Ludwig-Maximilians-Universität
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Bachelors Thesis

The role of excited atomic states in multiphoton ionization

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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

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2. Theory

Convention:
$\mathbf{\Psi}$ wavefunction for the whole system
$\psi(\underline{x})$ for a wavefunction in position space without choosing explicit coordinates,
$\psi(\underline{p})$ for a wavefunction in momentum space,
$\mathbf{A}$ for abstract vector as element in vector space,
$\underline{x}$ for vector in $\mathbb{R}^n$
$|\mathbf{\Psi}\rangle$ an abstract element in Hilbert space $\mathscr{H}$,
$|\mathbf{\Phi}\rangle$ 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 $\underline{x} = (r, \theta, \phi)$

This chapter mainly follows [**?**] with some modifications.

2.1 Basic Formalism

Our goal is to come up with a expression were we can

2.1.1 Schrödinger Equation

Basic Definitions of schröfinger qe, light dyson series, and strong field s matrix

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

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

The formal solution depends on the time dependence of the hamiltonian and the physical setting. In the following we assume [1] (IMPORTANT) that $[\hat{H}(t), \hat{H}(t')] = 0$ so we assume some sort of quasi static approximation to the Hamiltons time evolution. The solution is then given by

$$|\Psi(t)\rangle = e^{-\frac{i}{\hbar} \int_{t_0}^{t} \hat{\mathcal{H}}(t')dt'} |\Psi(t=0)\rangle = \hat{\mathcal{U}}(t) |\Psi(0)\rangle \tag{2.2}$$

Now its time so establish a physical setting. We have Hydrogen Atom with nucleus and electron described by time indepentent Hamilton $\hat{\mathcal{H}}_0$. The external laser Field is described by

[1] How? Later. No physical setting bzw no approximations yet. Its better to juistify it later but have a working formalism instead of the other way around.

an time dependent part $\hat{V}(t)$. To describe the interaction of the atom with the laser field we use in the following the dipole approximation.

2.1.2 Light-Matter Interaction

A light wave is defined by the Maxwell equations

$$\nabla \cdot \mathbf{E} = \rho \qquad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$
$$\nabla \cdot \mathbf{B} = 0 \qquad \nabla \times \mathbf{B} = \mathbf{J} + \frac{\partial \mathbf{E}}{\partial t}$$

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 $\varphi(t)$. These are not unique such that different choices can result in the same physical setting. In general

$$\mathbf{A} \rightarrow \mathbf{A} + \nabla\chi$$
$$\varphi \rightarrow \varphi - \frac{\partial \chi}{\partial t}$$

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.

2.1.3 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 exaclty one makes this assumption, first we rewrite the Maxwell equations in the dependence of the vector potential and the scalar potential as defined in (2.3). 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

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

We are mainly interested in the second equation. The equation is known as the wave equation therefore **A** describes plane waves

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

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

$$\mathbf{A}(\underline{x}, t) \approx \mathbf{A}_0 \mathrm{e}^{-i\omega t} = \mathbf{A}(t)$$

In other words

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

It is also helpfull to look at the semi classical Hamilton function of our system [Jackson]:

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

Under the dipole Approximation this can be simplified to:

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

Now we perform another gauge transformation to the so called length gauge via

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

Our Hamilton then reads:

$$\mathcal{H}(\underline{x}, t) = \frac{\mathbf{p}^2}{2m} - e\varphi(\underline{x}, t) + V(x)$$

Therefore we can rewirte the time dependent part $\hat{V}$ of our Hamiltonian (HOW??) as

$$\hat{V}(t) = -\hat{\mathbf{d}}\cdot\mathbf{E}(t) \tag{2.4}$$

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

2.2 Strong Field Approximation

For making the strong field approximation we first have to obtain a point where is its good to use. When we treat $\hat{V}(t)$ as the interaction term, we can write an exakt solution to (2.1) using (2.4)

$$|\Psi(t)\rangle = -\frac{i}{\hbar}\int_{t_0}^{t} \mathrm{d}t' e^{-\frac{i}{\hbar}\int_{t'}^{t}\hat{\mathcal{H}}(t'')\mathrm{d}t''}\hat{V}(t')e^{-\frac{i}{\hbar}\int_{t_0}^{t'}\hat{\mathcal{H}}_0(t'')\mathrm{d}t''}|\Psi(0)\rangle + e^{-\frac{i}{\hbar}\int_{t_0}^{t}\hat{\mathcal{H}}_0(t')\mathrm{d}t'}|\Psi(0)\rangle \tag{2.5}$$

as can be checked by inserting the solution into the Schrödinger equation using the parameter Integral trick. To make this expression more appealing we can project it into an eigenstate in the continuum ie a electron state characterized by its velocity. As can be seen in the following, the last term in (2.5) is now gone because there can be no overlap between a continuum state and the initial state.

