



MAX-PLANCK-INSTITUT
FÜR QUANTENOPTIK



Bachelor's Thesis

The influence of excited atomic states in multiphoton ionization

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Der Einfluss angeregter atomarer Zustände auf die Mehrphotonenionisation

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Abstract

Multiphoton ionization of atoms in strong laser fields is a fundamental process in attosecond physics. In this work, we extend the strong-field approximation (SFA) by incorporating the influence of excited atomic states on ionization rates. Standard SFA formulations neglect these excited states, assuming that the laser field has no effect on the atom before ionization. However, in intense few-cycle laser pulses, the Stark shift and transient population of excited states can significantly modify ionization dynamics. We numerically solve the time-dependent Schrödinger equation (TDSE) using the tRecX code to extract time-dependent probability amplitudes for hydrogen's ground and excited states. These amplitudes are then integrated into the SFA formalism to evaluate their impact on ionization rates.

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1. Introduction

What motivates this thesis? Background: developement of SFA and GASFIR rates that doesnt have to numerically solve Schroedinger equation. Comparison of ion rates from tRecX, SFA and GASFIR. When the laser pulse is an even function in time, the SFA rate is that as well. But numerical simulations from tRecX tell us thats not the case and the time symmetry is broken. Idea: because of the neglected excitedt states in SFA. This brings up more questions: What role play excited states in ionization? Does the stark effect play an important role?

Why is this so complicated? First, $[\hat{\mathcal{H}}(t), \hat{\mathcal{H}}(t')] \neq 0$ because $\hat{\mathcal{H}}_0$ and \hat{V} dont share same eigenbasis, -> the electron is free. Also the thing with all these gauges.

why so promising? coulomb potential has little effect on ionization dynamics (found manoram)

The only thingmissing is excited states

2. Theory

Convention:

Ψ wavefunction for the whole system

$\psi(\underline{x})$ for a wavefunction in position space without choosing explicit coordinates,

$\phi(\underline{p})$ for a wavefunction in momentum space,

\mathbf{A} for abstract vector as element in vector space,

\underline{x} for vector in \mathbb{R}^n

$|\Psi\rangle$ an abstract element in Hilbert space \mathcal{H} ,

$|\Phi\rangle$ for the abstract Eigenstates of the whole Hamiltonian,

$Y_{l,m}(\theta, \phi) = \langle \theta, \phi | l, m \rangle$ definition of spherical harmonics,

$\psi_{n,l,m}(r, \theta, \phi)$ for the wavefunction of hydrogen in spherical coordinates, with $\underline{x} = (r, \theta, \phi)$

I use underlined vectors when they are the coordinates and bold vectors when they are abstract elements in a vector space.

Its the concept of a manifold. \mathbf{A} could be in a manifold and not easy accessible but with a basis \underline{x} it has a physical meaning.

The canonical momentum \underline{P} parametrises the phase space but the kinetic momentum does not so kinetic momentum $\hat{=}\mathbf{p}$.

The position and momentum operator are in boldface $\hat{\mathbf{x}}$ because they do not choose any kind of basis not even a representation in which they are displayed.

When i use $|\mathbf{k}\rangle$ I mean a plane wave solution so "special" a continuum state.

$\mathbf{A} \cdot$ denotes a scalar product between two vectors, \times is just normal multiplication.

The strucutre in this chapter mainly follows [?] with some modifications.

What im going to do in this chapter: derive an instantaneous ionization rate (IIR) by solving time dependent schroedinger equation (TDSE) using the strong field approximation (SFA) and the interaction picture. First I solve the TDSE without making any (strict/harsh) approximations and piece by piece establish our physical setting (hydrogen atom with external laser field, in multiphoton ionisation regime, ionpropability around 0.01

QUESTION: What does vlad mean with two ways of deriving the basic formula for ionization rates?

2.1 Basic Formalism

Our goal is to come up with an expression where we can use the strong field approximation effectively. We want the time evolution of a quantum system in the presence of an external time dependent field in order to describe the strong field ionization later on. For that we first need to solve the schrodinger equation for a given Hamiltonian.

We will come across some difficulties like gauge dependence.

2.1.1 Schrödinger Equation

The time evolution of a quantum system is given by the time dependent Schrödinger equation and a general hamiltonian

$$i \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{\mathcal{H}}(t) |\Psi(t)\rangle. \quad (2.1)$$

The formal solution depends on the time dependence of the hamiltonian and the physical setting. With no further assumptions about our Hamiltonian because $[\hat{\mathcal{H}}(t), \hat{\mathcal{H}}(t')] \neq 0$ we can write the formal solution to (2.1) as a Dyson series: The solution is then given by

$$|\Psi(t)\rangle = \hat{\mathcal{U}}(t, t_0) |\Psi(t_0)\rangle = \hat{1} + \sum_{n=1}^{\infty} (-i)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \hat{\mathcal{H}}(t_n) \hat{\mathcal{H}}(t_{n-1}) \cdots \hat{\mathcal{H}}(t_1) |\Psi(0)\rangle. \quad (2.2)$$

Since the time evolution depends mainly on the Hamiltonian, one could say the time evolution is generated by the Hamiltonian.

2.1.2 Interaction picture and Projection operators

Solving the schrodinger equation can be cumbersome, especially when we have to deal with a time dependent Hamiltonian that doesn't commute with itself at different times. To make the calculations easier we can use projection operators with a method called feshbach method within the interaction picture.

2.1.3 Light-Matter Interaction

A light wave is defined by the Maxwell equations

$$\begin{aligned} \nabla \cdot \mathbf{E} &= \rho & \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\ \nabla \cdot \mathbf{B} &= 0 & \nabla \times \mathbf{B} &= \mathbf{J} + \frac{\partial \mathbf{E}}{\partial t} \end{aligned}$$

The Maxwell equations are being solved by

$$\begin{aligned}\mathbf{E} &= -\nabla\varphi - \frac{\partial\mathbf{A}}{\partial t} \\ \mathbf{B} &= \nabla \times \mathbf{A}\end{aligned}\tag{2.3}$$

For these solutions we introduced the vector potential $\mathbf{A}(\underline{x}, t)$ and the scalar potential $\varphi(\underline{x}, t)$. These are not unique such that different choices can result in the same physical setting. In general

$$\begin{aligned}\mathbf{A} &\rightarrow \mathbf{A} + \nabla\chi \\ \varphi &\rightarrow \varphi - \frac{\partial\chi}{\partial t}\end{aligned}$$

also fulfill the Maxwell equations while $\chi(t)$ is an arbitrary smooth scalar function. The arbitrariness of χ is known as gauge freedom and a direct consequence of the Maxwell equations. Choosing a gauge (i.e., a specific χ) is a matter of convenience and can be used to simplify the calculations as presented in the following.

2.1.4 Dipole Approximation

Very important approximation. The dipole approximation is valid when the wavelength of the optical field is much larger than both the size of the relevant bound electron states and the maximum displacement of a free electron during the light-matter interaction. Additionally, it assumes that the magnetic field of the light has a negligible effect on the electron's motion, meaning the velocities of the charged particles must be nonrelativistic.

