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Bachelor's Thesis

# The influence of excited atomic states in multiphoton ionization

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Supervised by:

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Prof. Ulrich Schollwöck

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# Der Einfluss angeregter atomarer Zustände auf die Mehrphotonenionisation

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FAKULTÄT FÜR PHYSIK

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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

Ionization with an intense laser is one of the most fundamental processes in attosecond physics and quantum mechanics in general and has a broad range of applications such as medical physics or . Whether you want your system to ionize or not, it may be important to understand, how ionization works. However since it is a quantum mechanical process, one has to first ask what information are even experimentally accessible. Quantum mechanics at its very fundamental level tells us one can only measure probabilities and how likely the electron get ionized. Unfortunately, in an actual experiment that's the only option you got. Further one likes to know more about the "path" the electron takes after it gets struck by the laser pulse i.e the response of the electron to the laser pulse. Everytime you hear "path" in quantum mechanics, the first name to think of is Heisenberg. His uncertainty principle sets the boundaries for these type of questions and does not let measure all the information you wish to had. Further to see the electrons path, one has to probe the system just as lightwaves probe the matter around you letting you see. However probing a quantum mechanical system effectively changes the quantum mechanical state of the electron so eventually one has to restrict oneself to something different.

The challenge of a theoretical model is now to predict ionization probabilities and further explain the underlying mechanisms and in the best case allowing some insights what happens between initial state of the atom and measured electron. A clever way to do this is by establishing the concept of an instantaneous ionization rate (IIR) via the property  $P_{\text{ion}} = \int_{\mathbb{R}} \Gamma(t) dt$ . At first sight, "instantaneous" seems to conflict with the energy time uncertainty relation  $\Delta E \Delta t \geq \hbar/2$ . However, instantaneous refers to the response of the electron to the laser field, not the and does not contain any information on when exactly does the electron get ionized.

Lets make an example to show how an IIR can be beneficial. Suppose a measurement is made, a laser pulse hits an atom and the outcome is measured, so if the electron is ionized or not. Suppose the measurement is repeated sufficiently many times, one can define a ionization probability for instance 1%. An IIR now allows to investigate which parts of the laser pulse causes what effects in the total ionization probability. One could say, an IIR tells us how likely the electron gets ionized within a certain time interval but of course

averaged over all the measurements made. Note that the IIR does not tell us the electron will get ionized at a certain time because this would violate the energy time uncertainty relation, the value of  $\Gamma$  at a certain time does not have any physical interpretation.

This concept allows us to investigate the ionization process better and understand more about the underlying mechanisms such as defining different limits and regimes (2.4) or make use of the IIR by sampling a light pulse [?]. Due to the challenge that the IIR is not really a quantum mechanical observable, it is difficult to have a working notion of it that works for different systems and laser pulses. Eventually one has to start from scratch and derive the IIR from the time dependent schroedinger equation (TDSE) and varios approximations. One approximation most used in this context is called Strong field aproximation (SFA) mostly for its simplicity and the capability to derive ionization rates [?]. However, SFA has its limitations, especially when it comes to comparing ab initio ionization propabilities, i.e. to numerical solutions of the TDSE using dedicated numerical solver. An implicit assumption often made while using SFA is that the laser field has no effect on the atom until the moment of ionization, effectively neglecting excited atomic states. In principle this does not have anything to do with the SFA itself, making it a possible solution to the differences between SFA and ab initio ionization propabilities. This is one of the main goal of this thesis, investigate if the differences from SFA and ab initio ionization propabilities can be explained by the neglect of excited states. Further one would like to investigate the dynamics and effects of the electron before it gets ionized and how they contribute to the ionization dynamics. Particularly important would be to know what matters more, the stark shift or the distortion of the ground state wavefunction. That could lead to an improvement to existing rates, making them besser applicable in the cases mentioned before.

To achieve this, one has to review how the SFA was made previously and how it can be improved (Chapter 2). Later I will implement the extended SFA rate (Chapter 4) and compare the results with existing SFA rates and ab initio ionization propabilities (Chapter 5).

## 2. Theory

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

What I'm going to do in this chapter: derive an instantaneous ionization rate (IIR) by solving the time dependent Schrödinger 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, ionization probability around 0.01).

### 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 Schrödinger 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

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

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

### 2.1.2 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  $\chi$  is known as gauge freedom and a direct consequence of the Maxwell equations. Choosing a gauge (i.e., a specific  $\chi$ ) is a matter of convenience and can be used to simplify the calculations as presented in the following.

### 2.1.3 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 interested 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  $\chi$  that comes up when doing this calculation explicitly and is possible when  $\mathbf{A}$  and  $\varphi$  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 tough 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.

The dipole approximation holds well for most experimental setups and also for the calculations in this thesis. Nonetheless it has its limits for instance when very fast electrons are generated by strong field ionization it causes a breakdown of the dipole approximation ([?], [?]).

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

### 2.1.4 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 field<sup>1</sup>:

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

In the dipole Approximation, this can be simplified to:

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

Note that we could set  $\varphi$  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  $\varphi$  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  $\varphi$  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 rewrite the time dependent part  $\hat{V}$  of our quantum mechanical Hamiltonian as

$$\hat{\mathcal{H}}_L(t) = -\hat{\mathbf{d}} \cdot \mathbf{E}(t) \quad (2.5)$$

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

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<sup>1</sup>Derivation can be found in [?]

