Atoms and Molecules in Intense Laser Fields: Gauge Invariance of Theory and Models

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Abstract. Gauge invariance was discovered in the development of classical electromagnetism and was required when the latter was formulated in terms of scalar and vector potentials. It is now considered to be a fundamental principle of nature, stating that different forms of these potentials yield the same physical description: they describe the same electromagnetic field as long as they are related to each other by gauge transformations. Gauge invariance can also be included into the quantum description of matter interacting with an electromagnetic field by assuming that the wave function transforms under a given local unitary transformation. The result of this procedure is a quantum theory describing the coupling of electrons, nuclei and photons. Therefore, it is a very important concept: it is used in almost every fields of physics and it has been generalized to describe electroweak and strong interactions in the standard model of particles. A review of quantum mechanical gauge invariance and general unitary transformations is presented for atoms and molecules in interaction with intense short laser pulses, spanning the perturbative to highly nonlinear nonperturbative interaction regimes. Various unitary transformations for single spinless particle Time Dependent Schrödinger Equations (TDSE) are shown to correspond to different time-dependent Hamiltonians and wave functions. Accuracy of approximation methods involved in solutions of TDSE's such as perturbation theory and popular numerical methods depend on gauge or representation choices which can be more convenient due to faster convergence criteria. We focus on three main representations: length and velocity gauges, in addition to the acceleration form which is not a gauge, to describe perturbative and nonperturbative radiative interactions. Numerical schemes for solving TDSE's in different representations are also discussed. A final brief discussion is presented of these issues for the relativistic Time Dependent Dirac Equation (TDDE) for future super-intense laser field problems.

1. Introduction

Advances in current laser technology allow experimentalists to access new laser sources for probing and controlling molecular structure, function and dynamics on the natural time scale of atomic (nuclear) motion, the femtosecond (1 fs = 10^{-15} s) [1, 2], and electron motion on attosecond (1 as = 10^{-18} s) time scale [3, 4]. This new regime of nonlinear nonperturbative laser-matter interaction is leading to new physical phenomena such as nonlinear photoelectron spectra called Above Threshold Ionization (ATI) [5, 6, 7, 8] and High order Harmonic Generation (HHG) [9, 10]. In these two new examples of nonperturbative electron response, ionized electron trajectories are completely controlled by the electric laser field [3]. This can be understood qualitatively as follows. First, we introduce atomic units (a.u.), which are convenient in the study of laser-matter interaction. In these units, we set $\hbar = m_e = e = 1$ and $c = 1/\alpha$ where m_e is the mass of the electron, e is the electron charge and $\alpha = 1/137.035999074$ is the fine structure constant. The atomic unit of laser intensity is $I_0 = \varepsilon_0 c E_0^2 / 2 = 3.54 \times 10^{16}$ W·cm^{-2}, which corresponds to the atomic unit of electric field $E_0 = e/a_0^2 = 5.14 \times 10^9$ V·cm^{-1}. Then, the field at the atomic radius $a_0 = 1$ a.u. $= 0.0529$ nm of the $1s$ hydrogen (H) atom orbit is given by E_0. For an intensity of $I = 3.5 \times 10^{14}$ W·cm$^{-2} = 10^{-2}$ a.u., currently used in many high intensity experiments, the electron ponderomotive energy at typical wavelength $\lambda = 800$ nm ($\omega = 0.057$ a.u.) is given by $U_p = I/4\omega^2$ (a.u.) $= 0.77$ a.u. $= 21$ eV. The latter exceeds the

ionization potential $I_p = 0.5$ a.u. $= 13.6$ eV of the ground state H atom. The corresponding maximum field induced excursion of the electron is $\alpha = E/\omega^2 = 30.8$ a.u. $= 1.63$ nm, where the Coulomb potential becomes negligible and a field dressed electron description becomes appropriate. This new regime of nonperturbative radiative interactions has motivated the development of simple but highly predictive physical models and approximation techniques, such as the recollision model in atoms [11, 12, 13] or molecules [8], and the strong field approximation (SFA) [3, 5, 7]. Both have now become standard models for the advancement and development of this new field of nonlinear physics.

The theoretical description of perturbative and nonperturbative radiative interactions relies on one of the most important concepts of physics: *gauge invariance*. Gauge invariance was discovered in the development of classical electromagnetism when the latter was formulated in terms of scalar and vector potentials [14]. It is now considered to be a fundamental principle of nature, stating that different forms of potentials yield the same physical description, i.e. as long as they are related to each other by gauge transformations, different potentials describe the same electromagnetic fields [15]. More precisely, these gauge transformations are given by

$$\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla F, \tag{1}$$

$$U \rightarrow U' = U - \frac{\partial}{\partial t} F, \tag{2}$$

where $\mathbf{A}$ is the electromagnetic vector potential, U is the electromagnetic scalar potential and F is an arbitrary function, which depends on space-time coordinates. It will be shown latter using mathematical identities that these transformations do not modify the electromagnetic field, which is the physical quantity.

In the quantum description of matter interacting with electromagnetic fields, gauge invariance is obtained by transforming wave functions under local unitary transformations, resulting in different Hamiltonians in the corresponding TDSE's. For instance, the wave function transforms as

$$\psi^{(1)}(x) \rightarrow \psi^{(2)}(x) = \exp\left[iqF(x)/\hbar\right] \psi^{(1)}(x), \tag{3}$$

where q is the particle charge and $\psi^{(1,2)}$ are the wave functions in gauge 1 and 2, respectively. However unitary transformations can also give rise to "representations" which are not considered as "gauge" transformations (the latter are obtained rigorously only from transformations of classical Lagrangians leaving the dynamics invariant [2, 15]). This issue will be described in more details in following sections.

According to the gauge principle all "true" physical observables are gauge invariant. In quantum mechanics, an *observable* $\widehat{O}$ is defined as a Hermitian operator acting in the Hilbert space describing the system under consideration (for example, the momentum and spin operators). It is gauge invariant provided that it transforms as

$$\widehat{O}^{(1)} = G\widehat{O}^{(2)}G^{-1}, \tag{4}$$

where G is the gauge transformation shown in Eq. (3) and where $\widehat{O}^{(1,2)}$ are the observables expressed in two gauges. This transformation rule can be obtained explicitly in most cases. From this, gauge invariance can be shown as follows. First let us consider two wave functions related by a gauge transformation G as $\psi^{(1)} = G\psi^{(2)}$. Then, the following expectation value of observables will obey

$$\langle \widehat{O}^{(1)} \rangle := \langle \psi^{(1)} | \widehat{O}^{(1)} | \psi^{(1)} \rangle = \langle \psi^{(2)} | \widehat{O}^{(2)} | \psi^{(2)} \rangle =: \langle \widehat{O}^{(2)} \rangle, \tag{5}$$

The last equation (5) expresses the essence of the gauge principle, i.e. that "true" physical observables are independent of the gauge chosen. Also, it can be obtained easily by using the transformation rules. However, it is possible to construct Hermitian operators which transform differently from Eq. (4) under gauge transformations (one example of this is the Hamiltonian operator, see Section 2.7). These operators are also quantum observables according to the interpretation laws of quantum mechanics. But according to the gauge principle, they are not "true" quantum observables because they cannot be measured physically: a physical quantity cannot depend on the gauge choice, otherwise, it could take any arbitrary value. This feature is a very important aspect of gauge transformations and gauge theories.

Calculations of physical (gauge invariant) observables in quantum mechanics usually involve the evaluation of gauge dependent quantities: for instance, the expression of the electron wave function depends on the chosen gauge. When the exact analytical solution of the TDSE is known, it is possible to move from

one gauge to the other by a gauge transformation (see [16] for instance), and then, all gauges will yield the same physical result. In this case, the gauge choice is simply a matter of convenience: it may be easier to solve the TDSE in one specific gauge than in others. However, when approximations of gauge dependent quantities are involved (for instance, when using numerical methods or perturbation theory), the gauge invariance of physical observables may be lost as the error induced by the approximation scheme may not transform in the same way as the full solution. This can be illustrated as follows. Let us consider a single electron in interaction with an electromagnetic field expressed in two different gauges such that our system can be described equivalently by the following wave functions:

$$\psi^{(1)} = \tilde{\psi}^{(1)} + R^{(1)}, \tag{6}$$

$$\psi^{(2)} = \tilde{\psi}^{(2)} + R^{(2)}, \tag{7}$$

where $\psi^{(1)}$ is the general exact solution of the TDSE, coupled to the electromagnetic field expressed in gauge 1, while $\psi^{(2)}$ is given in gauge 2. The two wave functions are related by a gauge transformation G as $\psi^{(1)} = G\psi^{(2)}$ and we have again:

$$\langle\widehat{O}\rangle := \langle\psi^{(1)}|\widehat{O}^{(1)}|\psi^{(1)}\rangle = \langle\psi^{(2)}|\widehat{O}^{(2)}|\psi^{(2)}\rangle. \tag{8}$$

In Eqs. (6) and (7), $\tilde{\psi}^{(1,2)}$ are approximate wave functions, obtained from a solution of the TDSE using approximation methods. Thus, $R^{(1,2)}$ are the remainder or error of this method. Typically, it will be given by $R^{(1,2)} \sim h^n$ for numerical methods (where h is the grid size and $n \in \mathbb{N}^*$) or $R^{(1,2)} \sim g^n$ for perturbation theory (where g is a small parameter). If the approximate wave functions obey the same gauge transformation as the full solution, that is $\tilde{\psi}^{(1)} = G\tilde{\psi}^{(2)}$, the approximation of the observable will also be gauge invariant:

$$\langle\widehat{O}\rangle \approx \langle\tilde{\psi}^{(1)}|\widehat{O}^{(1)}|\tilde{\psi}^{(1)}\rangle = \langle\tilde{\psi}^{(2)}|\widehat{O}^{(2)}|\tilde{\psi}^{(2)}\rangle. \tag{9}$$

However, this is generally not the case because $\tilde{\psi}^{(1)}$ and $\tilde{\psi}^{(2)}$ usually transform differently in different gauges:

$$\langle\widehat{O}\rangle \approx \langle\tilde{\psi}^{(1)}|\widehat{O}^{(1)}|\tilde{\psi}^{(1)}\rangle, \tag{10}$$

$$\approx \langle\tilde{\psi}^{(2)}|\widehat{O}^{(2)}|\tilde{\psi}^{(2)}\rangle, \tag{11}$$

but

$$\langle\tilde{\psi}^{(1)}|\widehat{O}^{(1)}|\tilde{\psi}^{(1)}\rangle \neq \langle\tilde{\psi}^{(2)}|\widehat{O}^{(2)}|\tilde{\psi}^{(2)}\rangle, \tag{12}$$

and thus $\langle\widehat{O}^{(1)}\rangle \approx \langle\widehat{O}^{(2)}\rangle$. Therefore, we have lost gauge invariance by approximating the wave function. As the approximate wave functions get closer to the exact solution, the observables calculated in two different gauges converge towards each other

$$\langle\tilde{\psi}^{(1)}|\widehat{O}^{(1)}|\tilde{\psi}^{(1)}\rangle \xrightarrow{R^{(1,2)}\to 0} \langle\tilde{\psi}^{(2)}|\widehat{O}^{(2)}|\tilde{\psi}^{(2)}\rangle, \tag{13}$$

and of course, gauge invariance is recovered in the limit of the exact solution when $R^{(1,2)} = 0$.

The previous discussion illustrates the fact that approximating a gauge independent quantity (a physical observable) by implementing an approximation of a gauge dependent quantity (the wave function) may destroy the gauge independence of the former: the breaking of gauge invariance is an artifact of the approximation method. In this paper, we will compare the calculation of many observables in different gauges and show that certain gauge choices have better convergence properties towards the exact solution. One should always try to choose the gauge which gives the best approximation of the physical quantity under consideration. This has been studied extensively using either analytical or numerical approximations. For instance, it was remarked by Lamb in his celebrated study of the Hydrogen atom fine structure, that the theoretical results obtained in the length and velocity gauges (defined later) differ in perturbation theory [17]. Moreover, the result of the length gauge calculation was in better agreement with experiments, suggesting that this gauge would be more "fundamental". This apparent paradox was resolved latter when it was observed that the "naive" perturbation theory is not gauge invariant and that special care is required to calculate observables in a gauge independent way. In particular, this problem was encountered even earlier by Dirac in his discussion of the quantum Kramers-Heisenberg dispersion formula [18]. In second order perturbation theory, the $\mathbf{A} \cdot \mathbf{p}$ interaction must include the direct term $\mathbf{A}^2$ to be consistent (by power counting argument). Thus using the full interaction $\mathbf{A} \cdot \mathbf{p} + \mathbf{A}^2$ gives exactly the $(\mathbf{E} \cdot \mathbf{r})^2$ corresponding to perturbation expressions for Stark shifts. Moreover, it may happen that the electromagnetic potentials in

certain gauge are non-zero when the field is null (at $t = \pm\infty$ for instance). In this case, the eigenstates used in the perturbation theory has to be computed with great care (in the right gauge) or a gauge transformation has to be added in the perturbation expansion to get gauge independent results (see Section 5.1). Many papers have attempted to clarify this issue [19, 20, 21, 22, 23, 23, 24, 25, 15, 26]. The equivalence of the velocity and length gauge was also demonstrated in specific calculations for multiphoton transition probabilities [27] and induced polarization [28]. Other calculations have shown the equivalence of results in different gauge choices [29, 30]. Given the status and importance of this issue, we will attempt to formulate a consistent gauge invariant perturbation theory using general arguments in the following sections. Concerning numerical calculation and gauge independence, it is now generally admitted that certain gauge choices are better than others for the solution of the TDSE. For instance, it was concluded that the velocity gauge is more appropriate for calculations in dynamical laser-matter interactions [31]. Other calculations where gauge choices are compared can be found in [32] for HHG. It should be stressed here that these comparisons should be performed with great care because the structure of the mathematical equation may change under a gauge transformation and the resulting TDSE may require a different numerical scheme. This issue will be discussed in details in this work, along with the description of popular numerical methods.

Throughout this work, a single particle system is mainly considered but extension to N-particle problems exists naturally in the literature, and can often be easily deduced. Recent work has examined gauge invariance of coupled electron-nucleus dynamics using the time-dependent Hartree-Fock equation (TDHF) in [33] and the Time-dependent Kohn-Sham equation (TDKS) density functional theory [34] and also nonadiabatic molecular dynamics [35]. However, they are much more involved technically and are outside the scope of our discussion.

It is assumed in this tutorial that the electromagnetic field is not quantized and treated as a classical field. This approximation is valid when the number of photons is large (such as in a macroscopic laser field) such that quantum fluctuations can be neglected [15]. Concluding whether this approximation is true or not for the field induced by the particle is a non-trivial task and certainly depends on the dynamic of the system. Also, from the practical point of view, this approach simplifies the calculations significantly, which is certainly the main reason why it has been so popular among practitionners. It is important to note that using a classical theory spontaneous emission is not taken into account but must be introduced by "hand" as in HHG.

This article is organized as follows. In Section 2, the classical and quantum dynamics of particles coupled to an electromagnetic field is treated, with a special emphasis on gauge transformations. It will be shown how to obtain the TDSE from the classical dynamics of a scalar particle and how it interacts with the electromagnetic field. More generally, the gauge principle, which allows to derive the interaction of matter with force carriers will be described. In Section 3, the dipole approximation is detailed along with the regime where it can be used. The gauges commonly used in laser-matter interaction are reported in Section 4. More precisely, we will consider the length, the velocity and the acceleration gauges. The transformations allowing to change the gauge representation are also described. Section 5 contains details on analytical approximations used to evaluate quantum transition amplitudes. For instance, a general description of perturbation theory and the strong field approximation, with respect to gauge transformation, is included. The gauge invariance of these techniques is also shown in some specific examples. Section 6 contains a discussion of numerical methods for the solution of TDSE's. It is emphasized that the mathematical structure of the TDSE depends on the gauge and thus, the numerical scheme used to solve the equation should be accordingly chosen. Finally, gauge transformations in relativistic quantum mechanics, which is relevant for ultra-intense laser field, is considered in Section 7.

2. Classical and quantum dynamics of particles coupled to an electromagnetic field

In this section, we recall Maxwell's equations and the notion of gauge transformations and gauge choice, as well as some basic facts about the Hamiltonian and Lagrangian formulations of classical mechanics. The latter will then be applied to the case of a single particle interacting with a classical electromagnetic field. The corresponding quantum dynamics will be derived at the end of this section using the usual canonical quantization scheme. This allows to obtain a TDSE describing the quantum dynamics of a particle coupled

4

to an electromagnetic field: this equation is the basis of this paper. Finally, we will discuss the derivation of the TDSE from the point of view of the *Gauge principle* and show how a general symmetry principle can be used to obtain an interaction of matter with an electromagnetic field. This non-exhaustive survey will allow us to set the framework. This first part is a summary of some key sections of [15] (in particular we use similar notations).

2.1. Maxwell's equations

The electromagnetic field can be characterized by two physical quantities: the electric field $\mathbf{E}(x)$ and the magnetic field $\mathbf{B}(x)$, where $x := (\mathbf{r}, t)$ is a four-vector. These are vector fields which exist only in the presence of electric charges: an electric field is produced by a stationary charge while the magnetic field is induced by charges in motion (currents). Their dynamics and the relation between them is governed by Maxwell's equations. Denoting the electromagnetic field by $\mathcal{E} := (\mathbf{E}, \mathbf{B})$, microscopic Maxwell's equations in non-Gaussian (SI) units are written as:

$$
\begin{cases}
\nabla \cdot \mathbf{E}(x) &= \dfrac{1}{\varepsilon_0}\rho(x), \\
\nabla \cdot \mathbf{B}(x) &= 0, \\
\nabla \times \mathbf{E}(x) &= -\dfrac{\partial}{\partial t}\mathbf{B}(x), \\
\nabla \times \mathbf{B}(x) &= \dfrac{1}{c^2}\dfrac{\partial}{\partial t}\mathbf{E}(x) + \dfrac{1}{\varepsilon_0 c^2}\mathbf{j}(x),
\end{cases}
\tag{14}
$$

where ρ is the charge density, $\mathbf{j}$ is the current density, ε_0 is the vacuum permittivity and c is the velocity of light. When we are considering a system of ℓ point-like particles of charges q_i (here $q_i = -|e|$ for the electron) located at $\mathbf{r}_i(t)$ at time t, the charge density is given by [15]

$$
\rho(x) = \sum_{i=1}^{\ell} q_i \delta(\mathbf{r} - \mathbf{r}_i(t)),
\tag{15}
$$

and the current density by

$$
\mathbf{j}(x) = \sum_{i=1}^{\ell} q_i \mathbf{v}_i(t)\delta(\mathbf{r} - \mathbf{r}_i(t)),
\tag{16}
$$

where $\mathbf{v}_i(t) := d\mathbf{r}_i(t)/dt$ is the ith particle velocity. Of course, there exists a generalization of these last two formulas to the case of a continuous distribution of charges [14], but it is not required in this paper because we will consider point-like particles like the electron. The particle positions are determined from the Newton-Lorentz equations, which describes the non-relativistic dynamics of point-particles immersed in an electromagnetic field. Thus, the classical particles trajectories are solution of:

$$
\begin{cases}
m_i \dfrac{d^2\mathbf{r}_i(t)}{dt^2} = q_i \left[\mathbf{E}(\mathbf{r}_i(t), t) + \mathbf{v}_i(t) \times \mathbf{B}(\mathbf{r}_i(t), t)\right], \\
\mathbf{r}_i(t_0) = \mathbf{R}_i, \\
\mathbf{v}_i(t_0) = \mathbf{V}_i,
\end{cases}
\tag{17}
$$

for $i = 1 \cdots \ell$, and where we consider the electromagnetic field as external. Here, m_i are the particle masses, t_0 is the initial time and $\mathbf{R}_i, \mathbf{V}_i$ are the initial particle positions and velocities, respectively. Therefore, Eqs. (14) and (17) form a coupled system of equation where the coupling occurs via Eqs. (15) and (16). Together, these equations give the full classical dynamics of charged particles in an electromagnetic field.

From the divergence free equation $\nabla \cdot \mathbf{B} = 0$ implying the non-existence of magnetic monopoles, and the Maxwell-Faraday equation ($\nabla \times \mathbf{E}(x) = -\partial \mathbf{B}(x)/\partial t$), we deduce the existence of vector and scalar functions $\mathbf{A}$ and U such that

$$
\begin{cases}
\mathbf{B} &= \nabla \times \mathbf{A}, \\
\mathbf{E} &= -\dfrac{\partial}{\partial t}\mathbf{A} - \nabla U,
\end{cases}
\tag{18}
$$

5

where $\mathbf{A}$ is the vector electric potential and U the scalar electric potential. Substituting Eq. (18) into (14), Maxwell's equations can be rewritten in terms of $\mathbf{A}$ and U as a second order (in time and space) wave equation:

$$
\begin{cases}
\triangle U + \dfrac{\partial}{\partial t}(\nabla \cdot \mathbf{A}) = -\dfrac{1}{\varepsilon_0}\rho, \\[2mm]
\left(\dfrac{1}{c^2}\dfrac{\partial^2}{\partial t^2} - \triangle\right)\mathbf{A} + \nabla\left[\nabla \cdot \mathbf{A} + \dfrac{1}{c^2}\dfrac{\partial}{\partial t}U\right] = \dfrac{1}{c^2\varepsilon_0}\mathbf{j}.
\end{cases}
\tag{19}
$$

This system of equations is equivalent in principle to Maxwell's equations: it should give the same electromagnetic field $\mathcal{E}$. However, we will see in the following that this is not quite the case because the potentials are not defined uniquely and thus, we need another condition to obtain the appropriate dynamics. This can be understood in the following way. Let us consider a regular scalar function $F(x)$. It can be easily shown from (18) that the electromagnetic field $\mathcal{E}$ is unchanged (using the fact that $\nabla \times \nabla F = 0$, for any scalar) by the so-called *gauge transformation*:

$$
\begin{aligned}
\mathbf{A} &\rightarrow \mathbf{A}' = \mathbf{A} + \nabla F, \\[1mm]
U &\rightarrow U' = U - \dfrac{\partial}{\partial t}F.
\end{aligned}
\tag{20}
$$

As a consequence, the potentials are not uniquely defined: there exists an infinite number of potentials related by gauge transformations that yield the same electromagnetic field. Therefore, an additional equation (the *gauge condition*) is required to fix these superfluous "degrees of freedom" and to determine a unique definition of potentials: using such a gauge condition is called *gauge fixing*‡. There exists in principle an infinite number of these conditions but from a practical point of view, only a certain number of gauge choices are generally utilized because the resulting equations are simpler or have certain interesting properties. In the framework of electrodynamics coupled to non-relativistic classical particles, the most popular choices are the Lorentz and Coulomb gauges:

- Lorentz Gauge:
  Consists of imposing the condition

$$
\dfrac{\partial}{\partial t}U + c^2\nabla \cdot \mathbf{A} = 0,
\tag{21}
$$

  and Maxwell's equations become

$$
\begin{cases}
\dfrac{\partial^2}{\partial t^2}U - c^2\triangle U &= \dfrac{c^2}{\varepsilon_0}\rho, \\[2mm]
\dfrac{\partial^2}{\partial t^2}\mathbf{A} - c^2\triangle\mathbf{A} &= \dfrac{1}{\varepsilon_0}\mathbf{j}.
\end{cases}
\tag{22}
$$

  This gauge has the merit of being manifestly covariant, which is a very useful property when one is interested in symmetries of Maxwell's equations or in the covariant perturbation theory. It is to be noted that scalar U, and vector $\mathbf{A}$ potentials are decoupled in this gauge, as well as charge and current.

