# High-order harmonic generation in laser fields and investigation of plasmonic nanoparticles

Summary of Ph.D. thesis


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# 1. Introduction

Several aspects of light-matter interaction phenomena have become important in the world of science and technology over the past few decades. This development has been greatly facilitated by the emergence and spread of lasers since the 1960s, as new light-matter interaction parameter ranges have become available with lasers, enabling the exploration of new physical phenomena.

Important types of such phenomena are nonlinear optical effects, which mean the nonlinear response of the polarization of a given medium to the incoming laser field. This allows the appearance of new frequency components as a result of the interaction of laser light and the medium. These phenomena can typically be described by the perturbative orders of polarization, and accordingly higher-order processes become weaker and more difficult to detect.

However, with the development of high-intensity pico- and femtosecond lasers, laser fields became available that not only perturb the field strength within the atom, but also provide an external field that became comparable to the atomic field. This allows observation of new physical phenomena. One of the most typical examples is the discovery of above threshold ionization in 1979 [1], in which the weakest bound electron is not only able to absorb several photons at the same time (which leads to ionization) but also absorbs more photons than the minimum required, thus creating characteristic step-wise structure in the photo-ionization energy spectrum of atoms. At higher laser intensities, the laser field distorts the atomic potential to such an extent that electrons can escape by tunneling. These phenomena are collectively referred to as "extreme nonlinear optics" to distinguish them from conventional nonlinear optics.

In the course of the research that forms the basis of my dissertation, I also partially investigated an extreme nonlinear optical phenomenon, high-order harmonic generation (HHG). The basic phenomenon is that after the ionization by an intense laser field, the electron accelerates in the laser field and then recombines with its "parent ion" and emits energy in a coherent manner by emitting photons in the extreme ultraviolet (XUV) range [2]. This process was first demonstrated in atomic gases [3], but the potential for high-order harmonic generation has been demonstrated and predicted in a variety of physical systems since the early 1990s, including plasma surfaces, bulk solids, and nanostructures [4]. Such high-order harmonic spectra also allow the production of electromagnetic pulses shorter than 1 femtosecond, due to the significantly shorter optical cycle in the XUV range, and the wide spectrum and phase-correct oscillations of the harmonics [5]. The technology of generating attosecond pulses has facilitated the emergence of a new field of science roughly 20 years ago: attoscience, which deals with the ultrafast dynamics of electrons in atoms, molecules, solids and plasmas. The spread of attosecond technologies justifies the efforts that aim the development of new approaches to describe the high-order harmonic generation processes, and I present examples of this in my dissertation.

However, high optical field strengths can not only achieved with amplified laser systems with complex structures, being common in attophysics. This is because the energy of the laser light can be concentrated below the diffraction limit during the interaction with various physical systems in the nanometer range. This is accompanied by significant increases in field strength compared to the external field strength. The effect is also ap-

parent in the case of nanotips with a sufficiently small radius of curvature (see the lightning rod effect in static field). However, a really large increase in electric fields up to two orders of magnitude can be achieved if the light resonantly induces surface charge density waves or oscillations, so-called surface plasmon polaritons (SPP) (for flat surfaces) and localized surface plasmons (LSP) for nanoparticles. Such a large increase of the field also makes it possible to induce even extreme nonlinear optical phenomena in the environment of nanoparticles with simple femtosecond laser oscillators [6]. In my thesis I also present the results of my research on localized surface plasmons, which are related to the field enhancement of regular surface nanostructure arrays and the femtosecond plasmon transients that can be generated on them.

# 2. Objectives

Even though many have previously dealt with quantum mechanical modeling of HHG [7], it is worth studying this research field with novel methods in order to gain a deeper understanding of the quantum mechanical behavior of the system.

Therefore, I aimed to develop a numerical method for studying the behavior of hydrogen-like atoms placed in a continuous excitation field using the Floquet method [8] and the Sturmian basis [9] together. By developing this method, my goal was to study the quantum mechanical behavior of such a system and to take advantage of the smaller numerical computational requirements to deepen our knowledge about the generation of harmonic spectra. My goal was to compare the spectra of atomic systems that were initially in different quantum mechanical superposition

states using the generated program codes. I plan to investigate how the disappearance of the dipole moment matrix element between the initial state and the atomic ground state affects the qualitative properties of the spectrum.

