A numerical Maxwell-Schrödinger model for intense laser-molecule interaction and propagation

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Abstract

We present in this paper a numerical Maxwell-Schrödinger model and a methodology to simulate intense ultrashort lasers interacting with a 3D $H_2^+$-gas under and beyond Born-Oppenheimer approximation. After a presentation of the model and a short mathematical study, we will examine some issues on its numerical computation. In particular we will focus on the polarization computation allowing the coupling between the Maxwell and time dependent Schrödinger equations (TDSE), on the parallelization, and on the boundary conditions problem for the TDSE. Examples of numerical computations of high order harmonics generation and of electric fields propagations are presented.

Keywords: Maxwell, Schrödinger, laser, multiscales problem, transparent boundary conditions.

1 Introduction

From the theoretical point of view to the very practical point of view (controlled fusion [35] by inertial confinement, quantum dynamic imaging [10], attosecond pulse generation [4]), there exist numerous applications of ultrashort and intense lasers. Indeed current laser technology allows to create ultrashort pulses with intensities exceeding some molecules and atoms internal electric fields. Typically, for the hydrogen atom the period of circulation is $24.6$ attoseconds ($10^{-18}$s) and the intensity of its Coulomb field is $3 \times 10^{16}$W/cm$^2$ with a corresponding electric field $E = 5 \times 10^{11}$V/m$^{-1}$. Current laser intensities can reach around $10^{20}$W/cm$^2$ with pulse durations of $\sim 50$ femtoseconds ($10^{-15}$s). The main goal of this work is to study high order nonlinear phenomenons (Above Threshold Ionization (ATI), High Harmonics Generation (HHG), filamentation [24], etc) obtained with very intense lasers interacting with molecules and to study their dynamics. HHG is one of these nonlinear phenomenons that appears when the electric field is of same order as the Coulomb potential (ionization) and is created by electron rescattering [1], [20]. It is, moreover, the current source of coherent attosecond pulses [5], [4]: in a first step submitted to an intense electric field the electron leaves the ion vicinity and enters in the ionized continuum with an initial velocity equal to zero [1], [20]. Then the free electron is accelerated by the strong electric field and gains energy. In a last step the electron is driven back into the vicinity of the parent ion and recombined with it, leading to a multiphoton ionization (see [29] for description of HHG or [21] for their numerical aspects) then to the creation of high order harmonics. In this paper we will introduce a precise model to describe this dynamics, including ionization, dissociation of the molecule and including propagation effects in order to take into account the phase matching [14]. Whereas previous works dealt with laser-atom interactions [14], we propose here to study ultrashort pulses interacting with molecules, in particular we will focus on the one-electron $H_2^+$-molecule [14]. To model phase matching in molecular media such as propagation in the atmosphere [24], the most natural way is to consider a coupling

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between the Maxwell equations describing the behavior of the electric and magnetic fields and the TDSE describing the particles motions. In order to increase the precision of the model, we propose to go beyond the Born-Oppenheimer approximation taking into account the nuclear motions [17]. The Maxwell equations and the TDSE are then coupled with the polarization of molecules that describes the relative position of the particles constituting the molecule. The model is written first in its whole generality and then some approximations are proposed in order to solve it numerically efficiently. Note that the model we propose is close to the “one-dimensional” model presented in [33], [34], [19], [18].

In section 2, we will present our approach and we will briefly discuss some existing models. Then we will focus on the existence of solutions for the Schrödinger equation we consider. Section 3. will be devoted to the presentation of the numerical and parallel method we have used to solve the coupled system. In particular we will detail the polarization computation (and how to reduce it in CPU time) and on the numerical boundary conditions for the TDSE, crucial in this framework. We will demonstrate scalability as a function of number of particles for the $H^+_2$ gas system. In the last section some numerical results will be presented.

2 Mathematical Model

2.1 Presentation of the Maxwell-Schrödinger model

The TDSE describing the $H^+_2$ molecule behavior submitted to a laser field can be written [21] where we use atomic units ($e = h/2\pi = m_e = 1$):

$$i\partial_t \psi(r, R, r', t) = \left[-\frac{1}{2}\Delta_r + V_e(r, R) - \frac{i}{c}A(r', t) \cdot \nabla_r + \frac{1}{R} - \frac{1}{4m_p}\Delta_R + \frac{||A(r', t)||^2}{2c^2}\right] \psi(r, R, r', t),$$

where $\psi$ represents the molecular wavefunction. Electron-nuclea, $V_e$ and nuclear ion $V_i$ potentials are given by

$$V_e(r, R) = -\frac{1}{\sqrt{x^2 + (y - R/2)^2 + z^2}} - \frac{1}{\sqrt{x^2 + (y + R/2)^2 + z^2}}, \quad V_i(R) = \frac{1}{R}.$$  

The electronic position in the nuclear center of mass coordinates is denoted by $r = (x, y, z)^T$. $R$ represents the nuclear relative position and $m_p$ denotes the $H^+$ mass. We suppose in this paper that the nuclear motion is one-dimensional. The variable $r'$ denotes the spatial dependency of the electric and magnetic fields, and $A$ represents the electromagnetic potential. Note that in our orthogonal coordinates, $e_x = e_{x'}$, $e_y = e_{y'}$, $e_z = e_{z'}$. Next, if the laser wavelength is large enough we can assume that the electric and magnetic fields are constant in space at the molecular scale $\lambda/\ell >> 1$ (this corresponds to the dipole approximation [31], [9])
allowing us to reduce the numerical and mathematical complexity of the problem. Indeed, in this situation the Schrödinger equation can be written:

\[ i\partial_t \psi_{r'}(r, R, t) = \left[ -\frac{1}{2} \Delta_r + V_c(r, R) - \frac{i}{c} A_{r'}(t) \cdot \nabla_r + \frac{1}{R} - \frac{1}{4m_p} \Delta_R + \frac{\|A_{r'}(t)\|^2}{2c^2} \right] \psi_{r'}(r, R, t), \]

(3)

\( r' \) is now a parameter denoting the molecule position in the “Maxwell domain”. For each \( r' \) in the gas, one has to solve a 4D-TDSE. Let us remark that this approximation leads to \( [\Delta_r, A_{r'}(t) \cdot \nabla_r] = 0 \); a very useful feature for applying an error numerical splitting.

The previous TDSE is given is the so-called \textit{velocity gauge}. Another possible formulation is in the so-called \textit{length gauge}. Applying the unitary transformation

\[ \psi \mapsto \psi \exp \left( -\frac{i}{2c^2} \int_0^t \| A_{r'} \|^2(s) ds + \frac{i}{c} r \cdot A_{r'}(t) \right), \]

(4)

we get a new formulation of the TDSE [9], [15]:

\[ i\partial_t \psi_{r'}(r, R, t) = \left[ -\frac{1}{2} \Delta_r + V_c(r, R) + r \cdot E_{r'}(t) + V_i(R) - \frac{1}{m_p} \Delta_R \right] \psi_{r'}(r, R, t). \]

(5)

with \( E_{r'}(t) = -c\partial_t A_{r'}(t) dt \) denoting the electric field.

Ideally the electric field dynamics modeling is given by the microscopical Maxwell equations coupled with the Schrödinger equations and will be done in a future work. A full description of the microscopical Maxwell equations can be found in [26]. A close approach is proposed in [16], where the authors study the microscopical Maxwell equations but coupled with classical dynamics equations to describe the particles motions. We will here consider the macroscopical Maxwell equations that correspond to a spatial average of the microscopical ones. These equations are typically valid in a domain equal or exceeding a size of \( 10^{-18} cm^3 \) with a sufficiently high molecular density (see again [26]). The macroscopical 3D-Maxwell equations written in atomic units are:

\[
\begin{cases}
\partial_t B(r', t) = -c \nabla_{r'} \times E(r', t), \\
\partial_t E(r', t) = c \nabla_{r'} \times B(r', t) - 4\pi \partial_t P(r', t), \\
\nabla_{r'} \cdot (E(r', t) + 4\pi P(r', t)) = 0, \\
\nabla_{r'} \cdot B(r', t) = 0.
\end{cases}
\]

(6)
Under the dipolar approximation the polarization $P$ for a molecule located at $r'$ is given by:

$$P(r', t) = -n(r') \int \psi^*_r(r, R, t) \cdot r \cdot \psi^*_r(r, R, t) dR dr,$$

where $n(r')$ denotes the molecular density defined below. The sign comes from the electron charge. The polarization $P$ is then the coupling term between the Schrödinger and Maxwell equation. The model equations are then given by (5), (7), (6). A full description of the numerical polarization modeling will be presented in section 3.4.

The Maxwell domain is denoted by $\Omega_M$. The molecules are located in a sub-domain $\Omega_m$ and the vacuum regions are denoted by $\Omega_0$: $\Omega_M = \Omega_m \cup \Omega_0$. Initially the laser-pulse of frequency $\omega$ and intensity $I$ is defined as:

$$\left\{ \begin{array}{ll}
E(r', 0) = E_0(r') f_\omega(r'), & r' \in \Omega_0, \\
E(r', 0) = 0, & \text{elsewhere}.
\end{array} \right.$$ 

The function $f$ is usually a sinusoidal, and $E_0$ is a gaussian function $E_0(r') = I e^{-c_x(x'-x_c)^2-c_y(y'-y_c)^2-c_z(z'-z_c)^2} e^y$.

Even if for usual cases the beam is sufficiently large so that along the propagation axis, we can again neglect the $x'$ and $y'$ dependencies. The quantities $c_x, c_y, c_z$ depend on the pulse shape. The harmonics spectra of the transmitted field, denoted by $E_T$, possesses in theory [29], a frequency cut-off denoted by $\omega_c$ (see fig. 4) where $\omega_c = I_p + 3.17U_p = N \omega$ for recollision of the electron with the parent ion [35], [20]. $I_p$ is the ionization potential, $U_p = 1/4\omega^2$ (a.u.) for intensity $I$ and frequency $\omega$. $N$ is the harmonic order at the cut-off frequency. Collisions with neighboring ions such as in molecules produce larger orders $N$ due to large collision energies exceeding $3.17U_p$ [3]. It is then possible to filter this field around $\omega_c$ and to pick-up a shorter “intense” pulse denoted by $E_F$:

$$E_F(t) = \frac{1}{2\pi} \int_{\omega_c-\Delta\omega}^{\omega_c+\Delta\omega} E_T(\omega) e^{i\omega t} dt.$$ 

See for instance, [32], [2] or [4] for the control aspects. Note that, this problem constitutes typically a multiscale physical problem as the characteristic length and time of the TDSE are much smaller than the Maxwell equations characteristic ones.

There exist many models describing the physical phenomenon presented above. The most simplest ones are the nonlinear Maxwell models, and consist in calculating the polarization as an expansion of the susceptibility (linear, quadratic, cubic, and so on.):

$$P(r', t) = \Xi^{(1)} \cdot E + \Xi^{(2)} \cdot E^2 + \Xi^{(3)} \cdot E^3 + \cdots,$$

instead of deducing it from the molecular wave functions. These models allow for example to simulate the behavior of low intensity lasers with low harmonic generation. As our transmitted fields possess high order
harmonics these models are not applicable here due to the high nonlinear regime.