- Coulomb Gauge or minimal coupling:
  Consists of imposing the condition $\nabla \cdot \mathbf{A} = 0$, and as consequence Maxwell's equations are rewritten

$$
\begin{cases}
\triangle U &= -\dfrac{1}{\varepsilon_0}\rho, \\[2mm]
\dfrac{\partial^2}{\partial t^2}\mathbf{A} - c^2\triangle\mathbf{A} &= \dfrac{1}{\varepsilon_0}\mathbf{j} - \nabla\dfrac{\partial}{\partial t}U.
\end{cases}
\tag{23}
$$

There exist many other possibilities, such as the light-cone gauge, temporal gauge, axial gauge, Fock-Schwinger gauge and Poincaré gauge (for an exhaustive enumeration and definitions, see [15, 36]). Also, it is interesting to note that the null divergence of the vector potential $\mathbf{A}$ has interesting connections to the incompressibilty condition in fluid dynamics. This is discussed in more details in Section 6.

‡ It is interesting here to note that it took almost a century to understand this gauge fixing procedure[36].

2.2. Lagrangian and Hamiltonian formulation

This section is not an exhaustive presentation of the notion of Lagrangian and Hamiltonian operators. However simple facts are important to recall, in particular the least action principle, which lies as the basis of classical and quantum mechanics. Two cases will be treated: the discrete and the continuum cases. The former is used for the description of point-like particles. The latter is important when one is interested in the dynamics of a field variable such as the electromagnetic field, the velocity field in fluid dynamics and even the quantum wave function.

2.2.1. Discrete case: particle-like systems We denote by $(\mathbf{r}_i)_{i=1,\cdots,\ell}$ the set of trajectories of ℓ particles of mass $(m_i)_{i=1,\cdots,\ell}$. In the Lagrangian formalism the search of trajectories is equivalent to solving an extremum problem for the action S (the action is an extremum when $\mathbf{r}_i$ correspond to classical trajectories), between times t_1 and t_2 (see [37, 38]):

$$S := \int_{t_1}^{t_2} L\big(\mathbf{r}_1(t), \cdots, \mathbf{r}_\ell(t), \dot{\mathbf{r}}_1(t), \cdots, \dot{\mathbf{r}}_\ell(t), t\big)dt, \tag{24}$$

$$= \int_{t_1}^{t_2} K\big(\dot{\mathbf{r}}_1(t), \cdots, \dot{\mathbf{r}}_\ell(t)\big) - V\big(\mathbf{r}_1(t), \cdots, \mathbf{r}_\ell(t)\big)dt, \tag{25}$$

where $L := K - V$ is called the Lagrangian, with $K = \sum_i m_i(\dot{\mathbf{r}}_i)^2/2$ the kinetic energy and V the potential energy. Above and in the following, the notation $\dot{a}$ denotes the total time derivative of a ($\dot{a} = da/dt$). It should be noted here that the Lagrangian depends only on the variables $\mathbf{r}_i$, their time derivative $\dot{\mathbf{r}}$ (velocities) and possibly on time, but not on the acceleration $\ddot{\mathbf{r}}$, which is not included. The variables $\mathbf{r}_i, \dot{\mathbf{r}}_i$ are the *dynamical variables* and they completely specify the state of a classical system (this is the reason why the Lagrangian does not depend on higher time derivatives). The explicit time dependence of the Lagrangian is included to describe external forces acting on the dynamical system under consideration. In this latter case, it can be shown that the energy is not conserved.

The equations of motion are then obtained from the least action principle, which states that the particle paths minimize the action, that is: $\delta S = \int_{t_1}^{t_2} \delta L = 0$ where δL is the functional differential:

$$\delta L = \sum_{i=1}^{\ell} \Big(\frac{\partial L}{\partial \mathbf{r}_i}\delta\mathbf{r}_i + \frac{\partial L}{\partial \dot{\mathbf{r}}_i}\delta\dot{\mathbf{r}}_i\Big). \tag{26}$$

Assuming that the coordinate variation vanishes at $t = t_{1,2}$, the Euler-Lagrange equations can be obtained [37], for all $i = 1, \cdots, \ell$:

$$\frac{\partial L}{\partial \mathbf{r}_i} - \frac{d}{dt}\Big(\frac{\partial L}{\partial \dot{\mathbf{r}}_i}\Big) = 0. \tag{27}$$

These equations allow us to obtain a description local in time (equation of motion) from a global in time principle (least action principle).

Another important quantity can be obtained from the Lagrangian: the conjugate momentum. It is given, for the ith particle, by

$$\mathbf{p}_i = \frac{\partial L}{\partial \dot{\mathbf{r}}_i}. \tag{28}$$

It should also be noted that the conjugate momentum will be especially important when the theory is quantized and it will happen that $\mathbf{p}_i$ is *not* always equal to $m\dot{\mathbf{r}}_i$.

The last equation suggests that it is possible to obtain a description of the dynamics in terms of momenta $\mathbf{p}$ and coordinates $\mathbf{r}$, instead of the velocity $\dot{\mathbf{r}}$ used in the Lagrangian formulation. This is the Hamiltonian formulation, which is related to the Lagrangian by a Legendre transformation:

$$H(\mathbf{r}_1, \cdots, \mathbf{r}_\ell, \mathbf{p}_1, \cdots, \mathbf{p}_\ell) = \sum_{i=1}^{\ell} \dot{\mathbf{r}}_i\mathbf{p}_i - L = K + V. \tag{29}$$

Thus, the Hamiltonian represents the total energy (kinetic + potential energy) of the system. From the above equation it follows that if the Lagrangian is time-independent, the Hamiltonian or the total energy is conserved and thus, is a constant of motion.

2.2.2. Continuous case: classical field theory   In this section, we recall some basic facts about Hamiltonian and Lagrangian operators in classical field theory. The main difference with the preceding section is the fact that now, the object under study are fields, that is quantities which take a value at every point of space-time (they are defined everywhere in $\mathbb{R}^3 \times \mathbb{R}^+$). The latter come in various form depending on their transformation properties: scalar fields, vector fields or tensor fields for example. Also, they can be used to describe many physical entities such as the electromagnetic field, flow velocity in fluid mechanics, temperature distribution in a material, etc. Their dynamics can also be formulated in terms of Lagrangian and Hamiltonian mechanics, which is the subject of this section.

First, let us consider the dynamical variables given by $\phi_a(x)$ and $\partial_i \phi_a(x)$, that is the field under consideration. Here the index $a = 1, \cdots, n$ is an integer which denotes one of the n field vectorial components, that is:

$$\phi(x) := \begin{bmatrix} \phi_1(x) \\ \phi_2(x) \\ \vdots \\ \phi_n(x) \end{bmatrix}. \tag{30}$$

Also, the argument is $x = (t, \mathbf{r})$ such that ϕ has a value over $\mathbf{r} \in \mathbb{R}^3$ and $t \in [t_i, t_f]$. Finally, the index i denotes a derivative with respect to a space-time coordinate (when considering the Minkowski metric or in other words, when looking at relativistic systems, the usual notation is to have $i = \mu$ where μ is a Lorentz index).

Now, since the Lagrangian is a function of the dynamical variables, we can write the field action as

$$S = \int_{t_i}^{t_f} dt \int_{\mathbb{R}^3} d^3\mathbf{r} \mathcal{L}[\phi_a(x), \partial_i\phi_a(x), x], \tag{31}$$

where $\mathcal{L}$ is a Lagrangian density. This action is a scalar and is a generalization to the continuous case of the action for the discrete case. It can actually be derived from the discrete case in the limit of an infinite number of degrees of freedom and by assuming local interactions. The least action principle is unchanged in this procedure and can still be used to compute the equations of motion. The latter states that the field minimizes the action such that $\delta S = S[\phi'] - S[\phi] = 0$ where $\phi'_a(x) = \phi_a(x) + \delta\phi_a(x)$. In other words, the action is stationnary under the perturbation $\delta\phi_a(x)$. So under this infinitesimal variation, the action changes according to

$$\delta S = \int_{t_i}^{t_f} dt \int_{\mathbb{R}^3} d^3\mathbf{r} \left[\frac{\partial \mathcal{L}(x)}{\partial \phi_a(x)} - \partial_i \frac{\partial \mathcal{L}}{\partial [\partial_i \phi_a(x)]} \right] \delta\phi_a(x). \tag{32}$$

Of course, by requiring stationarity of the action, we get the usual Euler-Lagrange equation of motion:

$$\frac{\partial \mathcal{L}(x)}{\partial \phi_a(x)} - \partial_i \frac{\partial \mathcal{L}(x)}{\partial [\partial_i \phi_a(x)]} = 0. \tag{33}$$

Here, Einstein notation convention is assumed, that is repeated indices are summed.

The conjugate momenta (Π) and the Hamiltonian density ($\mathcal{H}$) can also be defined as in the discrete case. They are given by

$$\Pi_a(x) \qquad\qquad = \frac{\partial \mathcal{L}}{\partial \phi_a(x)}, \tag{34}$$

$$\mathcal{H}[\phi_a(x), \Pi_a(x)] = \sum_a \Pi_a(x)\phi_a(x) - \mathcal{L}. \tag{35}$$

Finally, it is often convenient to use the Lagrangian of a continuous system obtained from the Lagrangian density as $L = \int_{\mathbb{R}^3} d^3\mathbf{r} \mathcal{L}(x)$. This notation will be used frequently in the following sections.

2.2.3. Symmetry transformations   In both the discrete and the continuous cases, a physical system may have symmetries, that is a set of transformations which leave the dynamics (equation of motion) invariant. In the Lagrangian formulation, it can be shown that under such symmetry transformations, the Lagrangian

is unchanged, up to a divergence term. Among the general set of symmetries, we now focus on continuous symmetries, which are smooth mapping which can be parametrized by a real number. These are very important in all areas of physics and mathematics because they are related to conserved quantities via Noether's theorem. Also, gauge transformations are continuous symmetries.

First, we will look at the possible transformations that can be implemented on the Lagrangian. These exist in two varieties (for the discrete case, only the first type can be implemented):

(i) Transformations on coordinates:
    Examples of these are the Lorentz and Galilean transformations, which include translations and rotations.

(ii) Transformation on the fields:
    Examples of these are the phase transformation of the wave function ($\psi \to \psi' = e^{i\Lambda}\psi$). Note that in the following, we will consider a set of invertible transformations which depend only on the field itself (not its derivative).

Mathematically, a general way of writing these two transformations is to define a linear mapping T_Λ as:

$$T_\Lambda : \quad \begin{aligned} x &\to x_\Lambda, \\ \phi_a(x) &\to \phi_{\Lambda,a}(x_\Lambda), \end{aligned} \tag{36}$$

where Λ is a continuous parameter (which may depend on space-time) such that when $\Lambda = 0$, the transformation is the identity. Then, it can be shown that a condition to confirm that T_Λ is a symmetry transformation (for the continuous case) is that

$$\mathcal{L}[\phi_\Lambda(x_\Lambda), \partial_i^\Lambda \phi_\Lambda(x_\Lambda), x_\Lambda] = \mathcal{L}[\phi(x), \partial_i \phi(x), x] J(x, x_\Lambda) + \partial_i F_i^\Lambda[\phi(x), x], \tag{37}$$

where $J(x, x_\Lambda)$ is the Jacobian of the coordinate transformation (this is required because $\mathcal{L}$ is a density, meant to be integrated). Also, the function F is related to the transformation Λ, in the sense that its explicit expression depends on the mapping T_Λ, and obeys $F^\Lambda \xrightarrow{\Lambda \to 0} 0$.

In the discrete case, this symmetry condition is written as

$$L(x_\Lambda) = L(x) + \frac{d}{dt} f^\Lambda(x), \tag{38}$$

where f is an arbitrary functions similar to F^Λ: it is related to the mapping T_Λ and obeys $f^\Lambda \xrightarrow{\Lambda \to 0} 0$. If these conditions are fulfilled, the transformed and the initial Lagrangian will lead to the same dynamics (the equation of motion will have the same form).

2.3. Lagrangian of the electromagnetic field

In this section, we will look at the Lagrangian density describing the electromagnetic field. It is convenient for this discussion to use the manifestly covariant formulation of electrodynamics. In this case, we define the four vector potential and current as

$$A^\mu(x) := (U(x)/c, \mathbf{A}(x)), \tag{39}$$
$$J^\mu(x) := (c\rho(x), \mathbf{j}(x)). \tag{40}$$

These quantities are contravariant tensors which are related to their covariant counterparts by $A^\mu = \eta^{\mu\nu} A_\nu$, where $\eta^{\mu\nu} = \text{diag}[1, -1, -1, -1]$ is the Minkowski metric. It is also convenient to define the antisymmetric field strength tensor as

$$F^{\mu\nu}(x) := \partial^\mu A^\nu(x) - \partial^\nu A^\mu(x). \tag{41}$$

Then, within this formulation, Maxwell's equations can be written in a very compact and manifestly covariant (invariant under Lorentz transformations) form:

$$\partial_\mu F^{\mu\nu}(x) = \frac{1}{\varepsilon_0 c^2} J^\nu(x). \tag{42}$$

Also, the conservation of current is written as

$$\partial_\mu J^\mu(x) = 0. \tag{43}$$

This last equation can be obtained from Maxwell's equations presented in the last section. It expresses the fact that charge is conserved and cannot be created.

In this notation, the gauge transformation is

$$A^\mu(x) \to A'^\mu(x) = A^\mu(x) - \partial^\mu F(x), \tag{44}$$

where F is again an arbitrary scalar function. We would like to stress that the covariant formulation is equivalent to the set of Maxwell's equations presented before. However, it is independent of the choice of referential frame: the latter are related by Lorentz (or Poincaré) transformations.

From these equations, it is possible to obtain the corresponding Lagrangian density for the electromagnetism sector. It is given by

$$\mathcal{L}_\mathcal{E}(A^\mu, \nabla A^\mu, x) := \mathcal{L}_{\mathrm{kin}}(A^\mu, \nabla A^\mu, x) + \mathcal{L}_{\mathrm{int}}(A^\mu, \nabla A^\mu, x), \tag{45}$$

$$= -\frac{\varepsilon_0 c^2}{4} F_{\mu\nu}(x) F^{\mu\nu}(x) - J^\mu(x) A_\mu(x). \tag{46}$$

It is a straightforward calculation to show that the Euler-Lagrange equation for this Lagrangian density is given by Maxwell's equations.

The coupling of the electromagnetic field to matter is done through the source terms $J^\mu A_\mu$ which contain the charge density and current. In a classical setting, this would be related to the charge position and thus, another term should be included in the Lagrangian to take care of the particles dynamics. This is done in section 2.4. In the quantum setting however, the tensor J^μ is related to the wave function of the particle under study (in our case, a single electron). This is described is Section 2.6.

2.4. Lagrangian of a particle in an electromagnetic field

The Lagrangian for a system of ℓ non-relativistic free particles is given by $L_{\ell\mathrm{p}} := 1/2 \sum_{i=1}^\ell m_i \mathbf{v}_i^2$. To introduce its coupling with an electromagnetic field, we can add the electromagnetic field Lagrangian $L_\mathcal{E}$ and we get

$$L_{\ell\mathrm{p}+\mathcal{E}} := L_{\ell\mathrm{p}} + L_\mathcal{E}, \tag{47}$$

$$= \frac{1}{2} \sum_{i=1}^\ell m_i \mathbf{v}_i^2 + \int \mathcal{L}_\mathcal{E} d^3\mathbf{r}, \tag{48}$$

$$= \frac{1}{2} \sum_{i=1}^\ell m_i \mathbf{v}_i^2 + \frac{\varepsilon_0}{2} \int d^3\mathbf{r} \Big[(-\nabla U(x) - \dot{\mathbf{A}}(x))^2 - c^2 (\nabla \times \mathbf{A}(x))^2 \Big]$$

$$+ \int d^3\mathbf{r} \Big[\mathbf{j}(x) \cdot \mathbf{A}(x) - \rho(x) U(x) \Big], \tag{49}$$

$$= \frac{1}{2} \sum_{i=1}^\ell m_i \mathbf{v}_i^2 + \frac{\varepsilon_0}{2} \int d^3\mathbf{r} \Big[\mathbf{E}^2(x) - c^2 \mathbf{B}^2(x) \Big] + \int d^3\mathbf{r} \Big[\mathbf{j}(x) \cdot \mathbf{A}(x) - \rho(x) U(x) \Big], \tag{50}$$

where the current $\mathbf{j}$ and density $\rho(x)$ in the interaction terms of $\mathcal{L}_\mathcal{E}$ are given by Eq. (16) and (15), respectively. The Euler-Lagrange equation of motion are given by Maxwell's equations and by the Newton-Lorentz equation as the dynamical variables are $\mathbf{r}, \dot{\mathbf{r}}, \mathbf{A}, U$.

We now discuss the effect of a gauge transformation via F in Eq. (44), on this Lagrangian where we set $\ell = 1$, that is for the single particle case. Replacing $(\mathbf{A}, U)$ by $(\mathbf{A}', \mathbf{U}')$, leads to a new Lagrangian $\tilde{L}_{1\mathrm{p}+\mathcal{E}}$:

$$L_{1\mathrm{p}+\mathcal{E}} \to \tilde{L}_{1\mathrm{p}+\mathcal{E}} := L_{1\mathrm{p}+\mathcal{E}} + \int_{\mathbb{R}^3} \left[\nabla \cdot (\mathbf{j}F) + \frac{\partial}{\partial t}(\rho F) \right] d^3\mathbf{r} - \left(\nabla \cdot \mathbf{j} + \frac{\partial \rho}{\partial t} \right). \tag{51}$$

Due to charge conservation given in Eq. (43), which can be written as

$$\nabla \cdot \mathbf{j} + \frac{\partial \rho}{\partial t} = 0, \tag{52}$$

10

and the divergence theorem ($\int \nabla \cdot (\mathbf{j}F)d^3\mathbf{r} = 0$), we can deduce that

$$\tilde{L}_{1\text{p}+\mathcal{E}} = L_{1\text{p}+\mathcal{E}} + \frac{d}{dt}\int_{\mathbb{R}^3} \rho F d^3\mathbf{r}. \tag{53}$$

The new $\tilde{L}_{1\text{p}+\mathcal{E}}$ and old Lagrangians $L_{1\text{p}+\mathcal{E}}$ are then *equivalent* as they obey the symmetry condition in Eq. (38) and thus, lead to the same equation of motion. This transformation is called a *gauge transformation of the first kind*, according to Pauli [39].

The Lagrangian $L_{1\text{p}+\mathcal{E}}$ was written in a general way such that gauge invariance is explicitly satisfied. However, it contains redundant degrees of freedom and as discussed earlier, these can be discarded by the gauge fixing procedure, i.e. by imposing a certain gauge condition. Thus, it is possible to write Lagrangians for specific gauge choices. For instance, in the Coulomb gauge ((c)) where $B = \nabla \times \mathbf{A}$ with $\nabla \cdot \mathbf{A} = 0$, the Lagrangian (50) can be written:

$$L_{1\text{p}+\mathcal{E}}^{(c)} = \frac{m}{2}\mathbf{v}^2 - V_c + \frac{\varepsilon_0}{2}\int_{\mathbb{R}^3}\left[\dot{\mathbf{A}}^2 - c^2(\nabla \times \mathbf{A})^2 + \mathbf{j}\cdot\mathbf{A}\right]d^3\mathbf{r}, \tag{54}$$

and the corresponding Hamiltonian, is then given by (using (29), (34) and (35))

$$H_{1\text{p}+\mathcal{E}}^{(c)} = \frac{1}{2m}[\mathbf{p}-q\mathbf{A}]^2 + V_c + \frac{\varepsilon_0}{2}\int_{\mathbb{R}^3}d^3\mathbf{r}\left[\left(\frac{\mathbf{\Pi}}{\varepsilon_0}\right)^2 + c^2(\nabla \times \mathbf{A})^2\right], \tag{55}$$

where $\mathbf{\Pi}$ is defined in Eq. (34). There are a few interesting remarks to make about this Lagrangian:

- It is not gauge invariant, rather, it is obtained from the gauge invariant Lagrangian by gauge fixing. Thus, it is valid only for the Coulomb gauge choice.
- The electromagnetic field dynamics does not depend on the scalar potential U. The gauge fixing procedure ($\nabla \cdot \mathbf{A} = 0$) allowed to eliminate this degree of freedom.
- The Coulomb potential V_c of the particle appears naturally from the term involving the charge density [15]. Thus, in this gauge, the field of the particle is simply given by the usual Coulomb law.
- It is not manifestly covariant because the gauge condition is not invariant under Lorentz transformation.

For the first three reasons, the Coulomb gauge is a very popular choice to describe laser-matter interactions.

We would like to conclude this section by considering the special case of a single particle ($\ell = 1$) subject to an external electromagnetic field where we assume that the field is not part of the dynamical system. This approximation is often used to simplify the calculations. The simplified Lagrangian becomes

$$L_{1\text{p}+\mathcal{E}_e} = \frac{m}{2}\mathbf{v}^2 + \int d^3\mathbf{r}\left[\mathbf{j}(x)\cdot\mathbf{A}_e(x) - \rho(x)U_e(x)\right], \tag{56}$$

where $U_e, \mathbf{A}_e$ represent the potential of an external electromagnetic field $\mathcal{E}_e := (\mathbf{E}_e, \mathbf{B}_e)$. In this model, the Euler-Lagrange equation are given by the Newton-Lorentz equation for the particle and there is no backreaction of the particle on the field. The conjugate momentum is $\mathbf{p} = m\mathbf{v} + q\mathbf{A}_e$ while the Hamiltonian is

$$H_{1\text{p}+\mathcal{E}_e} = \frac{1}{2m}[\mathbf{p}-q\mathbf{A}_e]^2 + qU_e. \tag{57}$$

This Hamiltonian is then used in the special case where it is assumed that the backreaction on the electromagnetic field is negligible. Throughout this paper, we will refer to this case as the *external field approximation* (minimal gauge).

2.5. Quantization

The equations of motion obtained in the last section can be quantized in the usual canonical quantization procedure where the position and conjugate momentum become operators. This method attempts to quantize a classical system while keeping its symmetries. We would like to stress again that in this work, we are not quantizing the electromagnetic field: only the single particle described by the Newton-Lorentz equation will

be quantized. The canonical quantization states that the classical dynamical variables, that is the position $\mathbf{r}$ and conjugate momentum $\mathbf{p}$, become operators with the following commutation relations:

$$[\widehat{r}_i, \widehat{r}_j] = 0, \tag{58}$$

$$[\widehat{p}_i, \widehat{p}_j] = 0, \tag{59}$$

$$[\widehat{r}_i, \widehat{p}_j] = i\hbar\delta_{ij}. \tag{60}$$

Throughout this work, we will work in the "position representation" where $|\mathbf{r}\rangle$ is a vector in the Hilbert space describing the quantum state of our system. The position operator has the property that $\widehat{\mathbf{r}}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle$. From this result and the commutation relation, it is straightforward to obtain that $\widehat{\mathbf{p}} = -i\hbar\nabla$ (in the free case).

