Spin dynamics in photon ionization processes in hydrogenic atoms

Master Thesis in Physics, Atomic Physics
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Contents

1 Introduction

Laser is an acronym standing for Light Amplification by Stimulated Emission of Radiation. In other words, a laser is simply something that amplifies light, that is the light's intensity is increased, through the process which is called stimulated emission. Stimulated emission is a quantum mechanical phenomenon in which an incoming photon (light) interacts with an excited atom causing it to emit itself a photon. The emitted amplified light not only can be adjusted to extremely high intensities, but also to be coherent. Coherence of the emitted light allows for very high precision when applying the laser making it a suitable tool for studying incredibly small systems, such as quantum mechanical ones.
Ever since the laser's invention in 1960, the laser has become more and more valuable in the experimental study of atomic systems such as molecules. This is mainly due to the advancements in laser technology. Lasers are becoming more and more intense, enabling, among many other things, the acceleration of electrons to relativistic speeds, making yet another way to study relativistic effects in quantum systems possible.
As such, this thesis is concerned with studying relativistic effects in quantum systems when an external laser has been applied. The simplest (physical) quantum mechanical system is the hydrogen atom. The hydrogen atom consists of its nucleus, the proton, and an electron. When studying the hydrogen atom, the dipole approximation, a much used approximation in theoretical physics, has been used in this work, though some discussions are given on how one may study beyond dipole effects in regard to what has been considered in this thesis. Put shortly, the dipole approximation assumes that the dimensions of the studied system (hydrogen) are much smaller than the wave length of the applied field (due to the laser), as well as that the intensity is assumed low enough so that the magnetic field component can be neglected. This implies then that the spatial dependence of the field generated by the laser can be ignored. The validity of the dipole approximation has been shown to break down at large laser frequencies and/or intense lasers [1],[2],[3],[4].Therefore, the laser frequencies/intensities considered in this thesis have been assumed to be small enough to stay in the regime of the dipole approximation's validity, unless otherwise stated.

The purpose of this thesis has been to find a suitable Pauli equation that can describe relativistic effects, including spin effects, appearing in the study of an electron (bound to a hydrogen nucleus) in the presence of an applied laser, whilst still being not too demanding when doing numerical computations. The reason is that using the exact model (Dirac equation) quickly becomes a formidable task numerically as there appear numerical technicalities. An example would be that one has to be careful with the choice of basis as one otherwise might get spurious states [5].

The developed model has been tested numerically by looking at the cross section for photon ionization which is then compared to the solution obtained from the

Dirac equation up to photon energies around 2500 atomic units (a.u.).
All programs have been written in Python in order to calculate the interaction matrices and in order to plot the cross sections of interest.

2 Quantum mechanics

2.1 Single-Particle States

The state of any particle is assumed to be described by a wave function $\Psi(\bar{r}, t)$, where $\bar{r}$ is the position vector and t is time. This means that if one knows a particle's wave function Ψ, one can in principle calculate all its observables. The wave function Ψ has in and of itself no physical interpretation, however its absolute value squared is to be interpreted as a probability density (probability per unit volume). In order for such an interpretation to be possible, Ψ is always assumed to be normalised to unity, that is, any wave function Ψ corresponding to a physical particle has to be such that

$$\int_{\mathcal{R}^3} d^3r \ |\Psi(\bar{r}, t)|^2 = 1. \tag{1}$$

2.2 Operators

Any observable quantity O has a corresponding operator $\hat{O}$. For instance, the momentum $\bar{p}$ of a particle has a corresponding momentum operator $\hat{\bar{p}}$. Each such operator can act on a given wave function Ψ in a linear fashion. The only measurable values corresponding to an observable are the eigenvalues of the associated operator. As an example, measuring the kinetic energy $\frac{\bar{p}^2}{2m}$ of a particle of mass m, one could only possibly obtain measurements equalling (assuming no measuring error) the eigenvalues of the associated operator $\frac{\hat{\bar{p}}^2}{2m}$. In order for this to hold, the eigenvalues of every such operator need to be real. This is ensured by demanding that any operator corresponding to an observable is to be hermitian, i.e.

$$\hat{O}^\dagger = \hat{O}. \tag{2}$$

Next, the expectation value of a given operator $\hat{O}$ with respect to some wave function Ψ is defined as

$$< \hat{O} >:= \int_{\mathcal{R}^3} d^3x \ \Psi^*(\bar{x}, t)\hat{O}\Psi(\bar{x}, t). \tag{3}$$

The expectation value of an operator is to be interpreted as the mean value of an infinite number of repeated measurements on the given system.

The two fundamental operators $\hat{\bar{r}}$ and $\hat{\bar{p}}$ that correspond to position and momentum, respectively, are defined as

$$\begin{aligned} \hat{\bar{r}}\Psi(\bar{r}, t) &= \bar{r}\Psi(\bar{r}, t) \\ \hat{\bar{p}}\Psi(\bar{r}, t) &= -i\hbar\nabla\Psi(\bar{r}, t). \end{aligned} \tag{4}$$

2.3 Non-relativistic equation of motion

In order to obtain the wave function Ψ of a physical system, one proceeds by solving the equation of motion. In the non-relativistic case, the equation of motion is given by the time dependent Schödinger equation (TDSE) [6]

$$i\hbar\partial_t\Psi(\bar{r},t) = (\frac{\bar{\hat{p}}^2}{2m} + \hat{V}(\bar{r},t))\Psi(\bar{r},t), \tag{5}$$

where $\hat{H} = \frac{\bar{\hat{p}}^2}{2m} + \hat{V}(\bar{r},t)$ is the Hamilton operator of the system with $\hat{V}(\bar{r},t)$ being the potential energy operator and m being the mass of the particle under consideration. The Hamiltonian is in most cases the energy operator of the system. In fact, throughout this thesis, the Hamiltonian will always be the energy operator.

Often one may only be interested in a system's energy spectrum, that is the set of all possible energy values that the particle can acquire. Then, the problem of solving the Schrödinger equation reduces to diagonalising the given Hamiltonian operator in order to find its eigenvalues (the energy spectrum).

2.3.1 Spin for non-relativistic particles

It is a known fact that the spin of particles plays, even in the non-relativistic regime, a major role when studying quantum systems due to the Pauli exclusion principle. The prime example is typically given by the study of the Helium atom where the Pauli exclusion principle explains the existence of Para- and Ortho helium [7]. As the Schrödinger equation (5) does not contain any spin operators, one has to resort to a different equation of motion when talking about spin. The non-relativistic equation used when considering spin effects is usually the Pauli equation. The major difference between the Pauli equation and the corresponding Schrödinger equation is that the Pauli equation contains the spin operator $\bar{S}$ coupled to the external magnetic field $\bar{B}$. In this thesis however, the dipole approximation (see chapter 4.2) is invoked, implying an absent magnetic field, thus making the term containing the spin operator in the Pauli equation vanish. The resulting Pauli equation is then effectively given by two (identical) Schrödinger equations, one for each spin state. Further, in this thesis only one particle systems (ignoring the photon) are considered, thus making the non-relativistic Pauli equation obsolete when studying spin effects in the dipole approximation, as the symmetry constraints on the wave function in order to respect the Pauli exclusion principle are trivially satisfied.
Instead, one has to take into account higher order relativistic effects when wanting to study spin effects in the dipole approximation. This is exactly what will be done in chapter 6.

2.4 Relativistic equation of motion

The equation of motion that describes the dynamics of a relativistic electron is given by the Dirac equation [8]. The free Dirac equation reads

$$i\hbar\Psi(\bar{r},t) = (c\bar{\alpha}\cdot\bar{\hat{p}} + mc^2\beta)\Psi(\bar{r},t), \tag{6}$$

where now the Hamiltonian is given by $H = c\bar{\alpha}\cdot\bar{\hat{p}} + mc^2\beta$ with m being the mass of the particle, c being the speed of light and $\bar{\alpha}$ and β being operators.
The wave function Ψ is now a four component object instead of one, as it was the case in the Schrödinger equation. This has to do with the fact that in a relativistic treatment of the electron, one has to take into account the spin degrees of freedom (2), as well as its antiparticle, the positron (2). The necessity of having to solve for the wave function of the positron is explained by the fact that electron-positron pairs may be spontaneously created and annihilated in the vacuum, implying that one cannot talk about an electron without talking about its antiparticle, the positron.
The operators $\bar{\alpha}$ and β in (6) may be written as 2×2 block diagonal matrices given by

$$\begin{aligned} \beta &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \\ \alpha_j &= \begin{pmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{pmatrix} \text{ j = 1, 2, 3,} \end{aligned} \tag{7}$$

where σ_j are the Pauli matrices. These matrices may look different depending on which representation is being used.
An often used representation is the Weyl-representation, also known as the chiral representation [9]. In the Weyl-representation the α_j and β matrices will still be block diagonal, however this representation is not used in this thesis because then the 2 component objects χ and ξ in the wave function $\Psi = (\chi, \xi)$ would not directly correspond to the electron and the positron anymore. Instead, these would correspond to different chiralities and would therefore each be linear combinations of an electron wave function and a positron wave function.
In chapter (6), we wish to derive an approximate Hamiltonian, starting with the relativistic Hamiltonian in the Dirac theory, that in the end may be cast into an approximate block diagonal form, such that the positron wave function will be (approximately) decoupled from the electron wave function, enabling the isolated study of the electron. Therefore, throughout this thesis, we will make use of the above representation (7), usually referred to as the Pauli-Dirac representation.

3 Hydrogenic atoms

A hydrogenic atom is usually referred to as any atomic nucleus/ion that has a net charge of $-e$ ($e < 0$) and can thus bind exactly one electron. The atomic nucleus/ion is to a first approximation assumed to be point like with infinite mass. Then, an electron interacting with such a system interacts only through the Couloumb force. Therefore, the Hamilton operator of an electron in a hydrogenic system with nuclear charge $-Ze$ is given by

$$\hat{H}_Z = \frac{\hat{\bar{p}}^2}{2m} - \frac{Ze^2}{r}, \tag{8}$$

where r is the distance from the nucleus to the electron and m is the electron's mass.
The outline of the following derivation of the solutions to the above equation follows closely what is presented in [7].

To solve (8), one starts by inserting the Hamiltonian $\hat{H}_Z$ into the TDSE (5). As $\hat{H}_Z$ is time independent, one may make the Ansatz $\Psi(\bar{r}, t) = T(t)\psi(\bar{r})$. Inserting this into the TDSE, one gets that $T(t) = e^{-\frac{iE_n}{\hbar}t}$, where E_n is such that

$$\hat{H}_Z\psi_n(\bar{r}) = E_n\psi_n(\bar{r}). \tag{9}$$

$\{\psi_n\}$ are then the spatial eigenstates of the Hamiltonian H_Z.
This equation is referred to as the time independent Schrödinger equation (TISE). Since the Coulomb potential is spherically symmetric, spherical coordinates will be used. This enables one to write the Hamiltonian as

$$\hat{H}_Z = -\frac{\hbar^2}{2m}\frac{1}{r^2}\partial_r(r^2\partial_r) - \frac{Ze}{r} + \frac{\hat{L}^2(\phi,\theta)}{2m\hbar^2r^2}, \tag{10}$$

where $\hat{\bar{L}} := \hat{\bar{r}} \times \hat{\bar{p}}$ is the angular momentum operator.
It is evident that if we were to insert the above expression into the TISE, we would get the sum of a purely radially dependent operator and a purely angular dependent operator. In analogy to the previous Ansatz, one may proceed by assuming that the eigenstates of $\hat{H_Z}$ are of the form $\psi(\bar{r}) = R_{nl}(r)\mathcal{Y}_{lm}(\phi,\theta)$. Upon inserting this Ansatz into (9) using (10), one gets the two uncoupled differential equations

$$\begin{aligned} &\hat{\bar{L}}^2\mathcal{Y}_{lm}(\phi,\theta) = \hbar^2 l(l+1)\mathcal{Y}_{lm}(\phi,\theta) \\ &(-\frac{\hbar^2}{2mr^2}\partial_r(r^2\partial_r) - \frac{Ze}{r})R_{nl}(r) = E_{nl}R_{nl}(r). \end{aligned} \tag{11}$$

One observes that the first equation is seperable in ϕ and θ. We can thus make the Ansatz $\mathcal{Y}_{lm}(\phi,\theta) = \Phi_m(\phi)\Theta_{lm}(\theta)$. It is noted that the $\hat{\bar{L}}^2$ opertor commutes with any of the three $\hat{L_j}, j = x, y, z$ operators. It thus follows that one can find

a simultaneous set of eigenstates of both $\hat{\hat{L}}^2$ and $\hat{L_z}$. That is, we may find $\mathcal{Y}_l^m = \Phi^m(\phi)\Theta_l^m(\theta)$ by solving the differential equations

$$\begin{aligned} \hat{\hat{L}}^2\mathcal{Y}_l^m &= \hbar^2 l(l+1)\mathcal{Y}_l^m \\ \hat{L}_z\Phi^m(\phi) &= \hbar m\Phi^m(\phi). \end{aligned} \tag{12}$$

It can be shown that the constant l and m are limited to $l = 0, 1, ..., n-1$ and $m = 0-l, -l+1, ..., l$. The solutions of (12) are referred to as spherical harmonics and are known functions which are typically given in terms of associated Legendre polynomials P_l^m as

$$\mathcal{Y}_l^m(\theta) = (-1)^m\sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}P_l^m(\cos(\theta))e^{im\phi}. \tag{13}$$

The specific form of the Legendre polynomials may be found in sources such as [10].
The second equation of (11) is referred to as the radial equation. For convenience, one may rewrite this equation by introducing the reduced radial function $u_{nl}(r) := rR_{nl}(r)$. In doing so, one obtains the reduced radial equation which reads

$$(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} - \frac{Ze}{r} + \frac{\hbar^2 l(l+1)}{2mr^2})u_{nl}(r) = E_n u_{nl}(r). \tag{14}$$

The radial equation can then be solved analytically. Its solutions are usually given in terms of associated Laguerre polynomials L_{n+l}^{2l+1} as

$$R_{nl}(r) = -\sqrt{(\frac{2mZ}{n})^3\frac{(n-l-1)!}{2n[(n+l)!]^3}}e^{-\frac{mZr}{n}}(\frac{2mZr}{n})^l L_{n+l}^{2l+1}(\frac{2mZr}{n}), \tag{15}$$

where different sign conventions for R_{nl} may be found in different sources.
An explicit form of the associated Laguerre polynomials may be found in [10].
The energy eigenvalues are then seen to yield

$$E_n = -\frac{mc^2\alpha^2}{2}\frac{Z^2}{n^2}, n = 1, 2, .., \tag{16}$$

where α is the fine structure constant. In atomic units this reduces neatly to $E_n = -\frac{1}{2}\frac{Z^2}{n^2}$.