The Maxwell-Bloch equations constitute a more precise model where the polarization $\mathbf{P}$ is obtained from the TDSE via the Bloch equation coupled with the Maxwell equations. More precisely, supposing the nuclei fixed, the TDSE can be written in a compact form:

$$i\partial_t \psi = [H_0 + L(E)] \psi,$$

where $H_0$ is the free Hamiltonian (without laser) and $L(E)$ denotes the laser operator and $E$ the electric field. We then compute the $N$ first eigenvalues and associated eigenvectors of the Hamiltonian operator (energy levels $(\omega_j)_j$ and associated eigenfunctions, $(\phi_j)_j$), that is, supposing no degeneracy:

$$H_0 \phi_j = \omega_j \phi_j, \; \forall j \in \{1, \cdots, N\}.$$

We can then deduce the so-called dipolar matrix $\mu_j \in M_N(\mathbb{C}^3)$ obtained using the position operator and the eigenfunctions of the free Hamiltonian. Then we have to solve a set of differential equations on the electronic density matrix $\rho_j = (\rho_{jk})_{jk} \in M_N(\mathbb{C})$:

$$\begin{cases} 
\partial_t \rho_{jk} = -i(\omega_j - \omega_k)\rho_{jk} - \frac{2i\pi}{\hbar}[V, \rho], \; (j,k) \in \{1, \cdots, N\}^2; \\
\rho(\cdot, t = 0) = (\int \phi_j \phi_k^* \rho_{jk}).
\end{cases}$$

with $V = -\mu \cdot E$ under the dipolar approximation, and where $[\cdot, \cdot]$ is the Lie bracket. Finally denoting by $\mathcal{N}$ the molecular density, the polarization is given by: $\mathbf{P} = \mathcal{N} \text{tr}(\mu \cdot \rho)$. A detailed numerical study of this model can be found in [13] and [37]. To understand the validity of this model, let us observe that the polarization $\mathbf{P}$ is obtained from the energy levels of the free Hamiltonian. As is well known the computation of the eigenelements of the Hamiltonian operator is numerically very costly, so that $N$ is in practice limited to very small numbers (less than 5 usually). With such a limited model it is then $a\ priori$ not possible to reach the continuous part of the Hamiltonian to compute high order harmonics with very intense laser pulses (typically of the order of the Coulomb potential intensity).
Theorem 2.1

Let us consider the following TDSE:

\[ y \text{ and } \chi \text{ obviously not true, so that we will consider a function } \chi \text{ defined as follows: } \chi(r, t) = N a(t - z'/c + \phi(z', t)), \]

where \( \phi \) denotes the electric field envelope phase. The polarization \( P \) is then coupled with the Maxwell equations. The main advantage of this approximate technique comes from the fact that it is only necessary to solve one single TDSE to deduce the polarization \( P \) in the whole gas. However such a strong approximation induces a "loss of informations" difficult to evaluate, [28].

2.2 Existence and regularity for the TDSE model

In this section we are interested in the existence and regularity of solutions for the TDSE (5). To do this, we will use the Fourier transform set of \( H^1 \):

\[ H_1 = \{ u \in L^2(\mathbb{R}^4), \int_{\mathbb{R}^4} (1 + ||(r, R)||^2)|u(r, R)|^2 dRdR < \infty \} \]

From Baudouin and Puel [12], [11], we can easily deduce that for \( L \in L^\infty(0, T; C^0_b(\mathbb{R}^4)) \) and if \( u_0 \in H^1 \cap H_1 \), then there exists a unique solution \( u \) in \( C^0(0, T; H^1 \cap H_1) \) such that

\[ (i\partial_t + \frac{\Delta_y}{2} + \frac{\Delta_R}{m_p} + \mathcal{L}(r, R, t) )u(r, R, t) = 0, \quad u(r, R, 0) = u_0(r, R). \]

Furthermore, for \( K > 0 \) such that

\[ \| V \|_{L^\infty(0, T; C^0_b(\mathbb{R}^4))} \leq K \]

then there exists \( C_{T, K} \) such that

\[ \| u \|_{C^0(0, T; H^1 \cap H_1)} \leq C_{T, K} \| u_0 \|_{H^1 \cap H_1}. \]

Considering now (5), let us suppose that for all \( T > 0, \ E \in L^\infty(0, T) \) and \( \partial_t E \in L^1(0, T) \). The laser field \( r \cdot E(t) \) we consider is a priori non-zero in the whole space it is defined for all \( r \in \mathbb{R}^3 \). Physically it is obviously not true, so that we will consider a function \( \chi \) defined as follows: \( \chi : (r, R) \mapsto \chi(r, R) \in C^0_b(\mathbb{R}^4) \) and \( \chi(r, R) = r \) on a compact set \( \Omega_1 \) of \( \mathbb{R}^4 \) and \( \chi(r, R) \) is zero outside a set \( \Omega_2 \) containing strictly \( \Omega_1 \). Such a function can easily be constructed by convolution of \( y \) and a plateau function. Then we can prove:

Theorem 2.1 Let us consider the following TDSE:

\[ i\partial_t \psi(r, R, t) = \left[ -\frac{1}{2} \Delta_y + V_c(r, R) - \frac{1}{m_p} \Delta_R + V_i(R) - \chi(r, R) \cdot E(t) \right] \psi(r, R, t). \]

\[ \forall T > 0, \text{ suppose that } E \in L^\infty(0, T) \text{ and } \partial_t E \in L^1(0, T). \text{ Then there exists } C_T > 0 \text{ such that, for all } \psi_0 \in H^1 \cap H_1, \text{ there exists a solution unique } \psi \in L^\infty(0, T; H^1 \cap H_1) \text{ and } \]

\[ \| \psi(t) \|_{L^\infty(0, T; H^1 \cap H_1)} \leq C_T \| \psi_0 \|_{H^1 \cap H_1}. \]
The proof is based on an energy estimate in \(H_1 \cap H^1\) via a Gronwall inequality and a compactness argument to extract a convergent subsequence. As it can be derived with some elementary modifications from the proof of theorem 2.1 in [11] and is very close of existing results, for instance [25] we present it in appendix.

We can in fact improve the previous results. Under regularity assumptions on the electric field we could prove (using again [12]) that for \(u_0 \in H^2_{mp} \cap H_2\) the existence of a unique solution in \(L^\infty(0,T;H^2_{mp} \cap H_2)\).

The existence of solutions for the coupled systems Maxwell-Schrödinger has yet to be proved; in particular the regularity of the polarization (linking the two systems) is useful in our numerical approach. We can expect that the polarization regularity on \(r\) comes from the incoming electric field spatial regularity. Some interesting results about this coupling can be found for instance in [22], where the existence of global smooth and weak Maxwell-Bloch solutions is presented.

3 Numerical approach

We describe in this section our numerical method to approximate the Maxwell-Schrödinger system presented above. We will focus on the polarization computation that allows the coupling between the Maxwell and TDSE and on the boundary conditions for the TDSE and finally on the parallelization of the coupled system. Suppose to simplify the notations that the Maxwell computational domain is given by \(\Omega_M = [-L_x, L_x] \times [-L_y, L_y] \times [-L_z, L_z]\), and the vacuum region is \(\Omega_0 = [-L_x, L_x] \times [-L_y, L_y] \times [-L_z, L_z] \times /[-\ell_x, \ell_x] \times [-\ell_y, \ell_y] \times [-\ell_z, \ell_z]\). In this framework, introducing some positive constants \(0 < a < \ell < \lambda\), the molecular density can be given by:

\[
n(r') = \begin{cases} 
0, & \text{if } \ell < ||r'|| < \lambda, \\
n_0 \exp\left(-\frac{||r'||^2}{\ell^2}\right), & \text{if } a < ||r'|| < \ell, \\
n_0, & \text{if } ||r'|| \leq a,
\end{cases}
\]

where \(n_0 \in \mathbb{R}_+^*\) (mol/cm\(^3\)). Such a density choice will allow us in particular to numerically reduce the reflections of the incoming electric field on the “boundaries” of the gas. The TDSE is approximated by a finite difference Crank-Nicolson scheme in time, and the Laplace operator is approximated using a 3-points stencil. Such a scheme, allows to preserve the \(\ell^2\)-norm and is a second order scheme. The Yee scheme is used to solve the Maxwell equations [39] that consists in a finite difference scheme where the electric and magnetic fields are computed on two spatial and temporal staggered grids. Under a CFL condition this is a stable and order two scheme. At this point it is important to recall that to be valid the macroscopical Maxwell equations have to be applied on a sufficiently large domain (as it is obtained by a spatial average on microscopical Maxwell equations). Typically if we denote by \(\Delta z'M\) the Maxwell space step in the \(z'\)-direction, we should have: \(\Delta z'M \times n_0^{1/3} >> 1\) but also have \(\Delta z'M < \lambda_{\text{min}}\), with \(\lambda_{\text{min}}\) corresponding to the highest harmonics created during the HHG process. In each Maxwell cell, a large number of molecules is contained, but in practice we solve only one TDSE to determine a local polarization \(\mathbf{P}\). The simulation has then some multiple scales as \(\Delta'z'M >> \Delta y_S\) where \(\Delta y_S\) is the Schrödinger grid space step in the \(y\)-direction. We also have the condition \(\Delta t_M >> \Delta t_S\) where \(\Delta t_S, \Delta t_M\) are respectively the Schrödinger and Maxwell solvers time steps. We then set

\[
\tilde{N} = E[\frac{\Delta t_M}{\Delta t_S}] + 1.
\]

Now denoting by \(S\) the Schrödinger operator and by \(B\) the Maxwell operator, the global coupled numerical scheme is written as the following splitting scheme (here written at order 1, but is computed at order 2 to
preserve the Maxwell and Schrödinger solvers order), from time $t^n$ to time $t^{n+1}$:

$$
\begin{align*}
E^{n+1} &\leftarrow e^{\Delta t_M B^r} E^n, \quad \forall r' \in \Omega_M, \text{ solving the Maxwell equations}, \\
\psi^{n+1} &\leftarrow e^{[\Delta t_M - (\bar{N} - 1) \Delta t_S]} S^n e^{(\bar{N} - 1) \Delta t_S} S^n \psi^n, \quad \text{solving the TDSE in each “Maxwell cell”}, \\
P^{n+1} &\leftarrow \psi^{n+1}, \quad \text{by definition of the polarization}.
\end{align*}
$$

3.1 Time Dependent Schrödinger Equation

The TDSE can be summarized as,

$$
\begin{align*}
\frac{i}{\hbar} \partial_t \psi_{r'}(r, R, t) &= (A + B + C_{r'}) \psi_{r'}(r, R, t),
\end{align*}
$$

with

$$
A = -\frac{1}{2} \Delta_r + V_c, \quad B = -\frac{1}{4m_p} \Delta_R + V_i, \quad C_{r'} = r \cdot E_{r'}(t).
$$

The domain we work on is then given by $\Omega_S \times [0, R_c]$. The space steps are given by $\Delta r = (\Delta x_S, \Delta y_S, \Delta z_S)^T$ and $\Delta R$ and in the following $\Delta t_S$ will denote the time step of the numerical scheme for solving the TDSE.