To see where exactly one makes this assumption, first we rewrite the Maxwell equations in the dependence of the vector potential and the scalar potential as defined in (??). This will result in two coupled differential equations, what does not bring us any further. However we are interestet in making a simple expression for the vector potential \mathbf{A} . We achieve this by choosing a certain gauge, the so called Lorentz gauge

$$\partial_\mu \mathbf{A}^\mu = 0 \quad \text{or} \quad \nabla \cdot \mathbf{A} + \frac{\partial\varphi}{\partial t} = 0$$

This can be achieved by solving the inhomogenous wave equation for χ that comes up when doing this calculation explicitly and is possible when \mathbf{A} and φ are know. Now the Maxwell equations are uncoupled and can be written as

$$\begin{aligned}\nabla^2\varphi - \frac{\partial^2\varphi}{\partial t^2} &= \rho \\ \nabla^2\mathbf{A} - \frac{\partial^2\mathbf{A}}{\partial t^2} &= \mathbf{J}\end{aligned}$$

We are mainly interested in the second equation. The equation is known as the wave equation therefore \mathbf{A} describes plane waves

$$\mathbf{A}(\underline{x}, t) = \mathbf{A}_0 e^{\pm i(\underline{k} \cdot \underline{x} - \omega t)}$$

The dipole approximation is mathematically speaking just the leading term in Taylor expansion of $e^{i\mathbf{k} \cdot \mathbf{x}}$. The vector potential is therefore independent of the spatial coordinates and can be written as

$$\mathbf{A}(\underline{x}, t) = \mathbf{A}_0 e^{\mp i\omega t} \exp \left\{ \pm 2\pi i \frac{|\underline{x}|}{\lambda} \underline{e}_k \cdot \underline{e}_x \right\} \approx \mathbf{A}_0 e^{\mp i\omega t} \left(1 + \mathcal{O} \left(\frac{|\underline{x}|}{\lambda} \right) \right) = \mathbf{A}(t)$$

As long as the Wavelength is big enough this approximation is valid. It follows:

$$\mathbf{B} = \nabla \times \mathbf{A} \approx 0$$

Even though we will later choose another gauge, the physics in our system remains the same. The dipole Approximation is not gauge dependent, so in another gauge \mathbf{B} remains approximately zero. Choosing the Lorentz gauge here is just a matter of convenience, because just expanding the vector potential to the linear term is very intuitive.

This was the essence of the dipole approximation but we also want a intuitive expression for our Laser Field in the Hamiltonian. For that we need to think more about the gauge of our system.

2.1.5 Gauges

What makes calculating ionisation rates in strong field physics so difficult is the gauge, ie deciding which one you want to choose and when.

First, I will derive two basic expressions for the Hamiltonian in the so called velocity gauge and length gauge using the dipole approximation. It will be helpful to look at the semi classical Hamilton function of a free electron in an electric field¹:

$$\hat{\mathcal{H}}(\underline{x}, t) = \frac{1}{2m} (\hat{\mathbf{P}} - e\mathbf{A}(\underline{x}, t))^2 + e\varphi(\underline{x}, t) \quad (2.4)$$

In the dipole Approximation, this can be simplified to:

$$\hat{\mathcal{H}}(\underline{x}, t) = \frac{\hat{\mathbf{P}}^2}{2m} + \frac{e}{m} \hat{\mathbf{P}} \cdot \mathbf{A}(t) + \frac{e^2}{2m} \mathbf{A}^2(t) - e\varphi(\underline{x}, t)$$

¹Because its interesting it will be derived in ??

Note that we could set φ to zero because the source of the em wave are outside of our region of interest but the dipole approximation can be made without this assumption. We will however set φ to zero later. Another general assumption one made when working with semi classical Hamiltonians is that only the vectorpotential causes the electron to change its state but not vice versa (Bosßmann). This is reasonable approximation because in our case the intensity of the Laser is sufficiently high, so we dont have to worry about that(is it really??). Now we perform our desired gauge transformation, called length gauge via:

$$\chi = -\mathbf{A}(t) \cdot \underline{x}$$

This gauge sets \mathbf{A} to zero, and φ will have the following form:

$$\nabla\varphi \rightarrow \nabla \cdot (\varphi + \mathbf{x} \cdot \frac{\partial \mathbf{A}}{\partial t}) = \nabla\varphi + \frac{\partial \mathbf{A}}{\partial t} = -\mathbf{E}$$

Integrating this equation from the origin to \mathbf{x} gives us the electric potential in the length gauge. Furthermore, \mathbf{r} is now quantized and our Hamilton therefore reads:

$$\hat{\mathcal{H}}(\underline{x}, t) = \frac{\hat{\mathbf{P}}^2}{2m} - e\hat{\mathbf{x}} \cdot \mathbf{E}$$

We can rewirte the time dependent part \hat{V} of our quantum mechanical Hamiltonian as

$$\hat{V}_L(t) = -\hat{\mathbf{d}} \cdot \mathbf{E}(t) \tag{2.5}$$

where $\hat{\mathbf{d}} = e\hat{\mathbf{x}}$ is the dipole operator and $\mathbf{E}(t)$ is the electric field.

This is a common way to write the interaction Hamiltonian. **However if we choose another gauge transformation, the equations will have a different form. look bossmann!!!**

2.2 Strong Field Approximation

The difficulty with ionisation arises because we now have in some sense two Hilbert spaces, one for the states in the Hydrogen atom that deals with some distortion of the wavefunction because of the Laser field and one for the continuum states that are affected mainly by the Laser field but also by the binding potential.

We will see SFA will take care about the second Hilbertspace and make it easier. The main goal of this thesis is to see how much the Laser field has an effect on the wavefunction before ionisation happens. Previous work neglects this part so there is just one hilbertspace for the eigenstates unaffected by the laser field and one hilbertspace for the continuum states that are unaffected by the binding potential.

2.2.1 Subspaces

First we project the full timedependent Hamiltonian $\hat{\mathcal{H}}(t)$ onto subspaces using projection operators defined by:

$$\hat{X} = \sum_n |\Psi_n\rangle \langle \Psi_n| \quad \text{and} \quad \hat{Y} = \hat{1} - \hat{X}$$

With $|\Psi_n\rangle$ being the bound states of our atom. We can write:

$$\hat{\mathcal{H}}(t) = \underbrace{\hat{X}\hat{\mathcal{H}}(t)\hat{X}}_{\hat{\mathcal{H}}^{XX}(t)} + \underbrace{\hat{Y}\hat{\mathcal{H}}(t)\hat{Y} + \hat{X}\hat{\mathcal{H}}(t)\hat{Y} + \hat{Y}\hat{\mathcal{H}}(t)\hat{X}}_{\hat{\mathcal{H}}^{YY}(t) + \hat{\mathcal{H}}^{XY}(t) + \hat{\mathcal{H}}^{YX}(t) = \hat{\mathcal{H}}_I(t)}$$

Lets think about what these terms mean. $\hat{\mathcal{H}}^{XX}(t)$ can be seen as just our quantum system but with a small distortion by our electric field. This part causes effects like Stark shift both in the eigenstates and eigenenergies of our atom. As long as the laser pulse is not too strong and no ionisation has happened, we can treat the pulse like a perturbation to the system. The distortion may be time dependent but the good thing is that we can easily determine the propagator with respect to $\hat{\mathcal{H}}^{XX}(t)$ by using the interaction picture and solving a system of coupled differential equations. In other words this Hamiltonian determines the time evolution of the first hilbert space, as mentioned above.

Lets think about the other terms. For that we need to establish a setting. Say our Atom sits in the ground state and gets ionised. Based on this image we can say two from three parts are unnecessary. First $\hat{\mathcal{H}}^{YY}(t)$ plays no role because we project the initial state into the continuum state, and since there can be no overlap between them this part will play no role. This term actually just describes the evolution of a continuum state that remains a continuum state after the interaction so the laser pulse has happened. Second $\hat{\mathcal{H}}^{XY}(t)$ plays no role either since we project the initial (bound) state into the continuum. This term

would determine the time evolution of a continuum state that recombines with the atom after the interaction has happened. Obviously that's not what we want. The only term that remains is $\hat{\mathcal{H}}^{\text{YX}}(t)$ which describes the time evolution of a bound state that gets ionised in the continuum by the laser pulse. This is the perfect part to later start the strong field approximation with.

2.2.2 Dyson equation

NEED TO CHECK WITH VLADS DOCUMENT IF U_0 IS RIGHT!! For determining the time evolution we need to be careful since the whole Hamiltonian doesn't commute with itself at different times so we need to be exact. Since the full Dyson series (??) can be cumbersome to deal with, we choose a different way. What helps us is the fact that we can split the Hamiltonian by projecting it into subspaces in two parts of which one can be solved directly as mentioned above. Let's first write our ansatz:

$$\hat{\mathcal{U}}(t, t_0) = \hat{\mathcal{U}}_{\text{XX}}(t, t_0) - i \int_{t_0}^t \hat{\mathcal{U}}(t, t') \hat{\mathcal{H}}_I(t') \hat{\mathcal{U}}_{\text{XX}}(t', t_0) dt' \quad (2.6)$$

It is very easy to show that (??) is a solution to (??).