In addition to the continuous excitation field, my goal was to study the dynamics of pulsed excitation, as the discrete Sturmian basis is also suitable for this. To this end, I developed another numerical method, which allows to study the harmonic spectra as a function of the polarization of the excitation field. By reproducing the experimental results, namely that there is no high-order harmonic generation in this system with circularly polarized excitation, I validated the accuracy of my method. The question I was looking for an answer to: Is there a deeper (interferometric) picture beyond the usual explanation?

During the course of my experimental work, following the goals of our research group, I also participated in the process of creating nanostructures. By the better understanding of the equipment used for this purpose, we have developed a robust process for the fabrication of nanoparticles by electron beam lithography (EBL). Based on this experience, I had the goal to produce nanoparticle arrays that are designed by our group using FDTD model calculations. The arrays are written by EBL. I also planned to record the extinction spectra of the prepared nanoparticle arrays and to show the correlation with the field enhancement obtained in the FDTD model calculations. More specifically, my intention was investigating the field enhancement as a function of the excitation and the overlap of the extinction spectrum by modeling both isolated nanorods and nanorod arrays. This comparison later led to the results related to thesis 5.

# 3. Research methods

I began the modeling of high-order harmonic generation with the time-dependent Schrödinger equation of an atom placed in an external field. For monochromatic excitation, the set of Floquet states forms a complete basis at all times, therefore the time evolution can be explained by any initial state. That is, after determining the Floquet quasi-energies and the periodic states at the appropriate time, I was able to calculate the dynamics of any initial state. This is because the time-dependent differential equation takes the form of a matrix eigenvalue equation using this method.

Hydrogen-like bound states are orthogonal to the positive energy states in the continuum, but the usual picture of the process of high-order harmonic generation in the gas sample (three-step model) suggests that the role of positive energy states is significant. Therefore, to properly describe the problem, I use another set of basis functions, the Sturmian states [10]. These form basis in the space of normalizable states. The Sturmian-Floquet method is numerically efficient and convenient for describing the state of the system, since the eigenvalue equation only needs to be solved once within the truncated subspace to obtain the time evolution of the different initial states. Depending on the duration of the excitation pulse, the TDSE-based and Sturmian-Floquet methods complement each other: the first approach is preferable to few cycle laser pulses, while the method I have developed is more suitable for multi-cycle or continuous excitation.

A highly nonlinear process for producing high-order harmonics belonging to the central frequency of high-intensity optical excitation has already been observed using different physical systems as targets [3, 11]. In addition to deepening the understand-

ing of the underlying strong spatial mechanisms, the role of the phenomenon is also fundamental in laser technology: the appearance of short (even attosecond) pulses of electromagnetic radiation is based on the corresponding phase summation of harmonics [2, 5]. In my thesis I also use the Sturmian basis in dynamic equations, by considering an elliptically polarized laser field using a length gauge and dipole approximation. I only consider the interaction with the electric field and neglect the influence of the magnetic field. I examine the ellipticity dependence of the harmonic generation process. The accuracy of my numerical approach can also be checked by monitoring the orientation independence.

In the classical picture, the polarization dependence of the high-order harmonic generation (HHG) process is clear. When the excitation field is circularly polarized, the classical electron orbits never return to the nuclei, that leads to a lack of high-order harmonic radiation. A similar result can be obtained using a quantum mechanical description when the dynamics of the electrons is given by the time-dependent Schrödinger equation, where the bound and continuum parts of the wave functions show negligible overlap in the case of circular polarization. In fact, the finite spatial extent of the electron wave packet may explain the gradual disappearance of high-order harmonics as the degree of ellipticity increases.

However, in the quantum mechanical description, coordinate representation is not the only option. We are free to use, for example, a different discrete basis. It is obvious that all elements of the Sturmian basis [10, 12] correspond to a well-defined wave function, so my results are physically equivalent to the real space description. The main advantage of my method is that it reveals

the basic aspects of the symmetry of the polarization dependence of HHG.

In the course of my research, I also performed studies on the field enhancement of plasmonic nanoparticles. I used the commercially available Lumerical software package to model both the optical response (extinction) and the field enhancement. I performed my simulations using the finite difference time-domain (FDTD) method. The FDTD method is a numerical technique used for electrodynamic modeling. Because it is a time domain method, FDTD solutions are able to cover a wide frequency range with a single simulation run and handle nonlinear material properties in a natural way.