3.1.1 Initial data and numerical scheme

The first step consists in computing the initial data of the TDSE given by the smallest eigenvalue and associated eigenvector of the free Hamiltonian $A + B$; that corresponds to the initial energy state. This is done here using a splitting scheme. Indeed, even if it is possible in theory to compute directly the eigenelements of the operator $A + B$ in multidimensions this constitutes a sparse eigenvalue problem that can become computationally very costly in terms of storage and algorithmic complexity. That is why we propose the following two-step process.

We first solve:

$$
A \phi(r, R) = \lambda(R) \phi(r, R),
$$

that gives a set of eigenvalues $\lambda(R)$ and associated eigenvectors $\phi(r, R)$ corresponding to $R$ fixed (Born-Oppenheimer), to the smallest eigenvalues of $A$. This is numerically obtained by a simple three point scheme to approximate the Laplace operator and by the ARPACK (www.arpack.org) Arnoldi method to compute the smallest eigenvalue and associated eigenvector of the associated sparse matrix.

In a second time, we compute:

$$
[B + \lambda(R) \text{Id}] \xi(R) = \mu \xi(R)
$$

using again a three point scheme for the Laplacian operator and an Arnoldi method to compute the smallest eigenvalue $\mu$ and associated eigenvector $\xi$.

Finally the initial data corresponding to an approximation of the initial state wave function for the considered molecule is given by:

$$
\psi(r, R) = \phi(r, R) \xi(R).
$$

in the sense that it approximates $\tilde{\psi}(r, R)$ obtained from the calculation of the smallest eigenvalue and associated eigenvector of $A + B$. This approximation can be easily justified neglecting the term $\phi(R) B \psi(r, R)$ due to the mass ratio between nuclea and electrons.

Setting $\psi^n$ an approximation of $\psi(\cdot, \cdot, t^n)$ the Crank-Nicolson scheme writes:
Figure 5: Initial data: probability $|\psi|^2(R = R_0)$

\[
\begin{align*}
\dot{\psi}^{n+1/2} - \psi^n &= -\frac{\Delta_r \psi^{n+1/2}}{4} + \left(\frac{V_c}{2} + r \cdot E^{n+1/2}\right)\psi^{n+1/2} - \frac{\Delta_r \psi^n}{4} + \left(\frac{V_c}{2} + r \cdot E^n\right)\psi^n, \\
\dot{\psi}^{n+1} - \psi^{n+1/2} &= -\frac{\Delta_R \psi^{n+1}}{2m_p} + \frac{V_i}{2}\psi^{n+1} - \frac{\Delta_R \psi^{n+1/2}}{2m_p} + \frac{V_i}{2}\psi^{n+1/2},
\end{align*}
\]

This approach is very classical and allows in particular to preserve, when the electric field is zero, the $\ell^2$-norm of $\psi$ and is of order 2. Numerically, the resolution of the sparse linear system coming from the semi-implicit Crank-Nicolson scheme is given by a LU-preconditionned GMRES iterative method (see [36]). The storage is a compressed row storage (C.R.S.).

3.1.2 Parallelization of the TDSE beyond Born-Oppenheimer approximation

The operator splitting proposed above induces a natural parallelization. Indeed, the “electronic” step:

\[
\begin{align*}
\frac{\psi^{n+1/2} - \psi^n}{\Delta t_S} &= -\frac{\Delta_r \psi^{n+1/2}}{4} + \left(\frac{V_c}{2} + r \cdot E^{n+1/2}\right)\psi^{n+1/2} - \frac{\Delta_r \psi^n}{4} + \left(\frac{V_c}{2} + r \cdot E^n\right)\psi^n, \\
\frac{\psi^{n+1} - \psi^{n+1/2}}{\Delta t_S} &= -\frac{\Delta_R \psi^{n+1}}{2m_p} + \frac{V_i}{2}\psi^{n+1} - \frac{\Delta_R \psi^{n+1/2}}{2m_p} + \frac{V_i}{2}\psi^{n+1/2},
\end{align*}
\]

has to be computed for all $k \in \{-M, \ldots, M\}$ (that is for all $R$ in $[0, R_\infty]$), but the differential Laplace operator is independent of $R$ (then of $k$). So that we have to solve $\mathcal{M} := 2M + 1$ independent sparse linear systems. These numerical resolutions are done using a Krylov iterative method with initial data depending on $k$.

\[
P \psi_k^{n+1} = Q \psi_k^n, \quad k \in \{-M, \ldots, M\}, \forall r_j
\]

where $P$ and $Q$ are some matrices of $\mathcal{M}_N \mathcal{N}(\mathbb{C})$. We then sample $\{-M, \ldots, M\}$ on the nodes of the parallel computer. In term of algorithmic complexity each linear system preconditionned resolution is of order $O(N^{3/2})$. As the number of resolutions is equal to the number of cells $\mathcal{M}$ in the $R$–grid the total algorithmic complexity at each iteration is given by $O(\mathcal{M}N^{3/2})$. By independence of the linear systems, and for a number of processors equal to $p$, each processor computes $O(\mathcal{M}N^{3/2}/p)$ operations.

Considering now the parallelization of the nuclear step: $k \in \{-M, \ldots, M\}$

\[
\frac{\psi^{n+1} - \psi^{n+1/2}}{\Delta t_S} = -\frac{\Delta_R \psi^{n+1}}{8m_p} + \frac{V_i}{2}\psi^{n+1} - \frac{\Delta_R \psi^{n+1/2}}{8m_p} + \frac{V_i}{2}\psi^{n+1/2}, \forall r_j
\]

the processing is different due to the fact that applying the previous parallelization would be very costly in 3D (as the number of a cells is of order $N^3$). We propose an approach based on the fact that numerically
the number of cells in the $R$–grid is much smaller than in the electronic grid. The numerical nuclear step can be summarized by the compact form:

$$H\psi_{n+1}^r = K\psi_n^r,$$

where $H$ and $K$ are matrices of $M_M M_C$, where $M$ is the number of grid-points in the $R$-grid. We then propose to compute and store the constant operator $H^{-1} K$. This operation has to be done only one time. We are led to compute $N$ matrix-vector products to deduce the global wavefunction. The natural parallelization then consists in the well-known parallelization of the matrix-vector product $H^{-1} K \times \psi_n^{n+1}$. The use of this technique implies an adapted numerical code design that is not detailed here.

In 7, we represent the computational time with respect to the number of processors. The simulations use a computer of 576 nodes Dell 1425SC (1152 CPU Intel Xeon, 3.6 GHz) 8 GB RAM / node with infiniband network 4X. The baby-benchmark consists in a one-dimensional laser-molecule interaction with 100 points in the “electronic”-grid, 100 points in the “nuclear”-grid.

To conclude this section, here is a detail of the communications between processors for the construction of the initial data. To simplify the presentation let us suppose that we use only two processors.

1. The processor 1 (root) first computes $\phi_{R_1}(r, R)$ and $\lambda_{R_1}(R)$ solutions of the eigenvalue problem for the electronic Hamiltonian, for $R \in [0, R_1]$, $0 < R_1 < R_{\infty}$. The second processor (slave) computes $\phi_{R_2}(r, R)$ and $\lambda_{R_2}(R)$ solution of the eigenvalue problem for the electronic Hamiltonian, for $R \in [R_1, R_{\infty}]$. 

- Figure 6: Sampling
- Figure 7: Speed-up: 1 → 16 processors

10
2. Then \( \lambda_{R_2}(R) \) is sent by the slave processor to the root processor in order to compute the solution of the eigenvalue problem of the nuclear Hamiltonian. This then gives \( \xi(R) \) for all \( R \in [0, R_∞] \).

3. Then \( \xi(R) \) is sent to the slave in order to construct \( \phi_{R_2}(r, R)\xi(R) \) for \( R \in [R_1, R_∞] \). In the same time, the root processor gets \( \phi_{R_1}(r, R)\xi(R) \) for \( R \in [0, R_1] \).

4. Then the two processors compute the square integral of their wavefunction part that gives \( I_1^2 \) and \( I_2^2 \) respectively for the root and slave processor.

5. Finally the value \( I_2 \) is sent to the root processor to compute the total integral \( I = \sqrt{I_1^2 + I_2^2} \) and the root processor normalizes its part of the wavefunction: \( \phi_{R_1}(r, R)\xi(R)/I \),

6. and sends to the slave processor \( I \) for normalization: \( \phi_{R_2}(r, R)\xi(R)/I \).

At the end, the total normalized wavefunction \( \phi(r, R)\xi(R)/I \) is then given by

\[
(\phi_{R_1}(r, R)\xi(R)/I, \phi_{R_2}(r, R)\xi(R)/I),
\]

### 3.2 Boundary conditions for the TDSE

Let us now discuss the boundary conditions problem for the TDSE. The initial wavefunction (initial state) support is located in the Schrödinger computational domain center. Then the laser interacts with a molecule expanding the wavefunction by ionization whose support that can become very large. Numerically this means that it is necessary to discretize the Schrödinger equation in a very large domain. To overcome this well-known problem in numerical scattering theory, we have to find an adapted method. The usual idea to circumvent this difficulty is to reduce the computational domain and to impose some particular numerical boundary conditions on the reduced domain. It is well-known that imposing Dirichlet or Neumann boundary conditions leads to important numerical oscillations and reflections on the boundary of the domain interacting with the “physical” waves inside the domain. Absorbing boundary conditions are also used in order to absorb the numerical spurious reflections. Even if this kind of methods allows effectively to reduce the spurious reflections, they are often empirical (see for instance [17] in this framework), as some parameters have to be adapted for each numerical situation. Moreover the spurious reflections are made to vanish but a part of the wavefunction can also be partially absorbed by the absorber. In particular the \( ℓ^2 \)-norm of the wavefunction can hardly be preserved. Ideally we would like to impose particular boundary conditions such that the solution of the whole space problem restricted to the compact domain is equal to the solution on the compact domain (i.e. without spurious reflections).