In our setting we start with the ground state of the atom so the time evolution is given by $\hat{\mathcal{U}}(t, t_0) |\Psi_0(t_0)\rangle$. To make things even simpler, we project into a continuum state $|\Pi(t_c)\rangle$ at time t_c with t_c being sufficiently big enough for the electron to be in the continuum ($t_c \gg t'$).

Of course, there is no overlap between $|\Pi(t_c)\rangle$ and $\hat{\mathcal{U}}_{\text{XX}}(t, t_0) |\Psi_n(t_0)\rangle$ since the electron did not get ionised yet. Furthermore, if we expand $\hat{\mathcal{H}}_I(t')$ and remind ourselves about the orthogonality of the bound states and the continuum states, we see that most of the terms of $\hat{\mathcal{H}}_I(t')$ vanish. We are being left with:

$$\langle \Pi(t_c) | \Psi_n(t) \rangle = -i \int_{t_0}^t \langle \Pi(t_c) | \hat{\mathcal{U}}(t, t') \hat{Y} \hat{\mathcal{H}}(t') \hat{X} \hat{\mathcal{U}}_{\text{XX}}(t', t_0) | \Psi_0(t_0) \rangle dt' \quad (2.7)$$

Note: No approximations have been made, (??) is exact.

2.2.3 Strong Field Approximation

Before making the strong field approximation, let's think about (??) again. It is best to read this equation from right to left, starting with the initial state of our system and the propagation of the system in presence of a weak electric field before ionisation. At moment t' the Laser starts to interact with the system and it transitions into a virtual state. From time t' to the observed time t the system is described by the full Hamiltonian including

both Laser Field and the binding potential.

In principle, SFA is the neglecting of exactly this binding potential once the electron is in the continuum because the Laser Field is now the dominant force acting on the electron. We can therefore write time evolution operator after ionisation as:

$$\hat{\mathcal{U}}(t, t') \approx \hat{\mathcal{U}}_{\text{SFA}}(t, t') = e^{-i \int_{t'}^t \hat{\mathcal{H}}_{\text{SFA}}(t'') dt''} \quad \text{and} \quad \mathcal{H}_{\text{SFA}}(t') = \hat{\mathcal{H}}(t) - \hat{V}_C$$

This is very usefull because for the eigenstates of $\hat{\mathcal{H}}_{\text{SFA}}$ we know an exact analytical solution; the Volkov states. Note that we can explicetely write $\hat{\mathcal{U}}_{\text{SFA}}(t, t')$ in (??) since after ionisation the hamiltonian commutes with itself at different times. For that lets take another look at the semi classical Hamilton (??). Classically, the physics driven by the momentum operator $\hat{\mathbf{P}}$ is known as the canonical momentum and given by:

$$\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{x}}} = \underline{P} = m \dot{\mathbf{x}} + \frac{e}{c} \mathbf{A} \stackrel{\text{a.u.}}{=} \mathbf{p} + \mathbf{A} \quad (2.8)$$

With \mathcal{L} being the Lagrangian of the system. In our case the canonical momentum is conserved. To see this, lets finally set $\varphi = 0$ so we have $\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}$ as justified above and recall the equation of motion for a charged particle in an electromagnetic field [?]:

$$\frac{d\mathbf{p}}{dt} = \mathbf{E} + (\dot{\mathbf{x}} \times \mathbf{B}) \approx -\frac{\partial \mathbf{A}}{\partial t} = -\frac{d\mathbf{A}}{dt}$$

so $\frac{d}{dt} \underline{P} = 0$. And also the energy of the system is clear:

$$E(t) = \dot{\mathbf{x}} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{x}}} - \mathcal{L} = \frac{\mathbf{p}^2}{2} \quad (2.9)$$

Note that the energy is not conserved because the argument we made bevor does not hold for the kinetic momentum only for the canonical momentum. Now comes the interesting part. Clearly $|\Pi(t_c)\rangle$ (not $|\mathbf{p}(t_c)\rangle$!) is a solution of $e^{-i \int_{t'}^t \hat{\mathcal{H}}_{\text{SFA}}(t'') dt''}$ so combining (??) and (??) gives us:

$$e^{-i \int_{t'}^t \hat{\mathcal{H}}_{\text{SFA}}(t'') dt''} |\Pi(t_c)\rangle = e^{-i \int_{t'}^t (\underline{P} - \mathbf{A}(t''))^2 dt''} |\Pi(t_c)\rangle$$

\underline{P} is of course independent of time, but \mathbf{A} is not. Since dealing with canonical momentum in numerical simulations is not very convenient, we use the fact that its conserved and calculate the momentum at other times. In particular we are interested in times where the laser field is long gone:

$$\underline{P} = \mathbf{p}(t'') + \mathbf{A}(t'') = \mathbf{p}(t \rightarrow \infty) + \mathbf{A}(t \rightarrow \infty) = \mathbf{p}$$

Furthermore (how??)

$$|\Pi\rangle = |\underline{P}\rangle = |\mathbf{p} + \mathbf{A}\rangle$$

Combining all these equations give us the following expression:

$$\langle \Pi(t_c) | \Psi_n(t) \rangle = -i \int_{t_0}^t e^{-i \int_{t'}^t (\underline{P} - \mathbf{A}(t''))^2 dt''} \langle \mathbf{p} + \mathbf{A} | \hat{Y} \hat{\mathcal{H}}(t') \hat{X} \hat{\mathcal{U}}_{XX}(t', t_0) | \Psi_0(t_0) \rangle dt'$$

Now comes the crucial part and a second, big approximation about $\hat{\mathcal{U}}_{XX}$. Whatever the final form if this will be, it can be expanded in the bound states $|n\rangle$ since we are projecting onto them. With this in mind we make an ansatz using the interaction picture as:

$$\hat{\mathcal{U}}_{XX}(t', t_0) | \Psi_0(t_0) \rangle = \sum_n c_n(t') e^{-i E_n t'} | \Psi_n(t_0) \rangle$$

The main problem with this ansatz is how can we get the coefficients $c_n(t')$. There are two ways. Solve the TDSE for the coefficients in the subspace spanned by the bound states or solve the TDSE for the coefficients in the whole hilbertspace and then project into the bound states. The derivation here suggests the second way. For a detailed analysis which way is better see chapter 4.

In contrast to other literature ([?], [?]) I am not neglecting transitions between different bound states before the ionisation. For instance it can happen that the laserpulse excites the electron but doesnt ionise it quite yet. IMPORTANT: I have to be more carefull here. There is a difference between solving the schroedinger euqation in the whole hilbert space and then projecting it into the subspace spanned by the bound states, and solving the schroedinger equation in the subspace.

In our case it doesnt make much difference becaus the ionization propability is still small so solving it in the sub hilbertspace should not make much difference. But fundamentally they are rally different ways on going about this problem and jsut 2 different approximations, both are not the truth!!.

We will later see how well these two approximations perform but for now I stick with solving the schroedinger equation in the subsoace spanned by the bound states since that is whats most natural in the dyson equation.

Using this leads to a system of ordinary differential equaitons in an ansatz called interaction picture. Solving this system of ODE's results in the coefficients $c_n(t)$. They should contain all the relevant information that happe inside a hydrogen atom before ionization (effects like DC/AC stark shift, muktiphoton transitions, etc.).

Lets first write the final expression. $\langle \mathbf{p} + \mathbf{A} | \hat{Y} \hat{\mathcal{H}}(t') \hat{X} | \Psi_n(t_0) \rangle$ is just the transition dipole

matrix element $\mathbf{d}_n(\mathbf{p} + \mathbf{A})$ between the bound state and the continuum state, generated by the laser pulse (ionisation). Some simple manipulations of this expectation value lets us apply the dipole approximation (??) and lets us write:

$$\langle \Pi(t_c) | \Psi_n(t) \rangle = -\frac{i}{2} \int_{t_0}^t e^{-i \int_{t'}^t (E - A_z(t''))^2 dt''} E_z(t') \sum_n c_n(t) e^{-i E_n t'} \langle \mathbf{p} + A_z | \hat{d}_z | \Psi_n \rangle dt'$$

Where we used the fact that the electric field is polarized along the z axis. This is the equation where most papers start with [?] known as Strong field s matrix.

Note that SFA is not about strong laser pulses since here we are also dealing with small ionisation probabilities (< 0.01) so SFA states that when ionisation does happen (regardless if its unlikely) the laser pulse will then be the dominant force.