A general state is obtained by the linear superposition $|\psi\rangle = \int d^3\mathbf{r}\psi(\mathbf{r})|\mathbf{r}\rangle$. The wave function is a projection of such a state on the position state, that is $\psi(\mathbf{r}) := \langle\mathbf{r}|\psi\rangle$. The dynamics of the wave function is given by the TDSE:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \widehat{H}(t)|\psi(t)\rangle, \tag{61}$$

where $\widehat{H}$ is the Hamiltonian operator for the system under consideration. Projecting this equation on position space, we get the usual TDSE in coordinate space:

$$i\hbar\frac{\partial}{\partial t}\psi(t,\mathbf{r}) = \widehat{H}(t,\mathbf{r})\psi(t,\mathbf{r}), \tag{62}$$

where the quantum Hamiltonian is obtained from the classical Hamiltonian by using the following prescription: $\mathbf{p} \to -i\hbar\nabla$. This procedure will be used in the rest of this paper to obtain wave equations describing the quantum dynamics of a single particle interacting with different electromagnetic fields.

To end this section, we note that Eq. (62) can be solved formally as

$$\psi(t_f,\mathbf{r}) = \widehat{U}(t_f, t_i)\psi(t_i,\mathbf{r}) \tag{63}$$

$$= \widehat{T}\exp\left[-\frac{i}{\hbar}\int_{t_i}^{t_f} d\tau\widehat{H}(\tau,\mathbf{r})\right]\psi(t_i,\mathbf{r}), \tag{64}$$

where $t_{i,f}$ are initial and final times, $\widehat{U}(t_f, t_i)$ is the evolution operator and $\widehat{T}$ is the time-ordering operator. The latter is required when the Hamiltonian does not commute with itself at different times.

2.6. Time dependent Schrödinger equation coupled to an electromagnetic field and the gauge principle

In this section, we consider the gauge invariance of the TDSE coupled to an electromagnetic field from the Lagrangian viewpoint and the gauge principle. It should be noted here that the wave function is also a field (a complex scalar field) in the sense that it is a function that is defined over all $\mathbb{R}^3$. Therefore, its dynamics can be understood from a variational principle analogous to the treatment of the electromagnetic field. This will be presented in the first section. Finally, the coupling of the two along with gauge invariance and physical consequences will be proven.

2.6.1. Schrödinger scalar field The free Schrödinger equation for a particle of mass m is given by

$$i\hbar\partial_t\psi(x) = -\frac{\hbar^2}{2m}\nabla^2\psi(x). \tag{65}$$

Then, it can be shown that the free Schrödinger equation is given by the Euler-Lagrange equation of the following Lagrangian density:

$$\mathcal{L}_{\mathrm{S}}(\psi, \partial\psi, \psi^*, \partial\psi^*, x) = i\frac{\hbar}{2}\left[\psi^*(x)\dot{\psi}(x) - \dot{\psi}^*(x)\psi(x)\right] - \frac{\hbar^2}{2m}|\nabla\psi(x)|^2. \tag{66}$$

This Lagrangian describes matter (it gives the quantum dynamics of a particle of mass m) and thus, ψ will be denoted as the "matter field" in the following. It should be noted that since the field ψ is complex, both ψ and ψ^* should be considered as dynamical variables [15], leading to two different Euler-Lagrange equations

which are complex conjugate of each other. Also, the Schrödinger Lagrangian is not invariant under Lorentz transformations because of course, it describes a non-relativistic particle. It is however invariant under the Galilean transformations which relates different referential frames in the non-relativistic setting. There exists relativistic generalizations of the Schrödinger wave equation, such as the Klein-Gordon (spin-0) and the Dirac (spin-1/2) equations, which are invariant under Lorentz transformations.

2.6.2. Minimal coupling prescription and gauge invariance Now, we would like to couple the matter field, described by the Schrödinger Lagrangian, with the electromagnetic field. This can be achieved by imposing a symmetry on the Lagrangian $\mathcal{L}_S$. Let us assume that the theory describing our system (particle and electromagnetic field) is invariant under local phase transformations ($U(1)$ symmetry). The latter are given by:

$$\psi(x) \to \psi'(x) = e^{iqF(x)/\hbar}\psi(x), \tag{67}$$

where F depends on space-time and thus, corresponds to a local transformation. An explicit calculation shows that $\mathcal{L}'_S \neq \mathcal{L}_S$. Rather, we have

$$\mathcal{L}'_S(\psi, \partial\psi, \psi^*, \partial\psi^*, x) = i\frac{\hbar}{2}\left[\psi^*(x)\dot{\psi}(x) - \dot{\psi}^*(x)\psi(x)\right] - \frac{1}{2m}|\left[-i\hbar\nabla - q\nabla F(x)\right]\psi(x)|^2 + q\partial_t F(x), \tag{68}$$

and thus, *a priori*, the matter field is not invariant under this transformation. There is a way however to cancel the extra terms in Eq. (68) by adding a new (gauge) field with appropriate transformations. This new field is the electromagnetic field and it is added via the minimal coupling prescription, that is partial derivatives in $\mathcal{L}_S$ are replaced by:

$$\partial_\mu \to D_\mu = \partial_\mu + i\frac{q}{\hbar}A_\mu(x), \tag{69}$$

or

$$\nabla \to \nabla - i\frac{q}{\hbar}\mathbf{A}(x), \tag{70}$$

$$\partial_t \to \partial_t + i\frac{q}{\hbar}U(x), \tag{71}$$

where D_μ is the covariant derivative. This is complemented by adding the kinetic term $F^{\mu\nu}F_{\mu\nu}$ such that the electrodynamic field becomes a dynamic variable. Then, the Lagrangian for the coupled system becomes

$$\mathcal{L}_{S+\mathcal{E}} := \mathcal{L}_{S+\mathcal{E}}(\psi, \partial\psi, \psi^*, \partial\psi^*, A^\mu, \partial A^\mu), \tag{72}$$

$$= i\frac{\hbar}{2}\left[\psi^*(x)\dot{\psi}(x) - \dot{\psi}^*(x)\psi(x)\right] - qU(x)|\psi(x)|^2$$

$$- \frac{1}{2m}|\left[-i\hbar\nabla - q\mathbf{A}(x)\right]\psi(x)|^2 - \frac{\varepsilon_0 c^2}{4}F^{\mu\nu}(x)F_{\mu\nu}(x). \tag{73}$$

This is invariant under gauge transformations, which are a combination of the $U(1)$ phase transformation and the transformations on electromagnetic potentials.

The Lagrangian $\mathcal{L}_{S+\mathcal{E}}$ represents physically the dynamics of the matter field with its "own" electromagnetic field, that is the magnetic field generated by the particle itself. However, it is also possible to add an external electromagnetic field by letting $A^\mu \to A^\mu + A^\mu_{\text{ext}}$. The corresponding Euler-Lagrange equation then becomes

$$\begin{cases} i\hbar\partial_t\psi(x) = \dfrac{1}{2m}\left[-i\hbar\nabla - q(\mathbf{A}(x) + \mathbf{A}_{\text{ext}}(x))\right]^2\psi(x) + q[U(x) + U_{\text{ext}}(x)]\psi(x), \\ \partial_\mu F^{\mu\nu}(x) = J^\nu(x), \end{cases} \tag{74}$$

where

$$J^\mu(x) = \begin{cases} q|\psi(x)|^2 & \text{for } \mu = 0, \\ \left[-i\hbar\nabla - q(\mathbf{A}(x) + \mathbf{A}_{\text{ext}}(x))\right]|\psi(x)|^2 & \text{for } \mu = 1, 2, 3. \end{cases} \tag{75}$$

Before continuing further, we summarize the above derivations. We started with a Lagrangian describing matter: the Schrödinger Lagrangian in Eq. (66). Then, we imposed a local $U(1)$ symmetry (note that $U(1)$ symmetry with a space-independent phase parameter is related to charge conservation) to this Lagrangian. The consequence of this is that we had to add a new field, the electromagnetic gauge field, such that the symmetry is obeyed. This field obeys the gauge transformation properties. This whole procedure is an example of the gauge principle which is used in many field of physics to obtain interaction terms between matter and force carriers. For example, the theory of Strong and Weak nuclear interaction are based upon this very principle, albeit on its non-abelian generalization (the symmetry groups are local $SU(3)$ and $SU(2)$ in these cases). Therefore, it is generally believed that gauge symmetries are one of the fundamental organizing principles of nature.

To summarize, the gauge transformation T_F can be written as

$$T_F : \begin{array}{ccccc} \psi(x) & \to & \psi'(x) & = & e^{iqF(x)/\hbar}\psi(x), \\ A^\mu(x) & \to & A'^\mu(x) & = & A^\mu(x) - \partial^\mu F(x). \end{array} \tag{76}$$

where F is an arbitrary function. This was shown to be a symmetry transformation because the Lagrangian is invariant and obeys Eq. (37).

The fact that matter, described here by the matter field, is coupled to potentials via the minimal coupling prescription (Eq. (69)) and the gauge principle, have very important physical consequences. One of the most striking example is that of the Aharonov-Bohm effect [40], which states that a confined electromagnetic field can have an effect on the quantum wave function (on the phase), even in space-time regions where the field is null. This occurs because although the field is zero, the potential can still be non-vanishing (see Eq. (18)). The experimental verification of this effect [41] gives a hint that gauge theory really describe the interaction of light with matter.

2.7. Gauge invariance, unitary transformation and quantum observables

The goal of this section is to show that although gauge transformations are unitary, not all unitary transformations correspond to a gauge transformation. This may occur when the transformation parameter F depends on dynamical variables such as $\dot{\mathbf{r}}$, etc. Also, the fact that transition matrix elements are invariant under any unitary transformations is discussed. This is crucial for our analysis because it states that physical observables are the same, for any unitary transformations of the wave function. The corollary to this is that observables are invariant under gauge transformations.

To describe these results, we will start by looking at the invariance of quantum observables under unitary transformations. Let us consider a transformation operator defined by

$$\mathcal{U}(t) := \exp(iF(t)/\hbar), \tag{77}$$

where F can be any space-time dependent operator. Of course, this transformation is unitary: $|\mathcal{U}(t)|^2 = 1$. The operator $\mathcal{U}$ acts on the wave function as $|\psi^{(2)}(t)\rangle = \mathcal{U}(t)|\psi^{(1)}(t)\rangle$, while the wave functions obey the following TDSE's:

$$i\hbar\frac{\partial}{\partial t}|\psi^{(1)}(t)\rangle = \widehat{H}^{(1)}(t)|\psi^{(1)}(t)\rangle \ ; \ i\hbar\frac{\partial}{\partial t}|\psi^{(2)}(t)\rangle = \widehat{H}^{(2)}(t)|\psi^{(2)}(t)\rangle. \tag{78}$$

It can be verified by using these TDSE's, along with the definition of unitary transformations, that the Hamiltonians in the two representations are related by

$$\widehat{H}^{(2)} = \mathcal{U}\widehat{H}^{(1)}\mathcal{U}^\dagger + i\hbar\frac{d\mathcal{U}}{dt}\mathcal{U}^\dagger. \tag{79}$$

Note here that this is derived in all generality by assuming that $[\partial_t\mathcal{U},\mathcal{U}] \neq 0$. The average energy then transforms as

$$\langle\psi^{(2)}|\widehat{H}^{(2)}|\psi^{(2)}\rangle = \langle\psi^{(1)}|\widehat{H}^{(1)}|\psi^{(1)}\rangle + i\hbar\langle\psi^{(2)}|\frac{d\mathcal{U}}{dt}|\psi^{(1)}\rangle. \tag{80}$$

Therefore, the average energy is not invariant under a general unitary transformation if the last term of the last equation is non-zero. However, it can be easily deduced that physical observables, which are given in

terms of transition amplitudes, are invariant under unitary transformations, even if the Hamiltonian does not. This result can be obtained as follows.

Denoting $\widehat{U}^{(1,2)}(t,t_0) := \widehat{T}\exp(-i\int_{t_0}^t \widehat{H}^{(1,2)}(t')dt'/\hbar)$ the evolution operator for $\widehat{H}^{(1,2)}$ (where $\widehat{T}$ stands for the time-ordering operator) see for instance [42] and Section 2.5, such that for $t \geqslant t_0$,

$$|\psi^{(1)}(t)\rangle = \widehat{U}^{(1)}(t,t_0)|\psi^{(1)}(t_0)\rangle. \tag{81}$$

Then, we have

$$\begin{aligned}|\psi^{(2)}(t)\rangle &= \mathcal{U}(t)|\psi^{(1)}(t)\rangle \\ &= \mathcal{U}(t)\widehat{U}^{(1)}(t,t_0)|\psi^{(1)}(t_0)\rangle \\ &= \mathcal{U}(t)\widehat{U}^{(1)}(t,t_0)\mathcal{U}^\dagger(t_0)|\psi^{(2)}(t_0)\rangle \\ &= \widehat{U}^{(2)}(t,t_0)|\psi^{(2)}(t_0)\rangle. \end{aligned} \tag{82}$$

Thus, we can deduce that the evolution operator transforms as

$$\widehat{U}^{(2)}(t,t_0) = \mathcal{U}(t)\widehat{U}^{(1)}(t,t_0)\mathcal{U}^\dagger(t_0) \tag{83}$$

under a unitary transformation. As a consequence, the transition amplitudes from $|\psi^{(1)}(t_0)\rangle$ to $|\psi^{(1)}(t)\rangle$ obey:

$$\langle\psi^{(1)}(t)|\widehat{U}^{(1)}(t,t_0)|\psi^{(1)}(t_0)\rangle = \langle\psi^{(2)}(t)|\widehat{U}^{(2)}(t,t_0)|\psi^{(2)}(t_0)\rangle. \tag{84}$$

This equation states that the transition amplitudes are equal and are invariant under a unitary transformation. This is a very important result because most physical observables can be obtained from the transition amplitudes and consequently, these observables are also invariant under unitary transformations. For instance, in HHG experiments, one can measure the amplitude and phase of each harmonic electric field, and these are related to photon emission transition moments, which can result in direct tomography of wave functions [9, 43].

We can now specialize the general unitary transformations to the special case of gauge transformations. Then, the unitary transformation takes the form:

$$\mathcal{U}(t) = G(t) = \exp\left[i\frac{q}{\hbar}F(\mathbf{r},\mathbf{A},U,t)\right]. \tag{85}$$

In this case, F and $\frac{\partial F}{\partial t}$ commute and the transformation of the Hamiltonian is given by

$$\widehat{H}^{(2)} = G\widehat{H}^{(1)}G^\dagger - q\frac{\partial F}{\partial t}. \tag{86}$$

It was shown in previous sections that under this transformation, the Lagrangian $L^{(1)}$ of a particle interacting with electromagnetic radiation transforms into an equivalent Lagrangian $L^{(2)}$ via

$$L^{(2)}(\mathbf{r},\mathbf{A},U,\dot{\mathbf{r}},\partial\mathbf{A},\partial U) = L^{(1)}(\mathbf{r},\mathbf{A},U,\dot{\mathbf{r}},\partial\mathbf{A},\partial U) + \frac{d}{dt}qF(\mathbf{r},\mathbf{A},U,t). \tag{87}$$

This is the more general unitary transformation that yields a Lagrangian respecting the symmetry condition in Eq. (38). Note that the function F is independent of $\dot{\mathbf{r}}$, $\partial\mathbf{A}$ or ∂U, to avoid any dependence in $\ddot{\mathbf{r}}$, $\partial^2\mathbf{A}$ or $\partial^2 U$ in the Lagrangian as these quantities are not required to specify the dynamics of the system. The consequence of adding these terms is that the new Lagrangian $L^{(2)}$ would not describe a physical system obeying Hamiltonian mechanics. Thus, certain unitary transformations change the classical dynamics of the system, such as

$$\mathcal{U}(t) = \exp\left[i\frac{q}{\hbar}F'(\mathbf{r},\mathbf{A},U,\dot{\mathbf{r}},\partial\mathbf{A},\partial U,t)\right]. \tag{88}$$

Although they leave transition amplitudes invariant, these are not gauge transformations because they may change the form of the Schrödinger equation. An example of these are the Kramers-Henneberger (also called Bloch-Nordsieck [44]) transformations, presented below, which allow to obtain the acceleration gauge from the length gauge.

3. Long wavelength or dipole approximation

In this section, we describe the long wavelength approximation which is relevant when the wavelength of the electromagnetic field λ is much larger than the dimension of the system d, that is $\lambda \gg d$. In that case, the spatial variation of the electromagnetic field over the size of the quantum system is very small and thus can be neglected. This approximation is often used in laser-matter interaction as it simplifies the calculations significantly.

More precisely, we consider a quantum system centered in $\mathbf{r} = 0$ and an electric field with a space-time dependence given by $\mathbf{E} = \mathbf{E}(\omega t - kz)$, where ω is the laser frequency and k is the wave number. Here, we assume that the z-axis of the coordinate system is in the direction of the wave propagation and thus, we define the wave number $k := |\mathbf{k}|$. This form of the electric field is relevant as $\mathbf{E}$ is a solution of a wave equation, which has plane wave solutions with this space-time dependence (for instance $E = E_0 \cos(\omega t - kx)$). A general solution can be written as the linear combination of plane waves. Then, making a Taylor expansion as in [45],

$$\mathbf{E}(\omega t - kz) \sim \mathbf{E}(\omega t) - kz \frac{\partial}{\partial(\omega t - kz)} \mathbf{E}(\omega t - kz)|_{z=0}. \tag{89}$$

This last equation can be re-written in two different but equivalent ways:

$$\mathbf{E}(\omega t - kz) \sim \mathbf{E}(\omega t) + z \frac{\partial}{\partial z} \mathbf{E}(\omega t - kz)|_{z=0}, \tag{90}$$

$$\mathbf{E}(\omega t - kz) \sim \mathbf{E}(\omega t) - \frac{kz}{\omega} \frac{\partial}{\partial t} \mathbf{E}(\omega t). \tag{91}$$

The first one allows us to understand the limit of the long wavelength approximation. Indeed, from this equation, we obtain the change in the electric field over the size of the system: $\Delta E \sim d\partial_z E(\omega t - kz)|_{z=0} \sim dk|\mathbf{E}| = d\omega|\mathbf{E}|/c$. To neglect the space variation of the electric field, we need the condition $\Delta E \ll |\mathbf{E}|$ and thus, we obtain:

$$\omega d \ll c. \tag{92}$$

When the laser frequency ω obeys this condition, the long wavelength approximation can be used.

The second equation allows us to get the vector potential in the velocity gauge associated with the electric field, in this long wavelength approximation. It is given by

$$\mathbf{A}(\omega t - kz) \sim \mathbf{A}(\omega t) + \frac{z}{c} \mathbf{E}(\omega t). \tag{93}$$

This form of vector potential with the second term neglected will be used extensively in the next sections.

We can focus now on the magnetic field, which is given, within the long wavelength approximation, by

$$\mathbf{B} \sim \frac{1}{c} \nabla \times [z\mathbf{E}(\omega t)]. \tag{94}$$

This is obtained by using the expression of the vector potential in Eq. (93). Thus, to first order in the approximation (if $\mathbf{A} = \mathbf{A}(\omega t)$), we have $\mathbf{B} = 0$. However, even if the condition in Eq. (92) is fulfilled, if the electric field is strong enough, the magnetic field cannot be neglected by virtue of Eq. (94). Therefore, we need another condition for the validity of this approximation. It can be obtained from considerations using classical mechanics. The condition is that the electron displacement δ due to the magnetic force should be smaller than the system size, that is $\delta \ll d$. From the Lorentz equation, we know that the magnetic force is $|\mathbf{F}_{\mathrm{mag}}| \sim q|\mathbf{v}||\mathbf{B}| = m|\mathbf{a}_{\mathrm{mag}}|$, with $\mathbf{a}_{\mathrm{mag}}$ the acceleration due to the magnetic field. The velocity of the electron can be estimated from the electric force as $|\mathbf{F}_{\mathrm{elec}}| = q|\mathbf{E}| = m|\mathbf{a}|$. The typical time for the electron acceleration is one cycle: $\delta t \sim \omega^{-1}$, so we get that $|\mathbf{v}| \sim q|\mathbf{E}|/(m\omega)$. Then, using the fact that $|\mathbf{B}| \sim |\mathbf{E}|/c$ and $|\mathbf{a}_{\mathrm{mag}}|\delta t^2$, we get the condition

$$|\mathbf{E}| \ll \frac{mc\omega}{q} \sqrt{\frac{d}{\lambda}}, \tag{95}$$

where $\lambda = 2\pi c/\omega$ is the wavelength of the electromagnetic radiation. This condition on the electric field is required to neglect the effect of the magnetic field so that we can use the long wavelength approximation to first order. The latter is usually referred to as the dipole approximation: higher order terms corresponds to a multipole expansion.

4. Length, velocity and acceleration gauges

In this section we detail the main gauge choices commonly used in non-relativistic laser-molecule interaction. The starting point of this discussion is the Hamiltonian in the external field approximation written in the Coulomb gauge, and given by (we assume here that $U = 0$). We refer to [46] for additional details.

$$\widehat{H}^{(c)} = \frac{1}{2m} [\widehat{\mathbf{p}} - q\mathbf{A}(x)]^2 + V_c, \tag{96}$$

where $\widehat{\mathbf{p}} = -i\hbar\nabla$. As discussed previously, this Hamiltonian is obtained from the general gauge invariant Hamiltonian by imposing the gauge condition $\nabla \cdot \mathbf{A} = 0$.

4.1. Dipole approximation

To obtain the Hamiltonian in the velocity gauge, we use the dipole approximation described in the last section. This allows us to neglect the space dependence of the vector potential and we get

$$\widehat{H}^{(v)} = \frac{1}{2m} \left[\widehat{\mathbf{p}} - q\mathbf{A}^{(v)}(\omega t)\right]^2 + V_c(\mathbf{r}), \tag{97}$$

which is the Hamiltonian in the *velocity gauge* §. The vector potential can be evaluated at $\mathbf{r} = 0$, that is $\mathbf{A}^{(v)}(\omega t) = \mathbf{A}(\mathbf{r}, \omega t)|_{\mathbf{r}=0}$ because in the dipole approximation, we are assuming slow spatial variations.

Implementing the following unitary transformation

$$G^{(vl)}(t) := \exp\left[-iq\mathbf{A}^{(v)}(\omega t) \cdot \mathbf{r}/\hbar\right], \tag{98}$$

along with the corresponding gauge transformations of potentials (in other words, $F = \mathbf{A}^{(v)}(\omega t) \cdot \mathbf{r}$), lead to the *length gauge* representation:

$$\widehat{H}^{(l)} = \frac{1}{2m}\widehat{\mathbf{p}}^2 - q\mathbf{r} \cdot \mathbf{E}(\omega t) + V_c(\mathbf{r}). \tag{99}$$

Here, $\mathbf{E}$ is the electric field. It is obtained because in this gauge transformation, there are terms like $\partial_t\mathbf{A}^{(v)}(\omega t)$ that appear.