4 Electromagnetism and lasers

When studying an electron (bound to some nucleus) in an applied laser field, the interactions will be electromagnetic. Therefore, a brief summary of electromagnetism relevant for this thesis will be given in the following.

Classically, any charged object described by the charge distribution ρ and the current density vector $\bar{j}$ in space will cause an electric field $\bar{E}$ and a magnetic field $\bar{B}$. These are to obey Maxwell's equations [11] which are neatly summarised in the following four equations:

$$\begin{aligned} \nabla \cdot \bar{B} &= 0 \\ \nabla \times \bar{E} + \frac{1}{c}\partial_t \bar{B} &= 0 \\ \nabla \cdot \bar{E} &= 4\pi\rho \\ \nabla \times \bar{B} - \frac{1}{c}\partial_t \bar{E} &= \frac{4\pi}{c}\bar{j}. \end{aligned} \tag{17}$$

Maxwell's equations imply that for reasonably well behaved (that is, physically realizable) charge distributions, the electric and magnetic fields can be expressed in terms of the scalar potential ϕ and the vector potential $\bar{A}$ as

$$\begin{aligned} \bar{E} &= -\nabla\phi - \partial_t \bar{A} \\ \bar{B} &= \nabla \times \bar{A}. \end{aligned} \tag{18}$$

The potentials are non-physical in the sense that they cannot be measured. This is the case as there is no pair of potentials that uniquely describes a given electric and magnetic field. That is to say that one can find two distinct sets of potentials ϕ and $\bar{A}$ that yield the excact same electric and magnetic field. This is easily seen by performing the following set of transformations:

$$\begin{aligned} \phi &\to \phi - \partial_t \chi \\ \bar{A} &\to \bar{A} + \nabla\chi. \end{aligned} \tag{19}$$

The set of transformations (19) is usually referred to as a gauge transformation and electromagnetism is in that regard a gauge invariant theory, meaning that a gauge transformation does not alter the physical consequences of the theory. As it is often advantageous to work with the potentials ϕ and $\bar{A}$ instead of the fields $\bar{E}$ and $\bar{B}$, one may derive a set of two equations for the potentials from Maxwell's equation via inserting the definitions (18) to yield (in CGS units)

$$\begin{aligned} &\nabla^2\phi + \partial_t(\nabla \cdot \bar{A}) = 4\pi\rho \\ &(\frac{1}{c^2}\partial_t^2 - \nabla^2)\bar{A} + \nabla(\nabla \cdot \bar{A} + \frac{1}{c^2}\partial_t\phi) = 4\pi\bar{j}. \end{aligned} \tag{20}$$

In this thesis, the Coulomb gauge is used implicitly throughout all the calculations and derivations presented.

To motivate the Coulomb gauge, we start with the Lorentz gauge (really a class of gauges), which is defined as choosing gauges that satisfy the Lorentz condition

$$\nabla \cdot \bar{A} + \frac{1}{c}\partial_t \phi = 0. \tag{21}$$

In this thesis, the potential ϕ will be purely space dependent due to the Coulomb potential. Therefore, ϕ will be time independent, implying $\partial_t \phi = 0$. Thus, within this thesis, the Lorentz condition will be equivalent to saying that

$$\nabla \cdot \bar{A} = 0. \tag{22}$$

The gauge condition (22) defines the Coulomb gauge. Inserting the condition (22) for the Coulomb gauge into (20), one obtains the Maxwell equations in terms of the potentials in the Coulomb gauge as given by

$$\begin{aligned} &\nabla^2 \phi = 4\pi\rho \\ &(\frac{1}{c^2}\partial_t^2 - \nabla^2)\bar{A} = 4\pi\bar{j}. \end{aligned} \tag{23}$$

One readily observes that the former equation in (23) is the Poisson equation, while the latter one is the inhomogeneous wave equation equation.

As a final note before moving on to the specifics of how to mathematically describe lasers, it is noted that in the literature one often finds, in a quantum mechanical context, claims stating that a gauge transformation is a unitary transformation. That is to say that, given a Hamiltonian operator H that describes a given quantum mechanical system, applying a gauge transformation (19) results in a final Hamiltonian with a set of wave functions $\{\Psi\}$ that equivalently may be obtained through the set of transformations [12]

$$\begin{aligned} &\Psi \to e^{iS}\Psi \\ &H \to e^{iS}(H - \dot{S})e^{S}, \end{aligned} \tag{24}$$

where S is (not to be confused with the spin operator) a hermitian operator. However, caution is to be taken when making use of this "equivalence", as will be eluded to in chapter 7.

4.1 Mathematical description of lasers

The scope of the mathematical description of lasers presented here is intended to cover the minimum needed to be able to follow the content of this thesis. Therefore, it is noted that the following is in no sense meant to represent an exhaustive description of the broad field of laser physics. For a more extensive covering one may refer to sources such as [13].

A laser is to be understood as radiation, that is one should be able to describe a laser by its electric and magnetic field. This on the other hand can be reduced to saying that a laser can be described by a set of potentials ϕ and $\bar{A}$ according to (18). It can be shown [14] that (in the Coulomb gauge) for monochromatic radiation propagating in the positive x-direction, the electric and magnetic fields depend on t and x as $E = E(\omega t - kx)$ and $B = B(\omega t - kx)$, thus implying that the vector potential is of the form $\bar{A} = \bar{A}(\omega t - kx)$, where k is the wave vector's magnitude, ω is the laser's angular frequency and t is time. By choosing a gauge in which $\phi = 0$, we conclude that a monochromatic laser with positive z-polarization propagating in the positive x-direction is described by a vector potential of the form $\bar{A} = \hat{z}A_0(\omega t - kx)$, where A_0 is the amplitude of the vector potential.

4.2 Dipole approximation

In general, studying a problem with an exact vector potential $\bar{A}$ that fully describes a given laser is often an extremely difficult and demanding task. More often than not, one is forced to approximate the vector potential in order to make studying the problem at hand more tangible. In our case, we may expand $\bar{A}(\omega t - kx)$ in powers of kx. That is, we write

$$\bar{A}(\omega t - kx) = \bar{A}(\omega t) + \bar{E}(\omega t)kx + ... \tag{25}$$

In many cases, only retaining the first term in the expansion above is sufficient. This approximation is usually referred to as the dipole approximation and it is heavily used in the field of atomic physics as well as in many other areas of theoretical physics. In the dipole approximation, the vector potential is purely time dependent, resulting in a vanishing magnetic field. In order to approximately describe a non-vanishing magnetic field one therefore has to at least go to first order in the above expansion. The explicit form of the vector potential used in this thesis to describe our applied laser is given by

$$\bar{A}(t) = A_0 \sin(\omega t)\hat{z}, \tag{26}$$

where ω is the angular frequency of the laser and A_0 is the magnitude of the vector potential.

5 Hydrogenic atoms in an applied laser

As a final preliminary step, this chapter outlines roughly how the interaction of an electron in a hydrogenic atom with an external electromagnetic field (laser) is modeled. This will be done for the non-relativistic and the relativistic case, respectively. Finally, the resulting Hamiltonian will be presented in the two most typically known gauges, the velocity gauge and the length gauge.
It is noted here that the definition of velocity and/or length gauge may vary depending on the source one is referring to (see [15] and references therein). Therefore, the definitions of the velocity and length gauge used in this chapter are stated explicitly to avoid confusion.

5.1 Non-relativistic hydrogenic atom in a laser

We start with the Hamiltonian for a free electron. For a free electron, the Hamiltonian is simply the kinetic energy, which reads

$$H_{free} = \frac{p^2}{2m}. \tag{27}$$

In analogy to classical mechanics, the correct interaction with an electromagnetic field is obtained through the minimal coupling rule. The minimal coupling rule states that the correct interaction is obtained by the following replacement in the free Hamiltonian (27)

$$\begin{aligned} H &\to H - e\phi \\ \bar{p} &\to \bar{p} - e\bar{A}, \end{aligned} \tag{28}$$

where ϕ is the scalar potential and $\bar{A}$ is the vector potential describing the net electromagnetic field acting on the electron. In our case, the net electromagnetic field is generated by the scalar potential $\phi = \frac{Ze}{r}$ due to the nucleus and the vector potential $\bar{A}$ describing our laser. Therefore, the Hamiltonian for a non-relativistic electron in an applied laser (ignoring spin) is given by

$$H = \frac{(\bar{p} - e\bar{A})^2}{2m} - \frac{Ze^2}{r}. \tag{29}$$

5.1.1 Velocity gauge

Applying the dipole approximation, we may write the above Hamiltonian more explicitly as

$$H^{dip} = \frac{\bar{p}^2}{2m} - \frac{Ze^2}{r} - \frac{e}{m}\bar{A}\cdot\bar{p} + \frac{e^2}{2m}\bar{A}^2. \tag{30}$$

Now, we note that the term quadratic in $\bar{A}$ is now purely time dependent. We can get rid of that term via a gauge transformation (19) with $\chi = \frac{e^2}{2m}\int^t d\tau\ \bar{A}^2(\tau)$. The resulting Hamiltonian is then given by

$$H_{vel} = \frac{\bar{p}^2}{2m} - \frac{Ze^2}{r} - \frac{e}{m}\bar{A}\cdot\bar{p} \tag{31}$$

The choice of gauge for the above Hamiltonian is usually referred to as the *velocity gauge* [16].

5.1.2 Length gauge

An alternative gauge that may be used is the so called *length gauge* [16]. The length gauge has more of an analytical appeal, as the Hamiltonian in general becomes much more neat, as a lot of terms simply drop out. This is much more apparent in the relativistic treatment, as will be seen later while not as much in the non-relativistic case here.

In order to obtain the length gauge, one starts with the velocity gauge Hamiltonian (31) and performs yet another gauge transformation (19) with $\chi = -\bar{A}\cdot\bar{r}$. One then obtains the length gauge Hamiltonian given by [16]

$$H_{len} = \frac{\bar{p}^2}{2m} - \frac{Ze^2}{r} - e\bar{E}_L\cdot\bar{r}, \tag{32}$$

where $\bar{E}_L = -\partial_t\bar{A}$ is the electric field due to the laser.

5.2 Relativistic hydrogenic atom in a laser

In order to obtain the relativistic analog of (29) we start again by considering the free (now relativistic) Hamiltonian (6). As in the non-relativistic case, we proceed by applying the minimal coupling rule, resulting in the Hamiltonian describing the relativistic electron in a hydrogenic atom in an applied laser field, given by

$$H = c\bar{\alpha} \cdot (\bar{p} - e\bar{A}) + e\phi + mc^2\beta. \tag{33}$$

This Hamiltonian will be referred to as the minimal coupling Dirac Hamiltonian.
Recall that the relativistic Hamiltonian may be thought of as a 2×2 block matrix due to the fact that we now have in addition to the electron its antiparticle, the positron. Further, we are considering spin, too, which additionally yields two degrees of freedom per particle. Recall that while β is diagonal, $\alpha_j, j = 1, 2, 3$ is not as may be seen explicitly in (7). This means that when trying to solve for the wave function Ψ, we cannot merely solve for a single particle. As the differential equations will be coupled, we are forced to solve for both the electron's *and* the positron's wave function.

In this thesis, however, the electron in the non-relativistic limit is studied. Therefore, we are not interested in finding the wave function for the positron. In order to decouple the electron's wave function from the positron's wave function, the non-relativistic limit is invoked. A complication arises however in the fact that, as mentioned, the Hamiltonian above couples the particle's wave functions. Thus, before invoking the non-relativistic limit, one has to obtain a Hamiltonian that has off diagonal block matrices of negligible order. For us, this will mean that we want to write the Hamiltonian (33) of the form

$$H = \begin{pmatrix} H_{e^-} & \mathcal{O}(\frac{1}{m^4}) \\ \mathcal{O}(\frac{1}{m^4}) & H_{e^+} \end{pmatrix}, \tag{34}$$

where m is the mass of the electron and H_{e^-} is the 2×2 relativistic Hamiltonian of the electron up to order $\mathcal{O}(\frac{1}{m^3})$ while H_{e^+} is the 2×2 dimensional Hamiltonian corresponding to the positron. Going to the non-relativistic limit, then, is done by merely considering the Hamiltonian for the electron H_{e^-} up to order $\mathcal{O}(\frac{1}{m^3})$, while ignoring the positron's Hamiltonian.

The method used to perform the above mentioned process is referred to as the Foldy-Wouthuysen transformation [17], which will be outlined in the following chapter.

6 Theoretical model

In this section we will outline and motivate the choice of the theoretical model used in this thesis.

The main Hamiltonian in this thesis on which most is based on will be first derived via the Foldy-Wouthuysen transformation [17]. Then, the obtained Hamiltonian will be presented in three different gauges. The first gauge, the so called propagation gauge [18], will be given to illustrate how the derived model may be applied to phenomena where the dipole approximation is not valid. Then, the dipole approximation will be invoked and the resulting Hamiltonian will be given in two different gauges. These gauges are generalizations of the velocity gauge (31) and the length gauge (32) that were given in the non-relativistic treatment in chapter 5. The generalized length and velocity gauges are what have been considered when applying the model later on in chapter 7.

6.1 Foldy Wouthuysen transformation

The approximate block diagonalization of the minimal coupling Dirac Hamiltonian (33) via a unitary transformation of the 4 component wave function Ψ is usually referred to as the Foldy-Wouthuysen transformation (FWT) [17]. In the following we will illustrate how to obtain (33) in a block diagonal form that includes terms of order $O(\frac{1}{m^3})$ by applying the FWT. The derivation outlined here follows closely the one used in [19].

Before applying the FWT however, we first define two types of operators and name their most important properties with regard to the FWT.

An operator E is called even if it is of the block diagonal form

$$E = \begin{pmatrix} X & 0 \\ 0 & Y \end{pmatrix}, \tag{35}$$

while an operator O is called odd if it is of the block diagonal form

$$O = \begin{pmatrix} 0 & A \\ B & 0 \end{pmatrix}. \tag{36}$$

Put differently, even operators do not couple large and small components, while odd operators do. It is easy to show that for any even operator E we have

$$E\beta = \beta E, \tag{37}$$

while for any odd operator O we have

$$O\beta = -\beta O. \tag{38}$$

When applying the FWT our goal is to choose a unitary transformation such that our new Hamiltonian only contains odd operators of order $\frac{1}{m^4}$ or less.