However, there is a different gauge transformation that will also be used in the context of this thesis. Using the velocity transformation

$$\chi = -\frac{e^2}{2m} \int_{-\infty}^t \mathbf{A}^2(t') dt'$$

and because of the dipole approximation, it leaves  $\mathbf{A}$  unchanged but  $\varphi$  changes as

$$\varphi \rightarrow \varphi - \frac{e^2}{2m} \mathbf{A}^2(t)$$

resulting in the following Hamiltonian:

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

and

$$\hat{\mathcal{H}}_V(t) = -\frac{e}{m} \hat{\mathbf{P}} \cdot \mathbf{A}(t) \tag{2.6}$$

where  $\varphi$  is set to zero. These are common ways to write the interaction Hamiltonian for light matter interaction. As with any kind of gauge transformation there are scenarios where one gauge is more convenient than the other (chapter 4).

## 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. However, previous SFA's simplifies the first Hilbertsubspace so much that 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.

SFA is in principle just the second part, neglecting the dynamics even before ionization is not really a part of it. In this section I derive an expression that does not simplify the first Hilbert space to some extent. However we will also see that there are two equivalent ways of solving the TDSE that later differ when approximations are made. Nonetheless it becomes clear that in the end they "come together" again and yield the same analytical result.

### 2.2.1 Subspaces

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

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

The idea for using projecting operators for this kind of problem comes from this [?]. Projection operators are indempotent, i.e  $\hat{X}^2 = \hat{1}$  so they are its own inverse. This can be seen as the defining property of projecting operators so applying it twice makes no difference.

With  $|\Psi_n\rangle$  being the bound states of our atom. Using  $\hat{X} + \hat{Y} = \hat{1}$  we are free to choose any partition of the Hamiltonian we can think of. First lets write the most natural partitioning::

$$\hat{\mathcal{H}}(t) = \underbrace{\hat{X}\hat{\mathcal{H}}(t)\hat{X}}_{\hat{\mathcal{H}}^{XX}(t)=\hat{\mathcal{H}}_0^{\text{ODE}}(t)} + \underbrace{\hat{Y}\hat{\mathcal{H}}(t)\hat{Y} + \hat{X}\hat{\mathcal{H}}(t)\hat{Y} + \hat{Y}\hat{\mathcal{H}}(t)\hat{X}}_{\hat{\mathcal{H}}^{YY}(t)+\hat{\mathcal{H}}^{XY}(t)+\hat{\mathcal{H}}^{YX}(t)=\hat{\mathcal{H}}_1^{\text{ODE}}(t)} = \hat{\mathcal{H}}_0^{\text{ODE}}(t) + \hat{\mathcal{H}}_1^{\text{ODE}}(t)$$

Just like with  $\hat{H}s(t) = \hat{\mathcal{H}}_0(t) + \hat{\mathcal{H}}_1(t)$  where  $\hat{\mathcal{H}}_1(t)$  is the interacting pertubation like part for instance in length gauge (??), now just with the full hamiltonian and projecting onto supspaces. For reasons elaborated later I will call this the ODE partition. ODE stands for Ordinary Differential Equation and it will be used later to solve for the coefficients that



weights our wavefunction. Now the notation falls from the sky but later it will make sense. However the Hamiltonian can also be partitioned into a different form:

$$\hat{\mathcal{H}}(t) = \underbrace{\hat{X}\hat{\mathcal{H}}(t)\hat{X} + \hat{Y}\hat{\mathcal{H}}(t)\hat{Y} + \hat{X}\hat{\mathcal{H}}(t)\hat{Y}}_{\hat{\mathcal{H}}^{XX}(t) + \hat{\mathcal{H}}^{YY}(t) + \hat{\mathcal{H}}^{XY}(t) = \hat{\mathcal{H}}_0^{\text{tRecX}}(t)} + \underbrace{\hat{Y}\hat{\mathcal{H}}(t)\hat{X}}_{\hat{\mathcal{H}}^{YX}(t) = \hat{\mathcal{H}}_1^{\text{tRecX}}(t)} = \hat{\mathcal{H}}_0^{\text{tRecX}}(t) + \hat{\mathcal{H}}_1^{\text{tRecX}}(t)$$

Lets think about what these terms mean specifcially. In  $\hat{\mathcal{H}}^{XX}(t)$  the electron never leaves the space an can always be described by a superposition of the bound states. If there would be no ionization this would be the only part determining the time evolution. In previos work this part of the Hamiltonian was suimplified so much that effects lake stark shift or coupling to excited states were neglected. But in principle  $\hat{\mathcal{H}}^{XX}(t)$  is were the approxima-tions that are not part of SFA are being made.

$\hat{\mathcal{H}}^{YY}(t)$  is basically the same but not in the subspace covered by the bound states, rather the continuum states. In reality you can not really seperate these two spaces but this is only to get a better view of it. This is the part where the SFA is being made later.

Lets think about the other terms. There are two processes that can happen, the elec-tron can get ionized or it can recombine with the atom. These processes are governed by the terms  $\hat{\mathcal{H}}^{XY}(t)$  and  $\hat{\mathcal{H}}^{YX}(t)$ . Of course in our case only one of the terms is relevant and further we will later see that  $\hat{\mathcal{H}}^{YX}(t)$  "cause" the ionization in the sense that it "kicks" the electron out of the atom [?].