#### 3.2.1 One-dimensional boundary conditions

To be more precise let us consider the following simplified one-dimensional model without laser:

\[
\begin{aligned}
(i\partial_t u + \Delta u + V(x) \cdot u)(x, t) &= 0, \\
u(x, 0) &= u_0(x), \quad u_0 \in H^1(\mathbb{R}).
\end{aligned}
\]

We suppose that the supports of \( u_0 \) and \( V \) are strictly included in a compact set \( \bar{\Omega} \). One then considers the domain \( \Omega \times [0, T] \) with \( \bar{\Omega} \subset \Omega \) and one denotes by \( \Gamma \) the boundary of \( \Omega \). One then looks for \( v \) solution of

\[
\begin{aligned}
(i\partial_t v + \Delta v + V(x) \cdot v)(x, t) &= 0, \quad x \in \Omega, \\
\mathcal{B}(x, \partial_x, \partial_t) v(x, t) &= 0, \quad x \in \Gamma, \\
v(x, 0) &= u_0(x), \quad x \in \Omega, \quad u_0 \in H^1(\mathbb{R}).
\end{aligned}
\]
such that

$$u|_{\Omega \times [0,T]} = v. \quad (10)$$

The main problem consists then in finding an adequate (pseudo-)differential boundary operator $B$ on $\Gamma$ such that (10) occurs. As it well-known these conditions, called Dirichlet-Neumann, are nonlocal in time (and in space in multidimension). To be more precise we can rewrite this system as follows:

$$
\begin{cases}
(i\partial_t v + \Delta v + Vv)(x, t) = 0, & x \in \Omega, \\
\partial_n v = Dv, & x \in \Gamma, \\
v(x, 0) = u_0(x), & u_0 \in H^1(\mathbb{R}).
\end{cases}
$$

with $n$ the outward normal of $\Gamma$ and $\partial_n$ is the trace operator on $\Gamma$. And $D$ is a first order nonlocal pseudo-differential operator. One then has to solve a TDSE outside $\Omega$. To do this one uses the Laplace transform in time, the Sommerfeld radiation condition and the solution of the second order complex ODE. One can finally obtain:

$$v = -e^{i\pi/4} \int_0^t \frac{\partial_n v(x, \tau)}{\sqrt{\pi(t-\tau)}} d\tau \quad \text{on } \Gamma. \quad (11)$$

So that one has the following set of continuous equations:

$$
\begin{cases}
(i\partial_t v + \Delta v + V \cdot v)(x, t) = 0, & x \in \Omega, \\
v(x, t) = -e^{i\pi/4} \int_0^t \frac{\partial_x v(x, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, & x \in \Gamma, \\
v(x, t) = -e^{i\pi/4} \int_0^t \frac{\partial_x v(-x, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, & x \in -\Gamma. 
\end{cases}
$$
This approach has been previously described in particular in [6], and some numerical issues can be found in [7], [8]. As unfortunately these conditions are nonlocal in time, some numerical methods have been devoted to find effective numerical approximations. At each iteration we can for instance decompose the integral (11) as the sum of a local part and historical part as proposed in [27]. Thus at time $t^{n+1}$:

$$v(x_{Γ}, t^{n+1}) = -e^{iπ/4} \int_{0}^{t^{n+1}} \frac{∂_x v(x_{Γ}, τ)}{√(π(t^{n+1} - τ))}dτ,$$

is decomposed into

$$v(x_{Γ}, t^{n+1}) = -e^{iπ/4} \int_{0}^{t^{n}} \frac{∂_x v(x_{Γ}, τ)}{√(π(t^{n+1} - τ))}dτ - e^{iπ/4} \int_{t^{n}}^{t^{n+1}} \frac{∂_x v(x_{Γ}, τ)}{√(π(t^{n+1} - τ))}dτ.$$

One can then compute the historical part $e^{iπ/4} \int_{0}^{t^{n+1}} \frac{∂_x v(x_{Γ}, τ)}{√(π(t^{n+1} - τ))}dτ$ using an explicit approximation and to implicit the local part $e^{iπ/4} \int_{t^{n}}^{t^{n+1}} \frac{∂_x v(x_{Γ}, τ)}{√(π(t^{n+1} - τ))}dτ$. Such an approach is known to reduce drastically the artificial reflections on the boundaries (see again [27]).

Now we present some ideas related to the boundary conditions for the TDSE coupled with a laser. As the laser operator does not depend on the inter-nuclear distance $R$ we suppose it here constant, so that the equation we consider here simply writes:

$$i∂_t \psi(y, t) = \left(-\frac{1}{2}Δ_y + V(y) + yE(t)\right)\psi(y, t). \tag{12}$$

It is important to note that the term $V(y) + yE(t)$ has not a compact support, so that it is no more possible to solve “easily” the free potential TDSE outside a bounded domain as done above. Indeed, outside a given domain containing the support of the Coulomb potential, the equation writes:

$$i∂_t \psi(y, t) = \left(-\frac{1}{2}Δ_y + yE(t)\right)\psi(y, t).$$

Using as above a Laplace transform in time would lead to a convolution product between the Laplace transforms of $E$ and $ψ$. We then propose not to solve exactly this equation but to give an approximate condition based on a splitting operator. With the known solution on the boundaries at time $t^n$ we search for it at time $t^{n+1}$ splitting the equation (12):

$$\begin{cases} i∂_t \psi(y, t) = yE(t)\psi(y, t), & x ∈ Γ, \ [t^n, t^{n+1/2}], \\ i∂_t \psi(y, t) = \left(-\frac{1}{2}Δ_y + V(y)\right)\psi(y, t), & x ∈ Γ, \ [t^{n+1/2}, t^{n+1}]. \end{cases}$$

The first equation provides the following solution:

$$ψ(x_{Γ}, t^{n+1/2}) = e^{-ix_{Γ}∫_{t^n}^{t^{n+1/2}} E(s)ds}ψ(x_{Γ}, t^n).$$

To approximate the second one we consider the solution at time $t^{n+1}$ when the laser is null:

$$ψ(x_{Γ}, t^{n+1}) = -e^{iπ/4} \int_{0}^{t^{n+1}} \frac{∂_x ψ(x_{Γ}, τ)}{√(π(t^{n+1} - τ))}dτ.$$

We then decompose this integral in two parts corresponding to the local and historical parts.

$$ψ(x_{Γ}, t^{n+1}) = -e^{iπ/4} \int_{0}^{t^{n}} \frac{∂_x ψ(x_{Γ}, τ)}{√(π(t^{n+1} - τ))}dτ - e^{iπ/4} \int_{t^{n}}^{t^{n+1}} \frac{∂_x ψ(x_{Γ}, τ)}{√(π(t^{n+1} - τ))}dτ.$$
The historical part depends on \( \psi \) at time \( t^n \) and is then known at time \( t^{n+1} \). For the local part we use \( \psi(x_T, t^{n+1/2}) \) in order to compute \( \psi(x_T, t^{n+1}) \). More precisely and following some approximations proposed by Greengard in [27], the historical part is approximated by:

\[
-e^{i\pi/4} \int_0^{t^n} \frac{\partial_x \psi(x_T, \tau)}{\sqrt{\pi(t^{n+1} - \tau)}} \sim -e^{i\pi/4} \sum_{j=1}^M w_j c_j(n),
\]

where \( (c_j(n))_j \) and \( (w_j)_j \) are sequences described in [27]. The local part is then approximated by a Gauss-Legendre formula,

\[
e^{i\pi/4} \int_{t^n}^{t^{n+1}} \frac{\partial_x \psi(x_T, \tau)}{\sqrt{\pi(t^{n+1} - \tau)}} d\tau \sim -e^{i\pi/4} \sqrt{\frac{\Delta t^{n+1}}{\pi}} \left( \frac{\Delta t^{n+1}}{\Delta x} \alpha \psi^{n+1/2}_x + (2 - \alpha) \psi^n_x \right), \quad 0 \leq \alpha \leq 2.
\]

With such an approach we then have the following boundary conditions. If \( J \) denotes the last cell index: \( J \Delta x = x_T \in \Gamma \).

\[
\begin{cases}
\psi_j^{n+1} = -e^{i\pi/4} \left( \sum_{j=1}^{J-1} w_j c_j(n) + \sqrt{\frac{\Delta t^{n+1}}{\pi}} \frac{\psi_j^{n+1/2} - \psi_{j-1}^{n+1/2}}{\Delta x} e^{-ix_T \int_{t^n}^{t_{n+1}} E(s) ds} (2 - \alpha) \psi^n_j \right), \\
c_j(n+1) = e^{\Delta t^n} c_j(n) + \frac{\Delta t^n}{2} \left( e^{-s^2 \Delta t^n} \psi_j^{n+1} - \psi_{j-1}^{n+1} \right),
\end{cases}
\]

With then,

\[
\psi_j^{n+1/2} = e^{-ix_T \int_{t^n}^{t_{n+1}} E(s) ds} \psi_j^n, \quad \psi_{j-1}^{n+1/2} = e^{-ix_T \int_{t^n}^{t_{n+1}} E(s) ds} \psi_{j-1}^n.
\]

Note that by induction, the historical part depends also on the laser. A symmetric approach is proposed in \( -x_T \). These 2 discrete equations in \( -J \) and \( J \) close the Crank-Nicolson system. Then the hermitian structure of the sparse matrix is lost so that a GMRES method is used to solve the linear system. Our strong assumption consists then in searching for a numerical boundary condition that behaves like \( \int_0^T \partial_\tau \psi(x, \tau)/\sqrt{\pi(t - \tau)} d\tau \). It is straightforward to apply the technique presented above in the velocity gauge as we do in the following numerical example.

To illustrate this technique we propose a simple benchmark on the TDSE for fixed \( R \), in the velocity gauge (4). We suppose that the Coulomb potential is equal to zero and the electron function solutions are Volkov states [17], [14].

\[
\begin{cases}
(i \partial_t u + \partial_{xx} u + i A(t) \partial_x u) = 0, \quad x \in \mathbb{R}, \quad t \geq 0, \\
u(x, 0) = u_0(x), \quad u_0 \in H^1(\mathbb{R}).
\end{cases}
\]

The benchmark we propose is as follows. The space grid \( \tau \) contains 100 cells with a space step equal to 0.1. The convective part is approximated using an upwind scheme and the diffusive one is approximated using a Crank-Nicolson scheme. The computational domain is divided in 3 equal regions. At each internal frontier (located in \( x_1 = -12.5 \) and \( x_2 = 12.5 \)), we impose Dirichlet-Neumann boundary conditions combined with Dirichlet boundary conditions for the convection operator. The laser field is stated in fig. 10. Note that the exact solution always remains inside \( \tau \); we can then apply Dirichlet boundary conditions at the extremal boundaries located in \( x = -25 \) and \( x = 25 \). We observe a good behavior of the numerical solution with respect to the exact one (fig. 10) despite the coarsiness of the grid: after 185 iterations (2 laser cycles), in \( \ell^\infty \)-norm the relative error between the exact and approximate solution is 6%.

### 3.2.2 Extension to cubic domains

As discussed in the one-dimensional case above, the treatment of the boundary conditions is crucial in order to limit the computational complexity. In practice adequate boundary conditions allow to limit the size of
the computational box for the TDSE. Thus instead of discretizing $\mathbb{R}^3$, we can reduce the domain of computation to a “small” box and then can reduce the algorithmic complexity. The Dirichlet-Neumann boundary conditions proposed are a possible solution. However a direct application of the method seen above will introduce some numerical instabilities.