The interesting part is that the dynamics before ionizing the atom is exact so no approximations were made

2.3 Ionization rates

What is a ionization rate and why do we want to have it?

Dilemma: numerical simulations yield good ion propabilitiees but no ionization rate, analytical calculations yield good ionization rates but incorrect propabilities (see GASFIR paper).

Furthermore, no experimental method has been developed yet to measure ionization rates, only ionization propabilities - a quantum mechanical observable.

As long as the electromagnetic field is present, projecting onto bound/unbound states yields non-physical gauge-dependent predictions [14].

Tunneling time is imaginary, source???

2.3.1 Derivation of SFA Rate

This mainly follows [?] with some modification.

First we write the ionization propability as the amplitude of projection of the wavefunction onto the continuum supspace. The ionization rate integrated over the time domain should

yield the total ionization propability. Therefore we can write the SFA rate (??) as:

$$\begin{aligned} \lim_{t \rightarrow \infty} \langle \Psi(t) | \int d^3p |p\rangle \langle p| \Psi(t) \rangle &= \int_{-\infty}^{\infty} \Gamma_{\text{SFA}}(t) dt \\ &= \int d^3p \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt_1 dt_2 e^{\frac{i}{2} \int_{t_1}^{t_2} (\underline{p} + A_z(t''))^2 dt''} E_z(t_1) E_z(t_2) \\ &\quad \times \left(\sum_n e^{iE_n t_1} c_n^*(t_1) d_{z,n}^*(\underline{p} + A_z(t_1)) \right) \left(\sum_n e^{-iE_n t_2} c_n(t_2) d_{z,n}(\underline{p} + A_z(t_2)) \right) \end{aligned}$$

Changing variables to $t = \frac{t_2+t_1}{2}$ and $T = \frac{t_2-t_1}{2}$ and using the fact that our Laser pulse is polarized along the z Axis gives us:

$$\begin{aligned} \Gamma_{\text{SFA}}(t) &= \int d^3p \int_{-\infty}^{\infty} dT e^{\frac{i}{2} \int_{t-T}^{t+T} (\underline{p} + A_z(t''))^2 dt''} E_z(t-T) E_z(t+T) \\ &\quad \times \left(\sum_n e^{i(t-T)E_n} c_n^*(t-T) d_{z,n}^*(\underline{p} + A_z(t-T)) \right) \left(\sum_n e^{-i(t+T)E_n} c_n(t+T) d_{z,n}(\underline{p} + A_z(t+T)) \right) \\ &= \sum_{n_1} \sum_{n_2} \int_{-\infty}^{\infty} dp p^2 \int_0^{\pi} d\theta \sin \theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dT e^{\frac{i}{2} \int_{t-T}^{t+T} (\underline{p} + A_z(t''))^2 dt''} e^{i(t-T)E_{n_1} - i(t+T)E_{n_2}} \\ &\quad \times E_z(t-T) E_z(t+T) c_{n_1}^*(t-T) c_{n_2}(t+T) d_{z,n_1}^*(\underline{p} + A_z(t-T)) d_{z,n_2}(\underline{p} + A_z(t+T)) \end{aligned}$$

Now we change the integration from \mathbf{p} to $\mathbf{p} + \mathbf{A}$ and defining $\Delta(t') = \mathbf{A}(t+t') - \mathbf{A}(t)$ gives us:

$$\begin{aligned} &\sum_{n_1} \sum_{n_2} \int_{-\infty}^{\infty} dp p^2 \int_0^{\pi} d\theta \sin \theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dT e^{\frac{i}{2} \int_{t-T}^{t+T} (\underline{p} + \Delta_z(t''))^2 dt''} e^{i(t-T)E_{n_1} - i(t+T)E_{n_2}} \\ &\quad \times E_z(t-T) E_z(t+T) c_{n_1}^*(t-T) c_{n_2}(t+T) d_{z,n_1}^*(\underline{p} + \Delta_z(-T)) d_{z,n_2}(\underline{p} + \Delta_z(T)) \end{aligned}$$

Also the integrand in the exponential function can be further simplified:

$$\begin{aligned} \frac{i}{2} \int_{-T}^T (\mathbf{p} + \Delta_z(t''))^2 dt'' &= i\mathbf{p}^2 T + \frac{i}{2} \int_{-T}^T \Delta_z(t'')^2 + 2\mathbf{p} \cdot \Delta_z(t'') dt'' \\ &= i\mathbf{p}^2 T + ip \cos \theta \int_{-T}^T \Delta_z(t'') dt'' + \frac{i}{2} \int_{-T}^T \Delta_z(t'')^2 dt'' \end{aligned}$$

Because in the code as well as in [?] the notation

$$\bar{\Delta}^k = \int_{-T}^T \Delta^k(t') dt' = \int_{-T}^T (\mathbf{A}(t+t') - \mathbf{A}(t))^k dt'$$

was used, we can write the final SFA rate that's later being implemented as

$$\begin{aligned} \Gamma_{\text{SFA}}(t) = & \sum_{n_1} \sum_{n_2} \int_{-\infty}^{\infty} dp p^2 \int_0^{\pi} d\theta \sin \theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dT \\ & \times \exp \left(i\mathbf{p}^2 T + ip \cos \theta \bar{\Delta}_z^k + \frac{i}{2} \bar{\Delta}_z^2 + i(t-T)E_{n_1} - i(t+T)E_{n_2} \right) \\ & \times E_z(t-T)E_z(t+T)c_{n_1}^*(t-T)c_{n_2}(t+T)d_{z,n_1}^*(\underline{p} + \Delta_z(-T))d_{z,n_2}(\underline{p} + \Delta_z(T)) \end{aligned}$$

For numerical calculations it can be convenient to split a complex integrand into its phase and absolute value. Mostly this is being done with this formula, but the coefficients remain complex and may have a very fast oscillating phase.

2.4 Strong Field Ionization

This mostly follows [master manoram thesis] Ionization can occur in different ways, depending on the laser parameters and the atom or material used. To distinguish these two processes, we need to define some parameters. According to [?] the strong field ionization depends mostly on three parameters: the photon energy, the binding potential and the ponderomotive energy.

Ponderomotive Energy The ponderomotive energy is the cycle-averaged quiver energy of a free electron in an electromagnetic field. [cite wikipedia] Since the particle experiences harmonic motion, the time-averaged kinetic energy is given by

$$\frac{1}{2}m\omega^2 \langle x^2 \rangle = \frac{e^2 E^2}{4m_e \omega^2} = \frac{E^2}{4\omega^2}$$

Keldysh Parameter The Keldysh parameter γ compares the ponderomotive energy with the ionization potential. It is defined as

$$\gamma = \sqrt{\frac{I_p}{2U_p}}$$

The ionization potential in the hydrogen atom is $I_p = 13.6\text{eV} = 0.5\text{au}$. Depending on what the keldysh parameter is, one can define different regimes of ionization with different physical interpretations.

2.4.1 Tunneling ionization

Usually one can define this regime with $\gamma \ll 1$. The laser pulse is so strong that it distorts the potential barrier. However one can also define it with saying the tunneling regime is where the quasi static approximation holds, i.e the instantaneous ionization rate is entirely defined by the absolute value of the electric field at that time [?]. That makes it possible to calculate the ionization rate for DC and AC fields in this regime analytically [?].

$$\Gamma_{\text{SFA}}(t) \propto \exp\left(-\frac{2}{3} \frac{(2I_p)^{3/2}}{F}\right)$$

With F being the peak of the electric field for an AC field.

2.4.2 Multiphoton ionization

The regime where $\gamma \gg 1$ is mostly called multiphoton ionization. This is especially when the field strength is far weaker than in the tunneling regime. In other words, multiphoton regime can be defined as the regime where

$$\Gamma_{\text{SFA}}(t) \propto \mathbf{E}^{2N} \quad \text{with} \quad N = \frac{I_p}{E_e}$$

is valid [?]. You can imagine it as the electron is being heated up, gaining energy while still under the barrier. That makes it the complete opposite of the tunneling regime, being non adiabatic. For deeper insight, refer to [?] and [?].