We now start applying the FWT to our Hamiltonian (33). As stated above, we start by performing a unitary transformation e^{iS} to our 4 component wave function Ψ, that is

$$\Psi \to e^{iS}\Psi. \tag{39}$$

Accordingly, our Hamiltonian will transform into the new Hamiltonian given by

$$H' = e^{iS}(H - i\partial_t)e^{-iS}. \tag{40}$$

We will choose our unitary transformation to be small, that is we choose S : $S = O(\frac{1}{m})$. Further, as we want to "transform away" the odd operators in (33), we demand further that S be an odd operator. As we are interested in (40) only to a finite order in $\frac{1}{m}$, we will rewrite (40) using the Baker-Hausdorff formula

$$e^A B e^{-A} = \Sigma_{n=0}^{\infty} \frac{i^n}{n!} \Omega_n(A, B), \tag{41}$$

where $\Omega_n(A, B) = [A, \Omega_{n-1}(A, B)]$ and $\Omega_0(A, B) := B$. Using this relation, we may write

$$-e^{iS} i\partial_t e^{-iS} = -\Sigma_{n=0}^{\infty} \frac{i^{n+1}}{n!} \Omega_n(S, \partial_t). \tag{42}$$

Note that $[S, \partial_t]$ = -$(\partial_t S)$, such that we get

$$H' = \frac{i^0}{0!}\Omega_0(S, H) + \Sigma_{n=1}^{\infty} \frac{i^n}{n!}(\Omega_n(S, H) + i\Omega_{n-1}(S, \partial_t S)). \tag{43}$$

By definition, we have that $\Omega_0(S, H) = H$. We can rename the summation index in the equation above as

$$H' = H + \Sigma_{n=0}^{\infty} \frac{i^{n+1}}{(n+1)!}(\Omega_{n+1}(S, H) + i\Omega_n(S, \partial_t S)). \tag{44}$$

We use the fact that $[S, \Omega_n(S, H)] + \Omega_n(S, i\partial_t S) = \Omega_n(S, [S, H] + i\partial_t S)$, which one can verify via mathematical induction. Equation (44) then takes the form

$$H' = H - \Sigma_{n=0}^{\infty} \frac{i^n}{(n+1)} \Omega_n(S, i[H, S] + \partial_t S). \tag{45}$$

We now make use of the Heisenberg equation of motion for S which states that

$$\dot{S} = i[H, S] + \partial_t S, \tag{46}$$

where $\dot{S} := \frac{dS}{dt}$. As will be shown later, S will be such that it commutes with all terms in H, except for $e\phi$. To shorten notation, we define

$$\begin{aligned} T &= c\bar{\alpha} \cdot (\bar{p} - e\bar{A}), \\ V &= e\phi. \end{aligned} \tag{47}$$

Then we have that

$$H = T + V + mc^2\beta. \tag{48}$$

Equation (45) then takes the form

$$H' = T + V + mc^2\beta - i\Sigma_{n=0}^{\infty}\frac{i^n}{(n+1)!}\Omega_n(S,[T+mc^2\beta,S]). \tag{49}$$

Using the fact that

$$\Omega_n(S,[T+mc^2\beta,S]) = -\Omega_n(S,[S,T+mc^2\beta]) = -\Omega_{n+1}(S,T+mc^2\beta), \tag{50}$$

we obtain that

$$\begin{aligned} H' = V + mc^2\beta + T + \Sigma_{n=0}^{\infty}\frac{i^{n+1}}{(n+1)!}\Omega_{n+1}(S,T+mc^2\beta) \\ - \Sigma_{n=0}^{\infty}\frac{i^n}{(n+1)!}\Omega_n(S,\dot{S}). \end{aligned} \tag{51}$$

Finally, we remark that $T + mc^2\beta = \Omega_{-1+1}(S, T + mc^2\beta)$, such that we may rewrite the above equation (51) as

$$H' = V + \Sigma_{n=0}^{\infty}\Omega_n(S,T+mc^2\beta - \frac{1}{n+1}\dot{S}). \tag{52}$$

If we were now to expand S in a power series in $\frac{1}{m}$, we would obtain an expression for our Hamiltonian in powers of $\frac{1}{m}$. However, since we in addition are interested in (approximately) block diagonalizing our Hamiltonian, we further proceed in trying to rewrite our Hamiltonian as a sum of even and odd operators. We do this by noting the following:
Since S is an odd operator, we know that $S\beta = -\beta S$. This, together with the fact that $\beta^2 = 1$, may be used to show that

$$\Omega_n(S,\beta) = \beta(-2S)^n, \tag{53}$$

for $n = 0, 1, \ldots$. We can then write our Hamiltonian (52) as

$$H' = V + mc^2\beta\Sigma_{n=0}^{\infty}\frac{(-2iS)^n}{n!} + \Sigma_{n=0}^{\infty}\frac{i^n}{n!}\Omega_n(S,T-\frac{1}{n+1}\dot{S}). \tag{54}$$

Since S is odd, we have that S^n is odd (even) if n is odd (even). Further, since T and S are odd, we have that $\Omega_n(S, T - \frac{1}{n+1}\dot{S})$ is even (odd) if n is odd (even). Therefore, we obtain the expression

$$\begin{aligned} H' = V + mc^2\beta\Sigma_{n=0,2,\ldots}^{\infty}\frac{(-2iS)^n}{n!} + \Sigma_{n=1,3,\ldots}\frac{i^n}{n!}\Omega_n(S,T-\frac{1}{n+1}\dot{S}) \\ + mc^2\beta\Sigma_{n=1,3,\ldots}^{\infty}\frac{(-2iS)^n}{n!} + \Sigma_{n=0,2,\ldots}\frac{i^n}{n!}\Omega_n(S,T-\frac{1}{n+1}\dot{S}). \end{aligned} \tag{55}$$

Equation (55) thus yields an expression for our Hamiltonian (33) as a sum of even and odd operators only.
Finally, we write

$$S = m^{-1}S_1 + m^{-2}S_2 + m^{-3}S_3 + ... \tag{56}$$

and plugg this into the equation (55) above, which will yield an expression of the form

$$H' = H^{(0)}_{even} + H^{(0)}_{odd} + \Sigma^{\infty}_{n=1} H^{(n)}_{even} m^{-n} + H^{(n)}_{odd} m^{-n}. \tag{57}$$

When calculating (57) up to order $\mathcal{O}(\frac{1}{m^3})$, we want only to retain terms proportional to $\frac{1}{m^3}$ and below. Therefore, we need to find S_1, S_2, S_3 such that H' is block diagonal up to order $O(\frac{1}{m^3})$. We do so by choosing S_1, S_2 and S_3 such that $H^{(0)}_{odd} = H^{(1)}_{odd} = H^{(2)}_{odd} = 0$. This yields a system of equations, linear in S_1, S_2 and S_3, which may be solved readily. Upon doing so, one obtains the following expressions

$$\begin{aligned} S_1 &= -\frac{i}{2c^2}\beta T \\ S_2 &= \frac{1}{(2c^2)^2}\dot{T} \\ S_3 &= \frac{i}{(2c^2)^3}(\frac{4}{3}T^3 + \ddot{T}). \end{aligned} \tag{58}$$

Finally, these expressions may be used to calculate $H^{(n)}_{even}$ for $n = 0, 1, 2, 3$. Upon doing so, one obtains a block diagonal Hamiltonian, accurate to order $O(\frac{1}{m^3})$:

$$\begin{aligned} H' = mc^2\beta + V + \frac{1}{2mc^2}\beta T^2 - \frac{i}{8m^2c^4}\{T, \dot{T}\} - \frac{1}{8m^3c^6}\beta T^4 \\ - \frac{1}{16m^3c^6}\{T, \ddot{T}\} + O(\frac{1}{m^4}). \end{aligned} \tag{59}$$

As we have written our Hamiltonian in a block diagonal form, we may now proceed to the non-relativistic limit, i.e. we may now neglect the small component of the 4 component spinor to obtain an equation for the 2 component spinor describing an electron in an external electromagnetic field, as we now have (approximately) uncoupled the large component from the small component. Before considering the non-relativistic limit, though, we note that
$T^2 = c^2(\alpha \cdot (\bar{p} - e\bar{A}))^2 = c^2(\bar{p} - e\bar{A})^2$ by using the fact that we assume Coulomb gauge and $\frac{1}{2}(\alpha_i\alpha_j + \alpha_j\alpha_i) = \delta_{ij}$. Further, we have that $[\alpha_i, \alpha_j] = \Sigma_k i\epsilon_{ijk}\alpha_k := \Sigma_k$, where Σ_k is the four dimensional spin operator. The non-relativistic limit is then obtained by simply taking the Hamiltonian in (59) and replacing $\beta \to 1$ and $\bar{\Sigma} \to \bar{S}$, where $\bar{S}$ is the 2 dimensional spin operator vector. Upon doing so, we obtain the final non-relativistic expression for our Hamiltonian describing an

electron in an external electromagnetic field:

$$
\begin{aligned}
H_{FWT} &= mc^2 + e\phi + \frac{(\bar{p} - e\bar{A})^2}{2m} - \frac{(\bar{p} - e\bar{A})^4}{8m^3c^2} \\
&- \frac{e}{16m^3c^4}([\bar{p} - e\bar{A}], \partial_t \bar{E}) \\
&- \frac{e}{2m}\bar{\sigma} \cdot (\bar{B} + \frac{i}{8m^2c^4}(\partial_t \bar{E} \times (\bar{p} - e\bar{A}) + (\bar{p} - e\bar{A}) \times \partial_t \bar{E})) \\
&+ \frac{e}{8m^3c^2}([\bar{p} - e\bar{A}]^2, \bar{\sigma} \cdot \bar{B}) - \frac{e^2}{8m^3c^2}\bar{B}^2 - \frac{e}{8m^2c^2}\nabla \cdot \bar{E} \\
&- \frac{e}{8m^2c^2}\bar{\sigma} \cdot (\bar{E} \times [\bar{p} - e\bar{A}] - [\bar{p} - e\bar{A}] \times \bar{E}) + O(\frac{1}{m^4}),
\end{aligned}
\tag{60}
$$

where we have set $\bar{E} = -\nabla\phi - \partial_t \bar{A}$ and $\bar{B} = \nabla \times \bar{A}$. This is the non-relativistic Hamiltonian that is to describe the electron containing relativistic corrections up to order $O(\frac{1}{m^3})$.

6.2 The Theoretical Model in different Gauges

We now start by considering the Hamiltonian (60) that was obtained through the FWT in different gauges. For each gauge, we will explain in which situations the presented gauge may be useful/not so useful.

6.2.1 Propagation gauge

We start by considered the propagation gauge [18]. The propagation gauge may be obtained from the exact Dirac Hamiltonian (33) by applying a gauge transformation (19) with

$$\chi = -\frac{e^2}{2m\omega}\int_{-\infty}^{\eta} d\eta' A^2(\eta'), \tag{61}$$

where $\eta = \omega t - \bar{k}\cdot\bar{r}$. ω is the applied laser's frequency, $\bar{k} = \hat{k}\frac{\omega}{c}$ is the wave vector, pointing in the propagation direction $\hat{k}$ of the applied laser, and c is the speed of light. Applying the gauge transformation (61) to the minimal coupling Dirac Hamiltonian (33), we obtain the propagation gauge Hamiltonian in the fully relativistic Dirac theory, given by

$$H_{prop} = c\bar{\alpha}\cdot\bar{d} + mc^2\beta + (V - \frac{e^2}{2m}A^2), \tag{62}$$

where $V = e\phi$ with ϕ being the scalar potential and $\bar{d} = \bar{p} - e\bar{A} + \frac{e^2}{2mc}\bar{A}^2\hat{k}$. In order to obtain an approximate Hamiltonian to (62), we apply the FWT formula (59) and get

$$\begin{aligned} H_{prop}^{FWT} = mc^2\beta + V' + \frac{\beta T^2}{2mc^2} - \frac{i}{8m^2c^4}[T,\dot{T}] \\ - \frac{\beta T^4}{8m^3c^6} - \frac{\beta}{16m^3c^6}\{T,T\} + ..., \end{aligned} \tag{63}$$

where $T = c\bar{\alpha}\cdot(\bar{p} - e\bar{A} + \frac{e^2}{2mc}A^2\hat{k})$ and $V' = V - \frac{e^2}{2m}A^2$.
For brevity, we introduce the following definitions:

$$\begin{aligned} T_0 &= c\bar{\alpha}\cdot(\bar{p} - e\bar{A}) \\ \tau &= c\bar{\alpha}\cdot\hat{k}\frac{e^2}{2mc}A^2 \\ \nu &= -\frac{e^2}{2m}A^2, \end{aligned} \tag{64}$$

which allow us to write $T = T_0 + \tau$ and $V' = V + \nu$. Making use of these definitions, we may write (63) more neatly as

$$H_{FWT} = H_0 + \nu + \frac{\beta}{2mc^2}(\{T_0,\tau\} + \tau^2) + \mathcal{O}(\frac{1}{c^3}), \tag{65}$$

where H_0 simply is the Hamiltonian (60) derived previously.
In order to simplify (65) we use the two identities

$$\begin{aligned}(\bar{\alpha}\cdot\bar{M})(\bar{\alpha}\cdot\bar{N}) &= \bar{M}\cdot\bar{N} + i\bar{\Sigma}\cdot(\bar{M}\times\bar{N})\\ (\hat{k}\cdot\bar{\alpha})^2 &= 1,\end{aligned} \tag{66}$$

where $\bar{\Sigma}$ =diag$(\bar{\sigma},\bar{\sigma})$, with $\bar{\sigma} = (\sigma_1,\sigma_2,\sigma_3)$ being the pauli matrix vector. Applying the identities (66) we get that

$$\begin{aligned}\{T_0,\tau\} &= \frac{e^2c}{2m}\hat{k}\cdot(\{\bar{p}-e\bar{A},A^2\} + i\bar{\Sigma}\times[\bar{p},A^2]).\\ \tau^2 &= (\frac{e^2A^2}{2m})^2.\end{aligned} \tag{67}$$