We next consider the computational domain in a cubic box. The Crank-Nicolson scheme for the TDSE requires boundary conditions to be imposed at the cube faces. These faces are planar it is then trivial to extend the modified Dirichlet-Neumann conditions seen above. We denote by $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5, \Gamma_6$ the six faces of the domain, located in $x = x_{\Gamma_1}, x = x_{\Gamma_2}, y = y_{\Gamma_3}, y = y_{\Gamma_4}, z = z_{\Gamma_5}, z = z_{\Gamma_6}$. Then, supposing that the propagation is one-dimensional (in $z'$) and polarized in $y$ the boundary conditions are:

$$
\begin{aligned}
-\partial_{n_1} u(x_{\Gamma_1}, y, z, t) &= e^{i\pi/4} \int_0^t \frac{\partial_x u(x_{\Gamma_1}, y, z, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \ (x, y, z) \in \Gamma_1, \ t \geq 0, \\
-\partial_{n_2} u(x_{\Gamma_2}, y, z, t) &= e^{i\pi/4} \int_0^t \frac{\partial_x u(x_{\Gamma_2}, y, z, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \ (x, y, z) \in \Gamma_2, \ t \geq 0, \\
-\partial_{n_3} u(x, y_{\Gamma_3}, z, t) &= e^{i\pi/4} \int_0^t \frac{\partial_y u(x, y_{\Gamma_3}, z, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \ (x, y, z) \in \Gamma_3, \ t \geq 0 + \text{ laser conditions,} \\
-\partial_{n_4} u(x, y_{\Gamma_4}, z, t) &= e^{i\pi/4} \int_0^t \frac{\partial_y u(x, y_{\Gamma_4}, z, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \ (x, y, z) \in \Gamma_4, \ t \geq 0 + \text{ laser conditions,} \\
-\partial_{n_5} u(x, y, z_{\Gamma_5}, t) &= e^{i\pi/4} \int_0^t \frac{\partial_z u(x, y, z_{\Gamma_5}, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \ (x, y, z) \in \Gamma_5, \ t \geq 0, \\
-\partial_{n_6} u(x, y, z_{\Gamma_6}, t) &= e^{i\pi/4} \int_0^t \frac{\partial_z u(x, y, z_{\Gamma_6}, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \ (x, y, z) \in \Gamma_6, \ t \geq 0.
\end{aligned}
$$

The coupling with the laser field is done the same way as for 1D. We extend therefore the idea developed in 1D on $\Gamma_3, \Gamma_4$. Let us consider the conditions on $\Gamma_3$ at time $t^n$:

$$
\begin{aligned}
u(x, y_{\Gamma_3}, z, t^n+1) &= e^{i\pi/4} \int_0^{t^n+1} \frac{\partial_z u(x, y_{\Gamma_3}, z, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \ (x, z) \in \Gamma_3.
\end{aligned}
$$

Numerically:

$$
\begin{aligned}
u(x, y_{\Gamma_3}, z, t^{n+1}) &= e^{i\pi/4} \int_0^{t^n} \frac{\partial_z u(x, y_{\Gamma_3}, z, \tau)}{\sqrt{\pi(t-\tau)}} d\tau + e^{i\pi/4} \int_{t^n}^{t^{n+1}} \frac{\partial_z u(x, y_{\Gamma_3}, z, \tau)}{\sqrt{\pi(t-\tau)}} d\tau.
\end{aligned}
$$

15
For the historic part we use the previous computed solutions on the boundary and depending on the laser. In this goal we then compute the numerical solution of

\[ u_t + yE_z(t)u = 0, \quad (x, y, z) \in \Gamma_3, \quad t \in [t^n, t^{n+1}]. \]

Between \([t^n, t^{n+1}]\) we have

\[ u(x, y_{\Gamma_3}, z, t^n)e^{-i \int_{t^n}^{t^{n+1}} E(s)ds} \text{ denoted by } u^{n+1/2}_{\Gamma_3}(x, z). \]

We then use this solution in order to approximate the local part in (13) using the same approach as above:

\[ e^{i\pi/4} \int_{t^n}^{t^{n+1}} \frac{\partial_z u(x, y_{\Gamma_3}, z, \tau)}{\sqrt{\pi(t^{n+1}-\tau)}} d\tau \sim -e^{i\pi/4} \sqrt{\frac{\Delta t^{n+1}}{\pi}} (\frac{4}{3} u^{n+1/2}_{\Gamma_3}(x, z) + \frac{2}{3} u^2_{\Gamma_3}(x, y_{\Gamma_3}, z)), \forall (x, z) \in \Gamma_3. \]

However the computational domain is singular and these conditions are no more valid on the plane intersections and corners of the domain. We propose a more adequate way to treat the boundary conditions in multidimensions. In order to limit the effect of the singularities we propose to work on a “more regular” grid, a circular cylinder.

3.2.3 Using real 2D Dirichlet-Neumann boundary conditions - Application to 3D domains

In this section we examine some possible solutions to improve the boundary conditions treatment in multiD. The numerical computation of these boundary conditions are in progress. As seen above the singularities of the 3D domain (cubic box) lead to construct truly multi-dimensional Dirichlet-Neumann boundary conditions. In this goal let us recall some important results. Considering the 2D problem (with \( r = (x, y) \) here).

\[ \begin{cases} 
    i\partial_t u = -\left(\Delta_r + V(r)\right)u, & r \in \mathbb{R}^2, \\
    u(r, 0) = u_0(r).
\end{cases} \]

To determine the Dirichlet-Neumann boundary conditions we have to solve outside a compact domain \( \Omega \) containing the supports of \( u_0 \) and \( V \), the equation:

\[ i\partial u = -\Delta_r u, \quad r \in \Omega^C. \]
The solution is obtained using the Laplace transform in space (see [38]) and the Sommerfeld radiation condition that ensures unicity and positivity of the energy flux and is nonlocal in space and in time. That is the condition on each point of the boundary depends on all the boundary points at all previous times. It is then computationally very complex to apply directly such a method. It is necessary to establish an appropriate numerical method effective in space and time or at least in time or in space. With this aim, we propose to use the approach of Antoine and Besse as a starting point. They proved that the Dirichlet-Neumann conditions (nonlocal in space and time) can be approximated (to order 3) by some differential operators. That is the spatial nonlocality is replaced by local differential operators even if the formulation remains nonlocal in time. In particular they proved in 2D the following theorem (see [7]):

\[ \text{Theorem 3.1 [Antoine & Besse, '01] } \text{The TDSE with artificial boundary conditions of Dirichlet-Neumann type of order } m/2 \text{ with } m \in \{1, \cdots, 4\} \text{ is defined by the initial boundary value problem:} \]

\[
\begin{cases}
  i\partial_t u(r, t) + \Delta_r u(r, t) = 0, & (r, t) \in \Omega \times \mathbb{R}^*_+,
  \\
  \partial_n u(r, t) + T_{m/2} u(r, t) = 0, & (r, t) \in \Omega \times \mathbb{R}^*_+,
  \\
  u(r, 0) = u_0(r), & r \in \Omega.
\end{cases}
\]

where \( T_{m/2} \) are pseudo-differential in time and differential in space operators given by:

\[
\begin{aligned}
  T_{1/2}^2 u &= e^{-i\pi/4} \partial_t^{1/2} u, \quad \partial \Omega \times \mathbb{R}^*_+ \\
  T_1 u &= T_{1/2}^2 u + \frac{\kappa}{2} u, \quad \partial \Omega \times \mathbb{R}^*_+ \\
  T_{3/2}^2 u &= T_1 u - e^{i\pi/4} \left( \frac{\kappa^2}{8} + \frac{1}{2} \Delta_{\partial \Omega} \right) I_t^{1/2} u, \quad \partial \Omega \times \mathbb{R}^*_+ \\
  T_2 u &= T_{3/2}^2 u + i \left( \frac{\kappa^3}{8} + \frac{1}{2} \partial_s (\kappa \partial_s) + \frac{\Delta_{\partial \Omega}}{8} \right) I_t u, \quad \partial \Omega \times \mathbb{R}^*_+
\end{aligned}
\]

The operator \( \Delta_{\partial \Omega} \) is the Laplace-Beltrami operator and \( \kappa \) is the local curvature of \( \partial \Omega \). The pseudo-differential convolution \( I_t^{1/2} \) and \( \partial_t^{1/2} \) are defined by:

\[
\partial_t^{1/2} u(t) = \frac{1}{\sqrt{i}} \frac{d}{dt} \int_0^t \frac{u(y)}{\sqrt{t-y}} dy, \quad I_t^{1/2} u(t) = \frac{1}{\sqrt{\pi}} \frac{d}{dt} \int_0^t \frac{u(y)}{\sqrt{t-y}} dy.
\]

These conditions in the twodimensional case allow to reduce drastically the spurious reflexions on \( \partial \Omega \) (see [8]). The extension of these formulas to the 3D case are of course possible and are based on the Laplace transform in time of the TDSE, the resolution of the obtained Helmholtz equation under the Sommerfeld radiation condition and then by inverse Laplace transform. We then propose to combine these boundary conditions with the electric field operator. In order to use the 2D approach, we propose to work in cylindrical coordinates for the 3D problem.

We suppose for the presentation that the nuclei are fixed (Born-Oppenheimer approximation) and the potential are set to zero. This assumption is only imposed for the sake of simplicity. This has no consequence on the method for the global problem with potentials and with moving nuclei. In cylindrical coordinates our equations write:

\[
\begin{cases}
  \left( i\partial_t + \Delta_r + \frac{1}{r} \partial_r + \frac{1}{r^2} \Delta_\theta + \Delta_z \right) u(r, \theta, z, t) = 0, & (r, \theta, z, t) \in \mathbb{R}^+ \times [0, 2\pi] \times \mathbb{R} \times \mathbb{R}^*_+,
  \\
  u(r, \theta, z, 0) = u_0(r, \theta, z), & (r, \theta, z) \in \mathbb{R}^+ \times [0, 2\pi] \times \mathbb{R}.
\end{cases}
\]
Finally $\Gamma = \Gamma_\theta \cup \Gamma_{-z} \cup \Gamma_z$. The finite difference discretization will be discussed later. The natural Dirichlet-Neumann boundary conditions are then given by extension of the previous formulas by:

$$
\begin{align*}
-\partial_{\nu_{r-z}} v(r, \theta, z, t) &= e^{i\pi/4} \int_0^t \frac{\partial_z u(r, \theta, z_{r-z}, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \quad (r, \theta, z) \in \Gamma_{-z}, \\
-\partial_{\nu_{r-z}} v(r, \theta, z, t) &= e^{i\pi/4} \int_0^t \frac{\partial_z u(r, \theta, z_{r-z}, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \quad (r, \theta, z) \in \Gamma_z, \\
-\partial_{\nu_{r}} v(r = R_{\text{max}}, \theta, z, t) + T_{m/2} u(r = R_{\text{max}}, \theta, z, t) &= 0, \quad (r, \theta, z) \in \Gamma_\theta.
\end{align*}
$$

In the particular case of a circular cylinder the Laplace-Beltrami operator $\triangle_{r_{\theta}}$ is given by $\triangle$.

