} | a \rangle / E_{\Omega_i},
\]

for the diagrams in Fig. 2 a) and c), where TO1 stands for first time-order, and

\[
M^{(2,a/c)}_{\text{TO2}} = \left( f | \text{ez} | \rho^{(1)}_{\pm\omega,a} \right) \langle \text{ez} | a \rangle / E_{\pm\omega},
\]

(31)

for the second time-order (TO2) diagrams in Fig. 2 b) and d) The final state f is here an eigenstate to the effective one-particle Hamiltonian at the sideband kinetic energy \(\epsilon = \epsilon_a + 2n\hbar \omega\). As described in Ref. [16, 24] the numerical representation of radial part \(u_{f,\ell}\) with angular momentum \(\ell\) is found by solution of

\[
h_{\ell} u_{f,\ell}(r) = \epsilon_{f,\ell}(r),
\]

which can be reformulated as a system of linear equations for the unknown coefficients \(c_i\) when expanded in B-splines

\[
u_{f,\ell}(r) = \sum_i c_i B_i(r).
\]

(33)

For the case in Fig. 2 a), where the first photon is of an XUV-wavelength causing ionization, and the second integral is between two continuum states, the integral in Eq. (30) will not converge for any finite interval on the real axis. The integration is instead performed numerically out to a distance far outside the atomic core, but within the unscathed region \((a_0 \ll r < R_c)\), while the final part of the integral is carried out using analytical Coulomb waves along the imaginary r-axis as described in Ref. [16]. The numerical stability is monitored by comparison of different “break points” between the numerical and analytical descriptions. The integrals in Eq. (31), on the other hand, converge inside the numerical box since the IR-field can only induce a localized correction to the wave function.

The diagrams in Fig. 2 e-j) can all be calculated by connecting converged first order corrections for the XUV photon \(\rho^{(1)}_{(2n+1)\omega,a}\) and the laser photon \(\rho^{(1)}_{\pm\omega,a}\) with the Coulomb interaction. Finally the diagrams in Fig. 2 k-l) are found in an iterative procedure following that for the first order correction, Eq. 26. With the use of the projected potential, Eq. (25) all monopole terms are removed from the iterative procedure and the integral over the remaining Coulomb interaction does indeed converge on a finite interval and it can thus be treated numerically inside the computational box. Separating the two-photon perturbed wave function in the lowest order contributions (Fig. 2 a-d)) and the rest \(\rho^{(2)}_{\pm\omega,a} = \rho_{\pm\omega,a}^{(0)} + \delta \rho_{\pm\omega,a}^{(2)}\) and the remaining contribution to the two-photon matrix element, \(\delta M^{(2,a/c)}\), can be deduced directly from \(\delta \rho_{\pm\omega,a}^{(2)}\), giving the final result:

\[
M^{(2,a/c)} = M^{(2,a/c)}_{\text{TO1}} + M^{(2,a/c)}_{\text{TO2}} + \delta M^{(2,a/c)}.
\]

(34)

Of the four contributions in Eq. (30 - 31) it is natural to assume that the first integral in Eq. (30), Fig. 2 a), is by far the dominating one since both steps can be on-shell. In the general case Fig. 2 b-d) are indeed all connected with rather large denominators. The analytical form of the cc-delay [12, 13] accounts only for Fig. 2 a) and the same is true for the numerical calculations in [16, 23]. Here we will show that this assumptions is close to the truth for calculations in length gauge, but wrong in velocity gauge.
FIG. 2: Goldstone diagrams illustrating two-photon RPAE. Only forward propagation, and only direct diagrams, are shown. Diagrams g-j are also to be calculated with the order of the two photons interchanged.

D. Gauge-invariance

As discussed above the RPAE-approximation can be shown to produce gauge-invariant results [18] for the one-photon processes. This holds when the approximation is used without truncations. For example, the sum over core orbitals in Eq. (26) cannot be truncated and the orbital energies should be eigenvalues to the one-particle Hamiltonian used and cannot be replaced with experimental ionization energies. The latter is a common practice to improve the comparison with experiments. With these constraints we are here able to demonstrate gauge invariance also for the two-photon RPAE-approximation as will be seen below.