Inserting (67) into (65), one obtains the 4×4 propagation gauge Hamiltonian (62) up to order $\mathcal{O}(\frac{1}{c^2})$. As we are only interested in the part of the Hamiltonian describing the electron, we apply the substution rules $\bar{\Sigma}\to\bar{\sigma}$ and $\beta\to 1$. This then yields the propagation gauge Hamiltonian (62) up to order $\mathcal{O}(\frac{1}{c^2})$ that describes the electron in an applied laser, given by

$$\begin{aligned}H_{prop} = mc^2 + V + \frac{(\bar{p}-e\bar{A})^2}{2m} - \mathbf{\frac{e^2}{2m}A^2} - \frac{(\bar{p}-e\bar{A})^4}{8m^3c^2} + \mathbf{\frac{e^4}{8m^3c^2}A^4}\\ - \frac{e}{2m}\bar{\sigma}\cdot\bar{B} + \mathbf{\frac{e^2}{4m^2c}\hat{k}\cdot\{\bar{p}-e\bar{A},A^2\}}\\ + \frac{e}{8m^3c^2}\{(\bar{p}-e\bar{A})^2,\bar{\sigma}\cdot\bar{B}\} - (\frac{e}{2m})^2\frac{\bar{B}^2}{2mc^2} - \frac{e}{8m^2c^2}\nabla\cdot\bar{E}\\ - \frac{e}{8m^2c^2}\bar{\sigma}\cdot(\bar{E}\times(\bar{p}-e\bar{A}) - (\bar{p}-e\bar{A})\times\bar{E}) + \mathcal{O}(\frac{1}{c^3}),\end{aligned} \tag{68}$$

where $\bar{B} = \nabla\times\bar{A}$ and $\bar{E} = -\partial_t A\hat{k}$. The bold faced terms are the terms that appear due to being in propagation gauge. As one can see, the first two terms simply cancel the purely A dependent terms that one gets from the kinetic terms of the form $(p-eA)^2$ and $(p-eA)^4$. This ensures that one avoids the problem of catastrophic cancellation [3]. In essence, catastrophic cancellation refers to the case where the sum of two terms contributes little, while the effect of each individual one is very large. This in turn, causes difficulties when doing numerical computations.
The third bold faced term in (68) is a mere artefact of being in propagation gauge. When considering beyond dipole effects, that is when one is not assumimg the dipole approximation (see chapter 4.2), this term will be of much importance.
The propagation gauge Hamiltonian (68) is most suitable when studying beyond dipole effects [20]. One reason would be that, as mentioned previously, one avoids the numerical problem of catastrophic cancellation due to the exact cancellation of the terms proportional to A^2 and A^4 appearing in (68). Another advantage with using the propagation gauge when studying beyond dipole effects is that, in contrast to the dipole approximation, one does not have to make

any assumptions about the importance of the magnetic field [20] while still being able to apply the approximation $\bar{A} = \bar{A}(t)$. Yet another advantage with using the propagation gauge is that, instead of the term $\frac{\mathring{eA}2}{2m}A^2$, one has to deal with the propagation gauge operator $\frac{e^2}{4mc}\hat{k}\cdot\{\bar{p}-e\bar{A},\bar{A}^2\}$. This is an advantage, as the operator $\frac{e^2}{2m}\bar{A}^2$ is much more difficult to handle when doing numerical computations than the term $\frac{e^2}{4mc}\hat{k}\cdot\{\bar{p}-e\bar{A},\bar{A}^2\}$.
To illustrate how one would go about when studying beyond dipole effects with the presented propagation gauge Hamiltonian (68), we consider here a monochromatic laser generating radiation propagating in the positive x-direction while being linearly polarised in the positive z-direction. We then know from (24) that we can write our vector potential $\bar{A} = A_0\hat{z}$ as

$$\bar{A}(\omega t - kx) = \hat{z}A_0(\omega t) + \hat{z}E_0(\omega t)kx + \mathcal{O}((kx)^2), \tag{69}$$

where $E_0(t) = \frac{dA_0(t)}{dt}$ is the electric field amplitude due to the applied laser. Then, inserting (69) into the propagation gauge Hamiltonian (68) while only retaining terms linear in kx, we obtain (in atomic units)

$$\begin{aligned} H^1_{prop} = {} & c^2 + \frac{p^2}{2} - \frac{Z}{r} - \frac{p^4}{8c^2} + \frac{1}{2c^2r^3}\bar{L}\cdot\bar{S} + \frac{\pi}{2c^2}\delta(\bar{r}) \\ & - \frac{E_0(t)}{2c}\sigma_y + (A_0(t) - \frac{A_0(t)^3}{2c^2})p_z + \frac{1}{4c^2}p_x - \frac{A_0(t)^2}{2c^2}p_z^2 \\ & - \frac{A_0(t)^2}{4c^2}p^2 - \frac{A_0(t)}{2c^2}p_zp^2 + \frac{E_0(t)}{c}xp_z \\ & + \frac{E_0(t)}{4c^2}\hat{z}\cdot(\bar{\sigma}\times\bar{p}) - \frac{ZA_0(t)}{4c^2r^3}\hat{z}\cdot(\bar{\sigma}\times\bar{r}). \end{aligned} \tag{70}$$

The Hamiltonian (70) then yields a model accurate to order $\mathcal{O}(\frac{1}{c^2})$, that may be used when studying beyond dipole effects of an electron in an applied laser field. A quick glance at (70) reveals that a study of beyond dipole effects is a fairly demanding task, as there are many matrix elements that one needs to numerically calculate.

In this thesis, the study of the electron in an applied laser is done in the dipole approximation. Therefore, the propagation gauge Hamiltonian (68) has not been considered further and has been added here for completeness, as well as to illustrate how the Hamiltonian (60) derived through the FWT could be used to study beyond dipole effects.

6.2.2 Velocity gauge

We now proceed by invoking the dipole approximation. This means that our laser can be modeled by a vector potential $\bar{A} = \bar{A}(t)$ that is only time dependent. Inserting this assumption into the Hamiltonian (60) obtained through the FWT, valid to order $\mathcal{O}(\frac{1}{c^2})$, one obtains the following expression

$$\begin{aligned} H^{dip} &= mc^2 + e\phi + \frac{(\bar{p} - e\bar{A})^2}{2m} \\ &- \frac{(\bar{p} - e\bar{A})^4}{8m^3c^2} - \frac{e}{8mc^2}\nabla \cdot \bar{E} + \frac{\pi Ze^2}{2m^2c^2}\delta(\bar{r}) + \frac{e^2}{2m^2c^2r^3}\bar{S} \cdot \bar{L} \\ &- \frac{e}{2mc^2}\bar{S} \cdot (\partial_t \bar{A} \times \bar{p}) + \frac{Ze^2}{2mc^2}\frac{1}{r^3}\bar{S} \cdot (\bar{r} \times \bar{A}). \end{aligned} \tag{71}$$

In order to obtain the Hamiltonian (71) in the velocity gauge, we proceed in analogy to what has been done for the non-relativistic velocity gauge (71) by applying a gauge transformation (19) with

$$\chi = \int^t d\tau (\frac{e^2}{2m}\bar{A}^2(\tau) - \frac{e^4}{8m^3c^2}\bar{A}^4(\tau)), \tag{72}$$

in order to get rid of all the purely time dependent terms in (71). Upon doing so, one obtains the Hamiltonian H_{vel} given by

$$\begin{aligned} H_{vel} &= mc^2 + e\phi + \frac{(\bar{p} - e\bar{A})^2}{2m} - \frac{e^2}{2m}\bar{A}^2 \\ &- \frac{(\bar{p} - e\bar{A})^4}{8m^3c^2} + \frac{e^4}{8m^3c^2}\bar{A}^4 - \frac{e}{8mc^2}\nabla \cdot \bar{E} + \frac{\pi e^2}{2m^2c^2}\delta(\bar{r}) + \frac{e^2}{2m^2c^2r^3}\bar{S} \cdot \bar{L} \\ &- \frac{e}{2mc^2}\bar{S} \cdot (\bar{E}_L \times \bar{p}) + \frac{Ze^2}{2mc^2}\frac{1}{r^3}\bar{S} \cdot (\bar{r} \times \bar{A}), \end{aligned} \tag{73}$$

where $\bar{E}_L = -\partial_t \bar{A}$ denotes the electric field due to the applied laser.
The Hamiltonian (73) is the generalization of the non-relativistic velocity gauge Hamiltonian (31). The main difference is that now, relativistic effects up to order $\mathcal{O}(\frac{1}{c^2})$ are included.

The velocity gauge is usually a good choice for performing numerical computations, in that it has good convergence properties [21]. The possible downside is that one has to compute a respectable amount of terms, making it a less preferable candidate for doing analytical computations.

6.2.3 Length gauge

In analogy to the non-relativistic case, one may perform yet another gauge transformation to (73) in order to obtain a Hamiltonian with fewer terms in total. This will be the generalization of the non-relativistic length gauge Hamiltonian (32).
To obtain the length gauge Hamiltonian, we apply a gauge transformation (19) with

$$\chi = -\bar{A}(t) \cdot \bar{r} \tag{74}$$

to the velocity gauge Hamiltonian (73). This essentially results in the following replacement rules

$$\begin{aligned} &\bar{A} \to 0 \\ &\partial_t \bar{A} \to 0 \\ &\phi \to \phi - \bar{E}_L \cdot \bar{r} \\ &\frac{e^2}{2m^2c^2r^3} \bar{S} \cdot \bar{L} \to \frac{e^2}{2m^2c^2r^3} \bar{S} \cdot \bar{L} - \frac{e}{2mc^2} \bar{S} \cdot (\bar{E}_L \times \bar{p}), \end{aligned} \tag{75}$$

that are to be applied to the velocity gauge Hamiltonian (73). Upon applying the replacement rules (75), one obtains the Hamiltonian H_{len} given by

$$\begin{aligned} H_{len} = mc^2 + e\phi + \frac{\bar{p}^2}{2m} \\ - \frac{\bar{p}^4}{8m^3c^2} + \frac{e^2}{2m^2c^2r^3} \bar{S} \cdot \bar{L} + \frac{\pi e^2}{2m^2c^2} \delta(\bar{r}) \\ - \frac{e}{2m^2c^2} \bar{S} \cdot (\bar{E}_L \times \bar{p}) - e\bar{E}_L \cdot \bar{r}. \end{aligned} \tag{76}$$

Comparing the length gauge Hamiltonian (76) to the velocity gauge Hamiltonian (73), one immediately sees that the length gauge Hamiltonian has much fewer terms. Hence, the length gauge would be the preferred choice for analytical analysis and computation. However, when using the length gauge for numerical computations, one is quickly faced with the problem of slow convergence [21]. This is usually reflected in the need of a comparatively large basis in order to obtain sufficient precision, though this usually only becomes a problem when considering eigenstates of the Hamiltonian (76) with higher angular momentum quantum numbers.

7 Results

Having developed a framework (71) to describe our hydrogenic electron in an applied laser field, we may now proceed to use this model to study its domain of applicability, as well as its limitations. To this end, we will in this section start by looking at photon ionization.
Before applying the model, though, we have the freedom of choosing any of the gauges presented, that is we may choose between the propagation gauge (68), the velocity gauge (73) and the length gauge (76). As already mentioned in the previous chapter, we are only interested in applying the model in domains where the dipole approximation is valid. Therefore, the choice of gauges reduces to choosing between the velocity gauge (73) and the length gauge (76). Previously we commented on the fact that the length gauge Hamiltonian (76) has notably fewer terms than the velocity gauge Hamiltonian (73). In addition, we are going to apply the model to photon ionization processes, hence when doing numerical computations we only need to consider states with small angular momentum quantum numbers, thus making the length gauge Hamiltonian (76) a suitable choice. Therefore, for the following calculations the length gauge Hamiltonian has been used, which in atomic units looks like

$$\begin{aligned} H_{len} = \frac{\bar{p}^2}{2} - \phi - \frac{\bar{p}^4}{8c^2} + \frac{1}{2c^2 r^3}\bar{S}\cdot\bar{L} + \frac{\pi}{2c^2}\delta(\bar{r}) \\ + \frac{1}{2c^2}\bar{S}\cdot(\bar{E}_L \times \bar{p}) + \bar{E}_L \cdot \bar{r}. \end{aligned} \tag{77}$$

Note that the rest mass energy c^2 has been neglected, as this simply yields a constant shift in the energies which will not be of importance for us.
In order to be able to judge how important the relativistic effects appearing in (77) are, we need to have a non-relativistic model to compare (77) to. To this end, we will use the non-relativistic length gauge Hamiltonian (32) given by (in atomic units)

$$H_{nonrel} = \frac{p^2}{2} - \frac{Z}{r} + \bar{E}_L \cdot \bar{r}. \tag{78}$$

Now that we have chosen a suitable gauge in which to express our model (77) which will be compared to (78), we will give a brief overview over the theory of photon ionization.

7.1 Photon ionization

Photon ionization is the process in which an incoming photon collides and interacts with an electron, bound to a nucleus, which causes the electron to gain enough momentum to escape the attractive force of the nucleus. More succinctly, photon ionization may be written as $Atom + \gamma \rightarrow Atom^+ + e^-$, where $Atom^+$ denotes the initial atom minus one electron, γ is the initial photon and e^- is the final electron.
An observable that is typically measured in this regard is the cross section. Here we will look at the cross section for photon ionization in a hydrogen-like atom to which a laser field has been applied. Before doing so, however, we will explain how to calculate the cross section for photo ionization with the use of our Hamiltonian (77) and the non-relativistic analogue (78) thereof.

7.1.1 Cross sections

We consider here an electron that is initially bound to a hydrogen like atom, which then interacts with a (or possibly multiple) photon(s), and is therefore accelerated and ends up in a different final state. Let us denote by α the initial state of the electron and by β its final state. Similarly, we denote by E_β and E_α the energy of the final and initial state of the electron, respectively. As energy will be conserved, we can express the energy of the photon(s) as $\omega_{\beta\alpha} = E_\beta - E_\alpha$. Denoting by $I(\omega)$ the intensity of a coherent laser beam with energy ω per photon, we define the cross section for the process considered here (in atomic units) as

$$\sigma_{\beta\alpha} = \frac{\omega_{\beta\alpha} W_{\beta\alpha}}{I(\omega_{\beta\alpha})}, \tag{79}$$

where $W_{\beta\alpha}$ gives the number of transitions occurring per unit time. In order to find $W_{\beta\alpha}$, we invoke Fermi's Golden rule. This mean that we will be working in the perturbative limit, which presupposes that we are considering only weak interactions. As the interactions here considered are due to the applied laser field, we need to assume that the vector potential's amplitude A_0 is sufficiently small for the perturbative limit to be valid. In addition, we need to write our Hamiltonian (77) as a sum of two terms, where one of those terms will be the small time-dependent perturbation considered. To this end, we write our Hamiltonian (77) as

$$\begin{aligned} H_{len} &= H_0 + H_I, \text{ where} \\ H_0 &= \frac{\bar{p}^2}{2} - \phi - \frac{\bar{p}^4}{8c^2} + \frac{1}{2c^2 r^3}\bar{S}\cdot\bar{L} + \frac{\pi}{2c^2}\delta(\bar{r}) \text{ and} \\ H_I &= \frac{1}{2c^2}\bar{S}\cdot(\bar{E}_L \times \bar{p}) + \bar{E}_L \cdot \bar{r}. \end{aligned} \tag{80}$$

Similarly for the non-relativistic Hamiltonian (78) we write

$$\begin{aligned} H_{nonrel} &= H_0 + H_I, \text{ where} \\ H_0 &= \frac{\bar{p}^2}{2} - \phi \text{ and} \\ H_I &= \bar{E}_L \cdot \bar{r}. \end{aligned} \tag{81}$$