Still working under the dipole approximation and introducing the following unitary Kramers-Henneberger's transformation [47], also called Bloch-Nordsiek and introduced for the Dirac equation [44, 2, 48, 49]:

$$G^{(la)}(t) := \exp\left[-\frac{i}{\hbar}q\dot{\mathbf{r}} \int^t \mathbf{A}(\omega s)ds\right], \tag{100}$$

the length gauge Hamiltonian is transformed into

$$\widehat{H}^{(a)} = \frac{1}{2m}\widehat{\mathbf{p}}^2 + \frac{q^2}{2m}\mathbf{A}^2(\omega t) + V_c\left(\mathbf{r} - \frac{q}{m}\int^t \mathbf{A}(\omega s)ds\right). \tag{101}$$

It is important to note here that in this case, there is no gauge transformation on the electromagnetic potential because the Kramers-Henneberger transformation is not a gauge transformation, although it preserves the value of transition amplitudes at all times. Physically, it corresponds to a change of reference frame because the operator $G^{(la)}$ is a translation operator. Although this choice is often referred to as the *acceleration gauge*, it is actually not a gauge choice. For this reason, it has been called the *acceleration frame* by some authors [26], which is certainly a more precise terminology. The main interest of this transformation is to remove the transport operator $\mathbf{r} \cdot \mathbf{E}$ from the Hamiltonian: the reference frame "follows" the classical motion of the particle (without the Coulomb field). The counter-part is that the Coulomb potential is moving [50], which requires a special treatment in numerical calculations. Its main advantage is that the radiative interaction becomes negligible at large distances, such as in ionization, whereas the length gauge with action $\mathbf{r} \cdot \mathbf{E}$ diverges for $|\mathbf{r}| \to \infty$.

§ It should be noted here that the definition of velocity gauge used in laser-matter interaction is different from the one found in other contexts, such as in [16]. In the latter, the velocity gauge is a gauge condition which interpolates between the Coulomb and Lorentz gauge condition.

4.2. First order approximation

In the first order approximation, we neglect terms in $\dfrac{|\mathbf{k} \cdot \mathbf{r}|^2}{c^2}$ and of higher order and keep the first correction to the dipole approximation. This may be useful when we are interested in the effect of magnetic field and thus, this approach allows for a beyond-dipole approximation study. Starting from the Coulomb gauge and keeping the second order term in the long wavelength approximation, we get

$$\widehat{H}^{(2,v)} = \frac{1}{2m}\left[\widehat{\mathbf{p}} - q\mathbf{A}^{(v)}(\omega t)\right]^2 + \frac{1}{c}\mathbf{k}\cdot\mathbf{r}\left[\widehat{\mathbf{p}} - q\mathbf{A}^{(v)}(\omega t)\right]\cdot\mathbf{E}(\omega t) + V_c(\mathbf{r}), \tag{102}$$

where we neglected terms in $\dfrac{|\mathbf{k} \cdot \mathbf{r}|^2}{c^2}$ and of higher order. Note that the term $\mathbf{A}(\omega t) \cdot \mathbf{E}(\omega t)$ obtained in this way is a drift term induced by the magnetic fields.

The length gauge and acceleration frame representation are obtained in the same way as in the dipole approximation, using the same transformations. The corresponding Hamiltonians are given by

$$\widehat{H}^{(2,l)} = \frac{1}{2m}\widehat{\mathbf{p}}^2 + \left[\mathbf{r} - \frac{i}{c}(\mathbf{k}\cdot\mathbf{r})\nabla\right]\cdot\mathbf{E}(\omega t) + V_c(\mathbf{r})$$

$$H^{(2,a)} = \frac{1}{2m}\widehat{\mathbf{p}}^2 + \frac{q^2}{2m}\mathbf{A}^2(\omega t) + V_c\left(\mathbf{r} - \frac{q}{m}\int^t \mathbf{A}(\omega s)ds\right), \tag{103}$$

$$- \mathbf{r}\cdot\mathbf{E}(\mathbf{r},t) + q\mathbf{r}\cdot\nabla U(\omega t) + \frac{q^2}{m}\int^t \mathbf{A}(\omega s)ds\cdot\nabla U(\omega t). \tag{104}$$

4.3. Beyong long wavelength approximations

When the fields are sufficiently strong or when the frequency is large enough, the long wavelength approximation cannot be used. However, as shown in [51], it is still possible to derive equivalent Hamiltonians in the length gauge and acceleration frame, although their form is more intricate. Starting from the Hamiltonian in the Coulomb gauge, we can perform the unitary transformation given by

$$G^{(\text{all},vl)} := \exp\left(-i\frac{q}{\hbar}\mathbf{A}(\eta)\cdot\mathbf{r}\right), \tag{105}$$

where we defined $\eta := \omega t - \mathbf{k}\cdot\mathbf{r}$. From this unitary transformation, the Hamiltonian in the "generalized" length gauge without the long wavelength approximation, is given by [51]

$$\widehat{H}^{(\text{all},l)} = \frac{1}{2m}\widehat{\mathbf{p}}^2 - q\mathbf{E}(\eta)\cdot\mathbf{r} + V_c(\mathbf{r})$$

$$+ \frac{1}{2m}\left[\left(qk\mathbf{r}\cdot\frac{d\mathbf{A}}{d\eta}\right)^2 - q\mathbf{r}\cdot\left((\mathbf{k}\cdot\widehat{\mathbf{p}})\frac{d\mathbf{A}}{d\eta} + \frac{d\mathbf{A}}{d\eta}(\mathbf{k}\cdot\widehat{\mathbf{p}})\right)\right]. \tag{106}$$

The resulting Hamiltonian is similar to the one in the dipole approximation but has three new terms (shown on the second line of the last equation).

The generalization of the Kramers-Henneberger transformation can also be performed. The transformation is defined as

$$G^{(\text{all},la)} := \exp\left(\frac{i}{\hbar}\boldsymbol{\Sigma}\cdot\mathbf{p}\right), \tag{107}$$

where

$$\boldsymbol{\Sigma} := -\frac{q}{\omega m}\int_{\eta_0}^{\eta} \mathbf{A}(\eta')d\eta'. \tag{108}$$

This transformation yields a Hamiltonian given by

$$\widehat{H}^{(\text{all},l)} = \frac{1}{2m}\widehat{\mathbf{p}}^2 + \frac{q^2}{2m}\mathbf{A}^2(\eta) + V_c(\mathbf{r}+\boldsymbol{\Sigma})$$

$$+ \frac{1}{2m}\left[\left(k\frac{d\boldsymbol{\Sigma}}{d\eta}\cdot\mathbf{p}\right)^2 + \mathbf{k}\cdot\mathbf{p}\left(\frac{d\boldsymbol{\Sigma}}{d\eta}\cdot\mathbf{p}\right) + \left(\frac{d\boldsymbol{\Sigma}}{d\eta}\cdot\mathbf{p}\right)\mathbf{k}\cdot\mathbf{p}\right]. \tag{109}$$

Again, this gives a Hamiltonian which is similar to the one in the dipole approximation, with some additional terms.

Within this generalization to all orders of the wavelength approximation, the resulting expressions for the Hamiltonian is much more intricate and thus, certainly harder to solve. However, they may be useful to find other approximation schemes, as discussed in [51].

5. Analytical approximations

There are many approximation schemes that can be used to obtain solutions of the TDSE wave function. In this section, we focus on the usual perturbation theory, where the expansion parameter is the weak field, or the strong field approximation. We show that observables calculated in different gauges using these techniques are invariant under gauge transformations and describe some specific well-known examples.

5.1. Perturbation theory

In this paragraph, we describe gauge invariance of transition amplitudes when the electromagnetic field vanishes at the initial time $t = t_0$ and final time t_f. Although this may seem academic at first sight, this is a very important topic because this may be the source of computational errors if proper care is not taken. Our discussion starts with the effect of gauge transformations on the energy spectrum and eigenstates of the time-independent Schrödinger equation as this is used as a basis for time-dependent perturbation theory.

Let us consider a general gauge transformation G which relates the wave function in two different gauge choices. As usual, the wave functions obey (in this section, we use units in which $\hbar = 1$)

$$i\partial_t|\psi^{(1)}(t)\rangle = \widehat{H}^{(1)}(t)|\psi^{(1)}(t)\rangle \; , \; i\partial_t|\psi^{(2)}(t)\rangle = \widehat{H}^{(2)}(t)|\psi^{(2)}(t)\rangle. \tag{110}$$

Assuming the electromagnetic field vanishes at $t = t_0$ and $t = t_f$, we consider that the Hamiltonian will be time-independent in these limits‖ and thus, the solution of the Schrödinger equation reduces to an eigenvalue problem, for $t \in (-\infty, t_0] \cup [t_f, \infty)$:

$$E_{a,b}^{(1)}|\phi_{a,b}^{(1)}\rangle = \widehat{H}_{a,b}^{(1)}|\phi_{a,b}^{(1)}\rangle, \tag{111}$$

$$E_{a,b}^{(2)}|\phi_{a,b}^{(2)}\rangle = \widehat{H}_{a,b}^{(2)}|\phi_{a,b}^{(2)}\rangle, \tag{112}$$

where the subscript a refers to quantities or operator evaluated at $t = t_0$ while b is for $t = t_f$ (for instance, we have $\widehat{H}^{(1)}(t_0) = \widehat{H}_a^{(1)}$ and $\widehat{H}^{(1)}(t_f) = \widehat{H}_b^{(1)}$). It should be noted here that the eigenenergies for the two gauges may differ. This occurs because although the electromagnetic field vanishes in these limits, it is possible that the potentials (scalar or vector) still has a non-zero value and this will change the value of the eigenenergies: they will be shifted by a certain amount. This can be seen as follows. We have shown earlier that the Hamiltonian is not invariant but is changed under a gauge transformation. This transformation evaluated at $t = t_0, t_f$ is given by

$$\widehat{H}_{a,b}^{(2)} = G\widehat{H}_{a,b}^{(1)}G^\dagger - \partial_t F(\mathbf{x}, t)|_{t=t_0, t_f} \, , \tag{113}$$

where F is the arbitrary function defining the gauge transformation ($G = \exp(iF)$). Substituting this transformation into Eq. (112), we get

$$E_{a,b}^{(2)}|\phi_{a,b}^{(2)}\rangle = \left[G\widehat{H}_{a,b}^{(1)}G^\dagger - \partial_t F(\mathbf{x}, t)|_{t=t_0, t_f} \right] |\phi_{a,b}^{(2)}\rangle. \tag{114}$$

Using the gauge transformation of the wave function and multiplying by $\langle \phi_{a,b}^{(2)}|$ on the left, we obtain the following important condition:

$$\Delta E_{a,b} := E_{a,b}^{(1)} - E_{a,b}^{(2)} = \langle \phi_{a,b}^{(2)}| \, \partial_t F(\mathbf{x}, t)|_{t=t_0, t_f} \, |\phi_{a,b}^{(2)}\rangle. \tag{115}$$

This expression gives the relation between the eigenenergies expressed in different gauges, in the limit where the external electromagnetic field vanishes. At this point, it has been advocated by certain authors that the

‖ This however is not the most general case for the vanishing of the electromagnetic potential. Generally, a gauge where the potential is given by $\mathbf{A}(\mathbf{x}, t) = \nabla\phi(\mathbf{x}, t)$ and $U(\mathbf{x}, t) = \partial_t\phi(\mathbf{x}, t) + C$ also gives a vanishing potential for an arbitrary function, ϕ, and an arbitrary constant, C. In this case, the Hamiltonian is not time-independent.

most general transformation should be given by $F = f(\mathbf{x})$ (f here is an arbitrary function of $\mathbf{x}$, independent of time) such that $\partial_t F = 0$ and the energy shift is $\Delta E = 0$, on the basis that the spectrum should be invariant under gauge transformations [52, 53]. Our point of view on this is different: rather, we assume that the term $\partial_t F(\mathbf{x}, t)|_{t=t_0, t_f}$ is an analytical function of $\mathbf{x}$, such that it can be expanded as a Taylor series. We obtain

$$\Delta E_{a,b} = \sum_{n_x, n_y, n_z = 0}^{\infty} \frac{a_{n_x, n_y, n_z}}{n_x! n_y! n_z!} \mu_{a,b}^{(n_x, n_y, n_z)}, \tag{116}$$

where a_{n_x, n_y, n_z} are the coefficients of the Taylor series and $\mu_{a,b}^{(n_x, n_y, n_z)} := \langle \phi_{a,b}^{(2)} | x^{n_x} y^{n_y} z^{n_z} | \phi_{a,b}^{(2)} \rangle$ are the n_x, n_y, n_z'th moments. When only the zeroth moment is non zero, every eigenstate is shifted by the same amount under a gauge transformation: thus, the latter corresponds to an overall shifting of the zero point energy. However, when higher moments are involved, such as the first moment ($n_{x,y,z} = 1$) which corresponds to the average position of the electron in state a, then the energy shift of each state is different¶. Nevertheless, the transition amplitudes will be gauge invariant, as proven below.

Transition amplitudes between two energy states $(E_a^{(1,2)}, |\phi_a^{(1,2)}\rangle)$ to $(E_b^{(1,2)}, |\phi_b^{(1,2)}\rangle)$ are now considered. Physically, this corresponds to preparing the system in states $(E_a^{(1,2)}, |\phi_a^{(1,2)}\rangle)$ at $t = t_0$ where the external field vanishes, evolving these states to $t = t_f$ and projecting on the states $(E_b^{(1,2)}, |\phi_b^{(1,2)}\rangle)$. In laser-atoms or laser-molecule interactions, the states $\phi_{a,b}^{(1,2)}$ would typically corresponds to states of the atom or molecule (for states in the continuum, the sum on eigenenergies should be replaced by an integral on energy and a spectral density) while the time evolution would include the laser field. Thus, a certain gauge has to be chosen to compute these observables. We now show that the transition amplitudes are invariant under gauge transformations, which is in fact a particular case of a result that was discussed above. The transition amplitude from time t_0 to t_f (assuming the electromagnetic field vanishes at $t \in (-\infty, t_0] \cup [t_f, \infty)$) can be written as

$$A^{(1)} := \langle \psi^{(1)}(t_f) | \widehat{U}^{(1)}(t_f, t_0) | \psi^{(1)}(t_0) \rangle = \langle \phi_b^{(1)} | \widehat{U}^{(1)}(t_f, t_0) | \phi_a^{(1)} \rangle, \tag{117}$$

$$A^{(2)} := \langle \psi^{(2)}(t_f) | \widehat{U}^{(2)}(t_f, t_0) | \psi^{(2)}(t_0) \rangle = \langle \phi_b^{(2)} | \widehat{U}^{(2)}(t_f, t_0) | \phi_a^{(2)} \rangle, \tag{118}$$

where we take a single eigenstate as initial and final states. Using the gauge transformation on the eigenstates and the evolution operator, it is easy to show that $A^{(1)} = A^{(2)}$. What is more interesting however is that in some cases, it is more convenient to solve the time-independent Schrödinger equation in a specific gauge choice, say in gauge 1, but implement the time evolution in gauge 2. Then, we have that

$$A^{(2)} = \langle \phi_b^{(1)} | G^\dagger(t_f) \widehat{U}^{(2)}(t_f, t_0) G(t_0) | \phi_a^{(1)} \rangle. \tag{119}$$

The gauge operator included in this last expression is very important to preserve the gauge invariance of the transition amplitudes in this "mixed" representation and can be omitted only if $F(t_{0,f}) = 0$ [15, 26]. Once we have this expression, it is possible to calculate transition amplitudes using perturbation theory in a gauge independent way where the perturbation is the weak external field. However, obtaining a consistent perturbation expansion from this starting point requires the resummation of an infinite number of terms, which may be impossible in certain cases. This expansion can be performed much more easily if the preceding expression is given in the *interaction picture*, to which we now turn. The latter is required to obtain a perturbation theory where each term of the series is at a given order in the expansion parameter.

It is well-known that the evolution operator in the Schrödinger picture is related to the interaction picture by the following relation [54]:

$$\widehat{U}_{I,a,b}^{(1)}(t_f, t_0) = e^{i\widehat{H}_{a,b}^{(1)} t_f} \widehat{U}^{(1)}(t_f, t_0) e^{-i\widehat{H}_{a,b}^{(1)} t_0}, \tag{120}$$

$$\widehat{U}_{I,a,b}^{(2)}(t_f, t_0) = e^{i\widehat{H}_{a,b}^{(2)} t_f} \widehat{U}^{(2)}(t_f, t_0) e^{-i\widehat{H}_{a,b}^{(2)} t_0}. \tag{121}$$

¶ It may seem counterintuitive that the eigenvalues of the Hamiltonian operator are not gauge invariant. However, we would like to stress that these eigenenergies are not observable quantities. Rather, what is observable are the resonances in the transition amplitudes: these appear as peak in the spectrum which are detected as spectral lines in spectroscopic measurement. The position of these peaks are gauge invariant because they are physical observables. For certain gauge choices, these resonances have the same energies as the eigenvalues of $\widehat{H}$, in which case, it is possible to give a one-to-one correspondence between them (as in the length gauge, for instance). This correspondence is possible when the canonical momentum is equal to the mechanical momentum, but this is not true in general.

where the interaction Hamiltonian appearing in the evolution operator ($U_I(0,t) = \widehat{T}\exp(\int_0^t d\tau H_I(\tau))$ with $\widehat{T}$ being the time-ordered operator) are given by $\widehat{H}_{I,a,b}^{(1,2)}(t) = \widehat{H}^{(1,2)}(t) - \widehat{H}_{a,b}^{(1,2)}$. When we have $\widehat{H}_a^{(1,2)} = \widehat{H}_b^{(1,2)}$, the transition amplitudes in the interaction picture simply become

$$A^{(1)} := e^{-i(E_b^{(1)}t_f - E_a^{(1)}t_0)}\langle\phi_b^{(1)}|\widehat{U}_I^{(1)}(t_f,t_0)|\phi_a^{(1)}\rangle, \tag{122}$$

$$A^{(2)} := e^{-i(E_b^{(2)}t_f - E_a^{(2)}t_0)}\langle\phi_b^{(2)}|\widehat{U}_I^{(2)}(t_f,t_0)|\phi_a^{(2)}\rangle. \tag{123}$$

In the more general case, where $\widehat{H}_a^{(1,2)} \neq \widehat{H}_b^{(1,2)}$, first, we need to use the property of the evolution operator that $\widehat{U}^{(1,2)}(t_f,t_0) = \widehat{U}^{(1,2)}(t_f,t)\widehat{U}^{(1,2)}(t,t_0)$ for an arbitrary time $t \in]t_0, t_f[$. Then, using the transformation to the interaction picture, we get

$$A^{(1)} := e^{-i(E_b^{(1)}t_f - E_a^{(1)}t_0)}\langle\phi_b^{(1)}|\widehat{U}_{I,b}^{(1)}(t_f,t)e^{-i\widehat{H}_b^{(1)}t}e^{i\widehat{H}_a^{(1)}t}\widehat{U}_{I,a}^{(1)}(t,t_0)|\phi_a^{(1)}\rangle, \tag{124}$$

$$A^{(2)} := e^{-i(E_b^{(2)}t_f - E_a^{(2)}t_0)}\langle\phi_b^{(2)}|\widehat{U}_{I,b}^{(2)}(t_f,t)e^{-i\widehat{H}_b^{(2)}t}e^{i\widehat{H}_a^{(2)}t}\widehat{U}_{I,a}^{(2)}(t,t_0)|\phi_a^{(2)}\rangle. \tag{125}$$

Now, as in the Schrödinger picture, we write the transition amplitude in the second gauge choice as

$$A^{(2)} := e^{-i(E_b^{(2)}t_f - E_a^{(2)}t_0)}\langle\phi_b^{(1)}|G^\dagger(t_f)\widehat{U}_{I,b}^{(2)}(t_f,t)e^{-i\widehat{H}_b^{(2)}t}e^{i\widehat{H}_a^{(2)}t}\widehat{U}_{I,a}^{(2)}(t,t_0)G(t_0)|\phi_a^{(1)}\rangle. \tag{126}$$

This is the most general formula allowing to derive a perturbation expansion which is obtained by expanding the evolution operators and the exponentials. It is very important to note that if the gauge operator contains the electromagnetic potential, G should also be expanded to obtain the "true" leading order contribution.

5.1.1. Transition amplitude: a specific example   Although the transition amplitudes are identical in theory, some important differences may occur between different gauges when they are evaluated explicitly. This occurs because this usually requires the evaluation of infinite sums on intermediate states and although these sums yields the same result, their convergence depends on the gauge chosen. We will show this feature in a specific example which involves the the one and two-photon processes. We compare the perturbative calculation in the length and velocity gauges. As they are related by a unitary transformation, their corresponding transition matrices are identical, whether the resonance condition is fulfilled or not. Again, we refer to [15] for more complete explanations and calculations.

Following [15], we consider a linearly polarized laser pulse in the dipole approximation for which the vector potential, in the velocity gauge, can be written as $\mathbf{A}(t) = A(t)\cos(\omega t)\mathbf{e}_x$ where $t \in [0, T]$, with $T\omega \gg 1$. Here, $A(t)$ is an envelope function which gives the temporal pulse shape. We also assume a system with a single electron in the presence of an atom or molecule having bound states and characterized by a time-independent scalar potential V_c. We recall that the transition element from $|\phi_a\rangle$ to $|\phi_b\rangle$ is written as [15]

$$S_{a,b} = S_{ab}^{(l,v,a)} = \lim_{t_2\to+\infty}\lim_{t_1\to-\infty}\langle\phi_b^{(l,v,a)}|U^{(l,v,a)}(t_2,t_1)|\phi_a^{(l,v,a)}\rangle, \tag{127}$$

where $U^{(l,v,a)}$ is the evolution operator for (l) length, (v) velocity and (a) acceleration gauges. It is very convenient to evaluate the eigenstates of the system in the length gauge: in this case, the vector and scalar potential at $t = \pm\infty$ vanish for any pulse shapes because the electric field in these limits is zero and thus, the eigenenergies correspond to the physical bound states energies. Then, according to the discussion of the last section, we can write [15, 26]

$$S_{a,b} = \lim_{t_2\to+\infty}\lim_{t_1\to-\infty}\langle\phi_b^{(l)}|U^{(l)}(t_2,t_1)|\phi_a^{(l)}\rangle, \tag{128}$$

$$= \lim_{t_2\to+\infty}\lim_{t_1\to-\infty}\langle\phi_b^{(l)}|G^{(lv)\dagger}(t_2)U^{(v)}(t_2,t_1)G^{(lv)}(t_1)|\phi_a^{(l)}\rangle, \tag{129}$$

$$= \lim_{t_2\to+\infty}\lim_{t_1\to-\infty}\langle\phi_b^{(l)}|G^{(la)\dagger}(t_2)U^{(a)}(t_2,t_1)G^{(la)}(t_1)|\phi_a^{(l)}\rangle. \tag{130}$$

Then, these expressions can be expanded in powers of $q|A|$ to get an approximation of the transition amplitudes. Here however, it may be more convenient to use the interaction picture. It should be stressed again that since $G^{(la)}$ and $G^{(lv)}$ contain the potential, they should also be expanded.

It can be proven (see [15]), from a perturbative approach at order 1 in q (for 1-photon process) and order 2 in q (for 2-photon processes) and under the dipole approximation, that (here and in the following, we define $\hbar\omega_{ab} = E_a - E_b$):

- for a resonant 1-photon process $S_{ab}^{(v)} = S_{ab}^{(l)} = S_{ab}^{(a)}$.
- for a resonant 2-photon process, the transition element satisfy, in velocity gauge:

$$S_{ab}^{(v)} = q^2 \frac{2\pi}{i\hbar} Q_{ba}^{(v)} \left(\frac{A_0}{2}\right)^2 \delta(\omega_{ba} - 2\omega), \tag{131}$$

where the infinite sum over intermediate states is given by

$$Q_{ab}^{(v)} = \frac{1}{m^2} \sum_r \frac{\langle \phi_b | \mathbf{e}_x \cdot \mathbf{p} | \phi_r \rangle \langle \phi_r | \mathbf{e}_x \cdot \mathbf{p} | \phi_a \rangle}{\hbar(\omega - \omega_{ra})}, \tag{132}$$

and where $|\phi_r\rangle$ are the transition states. We note that in this case, because we are using the dipole approximation, the interaction term $\mathbf{A}^2$ has a zero contribution [15].