For now this seems to a very useless thing to do, but it sets the boundarys for what the electron is going to do and builds some intuition for that.

### 2.2.2 Dyson equation

For determining the time evolution we need to be carefull since the whole Hamiltonian doesnt 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. The ansatz choosen here is called dyson equation. It relies on the time evolution operator and is completely equaivalent to the TDSE and therefore the dyson series (??). It can be written in two ways that are in its raw form equivalent to each other but when approximations such as SFA are made, it may yield different results.

Lets write the in my opinion more inuitive form of the dyson equation for this physical setting:

$$\hat{\mathcal{U}}(t, t_0) = \hat{\mathcal{U}}_0^{\text{ODE}}(t, t_0) - i \int_{t_0}^t \hat{\mathcal{U}}(t, t') \hat{\mathcal{H}}_I^{\text{ODE}}(t') \hat{\mathcal{U}}_0^{\text{ODE}}(t', t_0) dt' \quad (2.7)$$

Note that the ODE propagators are of course not the same as the tRecX propagators but within the dyson ansatz the full propagator  $\hat{\mathcal{U}}$  remains the same. But this will change later when SFA comes into play. Most of the formulas in this thesis can be best read from right to left such as this one. It starts with the time evolution generated by the Hamiltonian projected onto the bound states. I find this intuitive since the initial state before the laser hits the atom is the ground state.

Furthermore we can also write the dyson equation in a slightly different form:

$$\hat{\mathcal{U}}(t, t_0) = \hat{\mathcal{U}}_0^{\text{tRecX}}(t, t_0) - i \int_{t_0}^t \hat{\mathcal{U}}_0^{\text{tRecX}}(t, t') \hat{\mathcal{H}}_I^{\text{tRecX}}(t') \hat{\mathcal{U}}(t', t_0) dt' \quad (2.8)$$

It can be eaily checked that both equations indeed satisfy the TDSE by simple plugging in  $\hat{\mathcal{U}}(t, t_0)$ . The main differences between tRecX and ODE is that the "initial" propagator on the right side is now the full time proopagator instead of a part of it.

To make things easier we concretize the physical setting. Starting 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 onto a continuum state  $|\Pi(t_c)\rangle$  at time  $t_c$ .  $|\Pi(t_c)\rangle$  does not represent a plane wave, it is more an abstract state charaterized by its momentum. Of course, there is no overlap between  $|\Pi(t_c)\rangle$  and  $\hat{\mathcal{U}}_0^{\text{ODE}}(t, t_0) |\Psi_0(t_0)\rangle$  nor with  $\hat{\mathcal{U}}_0^{\text{tRecX}}(t, t_0) |\Psi_0(t_0)\rangle$  since the electron did not get ionisaed yet and we assume no initial population in the continuum [?]. Furthermore, if we expand  $\hat{\mathcal{H}}_I^{\text{ODE}}(t')$  and  $\hat{\mathcal{H}}_I^{\text{tRecX}}(t')$  and remind ourself 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:

$$\langle \Pi(t_c) | \hat{\mathcal{U}}_0^{\text{ODE}}(t, t_0) | \Psi_0(t_0) \rangle = -i \int_{t_0}^t \langle \Pi(t_c) | \hat{\mathcal{U}}(t, t') \hat{Y} \hat{\mathcal{H}}(t') \hat{X} \hat{\mathcal{U}}_0^{\text{ODE}}(t', t_0) | \Psi_0(t_0) \rangle dt' \quad (2.9)$$

and

$$\langle \Pi(t_c) | \hat{\mathcal{U}}_0^{\text{tRecX}}(t, t_0) | \Psi_0(t_0) \rangle = -i \int_{t_0}^t \langle \Pi(t_c) | \hat{\mathcal{U}}_0^{\text{tRecX}}(t, t') \hat{Y} \hat{\mathcal{H}}(t') \hat{X} \hat{\mathcal{U}}(t', t_0) | \Psi_0(t_0) \rangle dt' \quad (2.10)$$

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

### 2.2.3 Strong Field Approximation

Before making the strong field approximation, let's think about (??) and (??) 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 both the physical consequences of laser field and the binding potential.

In principle, SFA is the neglecting of the binding potential once the electron after the ionization. Intuition wise this makes sense because the Laser Field is now the dominant force acting on the electron and likely have much more influence on the electrons ionization dynamics than the coulomb potential. Also note that SFA is not about high intensity laser pulses since even if we were dealing with for instance small ionisation probabilities ( $<0.01$ ), SFA states that when ionisation does happen (regardless if its unlikely) the laser pulse will then be the dominant force.

First let's deal with the ODE partitioning. We can write time evolution operator after ionisation as:

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

Similar with the tRecX partitioning:

$$\hat{U}_0^{\text{tRecX}}(t, t') \approx \hat{U}_{\text{SFA}}(t, t') = e^{-i \int_{t'}^t \hat{\mathcal{H}}_{\text{SFA}}(t'') dt''} \quad \text{and} \quad \mathcal{H}_{\text{SFA}}(t') = \hat{\mathcal{H}}(t) - \hat{V}_C$$

It is even possible to write an exact expression for the SFA time evolution operator because now it does indeed commute with itself at different times.