In the simulations, I investigated gold nanostructures placed on top of a bulk quartz glass plate coated with an indium tin oxide (ITO) layer. For faster and more efficient runs, I considered a single nanoparticle and its close environment in the simulation. In order to be able to describe the effect of adjacent and distant particles, I prescribed periodic boundary conditions at the boundaries of the simulation volume in directions perpendicular to the surface of the substrate, which coincided with the axes of the nanoparticle array. I set an absorbing boundary condition in a direction parallel to the substrate.

The time shape of a linearly polarized short laser pulse was set as excitation, which was calculated from the broadband spectrum of the HR laser system operating at the ELI-ALPS institute. The extinction spectrum of the nanorods was modeled using a linearly polarized full-field scatter-field (TFSF) plane wave source. The extinction spectrum of the particles can be determined by calculating the absorbed and scattered power inside and outside the source region. For this reason, I illuminated

the particle matrices with a plane wave source with the same characteristics as the TFSF source. The extinction curves determined by the far-field simulations were later compared with the measured ones.

The spectroscopic characterization of the plasmonic properties of the samples, i.e. the examination of the extinction properties of the nanostructure arrays, was measured using a Zeiss Axio Imager.z2m light microscope in transmission mode. The transmitted light is provided by a built-in tungsten halogen lamp with a spectrum very close to that of a black body at the temperature of 3080 K. The results presented in the thesis stemmed from such extinction measurements.

# 4. New scientific results

1. In this work, I have combined the concept of the Sturmian basis, which contains both the bound and continuum states of hydrogen and the Floquet method to handle the periodic excitation of the hydrogen atom. To this end, I have developed a numerical method based on the combined Sturmian-Floquet method to describe the interaction of strong laser fields and hydrogen like atoms. My numerical calculations have shown that the method is suitable for predicting HHG spectrum of these hydrogen-like atoms [P1].

2. I investigated the influence of the initial atomic state on the process of high-order harmonic generation. By using the Sturmian-Floquet method, I have shown that the charge dynamics started from an initial superposition of the usual energy eigenstates resulted in atomic energy eigenstates

produced noticeable change in the spectra in the case when the transition to the 1s ground state is forbidden. In this case, the position of the cut-off of the spectra shifted towards the lower frequencies, which comes from the reduction of the ionization energy as a result of the forbidden nature of transition to the ground state. We have found that certain weighting in the superposition of eigenstates will result in a double plateau in the energy spectrum. The dynamics calculated based on the expectation value of the dipole moment show sensitivity to the phases of the individual eigenstates in the superposition, namely a 180 degree phase difference resulted in a completely different time dependent signal [P1].

3. With the generalization of my results with the Sturmian basis, I investigated the excitation of a hydrogen atom by a short laser pulse. I determined the equations of the dynamics by using transient dipole moment matrix elements and I developed a numerical method to solve them. I calculated the time evolution of the expectation value of the dipole moment and I determined the harmonic spectrum emitted by the atom at different polarized excitations [P2].

4. The polarization dependence of the high-order harmonic spectrum can be determined by my method which was described in point 3 above. My results showed that with circularly polarized excitation high harmonics do not appear, consistently with the experiments. I have formulated an alternative of the usual spatial interpretation of the phenomenon using discrete Sturmian basis. In this approach I showed that the selection rules and circular polarization to-

gether lead to a temporal and spatial symmetry that eliminate the appearance of the high harmonics [P2].

5. By measuring and calculating extinction spectra of nanostructure arrays and also by calculating plasmonic field enhancement, I showed that the higher the overlap is between the excitation spectra and the extinction spectra of nanostructures, the higher is the field enhancement of nanostructure arrays. I characterized the overlap of the two spectra by the integration of the curve obtained by multiplying these two spectra (i.e. excitation and extinction spectra). I demonstrated linear relationship between this function and the available field enhancement. To prove the general nature of its correlation, I have calculated the field enhancement of single nanoparticles and found that the data points fit into a trend observed on nanostructure arrays [P3].

# 5. Summary

I examined high-harmonic generation in hydrogen-like atoms, and I showed that the combination of the Sturmian basis and the Floquet method in numerical calculations is suitable for describing the process in the case of continuous excitation field. The method I have developed is useful because it can calculate the resulting harmonic spectrum with much less computational requirements. Using the method, I showed that the quantum mechanical coherence of the initial states strongly influences the HHG spectra. Using superpositions formed from hydrogen energy eigenstates as an initial state, I have shown that the weights of the eigenstates play an important role in the high-order har-

monic radiation. In addition, if the components of the initial superposition state are dipole coupled, the time-dependent HHG signal is also sensitive to the quantum mechanical phase difference of the components of the initial superposition state. This may also be important from an experimental point of view because atomic coherence can be used to control the properties of the generated HHG radiation.