In the case of the length gauge we obtain an equation of the same form:

$$S_{ab}^{(l)} = q^2 \frac{2\pi}{i\hbar} Q_{ba}^{(l)} \left(\frac{A_0}{2}\right)^2 \delta(\omega_{ba} - 2\omega), \tag{133}$$

but now, the sum is

$$Q_{ab}^{(l)} = -\omega^2 \sum_r \frac{\langle \phi_a | \mathbf{e}_x \cdot \mathbf{r} | \phi_r \rangle \langle \phi_r | \mathbf{e}_x \cdot \mathbf{r} | \phi_a \rangle}{\hbar(\omega - \omega_{ra})}. \tag{134}$$

Using the fact that for any $|\phi_s\rangle$, $|\phi_t\rangle$, we have

$$\langle \phi_s | \mathbf{e}_x \cdot \mathbf{p} | \phi_t \rangle = i\omega_{st} m \langle \phi_s | \mathbf{e}_x \cdot \mathbf{r} | \phi_t \rangle \quad, \tag{135}$$

we can deduce

$$Q_{ab}^{(v)} = \sum_r \frac{\omega_{br}\omega_{ar}}{\hbar(\omega - \omega_{ra})} \langle \phi_a | \mathbf{e}_x \cdot \mathbf{r} | \phi_r \rangle \langle \phi_r | \mathbf{e}_x \cdot \mathbf{r} | \phi_a \rangle. \tag{136}$$

Out of resonance, when $2\omega \neq \omega_{ab}$, the transition amplitudes are equal $S_{ab}^{(l)} = S_{ab}^{(v)} = 0$ because the delta function $\delta(\omega - \omega_{ab})$ has a support only at resonance. It can then be proven that the contributions $Q_{ab}^{(l)}$ and $Q_{ab}^{(v)}$ are equal as infinite series at resonance, when $2\omega = \omega_{ab}$ [15]. Therefore, clearly, the transition amplitudes are gauge invariant to second order in perturbation theory in the example considered.

However, to obtain an explicit result for an observables related to these transition amplitudes, only a limited number of intermediate state can be evaluated: the sums has to be truncated because they cannot be evaluated in closed-form. It is clear that the convergence rate of series $Q_{ab}^{(l)}$ and $Q_{ab}^{(v)}$ are dependent on ω. That is: for $\omega \ll \omega_{mn}$, in the length gauge, we notice that the series converges more rapidly than in the velocity gauge as ω^2 is (much) smaller than $\omega_{br}\omega_{ra}$, for energy states $|\phi_r\rangle$ such that $|E_r - E_a| \gg 1$ and $|E_r - E_b| \gg 1$. The opposite occurs for $\omega \gg \omega_{mn}$. Denoting

$$q_{abr}^{(v)} = \frac{\omega_{br}\omega_{ar}}{\hbar(\omega - \omega_{ra})} \langle \phi_a | \mathbf{e}_x \cdot \mathbf{r} | \phi_r \rangle \langle \phi_r | \mathbf{e}_x \cdot \mathbf{r} | \phi_a \rangle, \tag{137}$$

$$q_{abr}^{(l)} = \frac{\omega^2}{\hbar(\omega - \omega_{ra})} \langle \phi_a | \mathbf{e}_x \cdot \mathbf{r} | \phi_r \rangle \langle \phi_r | \mathbf{e}_x \cdot \mathbf{r} | \phi_a \rangle, \tag{138}$$

we get the following results:
  - when ω is a low frequency compared to the transition energies ω_{ab}, for most r
$$\frac{q_{abr}^{(l)}}{q_{abr}^{(v)}} = \frac{\omega^2}{\omega_{br}\omega_{ar}} \ll 1, \tag{139}$$
  so that length gauge has a faster convergence.
  - when ω is a high frequency larger than ω_{ab}, for most r
$$\frac{q_{abr}^{(v)}}{q_{abr}^{(l)}} = \frac{\omega_{br}\omega_{ar}}{\omega^2} \ll 1, \tag{140}$$
  so that velocity gauge has a faster convergence.

This justifies the use of distinct gauges for different regimes.

5.1.2. Dynamic Stark shifts In the following we shortly discuss the frequency dependent shift in energy of any n'th atomic level (see [55, 56] for details). Physically, an atom (or molecule) immersed into a laser field of frequency ω. In the dipole approximation, we can assume that the electric field is given by $\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega t)$, where $\mathbf{E}_0$ is the electric field strength. The latter is used as a perturbation parameter in the weak field approximation such that perturbation theory can then be used to compute the energy shifts of atomic energy levels. A gauge independent expression of the Stark shift to second order in perturbation theory can be found in [56]. The general expression gives the energy of a given atomic level as a function of time. However, when the duration of the measurement ΔT is large compared to the period of the field, that is when $\Delta T \ll 2\pi/\omega$, a time-averaging procedure is required. It can then be shown that the energy shifts in the length gauge of the n'th level ($\delta E_n^{(l)}$) are (see [55, 56]):

$$\delta E_n^{(l)} = \frac{1}{2\hbar} \mathcal{P} \sum_m \frac{\omega_{nm}}{\omega_{nm}^2 - \omega^2} |\mathbf{E}_0 \cdot \mathbf{r}_{mn}|^2, \tag{141}$$

where $\hbar\omega_{nm} = E_n - E_m$ and where $\mathcal{P}$ stands for the principal part (which is only relevant for continuum states included in the sum). Also, we defined the matrix element $\mathbf{r}_{mn} := \langle \phi_m | \mathbf{r} | \phi_n \rangle$, where $\phi_{m,n}$ are the eigenstates of the laser-free Hamiltonian. For large laser frequency ω, the energy shift tends to the ponderomotive energy U_p which is positive. That is for $\omega \gg \omega_{nm}$

$$\delta E_n^{(l)} \sim -\frac{1}{2\hbar\omega^2} \sum_m \omega_{mn} |\mathbf{E}_0 \cdot \mathbf{r}_{mn}|^2 = \delta E_c := \frac{E_0^2}{4\omega^2} = U_p. \tag{142}$$

This is a simple consequence of the Thomas-Reiche-Kuhn sum formula $\sum_m \omega_{mn} |\mathbf{r}_{mn}|^2 = -1/2$. The total energy shift contains a continuum, I, contribution and a bound state, b, contribution

$$\delta E_c = \Delta E_b^{(l)} + \Delta E_I^{(l)}. \tag{143}$$

from (141) and (143), we deduce that

$$(\delta E_I^{(l)})_n = -\frac{1}{2\omega^2} \sum_m \frac{\omega_{nm}^3}{\omega_{nm}^2 - \omega^2} |\mathbf{E}_0 \cdot \mathbf{r}_{mn}|^2, \tag{144}$$

and for large frequencies $\omega \gg \omega_{nm}$

$$(\delta E_I^{(l)})_n \sim -\frac{E_0^2}{4\omega^4} \langle (\nabla \cdot \mathbf{E}_0)^2 V \rangle_n. \tag{145}$$

Similar computations in the velocity gauge, leads to, for $\omega \gg \omega_{mn}$,

$$(\delta E_b^{(a)})_n = -\frac{1}{2\hbar\omega^2} \sum_m \frac{\omega_{nm}^3}{\omega_{nm}^2 - \omega^2} |\mathbf{E}_0 \cdot \mathbf{r}_{mn}|^2 \sim 4\pi \frac{E_0^2}{4\omega^4} \rho_n(0), \tag{146}$$

where ρ_n denotes the nucleus electronic density and explain the Lamb shift of s atomic states. Details can be found in [55]

5.1.3. Radiative matrix element approximation We recall that the elements of the radiative matrix, for states $|\phi_a\rangle$, $|\phi_b\rangle$ are written as:

$$i\hbar \frac{\mathbf{p}_{ab}}{m} = \langle \phi_a | [\mathbf{r}, \widehat{H}_0] | \phi_b \rangle = \hbar\omega_{ab} \mathbf{r}_{ab}, \tag{147}$$

where $\hbar\omega_{ab} = E_a - E_b$ and $\widehat{H}_0$ the laser-free Hamiltonian. This gives directly a relation between the momentum radiative matrix elements (velocity gauge) and the dipole radiative matrix elements (length gauge) and $\mathbf{A}(t) = \mathbf{E}c/\omega$:

- In the length gauge, the dipole radiative matrix element is written as: $\mathbf{r}_{ab} \cdot \mathbf{E}$.
- In the velocity gauge the momentum radiative matrix elements is written as:

$$\frac{\mathbf{A} \cdot \mathbf{p}_{ab}}{mc} = i \frac{\omega_{ba}}{\omega} \mathbf{r}_{ab} \cdot \mathbf{E}, \tag{148}$$

The equality between this two quantities occurs only in resonance $\omega = \omega_{ba}$. As a consequence for $\omega \ll \omega_{ba}$, such transitions will be important in the calculation of transition amplitudes in the Coulomb gauge, see [2].

23

- In the acceleration gauge for perturbative fields, from Taylor's expansion of the shifted Coulomb potential:

$$V(\alpha(t) + \mathbf{r}) = V(\mathbf{r}) + \alpha(t) \cdot \nabla V + ..., \tag{149}$$

with $i\hbar = \nabla V = [H_0, \mathbf{p}]$, then $(\nabla V)_{ab} = i\omega_{ba}\mathbf{p}_{ab}$, we obtain the realation linking the radiative transition matrix elements in velocity and acceleration gauges

$$\alpha(t) \cdot (\nabla V)_{ab} = i\frac{\omega_{ba}}{\omega}\Big(\frac{\mathbf{A} \cdot \mathbf{p}_{ab}}{mc}\Big) = -\frac{\omega_{ba}^2}{\omega^2}\mathbf{E} \cdot \mathbf{r}_{ab}. \tag{150}$$

At near resonance, there is again agreement with the Coulomb gauge radiative coupling.

At high frequency $\omega \gg \omega_{ab}$, we remark that the acceleration matrix elements will be smaller than the corresponding ones in the 2 other gauges. As a consequence we can expect a faster convergence of perturbative computations in the acceleration gauge, in this regime.

5.2. Strong Field Approximation (SFA)

SFA is a very common non-perturbative approach to study the interaction of bound systems with intense lasers: only the ground state and continuum contributions are taken into account to represent the wave function for an intense laser-molecule interaction and is usually based on a Single Active Electron approximation, which allows the extension to multi-electron systems [6]. Early work on the equivalent gauges for strong field physics has emphasized the difference between the length and the velocity gauges. It was shown that the TDSE expressed in center of mass (c.m.) coordinates and relative coordinates is nonseparable beyond the dipole approximation in the length gauge, whereas in the velocity gauge, separation of variables is straightforward [57, 58]. In the dipole approximation and length gauge, the radiative interaction is described by a scalar potential $-\mathbf{E}\cdot\mathbf{r}$ whereas in the velocity gauge the interaction involves a gradient, $\mathbf{A}\cdot\nabla$, reminiscent of nonradiative interaction in molecular physics [2]. Recently the acceleration representation has been generalized beyond the dipole approximation [59] as this representation is most convenient for high frequencies where "atomic stabilization" is expected to occur at high intensities. The SFA theory of HHG is basically a time-dependent two potential Distorted Wave Born-Approximation (DWBA), where the final state of the electron can be described as a time dependent dressed state, called a Volkov state [60] (see also Appendix A), whereas the initial state, due to its high ionization potential energy I_P, is considered unperturbed. Calculations of photoionization based on Volkov final state wave functions were first done by Keldysh [61], and later by Faisal [62] and Reiss [63]. It was also re-examined recently for circular polarization [64, 65]. This strong field approach produces very accurate results for multiphoton detachment for negative ions since Coulomb potentials are absent in the ionization process in both length and velocity gauges [66, 67]. Later work by Bauer et al. [68] showed that the prediction of the two gauges can differ qualitatively for ionization of negative ions and that the length gauge SFA matches the exact TDSE numerical solutions [68]. More recently, it has been shown that the SFA used in models for computing HHG invalidates the Ehrenfest theorem [69]. Gordon and Kartner have shown in fact that the SFA can be improved by using the acceleration radiative interaction ∇V in the emission matrix element since then the SFA HHG amplitude is correct to first order in the Coulomb potential $V(\mathbf{r})$ [70]. The SFA encounters further difficulties in interpreting Molecular High Order Harmonic Generation (MHOHG) spectra due to multi-center nuclear interference effects both in the ionization and the recombination processes [71, 72]. In the acceleration representation, each nucleus contributes to the MHOHG amplitude via the multicenter nature of the total Coulomb force, $-\nabla V$. This multicenter effect is absent in both length and velocity gauges [72].

The non-invariance of SFA under gauge transformation is an issue which is also studied in [73], [74]. We here give some details about this issue. As often noticed (see also [75]) and recalled above, the ionization rates and energy distributions of strong-field photo-ionization differ depending of the choice of the gauge (length, velocity or acceleration). However, there is no definitive conclusion regarding the most appropriate (all give relevant results depending of the physical problem under consideration [76], [68]). We note that Faisal [77] showed that length and velocity gauge SFA amplitudes under the dipole approximation are equivalent at all orders under some assumptions on the initial and final state partitions of the Hamiltonian. Details of

what follows can be found in [76]. We recall that the ionization amplitude from $|\psi_0\rangle$ (ground state) to the continuum $|\psi_I\rangle$ is defined as

$$S_{0,I} = \lim_{t_2 \to +\infty} \lim_{t_1 \to -\infty} \langle \phi_I | \widehat{U}(t_2, t_1) | \phi_0 \rangle. \tag{151}$$

The propagator $\widehat{U}$ is a priori gauge dependent and is defined as follows:

$$\widehat{U}(t_1, t_2) = \widehat{U}_0(t_1, t_2) - i \int_{t_1}^{t_2} d\tau \, \widehat{U}(t_1, \tau) \widehat{H}_{\text{laser}}(\tau) \widehat{U}_0(\tau, t_2), \tag{152}$$

where $\widehat{U}_0$ is the time-evolution propagator associated to the laser-free operator and $\widehat{H}_{\text{laser}}^{(l,v)}$ is the interaction Hamiltonian that includes the laser field in the length or velocity gauge, respectively. Then, the transition amplitude is given by

$$S_{0,I} = -i \lim_{t_2 \to +\infty} \int_{-\infty}^{t_2} d\tau \langle \phi_I(t_2) | \widehat{U}(t_2, \tau) \widehat{H}_{\text{laser}}^{(l,v)}(\tau) | \phi_0(\tau) \rangle. \tag{153}$$

The SFA approximation for the ionization amplitude consists of replacing the exact final state wave function $|\psi_I\rangle$ by the Volkov one $|\psi_{\text{volkov}}\rangle$ (see Appendix A for the definition of Volkov solution):

$$\lim_{t_2 \to \infty} \langle \psi_I | \widehat{U}(t_2, t_1) = \langle \psi_{\text{volkov}}(t_1) |, \tag{154}$$

with $\mathbf{A}(\pm\infty) = \mathbf{0}$. Under some assumptions [76]'s authors show that the two representations (in fact in any gauge) are equivalent to the length gauge representation.

$$S_{0,I} = -i \int_{\mathbb{R}} dt \langle \psi_{\text{volkov}}(\tau) | \widehat{H}_{\text{laser}}^{(l,v)}(\tau) | \psi(t) \rangle. \tag{155}$$

As mentioned in [68], for $t < \tau$ the electron is bound and the laser-electron interaction is neglected. For $t = \tau$, ionization occurs and the electron then moves rapidly out of the range of the Coulomb potential. Keitel et al. have studied a gauge-invariant relativistic version of SFA in [78]. They also provide a gauge invariant ionization amplitude expression which coincides with the SFA in the length gauge, considered as more adequate for ionization process (ATI or nonsequential double-ionization (NSDI)).

6. Numerical approximations

This section is devoted to the numerical computation of TDSE in the velocity, length and acceleration gauges. The motivation comes from the fact that although in theory, the transition probability, dipole moments, velocities and accelerations are equal in all the discussed gauges, in practice due to approximations (continuous or discrete) the equality of these quantities does not hold in general. In addition, the choice of the mathematical structure (which is gauge dependent) of the TDSE often guides the choice of the numerical method. TDSE in the velocity gauge, contains a transport operator which is more accurately approximated using finite difference or finite volume techniques. In contrast, the Laplace operator is particularly well approximated using variational techniques, such as finite element or spectral methods. These aspects will be discussed in this section. For each approach, the principle of the numerical method is summarized and an appropriate application (at least the first steps of the discretization) of TDSE's is proposed. After detailing numerical methods, we describe the non-perturbative process of harmonic generation. This phenomenon, which is usually studied theoretically by using numerical solutions of TDSE, is an example where the gauge choice is instrumental in obtaining accurate results.

6.1. Numerical methods

We start this section with a discussion of a fundamental tool used to numerically solve Partial Differential Equation (PDE): the time splitting method. We then present several numerical techniques which are commonly used to solve TDSE's in different gauges.

6.1.1. Splitting The TDSE involves the coupling of several operators of different type: hyperbolic $(\partial_t - \mathbf{A} \cdot \nabla)$, parabolic $(\partial_t - \triangle)$ and algebraic $(V_c$ or $\mathbf{r} \cdot \mathbf{E})$. The general idea of splitting methods is to separate the main equation into simpler equations which can be solved more easily. Direct (no splitting) approaches are also commonly used and will be discussed later, especially since this can lead to very accurate numerical solutions (spectral convergence, exact). We start by detailing the general principle of splitting methods.

- **Mathematical Splitting: Trotter's formula** [79]. We consider the following equation:

$$u_t = \sum_{k=1}^{M} \widehat{A}_k u, \ u(\mathbf{r}, 0) = u_0(\mathbf{r}) \tag{156}$$

where $(\widehat{A}_k)_{k=\{1,\cdots,M\}}$ is a finite sequence of (spatial differential and algebraic) operators. Formally, the solution (via time propagators) can be written as $u(\mathbf{r}, t) = e^{t \sum_{k=1}^{M} \widehat{A}_k} u_0(\mathbf{r})$ if the operators are time-independent[+]. The exponential is defined by the Trotter-Kato's formula which states that

$$e^{t \sum_{k=1}^{M} \widehat{A}_k} = \lim_{N \to \infty} \left(\Pi_{k=1}^{M} e^{t \widehat{A}_k / N} \right)^N. \tag{157}$$

- **Numerical Splitting**. A discrete version of Trotter-Kato's formula is the well-known time-splitting method. From $[0, dt]$ and rather than solving (156) [81], we set

$$\begin{cases} u_t &= \widehat{A}_1 u, & u(\mathbf{r}, 0) = u_0(\mathbf{r}), \\ u_t &= \widehat{A}_2 u, & u(\mathbf{r}, 0) = u_1(\mathbf{r}), \\ \cdots & \cdots & \cdots & \cdots, \\ u_t &= \widehat{A}_M u, & u(\mathbf{r}, 0) = u_M(\mathbf{r}), \end{cases} \tag{158}$$

where $u_k(\mathbf{r}, dt)$ is solution on $[0, dt]$, to

$$u_t = \widehat{A}_k u, \ u(\mathbf{r}, 0) = u_{k-1}(\mathbf{r}), \ k \in \{1, \cdots, M\}. \tag{159}$$

This in fact is equivalent to applying Trotter-Kato's formula as follows:

$$e^{dt \sum_{k=1}^{M} \widehat{A}_k} = \lim_{N \to \infty} \left(\Pi_{k=1}^{M} e^{dt \widehat{A}_k / N} \right)^N, \tag{160}$$

and taking $N = 1$. The error between the exact solution to (156) and approximate solution to (158) can easily be evaluated and is equal in that case to:

$$u(\mathbf{r}, dt) = e^{dt \sum_{k=1}^{M} \widehat{A}_k} u_0(\mathbf{r}) = \Pi_{k=1}^{M} e^{dt \widehat{A}_k} u_0(\mathbf{r}) + \mathcal{O}(dt^2). \tag{161}$$

Errors are due to the non-commutativity of operators, [81]. More precisely for $M = 2$

$$\begin{cases} u_t = \widehat{A}_1 u, & u(\mathbf{r}, 0) = u_0(\mathbf{r}), \\ u_t = \widehat{A}_2 u, & u(\mathbf{r}, 0) = u_1(\mathbf{r}). \end{cases} \tag{162}$$

For $t \in [0, dt]$, we formally have the identity

$$\exp\left(dt(\widehat{A}_1 + \widehat{A}_2) \right) = \exp(dt\widehat{A}_1) \exp(dt\widehat{A}_2) + dt^2[\widehat{A}_1, \widehat{A}_2]/2 + \cdots, \tag{163}$$

where $[\widehat{A}_1, \widehat{A}_2] = \widehat{A}_1 \widehat{A}_2 - \widehat{A}_2 \widehat{A}_1$ is the commutator. When $\widehat{A}_1$ and $\widehat{A}_2$ commute the splitting is exact. More generally for M operators, if $[\widehat{A}_k, \widehat{A}_l] = 0$ for all k and l in $\{1, \cdots, M\}$, splitting the equation in M equations does not introduce any error.

Higher order splitting approaches are naturally possible, such as the famous Strang splitting [82]. Considering the equation

$$u_t(\mathbf{r}, t) = \widehat{A}_1 u(\mathbf{r}, t) + \widehat{A}_2 u(\mathbf{r}, t) \text{ on } [0, dt], \qquad u(\mathbf{r}, 0) = u_0(\mathbf{r}), \tag{164}$$

[+] If the operators are time-dependent and do not commute at different times, the solution will be given by $u(\mathbf{r}, t) = \widehat{T} \exp\left[\int_0^t dt' \sum_{k=1}^{M} \widehat{A}_k(t') \right] u_0(\mathbf{r})$, where $\widehat{T}$ is the time-ordering operator. Splitting methods can be extended to this latter case (see [80]).

where $\widehat{A}_1$ and $\widehat{A}_2$ are two algrebraic or differential spatial operators, the principle of Strang's splitting consists of approximating the exact solution $u_{\text{exact}}(\mathbf{r}, dt) = \exp\left((\widehat{A}_1 + \widehat{A}_2)dt\right)u_0(\mathbf{r})$, by solving

$$\begin{cases} u_t = \widehat{A}_1 u \text{ on } [0, dt/2], & u(\mathbf{r}, 0) = u_0(\mathbf{r}), \\ u_t = \widehat{A}_2 u \text{ on } [0, dt], & u(\mathbf{r}, 0) = u_1(\mathbf{r}), \\ u_t = \widehat{A}_1 u \text{ on } [0, dt/2], & u(\mathbf{r}, 0) = u_2(\mathbf{r}), \end{cases} \tag{165}$$

The calculated solution is given by

$$u_{\text{approx}}(\mathbf{r}, dt) = \exp\left(\widehat{A}_1 dt/2\right) \exp\left(\widehat{A}_2 dt\right) \exp\left(\widehat{A}_1 dt/2\right) u_0(\mathbf{r}). \tag{166}$$

It can easily be proven that in that case the error between the exact and approximate solution is a $\mathcal{O}(dt^3)$. In practice, for TDSEs, we will take $\widehat{A}_1 = \triangle$, $\widehat{A}_2 = V_c + \mathbf{A} \cdot \nabla$ or $\widehat{A}_2 = V_c + \mathbf{r} \cdot \mathbf{E}$. The advantage of this approach comes from the fact that $u_t = \widehat{A}_k u$ $(k = 1, 2)$ can be very accurately solved, at least more than $u_t = \widehat{A}_1 u + \widehat{A}_2 u$. The price to pay is that using a splitting method requires to choose dt sufficiently small to reduce the error. The splitting error is obviously added to the discretization errors coming from the approximation of equations (158). Splittings are extensively used with spectral, real space or even exact methods.