Now, keeping in mind that our interaction Hamiltonians H_I in (80) and (81) are time dependent, we need to use a form of Fermi's Golden rule which takes this time dependence into account. As the dipole approximation is assumed, we may more explicitly write our interaction Hamiltonian (77) (and (78) for that matter) as $H_I = A\cos(\omega t) + B\sin(\omega t)$. Alternatively, this can be written as

$$\begin{aligned} H_I &= V^+ e^{i\omega t} + V^- e^{-i\omega t} \text{ with} \\ V^\pm &= \frac{1}{2} E_0 (-z + \frac{1}{2c^2} \hat{z} \cdot (\bar{S} \times \bar{p}) \text{ for (77) and,} \\ V^\pm &= -\frac{1}{2} E_0 z \text{ for (78),} \end{aligned} \tag{82}$$

where E_0 is the amplitude of the electric field due to the applied laser and ω is the laser's angular frequency.
Having written our interaction Hamiltonians in the form (82) above, it can be shown [22] that Fermi's Golden rule now takes the form (in atomic units)

$$W_{\beta\alpha} = 2\pi |V^-_{\beta\alpha}|^2 \delta(\omega_{\beta\alpha} - \omega) + 2\pi (|V^+_{\beta\alpha}|^2 \delta(\omega_{\beta\alpha} + \omega), \tag{83}$$

The delta functions in (83) ensure energy conservation and one may therefore readily see that the prefactor of $e^{\pm i\omega t}$ in (82) may be identified with emission/absorption of a single photon. As we are only interested in photon ionization where photon emission cannot take place, we only need to consider here photon absorption. Thus, applying Fermi's Golden rule (83) to our formula (79) for the cross section as well as inserting $I(\omega) = 2\pi c E_0^2$, we obtain the final expressions (in atomic units)

$$\begin{aligned} \sigma_{\beta\alpha} &= \frac{4\pi^2}{E_0^2 c} \omega_{\beta\alpha} |V^-_{\beta\alpha}|^2 \rho(E_\beta) \text{ with} \\ V^-_{\beta\alpha} &= \frac{1}{2} E_0 (-z + \frac{1}{2c^2} \hat{z} \cdot (\bar{S} \times \bar{p})) \text{ for (77) and} \\ V^-_{\beta\alpha} &= -\frac{1}{2} E_0 z \text{ for (78),} \end{aligned} \tag{84}$$

where ρ denotes the density of states per unit energy.
Thus, we see that to calculate the cross section for photon ionization we simply need to compute the energy spectrum $\{E_n\}_n$ of the system, the matrix elements $V^-_{\beta\alpha}$ and the density of states function ρ.

Having found an expression (84) for calculating the cross section, we now proceed by considering specific transitions. In the following, the initial and final

states of the electron are eigenstates of the unperturbed Hamiltonian H_0 (80). These eigenstates are fully characterised by the set of quantum numbers given by $\{n, j, l, s, m_j\}$, where n is the energy quantum number, analogous to the energy quantum number in non-relativistic hydrogen (16). The quantum number l is the angular momentum quantum number which is the same as the one appearing in non-relativistic hydrogen (12), as well. The spin quantum number s is equal to $\frac{1}{2}$ as we are considering the electron. As s remains a constant throughout all calculations, it will be implicitly assumed and therefore omitted. Further, the quantum number j can be though of as a generalised quantum number that takes into account both angular momentum and spin and here it can take the values $j = l \pm \frac{1}{2}$. The states need to be characterised by the quantum number j since the operator proportional to $\bar{S} \cdot \bar{L}$ in (80) does not commute with the operators $\bar{L}^2$, L_z, $\bar{S}^2$ and S_z, though it commutes with the operator $\bar{J}^2 = (\bar{L} + \bar{S})^2$, having eigenvalues $j(j+1)$. Finally, for a fixed j, the quantum number m_j can take the values $-j, -j+1, ..., j$.

7.1.2 $\mathbf{j = \frac{1}{2} \rightarrow j = \frac{1}{2}/\frac{3}{2}}$

We now consider the specific transitions where the initial electron is in the ground state. The ground state will be described by the set of quantum numbers $(n = 1, l = 0, j = \frac{1}{2}, m_j = \frac{1}{2})$. Though the ground state could also have the quantum number $m_j = -\frac{1}{2}$, it does not alter any of the calculations done in this chapter, neither does it affect the outcome thereof. Therefore, the case where $m_j = -\frac{1}{2}$ has not been considered.
As shown in (83), photon absorption in the perturbative limit allows only for the absorption of one photon. Therefore, the final state will have the angular quantum number $l = 1$. This allows for the possible quantum numbers $j = \frac{1}{2}$ and $j = \frac{3}{2}$, of which both will be considered. For bound states (energy less than zero), n will denote the quantum number that can be any integer larger than 1. For the case where the final state is in the continuum (energy larger than 0), n denotes the energy of that state and may thus be any real number larger than 0. At last, the quantum number m_j will remain unchanged due to the selection rule stating that the change in m_j in the dipole approximation must be zero. Therefore, the final state may be summarised by any of the sets of numbers $(n, l = 1, j = 1 \pm \frac{1}{2}, m_j = \frac{1}{2})$. In summary, we are considering the two transitions

$$\begin{aligned} &(n = 1, l = 0, j = \frac{1}{2}, m_j = \frac{1}{2}) \rightarrow (n, l = 1, j = \frac{3}{2}, m_j = \frac{1}{2}), \\ &(n = 1, l = 0, j = \frac{1}{2}, m_j = \frac{1}{2}) \rightarrow (n, l = 1, j = \frac{1}{2}, m_j = \frac{1}{2}). \end{aligned} \tag{85}$$

These transitions will be abbreviated by $j = \frac{1}{2} \rightarrow j = \frac{3}{2}$ and $j = \frac{1}{2} \rightarrow j = \frac{1}{2}$, or simply $\frac{1}{2} \rightarrow \frac{3}{2}$ and $\frac{1}{2} \rightarrow \frac{1}{2}$, respectively. To calculate the cross sections for the transitions (85) then, we may use equation (84). In order to do so, we start by finding the density of states function ρ.

When doing the calculations numerically, a finite (large) box will be used and accordingly all the calculated quantities will be box normalized. Box normalization simply means that quantities have been normalized in a box dependent way, that is the normalization constants depend in some fashion on the size of the box. In theory one supposes all of space instead of a finite box. Hence, when computing the cross section (an observable) all box dependent terms ought to cancel in the end. In order for this to happen, we need to choose the density of states function accordingly. In order to get a cross section that is independent of the chosen size of the box, the density of state function will be chosen to be

$$\rho(E_n) = \frac{2}{E_{n+1} - E_{n-1}}. \tag{86}$$

More information about the specifics of how the numerical computations in this thesis have been performed is given in the appendix.
The remaining step involves calculating the matrix elements of the interaction Hamiltonians (80) and (81). This means that we need to calculate the integrals $I_n^{\pm}$ and $I_{n_{nonrel}}^{\pm}$ given by

$$\begin{aligned} I_{n_{rel}}^{\pm} &= \frac{E_0}{2} \int_{\mathcal{R}^3} d^3\bar{x}\ \Psi_{n1\frac{1}{2}}^{\pm *}(-z + \frac{1}{2c^2}\hat{z}\cdot(\bar{S}\times\bar{p}))\Psi_{10\frac{1}{2}}^{+} \text{ for (80) and} \\ I_{n_{nonrel}}^{\pm} &= -\frac{E_0}{2} \int_{\mathcal{R}^3} d^3\bar{x}\ \Psi_{n1\frac{1}{2}}^{\pm *} z \Psi_{10\frac{1}{2}}^{+} \text{ for (81),} \end{aligned} \tag{87}$$

where $\Psi_{nlm_j}^{\pm}$ denotes the wave function describing the state characterised by the numbers $(n, j = l \pm \frac{1}{2}, l, m_j)$ as mentioned in (85). The $\pm$ superscript represents the final state's j quantum number given by $j = 1 \pm \frac{1}{2}$. The specifics of how to calculate the above integrals are given in the appendix.
Inserting (87) into (84), we obtain the final expressions for calculating the cross sections for the processes (85) described by the Hamiltonians (77), reading

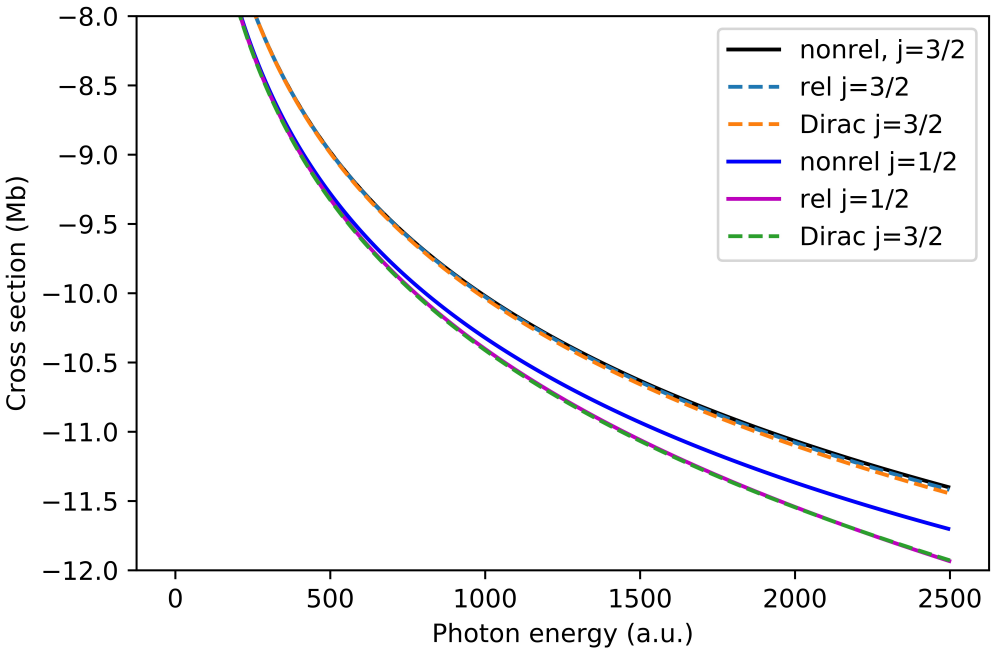
$$\sigma_{n_{rel}}^{\pm} = \frac{2\pi^2}{c} \frac{E_n^{\pm} - E_1^{+}}{E_{n+1}^{\pm} - E_{n-1}^{\pm}} \left| \int_{\mathcal{R}^3} d^3\bar{x}\ \Psi_{n1\frac{1}{2}}^{\pm *}(-z + \frac{1}{2c^2}\hat{z}\cdot(\bar{S}\times\bar{p}))\Psi_{10\frac{1}{2}}^{+} \right|^2 \tag{88}$$

as well as for the Hamiltonian (78), stating

$$\sigma_{n_{nonrel}}^{\pm} = \frac{2\pi^2}{c} \frac{E_n - E_1}{E_{n+1} - E_{n-1}} \left| \int_{\mathcal{R}^3} d^3\bar{x}\ \Psi_{n1\frac{1}{2}}^{\pm *} z \Psi_{10\frac{1}{2}}^{+} \right|^2. \tag{89}$$

We are now able to compute the cross sections for the processes (85) for both the relativistic model (77) and the non-relativistic model (78). These cross sections will be calculated and compared to each other, as well as to the cross section that one would get from the exact minimal coupling Dirac Hamiltonian (33). The data for the Dirac cross section has been obtained from [23].

Figure 1



Cross section for process $j = \frac{1}{2} \to j = \frac{3}{2}$ plotted against emitted photon energy for the non-relativistic, relativistic and the Dirac minimal coupling Hamiltonian.

In figure 1 the cross sections are plotted against the energy of the absorbed photon. The unit chosen to express the cross sections is megabarn (Mb) which is defined by 1 Mb= 10^{-18} cm^2. The photon energy axis is expressed in atomic units.

In figure 1, the plotted cross sections describe the transitions (85). The first three lines at the top represent the cross sections for the process $\frac{1}{2} \to \frac{3}{2}$. The uppermost lying curve in black has been obtained through the formula (89). Below the black curve one can see the blue dotted curve, representing the cross section obtained by using our model (88). Next, the dotted orange line in figure 1 represents the Dirac cross section based on the exact minimal coupling Dirac Hamiltonian (33). The remaining three curves in figure 1 are the cross sections for the process $\frac{1}{2} \to \frac{1}{2}$. The largest curve out of those three is the one in blue, yielding the cross section (89) for the non-relativistic model (78). Below the blue curve, one can see the dotted green line representing the cross section obtained through the minimal coupling Dirac Hamiltonian (33). At last, the curve in magenta lying on top of the Dirac curve represents the cross section (88) based on our model (77).

To analyze figure 1, we start by considering the three upper most curves that

yield the cross sections for the process $\frac{1}{2} \to \frac{3}{2}$. As can be seen by inspecting figure 1, the non-relativistic cross section is above the Dirac cross section, while the relativistic cross section obtained through our model is in between the Dirac cross section and the non-relativistic one. Therefore, we conclude that taking into account relativistic effects for this transition results in a smaller cross section. This can be understood by the fact that the most dominating relativistic correction appearing in (77) at high energies is the operator $-\frac{p^4}{8c^2}$, which is negative, causing the non-relativistic cross section (black) in figure 1 to be shifted down.
Though one can see from figure 1 that relativistic effects in the $\frac{1}{2} \to \frac{3}{2}$ transition contribute, their effect seems to be small. However, the relativistic approximation (dotted blue) yields a better approximation to the Dirac curve (dotted orange) than the non-relativistic one (black).
Continuing the analysis of figure 1, we consider now the three lowest lying curves that represent the cross sections for the process $\frac{1}{2} \to \frac{1}{2}$. Similarly to the $j = \frac{3}{2}$ case, the non-relativistic cross section (blue) lies above the Dirac curve (dotted green) and above the relativistic cross section (magenta). Here, the same explanation as given for the $j = \frac{3}{2}$ is valid. In contrast to the $j = \frac{3}{2}$ case, however, we can now see from figure 1 that the non-relativistic cross section (blue) is far longer apart from the Dirac cross section (dotted green) than the relativistic cross section (magenta) is, implying that relativistic effects are more important for the $j = \frac{1}{2}$ case than for the $j = \frac{3}{2}$ case. This can be explained through the following argument:
In (77), the Darwin term only affects the ground state which is the same in both cases. Also, the term $-\frac{p^4}{8c^2}$ is roughly of equal importance in both cases. The remaining two relativistic operators are the operator proportional to $\bar{S} \cdot \bar{L}$ and the operator proportional to $\bar{S} \times \bar{p}$. Starting with the LS operator, one can show that

$$\begin{aligned} \bar{S} \cdot \bar{L} \Psi_{njlm_j} &= \frac{l}{2} \Psi_{njlm_j} \text{ if } j = l + \frac{1}{2}, \\ \bar{S} \cdot \bar{L} \Psi_{njlm_j} &= -\frac{l+1}{2} \Psi_{njlm_j} \text{ if } j = l - \frac{1}{2}. \end{aligned} \tag{90}$$

Therefore, setting $l = 1$, we see that for the $j = \frac{1}{2}$ case the LS term contributes twice as much than it does for the $j = \frac{3}{2}$ case. As for the remaining operator in (77) which is given by $\frac{1}{2c^2} \bar{S} \cdot (\bar{E}_L \times \bar{p})$, we can again show that this operator contributes twice as much in the $j = \frac{1}{2}$ case than in the $j = \frac{3}{2}$ case by making use of the formula (121) which has been derived in the appendix. In our case it tells us that

$$\begin{aligned} \int_{\mathcal{R}^3} d^3\bar{x} \ \Psi^{+*}_{n1\frac{1}{2}} \frac{1}{2c^2} \hat{z} \cdot (\bar{S} \times \bar{p}) \Psi^{+}_{10\frac{1}{2}} &= -\frac{1}{4c^2} Q \text{ for } j = \frac{3}{2} \\ \int_{\mathcal{R}^3} d^3\bar{x} \ \Psi^{-*}_{n1\frac{1}{2}} \frac{1}{2c^2} \hat{z} \cdot (\bar{S} \times \bar{p}) \Psi^{+}_{10\frac{1}{2}} &= -2\frac{1}{4c^2} Q \text{ for } j = \frac{1}{2}, \end{aligned} \tag{91}$$

where Q is some integral that is not important here. (90) then shows that we get twice the contribution in the $j = \frac{1}{2}$ case than we get in the $\frac{3}{2}$ case.