Further SFA is very useful because for the eigenstates of  $\hat{\mathcal{H}}_{\text{SFA}}$  we know an exact analytical solution; the Volkov states. For that let's 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:

$$\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{x}}} = \underline{P} = m \dot{\mathbf{x}} + \frac{e}{c} \mathbf{A} \stackrel{\text{a.u.}}{=} \mathbf{p} + \mathbf{A} \quad (2.11)$$

With  $\mathcal{L}$  being the Lagrangian of the system. In our case the canonical momentum is conserved. To see this, let's 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:

$$E(t) = \dot{\underline{x}} \frac{\partial \mathcal{L}}{\partial \dot{\underline{x}}} - \mathcal{L} = \frac{\mathbf{p}^2}{2} \quad (2.12)$$

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  $\langle \Pi(t_c) |$  (not  $\langle \mathbf{p}(t_c) |$ ) is an eigenstate of  $e^{-i \int_{t'}^t \hat{\mathcal{H}}_{SFA}(t'') dt''}$  so combining (??) and (??) gives us:

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

$\underline{P}$  is of course independent of time, but  $\mathbf{A}$  is not. Now we use the fact that the canonical momentum is 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 for both tRecX and ODE:

$$\langle \Pi(t_c) | \hat{\mathcal{U}}_0^{\text{ODE}}(t, t_0) | \Psi_0(t_0) \rangle = -i \int_{t_0}^t e^{-i \int_{t'}^t (\underline{P} - \mathbf{A}(t''))^2 dt''} \langle \mathbf{p} + \mathbf{A} | \hat{\mathcal{H}}(t') \hat{X} \hat{\mathcal{U}}_0^{\text{ODE}}(t', t_0) | \Psi_0(t_0) \rangle dt' \quad (2.13)$$

and

$$\langle \Pi(t_c) | \hat{\mathcal{U}}_0^{\text{tRecX}}(t, t_0) | \Psi_0(t_0) \rangle = -i \int_{t_0}^t e^{-i \int_{t'}^t (\underline{P} - \mathbf{A}(t''))^2 dt''} \langle \mathbf{p} + \mathbf{A} | \hat{\mathcal{H}}(t') \hat{X} \hat{\mathcal{U}}(t', t_0) | \Psi_0(t_0) \rangle dt' \quad (2.14)$$

Note that SFA wiped out the difference in the left part of the integrand between ODE and tRecX so now both equation are indeed different from each other. Now comes the part thats actually new, an approximation about  $\hat{\mathcal{U}}_0^{\text{ODE}}(t', t_0) | \Psi_0(t_0) \rangle$  and  $\hat{\mathcal{U}}(t', t_0) | \Psi_0(t_0) \rangle$ .

**ODE** Whatever the final form may look like, it can certainly be expanded in the bound states  $|\Psi_n\rangle$ . This can be seen by writing the defining equation of the time evolution operator and noting that if the  $\hat{\mathcal{U}}_0^{\text{ODE}}(t', t_0) | \Psi_0(t_0) \rangle$  would have any overlap with a state not representable by the bound state, it would cancel out due to  $\hat{X}$ . With this in mind we can make an ansatz using the interaction picture as:

$$\hat{\mathcal{U}}_0^{\text{ODE}}(t', t_0) | \Psi_0(t_0) \rangle = \sum_n c_n(t') e^{-i E_n t'} | \Psi_n \rangle$$

The factors  $e^{-iE_n t'}$  were factored out because they might cause some numerical problems later on because they oscillate very fast.

In theory this ansatz is exact but with the implicit assumption that the hilbertspaces can be separated that easily. Also I assumed that the bound states are not affected by the laser field, which is not true in reality. However, this can be justified later by the fact that the laser intensity is low enough and the ionization probability does not exceed 0.01.

**tRecX** This time its a much harder approximation. The only thing that benefits here is that we only want the time evolution until moment of ionization  $t'$ . We also make the same assumptions about the laser intensity and the ionization probability as before. That justifies that this time evolution can also be approximated by a superposition of the bound states:

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

The only thing that differs from both ansatzes are the coefficients  $c_n(t')$ . In the ODE case they are retrieved by solving the TDSE in the subspace spanned by the boundstates. In other words, we cut off ionization and force the electron to stay inside the subspace (even if we would increase the laser intensity arbitrarily high). If one tries to do this this will lead you to an system of ordinary differential equations that solve for the coefficients, there the name. However, the tRecX approach is fundamentally different. In this case one has to solve the TDSE in the whole hilbertspace and then extract the coefficients at the times  $t'$ . In the atto/femtosecond regime this requires a lot of computational power and efficiency since the electron leaves the subhilbertspace within this process. For these numerical simulations I used a numerical solver (chapter 3) called tRecX. That motivates the name.

In contrast to other literature ([?], [?]) this ansatz does not neglect 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. The coefficients should contain all the relevant information that happen inside a hydrogen atom before ionization (effects like DC/AC stark shift, distortion of ground state etc.).

Lets first write the final expression. With some simplification of the dipole matrix element  $\mathbf{d}_n(\mathbf{p} + \mathbf{A}) = \langle \mathbf{p} + \mathbf{A} | \hat{\mathcal{H}}(t') | \Psi_n \rangle$  between the bound state and the continuum state one can apply the dipole approximation (??) and lets us write:

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

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 in length gauge but with the key difference that this equation does not neglect excited states.

## 2.3 Ionization rates

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

Dilemma: numerical simulations yield good ion propabiltiees 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:

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

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:

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

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 thats 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 beong 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]. This section is not directly needed for this thesis but in most literature these terms are often used so I quickly mention them. 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  $\gamma$  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 in the right direction.