The generalization to high order splitting methods for solving TDSE's is described in [83, 42].

Before describing other numerical methods and discretization, we propose a short discussion which attempts to link the TDSE to fluid dynamics equations (such as the transport and Navier-Stokes equations). These fluid equations have been studied extensively by mathematicians and physicists, and many techniques have been developed to analyze and solve numerically these equations. Thus, the formal analogy existing between TDSE's and fluid dynamics equations allows to use these techniques in the context of quantum mechanics, [84, 50]. Our remark is more specifically devoted to find connections between the TDSE written in the velocity gauge, with usual transport problems as well as incompressible viscous or non-viscous fluid flow equations. The TDSE involves a kinetic operator, $\triangle$, as well as a transport operator ∇:

$$i \frac{\partial}{\partial t}\psi = -\frac{1}{2m}\triangle\psi + i\mathbf{A} \cdot \nabla\psi + \frac{1}{2m}\mathbf{A}^2\psi. \tag{167}$$

It is possible to solve numerically this equation by splitting it into two parts (following the previous discussion):

$$i \frac{\partial}{\partial t}\psi = -\frac{1}{2m}\triangle\psi + \frac{1}{2m}\mathbf{A}^2\psi, \tag{168}$$

and

$$\frac{\partial}{\partial t}\psi + \mathbf{A} \cdot \nabla\psi = 0. \tag{169}$$

Under the Coulomb gauge, the last equation is a transport equation equivalent to the following conservation law:

$$\frac{\partial}{\partial t}\psi + \text{div}(\mathbf{A}\psi) = 0. \tag{170}$$

The general solution to this equation is obtained using the method of *characteristics*. Defining the characteristics as integral curves of

$$\dot{\mathbf{X}}(t) = \mathbf{A}\left(\mathbf{X}(t), t\right), \mathbf{X}(0) = \mathbf{X}_0. \tag{171}$$

The solution is constant $\frac{d\psi}{dt}\left(\mathbf{X}(t), t\right) = 0$ along these curves, which allows to deduce the exact solution. This approach naturally fails when viscosity (real or complex) is added.

A simple connection can be found with incompressible fluid flows. Under incompressibility condition $\nabla \cdot \mathbf{u} = 0$, the conservation of momentum of a non-viscous fluid of density ρ, becomes

$$\frac{\partial}{\partial t}\mathbf{u} + \text{div}(\rho\mathbf{u} \otimes \mathbf{u} + P) = \mathbf{0}, \tag{172}$$

where P is the pressure and $\mathbf{u}$ the fluid velocity. Although it is tempting to generalize the comparison between TDSE in the velocity gauge and the momentum equation for incompressible flows, the solution type for (170) (which is linear) and (172) (which is nonlinear, in fact quasi-linear) maybe very different [85]. Including now viscous effects, the Navier-Stokes equations is written as:

$$\rho\frac{\partial}{\partial t}\mathbf{u} + \rho\mathbf{u}\cdot\nabla\mathbf{u} = \nabla\cdot\sigma, \tag{173}$$

where for Newtonian fluids, the fluid viscosity μ is constant and $\nabla\cdot\sigma$ writes $\mu\triangle\mathbf{u} - \nabla P$. For non-newtonian fluids μ is no more constant and can even be complex. We refer to [86] for the interested readers. It is then interesting to notice the presence of a "complex viscous" term, which allows now to make a direct connection via the complex viscous and transport terms, with (167) and (168). Therefore, some mathematical and numerical techniques to solve the TDSE can be derived or adapted from fluid mechanics. The interested readers could explore further this question.

6.1.2. Galerkin Methods The main principle of Galerkin's method is to search for the wave function ψ in the form:

$$\psi(\mathbf{r},t) = \sum_n c_n(t)\phi_n(\mathbf{r}), \tag{174}$$

where $(\phi_n)_n$ is a basis of $L^2(\mathbb{R}^3,\mathbb{C})$ containing the exact wave function. Note that by doing this, the continuous states become discrete in the numerical calculation. The Galerkin methods are more adapted to solve TDSE in the length gauge than in the velocity gauge. This comes from the fact that for stability reasons, the discretization of transport operators (such as $\mathbf{A}\cdot\nabla$ in TDSE written in the velocity gauge) necessitates a numerical upwinding (see details in Section 6.1.3). By default, Galerkin's methods are centred and as a consequence provide unstable approximate transport operators (some empirical techniques exist to circumvent this issue, such as the Streamline Upwind Petrov Galerkin method usually used in computational fluid dynamics). The Galerkin method proceeds in the following way. We formally write the TDSE as $(\widehat{H} = -\triangle + V_c + \mathbf{r}\cdot\mathbf{E})$

$$i\frac{\partial}{\partial t}\psi = \widehat{H}\psi. \tag{175}$$

We multiply by a test function $\phi_k \in L^2(\mathbb{R}^3)$ and integrate on space, which transforms the partial differential equation into a variational formulation. Denoting $\langle\cdot,\cdot\rangle$ the inner product in $L^2(\mathbb{R}^3,\mathbb{C})$, that is

$$\langle\phi_1,\phi_2\rangle = \int_{\mathbb{R}^3}\phi_2^*(\mathbf{x})\phi_1(\mathbf{x})d^3\mathbf{x}, \qquad \int_{\mathbb{R}^3}|\phi|^2(\mathbf{x})d^3\mathbf{x} = \langle\phi,\phi\rangle, \tag{176}$$

this becomes

$$i\sum_n \dot{c}_n(t)\langle\phi_n,\phi_k\rangle = \sum_n\langle\widehat{H}\phi_n,\phi_k\rangle. \tag{177}$$

By integrating by parts:

$$\begin{aligned} i\sum_n \dot{c}_n(t)\langle\phi_n,\phi_k\rangle &= -\sum_n c_n(t)\langle\nabla\phi_n,\nabla\phi_k\rangle \\ &\quad + \sum_n c_n(t)\langle[V_c(\mathbf{r}) + \mathbf{r}\cdot\mathbf{E}(t)]\phi_n,\phi_k\rangle. \end{aligned} \tag{178}$$

Trucating the sum and keeping the N first terms, the set of equations can be rewritten as:

$$A\dot{\mathbf{C}}(t) = \big(B + D(t)\big)\mathbf{C}(t), \tag{179}$$

where $A_{nk} = \langle\phi_n,\phi_k\rangle$, $B_{nk} = \langle\nabla\phi_n,\nabla\phi_k\rangle$ and $D_{nk}(t) = \langle V_c(\mathbf{r}) + \mathbf{r}\cdot\mathbf{E}(t)\phi_n,\phi_k\rangle$ are $N\times N$ complex matrices and $\mathbf{C}(t) = \big(c_1,(t),\cdots,c_N(t)\big)^T \in \mathbb{C}^N$.

The time discretization leads to the solving of a linear system. For instance if a simple forward Euler discretization of the time derivative is applied, (179) becomes

$$A\mathbf{C}^{n+1} = A\mathbf{C}^n + dt\big(B + D^n\big)\mathbf{C}^n. \tag{180}$$

More elaborated time discretizations are of course more appropriate from a stability as well as accuracy points of view.

Spectral Methods What characterizes spectral methods is the non-locality of the basis function, which have support in all the spatial domain. Different choices of basis are possible, the most common being:

- $\phi_n(\mathbf{r}) = \exp(in\mathbf{r})$, corresponding to Fourier series expansion.
- Orthogonal polynomials (Hermite, Legendre,...).
- Spherical harmonics.
- Eigenfunction decomposition. This method requires the eigenfunctions:

$$\widehat{H}_0\phi_n = E_n\phi_n. \tag{181}$$

Although this is the most accurate basis (as the solution is decomposed on the exact orbitals), it requires important preliminary work, consisting of determining large sets of bound states of the laser-free Hamiltonian. Perturbation theory for solving TDSE's is also based on this decomposition.

The spectral approach is particularly appropriate for approximating the kinetic operator, in particular using a Fourier decomposition (which transforms the kinetic operator into -$\|\mathbf{k}\|^2$). Spectral (or exponential) convergence is possible in general, and Gibbs' phenomena (oscillations near singularities) do not appear (in general) due to the regularity of the solution. The consequence is then a fast convergence. For any smooth function ψ, say 2π-periodic, a $N-$term Fourier series approximation ψ_h^N is such that (spectral convergence)

$$\|\psi - \psi_h^N\| \leqslant C(q)\exp(-N)\|\psi\|_{L^2([0,2\pi])}, \tag{182}$$

where

$$\psi_h^N(x) = \sum_{|n|\leqslant N} \widehat{\psi}_n \exp(inx), \tag{183}$$

and

$$\widehat{\psi}_n = \frac{1}{2\pi}\int_0^{2\pi} \psi(x)\exp(-inx)dx. \tag{184}$$

These methods are then very attractive (easy to implement and very fast convergence). We refer to [87] for interested readers.

Finite Element Methods (FEM) [88], [89], [90]. As a Galerkin method, the finite element approximation is very similar to spectral methods. The main difference comes from the fact that the basis functions have a bounded support and are only piecewise regular. Again, this method allows to consider non-regular domains and non-uniform meshes (useful to capture singularities or large gradients). It is also based on the variational principle given by Eq. (178). The basis functions $(\phi_k)_k$ are for instance, piecewise Lagrange polynomials (or B-splines [91, 92, 93]) with a localized support. This allows in particular to increase the sparsity of the "mass" ($\langle\int \phi_i\phi_j\rangle_{ij}$) and "stiffness" ($\langle\nabla\phi_i\nabla\phi_j\rangle_{ij}$) matrices. Sparsity of the matrices (many zero entries) is crucial for computational efficiency (data storage and computational complexity). In addition, non regular solutions can be accurately captured provided.

Many convergence results exist, in particular for Lagrange finite element methods. The basis functions are piecewise polynomials of degree k equal to 1, at one node and 0 otherwise. Typical error estimates for the wave function in Sobolev space, that is for $\psi \in H^k(\mathbb{R}^n)$ $(\nabla^{(l)}\psi \in (L^2(\mathbb{R}^n))^3$, $l = 0, ..., k)$ and piecewise approximation by polynomials of degree k is:

$$\|\psi - \psi_h\| \leqslant Ch^{k+1}\|\psi\|_{L^2([0,2\pi])}, \tag{185}$$

for h, the largest cell area and C a positive constant.

Collocation Methods. Starting again from

$$\psi(\mathbf{r}, t) = \sum_n c_n(t)\phi_n(\mathbf{r}), \tag{186}$$

where $(\phi_n)_n$ is a basis of $L^2(\mathbb{R}^3)$. We again formally write the equation

$$i\frac{\partial}{\partial t}\psi = \widehat{H}\psi. \tag{187}$$

We multiply this time by test functions which are δ-functions in freely (typically closer to each other close to singularities) selected grid points $(\mathbf{r}_k)$. Defining the test functions by $\theta_k = \delta(\mathbf{r}_k)$, we get

$$i\sum_n \dot{c}_n(t)\langle\phi_n, \theta_k\rangle = -\sum_n c_n(t)\langle\triangle\phi_n, \theta_k\rangle + \sum_n c_n(t)\langle V_c(\mathbf{r}) + \mathbf{r}\cdot\mathbf{E}(t)\phi_n, \theta_k\rangle, \tag{188}$$

which this time leads to a set of equations:

$$i\sum_n \dot{c}_n(t)\phi_n(\mathbf{r}_k) = -\sum_n c_n(t)\triangle\phi_n(\mathbf{r}_k) + \sum_n c_n(t)\big(V_c(\mathbf{r}_k) + \mathbf{r}_k\cdot\mathbf{E}(t)\big)\phi_n(\mathbf{r}_k). \tag{189}$$

In particular a space discretization (on a unstructured grid) of the Laplacian is then necessary. This is usually done using Taylor expansion techniques. The time discretization leads to a system of the form (180).

In general, these collocation approaches do not necessitate any splitting to be highly accurate. Due to the total freedom on the grid point locations, they are very attractive for approximating (smoothly) singularities. The full convergence analysis of this approach is however still largely open.

6.1.3. Direct Real Space Methods **Finite Difference Methods (FDM)**. These methods constitute the most simple approaches to discretize TDSE's. The principle consists of approximating the spatial derivatives as follows. In $\mathbf{r}_0 = (x_0, y_0, z_0)$ and time t_0

$$\partial_x\psi(x_0, y_0, z_0, t_0) \sim \frac{\psi(x_0, y_0, z_0, t_0) - \psi(x_0 - dx, y_0, z_0, t_0)}{dx}, \tag{190}$$

or

$$\partial_x\psi(x_0, y_0, z_0, t_0) \sim \frac{\psi(x_0 + dx, y_0, z_0, t_0) - \psi(x_0 - dx, y_0, z_0, t_0)}{2dx}. \tag{191}$$

Consistency (correct approximation of the equation), stability (numerical solution remains bounded) and accuracy questions are discussed in details in [94]. Typically, Crank-Nicolson's scheme is used to approximate (here in 1-d) TDSE in the length gauge:

$$\partial_t\psi = i\partial_{xx}\psi - iV_c(x)\psi + ixE(t)\psi, \tag{192}$$

Denoting by ψ_j^n an approximation of $\psi(x_j, t_n)$ ($x_j = jdx$, $t_n = ndt$), the scheme writes

$$\begin{aligned}\frac{i}{dt}(\psi_j^{n+1} - \psi_j^n) =&\ -\frac{1}{2}\big(x_j E(t_{n+1}) + V_c(x)\big)\psi_j^{n+1} \quad - \quad \frac{1}{2dx^2}(\psi_{j+1}^{n+1} - 2\psi_j^{n+1} + \psi_{j-1}^{n+1})\\ &\ -\frac{1}{2}\big(x_j E(t_n) + V_c(x)\big)\psi_j^n \qquad - \quad \frac{1}{2dx^2}(\psi_{j+1}^n - 2\psi_j^n + \psi_{j-1}^n)\end{aligned} \tag{193}$$

This scheme is of order 2 (error divided by 4 when space step is divided by 2) in space and time and is unconditionally stable (that is, is stable for any choice of dx and dt). Stability is an important criterium with consistency (that is the numerical scheme approximates the continuous equation) to ensure the convergence of the numerical solution to the solution of the continuous TDSE. Roughly speaking, stability has to be understood in the sense that the numerical solution will remain bounded. Or more precisely, in ℓ^2-norm and for all n, the stability condition is

$$\Delta x\sum_j |\psi_j^n|^2 =: \|\psi^n\|^2 \geqslant \|\psi^{n+1}\|^2. \tag{194}$$

The finite difference scheme is also appropriate to solve TDSE in the velocity gauge. Indeed the transport operator can be discretized easily in a stable way as described below. First, it is recalled that the TDSE is given by

$$\partial_t\psi = i\partial_{xx}\psi - iV_c(x)\psi + iA(t)\partial_x\psi. \tag{195}$$

The transport operator (hyperbolic) necessitates to upwind the discrete the operator

$$
\begin{cases}
A(t_n)\partial_x\psi(jdx, t_n) & \sim \quad A(t_n)\dfrac{\psi_j^n - \psi_{j-1}^n}{dx}, \quad \text{if } A(t_n) > 0, \\[3mm]
A(t_n)\partial_x\psi(jdx, t_n) & \sim \quad A(t_n)\dfrac{\psi_{j+1}^n - \psi_j^n}{dx}, \quad \text{if } A(t_n) < 0
\end{cases}
\tag{196}
$$

The upwinding ensures the stability of the numerical scheme. The approximation of $A(t)\partial_x$ should then be done accordingly to the sign of $A(t)$, or equivalently the approximation of the derivative in jdx is done accordingly to where the information comes from: from the left $(\partial_x\psi \sim (\psi_j^n - \psi_{j-1}^n)/dx)$ if $A(t_n) > 0$, and from the right $(\partial_x\psi \sim (\psi_{j+1}^n - \psi_j^n)/dx)$ if $A(t_n) < 0$. If this rule is not satisfied, the scheme becomes unstable, the solution blows up and as a consequence does not converge.

In the velocity gauge, an order 2 (in space and time) scheme, on a N point grid writes:

$$
\begin{aligned}
\frac{i}{dt}(\psi_j^{n+1} - \psi_j^n) \quad = \quad & -\frac{\psi_{j+1}^{n+1} - 2\psi_j^{n+1} + \psi_{j-1}^{n+1}}{2dx^2} - \frac{\psi_{j+1}^n - 2\psi_j^n + \psi_{j-1}^n}{2dx^2} \\[3mm]
& -\frac{A^n + A^{n+1}}{4dx}\Big(\psi_{j+1}^{n+1} - \psi_{j-1}^{n+1} + \psi_{j+1}^n - \psi_{j-1}^n\Big).
\end{aligned}
\tag{197}
$$

The scheme can then be rewritten in the form

$$
A^{n+1}\psi^{n+1} = dt\big(B^n\psi^n + \mathbf{F}^n + \mathbf{F}^{n+1}\big),
\tag{198}
$$

where A^{n+1} and B^n are sparse $N \times N$ matrices. Thus, the equation has become a linear system of equation. The latter can be stored on a computer by compressed sparse row storage [95] in order to avoid or limit storage issues. For sparse symmetric matrices A, the linear system can be solved by the conjugate gradient method, which is among the most efficient solvers. GMRES and Bi-conjugate gradient techniques are most efficient in non-symmetric cases [95], which occur for instance when non-uniform spatial discretizations are used. The multi-dimensional TDSE can be solved similarly on a N^3 point grids. As a consequence, for N large, this necessitates the storage of huge matrices and the solving of sparse linear systems. In order to limit the storage and computational time issues, Alternate Direction Implicit (ADI) methods are often used, which mainly consists of splitting the equation in each spatial direction and necessitate the solving of one-dimensional TDSE's. The consequence of this splitting is that the time step has to be reduced in comparison to direct methods to maintain a good accuracy.

Finite volume method (FVM) for TDSE in the velocity gauge. We roughly describe how to derive a finite volume scheme for the TDSE. The interest of such a method is multiple. First it allows to consider any geometrical domains, with non-uniform cells (or volumes) as for the finite element method (the mesh can be designed to have finer cells in regions where the solution have strong gradients or singularities). Then, this approach, based on a weak formulation of the equation, allows a very simple upwinding of transport operators (more generally hyperbolic operators) ensuring (under condition on the time step) the stability (no blow-up of the numerical solution) and then, the convergence of the numerical scheme.

For the sake of notation simplicity, we suppose that the physical domain Ω is a polygon (in 2-d) or polyhedron (in 3-d). Domain Ω is decomposed in cells or volumes (typically triangles in 2-d and tetrahedra in 3-d) denoted by K_i, then $\Omega = \cup_i K_i$. The FVM which is presented, can in fact be seen as a Galerkin method with basis functions $\mathbf{1}_{K_i}(\mathbf{r})$ (equal to 1 if $\mathbf{r} \in K_i$, 0 otherwise). The starting point is the TDSE given by

$$
i\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = -\frac{1}{2m}\triangle\psi(\mathbf{r}, t) + V_c(\mathbf{r})\psi(\mathbf{r}, t) + i\mathbf{A}(t) \cdot \nabla\psi(\mathbf{r}, t).
\tag{199}
$$

Then, integrating over the volume K_i, we get

$$
\begin{aligned}
i\frac{d}{dt}\int_{K_i}\psi(\mathbf{r}, t)d^3\mathbf{r} = \quad & -\frac{1}{2m}\int_{K_i}\triangle\psi(\mathbf{r}, t)d^3\mathbf{r} + \int_{K_i}V_c(\mathbf{r})\psi(\mathbf{r}, t)d^3\mathbf{r} \\[3mm]
& + i\int_{K_i}\mathrm{div}\big(\mathbf{A}(t)\psi(\mathbf{r}, t)\big)d^3\mathbf{r}.
\end{aligned}
\tag{200}
$$

31

We denote $\psi_{K_i}^n$ the average of ψ in K_i at time t_n, that is

$$\psi_{K_i}^n = \frac{1}{\text{vol}(K_i)} \int_{K_i} \psi(\mathbf{r}, t_n) d^3\mathbf{r}, \tag{201}$$

where $\text{vol}(K_i)$ is the volume of the region K_i. By the divergence theorem, where $\mathbf{n}_{K_i}$ is an outward normal vector to K_i and σ_i a surface on K_i's boundary, integrating now in time, we have

$$\begin{aligned} \psi_{K_i}^{n+1} &= \psi_{K_i}^n + \frac{i}{2m\text{vol}(K_i)} \int_{t_n}^{t_{n+1}} \int_{K_i} \triangle\psi(\mathbf{r}, t) d^3\mathbf{r} dt \\ &+ \frac{1}{\text{vol}(K_i)} \int_{t_n}^{t_{n+1}} \int_{\partial K_i} \mathbf{A}(t) \cdot \mathbf{n}_{K_i} \psi(\mathbf{r}, t) d\sigma_i dt - \frac{i}{\text{vol}(K_i)} \int_{t_n}^{t_{n+1}} \int_{K_i} V_c(\mathbf{r}) \psi(\mathbf{r}, t) d^3\mathbf{r} dt, \end{aligned} \tag{202}$$

Approximating the time integrals by left-rectangle rules, leading to explicit scheme (right-rectangle rule would lead to an implicit scheme), and because we are considering polyhedron volumes, the integration on the surface ∂K_i can be rewritten as

$$\begin{aligned} \psi_{K_i}^{n+1} &= \psi_{K_i}^n + \frac{i\Delta t_n}{2m\text{vol}(K_i)} \int_{K_i} \triangle\psi(\mathbf{r}, t_n) d^3\mathbf{r} + \frac{\Delta t_n}{\text{vol}(K_i)} \sum_{e^{(i)}} \int_{e^{(i)}} \mathbf{A}(t_n) \cdot \psi(\mathbf{r}, t_n) d\sigma_{e^{(i)}} \\ &- i\frac{\Delta t_n}{\text{vol}(K_i)} \int_{K_i} V_c(\mathbf{r}) \psi(\mathbf{r}, t_n) d^3\mathbf{r}, \end{aligned} \tag{203}$$

where $e^{(i)}$ denotes the faces (or edges in 2-d) of volume K_i. Now, V_i^n is an approximation of $\psi_{K_i}^n$ and $V_{i_e}^n$ an approximation of $\int_{e^{(i)}} \mathbf{A}(t_n)\psi(\mathbf{r}, t) d^3\mathbf{r}/\text{vol}(K_i)$. Finally we have denoted $\Delta t_n = t_{n+1} - t_n$. Usual first order, explicit, finite volume schemes write

$$V_i^{n+1} = V_i^n + \frac{i\Delta t_n}{2m} L_i^n + \Delta t_n \sum_{e^{(i)}} V_{e^{(i)}}^n - i\Delta t_n V_{c,i} V_i^n, \tag{204}$$

where $V_{c,i} = \int_{K_i} V_c(\mathbf{r}) d^3\mathbf{r}$, and L_i^n is an approximation to $\int_{K_i} \triangle\psi(\mathbf{r}, t_n) d^3\mathbf{r}/\text{vol}(K_i)$. Usually, L_i^n is evaluated by reconstructing the Laplacian, using K_i's neighboring cell values. Another approach consists of rewritting and approximating this term as $\int_{\partial K_i} \nabla\psi(\mathbf{r}, t_n) \cdot \mathbf{n}_{K_i} d\sigma_i$. The presence of L_i^n imposes a restrictive stability conditions on Δt_n (typically in $\Delta t_n \leqslant C\big(\min_K \text{vol}(K)\big)^2$). The most important point to consider, and this is why FVM are well adapted to transport problem is the simple and stable approximation of the solution at the faces (or edges) of K_i. It is based on an upwinding process, which again ensures the stability of the scheme. More precisely, at a face $e^{(i)}$, if we denote by K_j the cell sharing the edge $e^{(i)}$ with K_i, then a stable approximation of $V_{e^{(i)}}^n$ is given by

$$V_{e^{(i)}}^n = \begin{cases} V_i^n & \text{if } \mathbf{A}^n \cdot \mathbf{n}_{e^{(i)}} > 0, \\ V_j^n & \text{if } \mathbf{A}^n \cdot \mathbf{n}_{e^{(i)}} < 0 \end{cases} \tag{205}$$

where $\mathbf{n}_{e^{(i)}}$ is the outward normal vector to the edge $e^{(i)}$ of K_i. For instance, a naive approximation such as $V_{e^{(i)}}^n = (V_i^n + V_j^n)/2$ would lead to numerical instability (for the same reasons as (196)), then to non-convergence. This is a natural extension of the approximation (196) for FDM. To the best of our knowledge, FVM is not commonly used for approximating TDSE, although this approach has very nice computational and mathematical properties. In the length gauge, the use of FVM is less natural, but still applicable, due to the absence of transport term. Theory about FVM is very well developed, in particular for application in fluid dynamics and to a certain extent to electromagnetism. In the framework of quantum mechanics, however a lot has still to be done.