Using the Sturmian basis, I also investigated short pulse excitation. Based on the transient dipole moment matrix elements, the method is suitable for calculating the polarization dependence of the harmonic spectrum. Among other things, it describes the disappearance of high-order harmonics in the case of circularly polarized excitation, which also reflects the experimental results. The method which I have developed is useful because it provides a deeper insight into how quantum mechanical interference effects and selection rules explain the polarization dependence of the process. This allowed me to point out that essentially the conservation of angular momentum is responsible for the lack of harmonics in a circularly polarized excitation field.

My results on plasmonic nanostructures help to optimize the field enhancement in such systems, especially when we generate plasmon transients with short-pulse, femtosecond excitation. This endeavor is important not only for applications, but also for answering many fundamental research questions. For example, the behavior of the dynamics of the so-called hot electrons, which show particularly interesting properties during plasmon excitation. Based on this, the results discussed in my dissertation contributed to the development of the ultrafast plasmonics research field.

## 6. Refereed research papers related to the thesis

**[P1]** J. Kasza, P. Dombi, and P. Földi, Sturmian-Floquet approach to high-order harmonic generation, J. Opt. Soc. Am. B 35, pp. A126-A130, 2018.

**[P2]** Z. Pápa, J. Kasza, J. Budai, Z. Márton, G. Molnár, and P. Dombi, Tuning plasmonic field enhancement and transients by far-field coupling between nanostructures, Appl. Phys. Lett. 117, 081105, 2020.

**[P3]** J. Kasza, I. Magashegyi, P. Dombi, and P. Földi, Polarization dependence of atomic high-order harmonic generation: Description using a discrete basis, Phys. Rev. A 105, 033105, 2022

## 7. References


[1] P. Agostini, F. Fabre, G. Mainfray, G. Petite, and N. K. Rahman, "Free-free transitions following six-photon ionization of xenon atoms," *Physical Review Letters* **42**(17), p. 1127, 1979.

[2] G. Farkas and C. Tóth, "Proposal for attosecond light pulse generation using laser induced multiple-harmonic conversion processes in rare gases," *Physics Letters A* **168**(5), pp. 447 – 450, 1992.

[3] M. Ferray, A. L'Huillier, X. F. Li, L. A. Lompre, G. Mainfray, and C. Manus, "Multiple-harmonic conversion of 1064

nm radiation in rare gases," *Journal of Physics B: Atomic, Molecular and Optical Physics* **21**(3), p. L31, 1988.

[4] M. F. Ciappina, J. A. Pérez-Hernández, T. Shaaran, M. Lewenstein, M. Krüger, and P. Hommelhoff, "High-order-harmonic generation driven by metal nanotip photoemission: Theory and simulations," *Phys. Rev. A* **89**, p. 013409, 2014.

[5] F. Krausz and M. Ivanov, "Attosecond physics," *Rev. Mod. Phys.* **81**, pp. 163–234, 2009.

[6] P. Dombi, A. Hörl, P. Rácz, I. Márton, A. Trügler, J. R. Krenn, and U. Hohenester, "Ultrafast strong-field photoemission from plasmonic nanoparticles," *Nano letters* **13**(2), pp. 674–678, 2013.

[7] M. Lewenstein, P. Balcou, M. Y. Ivanov, A. L'Huillier, and P. B. Corkum, "Theory of high-harmonic generation by low-frequency laser fields," *Phys. Rev. A* **49**, pp. 2117–2132, 1994.

[8] G. Floquet, "Sur les équations différentielles linéaires a coefficients périodiques," *Ann. École Norm. Sup.* **12**, pp. 46–88, 1883.

[9] O. Goscinski, "Preliminary research report no. 217, quantum chemistry group, uppsala university, (1968).".

[10] J. Avery and J. Avery, *Generalized Sturmians and Atomic Spectra*, World Scientific, 2006.

[11] A. L'Huillier and P. Balcou, "High-order harmonic generation in rare gases with a 1-ps 1053-nm laser," *Phys. Rev. Lett.* **70**, pp. 774–777, 1993.

[12] J. Avery and J. Avery, *Solving the Schrödinger Equation: Has Everything Been Tried?*, ch. 6. The generalized Sturmian method, pp. 111–140. Imperial College Press, 2011.