### 3.1 Numerical Methods

To implement formula ?? we need to solve the TDSE in two different ways numerically in order to obtain the coefficients  $c_n(t)$ . For that I used two different methods (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.

### 3.1.2 ODE

To access the coefficients of the wavefunction inside the subspace of the bound states I used the interaction picture and the coupled system of differential equations. To implement the calculation I used Python and the ODE solver from SciPy integrate called `solve_ivp`. For initial values I choosed  $c_n(0) = 1$  for the ground state and  $c_n(0) = 0$  for all other states. The code can be found in the electronic appendix in the class `HydrogenSolver`. For more details about the implementation, see chapter 4.

## 3.2 TIPTOE

This mostly follows [?] and [?].

**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 instantaneous 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 measuren the ionization yield for a certain medium. In the first order we can approximate the ionization rate as

$$\Gamma(E_F + E_S) \approx \Gamma(E_F) + E_S \left. \frac{d\Gamma(E_S)}{dE} \right|_{E=E_F}$$

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

$$N_{\text{total}} = N_0 + \delta N = \int dt \Gamma(E_F(t)) + \int dt E_S(t) \left. \frac{d\Gamma(E_S(t))}{dE} \right|_{E=E_F(t)}$$

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

$$\delta N(\tau) \propto E_S(\tau) \quad (3.1)$$

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.

Now we have a method to compare both ways and get insight in the dynamics of the electron. This method is very usefull because the problem of numerical simulations giving good predicitions about ionization propabilities and analytical models about ionization rates. Making a TIPTOE simulation can help to "reconstruct" the ionization dynamics which is particulary usefull in the context of this thesis. 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. The results of the TIPTOE simulation from the numerical solution of the TDSE (tRecX) compared to the approximative methods (variations of SFA) are shown in the figures in chapter 5. To have a better view on the actual physics in TIPTOE I subtracted the "background" ionization from  $E_F(t)$  and normalized the ionization yield so the formula in plot ???? reads

$$\frac{N_{\text{total}} - N_0}{N_{\text{max}}} = \frac{\delta N(\tau)}{N_{\text{max}}}$$

Nevertheless, one can also find some interesting physics by just comparing the net ionization yield  $N_{\text{total}}$  but later in chapter 5.

Usually TIPTOE is not used for this kind of analysis, rather for the sampling aspect. This makes instantanious ionization rates are so usefull because with TIPTOE it allows to sample the electric field of a laser pulse in the femtosecond to attosecond regime which has of course a broad range of applications for instance in laser spectroscopy or medical physics.

### 3.3 GASFIR

GASFIR is short for general approximator for strong field ionization rates. It is an analytical retrieval tool for reconstructing data obtained 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

In this chapter I will explain how I implemented formula (??) in the code. Most of the code was already written by the authors of [?]. The exact changes I made can be found in the electronic appendix. Since I am using git, you can also see the changes in the commit history. The main two parts that were new in this implementation now are the coefficients  $c_n(t)$  and the dipole matrix elements  $\mathbf{d}_n(\underline{p})$ .

### 4.1 Coefficients

As mentioned in chapter 2, there are two ways to write the dyson equation which results in two different expressions for the s-matrix. The only difference between both approaches are the coefficients. The ODE coefficients are with respect to the subspace spanned by the bound states, while tRecX coefficients are with respect to the full Hilbert space.

#### 4.1.1 ODE

To see how to solve for the coefficients, let's look at the defining equation again:

$$\hat{\mathcal{U}}_0^{\text{ODE}}(t', t_0) |\Psi_0(t_0)\rangle = \sum_n c_n(t') e^{-iE_n t'} |\Psi_n\rangle$$

with

$$i\partial_{t'} \hat{\mathcal{U}}_0^{\text{ODE}}(t', t_0) = \hat{X} \hat{\mathcal{H}}(t') \hat{X} \hat{\mathcal{U}}_0^{\text{ODE}}(t', t_0) \quad (4.1)$$

One can think of it as the wavefunction is not "allowed" to leave the subspace. Let's do the derivation for the coefficients real quick.

We start by splitting the  $\hat{\mathcal{H}}(t)$  into two parts  $\hat{\mathcal{H}}_0$  and  $\hat{\mathcal{H}}_I(t)$  where the eigenstates of  $\hat{\mathcal{H}}_0$  are  $\{|\Psi_n\rangle\}$  and the eigenenergies  $\hat{\mathcal{H}}_0$  are  $\{E_n\}$ . The next step is to plug the ansatz above into (??) and multiply with  $\langle\Psi_m|$  to get the coefficients  $c_n(t)$ .

$$i\dot{c}_m(t) = \sum_n c_n(t) e^{-i\omega_{nm}t} \langle\Psi_m|\hat{\mathcal{H}}_I(t)|\Psi_n\rangle$$

with  $\omega_{nm} = E_n - E_m$ .

Now this has its problems. First,  $\sum_n$  goes from 0 to  $\infty$ , but since we are in numerical simulations we have to limit ourselves to a finite number of states. How can we justify the number chosen? How can we make shure that the abrupt end of the sum does not cause any numerical problems?