6.1.4. Summary of numerical methods As seen in previous sections, the choice of numerical methods is closely related to the mathematical structure of the equation we plan to approximate. We have recalled above that transport operator approximation necessitates for stability reasons, an upwinding of the spatial derivatives. As a consequence finite difference or finite volume methods are perfectly adapted to this operator (Galerkin methods are by default centred techniques). The kinetic operator which is transformed into a symmetric bilinear form, by variational computations and is then well adapted to Galerkin approaches (finite element, spectral methods). To summarize the numerical solvers should be chosen accordingly to the fact that:

- Kinetic operators: Galerkin methods (finite element, spectral methods).
- Transport operator: upwind finite difference or volume methods. Galerkin's methods can also be used to approximate transport problem (using the Petrov-Galerkin Streamline Upwind, SUPG method). It consists of adding artificial numerical viscosity to stabilize the scheme.

Note that in Coulomb gauge $\nabla \cdot \mathbf{A} = 0$, it is possible to use a Lagrangian approach because in that case

$$\mathbf{A} \cdot \nabla \psi = \mathrm{div}(\mathbf{A}\psi) = 0. \tag{206}$$

We denote by $(\mathbf{r}_i)_i$ the set of grid points. The principle of Lagrangian methods consists of considering grid points as particles of a fluid propagating at velocity $\mathbf{A}$. The kinetic equation

$$i\partial_t \psi = -\triangle \psi + V_c(\mathbf{r})\psi, \tag{207}$$

is solved by discretizing on a moving grid. That is at time t_n, we search for $\psi(\mathbf{r}^n, t_{n+1})$, that is the solution at time t_{n+1} defined on the grid points located in $\mathbf{r}^n$ at time t_n and moving at velocity $\mathbf{A}^n$. This technique is in particular appropriate to the acceleration gauge.

All the presented methods can usually be coupled with mesh adaption. Mesh adaptation which can be based on wavelet decomposition [96] or local error estimators [97], AMR [98], is a very useful tool from a practical point of view. These are technical methods that dynamically adapt the spatial mesh, in function of the solution regularity: where the solution have large gradients or singularities, degrees of freedom (mesh points) are dynamically added; where the solution has slow spatial variation, degrees of freedom are removed. In fine, mesh adaptation allows for very accurate numerical solutions with acceptable computational times and data storage.
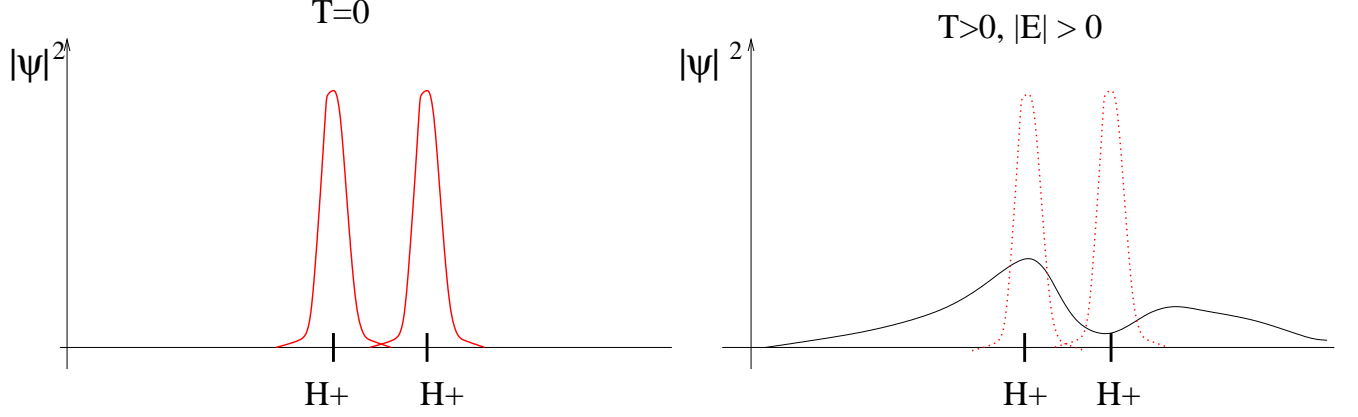
6.2. Boundary Conditions

The boundary condition question is essential in the discretization of TDSE's. Due to the intensity of the laser pulse, the wave function is delocalized necessitating a large computational domain. In multidimension and for multi-electron systems it is important to choose appropriate boundary conditions to avoid spurious reflection of the wave function at the computational domain boundaries. From a gauge invariance point of view, it is also crucial, as non-exact boundary conditions will necessarily lead to a discrepancy of the gauge invariance. As far as we know, no study exists on the effect of (the choice of) the boundary conditions on the gauge invariance. Taking Dirichlet or Neumann boundary conditions leads to important numerical oscillations and reflections at the boundary of the domain, interacting with "physical" waves inside the domain. Even if this kind of methods allows effectively to reduce spurious reflections, there are often empirical (see for instance [99] in this framework), as some "parameters" have to be adapted for each numerical situation. Outside the bounded domain, the Coulomb potential is assumed to be negligible and the laser-molecule TDSE can then be solved "exactly" using for instance the Volkov state propagator (see [99]). Ideally we would like to impose boundary conditions such that the solution in the whole space restricted to a bounded domain Ω is equal to the solution in Ω (that is without spurious reflections). Then outside this fictitious domain the wave function is accurately approximated and can be updated using for instance Volkov state propagator, or by another TDSE solver associated to other nuclei. As an illustration of this issue let us consider the following case: Let us consider the following simplified model *without laser field*:

$$\begin{cases} i\partial_t u(y,t) + \frac{1}{2}\partial_{yy}^2 u(y,t) - V_c(y) \cdot u(y,t) = 0, \\ \\ u(y,0) = u_0(y) \end{cases}$$

One considers the domain $\Omega \times [0,T]$ and denotes by Γ the boundary of Ω. One then looks for v solution of

$$\begin{cases} i\partial_t v(y,t) + \frac{1}{2}\partial_{yy}^2 v(y,t) - V_c(y) \cdot v(y,t) = 0, \ y \in \Omega, \\ \\ \mathcal{B}(y, \partial_y, \partial_t)v(y,t) = 0, \ y \in \Gamma, \\ \\ v(y,0) = u_0(y), \ y \in \Gamma \end{cases}$$
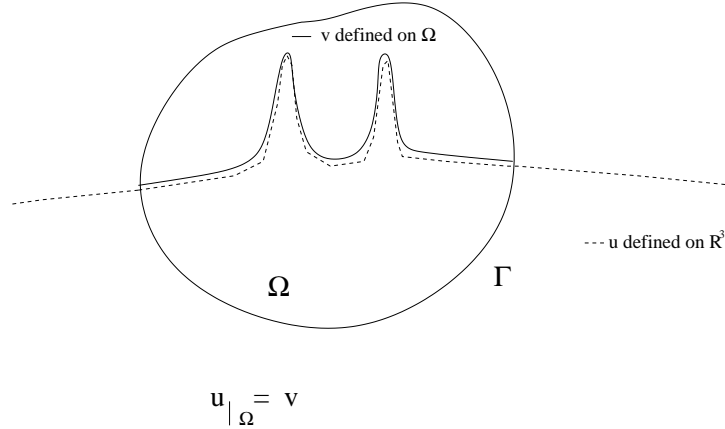
Figure 1. Electronic wave function delocalization

such that

$$u_{|_{\Omega \times [0,T]}} = v. \tag{208}$$

The main problem consists then of finding an adequate (pseudo-)differential boundary operator $\mathcal{B}$ on Γ such

$$u_{|_\Omega} = v$$

Figure 2. Transparent boundary conditions

that (208) occurs, see Fig. 2. As is well known these conditions, called Neumann-Dirichlet (or Dirichlet-Neumann), see Appendix A, are non-local in time (and in space in higher dimension). Denoting by $\mathbf{n}$ the outward normal of Γ and $\partial_\mathbf{n}$ is the trace operator on Γ we obtain:

$$\begin{cases} i\partial_t v(y,t) + \dfrac{1}{2}\partial^2_{yy}v(y,t) - V_c(y) \cdot v(y,t) = 0, \ y \in \Omega, \\[2mm] v(y,t) = -e^{i\pi/4}\sqrt{2} \int_0^t \dfrac{\partial_\mathbf{n} v(y,\tau)}{\sqrt{\pi(t-\tau)}}d\tau, \ y \in \Gamma. \end{cases}$$

This approach has been very well described in particular in [100], and some results can be found in [101], [102] or [103]. We also refer to [104] for the first presented discretization of non-local transparent boundary conditions for TDSE's. As unfortunately these conditions are non-local in time, many attempts have been devoted to find efficient numerical approximations of these conditions.

To illustrate this technique, we propose again a simple benchmark. We suppose that the Coulomb potential is equal to zero.

$$\begin{cases} i\partial_t v(y,t) + \dfrac{1}{2}\partial_{yy} v(y,t) - yE(t)v(y,t) = 0, \ y \in (-10,10), \ t \geqslant 0, \\ \\ v(y,0) = v_0(y) = e^{8iy}e^{-y^2}. \end{cases}$$

The fictitious domain is $\Omega = (-5,5)$. We impose the Neumann-Dirichlet boundary conditions coupled with the laser as described above, at $x_{-\Gamma} = -5$ and $x_\Gamma = 5$. We compare our numerical solution with the solution obtained using Dirichlet boundary conditions at $x_{-\Gamma} = -5$ and $x_\Gamma = 5$ and with a reference solution obtained numerically on a large domain.

The "Neumann-Dirichlet numerical (fig. 3) solution" is then far less reflected (although some reflection exists) compared to the "Dirichlet solution". Here, note that the grid is coarse and small, so that the influence of spurious reflections can be obviously diminished using a larger grid and smaller space steps. We also represent the ℓ^2−norm error between the reference solution and the Dirichlet and Neumann-Dirichlet solutions.
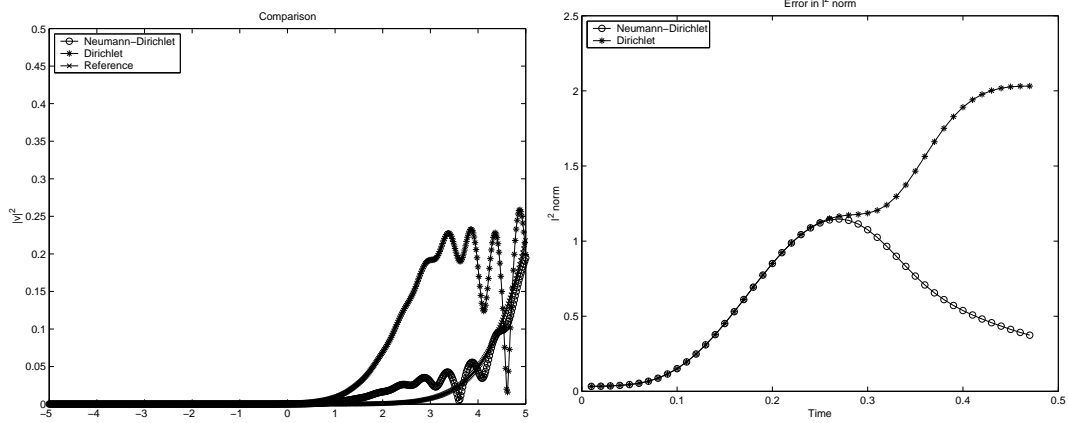
Figure 3. Comparison between the reference solution and the numerical solutions obtained with Dirichlet and Neumann-Dirichlet boundary conditions

Another approach is the Exterior Complex Scaling (ECS) method, in which the ionized electron coordinate is allowed to become complex [105, 106]. and avoids the standard complex absorbing potential method [107]. The ECS method allows for accurate computation of the electron flux through a distant surface, defined by the quiver motion, beyond which the outgoing flux is efficiently absorbed by the ESC in any gauge [105], avoiding reflections.

6.3. An example: harmonic generation

Harmonic generation is a process by which a laser of frequency ω is used to generate electromagnetic radiation of a different frequency (usually, a multiple of the incident photon frequency). This is generally achieved from laser-matter interactions: the laser excite or ionize an electron and while the latter is moving, it emits radiation of certain frequencies (the actual emitted spectrum depends on the electron dynamics). The radiation spectrum $S(\omega)$ is the Fourier transformed of the generated electric field:

$$S(\omega) := \frac{1}{4\pi^2}\left|\int_{-\infty}^{\infty} dt E(x,t)e^{i\omega t}\right|^2 \tag{209}$$

It can then be shown that $S(\omega)$ is proportionnal to the square of the velocity form, i.e. it is given by [108, 109]

$$S(\omega) \propto \left|\int_{-\infty}^{\infty} dt \langle \psi(t)|\dot{z}|\psi(t)\rangle e^{i\omega t}\right|^2. \tag{210}$$

In the following, we discuss alternative formulas for HHG processes which include dipole, velocity and acceleration forms. Prior to this, we recall Ehrenfest's theorem. For any operator $\widehat{O}$, the time dependence is governed by

$$\frac{d}{dt}\langle\widehat{O}\rangle = \frac{1}{i\hbar}\langle[\widehat{O},\widehat{H}]\rangle + \left\langle\frac{\partial\widehat{O}}{\partial t}\right\rangle. \tag{211}$$

The latter will be useful in the following to change from one form to the other. In the dipole approximation, one can derive simply the electric field $E(t)$ via the vector potential:

$$A(t) = -\frac{\mathcal{E}(t)}{\omega}\sin\left(\omega(t-t_c)\right). \tag{212}$$

and

$$E(t) = -\partial_t A(t) = \mathcal{E}(t)\cos\left(\omega(t-t_c)+\phi\right) + E_{cor}, \tag{213}$$

where t_c is the peak of the field and ϕ is the Carrier Envelope Phase (CEP), $\mathcal{E}(t)$ is the envelope of the pulse and

$$E_{cor} = \sin\left(\omega(t-t_c)+\phi\right)\frac{\partial_t\mathcal{E}(t)}{\omega}, \tag{214}$$

is the correction to the simple form (213) arising from the derivative of the envelope of the vector potential. E_{cor} is negligible near the peak, $t = t_c$, for long pulses and for slowly varying envelopes $\mathcal{E}(t)$. For short pulses such that the envelope varies rapidly, one must use the complete form (213), which ensures the zero-area theorem:

$$\int_{t_1}^{t_2} E(t)dt = A(t_1) - A(t_2) = 0. \tag{215}$$

One usually chooses $A(t_1) = A(t_2) = 0$ that is $\mathcal{E}(t_1) = \mathcal{E}(t_2) = 0$ in (212). If the total area of the electric field is not zero, a simple Fourier transform of (215) shows that $\int_{\mathbb{R}} E(t)dt = E_0$, that is a static field component is present in the pulse, contrary to Maxwell's equations. A more recent discussion of the related problem of adiabatic cut-offs of fields in gauge invariant electrodynamics emphasizes the importance of the electromagnetic potentials (212), to generate the physical field (213) [110].

In general the dipole velocity is related to the momentum as

$$\dot{z} = -i[z,H] = \frac{\partial H}{\partial p_z} = p_z. \tag{216}$$

for which we define $\langle\dot{z}(t)\rangle = \langle\psi(t)|p_z|\psi(t)\rangle$, where ψ is a converged numerical solution in any gauge, and $\widehat{p}_z = -i\partial/\partial z$. By abuse of notation, we denote the Fourier transform $\dot{z}(\omega) = \int_{t_i}^{t_f} dt e^{-i\omega t}\langle\dot{z}(t)\rangle$, which is given by

$$\dot{z}(\omega) = e^{i\omega t}\langle z(t_f)\rangle + i\omega z(\omega), \tag{217}$$

where the initial condition $\langle z(t_i)\rangle = 0$ for symmetric states. A similar procedure for the acceleration [111] gives

$$\ddot{z} = -i[\dot{z},H] = -i[p_z,H] = -\frac{\partial H_I}{\partial z}, \tag{218}$$

where H_I is the interaction Hamiltonian, then

$$\ddot{z}(\omega) = i\omega\dot{z}(\omega) - e^{i\omega t_f}\langle\dot{z}(t_f)\rangle, \tag{219}$$

with the initial symmetry dictated condition $\langle\dot{z}(t_i)\rangle = 0$. We note that this condition differs from that imposed in the tunnel ionization model [10, 11, 111, 112], which assumes instantaneous initial condition $\dot{z}(t_i) = 0$. Equations (214), (216) demonstrate that the three forms of the particle operators involved in radiative interactions, $z(\omega)$, $\dot{z}(\omega)$ and $\ddot{z}(\omega)$ are related. When $\langle z(t_f)\rangle = \langle\dot{z}(t_f)\rangle = 0$, then the HHG spectrum intensities satisfy

$$D_{\ddot{z}}(\omega) = \omega^2 D_{\dot{z}}(\omega) = \omega^4 D_z(\omega), \tag{220}$$

36

where $D_\xi(\omega) = |\xi(\omega)|^2$, and $\xi(\omega) = \int_{t_1}^{t_f} dt e^{-i\omega t}\xi(t)$. In the opposite case, when $\langle z(t_f)\rangle \neq 0, \langle \dot{z}(t_f)\rangle \neq 0$, the spectra may differ radically depending on the final values of the expectation value of the position $\langle z(t_f)\rangle$ and velocity $\langle \dot{z}(t_f)\rangle$. This issue originally raised by Burnett [113] was discussed in detail in [111] and we show another example in Figs 4, 5, 6, 7 where these differ significantly on the parameters that specify the laser pulse (duration, intensity, CEP).

Figures 4, 5, 6 and 7 illustrate the effect of pulse duration on the x and y components of MHOHG from the one electron molecular ion H_2^+ at internuclear distance $R = 22$ a.u. ionized by a linearly and circularly polarized pulse at wavelength 400 nm ($w = 0.114$ a.u.), and intensity $I = 2.1 \times 10^{14}$ W·cm^{-2} incident on the x, y plane of the molecule with the x direction parallel to the intermolular axis, i.e. R. The internuclear distance $R = 22$ a.u. is chosen to coincide with the laser induced collision radius for an electron ionized from one end of the molecule with its neighbor as predicted by a classical collision model. $P_{x,y}(\omega)$ correspond to the Fourier transform of the squared expectation value of the position, velocity and acceleration operators. We note in Fig. 6 for an ultrashort 2 cycle pulse that the MHOHG spectrum is the same for dipole and velocity forms since the expectation value of the position and velocity are nonvanishing after the pulse, whereas the acceleration operator, which does converge to zero average value, gives a completely different spectrum. Figs. 5 and 7 correspond to a long 20 cycle pulse for which all three expectation values of operators vanish after the pulse, thus giving basicallly identical MHOHG spectra. Figures 4 and 6 confirm the numerical difference in HHG calculations in different forms for ultrashort pulses due to the nonvanishing of average operators (position, velocity and acceleration) after the pulse.

Recent work has emphasized the direct relation of the velocity rather than dipole or acceleration forms to the harmonic fields generated in HHG [108, 109, 114]. On the other hand, as already noted by Gordon et al. [70], the acceleration form of HHG provides considerable computational advantages in SFA as the representation includes Coulomb potentials to first order, which is absent in the two other forms. Note that in [43, 71] numerical computations also show that the acceleration and dipole forms of the transition matrix lead to different results. It is shown that the acceleration form accurately predicts the interference effects, $\exp(i\mathbf{k} \cdot R/2) \pm \exp(-i\mathbf{k} \cdot R/2)$ in H_2^+, while the dipole form does not (see table II and eqs (34, 43) in [43]). This is due to the fact that the acceleration operator is made up of the forces from each Coulomb center, thus representing to first order the multicenter molecular structure, whereas the dipole operator emphasizes larger distances and contains no molecular structure information. In addition, the dipole form of the transition matrix indicates that the emission of harmonic photons is proportional to "momentum" derivative of the Fourier transform of the ground-state wave function. This feature is a key ingredient of the method for tomographic imaging of the ground-state molecular orbitals presented in [9] by exploiting the orientation dependence of MHOHG spectra. According to [43] a formulation of tomographic imaging based on the acceleration form could then be more accurate in reconstructing molecule orbitals from the harmonic spectrum. Moreover, in MHOHG, multicenter Coulomb effects are essential to predict maxima in the spectra and these are correctly predicted by the acceleration form [43, 71].