In summary, the spin dependent operators $\frac{1}{2c^2r^3}\bar{S}\cdot\bar{L}$ and $\frac{1}{2c^2}\bar{S}\cdot(\bar{E}_L\times\bar{p})$ appearing in our model (77) cause the relativistic effects to be more important in the transition $\frac{1}{2}\to\frac{1}{2}$ than in the transition $\frac{1}{2}\to\frac{3}{2}$ as shown in (90) and (91).

7.1.3 Spin Effects

After having shown that the presented model (77) is a good relativistic approximation to the minimal coupling Dirac Hamiltonian (33), we now wish to study spin effects that our model (77) predicts. To this end, we wish to isolate the spin dependent terms appearing in (77) as much as possible.
The spin dependent terms in (77) are given by

$$\begin{aligned} LS \text{ term} &= \frac{1}{2c^2r^3}\bar{S}\cdot\bar{L}, \\ S_1 &= \frac{1}{2c^2}\bar{S}\cdot(\bar{E}_L\times\bar{p}). \end{aligned} \tag{92}$$

It is well known that the LS term is of great importance when studying relativistic phenomena, especially when considering states with higher angular momentum quantum numbers l. We therefore wish to use a model based on (77) where, if possible, we can neglect the LS term, while still getting sensible results, in order to study the relevance of the spin term S_1. To this end, one might be tempted to simply discard the LS term appearing in (77), retaining only the other spin term S_1. This, however, would be non-sensible as the following argument will show:
Though observables are gauge invariant, this only holds when considering the full physical Hamiltonian, which in our case is either (73) or (76). As we are interested in discarding some of the terms such as the LS term, gauge invariance will be broken and we will no longer be left with a physical Hamiltonian, strictly speaking. Therefore, when discarding terms, we will have to decide which of the two gauges (73) and (76) we consider to be the "physical gauge". We will consider the velocity gauge Hamiltonian (73) to be the "physical gauge" from here on, as it most closely resembles the Hamiltonian (71) obtained from the physical minimal coupling Dirac Hamiltonian (33) which is known to yield extremely precise results when studying relativistic phenomena. Thus, starting off with the velocity gauge Hamiltonian (73) when trying to isolate the spin terms, we now have three spin terms which are given by

$$\begin{aligned} LS \text{ term} &= \frac{1}{2c^2r^3}\bar{S}\cdot\bar{L} \\ S_1 &= \frac{1}{2c^2}\bar{S}\cdot(\bar{E}_L\times\bar{p}) \\ S_2 &= \frac{Z}{2c^2r^3}\bar{S}\cdot(\bar{r}\times\bar{A}). \end{aligned} \tag{93}$$

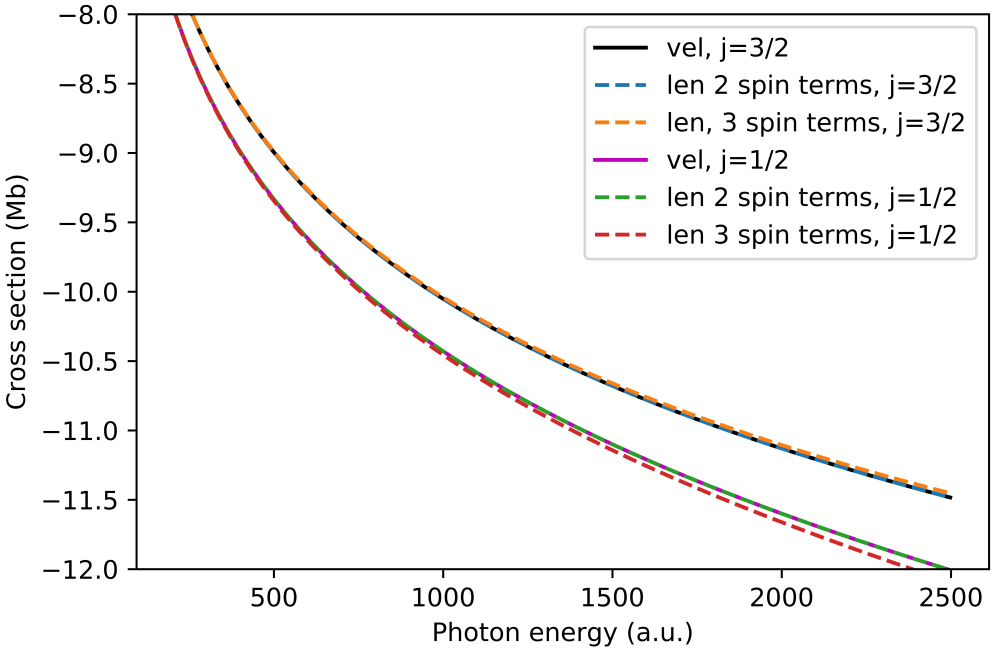
By comparing (92) with (93), we see that the velocity gauge Hamiltonian contains in addition to the spin terms present in the length gauge yet another spin

term S_2. This goes very much against intuition and has been a source for error [25] when studying relativistic effects perturbatively. To illustrate that gauge invariance between the velocity gauge (73) and the length gauge (76) implies such an asymmetry in spin terms, the cross sections for photon ionization have been calculated based on both gauges, as well as based on the Hamiltonian

$$H = H_0 + S_1 + S_2 + \bar{E}_L \cdot \bar{r}, \tag{94}$$

where H_0 is the same as the one given in (80), which represents the case in which the length gauge Hamiltonian would have the same amount of spin terms as the velocity gauge Hamiltonian (73). The cross sections are illustrated in figure 2.

Figure 2



Cross section in velocity gauge and length gauge (with two and three spin terms) for process $j = \frac{1}{2} \to j = \frac{3}{2}$ plotted against emitted photon energy.

In figure 2 there are six curves. The three uppermost lying curves represent the cross sections for the process $\frac{1}{2} \to \frac{3}{2}$, while the remaining three curves yield the cross sections for the process $\frac{1}{2} \to \frac{1}{2}$. Starting with the three curves at the top, the the black line is the cross section that has been obtained from the velocity gauge Hamiltonian (73), while the dotted blue line has been obtained from the length gauge Hamiltonian (76) with two spin terms (92). The orange dotted

line has been obtained from the length gauge Hamiltonian (94) with three spin terms. The curves for the velocity gauge and length gauge (black and dotted blue) are virtually identical, while the length gauge (94) with the additional spin term S_2 is slightly off, illustrating that gauge invariance between the velocity and length gauge for the $j = \frac{3}{2}$ case only holds if there is an asymmetry in spin terms. Of the remaining three curves, the solid magenta line yields the cross section that has been obtained in the velocity gauge (73), while the dotted green line has been obtained in the length gauge (76). The dotted red line has been obtained in the length gauge (94) with three spin terms. Here again one cannot tell any visual difference between the magenta and the dotted green curves, while the dotted red line is off, verifying that gauge invariance for the $j = \frac{1}{2}$ case only holds if there is an asymmetry in spin terms. As the spin terms S_1 and S_2 contribute non-trivially to the cross sections, this shows that one indeed needs to have 3 spin terms in the velocity gauge, while only 2 in the length gauge.

When now trying to discard the LS term in the length gauge, we are faced with the problem that the length gauge without the LS term is no longer connected to the velocity gauge (our physical gauge) by a gauge transformation. This is due to the fact that when going from the velocity gauge (73) to the length gauge (76), the LS term contributed non-trivially as can be seen from (75). In fact, the LS term contributes through yielding the spin term S_1 which is what we wish to study. Therefore, if we were to discard the LS term in the length gauge, we would also have to discard the spin term S_1 in order to preserve gauge invariance, i.e. in order for the length Hamiltonian to be physically equivalent to our (physical) velocity gauge Hamiltonian.

In summary, discarding the LS term in the length gauge Hamiltonian (76) forces us to discard the spin term S_1, which is what we wish to study. Therefore, we either have to retain the LS term, which makes the importance of the spin term S_1 less apparent as the LS term is known to be of much importance, or we have to choose the velocity gauge. As we want to be able to discard the LS term, we start by choosing the velocity gauge Hamiltonian (without the rest mass energy c^2), which in atomic units reads

$$\begin{aligned} H_{vel} = & \frac{\bar{p}}{2} - \phi + \bar{A} \cdot \bar{p} \\ & - \frac{(\bar{p} + \bar{A})^4}{8c^2} + \frac{1}{8c^2}\bar{A}^4 + \frac{\pi}{2c^2}\delta(\bar{r}) + \frac{1}{2c^2 r^3}\bar{S} \cdot \bar{L} \\ & + \frac{1}{2c^2}\bar{S} \cdot (\bar{E}_L \times \bar{p}) + \frac{Z}{2c^2}\frac{1}{r^3}\bar{S} \cdot (\bar{r} \times \bar{A}). \end{aligned} \tag{95}$$

As mentioned above, we now discard the LS term in order to isolate the effect of the remaining two spin terms S_1 and S_2, yielding the Hamiltonian

$$\begin{aligned} H_{vel} = &\frac{\bar{p}}{2} - \phi + \bar{A} \cdot \bar{p} \\ &- \frac{(\bar{p} + \bar{A})^4}{8c^2} + \frac{1}{8c^2}\bar{A}^4 + \frac{\pi}{2c^2}\delta(\bar{r}) \\ &+ \frac{1}{2c^2}\bar{S} \cdot (\bar{E}_L \times \bar{p}) + \frac{Z}{2c^2}\frac{1}{r^3}\bar{S} \cdot (\bar{r} \times \bar{A}). \end{aligned} \tag{96}$$

Besides the two spin terms S_1 and S_2 in the above Hamiltonian (96), the remaining relativistic terms are given by the Darwin term, proportional to the Dirac delta function, and the relativistic kinetic energy correction proportional to $(p + A)^4$.
The Darwin term contributes marginally. In fact, when computing the cross sections presented in figure 1, the same graphs have been obtained even when neglecting the Darwin term completely, which is why we are going to discard the Darwin term in (96), leaving us with the Hamiltonian

$$\begin{aligned} H_{vel} = &\frac{\bar{p}}{2} - \phi + \bar{A} \cdot \bar{p} \\ &- \frac{(\bar{p} + \bar{A})^4}{8c^2} + \frac{1}{8c^2}\bar{A}^4 \\ &+ \frac{1}{2c^2}\bar{S} \cdot (\bar{E}_L \times \bar{p}) + \frac{Z}{2c^2}\frac{1}{r^3}\bar{S} \cdot (\bar{r} \times \bar{A}). \end{aligned} \tag{97}$$

The above Hamiltonian (97) now only contains, besides the two spin terms S_1 and S_2, the relativistic correction to the kinetic energy, which is given by $-\frac{(p+A)^4}{8c^2}$. As we are interested in studying spin effects only, we will assume a case where the relativistic correction to the kinetic energy is not important, enabling us to discard the $-\frac{(p+A)^4}{8c^2}$ operator. An example for such a case would be given by Rydberg atoms [24] that can have extremely small kinetic energies. Upon discarding the kinetic energy correction, we are left with the final Hamiltonian that will be used to study the effects of the spin terms S_1 and S_2, given by

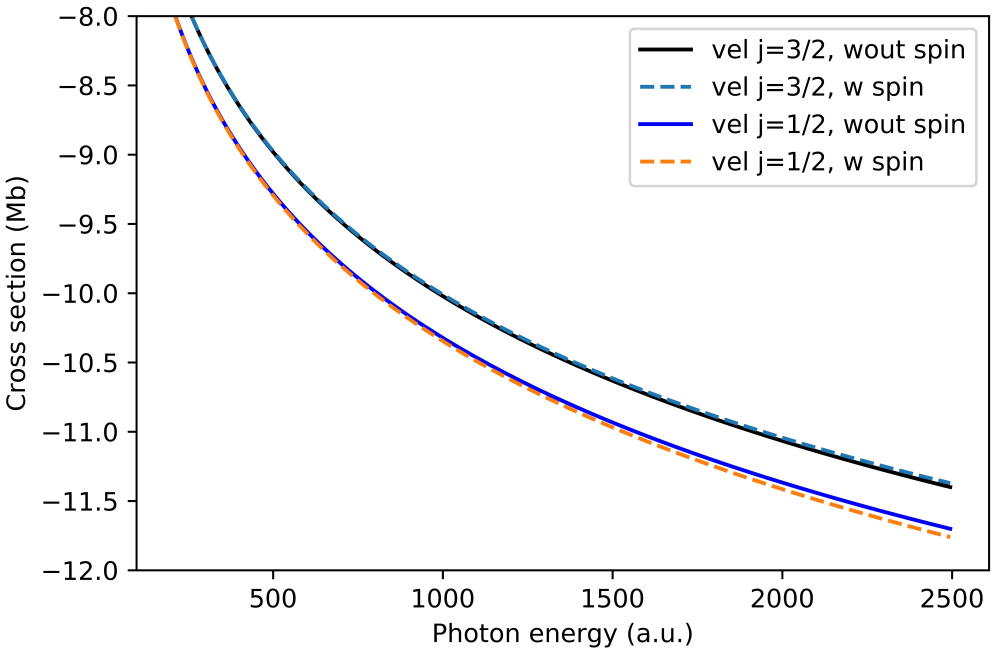
$$H_{vel} = \frac{\bar{p}}{2} - \phi + \bar{A} \cdot \bar{p} + \frac{1}{2c^2}\bar{S} \cdot (\bar{E}_L \times \bar{p}) + \frac{Z}{2c^2}\frac{1}{r^3}\bar{S} \cdot (\bar{r} \times \bar{A}). \tag{98}$$

The results obtained from this Hamiltonian (98) will then be compared to the non-relativistic Hamiltonian in the velocity gauge (31), given by (in atomic units)

$$H_{nonrel} = \frac{p^2}{2} - \phi + \bar{A} \cdot \bar{p}. \tag{99}$$

Then, both the Hamiltonian (99) without the spin terms and the Hamiltonian (98) with the spin terms have been used to calculate the cross sections for photon ionization for the transitions (85). The results are plotted in figure 3.