One way to think about it is just testing. By increasing the number of states used in the sum, the results (i.e. the rates) should converge. However, since we forced the electron to stay inside the subspace, going to higher and higher excited states can cause numerical problems as well. Especially for higher intensities and longer wavelengths, going to higher states caused unphysical oscillations in the rates. Eventually one has to find a certain number of states that is precise enough but does not cause numerical problems. For my simulations later, I used a maximum of  $n = 3$  for the calculation of the bound states. One could justify that by looking at the population; most of the dynamics before ionization is determined by the first few bound states, especially  $1s$ ,  $2s$ ,  $2p$  and  $3p$  so solving for more doesnt affect the previous coefficients not much.

Note: This was not about how many bound states I include in the final simulations, but how many I even considered when solving the ODE. I could have used only the ground state in the SFA rate later on, but there is still the question how many bound states have an effect on the ground state. This number was justified here.

Further, equation (??) is gauge dependent because of  $\langle m | \hat{\mathcal{H}}_I(t) | n \rangle$ . We can either choose length gauge (??) or velocity gauge (??). Which gauge should we use to get the most meaningful results?

To answer this question, lets think about the scenario again. An electron sits in ground state and bevore ionization its behavior is mainly described by the coulomb potential. After it gets ionized, SFA tells us it is now described as a plane wave oscillating in the laser pulse.

With this in mind, we can see that both gauges can be usefull. During the first part of the process, i.e. the electron being still bounded to the hydrogen atom, the length gauge is more appropriate since most of the behavior of the electron can be described better when knowing more about the position of the electron rather then its momentum. That is why in most elementary introductions on light matter interaction (for instance with rabi socillations and so on) length gauge because the system can not ionize. On the other hand, after ionization it is better to use velocity gauge since there is no potential anymore (because of SFA) and the elcetron is fully described by its momentum.

This makes length gauge a fitting candidate for the coefficients used in the ODE ansatz.



### 4.1.2 tRecX

The coefficients from the ODE are not the only one im using. I used tRecX to calculate 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 results 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.

### 4.1.3 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 carefull with the number of used bound states, but because of numerical reasons.

For my numerica 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 ne-

glected 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 schroedinger equation with tRecX and modyfied 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 cound states do we nodd (mentioned earlier)?

in E4 it was easy because laser had cosine shape. attosecond physics not the case, more a lase pulse, cos8 envelope so it doesnt make much sense to speak of rabi oszillations.

I also need to check how often I have to write the coefficients to the expec file. That depends on the characterisitc 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 dont want to exceed the length gauge regime, are best described in length not velocity gauge. Further: more phenomenological but most of the dynamics is int the first few bound states, like  $2s$ ,  $2p$ ,  $3p$  thats 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 propability of specified bound states, so the code prints out  $\langle \Psi(t) | \hat{P}_{\text{Occ}\{H0:n\}}^{-1} | \Psi(t) \rangle = |\langle \Psi(t) | n \rangle|^2$  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 eigenvalueporblem again, and pass the eigenstates down to the function calculating the expectation value. There is defenitely a more elegant way to do that, especially efficiency wise, since the eigenstates are already calculated elsewhere, but for now this works.

#### 4.1.4 Dipole matrix Elements

The dipole matrix elements are an essential part of the formula in (??). Calculating it generall is difficult, but in the case of hydrogen its even possible to do it analytically ??.

However, its that easy to calculate because we made a very coarse approximation, since the final state after ionisation is not in realtiy a plane wave, but we approximated it with that by using SFA.

Furthermore, our problem is

For the dipole matrix elements its also needed to simplify them as much as possible. Sometimes certain parts cancel out later in the integration (phi integral) but the computer is not good with that, even some small numerical errors will cause it to be not exactl zero and messes up the calculation.

## 4.2 tRecX TIPTOE Simulations

### 4.2.1 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.

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.