2.4.3 Intermediate regime

This is the most important regime for this thesis. Previous regimes just define limits, when the complementary process is negligible. But in reality it's more an coexistence of both processes. In this intermediate regime, the tunneling process is no longer adiabatic. This means the potential barrier oscillates significantly during the time it takes for the electron to tunnel through it. As a result, the electron can absorb energy from the laser field while it is tunneling.

3. Methods

The main reason for making these ionization models is because one wants to avoid solving the Schrödinger equation numerically because it is time consuming and contains numerical difficulties. However, for comparing and verifying the models, one needs to solve it numerically.

Furthermore, numerically solving the TDSE is just good for ionization probabilities and not rates.

Especially for expanding an already existing model, it is important to compare and see if the changes of the model are going into the right direction.

3.1 Numerical Methods

To implement formula ?? we need to solve the TDSE numerically in order to obtain the coefficients $c_n(t)$. For that I used two different tools (tRecX and ODE) each with its own advantages and disadvantages. Further, there is this dilemma with ionization rates not being quantum mechanical observables, so we need to have trustworthy ionization probabilities to compare my results.

3.1.1 tRecX

tRecX is a C++ code for solving generalized inhomogeneous time-dependent Schrödinger-type equations in arbitrary dimensions and in a variety of coordinate systems [?]. Usually ionization is difficult for a numerical solver because the electron "leaves" the subspace of the bound states, making the calculations very time consuming. tRecX uses different techniques (irECS and tSURFF) making it especially suitable for light atom interaction. Further, tRecX allows to specify the gauge in which the TDSE is solved, making it more flexible. This will be important later.

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3.1.2 ODE/Python

3.2 TIPTOE

This follows [?] and manorams master thesis.

Why do we need TIPTOE? In order to verify the ionization rates determined by the models, we need to compare it with something that is experimentally accessible. However an ionization rate is not a quantum mechanical observable, we can only measure the ionization yield so $\int \Gamma(t)dt$.

In some way, TIPTOE motivates this thesis, since TIPTOE's results showed us the break in time reversal symmetrie mentioned earlier. But what is TIPTOE? TIPTOE [?] is short for tunneling ionization with a perturbation for the time-domain observation of an electric field. It is used for direct sampling an electric pulse in the femtosecond to attosecond regime using quasistatic subcycle tunneling ionization in a gaseous medium or air. Tunneling ionization differs from multiphoton ionization in the sense that the laser field is so strong that it deforms the coulomb barrier of the atom, allowing the electron to tunnel through it. However, our motivation to establish an instantanious ionization rate remains promising, especially because in the models that describe tunneling ionization, the ionization rate only depends on the field strength of the laser pulse. A typical TIPTOE simulation consist of two linear polarised lase pulses, a "fundamental" and a "signal" pulse,

similar to common pump-probe experiments. The drive pulse is the pulse we want to sample at the end just by measure the ionization yield for a certain medium. In the first order we can approximate the ionization rate as

$$\Gamma(E_F + E_S) = \Gamma(E_F) + E_S \frac{d\Gamma(E_S)}{dE} \Big|_{E=E_F}$$

However in this approximation we are going to neglect the depletion of the ground state. Then the total ionisation yield N obtained by the two pulses is given by

$$N = N_0 + \delta N = \int dt \Gamma(E_F(t)) + \int dt E_{S(t)} \frac{d\Gamma(E_S(t))}{dE} \Big|_{E=E_F(t)}$$

By changing the delay τ between the two pulses, the ionization yield of course different values. With this we can find that:

$$\delta N(\tau) = E_S(\tau)$$

so we can sample the field amplitude of the signal pulse by measuring the ionization yield for different delays. The TIPTOE method can be applied for the broad spectral range of the signal pulse, as long as the fundamental pulse is shorter than 1.5 optical cycles.

This method is very usefull because the problem of numerical simulations giving good predicitions about ionization propabilities and analytical models about ionization rates. Now we have a method to compare both ways and egt insight in the dynamics of the electron. We will later integrate the ionization rate of $E_F + E_S$ over the full time domain and compare the ionization yield for different delay with the resluts from the numerical solution of the TDSE.

3.3 GASFIR

GASFIR is short for general approximator for strong field ionization rates. It is an analytical retrieval tool for reconstructing data obtaned from numerical solutions of the TDSE. It was validated for hydrogen and shows good agreement with existing theories in the quasi static limit of tunneling ionization not only for Hydrogen, also for Helim and Neon [cite GASFIR]. The way how GASFIR works is that it uses ionization probabilities to retrieve ionization rates. It uses the idea from SFA that the rates can be written as $\int dT K(t, T)$ with $K(t, T)$ being a kernel function. Later in the code you see also the kernel function, where the modifications happened. Its not really part of this thesis, but motivates it. Goal: make GASFIRs predictions better by improving SFA rates

4. Implementation

For retrieving ionisation rates, there are different ways of calculating the rates.

In this chapter I will explain some concepts and methods that are used to calculate the ionisation rates and what to do with them, how to verify them and so on.

4.1 SFA Implementation

4.2 SFA excited Implementation

The implementation of formula ?? was being done in python. Most of the implementation was already done by the Authors of [?]. The only part missing in the implementation was the extension to excited states. For that, major difficulty arises from the fact that we now need the coefficients $c_n(t)$ of the state before ionization. For the coefficients I used two different ways. The one is the most straight forward way. I solved a system of ordinary differential equations (ODE) to solve for the coefficients. Lets do the derivation real quick.

We start by splitting the $\hat{\mathcal{H}}$ into two parts $\hat{\mathcal{H}}_0$ and $\hat{\mathcal{H}}_{\text{Pert}}(t)$ where the eigenstates and eigenenergies of $\hat{\mathcal{H}}_0$ are known. Note that $\hat{\mathcal{H}}_{\text{Pert}}(t)$ has to be small enough such that our ansatz really works. We write our ansatz for the wavefunction as

$$|\alpha(t)\rangle = \sum_n c_n(t) e^{-iE_n t} |n\rangle$$

with E_n being the exact eigenstates of $\hat{\mathcal{H}}_0$ so just the hydrogen atom. Note that this ansatz does not represent the full wavefunction, we artificially force the electron to stay in the part of the Hilbert space covered by the bound states. In other words this ansatz doesn't even allow ionization, there is no notion to describe it. The next step is to plug this ansatz into the TDSE and multiply with $\langle m|$ to get the coefficients $c_n(t)$.

$$i\dot{c}_m(t) = \sum_n c_n(t) e^{-i\omega_{nm}t} \langle m|\hat{\mathcal{H}}_{\text{Pert}}(t)|n\rangle$$

with $\omega_{nm} = E_n - E_m$. Now we have two problems. First, \sum_n goes from 0 to ∞ , but since we are in numerical simulations we have to limit ourselves to a finite number of states. How can we justify the number we chosen? How can we make shure that the abrult end of the sum does not cause any numerical problems (like oszillations at the end)? Further, equation (??) is gauge dependent because of $\langle m | \hat{\mathcal{H}}_{\text{Pert}}(t) | n \rangle$. Which gauge should we use to get the most meaningful results? I will discuss these questions later.

The coefficients from the ODE are not the only one im using. I used tRecX to calcu- late solve the entire TDSE and extract the coefficients from the whole wavefunction. As mentioned earlier, there are two ways to think about $\hat{\mathcal{U}}(t', t_0) | \Psi \rangle$. First, solve the TDSE in the subspace of the bound states (we did that with the ODE) or solve the TDSE in the full Hilbert space and the project it onto bound states. tRecX does the second one, which is far more complicated than what I did using the ODE. However, tRecX results are also gauge dependent, so we need to be careful with the gauge. Also it is far more difficult to interpret the rsults from tRecX since many effects can determine the time evolution of the coefficients and therefore the ionization rate but its of course helpfull to have two independent sources of in some sense the same thing.

4.2.1 Coefficients

In theory, $|c_n(t)|^2$ or the amplitude of the coefficients is observable quantity and can be measured in experiment. It tells us how propable the system is to be in a certain state n at time t . Furthermore, and most importantly, they are gauge independent. But since SFA is gauge dependent theory, and now we are not even dealing with the amplitude instead the complex coefficients, we need to be extremely careful with the gauge.

In my thesis there are mostly two gauges used, the length gauge and the velocity gauge. In the following plot you see that the amplitudes are indeed not gauge independent. But why is that the case?