Figure 3



Cross section for process $j = \frac{1}{2} \to j = \frac{3}{2}$ with and without spin plotted against emitted photon energy.

In figure 3, the two curves lying at the top are the cross sections for the process $\frac{1}{2} \to \frac{3}{2}$, where the black curve is the cross section obtained from the non-relativistic spin-less Hamiltonian (99), while the blue dotted curve is the cross section that has been calculated using the Hamiltonian (98) that includes the spin terms S_1 and S_2. The two curves that lie the lowest are the cross sections for the process $\frac{1}{2} \to \frac{1}{2}$, of which the blue curve has been obtained through using the non-relativistic spin-less Hamiltonian (99). The orange dotted line has been calculated by using the Hamiltonian (98).

As can be seen in figure 3, the spin terms S_1 and S_2 contribute positively for the $j = \frac{3}{2}$ case, while contributing negatively for the $j = \frac{1}{2}$ case. Similarly to the results shown in figure 1, here too the spin terms contribute notably more in the $j = \frac{1}{2}$ case than in the $\frac{3}{2}$ case. We know from analyzing figure 1 that the spin term S_1 is twice as large in the $j = \frac{1}{2}$ case compared to the $j = \frac{3}{2}$ case. The question is then whether a similar statement holds true for the other spin term S_2.

To answer this question, we will here show that the spin term S_2 in fact is equivalent to the spin term S_1 when considering photon ionization, that is, when considering the transitions (85) in the perturbative limit. To this end, we start by noting that the spatial part of the ground state wave function is

independent of the angular variables ϕ and θ, while it only depends on the radial variable r. This means that

$$\Psi_f^* i\bar{p}\Psi_{gs} = \Psi_f^* \hat{r}\partial_r \Psi_{gs}, \tag{100}$$

where $\hat{r}$ is the unit vector pointing in the direction of $\bar{r}$, $\Psi_{gs} = \Psi_{100}$ is the ground state wave function and $\Psi_f = \Psi_{111}$ is the wave function of the final state. Both of the wave functions are eigenstates of the non-relativistic hydrogenic Hamiltonian H_Z (29), thus satisfying $H_Z\Psi = E\Psi$, E being the energy.
In addition to (100), we will make use of the identity

$$[\partial_r, H_z] = \frac{Z}{r^2}. \tag{101}$$

Using (100) and (5) enables us to rewrite the spin term S_2 when acting on the ground state as

$$\Psi_f^* S_2 \Psi_{gs} = -\Psi_f^* i(E_f - E_i)\frac{1}{2c^2}\bar{S}\cdot(\bar{p}\times\bar{A})\Psi_{gs}, \tag{102}$$

where E_f and E_i are the energies of the final and initial state, respectively. As a final step we note that the amplitude A_0 of the vector potential $\bar{A}$ is related to the amplitude E_0 of the electric field due to the laser through

$$A_0 = \frac{E_0}{\omega}, \tag{103}$$

where in our case ω is the energy of the absorbed photon. As energy is conserved, this means that $\omega = E_f - E_i$. Therefore we rewrite (100) as

$$\Psi_f^* S_2 \Psi_{gs} = -i\sin(\omega t)\Psi_f^* \frac{E_0}{2c^2}\hat{z}\cdot(\bar{S}\times\bar{p})\Psi_{gs}. \tag{104}$$

Rewriting the spin term S_1 as

$$S_1 = \cos(\omega t)\frac{E_0}{2c^2}\hat{z}\cdot(\bar{S}\times\bar{p}), \tag{105}$$

we see immediately upon comparing (104) with (105) that the spin term S_2, when considering photon ionization, acts very similarily to the spin term S_1, the only difference being a factor of $-i$ and the time dependent factor. If we were to calculate cross sections for photon ionization in the perturbative limit, we would, as we did for the results presented in figure 1, apply Fermi's Golden rule (83). This presupposes that our interaction terms, which in this case includes S_1 and S_2, have been written in the form (82). Then, as mentioned previously, for photon ionization only the term proportional to $e^{-i\omega t}$ will contribute. Therefore, we write both S_1 and S_2 in a suitable form, yielding

$$\begin{aligned}\Psi_f^* S_1 \Psi_{gs} &= \frac{1}{2}e^{-i\omega t}\frac{E_0}{2c^2}\hat{z}\cdot(\bar{S}\times\bar{p}) + ... \\ \Psi_f^* S_2 \Psi_{gs} &= \frac{1}{2}e^{-i\omega t}\frac{E_0}{2c^2}\hat{z}\cdot(\bar{S}\times\bar{p}) + ...,\end{aligned} \tag{106}$$

where we have used the Euler identity $e^{i\omega t}$ =cos(ωt)+$i$sin(ωt).
One can then see from (106) that the spin terms S_1 and S_2 contribute equally when considering photon ionization. Therefore, the spin term S_2 contributes twice as much to the cross section for the $j = \frac{1}{2}$ case than to the $j = \frac{3}{2}$ case.
In conclusion, the spin terms S_1 and S_2 contribute equally when considering photon ionzation in the perturbative limit. Further, the contribution of the total spin effect $S_1 + S_2$ in the $j = \frac{1}{2}$ case is four times that of the contribution in the $j = \frac{3}{2}$ case, albeit being relatively small compared to the case when taking into account all the other relativistic effects that have been neglected (see figure 1).

8 Summary and conclusion

The model presented in this thesis is summarised by the Hamiltonian (71) given by

$$\begin{aligned} H^{dip} &= mc^2 + e\phi + \frac{(\bar{p} - e\bar{A})^2}{2m} \\ &- \frac{(\bar{p} - e\bar{A})^4}{8m^3c^2} - \frac{e}{8mc^2}\nabla \cdot \bar{E} + \frac{\pi Ze^2}{2m^2c^2}\delta(\bar{r}) + \frac{e^2}{2m^2c^2r^3}\bar{S} \cdot \bar{L} \\ &- \frac{e}{2mc^2}\bar{S} \cdot (\partial_t \bar{A} \times \bar{p}) + \frac{Ze^2}{2mc^2}\frac{1}{r^3}\bar{S} \cdot (\bar{r} \times \bar{A}). \end{aligned} \tag{107}$$

This Hamiltonian is to describe an electron bound to a hydrogenic nucleus in an applied laser field. This Hamiltonian has been obtained by starting with the minimal coupling Dirac Hamiltonian (33)

$$H_D = c\bar{\alpha} \cdot (\bar{p} - e\bar{A}) + V + mc^2\beta, \tag{108}$$

which then has been approximately diagonalized (up to order $\mathcal{O}(\frac{1}{m^3})$) through the Foldy-Wouthuysen transformation [17]. The obtained Hamiltonian has then been presented in different gauges (68), (73) and (76), of which the former one was given to illustrate how to apply the model (60) to the beyond dipole case, while the latter two have been used extensively throughout this thesis under the assumption of the dipole approximation.

In order to study the validity of the derived model (71) in the dipole approximation, photon ionization has been studied by calculating and plotting their cross sections which have been compared to the analogous non-relativistic case (78) and to the exact Dirac theory (33). Based on the graphs plotted in figure 1, we conclude that our presented model (77) yields a good approximation to the Dirac theory, especially for the $\frac{1}{2} \to \frac{1}{2}$ transition, when calculating cross sections for processes concerned with photon ionization where the perturbative limit is valid. The fact that the relativistic correction in the $\frac{1}{2} \to \frac{3}{2}$ process as depicted in figure 1 has seemingly only improved the non-relativistic approximation a little may be thought to be due to the fact that the states involved, i.e. the ground state and the first excited state with $j = \frac{3}{2}$, are the "least relativistic" states of all the available states, thus making the relevance of relativistic effects minute. On the other hand, for the transition $\frac{1}{2} \to \frac{1}{2}$ where the final state was different, the model (77) yielded a much better approximation, in fact virtuallly no visible difference to the Dirac solution is apparent. Overall, the presented model yielded a good approximation to the Dirac theory.

Additionally, it has been found that there are 3 spin dependent operators present in the velocity gauge (93), while in the length gauge there are only 2 (92). A variation of the velocity gauge Hamiltonian (98) has then been used to study the effect of the present spin terms S_1 and S_2 by comparing the calculated cross sections to the non-relativistic velocity gauge Hamiltonian (31). It has been found and shown that the effect of the spin terms S_1 and S_2 is four times as important in the transition to the $j = \frac{1}{2}$ state than in the transition to the $j = \frac{3}{2}$

state. Further, the results obtained indicated that while the contribution from the spin terms S_1 and S_2 are apparent, they are small compared to the total relativistic correction obtained previously, where the LS term is the dominant spin dependent operator.

Everything studied in this chapter has been done in the perturbative limit, presupposing that the applied laser is weak. The effect of the spin terms S_1 and S_2 has been seen to only yield a small contribution to the cross section (figure 3) when compared to the total relativistic correction (figure 1). We know that the main relativistic corrections due to spin stem from the LS operator. One might now wonder if the same is true in the non-perturbative limit, where the laser now is strong, implying that A_0 and E_0 are large, as well as larger energies and thus larger momenta. Considering the spin term S_1 for example, we know that S_1 depends on both E_0 and $\bar{p}$, while the LS term only depends on p ($\bar{L} = \bar{r} \times \bar{p}$). Therefore, it might be possible that the spin term S_1 becomes more relevant than the LS term, though in the non-perturbative limit more than 1 photon may be absorbed, resulting in higher angular momentum quantum numbers l, making the LS term increase in importance. As the answers to such questions are seemingly not obvious, a suggestion for further studies might include considering the model (60) while assuming higher laser intensities in order to model the importance of the spin terms S_1 and S_2 in that regime. In order to isolate the importance of the spin terms S_1, S_2 and the LS term, it is suggested to study those effects in Rydberg atoms [24]. One of the reasons is that Rydberg atoms may have very small kinetic energies, thus making the relevance of the kinetic energy correction term $-\frac{p^4}{8c^2}$ less important. At the same time, one can consider higher angular momentum states where spin-orbit effects are known to be more important. This can then be used to model the importance of the spin terms S_1 and S_2 in comparison to the LS term for different regimes.

9 Appendix

This chapter is on the specifics on how the numerical computations done for this thesis have been performed. Among other things, the choice of basis is motivated and the general procedure is outlined.

The necessity of numerical computations for the work done in this thesis can be illustrated by formulating the problem that has been dealt with as follows:
At first, a suitable model has been chosen in order to describe the processes of interest correctly to the desired order of accuracy (76) (or any other of the presented gauges). The mathematical formulation of the quantum mechanical model is then given by a Hamiltonian, represented as a matrix, which is to be inserted into the TDSE (5).
When studying the dynamics of the given system through solving the TDSE, one is faced with the mathematical problem of solving a system of partial differential equations. In theory, the given Hamiltonian in this thesis (76) is to be infinite dimensional. In practice however, the Hamiltonian will be a large but finite dimensional matrix. The mathematical problem is then to diagonalize the given Hamiltonian, that is to find its eigenvalues together with its eigenvectors. Due to the difficulty of the calculations and the shear amount of matrix elements that need to be calculated, one naturally opts for a numerical approach. More about the numerical approach used in this thesis will be given in the following.

9.1 Numerical approach

The numerical approach that has been utilized throughout this thesis may be summarized as follows:

1. Step: Choosing a suitable basis

In theory a complete (usually infinitely large) set of basis functions is assumed. In the practical case, one has to choose a basis which is large enough to yield sufficient convergence to the real result, whilst still not being too large as to take up too much memory, making computations take longer than they otherwise would. As the basis states will be used to calculate matrix elements, it is considered an advantage if the chosen basis states also have some nice properties when being used for (approximate) methods of integration. As the integration domain has to be made finite when doing numerical computations, too, basis states that are non-zero only on a finitely large domain would be preferable. A set of basis states satisfying all these mentioned criteria are the so called B-spline functions. A brief explanation of B-splines will be given later.

2. Step: First diagonalization

One calculates the matrix elements of the non-reativistic hydrogenic Hamiltonian $\hat{H}_Z = \frac{\hat{p}^2}{2} - \frac{Z}{r}$ in the chosen B-spline basis. This means that one has to solve three-dimensional integrals. The angular integration is done analyti-

cally while the radial integration is done numerically using the so called Gauss-Legendre quadrature. A brief explanation of this integration method is given later. Having calculated the matrix elements of H_Z, its eigenvalues and eigenstates are found through diagonalization.

3. Step: Second diagonalization

Using the obtained eigenstates and eigenvalues, one proceeds in the same fashion as in step 2 by calculating matrix elements, now however of the relativistic Hamiltonian $H_{rel} = H_Z - \frac{p^4}{8c^2} + \frac{1}{2c^2 r^3}\bar{L}\cdot\bar{S} + \frac{\pi}{2c^2}\delta(\bar{r})$. After the computations have been performed, one again diagonalizes the newly calculated matrix in order to obtain the relativistic eigenstates and eigenvalues.

4. Step: Computation of the interaction of interest

Taking the length gauge Hamiltonian (76) as an example, one now uses the newly calculated relativistic eigenstates and eigenvalues to calculate the interaction Hamiltonian's $H_I^{len} = \bar{E}_L \cdot \bar{r} + S_1$ matrix elements. These can then be used to calculate observable quantities such as cross sections for photon ionization processes, as done for the plots presented in chapter 7 on photon ionization.

9.2 Numerical technicalities

9.2.1 B-Splines

The following will give a very brief explanation of what B-splines are from a practical perspective in regard to what has been done numerically in this thesis. For a more elaborate treatment of the subject, one may refer to other sources such as [26].