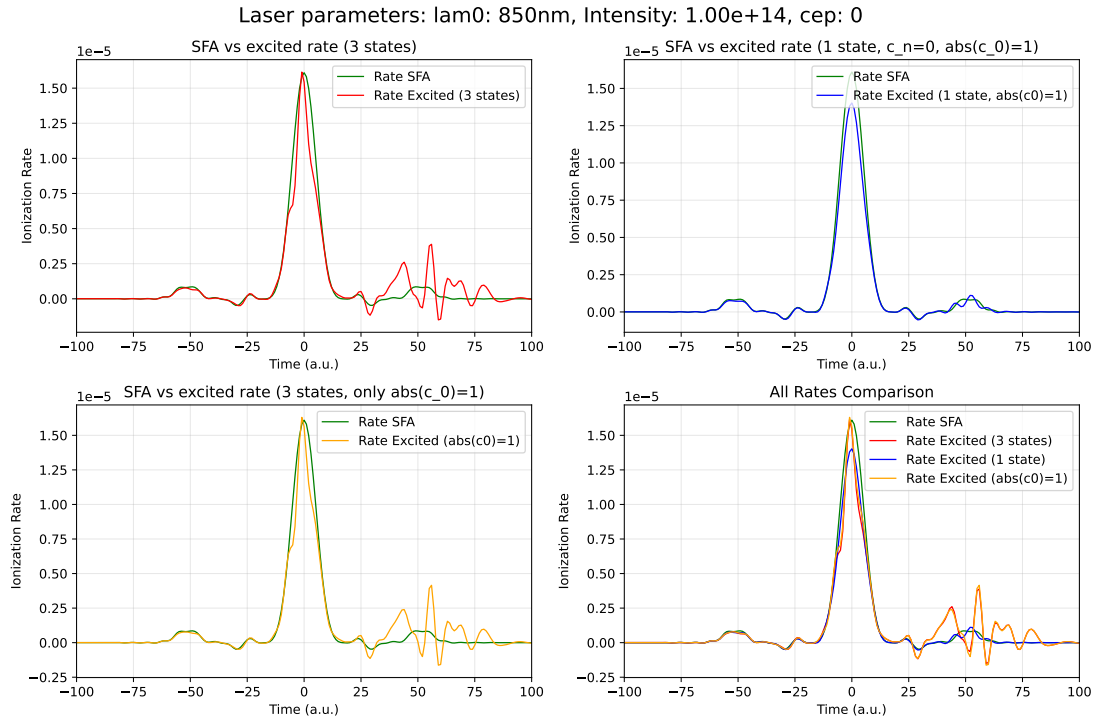


Figure 5.1: stark effect

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) but at least more than the polarisation of the ground state.

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 propabilitiy, 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

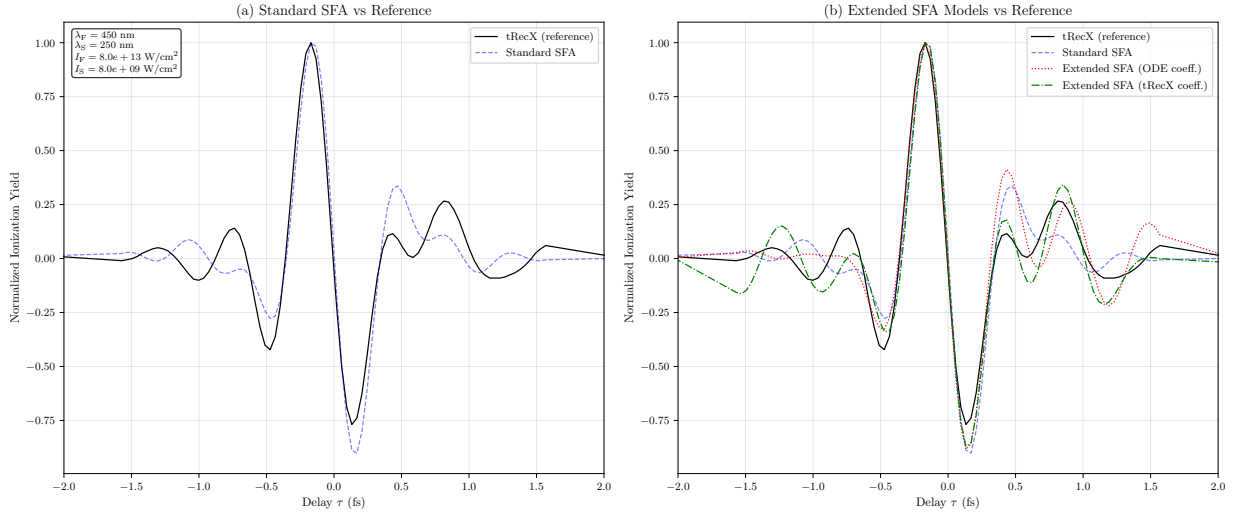


Figure 5.2: Comparison of ionization yields from TIPTOE simulations between different SFA models and reference data from tRecX. (a) Standart SFA overall does a good job reconstructing the ionization dynamics, but some parts it does not capture at all (b) Extended SFA to excited states indeed shows some improvements in the reconstructing

## 5.3 TIPTOE

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

Note that (??) is fulfilled and it actually looks like the signal pulse. 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 noticable 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 imple-

mented 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 its 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. 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:

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

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:

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

In principle, this integral or more precise the Fourier transformation of the wavefunction is all we need to do. Because of the structure of  $\psi_{nlm}$  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 Fourier transform 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  $\iota$ ) 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:

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

## Transition Element

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

new eq

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

$$\begin{aligned}
& \sum_{\iota=0}^{2l+1} \left( - \frac{(-1)^\iota n \text{Ip}^{-l-3} 2^{\iota-l-1} (in)^l (p^2)^{l/2} \left( \frac{1}{\sqrt{p^2}} - \frac{\text{pz}^2}{(p^2)^{3/2}} \right) \Gamma(2l + \iota + 3) \binom{l+n}{-l+n-\iota-1} \sqrt{\frac{\text{Ip}^3 \Gamma(n-l)}{\Gamma(l+n+1)}}}{\iota! \sqrt{1 - \frac{\text{pz}^2}{p^2}}} \right. \\
& \quad \times {}_2\tilde{F}_1 \left( l + \frac{\iota}{2} + 2, \frac{1}{2}(2l + \iota + 3); l + \frac{3}{2}; -\frac{n^2 p^2}{4\text{Ip}^2} \right) \left( \frac{m \text{pz} Y_l^m \left( \cos^{-1} \left( \frac{\text{pz}}{\sqrt{p^2}} \right), \tan^{-1}(\text{px}, \text{py}) \right)}{\sqrt{p^2} \sqrt{1 - \frac{\text{pz}^2}{p^2}}} \right. \\
& \quad \left. \left. + \frac{\sqrt{\Gamma(l-m+1)} \sqrt{\Gamma(l+m+2)} e^{-i \tan^{-1}(\text{px}, \text{py})} Y_l^{m+1} \left( \cos^{-1} \left( \frac{\text{pz}}{\sqrt{p^2}} \right), \tan^{-1}(\text{px}, \text{py}) \right)}{\sqrt{\Gamma(l-m)} \sqrt{\Gamma(l+m+1)}} \right) \right) \\
& \quad + \frac{(-1)^\iota l n \text{pz} \text{Ip}^{-l-3} 2^{\iota-l-1} (in)^l (p^2)^{\frac{l}{2}-1} \Gamma(2l + \iota + 3) \binom{l+n}{-l+n-\iota-1} \sqrt{\frac{\text{Ip}^3 \Gamma(n-l)}{\Gamma(l+n+1)}}}{\iota!} {}_2\tilde{F}_1 \left( l + \frac{\iota}{2} + 2, \frac{1}{2}(2l + \iota + 3); \right. \\
& \quad \left. - \frac{(-1)^\iota n^3 \text{pz} \text{Ip}^{-l-5} 2^{\iota-l-3} \left( \frac{\iota}{2} + l + 2 \right) (\iota + 2l + 3) (in)^l (p^2)^{l/2} \Gamma(2l + \iota + 3) \binom{l+n}{-l+n-\iota-1} \sqrt{\frac{\text{Ip}^3 \Gamma(n-l)}{\Gamma(l+n+1)}}}{\iota!} {}_2\tilde{F}_1 \left( l + \frac{\iota}{2} + 2, \frac{1}{2}(2l + \iota + 3); \right. \right. \\
& \quad \left. \left. \right) \right) \tag{A.3}
\end{aligned}$$