The gauge is a very fundamental problem. Not so fundamental is our ansatz, as mentioned erlier we artificially force the electron to stay in the part of the Hilbert space covered by the bound state. This restricts us to small ionization propabilities, and may also cause some numerical problems as will discussed later.

Also the numerical issue that we need to have infinitely many bound states for covering the aprt of the Hilbert space completely is not possible, so we have to limit ourselves. First this seems like a big problem, but we will see that most of the dynamics inside the electron before ionisation is in my simulations only determined by a few bound states. But one still

need to be careful with the number of used bound states, but because of numerical reasons.

For my numerical solution I used a system of ordinary differential equations (ODEs) to calculate the coefficients $c_n(t)$ using the interaction picture. In my implementation I neglected transitions to states that are forbidden via the dipole selection rules. However this is an approximation, since in reality two-photon processes can occur, effectively allowing transitions between $1s$ and $2s$ for instance. I numerically solved the Schrödinger equation with tRecX and modified the code to print out the coefficients $c_n(t)$ allowing me to get insight in the "real" dynamics of the electron.

Question: how many bound states do we need (mentioned earlier)?

in E4 it was easy because laser had cosine shape. attosecond physics not the case, more a laser pulse, cos² envelope so it doesn't make much sense to speak of Rabi oscillations.

I also need to check how often I have to write the coefficients to the expect file. That depends on the characteristic time of the state and on the frequency of the laser of course.

Naiv: as much as possible to be precise as possible. But: we don't want to exceed the length gauge regime, are best described in length not velocity gauge. Further: more phenomenological but most of the dynamics is in the first few bound states, like $2s$, $2p$, $3p$ that's mostly it. For that just look at the $|c_n(t)|^2$ which has the highest amplitudes.

For extracting the coefficients from tRecX so solving the full TDSE and then projecting onto bound states I modified the code as following: Already implemented was the Occupation probability of specified bound states, so the code prints out $\langle \Psi(t) | \hat{P}_{\text{Occ}\{H0:n\}} | \Psi(t) \rangle = |\langle \Psi(t) | n \rangle|^2$. In principle all I did was changing implementing a new function that changes the left bra $\langle \Psi(t) |$ to the eigenstate used in $\hat{P}_{\text{Occ}\{H0:n\}}$ and verifying that the eigenstates are normalized. This gives us

$$\langle \Psi(t) | \hat{P}_{\text{Occ}\{H0:n\}} | \Psi(t) \rangle \rightarrow \langle n | \hat{P}_{\text{Occ}\{H0:n\}} | \Psi(t) \rangle = \langle n | n \rangle \times \langle n | \Psi(t) \rangle = c_n(t)$$

For that I needed to solve the eigenvalue problem again, and pass the eigenstates down to the function calculating the expectation value. There is definitely a more elegant way to do that, especially efficiency wise, since the eigenstates are already calculated elsewhere, but for now this works.

4.2.2 ODE coefficients Implementation

4.2.3 Dipole matrix Elements

The dipole matrix elements are an essential part of the formula in (??). Calculating it generally can be cumbersome, but in the case of hydrogen it's even possible to do it analytically ???. However, it's that easy to calculate because we made a very coarse approximation, since the final state after ionisation is in reality a plane wave, but we approximated it with that by using SFA.

Furthermore, our problem is

4.3 tRecX TIPTOE Simulations

4.3.1 TIPTOE

TIPTOE [?] is a sampling method used for sub femtosecond processes. It is relevant for this thesis because it was used to verify the results from the Ionization model. TIPTOE is great because its fundamentals are very simple but it can tell you a lot about the dynamics in attosecond regime.

Now I used length gauge for the coefficients but velocity gauge for the ionization probabilities

5. Results and Discussion

Before discussing the results, first we have to formulate what we want to learn from this kind of generalisation. The main difference from previous literature was the use of transition to excited states before ionisation. In principle we want to investigate how this transition influences the ionisation process or in general the ionisation rate.

Previously: time reversal symmetry, what causes it?

Also we want to know what influences the ionization rate more, the Stark shift or the distortion of the ground state or the possibility for the electron to also get excited to higher states instead of direct ionization.

So let's start with the Stark effect.

Also we want to get closer to the tRecX TIPTOE results because that's all we really got (quantum mechanics fundamentals) maybe including excited states will help us.

All results are stored in a github repository and can be reproduced.

5.1 Stark Shift

The Stark effect is the shift of the energy levels of an atom or molecule due to the presence of an external electric field.

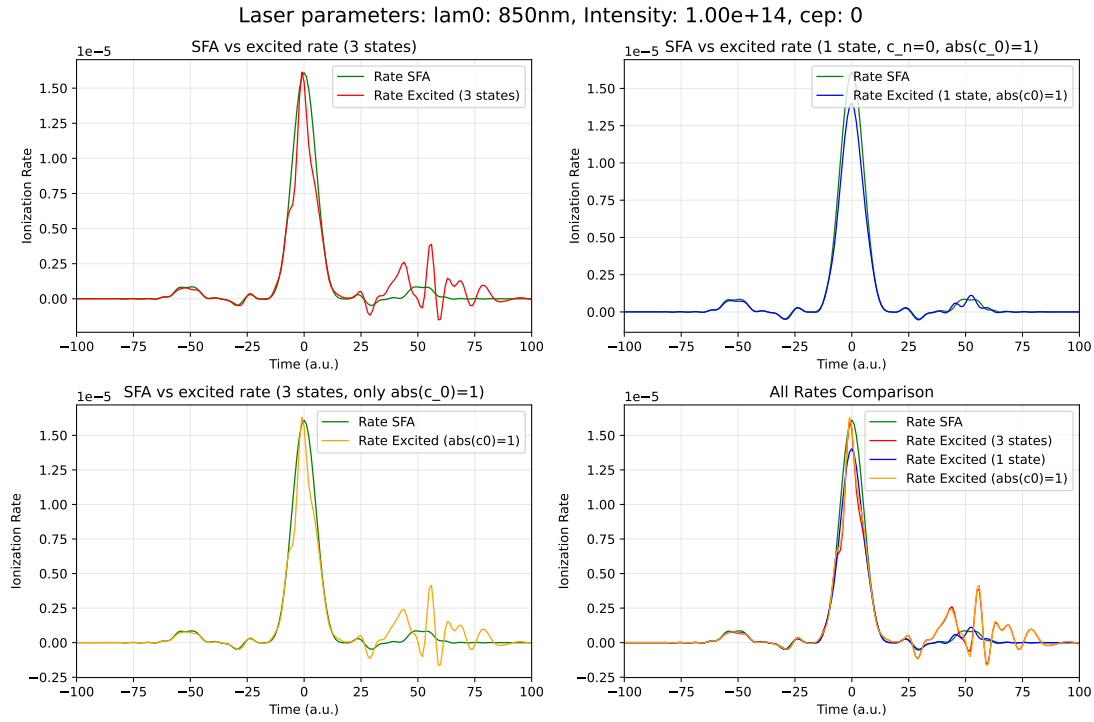


Figure 5.1: stark effect

Naiv: Stark effect changes energy in electron so its "harder" to ionise, thats why blue curve goes down (when excitedStates=1). But thats not certainly the case because of stark effect, thats why only set absc0 to 1 and phase remains. Example with oszillations with time dependent resonance frequency, and external force not at resonance but coincidence with oszillator resonance frequency so this may cause it.

5.2 Rates

Stark shift doesnt seem to have much contribution (sadly).

Lets investigate the influence of first coefficient, nothing more. Only the phase has a contribution, the amplitude is not important. Thats because the amplitude determines something occupation propability, but the phase is e^{-iEt} and if E is shifted by a bit you can isolate it by just using purely the phase.

Top right is the isolated stark effect

5.3 TIPTOE

From the TIPTOE results we want to learn, weither the tRecX coefficients or the SFA coefficients bring us closer to the tRecX ionProb results and if excited states help at all.