B-splines are to be understood as a set functions $\{B_i^r(x)\}_i$ that is linearly independent, making it possible to be used as a basis. Each B-spline $B_i^r(x)$ is a piecewise polynomial that has assignet to it an order r. B-splines as used in this thesis are defined in the following way:
One starts by considering a finite line segment, say, $[0, 2]$ on which the B-splines are to be defined. Then, one divides the line segment into equidistant subsegments, for example, $[0, 2] = [0, 1)U[1, 2]$. The set of all endpoints of the obtained subsegments is refered to as the knot vector t, which in this example reads $t = (0, 1, 2)$. The knot vector is by definition always ordered in a non-decreasing fashion, meaning that in the example given here $t' = (1, 0, 2)$ would not be the correct knot vector.
The dimension of the knot vector is referred to as the number of breaking points N_b, which in our example here is $N_b = 3$. The B-spline functions are then defined recursively, starting with defining the 0th order B-splines as

$$B_i^0(x) = \begin{cases} 1 & \text{if } t_i \leq x < t_{i+1} \\ 0 & \text{otherwise} \end{cases} \tag{109}$$

B-splines of order $r = 1$ or higher are then defined by

$$B_i^r(x) = \frac{x - t_i}{t_{i+k-1} - t_i} B_i^{k-1}(x) + \frac{t_{i+k} - x}{t_{i+k} - t_{i+1}} B_{i+1}^{k-1}(x). \tag{110}$$

The two equations above are often referred to as the Cox-de Boor recursion formula [26]. As can be seen from the above definitions, B-splines are only non-zero on a finite dimensional subset, making them ideal for numerical integration methods such as the Gauss-Legendre quadrature, which will be explained below. In this thesis, for all calculations done for the photon ionization cross sections presented in chapter 7, B-splines of order 6 have been used. Further, about 1400 breaking points have been used, yielding roughly 1400 B-splines in the first diagonalization, of which about 900 have been kept in the second diagonalization.

9.2.2 Gauss-Legendre Quadrature

All integrals that have been calculated numerically in this thesis have been done so through applying the so called Gauss-Legendre quadrature [27]. The Gauss-Legendre quadrature is an integration technique that expresses an integral as a sum of the integrand evaluated at certain points multiplied by a set of values which are called the weights. More succinctly, the Gauss-Legendre quadrature states that for a function f defined on an interval $[-1, 1]$, we may write

$$\int_{-1}^{1} dx\ f(x) = \Sigma_{k=1}^{n} w_k f(x_k) + \mathcal{E}_n, \tag{111}$$

where $\{w_k\}_{k=1}^{n}$ are the weights, $\{x_k\}_{k=1}^{n}$ are the roots of the nth Legendre polynomial $P^n(x)$ and $\mathcal{E}_n$ is the error, which may be written as

$$\mathcal{E}_n = \frac{2^{2n+1}(n!)^4}{(2n+1)((2n)!)^3} \frac{d^{2n} f(\rho)}{dx^{2n}}, \tag{112}$$

where ρ is some number in the interval $[-1, 1]$.
Looking at the above formula for the error, one easily sees that if f is a polynomial of order $2n-1$ or lower, then a Gauss-Legendre quadrature of order n will yield an exact result. This is important to note, as in our case, the function f will be a product of two basis states, expressed in terms of B-splines (polynomials) times x to some finite power. Therefore, for all calculations in this thesis the order of B-splines used has been matched such that Gauss-Legendre quadrature is exact, hence making the only source of computational error the finiteness of our box.

As a final note on Gauss-Legendre quadrature, the integrals that had to be solved in this thesis were radial integrals. Therefore the domain of integration was $[0, r_{max}]$, where r_{max} is the size of the box used. Therefore, in order to be able to apply the Gauss-Legendre quadrature formula (111), the radial integrals had to be rewritten at first. To this end, the radial integral had been written as a sum of the form

$$\int_{0}^{r_{max}} dr\ f(r) = \Sigma_{m=0}^{m_{max}} \int_{x1_m}^{x2_m} dx\ f(x), \tag{113}$$

where each integral in the sum has an integration domain of length 2.
Through a change of variables, each integral in the sum had been rewritten such that $x1_m \to -1$ and $x2_m \to +1$. Then, the remaining task was simply to invoke the Gauss-Legendre quadrature formula (111) on each of the integrals appearing in the sum above. For a more extensive treatment of Gauss-Legendre quadrature, one may consider more elaborate sources such as [27] or [28].

9.3 Calculation of the Interaction terms

In this section, the formulae that have been implemented numerically to study the problems presented in this thesis are derived and summarized. The Dirac notation has been used. The reader is referred to [29] for a comprehensible source on the Dirac notation. To understand the following, it is sufficient to simply consider the Dirac notation to be a shorthand for writing integrals, meaning that

$$< a|O|b >:= \int_{\mathcal{D}} dq\ \Psi_a^*(q) O \Psi_b(q), \tag{114}$$

where Ψ_a and Ψ_b are the wave functions corresponding to the (set of) quantum numbers a and b, respectively, while $\mathcal{D}$ is the domain to be integrated over. As an example, if we were to calculate the transition amplitude from the ground state ($b = 100$) to the first excited state ($a = 211$) in the hydrogen atom due to the operator x, we would have that

$$< 211|x|100 >= \int_{\mathcal{R}^3} d^3r\ \Psi_{211}^* x \Psi_{100}. \tag{115}$$

9.3.1 $S_x p_y - S_y p_x$ matrix elements

In the velocity gauge (73), for the problems studied in this thesis, there are effectively two interaction terms. One is of the form $S_y\Lambda_x - S_x\Lambda_y$, where $\Lambda_{x,y} = p_x, p_y$, while the other is of the form p_z. We start by considering the former interaction. In order to derive the desired expressions for those interaction terms, we may start by deriving an expression for the term $S_y\Lambda_x$. The analogous expression for the $S_x\Lambda_y$ term then follows easily.

We start by calculating the matrix element $< njl\frac{1}{2}m_j|S_y\Lambda_x|n'j'l'\frac{1}{2}m_j' >$.
From the selection rules that may be derived from the Dirac equation, we know that the only transitions allowed in the dipole approximation are the ones where $m_j' = m_j$. For simplicity, and since the particular choice of m_j is irrelevant for the problems studied in this thesis, we set $m_j = \frac{1}{2}$, as has been done throughout all computations for this thesis.
Yet another transition rule tells us that the only allowed transitions regarding the l quantum number are the ones where either $l' = l + 1$ or $l' = l - 1$. In this thesis the arrangement of the matrix that is being calculated has been chosen such that if the entry (i, j) corresponds to the transition from l to $l' = l + 1$, then the entry (j, i) corresponds to the process from l to $l' = l - 1$. Since our Hamilton matrix has to be hermitian, it is sufficient to calculate only, say, the matirx elements in the upper half. This implies that we only need to consider, say, the processes for which $l' = l + 1$. We thus set $l' = l + 1$ and $m_j = m_j' = \frac{1}{2}$ in the following computations.

To derive an expression for the matrix elements we start by expanding the coupled basis in the uncoupled one, yielding

$$\begin{aligned} < S_y \Lambda_x > = \Sigma_{m,m'} \Sigma_{m_s,m'_s} < l+1 m' \frac{1}{2} m'_s | j' \frac{1}{2} >< l m \frac{1}{2} m_s | j \frac{1}{2} > \\ < \frac{1}{2} m_s | S_y | \frac{1}{2} m'_s >< n l m | \Lambda_x | n' l+1 m' > . \end{aligned} \tag{116}$$

The first two factors in the above expression are Clebsch-Gordan coefficients. To further simplify, we write $< \frac{1}{2} m_s | S_y | \frac{1}{2} m'_s >= \frac{\lambda}{2i} (\delta_{m_s \frac{1}{2}} \delta_{m'_s -\frac{1}{1}} - \rho \delta_{m_s -\frac{1}{2}} \delta_{m'_s \frac{1}{1}})$, where $\lambda = \rho = 1$ have been inserted to make the calculation of the $S_x \Lambda_y$ matrix elements later on easier. We can then perform the sum over m_s and m'_s. This leaves us with

$$\begin{aligned} < S_y \Lambda_x > = \frac{\lambda}{2i} \Sigma_{m,m'} < n l m | \Lambda_x | n' l+1 m' > \\ (< l+1 m' \frac{1}{2} - \frac{1}{2} | j' \frac{1}{2} >< l m \frac{1}{2} \frac{1}{2} | j \frac{1}{2} > \\ - \rho < l+1 m' \frac{1}{2} \frac{1}{2} | j' \frac{1}{2} >< l m \frac{1}{2} - \frac{1}{2} | j \frac{1}{2} >). \end{aligned} \tag{117}$$

We may further simplify the above expression by noting that the Clebsch-Gordan coefficients vanish unless $m + m_s = m_j$. In addition, we may look up the Clebsch-Gordan coefficients to get that

$$\begin{aligned} < S_y \Lambda_x > = \frac{\lambda}{4i} \Sigma_{m,m'} < n l m | \Lambda_x | n' l+1 m' > \\ (\epsilon \sqrt{(1+\Delta)(1-\Delta')} \delta_{m'1} \delta_{m0} \\ - \rho \epsilon' \sqrt{(1+\Delta')(1-\Delta)} \delta_{m'0} \delta_{m1}), \end{aligned} \tag{118}$$

where $\epsilon = \pm 1$ depending on $j = l \pm \frac{1}{2}$ and $\Delta = \epsilon \frac{\frac{1}{2}}{l+\frac{1}{2}}$ as well as $\Delta' = \epsilon' \frac{\frac{1}{2}}{l+\frac{3}{2}}$. As a final step before setting Λ_x equal to p_x, we may derive the analogous expression for the matrix elements of the operator $S_x \Lambda_y$. To do so, we start by observing that for S_x, we have that $\lambda = i$ as well as that $\rho = -1$. Moreover, we may make use of the fact that $\Lambda_y = \exp^{-i \frac{\pi}{2} L_z} \Lambda_x \exp^{+i \frac{\pi}{2} L_z}$, implying that $< S_x \Lambda_y >= - < S_y \Lambda_x >$. We therefore get that

$$\begin{aligned} < S_x \Lambda_y - S_y \Lambda_x > = \frac{i}{2} \Sigma_{m,m'} < n l m | \Lambda_x | n' l+1 m' > \\ (\epsilon \sqrt{(1+\Delta)(1-\Delta')} \delta_{m0} \delta_{m'1} \\ - \epsilon' \sqrt{(1+\Delta')(1-\Delta)} \delta_{m'0} \delta_{m1}). \end{aligned} \tag{119}$$

The remaining part of the computation reduces to finding a suitable expression for the matrix elements of the operator Λ_x, which in our case will be the p_x operator.

Having set $\Lambda_x = p_x$, we may make use of the formula [23] stating that

$$< nlm|\partial_x|n'l+1m' >= (-a_{l+1,m'}\delta_{m',m+1} + a_{l+1,-m'}\delta_{m',m-1})G^l_{nn'}, \quad (120)$$

where $a_{lm} = \sqrt{\frac{(l+m)(l+m-1)}{4(2l-1)(2l+1)}}$ and $G^l_{nn'} = \int_0^\infty dr\ u_{nl}(\frac{du_{n'l+1}}{dr} + (l+1)\frac{u_{n'l+1}}{r})$. Inserting this into (119), we obtain the final expression

$$\begin{aligned} < S_x p_y - S_y p_x > = -\frac{1}{2}G^l_{nn'}\Sigma_{m,m'}(a_{l+1,-m'}\epsilon'\sqrt{(1+\Delta')(1-\Delta)}\delta_{m'0}\delta_{m1} \\ + a_{l+1,m'}\epsilon\sqrt{(1+\Delta)(1-\Delta')}\delta_{m'1}\delta_{m0}). \end{aligned} \quad (121)$$

9.3.2 z matrix elements

Here we will derive an expression for the z matrix elements which appear in the interaction Hamiltonian in the length gauge (76). To do so, we start by expanding the coupled basis in the uncoupled one yet again. Upon doing so, since z does not act on spin degrees of freedom, we get that

$$\begin{aligned} < z > = \Sigma_{m,m'}(< l+1m'\frac{1}{2}\frac{1}{2}|j'\frac{1}{2} >< lm\frac{1}{2}\frac{1}{2}|j\frac{1}{2} > \\ + < l+1m'\frac{1}{2}-\frac{1}{2}|j'\frac{1}{2} >< lm\frac{1}{2}-\frac{1}{2}|j\frac{1}{2} > \\ < nlm|z|n'l+1m' > . \end{aligned} \quad (122)$$

Again, we will make use of the fact that the Clebsch-Gordan coefficients vanish unless $m_j = m + m_s$. In addition, we look up the expressions for the resulting Clebsch-Gordan coefficients. Performing the sum over m', we are left with the following expression

$$\begin{aligned} < z >= \frac{1}{2}\Sigma_m(\delta_{m0}\epsilon\epsilon'\sqrt{(1+\Delta)(1+\Delta')} < nl0|z|n'l+10 > \\ + \delta_{m1}\sqrt{(1-\Delta)(1-\Delta')} < nl|z|n'l+11| > . \end{aligned} \quad (123)$$

As a last step, we make use of the formula

$$< nlm|z|n'l+1m' >= b_{l',m}\delta_{mm'}, \quad (124)$$

where $b_{l',m} = \sqrt{\frac{l^2-m^2}{(2l-1)(2l+1)}}$. Inserting this, we end up with the final expression given by

$$\begin{aligned} < z >= \frac{1}{2} < nl|r|n'l+1 > \Sigma_m \\ (\delta_{m0}b_{l+1,0}\epsilon\epsilon'\sqrt{(1+\Delta)(1+\Delta')} \\ + \delta_{m1}b_{l+1,1}\sqrt{(1-\Delta)(1-\Delta')}. \end{aligned} \quad (125)$$

9.3.3 $\hat{p}_z$ matrix elements

Here we will derive an expression for the matrix elements of the operator p_z that appears in the interaction Hamiltonian in the velocity gauge (73). We start again by expanding the coupled basis in the uncoupled one. Upon doing so, the sum over the spin quantum numbers m_s and m_s' are performed. Since p_z does not act on the spin degrees of freedom, this becomes trivial. Further, we again make use of the fact that the Clebsch-Gordan coefficients vanish unless $m_j = m + m_s$. Inserting the explicit expressions for the Clebsch-Gordan coefficients that we may look up, we may as a last step make use of the formula [3]

$$< nlm|p_z|n'l+1m' >= -ib_{l+1,m'}\delta_{m,m'}G^l_{n'n}, \tag{126}$$

where $G^l_{n'n} = \int_0^\infty dr\ u_{nl}(\frac{du_{n'l+1}}{dr} + (l+1)\frac{u_{n'l+1}}{r})$. We then end up with our final expression given by

$$\begin{aligned} < p_z >= &-\frac{i}{2}G^l_{n'n}\Sigma_m \\ &(\delta_{m0}b_{l+1,0}\epsilon\epsilon'\sqrt{(1+\Delta)(1+\Delta')} \\ &+ \delta_{m1}b_{l+1,1}\sqrt{(1-\Delta)(1-\Delta')}. \end{aligned} \tag{127}$$

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