Suppose now that a laser polarized in $z$ indpendant of $\theta$ interacts with the molecule. Then for $(r, \theta, z, R, t) \in \mathbb{R}^+ \times [0, 2\pi] \times \mathbb{R} \times \mathbb{R}^+ \times \mathbb{R}^+_z$:

$$
\begin{align*}
\left\{ \begin{array}{l}
(\partial_t + \Delta_r + \Delta_R + \frac{1}{r} \partial_r + \frac{1}{r^2} \Delta_\theta + \frac{1}{R^2} + \Delta_z + V_c(r, \theta, z, R) + V_i(R) + zE(t)) u(r, \theta, z, R, t) = 0, \\
u(r, \theta, z, R, 0) = u_0(r, \theta, z, R).
\end{array} \right.
\end{align*}
$$

We suppose that the nuclei are fixed (Born-Oppenheimer approximation). This also corresponds to the electronic step in the global scheme with moving nuclei:

$$
\begin{align*}
\left\{ \begin{array}{l}
(\partial_t + \Delta_r + \frac{1}{r} \partial_r + \frac{1}{r^2} \Delta_\theta + \Delta_z + V_c(r, \theta, z) + zE(t)) u(r, \theta, z, t) = 0, \quad (r, \theta, z, t) \in \mathbb{R}^+ \times [0, 2\pi] \times \mathbb{R} \times \mathbb{R}^+, \\
u(r, \theta, z, 0) = u_0(r, \theta, z), \quad (r, \theta, z) \in \mathbb{R}^+ \times [0, 2\pi] \times \mathbb{R}.
\end{array} \right.
\end{align*}
$$

Then, the coupling of the Dirichlet-Neuman boundary conditions is direct using the previous study. Indeed the TDSE with Dirichlet-Neumann boundary conditions on $\Gamma_{\theta}$ can be written as:

$$
\begin{align*}
\left\{ \begin{array}{l}
(\partial_t + \Delta_r + \frac{1}{r} \partial_r + \frac{1}{r^2} \Delta_\theta + V_c(r, \theta, z)) u(r, \theta, z, t) = 0, \quad (r, \theta, z, t) \in [0, R_{\text{max}}] \times [0, 2\pi] \times \mathbb{R} \times \mathbb{R}^+, \\
-\partial_{\nu_{r}} u(r = R_{\text{max}}, \theta, z, t) + T_{m/2} u(r = R_{\text{max}}, \theta, z, t) = 0, \quad (r, \theta, z) \in \Gamma_\theta, \ t \geq 0.
\end{array} \right.
\end{align*}
$$
As \( \Delta_r, \Delta_z = [\Delta_\theta, \Delta_z] = 0 \). So that we solve:

\[
\begin{cases}
(i\partial_t + \Delta_r + \frac{1}{r^2}\Delta_\theta + V_c(z, \theta, z))u(r, \theta, z, t) = 0, \ (r, \theta, z, t) \in [0, R_{\text{max}}] \times [0, 2\pi] \times \mathbb{R} \times \mathbb{R}_+^* \\
-\partial_{n_r} u(r = R_{\text{max}}, \theta, z, t) + T_{m/2}(r = R_{\text{max}}, \theta, z)u(r, \theta, z, t) = 0, \ (r, \theta, z) \in \Gamma_\theta, \ m \geq 1, t \geq 0, \\
(i\partial_t + \Delta_z + V_c(z, \theta, z) + gE(t))u(r, \theta, z, t) = 0, \ (r, \theta, z, t) \in [0, R_{\text{max}}] \times [0, 2\pi] \times \mathbb{R} \times \mathbb{R}_+^* \\
-\partial_{n_z} u(r, \theta, z, t) = e^{\pi/4} \int_0^t \frac{\partial_z u(r, \theta, z, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \ (r, \theta, z) \in \Gamma_z, \ t \geq 0 \ \text{+ laser conditions}, \\
-\partial_{n_z} u(r, \theta, z, t) = e^{\pi/4} \int_0^t \frac{\partial_z u(r, \theta, z, \tau)}{\sqrt{\pi(t-\tau)}} d\tau, \ (r, \theta, z) \in \Gamma_z, \ t \geq 0 \ \text{+ laser conditions}.
\end{cases}
\]

In the previous formula the pseudo-differential operators \( T_{m/2} \) are defined in [7] and theorem (3.1). The discretization we propose is again very classical and is based on the three-point Crank-Nicolson scheme. In the following we denote by \((r_i), (\theta_j), (z_k)\) the grid points.

- If \( r \neq 0 \):

\[
\begin{align*}
iv_{n+1}^{i,j,k} &= iv_n^{i,j,k} + \Delta t M \left( \frac{1}{2} \Delta_r \psi_n^{i,j,k} + \frac{1}{2} \Delta_z \psi_n^{i,j,k} + \frac{1}{2r_i^2} \Delta_\theta \psi_n^{i,j,k} + \frac{1}{2r_i} \partial_r \psi_n^{i,j,k} + \frac{1}{2r_i} \partial_\theta \psi_n^{i,j,k} + \frac{1}{2} \Delta_z \psi_n^{i,j,k} + \frac{1}{2} \Delta_\theta \psi_n^{i,j,k} \right),
\end{align*}
\]

- If \( r = 0 \) it is well known that the equation becomes:

\[
\begin{align*}
(i\partial_t + 2\Delta_r + \Delta_z)\psi(r, \theta, z, t) = 0, \ (r, \theta, z, t) \in \mathbb{R}^+ \times \mathbb{R} \times [0, 2\pi] \times \mathbb{R}_+^*,
\end{align*}
\]

so that:

\[
\begin{align*}
iv_{n+1}^{0,j,k} &= iv_n^{0,j,k} + \Delta t \left( \Delta_r \psi_n^{0,j,k} + \Delta_z \psi_n^{0,j,k} + \frac{1}{2} \Delta_\theta \psi_n^{0,j,k} + \frac{1}{2} \Delta_z \psi_n^{0,j,k} \right),
\end{align*}
\]

with obviously.

Figure 12: 3D domain
• If $r \neq 0$

$$\frac{\Delta \psi_{i,j,k}}{r_i} \sim \frac{\psi_{i+1,j,k} - 2\psi_{i,j,k} + \psi_{i-1,j,k}}{r_i^2 \Delta \theta^2}, \quad \forall j, i \neq 0,
\frac{\partial \psi_{i,j,k}}{r_i} \sim \frac{\psi_{i+1,j,k} - \psi_{i-1,j,k}}{2r_i \Delta r}, \quad \forall j, i \neq 0,$$

$$\Delta_r \psi_{i,j,k} \sim \frac{\psi_{i,j,k+1} - 2\psi_{i,j,k} + \psi_{i,j,k-1}}{\Delta r^2}, \quad \forall j, k, \quad \Delta_z \psi_{i,j,k} \sim \frac{\psi_{i+1,j,k} - 2\psi_{i,j,k} + \psi_{i-1,j,k}}{\Delta z^2}, \quad \forall i, j.$$

• If $r = 0$, then the approximation is given by $2\Delta_r \psi(0, z_k) \sim 4\frac{\psi(r_1, z_k) - \psi(0, z_k)}{\Delta r^2}, \quad \forall k.$

This corresponds to a free Hamiltonian Dirichlet-Neumann boundary conditions and has to be combined with the laser is polarized in the $y$-direction, the combination consists in coupling the laser field with the boundary conditions on $\Gamma_s$ and $\Gamma_{-z}$. On $\Gamma_{\theta}$ as long as the laser polarization remains one-dimensional and polarized in $y$ we can keep the same conditions than above.

### 3.3 Maxwell equations

The Maxwell equations are approximated using the Yee scheme [39] with Mur’s absorbing boundary conditions [30]. This is a stable order 2 scheme under a CFL condition:

$$\Delta t_M \leq \frac{1}{c} \sqrt{\frac{1}{\Delta x_M^2} + \frac{1}{\Delta y_M^2} + \frac{1}{\Delta z_M^2}}. \quad (14)$$

In vacuum we then use the classical Yee scheme and we add the polarization derivative in time $\partial_t \mathbf{P}$, when the laser interacts with the gas. An important issue is to ensure that inside the gas the divergence condition on $\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P}/c$, $\nabla \cdot \mathbf{D} = 0$ is effectively verified at the discrete level.

**Proposition 3.1** The condition $\nabla_h \cdot \mathbf{D}_h^n = 0$ is numerically verified by the modified Yee scheme for all $n \in \mathbb{N}$ provided that $\nabla_h \cdot \mathbf{D}_h^0 = 0$.

**Proof.** It is well-known that the Yee scheme in the vacuum leads to

$$\nabla_h \cdot \mathbf{E}_h^{n+1} = \nabla_h \cdot \mathbf{E}_h^n.$$

This allows to prove that the Yee scheme verifies $\nabla_h \mathbf{E}_h^n = 0$ provided that $\nabla_h \mathbf{E}_h^0 = 0$. In the non-homogeneous case, the same calculations lead us to the following discrete equation:

$$\nabla_h \cdot \mathbf{E}_h^{n+1} + 4\pi \Delta t_M \nabla_h \left( \partial_t \mathbf{P}_h^{n+1} \right) = \nabla_h \cdot \mathbf{E}_h^n.$$

That is suppose $\mathbf{P}$ regular enough in time and space (see next section):

$$\nabla_h \cdot \mathbf{E}_h^{n+1} + 4\pi \Delta t_M \partial_t \left( \nabla_h \mathbf{P}_h^{n+1} \right) = \nabla_h \cdot \mathbf{E}_h^n.$$

Now using the approximation of the partial derivative in time we have used:

$$\partial_t \left( \nabla_h \mathbf{P}_h^{n+1} \right) = \frac{\nabla_h \mathbf{P}_h^{n+1} - \nabla_h \mathbf{P}_h^n}{\Delta t_M},$$

then

$$\nabla_h \cdot \mathbf{E}_h^{n+1} + 4\pi \Delta t_M \left( \frac{\nabla_h \mathbf{P}_h^{n+1} - \nabla_h \mathbf{P}_h^n}{\Delta t_M} \right) = \nabla_h \cdot \mathbf{E}_h^n.$$

\(^1\mathbf{E}_h, \mathbf{D}_h, \nabla_h \) denote the discrete versions of $\mathbf{E}, \mathbf{D}$ and $\nabla$. 