IV. RESULTS

Here we present calculation of the Wigner delay (after one-photon) and the atomic delay (from the two-photon matrix elements) cf. Eq.(10)-Eq.(11) for electrons emitted along the polarization axis.

A. Neon

The results for Neon are presented in Fig. 3 (length gauge) and Fig. 4 (velocity gauge). The RPAE iterations account for effects from all three orbitals and the original Hartree-Fock orbital energies are used. It is striking that the length gauge results are completely dominated by the diagram in Fig. 2a). Only very small corrections, less than an attosecond, are found from other contributions. This finding is supported by the comparison with experiment in Ref. [27]. Good agreement was there found over a large energy interval with just Fig. 2a) included in the calculation. The situation is very different in velocity gauge where each added contribution change the result significantly. The full two-photon RPAE gives however identical results in velocity and length gauge as seen in Fig. 4. The agreement between the gauges can be viewed as a validation test of the implementation.
B. Argon 3p

The atomic delay for ionization from argon 3p is displayed in Fig. 5. The RPAE iterations account for effects from all five orbitals and the original Hartree-Fock orbital energies are used. The delay is larger and changes more dramatically in Argon as compared to Neon. The velocity gauge result from Fig. 2a) alone underestimate the delay with around 20 as below the Cooper minima and overestimate it above. Still the final agreement between the length and velocity result is within the numerical accuracy.

In a more restricted calculation, Fig. 6, where the RPAE iterations account only for effects from the two other shells there is a remaining difference between the two gauges. The deviation from the full result is, however of the same order of magnitude for the two gauges.

C. Argon 3s

The atomic delay for ionization from argon 3s, and photoelectrons emitted in the polarization direction, is displayed in Fig. 7. The RPAE iterations account for effects from all five orbitals and the original Hartree-Fock orbital energies have been replaced with the experimental ionization energies. For 3s the HF prediction for the ionization energy is ~34.8 eV, while the true ionization energy is only ~29.2 eV, and thus this replacement is important for comparison with experiment. From cross section studies it is known that the 3s cross section is strongly affected by the electron-electron coupling with the strong 3p channel. For the two-photon process such a coupling can also be provided by the second photon through the diagram in Fig. 2c-d), which might thus be of some importance in this case.

The Cooper minimum in the 3s ionization cross section can indeed be understood as a replica of the Cooper minimum in the 3p ionization cross. The effect on the delay is however very different. While the latter region shows large negative delays for photoelectrons originating from is however very different. While the latter region shows maximum in the 3s orbital energies have been replaced with the experimental ionization energies. For 3s the HF prediction for the ionization energy is ~34.8 eV, while the true ionization energy is only ~29.2 eV, and thus this replacement is important for comparison with experiment. From cross section studies it is known that the 3s cross section is strongly affected by the electron-electron coupling with the strong 3p channel. For the two-photon process such a coupling can also be provided by the second photon through the diagram in Fig. 2c-d), which might thus be of some importance in this case.

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D. The universality of the continuum-continuum delay

Fig. 8 shows the differences between the atomic and the Wigner delay for argon. The agreement with the estimated continuum-continuum delay (calculated from the analytical expression Eq. (100) in Ref. [12]) is very good for high kinetic energies, but there is a clear deviation for lower energies. For Ar 3p the deviation is still modest while Ar 3s shows a marked deviation which further is very dependent on if only Fig. 2a) is accounted for or if all the diagrams Fig. 2a-l) are included. It is clear that the analytical expression from Ref. [12] can be used to extract the Wigner delay from measured atomic delays in most cases, but also that there are exceptions from this rule, particularly for low photoelectron energies.

V. DISCUSSION

We have seen that much larger contributions arise in velocity gauge than in length gauge from the time-order where the less energetic photon is absorbed first. This can be quite easily understood.