Numerical simulations comparing the calculation of HHG intensities in the velocity versus the length gauge have shown a faster convergence in the velocity gauge by noting that the canonical momentum is reduced by the vector potential since $v = p - eA/mc$ [32], even if the spectra are very similar. These authors compare numerically the dipole moment computed using the length and velocity gauges for the hydrogen atom. As expected a very good agreement is obtained in these 2 gauges:

$$i\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = -\left(\triangle + W(\mathbf{r}, t) + \frac{1}{|\mathbf{r}|}\right)\psi(\mathbf{r}, t), \tag{221}$$
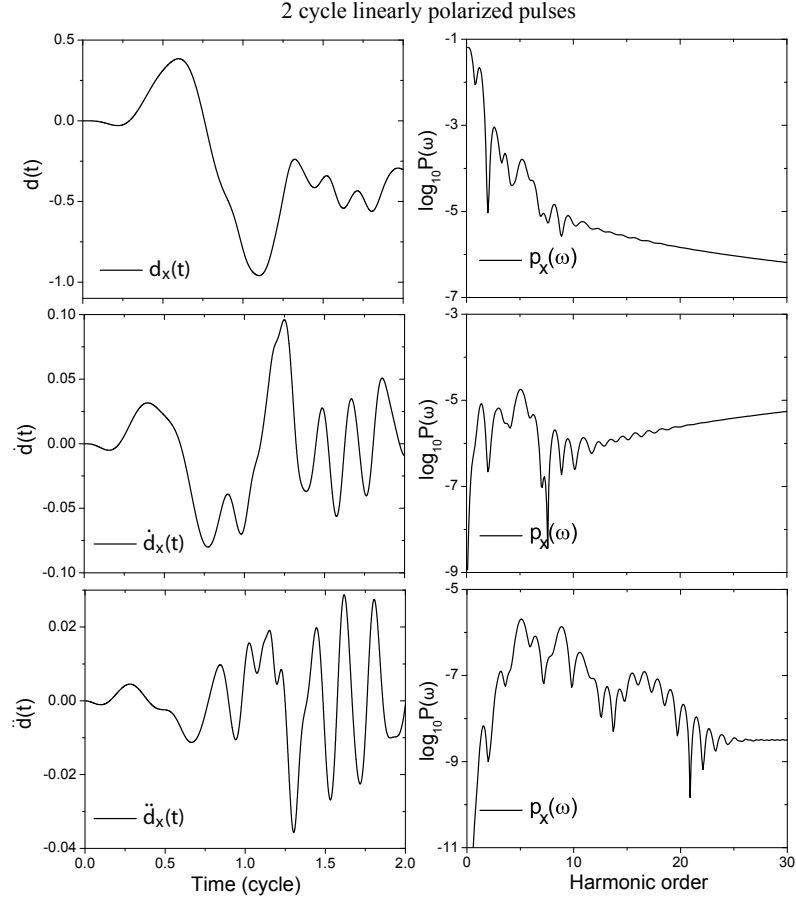
with in the length gauge (linear polarized laser field)

$$W(\mathbf{r}, t) = \mathbf{r} \cdot \mathbf{E}(t), \tag{222}$$

and in the velocity gauge

$$W(\mathbf{r}, t) = -i\mathbf{A}(t) \cdot \nabla(t), \tag{223}$$

where the laser pulse is chosen as:

$$\mathbf{E}(t) = E_0\left[\sin^2\left(\frac{\pi t}{T}\right)\sin(\omega_0 t) - \frac{\pi}{\omega_0 T}\sin\left(\frac{2\pi t}{T}\right)\cos(\omega_0 t)\right]\mathbf{e}_z, \tag{224}$$
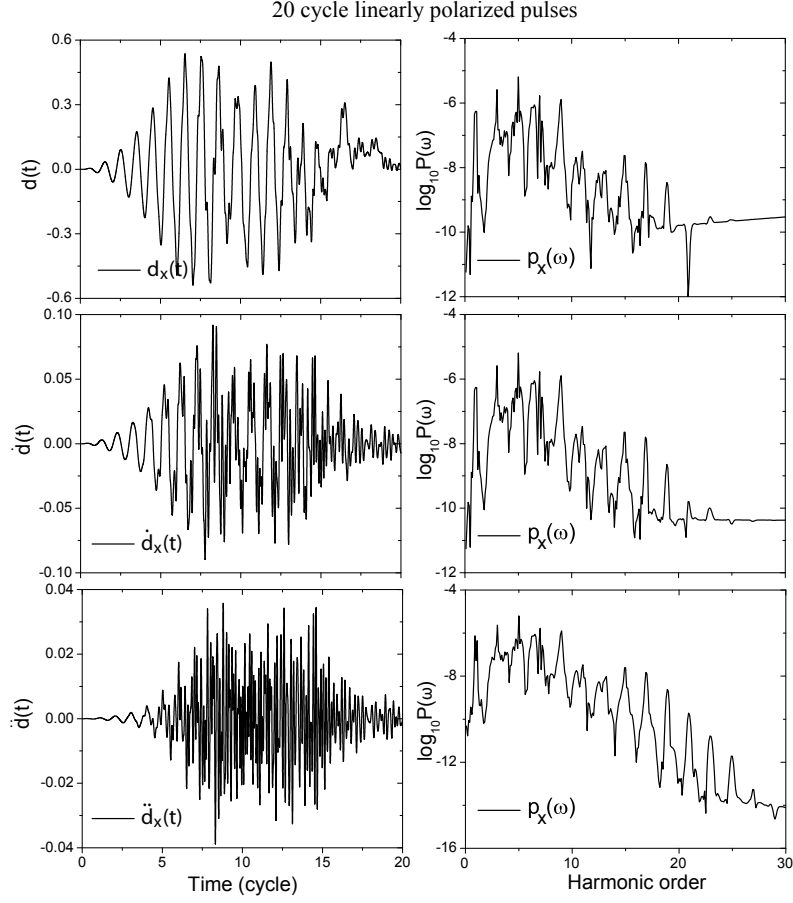
Figure 4. Expectation value of the position, velocity and acceleration operator, along with the dipole, velocity and acceleration forms of the HHG spectrum, for a 2 cycle linearly polarized pulse at 400 nm and $I = 10^{14}$ W·cm^{-2} and corresponding HHG spectrum for H_2^+ at distance $R = 22$ a.u.

with $\int_0^T \mathbf{E}(t)dt = \mathbf{0}$ and

$$\mathbf{A}(t) = \frac{E_0}{\omega_0} \sin^2\left(\frac{\pi t}{T}\right)\cos(\omega_0 t)\mathbf{e}_z, \tag{225}$$

$\lambda = 800$ nm and $T = 110.32$ a.u. and $I = 3 \times 10^{14}$ W·cm^{-2}. The equation was rewritten in spherical coordinates and the chosen numerical method was a spectral/finite element method with B-splines basis for
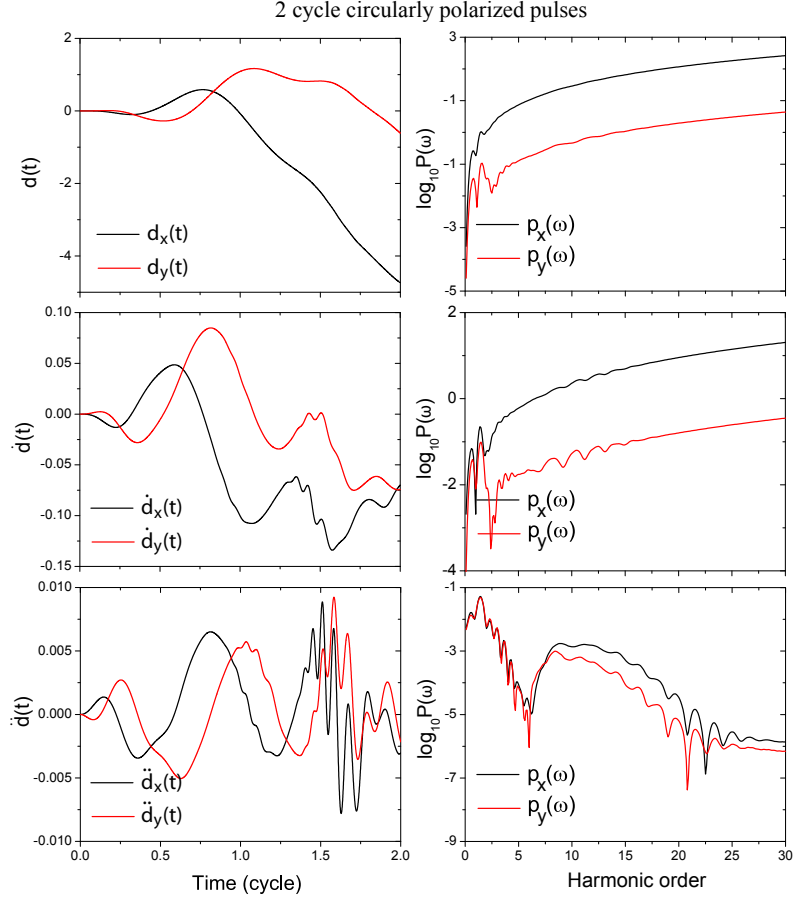
Figure 5. Expectation value of the position, velocity and acceleration operator, along with the dipole, velocity and acceleration forms of the HHG spectrum, for a 20 cycle linearly polarized pulse at 400 nm and $I = 10^{14}\mathrm{W\cdot cm^{-2}}$ and corresponding HHG spectrum for H_2^+ at distance $R = 22$ a.u.

the radial part and spherical harmonics for the angular part. Due to the choice of linear polarized laser field, the azimutal magnetic quantum number was taken null. Let us shortly recall the conclusion of this interesting paper. To obtain convergence (up to a certain fixed error):

- More grid points were required in the velocity gauge and larger angular basis in the length gauge.
- At high intensity the convergence was faster in the velocity gauge than in the length gauge.

Naturally, the convergence as function of physical parameters, is also highly dependent on the choice of
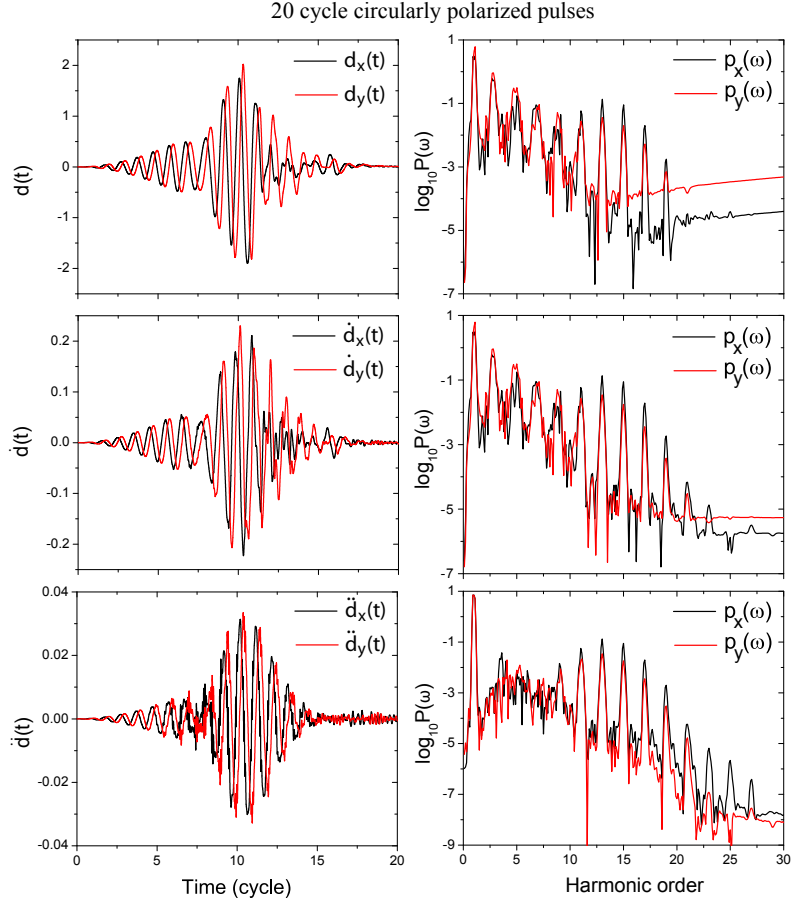
Figure 6. Expectation value of the position, velocity and acceleration operator, along with the dipole, velocity and acceleration forms of the HHG spectrum, for a 2 cycle circularly polarized pulse at 400 nm and $I = 10^{14}$W·cm^{-2} and corresponding HHG spectrum for H_2^+ at distance $R = 22$ a.u.

the numerical method to solve the TDSE. The above conclusions are of course a priori not valid for other methods, see [115].

When dealing with numerical computations of transition amplitudes, it is important to consider sufficiently large computational times. Indeed, theoretical estimation of these amplitudes necessitate in theory a computational time from $-\infty$ to $+\infty$. Time truncation introduces errors. For this reason in [116], [117] the authors focus on the solving of TDSE's using the acceleration gauge. The latter offers computational

20 cycle circularly polarized pulses

Figure 7. Expectation value of the position, velocity and acceleration operator, along with the dipole, velocity and acceleration forms of the HHG spectrum, for a 20 cycle circularly polarized pulse at 400 nm and $I = 10^{14}$W·cm^{-2} and corresponding HHG spectrum for H_2^+ at distance $R = 22$ a.u.

advantages in non Born-Oppenheimer molecular simulations: contrary to the divergent length gauge radiative term $zE(t)$, radiative terms vanish asymptotically so that projections can be made simply onto free electron Coulomb states [118]. Comparison of convergence between the same discretization schemes for all three gauges have demonstrated the superiority of the acceleration gauge due to its similarity to Lagrangian adaptive grid methods used in fluid dynamics [84, 81].

7. Gauge transformation and the Dirac equation

In the last few decades, laser intensities achieved in experiments have increased due to new technical advances. It is now possible to consider laser fields with $I \sim 10^{23}\text{W/cm}^2$, and higher [119]. In this new regime, the electron starts to move at relativistic velocities. For instance it is demonstrated in [120], by using an argument based on classical relativistic mechanics, that when

$$\frac{eE_0}{m\omega} > 1 \tag{226}$$

where E_0 is the electric field and ω is the laser frequency, an electron is accelerated to a regime where relativistic effects start to be important. The mathematical description of an electron subjected to such intense electromagnetic fields necessitates a relativistic treatment [121, 120] and thus, theoretical efforts should be based on the Dirac equation instead of the non-relativistic Schrödinger equation.

Most of the discussion concerning gauge invariance can be applied to the Dirac equation, which gives a quantum relativistic description of the electron. The latter, in covariant notation and for a free particle (no external potentials), is given by [122]

$$\left(i\hbar c\gamma^\mu \partial_\mu - mc^2\right)\psi(x) = 0 \tag{227}$$

where $\psi(t, \mathbf{x}) \in L^2(\mathbb{R}^3) \otimes \mathbb{C}^4$ is the time and coordinate dependent four-spinor and γ^μ are the Dirac matrices. The latter are given by

$$\gamma^0 := \begin{bmatrix} \mathbb{I}_2 & 0 \\ 0 & -\mathbb{I}_2 \end{bmatrix} \quad , \quad \gamma^i := \begin{bmatrix} 0 & \sigma_i \\ -\sigma_i & 0 \end{bmatrix}, \tag{228}$$

where $\mathbb{I}_2$ is the 2×2 unit matrix. The σ_i are the usual 2×2 Pauli matrices defined as

$$\sigma_x := \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad , \quad \sigma_y := \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \text{ and } \sigma_z := \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{229}$$

Written in this form, the Dirac matrices are in the Dirac representation. There exist many other representation of Dirac matrices as they are defined abstractly by their anti-commutation relations: $\{\gamma^\mu, \gamma^\nu\} = 2\eta^{\mu\nu}$. A list of representation can be found in [123, 122]. They are related to each other by unitary transformations.

This equation describes physically the relativistic dynamics of a single spin-1/2 particle like an electron or quark. As in the Schrödinger equation, the interaction with an external electromagnetic field is introduced by using the minimal coupling prescription: this allows to preserve the gauge invariance of the equation, as shown below. In this scheme, the partial derivative is replaced by a covariant derivative as

$$\partial_\mu \to D_\mu := \partial_\mu + i\frac{q}{\hbar}A_\mu, \tag{230}$$

and the Dirac equation becomes

$$\left(i\hbar c\gamma^\mu D_\mu - mc^2\right)\psi(x) = 0. \tag{231}$$

To show the gauge invariance of the Dirac equation, it is possible use the Lagrangian formulation and then, to demonstrate that the Dirac Lagrangian obeys the symmetry condition under a gauge transformation. The Lagrangian of Quantum Electrodynamics (QED) is given by

$$\mathcal{L}_{\text{QED}} = \bar{\psi}(x)\left[i\hbar c\gamma^\mu D_\mu - mc^2\right]\psi(x) - \frac{c^2\varepsilon_0}{4}F_{\mu\nu}F^{\mu\nu}, \tag{232}$$

where $\bar{\psi} := \psi^\dagger\gamma^0$. It is a straightforward calculation to show that the Euler-Lagrange equation for this Lagrangian are the Dirac and Maxwell equations. The gauge transformation is

$$\psi \to \psi' = e^{i\frac{q}{\hbar}F(x)} \tag{233}$$

$$A^\mu \to A'^\mu = A^\mu - \partial^\mu F(x), \tag{234}$$

where F is an arbitrary function, as usual. Therefore, the Lagrangian, under a gauge transformation, becomes

$$\mathcal{L}_{\text{QED}} \to \mathcal{L}'_{\text{QED}} = \bar{\psi}'(x)\left[i\hbar c\gamma^\mu\left(\partial_\mu + i\frac{q}{\hbar}A'_\mu\right) - mc^2\right]\psi'(x) - \frac{c\varepsilon_0}{4}F'_{\mu\nu}F'^{\mu\nu} \tag{235}$$

$$= \bar{\psi}(x)e^{-i\frac{q}{\hbar}F(x)}\left[i\hbar c\gamma^\mu\left(\partial_\mu + i\frac{q}{\hbar}A_\mu - i\frac{q}{\hbar}\partial_\mu F\right) - mc^2\right]e^{i\frac{q}{\hbar}F(x)}\psi(x)$$

$$- \frac{c^2\varepsilon_0}{4}F_{\mu\nu}F^{\mu\nu} \tag{236}$$

$$= \bar{\psi}(x)\left[i\hbar c\gamma^\mu\left(\partial_\mu + i\frac{q}{\hbar}A_\mu\right) - mc^2\right]\psi(x) - \frac{c^2\varepsilon_0}{4}F_{\mu\nu}F^{\mu\nu} \tag{237}$$

$$= \mathcal{L}_{\text{QED}}. \tag{238}$$

Thus, the Dirac equation is invariant under gauge transformations. This is the same result as for the Schrödinger equation considered previously. Therefore, many of the results presented earlier can also be applied to the Dirac equation.

Acknowledgments

Appendix A. Exact solutions

In many situations, the laser-molecule TDSE can be solved explicitly or approximately. We here shortly recall some of these particular situations.

- **Volkov**: Exact solution to potential-free (vacuum) TDSE or TDDE can be obtained analytically. Considering first the TDSE in velocity gauge:

$$i\partial_t\psi = \frac{1}{2m}\left(-i\nabla - \mathbf{A}\right)^2\psi \tag{A.1}$$

with initial data $\psi(\mathbf{r}, 0) = \phi(\mathbf{r})$. We assume that ϕ is a plane wave $e^{i\mathbf{p}\cdot\mathbf{r}}$ and that $\mathbf{A}$ is time dependent only. Approximate generalized Volkov wave functions can also be derived for space-time potentials [124]. Applying a Fourier transform in space and solving the induced differential equation and applying the inverse Fourier transform leads to the following solution

$$\psi_p(\mathbf{r}, t) = \frac{1}{(2\pi)^{3/2}}\exp\left[i\mathbf{p}\cdot\mathbf{r} - \frac{i}{2}\int_0^t\left(p + \mathbf{A}(\tau)\right)^2 d\tau\right] \tag{A.2}$$

In length gauge, by application of the usual unitary transformation we get:

$$\psi_p(\mathbf{r}, t) = \frac{1}{(2\pi)^{3/2}}\exp\left[i\left(\mathbf{p} + \mathbf{A}(t)\right)\cdot\mathbf{r} - \frac{i}{2}\int_0^t\left(p + \mathbf{A}(\tau)\right)^2 d\tau\right]. \tag{A.3}$$

These Volkov solutions, expressed in different gauge, applies to one mode. To obtain a general solution, one has to form a Volkov wave packet, i.e. a superposition of these modes.
Another possibility to derive Volkov wave functions for general initial data ($\phi \in L^2(\mathbb{R}^3, \mathbb{C})$) is the following. Starting, say from:

$$i\partial_t\psi = -\frac{1}{2}\Delta\psi + \mathbf{r}\cdot\mathbf{E}\psi, \qquad \psi(\mathbf{r}, 0) = \phi(\mathbf{r}) \tag{A.4}$$

assuming again that $\mathbf{E}$ is time dependent only. We apply a Fourier transform in space, which leads to a transport equation which can be solved. Then, taking the inverse Fourier transform leads to the Volkov

wavefunction:

$$\psi(\mathbf{r},t) = \frac{1-i}{2\sqrt{\pi t}}\exp\left[-i\mathbf{r}\int_0^t \mathbf{E}(s)ds - \frac{i}{2}\int_0^t (\int_0^s \mathbf{E}(\tau)d\tau)^2 ds\right]$$
$$\times \int_{\mathbb{R}^3} \phi(\mathbf{r}')\exp\left[\frac{i(\mathbf{r} - \int_0^t(\int_0^s \mathbf{E}(\tau)d\tau)ds - \mathbf{r}')^2}{2t}\right] d^3\mathbf{r}'. \qquad (A.5)$$

From the numerical point of view the main issue comes from the non-locality of this solution. Naturally this method is presented in any quantum physics book and can be extended to relativistic situations (Dirac equation).

- **Lewenstein Model/SFA**. This approach (which was already discussed above), although not exact, allows to find solutions to TDSE for intense laser pulses, including the Hamiltonian continuum [12]. That is we search for wavefunctions of the form:

$$\psi(\mathbf{r},t) = \exp\left(iI_p t\right)\left(a(t)\psi_0 + \int d^3\mathbf{p}\, b(\mathbf{p},t)\psi_\mathbf{P}\right) \qquad (A.6)$$

which corresponds to a decomposition of the wavefunction in the ground ψ_0 state and the Volkov state $\psi_\mathbf{P}$ as described above. I_p denotes the ionization potential, the density b is the amplitude of the continuum state $\psi_\mathbf{P}$. This model has been extensively developed and validated as it gives a very good description of multiphoton ionization and high order harmonics generation. The dipole can be calculated as follows

$$\begin{aligned}\mathbf{d}(t) &= \int_{\mathbb{R}^3} |\psi(\mathbf{r},t)|^2 \mathbf{r}\, d^3\mathbf{r} \\ &= i\int_0^t dt' d^3\mathbf{p}\, E\cos(t')d_x(\mathbf{p}-\mathbf{A}(t'))d_x^*(\mathbf{p}-\mathbf{A}(t))\exp\left(-iS(\mathbf{p},t,t')\right) + c.c.\end{aligned} \qquad (A.7)$$

where

$$S(\mathbf{p},t,t') = \int_{t'}^t dt'' \left(\frac{\left|\mathbf{p}-\mathbf{A}(t'')\right|^2}{2} + I_p\right). \qquad (A.8)$$

is the action of the free electron in the vector potential $\mathbf{A}(t)$

- **Dirichlet-Neumann**. Laser-free TDSE in vacuum can be solved analytically in length gauge. We shortly recall the principle here. From the laser-free Schrödinger in vacuum (in 1-d)

$$\psi_t - i\partial_{xx}\psi = (\partial_t^{1/2} - e^{\frac{i\pi}{4}}\partial_x)(\partial_t^{1/2} + e^{\frac{i\pi}{4}}\partial_x)\psi = 0, \quad \psi(x,t)\to_{|x|\to\infty} 0 \qquad (A.9)$$

involving the Dirichlet-to-Neumann pseudo-differential operator, we can solve explicitly this equation (under the Somerfeld radiation condition)

$$\psi(x,t) = e^{i\pi/4}\sqrt{2}\int_0^t \frac{\partial_x \psi(x,\tau)}{\sqrt{\pi(t-\tau)}}d\tau$$

This is naturally a fundamental result to derive analytical solution to TDSEs. It is also a very used tool to derive absorbing boundary conditions [125, 126, 127].

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