$$|\Psi(t)\rangle = -\frac{i}{\hbar}\int_{t_0}^{t} \mathrm{d}t' \,\langle \Xi(t=t_c)|\, e^{-\frac{i}{\hbar}\int_{t'}^{t}\hat{\mathcal{H}}(t'')\mathrm{d}t''}\hat{V}(t')e^{-\frac{i}{\hbar}\overbrace{\int_{t_0}^{t'}\hat{\mathcal{H}}_0(t'')\mathrm{d}t''}^{\text{Esou}}}|\Psi(0)\rangle \tag{2.6}$$

With $|\Xi(t_c)\rangle$ being a continuum state with momentum p at time t_c with t_c being sufficiently big enough for the electron to be in the continuum ($t_c >> t'$). Equation (2.6) is known as the strong field S-matrix amplitude. Note that $|\Psi(0)\rangle$ is not the ground state of the Hydrogen atom, just the initial state of the system at $t = 0$. Now we have a good place to start with the strong field approximation.

$$\lim_{t\to\infty}|\Psi(t)\rangle = -i\int d^3p\ |\mathbf{p}\rangle \int_{-\infty}^{\infty} dt'\, e^{-\frac{i}{2}\int_{t'}^{\infty}[\mathbf{p}+\mathbf{A}(t')]^2\,dt'} e^{iI_{\mathrm{p}}t'}\langle \mathbf{p}+\mathbf{A}(t')|\hat{\mathbf{d}}\cdot\mathbf{E}(t')|\Psi_0\rangle \tag{2.7}$$

2.3 Strong Field Ionization

Phenomenology of strong field ionization.

2.4 Multiphoton Ionization

Different types of Ionization, tunneling Ionization, multiphoton

3. Ionization Model

3.1 TIPTOE

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4. Numerical Methods

4.1 tRecX

Difference between length gauge and velocity gauge in numerics Lorem ipsum dolor sit amet, consetetur sadipscing elitr, sed diam nonumy eirmod tempor invidunt ut labore et dolore magna aliquyam erat, sed diam voluptua. At vero eos et accusam et justo duo dolores et ea rebum. Stet clita kasd gubergren, no sea takimata sanctus est Lorem ipsum dolor sit amet. Lorem ipsum dolor sit amet, consetetur sadipscing elitr, sed diam nonumy eirmod tempor invidunt ut labore et dolore magna aliquyam erat, sed diam voluptua. At vero eos et accusam et justo duo dolores et ea rebum. Stet clita kasd gubergren, no sea takimata sanctus est Lorem ipsum dolor sit amet.

4.1.1 irECS

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4.1.2 tSURFF

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4.2 Python Implementation of Ionization Model

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5. Results and Discussion

5.1 Laser Fields

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$$\partial_t u = \mathcal{H}(t)\lambda \tag{5.1}$$

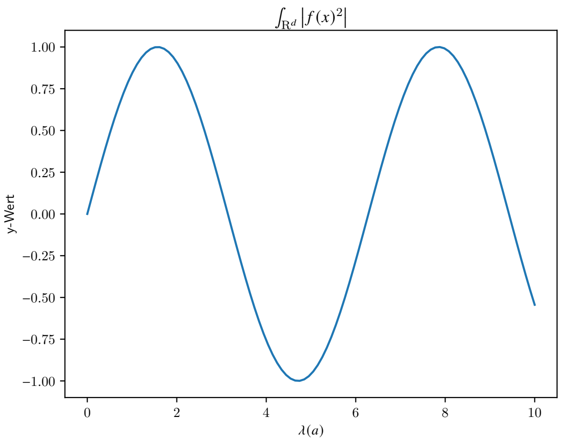

Figure 5.1: Sine function

$$\partial \mathbf{A} = \mathfrak{B}$$

$$\int_{\mathbb{R}^d} |f(x)|^2 \mathrm{d}x = \int_{\mathbb{R}^d} |\mathcal{F} f(\xi)|^2 \mathrm{d}\xi \tag{5.2}$$

$$\mathrm{i}\partial_t u = \mathcal{H}(t) \left|a\right\rangle \lambda \tag{5.3}$$

6. Conclusion and Outlook

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A. Appendix A

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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