For a Hamiltonian, \( h \), with a local potential the length and velocity form of the dipole operator satisfy

\[
[h, c_r] = -ie\hbar \frac{m}{e} p. \tag{35}
\]

The \( A \)-field can be written as:

\[
A_z \sim (a^+ e^{-i\omega t} + a e^{i\omega t}) \tag{36}
\]

where \( a^\dagger \) and \( a \) are photon creation and annihilation operators and any spatial dependence have been neglected. The expression for the \( E \) field is then

\[
E_z = \mp i\omega A_z \tag{37}
\]

for photon creation and annihilation respectively. For an on-shell matrix element identical results for the two gauges follow promptly from

\[
\frac{e\hbar}{m} \langle s | p_z | r \rangle A_z = \frac{e}{\mp \omega} (\epsilon_s - \epsilon_r) \langle s | z | r \rangle E_z, \tag{38}
\]
since then $(\epsilon_s - \epsilon_r) = -\omega$ for emission (photon creation) and $(\epsilon_s - \epsilon_r) = \omega$ for absorption (photon annihilation).

Off shell matrix elements are generally different. Consider the two-photon transition matrix element from initial state $|0\rangle$ to a final state with $\epsilon_f = \epsilon_0 + \Omega_1 + \Omega_2$ via an intermediate state $|i\rangle$:

$$\frac{\langle f | d\Omega_2 | i \rangle \langle i | d\Omega_1 | 0 \rangle}{\epsilon_0 + \Omega_1 - \epsilon_i} \quad (39)$$

the velocity gauge result is then

$$(\epsilon_i - \epsilon_0) (\epsilon_0 - \epsilon_i + \Omega_1 + \Omega_2) / \Omega_1 \Omega_2 \quad (40)$$

times the length gauge result. This function has a maximum at $\epsilon_i = \epsilon_0 + (\Omega_1 + \Omega_2) / 2$, and since this maximum amounts to

$$\left( \frac{\Omega_1 + \Omega_2}{2} \right) ^2 \frac{1}{\Omega_1 \Omega_2} \approx \Omega_\geq / 4 \Omega_\leq \quad (41)$$

we should be prepared to find large differences for individual diagrams when, as in in typical RABBITT situation, the XUV photon has an energy of $20 - 40$ IR photons. We have indeed seen that the second time-order (TO2) is much more important in velocity gauge than in length gauge. Here only off-shell matrix elements are possible and contributions for intermediate excited states and continuum states closely above the ionization threshold should dominate, i.e. contributions where the enhancement factor in Eq. (40) will be of quite some importance.

VI. CONCLUSION

We have shown that a full two-photon RPAE calculation of the atomic delay gives gauge-independent results and that effects beyond the commonly used approach for the continuum-continuum delay do play a role in some cases. Still it has not been possible to understand the discrepancy between theory and experiment for the...
Ar(3s – 3p) delay, stemming from 3s-delay.

FIG. 6: The atomic delay for ionization from Ar 3p for electrons emitted along the polarization axis using all diagrams in Fig. 2. The dashed and dashed-dotted lines show the results in both gauges when all five orbitals are included in the two-photon RPAE iterations, while the solid lines show the result with only the two outer orbitals included.

FIG. 7: The atomic delay for ionization from Ar 3s for electrons emitted along the polarization axis. The delay is calculated in length gauge. The solid blue line shows the result from Fig. 2a). The dashed blue line include also Fig. 2b) and the dashed-dotted blue line also Fig. 2c-d). The energy region shown is that of the Cooper minimum in the 3s - cross section. Here Hartree-Fock orbital energies have been replaced with experimental ionization energies.

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FIG. 8: The difference between the atomic delay and the Wigner delay for ionization from Ar 3p (blue) and Ar 3s (red). The solid gray line shows the continuum-continuum delay [12]. The results for Ar 3p agree well with the continuum-continuum delay, and a modest deviation can only be seen for low energies. For Ar 3s there are in contrast significant deviations from the continuum-continuum delay in the region close to the Cooper minimum.

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