## B. Code

This is a part of the code used to implement the SFA rate, where the calculations actually take place. One can see the usage of the coefficients and the dipole transition elements.

```

1  for state_idx in range(excitedStates):
2      for state_range_idx in range(excitedStates):
3          f0 = np.zeros((Tar.size, tar.size), dtype=np.cdouble)
4          phase0 = np.zeros((Tar.size, tar.size), dtype=np.cdouble)
5          cLeft = coefficients[state_idx, :]
6          cRight = coefficients[state_range_idx, :]
7          phaseleft = np.unwrap(np.angle(cLeft))
8          phaseright = np.unwrap(np.angle(cRight))
9          absleft = np.abs(cLeft)
10         absright = np.abs(cRight)
11
12         for i in prange(Tar.size):
13             Ti=Ti_ar[i]
14             for j in range(tar.size):
15                 tj=N+nmin+j*n
16                 tp=tj+Ti
17                 tm=tj-Ti
18                 if tp>=0 and tp<EF.size and tm>=0 and tm<EF.size:
19                     VPt = 0
20                     T= Ti*dT
21                     DelA = (intA[tp] - intA[tm]) - 2*VPt*T
22                     VP_p=VP[tp]-VPt
23                     VP_m=VP[tm]-VPt
24                     f_t_l= np.conjugate(transitionElement(config[state_idx], p, pz, VP_m, E_g))*
25                             transitionElement(config[state_range_idx], p, pz, VP_p, E_g)
26                     G1_T_p=np.trapz(f_t_l*np.exp(1j*pz*DelA)*np.sin(theta), Theta_grid)
27                     G1_T=np.trapz(G1_T_p*window*p_grid**2*np.exp(1j*p_grid**2*T), p_grid)
28                     DelA = DelA + 2 * VPt * T
29                     phase0[i, j] = (intA2[tp] - intA2[tm])/2 + T*VPt**2 - VPt*DelA + eigenEnergy[
30                         state_idx]*tp*dT - eigenEnergy[state_range_idx]*tm*dT - phaseleft[tm] +
31                         phaseright[tp]
32                     f0[i, j] = EF[tp]*EF[tm]*G1_T*absleft[tm]*absright[tp]
33                     current_state_rate = 2*np.real(IOF(Tar, f0, (phase0)*1j))*4*np.pi
34                     rate += current_state_rate
35
36     return rate

```

This is the main part where the tRecX coefficients are computed. It can be seen that in the `matrixElementUnscaled` method instead of computing  $\langle \Psi(t) | \Psi_n \rangle \langle \Psi_n | \Psi(t) \rangle = |c_n(t)|^2$  the left side of expectation has been modified to  $\langle \Psi_n | \Psi_n \rangle \langle \Psi_n | \Psi(t) \rangle = c_n(t)$ .

```

1  static std::complex<double> eigenProjection(int IOp, std::vector<OperatorAbstract*> Ops, double Time,
2      const Coefficients* Wf, bool Normalize, std::vector<std::shared_ptr<Coefficients>> Duals){
3      Ops[IOp]->update(Time,Wf);
4      if (IOp > 1 && !Duals.empty() && IOp - 2 < Duals.size()) {
5          const Coefficients* constdual_raw = Duals[IOp - 2].get();
6          complex<double> expec=Ops[IOp]->matrixElementUnscaled(*constdual_raw,*Wf);
7          expec=Threads::sum(expec);
8          if(Normalize){
9              std::complex<double> nrm=1.;
10             if (Ops[IOp]->name().find("Ovr(")==std::string::npos){
11                 for(auto o: Ops){
12                     if(o->name().find("Ovr(")!=std::string::npos){
13                         nrm=Threads::sum(o->matrixElementUnscaled(*constdual_raw,*Wf));

```

```
13|                 break;
14|             }
15|         }
16|     }
17|     if (nrm!=0.) expec/=nrm;
18| }
19| return expec;
20| }
```



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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

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Unterschrift