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So that:
\[ \nabla_h \cdot E_h^{n+1} + 4\pi \nabla_h P_h^{n+1} = \nabla_h \cdot E_h^n + 4\pi \nabla_h P_h^n. \]

Then, provided that \( \nabla_h \cdot D_h^0 = 0 \), it is true for all \( n \). \( \square \)

Typically the kind of initial data we consider is as fig. 13. And obviously we have:

**Theorem 3.2** The global scheme is an order 2 scheme, stable under the CFL condition (14).

---

### 3.4 Polarization computation

The polarization computation is central in this work as it allows to couple the Maxwell equations and TDSE. As said above the polarization is deduced from the TDSE by (7). In practice in each Maxwell-cell we will solve numerically one single TDSE and we will deduce the local polarization for a physical volume of size \( \Delta x'_M \times \Delta y'_M \times \Delta z'_M \) and containing \( n(r') \Delta x'_M \times \Delta y'_M \times \Delta z'_M \) molecules. For a one-dimensional gas prop-

<table>
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agation with a 100 cycles laser with a wavelength of 800nm interacting with molecules, we would have to solve numerically at each iteration 8000(80 \times 100) TDSE, for a Maxwell cell size equal to \( \Delta z'_M = 10nm \) (one TDSE per Maxwell cell). As noticed above, the non-Born-Oppenheimer TDSE we have to solve is 4D and is then costly in CPU time. We then propose a technique based on a simple Taylor expansion that allows to
reduce the numerical cost, supposing the polarization smooth in space. As discussed above, this assumption seems a priori valid when the electric field is smooth enough and its wavelength encompasses a large number of molecules (see fig. 14).

3.4.1 Decreasing the polarization computation cost

We make a partition of the domain $\Omega_M = \cup_{i=1,\ldots,I-1}[\omega_i, \omega_i+1]$ with $I$ a small integer. We suppose that each sub-domain $\omega_i$ contains a sufficiently large number of Maxwell cells. For each sub-domain $\omega_i$, we choose a reference cell $r_i^0$ (located for example in the center of the sub-domain). For this cell we compute the corresponding TDSE which in this framework is written as,

$$i\partial_t \psi_{r_i^0}(r, R, t) = \left( -\frac{1}{2} \Delta_r + V(r, R) - \frac{1}{m_p} \Delta_R + \frac{1}{R} + r \cdot E_{r_i^0}(t) \right) \psi_{r_i^0}(r, R, t).$$

and the corresponding polarization:

$$P(r_i^0, t) = -n(r_i^0) \int \psi_{r_i^0}^*(r, R, t) \cdot r \cdot \psi_{r_i^0}(r, R, t) dr dR.$$  \hspace{1cm} (15)

For every other cell located in $r' \in \omega_i$ we have:

$$P(r', t) = P(r_i^0, t) + \nabla_{r'} P(r_i^0, t) \cdot (r' - r_i^0) + O((r' - r_i^0)^2).$$

Then we deduce the value of the polarization for every cell of the sub-domain $\omega_i$. It is necessary to compute $\nabla_{r'} P(r_i^0, t)$. With this aim, by derivation in $r'$ of (15), we obtain

$$\nabla_{r'} P(r_i^0, t) = -n(r_i^0) \int \nabla_{r'} \psi_{r_i^0}^*(r, R, t) \cdot r \cdot \psi_{r_i^0}(r, R, t) dr dR - n(r_i^0) \int \psi_{r_i^0}^*(r, R, t) \cdot r \cdot \nabla_{r'} \psi_{r_i^0}(r, R, t) dr dR - (\nabla_{r'} n)(r_i^0) \int \psi_{r_i^0}^*(r, R, t) \cdot r \cdot \psi_{r_i^0}(r, R, t) dr dR.$$

Then to compute $\nabla_{r'} P(r_i^0, t)$ we compute $\nabla_{r'} \psi_{r_i^0}(r, R, t)$ and then we solve the following system obtained by derivation in $r'$ of the TDSE,

$$i\partial_t (\nabla_{r'} \psi_{r_i^0}(r, R, t)) = \left( -\frac{1}{2} \Delta_r + V(r, R) - \frac{1}{4m_p} \Delta_R + \frac{1}{R} + r \cdot E_{r_i^0}(t) \right) \nabla_{r'} \psi_{r_i^0}(r, R, t) + i(\nabla_{r'} E_{r_i^0}(t)) \cdot r \cdot \psi_{r_i^0}(r, R, t).$$  \hspace{1cm} (16)
The numerical scheme to solve the previous system is simply deduced from our Crank-Nicolson scheme:

\[
(\nabla_r' \psi'_{r_i,0})^{n+1} = \frac{(\nabla_r' \psi'_{r_i,0})^n}{2} + \frac{(\nabla_r' \psi'_{r_i,0})^n}{2} - \frac{i}{2} \mathcal{H}^n (\nabla_r' \psi'_{r_i,0})^{n+1} - \frac{i}{2} \mathcal{H}^n \nabla_r' \psi'_{r_i,0} + i (\nabla_r' \mathbf{E}_{r_i,0})^{n+1} \cdot \mathbf{r} \cdot \psi'_{r_i,0} + 1. (17)
\]

In (17) the quantity \(\psi'_{r_i,0}^{n+1}\) is supposed to have been previously computed by the numerical scheme for the TDSE with \(\mathcal{H}^n\) given by:

\[
\mathcal{H}^n = \left( -\frac{1}{2} \Delta_y + V(r, R) - \frac{1}{m_p} \Delta_R + \frac{1}{R} + r \cdot \mathbf{E}_{r_i,0}^n \right) (1, 1, 1)^T, \quad n > 0.
\]

Finally, for each sub-domain \(\omega_i\) we compute \(\psi'_{r_i,0}(r, R, t)\) and \(\nabla_r' \psi'_{r_i,0}(r, R, t)\) to deduce linearly from \(\mathbf{P}(r_i,0, t)\) the polarization for each cell located in \(r'\) of this sub-domain. The error due to this process is naturally here at order one. It is possible to increase the order using a higher order Taylor expansion. In this case, it would be necessary to compute \(\nabla^2_r' \psi'_{r_i,0}(r, R, t)\) obtained by double derivation in \(r'\) of the TDSE. We can then deduce easily the following result:

**Proposition 3.2** Supposing the polarization and the molecular density smooth enough, the approximation proposed above in each \(r' \in \omega_i\), is of order 1 or 2 depending on the Taylor expansion order.

In practice we can expect in some cases, a strong reduction of the number of TDSE to solve. Typically the sub-domains size will depend on the transmitted electric field harmonics, then on the intensity and frequency of the incoming laser. The higher the harmonics will be, the smaller the size of the sub-domains will be chosen.

Taking into account the previous method to reduce the computational cost of the polarization, that is the number of TDSE to solve, we have the following temporal scheme from \(t^n\) to \(t^{n+1}\), denoting by \(I - 1\) the number of sub-domains, with \(I <<\) number of cells in the Maxwell grid:

\[
\begin{align*}
\mathbf{E}^{n+1} &\leftarrow \mathbf{E}^n, \quad \forall r' \in \Omega, \\
\psi^{n+1} &\leftarrow \psi^n, \quad \text{for } r_i,0 \in \omega_i, \quad \forall i \in [1, I], \\
\mathbf{P}^{n+1} &\leftarrow \mathbf{P}^{n+1}, \quad \text{for } r_i,0 \in \omega_i, \quad \forall i \in [1, I], \\
\nabla_r' \psi^{n+1} &\leftarrow \psi^{n+1}, \quad \text{and eq. (16), for } r_i,0 \in \omega_i, \quad \forall i \in [1, I], \\
\nabla_r' \mathbf{P}^{n+1} &\leftarrow \nabla_r' \psi^{n+1}, \quad \text{for } r_i,0 \in \omega_i, \quad \forall i \in [1, I], \\
\mathbf{P}^{n+1} &\leftarrow \mathbf{P}^{n+1}, \quad (\nabla_r' \mathbf{n})(r_i,0) \quad \text{and } \nabla_r' \mathbf{P}^n, \forall r' \in \omega_i, \quad \forall i \in [1, I].
\end{align*}
\]

Note that from another point of view it would be interesting to investigate a coupling of the polarization solution with a local (in each Maxwell-cell) slowly varying envelope approximation (see section 2.).

### 3.4.2 Parallelization of the polarization computation in the Born-Oppenheimer approximation

Many approaches are possible to parallelize the Maxwell-TDSE. One of the most effective one is as follows. To simplify the presentation let us suppose that the Maxwell-grid possesses \(N\) cells and that we solve \(N\) TDSE (one by Maxwell-cell) with a code running on \(N\) processors. We also suppose in this paragraph that the Maxwell-domain is not “very large” so that it is possible to solve the Maxwell equations on one single processor. At each temporal Maxwell iteration, each processor solves one single Schrödinger equation, and
computes the corresponding polarization. Then it sends it to the root processor. Then with the polarization on the whole domain the root processor can solve the non-homogeneous Maxwell equations (recall that in our configuration (small Maxwell-domain) the CPU cost of the Maxwell equations computation is negligible compared to the TDSE computation cost). Then the root processor sends to the slaves the updated electric field (this process is summarized in fig. 16). Such a simple parallelization allows us to obtain a very good speed-up. Note also that the data are distributed between the computer nodes allowing to consider a large number of molecules with sufficiently large spatial grids. Fig. 17 represents for a given mesh: in abscissa

the number of TDSE (4, 16, 64, 256 TDSE) to solve also equal to the number of processors (one equation by processor) and in ordinate the real time for the 3D code to solve the corresponding Maxwell-TDSE. The ideal configuration would be “real time=constant”, corresponding to a speed-up equal to the number of processors. The coupling of our proposed reduced computation of the polarization with this parallelization

allows us to extend simulations to a very large number of molecules. Note also that the parallelization is almost totally independent of the way we solve numerically the Schrödinger and Maxwell equations.

We present next another approach used in particular for large 3D Maxwell-domains. In this case, the parallelization we propose is also based on a domain decomposition of the Maxwell domain. Let suppose that we have $N$ processors and $N_2$ TDSE to solve. We make a partition of the Maxwell domain in $N_1 = N - N_2$
sub-domains. In practice, $N_1 << N_2$ as the TDSE are more costly than the Maxwell ones. Suppose for instance that the gas is totally located in the $N_1$th sub-domain ($\bar{N} \leq N_1$). The computational steps become:

- the Maxwell equations are solved with processors $\{1, \cdots , N_1\}$ on each sub-domain with message passing at the sub-domains interfaces.
- the processor $\bar{N}$ sends its electric field to the molecules composing the gas that is to processors $\{N_1 + 1, \cdots, N\}$.
- independently, the $N_2$ TDSE are solved and give the associated polarization.
- each processor $\{N_1 + 1, \cdots, N\}$ sends to the $\bar{N}$th processor its computed polarization.

![Figure 18: Another parallelization approach for 5 TDSE and 8 processors](image)

The temporal process consists in two sub-iterations: computing the Maxwell equations on $N_1$ processors (first temporal sub-iteration) and then computing the TDSE on $N_2$ processors (second temporal sub-iteration). See figs. 18 and 19. Note also that such a decomposition allows us to distribute the memory between the nodes of the parallel-computer. This parallelization has been used for the largest computations (see numerical results section).

## 4 Numerical examples

In this part we present some results obtained using the numerical and parallel approaches introduced above. We consider Ti:sapphire pulses with intensity $I \sim 10^{14} W/cm^2$ at 800nm interacting with a $H_2^+$ gas.