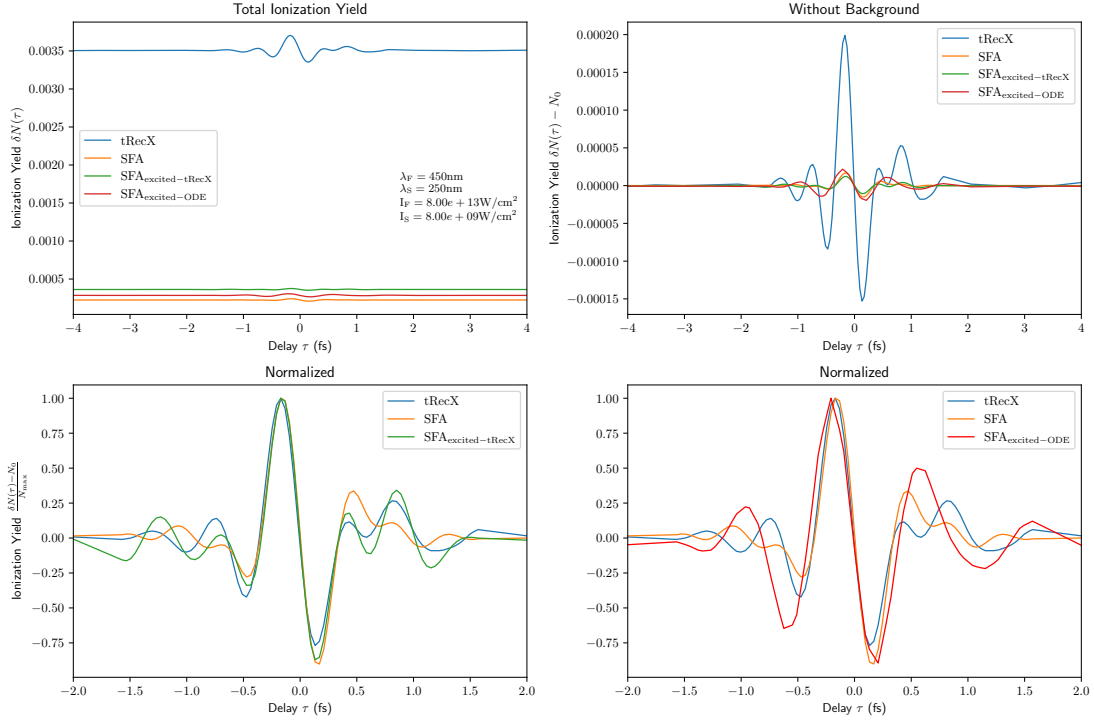


Figure 5.2: TIPTOE 3 excited states

On the left plot we see that tRecX is still orders of magnitude larger than the SFA results. However, with excited states it goes in the right direction as can be seen on the right plot. For three excited states there is not much improvement visible. Unfortunately, the results are nowhere close to the tRecX measurements. That indicates that there is some physics missing in the SFA model. If it's not the excited states, then it must be something else. And because the change is so big it has to be something more fundamental. The first idea is that the interaction with the coulomb potential after ionization cannot be completely neglected, as it is done in the SFA model. Even though it is counterintuitive, because if the coulomb potential is still noticeable for the electron after ionization, why would it increase the results we are seeing????? But this is in principle what our simulations are telling us. We can argue that we have two different ways of calculating the coefficients (ODE and tRecX) and then reproduce the same result.

However, it indicates that real ionization probabilities do have some characteristics that the improved SFA model does not capture.

One also should make clear what the ODE coefficients do not capture. First, I implemented the code such that it ignores transitions not allowed by the dipole selection rules.

So in principle, assuming my SFA modification was correct, the TIPTOE results tell us that the coulomb potential is not negligible after all. Maybe because the laser is not that intense (multiphoton ionization). But it's difficult to test that because if I increase the laser

intensity, the approximations I made with the coefficients is not valid anymore.

Looking at not normalized results, tRecX is much more sensitive to the shift of probe and pump pulse, while excited SFA coefficients are not. Maybe because tRecX takes into account all the dynamics and effects inside an atom, while excited SFA coefficients does not care that much. I would expect with tRecX coefficients more sensitive than with ODE coefficients???

5.4 Lorem

This might be how it is supposed to be – we are in the regime where the laser field is strong enough to ionize the atom, but we artificially force the electron to stay in the part of the Hilbert space covered by a few bound states. If the calculations are converged with respect to the time step, and you see convergence regarding the number of bound states in the weak-field regime, then it's fine if there is no convergence with respect to the number of bound states in the strong-field regime.

6. Conclusion and Outlook

Could be good for GASFIR because GASFIR learns from exact SFA rate.
What is more important, stark shift or else?

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A. Volkov states

We will derive Volkov states in different gauges, starting with velocity gauge since its the most natural for an electron in a laser field to be described that way.

Velocity gauge

Lets write the Schroedinger equation without the Coulomb interaction part with the interaction with the laser in velocity gauge ?? using atomic units:

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = \left(\frac{\hat{\mathbf{p}}^2}{2} + \hat{\mathbf{p}} \cdot \mathbf{A}(t) + \frac{\mathbf{A}^2}{2}\right)|\Psi(t)\rangle$$

Lets use the momentum basis for the representation of the wavefunction:

$$i\frac{\partial}{\partial t}\phi(\underline{p}, t) = \left(\frac{\underline{p}^2}{2} + \underline{p} \cdot \mathbf{A}(t) + \frac{\mathbf{A}^2}{2}\right)\phi(\underline{p}, t)$$

This equation can be solved easily by maing the ansatz:

$$\phi(\underline{p}, t) = e^{-\frac{i}{2} \int_{t_0}^t (\underline{p} + \mathbf{A}(t'))^2 dt'}$$

In coordinate space this will result in:

$$\psi(\underline{x}, t) = \mathcal{F}^{-1}\{\phi(\underline{p}, t)\} = (2\pi)^{-3/2} e^{\underline{x} \cdot \underline{p} - \frac{i}{2} \int_{t_0}^t (\underline{p} + \mathbf{A}(t'))^2 dt'} \quad (\text{A.1})$$

Length gauge

B. Dipole transition matrix elements

We want to derive the general transition dipole matrix elements into the continuum for an hydrogen-like atom. The general matrix element in our case is given by:

$$\underline{d}(\underline{p}) = \langle \Pi | \hat{\mathbf{d}} | \Psi_{nlm} \rangle \stackrel{\text{a.u.}}{=} \langle p | \hat{\mathbf{r}} | \Psi_{nlm} \rangle$$

With $|p\rangle$ being a plane wave. By partitioning the $\hat{\mathbf{1}}$, and using the fact that $\hat{\mathbf{r}} \rightarrow i\nabla_{\underline{p}}$ in momentum representation we find a general formula for the transition:

$$\underline{d}(\underline{p}) = i\nabla_{\underline{p}} \int d^3\underline{x} \psi_{nlm}(\underline{x}) e^{-i\underline{p}\cdot\underline{x}} = i\nabla_{\underline{p}} \phi_{nlm}(\underline{p})$$

In principle, this integral or more precise the Fouriertransformation of the wavefunction is all we need to do. Because of the structure of ψ_{nlm} we can expect a result similar to (eqref psi=RY). A posteriori we will see that:

$$\mathcal{F}\{\psi_{nlm}(\underline{x})\} = \phi_{nlm}(\underline{p}) = F_{nl}(p) Y_{lm}(\theta_p, \phi_p)$$

With $F_{nl}(p)$ being the Fouriertransform of the radial part of the wavefunction and $Y_{lm}(\theta_p, \phi_p)$ being the spherical harmonics in momentum space similar to the hydrogen atom in position space.

Momentum space

We start with the so called plane wave expansion [?] of the exponential part of the integral:

$$e^{i\underline{p}\cdot\underline{x}} = \sum_{l'=0}^{\infty} (2l' + 1) i^{l'} j_{l'}(pr) P_{l'}(\underline{p} \cdot \underline{x}) = 4\pi \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} i^{l'} j_{l'}(pr) Y_{l'm'}(\theta_p, \phi_p) Y_{l'm'}^*(\theta_x, \phi_x)$$

With $j_l(pr)$ being the spherical bessel functions. Also note that we are integrating over spherical kordinates now. At first it looks messy but we can use the orthogonality of the

spherical harmonics we can reduce the integral to:

$$\phi_{nlm}(\underline{p}) = 4\pi \sum_{m=-l}^l Y_{lm}(\theta_p, \phi_p) i^l \underbrace{\int_0^\infty dr r^2 j_l(pr) R_{nl}(r)}_{\tilde{R}_{nl}(p)}$$

This is the structure we were hoping for. Lets focus on the radial part $\tilde{R}_{nl}(p)$ of the integral. The term $R_{nl}(r)$ represents the radial function of the hydrogen atom in position space and is independent of the magnetic number m . An exponential term dependent of r , a polynomial term dependent of r , the generalized Laguerre polynomials and the normalization constant. It would be convenient to have a closed expression for the generalized Laguerre polynomials. I choose to represent them as following:

$$L_n^l(r) = \sum_{\iota=0}^n \frac{(-1)^\iota}{\iota!} \binom{n+l}{n-\iota} r^\iota$$

The Laguerre polynomials are therefore only dependent on an exponential term and finitely many polynomial terms. $\tilde{R}_{nl}(p)$ can be expressed (without prefactors and summation over ι) as:

$$\int_0^\infty dr r^{2+l+\iota} e^{-\frac{Zr}{n}} j_l(pr)$$

Before we can solve the Integral using computational methods, we need to transform the spherical bessel function into the ordinary ones:

$$j_l(pr) = \sqrt{\frac{\pi}{2pr}} J_{l+\frac{1}{2}}(pr)$$

Now it is a good time to write all the prefactors and summations in one expression and look at the integral as a whole:

$$\begin{aligned} \phi_{nlm}(\underline{p}) &= \frac{\pi^{3/2}}{\sqrt{2p}} \sqrt{\left(\frac{2}{n}\right)^3 \frac{(n-l-1)!}{n(n+1)!}} \\ &\times \sum_{m=-l}^l \sum_{\iota=0}^{n-l-1} i^l \frac{(-1)^\iota}{\iota!} \left(\frac{2}{n}\right)^{l+\iota} \binom{n+l}{n-l-1} \underbrace{\int_0^\infty dr r^{l+\iota+\frac{3}{2}} e^{-\frac{Zr}{n}} J_{l+\frac{1}{2}}(pr) Y_{lm}(\theta_p, \phi_p)}_{(*)} \end{aligned}$$

To calculate the remaining Integral, I used mathematica, so I can not give a detailed explanation of that. Interestingly, there is an analytical solution for that. The result for $(*)$ is:

$$(*) = {}_2\tilde{F}_1 \left(2+l+\frac{\iota}{2}, \frac{1}{2}(5+2l+\iota); \frac{3}{2}+l; -\frac{n^2 p^2}{Z^2} \right)$$

With ${}_2\tilde{F}_1$ being the regularized hypergeometric function defined by:

$${}_2\tilde{F}_1(a, b; c; z) = \frac{{}_2F_1(a, b; c; z)}{\Gamma(c)} = \frac{1}{\Gamma(a)\Gamma(b)} \sum_{n=0}^{\infty} \frac{\Gamma(a+n)\Gamma(b+n)}{\Gamma(c+n)} \frac{z^n}{n!}$$

The final formula $\phi_{nlm}(\underline{p})$ that can be also found in [atoms and molekulse] in slightly different form, can then be expressed as:

$$\begin{aligned} \phi_{nlm}(\underline{p}) = & \sum_{\iota=0}^{2l+1} \frac{(-1)^\iota 2^{\iota+\frac{1}{2}} n (in)^l (p^2)^{l/2} Z^{-l-3} \Gamma(2l + \iota + 3)}{\iota!} \\ & \times \binom{l+n}{-l+n-\iota-1} \sqrt{\frac{Z^3 \Gamma(n-l)}{\Gamma(l+n+1)}} \\ & \times Y_l^m(\theta_p, \phi_p) {}_2\tilde{F}_1\left(l + \frac{\iota}{2} + 2, \frac{1}{2}(2l + \iota + 3); l + \frac{3}{2}; -\frac{n^2 p^2}{Z^2}\right) \end{aligned} \quad (\text{B.1})$$

Transition Element

Now all thats left is to differentiate (??) with respect to \underline{p} .

new eq

$$\sum_{\iota=0}^{2l+1} \left(\frac{(-1)^\iota n \text{Ip}^{-l-3} 2^{\iota-1} (in)^l (p^2)^{l/2} \left(\frac{1}{\sqrt{p^2}} - \frac{\text{pz}^2}{(p^2)^{3/2}} \right) \Gamma(2l + \iota + 3) \binom{l+n}{-l+n-\iota-1} \sqrt{\frac{\text{Ip}^3 \Gamma(n-l)}{\Gamma(l+n+1)}} {}_2\tilde{F}_1\left(l + \frac{\iota}{2} + 2, \right.}{\dots} \right) \quad (\text{B.2})$$

$$\begin{aligned}
& \sum_{\iota=0}^{2l+1} \left(- \frac{(-1)^{\iota} n \text{Ip}^{-l-3} 2^{\iota-l-1} (in)^l (p^2)^{l/2} \left(\frac{1}{\sqrt{p^2}} - \frac{\text{pz}^2}{(p^2)^{3/2}} \right) \Gamma(2l + \iota + 3) \binom{l+n}{-l+n-\iota-1} \sqrt{\frac{\text{Ip}^3 \Gamma(n-l)}{\Gamma(l+n+1)}}}{\iota! \sqrt{1 - \frac{\text{pz}^2}{p^2}}} \right. \\
& \quad \times {}_2\tilde{F}_1 \left(l + \frac{\iota}{2} + 2, \frac{1}{2}(2l + \iota + 3); l + \frac{3}{2}; -\frac{n^2 p^2}{4\text{Ip}^2} \right) \left(\frac{m \text{pz} Y_l^m \left(\cos^{-1} \left(\frac{\text{pz}}{\sqrt{p^2}} \right), \tan^{-1}(\text{px}, \text{py}) \right)}{\sqrt{p^2} \sqrt{1 - \frac{\text{pz}^2}{p^2}}} \right) \\
& \quad + \sqrt{\Gamma(l - m + 1)}
\end{aligned}$$

C. Code

```
1  for state in range(excitedStates):
2      for stateRange in range(excitedStates):
3          cLeft = coefficients[state, :]
4          cRight = coefficients[stateRange, :]
5          f0 = np.zeros((Tar.size, tar.size), dtype=np.cdouble)
6          phase0 = np.zeros((Tar.size, tar.size), dtype=np.cdouble)
7          for i in prange(Tar.size):
8              Ti=Ti_ar[i]
9              for j in range(tar.size):
10                 tj=N+nmin+j*n
11                 tp=tj+Ti
12                 tm=tj-Ti
13                 if tp>=0 and tp<EF.size and tm>=0 and tm<EF.size:
14                     VPt = 0 # VP[tj]
15                     T= Ti*dT
16                     DelA = (intA[tp] - intA[tm])-2*VPt*T
17                     VP_p=VP[tp]-VPt
18                     VP_m=VP[tm]-VPt
19                     counter += 1
20                     #print("counter", counter) #
```

```

28         phase0[i, j] = (intA2[tp] - intA2[tm])/2 + T*
                VPt**2-VPt*DelA + eigenEnergy[state]*tm -
                eigenEnergy[stateRange]*tp
29         f0[i, j] = EF[tp]*EF[tm]*G1_T*np.conjugate(cLeft[
                tm])*cRight[tp]#(np.real(c[tp])*np.real(c[tm])
                +np.imag(c[tp])*np.imag(c[tm]))
30         print("state", state, "stateRange", stateRange)
31         print("config", config[state], "configRange", config[
                stateRange])
32         plt.plot(tar, 2*np.real(IOF(Tar, f0, (phase0)*1j)))
33         plt.show()
34         plt.close()
35         rate += 2*np.real(IOF(Tar, f0, (phase0)*1j))      #*c[np.
                newaxis, :]
36     return rate

```

testa

```

1     #include <iostream>
2
3     int main() {
4         std::cout << "Hello, World!" << std::endl;
5         return 0;
6     }

```

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Declaration of Authorship

Hiermit erkläre ich, die vorliegende Arbeit selbständig verfasst zu haben und keine anderen als die in der Arbeit angegebenen Quellen und Hilfsmittel benutzt zu haben.

München, den 20.6.2025

Unterschrift