We first present two results obtained when solving the Maxwell-TDSE in 1D and 3D for fixed nuclei with one-dimensional propagation. That is we neglect here the transversal effects of the gas on the electric field. The first one fig. 20 represents for a 1D computation, the transmitted electric field harmonics for a propagation in a $H_2^+$ media of length equal from 0.4nm (corresponding to 1 TDSE (molecule)), to 12.8nm (32 TDSE (molecules)). The Schrödinger equations are solved on a mesh containing 2000 points with a space step equal to 0.2a.u. Note that we obtain a quadratic scaling as expected (see [34] for instance) of the low electric harmonic intensities as a function of number of molecules from 1 to 32, when we increase the domain length. The second numerical result fig. 21 is the harmonic intensities of the transmitted electric field for a 3D computation, with a propagation in a $H_2^+$ media of length respectively equal to 15nm (corresponding to 4 TDSE), 60nm (16 TDSE), 240nm (64 TDSE). The Schrödinger equations are solved on a cartesian
The one-dimensional Maxwell equations are solve using space steps equal to 70 a.u. The code ran for \(\sim 22\) hours respectively on 4, 16 and 64 processors (see [www.ccs.usherbrooke.ca/mammouth](http://www.ccs.usherbrooke.ca/mammouth)). In this case, the molecules are located on a single line and the propagation is 1D, that is we here solve a 1D version of the Maxwell equations. Again we remark that the computation gives us a quadratic scaling as a function of number of molecules for the low harmonics with respect to the propagation length.

The next benchmark is the computation of our 3D Maxwell-Schrödinger model with the following datas: the Maxwell domain is a cubic box \([0, 2.25 \times 10^2]^3\) (in atomic units) with a uniform grid \(\Delta x_M = \Delta y_M = \Delta z_M = 750\) a.u. (allowing to consider rigorously at least the 20 first transmitted harmonics). The TDSE have been
Figure 21: 3D, $H_2^+$ harmonics for 15nm (4 molecules), 60nm (16 molecules), 240nm (64 molecules).

solved using the Crank-Nicolson scheme presented above with grid steps of length $\Delta x_S = \Delta y_S = \Delta z_S = 0.2\,\text{a.u.}$ The initial state for the molecules has been computed exactly in the Born-Oppenheimer approximation with $R = 3.2\,\text{a.u.}$ At such distance and $\lambda = 800\,\text{nm}$, there is a three-photon ionization resonance for the $1\sigma_g - 1\sigma_u$ excitation [17]. The initial electric field is presented in fig. 13. In this benchmark we have solved $3 \times 3 \times 56 = 504$ TDSE representing the $H_2^+$ molecules located in the middle of the Maxwell domain, in a box of size $2250 \times 2250 \times 4200$ (in atomic units). The total number of processors used in this numerical computation is 511. More precisely 504 processors have been used for the TDSE computation and 7 for the Maxwell equations computation, following the process presented in fig. 18. The real computation time is 1167 minutes and the physical computational one is $632\,\text{a.u}$ that is $\sim 15\,\text{fs}$. In fig. 22 we represent the electric field solution propagated in the vacuum and in the final electric field after interaction with gas. We also illustrate the modification of the transmitted pulses by substracting the vacuum pulse at the end of the propagation fig. 23.

Next, using the same data as above with $5 \times 5 \times 10$ TDSE (250 molecules), the electric field subtraction is given by 24, 25. We expect with this kind of simulations to have a better understanding of filamentation (see [24]) at the microscopical scale. This point will be more deeply studied in a forthcoming paper.

The next benchmark consists in comparing the effect of the molecular density on the transmitted electric

Figure 22: Electric field for a 3D-Maxwell-Schödinger propagation in the vacuum
Figure 23: Difference between the electric field for a 3D-Maxwell-Schödinger propagation in the gas and in the vacuum (504 TDSE)

Figure 24: Difference between the electric field for a 3D-Maxwell-Schödinger propagation in the gas and in the vacuum (250 TDSE)

Figure 25: Difference (250 TDSE) - other cut

field. A circular electric field (fig. 26) propagates through a $H_2^+$-gas of volume equal to $3750 \times 3750 \times 7500$ a.u. The number of Schrödinger equations to solve is equal to $5 \times 5 \times 10 = 250$ with the same numerical and
physical data than above (laser frequency, Maxwell domain, \( R = 3.2 \text{a.u.}, \text{etc} \)). The three cases we consider are for molecular densities equal to \( n_0 = 10^{-2}, n_0 = 10^{-3}, n_0 = 10^{-4} \) (figs. 27, 28, 29). We then observe as expected an amplification of the difference between the transmitted electric field in the vacuum and in the gas when the molecular density increases (see forthcoming papers for physical study of this phenomenon and consequences on filamentation).

![Figure 26: Transmitted Electric field in the vacuum](image)

![Figure 27: Difference between the electric field for a 3D-Maxwell-Schrödinger propagation in the gas and in the vacuum (250 TDSE) and \( n_0 = 10^{-4} \)](image)

We conclude this part on a remark on a numerical phenomenon noticed in [23]. The authors observed for high harmonics some minima in the harmonics spectra for \( H_2^+ \) molecules interacting with very short pulses (few cycles). In our simulations we also observe that these minima that seem not to vanish when the laser propagates in the gas on a length corresponding to 64 Schrödinger equations that is \( 0.250 \mu m \), figs 30, 31.

5 Conclusion

In this paper, we have presented a Maxwell-Schrödinger model for time dependent laser-matter interaction and some aspects of its numerical computation in 1D and 3D. In particular, we have proposed some methods to reduce the algorithmic complexity of the numerical problem due to the multiple scales (polarization computation for instance) but also due to the boundary conditions due to dissociative ionization of molecules. This has allowed us to develop a numerical code for a Maxwell-TDSE system of equations which guaranties
Figure 28: Difference between the electric field for a 3D-Maxwell-Schödinger propagation in the gas and in the vacuum (250 TDSE) and $n_0 = 10^{-3}$.

Figure 29: Difference between the electric field for a 3D-Maxwell-Schödinger propagation in the gas and in the vacuum (250 TDSE) and $n_0 = 10^{-2}$.

Figure 30: One-dimensional Maxwell-Schrödinger. Electric field harmonics.
scalability of intensities of harmonics as a function of the number of molecules in 1D and 3D, and the structure of the propagated pulses. Numerical simulations were obtained so far only for fixed $R$. the non-born-Oppenheimer TDSE for $H_2^+$ has been applied previously to single molecules only [17]. Computations with our Maxwell-Schrödinger code via equations (5), (7), (6) require Peta-Byte supercomputers. Among the important points to investigate note the following one. For a 10 Torr pressure, and supposing an ideal molecular equi-distribution, the distance between two molecules is on order of $12\text{nm}$. For a $800\text{nm}$ laser, the 67th harmonic wavelength is approximatively equal to $12\text{nm}$. This is raising new issues about the applicability of TDSE and macroscopic Maxwell equations.
APPENDIX - Proof of theorem 2.1

Proof. In the following we will denote by $\mathcal{E}$ the laser operator:
\[ \mathcal{E} : (r, R, t) \mapsto \mathcal{E}(r, R, t) = \chi(r, R) \cdot E(t). \]
In a first time we regularize the potentials, defining
\[ V_c^\varepsilon = -\frac{1}{\sqrt{\varepsilon^2 + x^2 + (y-R/2)^2 + z^2}} \quad V_i^\varepsilon = -\frac{1}{\sqrt{\varepsilon^2 + x^2 + (y+R/2)^2 + z^2}} \]
We then have $|V_c^\varepsilon| \leq |V_c|$ and $|V_i^\varepsilon| \leq 1/R$ and $\partial_t V_c^\varepsilon = \partial_t V_i^\varepsilon = 0$. Then
\[ i\partial_t \psi^\varepsilon(r, R, t) = \left[-\frac{1}{2} \Delta + V_c^\varepsilon(r, R) + \chi(r, R) \cdot E(t) + V_i^\varepsilon(R)\right] \psi^\varepsilon(r, R, t). \]
As remarked above there exists a unique $\psi^\varepsilon \in C^0(0, T; H^1 \cap H_1)$ as $V_i^\varepsilon, V_c^\varepsilon, \chi(r, R) \cdot E(t) \in L^\infty(0, T; C_0^2(\mathbb{R}^4))$. We now search for an estimation in $H_1$ of $\psi^\varepsilon$. First recall that:
\[ \|\psi^\varepsilon(t)\|^2_{H^1 \cap H_1} = \int_{\mathbb{R}^4} |\nabla y \psi^\varepsilon|^2 + |\nabla R \psi^\varepsilon|^2 + (1 + \|\chi(r, R)\|_{L^\infty}) |\psi^\varepsilon|^2. \]
Then there exists a constant $M_p > 0$ (= 1 for instance, as $m_p > 1$) such that:
\[ \int_{\mathbb{R}^4} \frac{|\nabla y \psi^\varepsilon|^2}{2} + \frac{|\nabla R \psi^\varepsilon|^2}{m_p} + (1 + \|\chi(r, R)\|_{L^\infty}) |\psi^\varepsilon|^2 \leq M_p \|\psi^\varepsilon(t)\|^2_{H^1 \cap H_1}. \] (18)
The main difficulty consists in finding a positive constant $C$ such that:
\[ \|\psi^\varepsilon(t)\|^2_{H^1 \cap H_1} \leq C \|\psi_0\|^2_{H^1 \cap H_1}. \] (19)
Supposing (19) is true and using a compacity argument, there exists a sequence $\varepsilon_n$ such that
\[ \psi^\varepsilon_n \rightharpoonup u \quad \text{in} \quad L^\infty(0, T; H^1 \cap H_1). \]
We finally get
\[ \|\psi(t)\|^2_{H^1 \cap H_1} \leq C \|\psi_0\|^2_{H^1 \cap H_1}. \]
That proves the existence of a solution in the set described above.

In order to obtain estimation (19) it is necessary to have an estimation of
\[ \frac{d}{dt} \int_{\mathbb{R}^4} (1 + \|\chi(r, R)\|_{L^\infty}) |\psi^\varepsilon|^2, \quad \text{and} \quad \frac{d}{dt} \int_{\mathbb{R}^4} \frac{|\nabla y \psi^\varepsilon|^2}{2} + \frac{|\nabla R \psi^\varepsilon|^2}{m_p}. \]
With this aim and as proposed in [11], we multiply the TDSE by $(1 + \|\chi(r, R)\|_{L^\infty}) \overline{\psi^\varepsilon}$ we integrate on $\mathbb{R}^4$ and we take the imaginary part:
\[ \frac{d}{dt} \int_{\mathbb{R}^4} (1 + \|\chi(r, R)\|_{L^\infty}) |\psi^\varepsilon|^2 = \text{Im} \int_{\mathbb{R}^4} \nabla y \left[ (1 + \|\chi(r, R)\|_{L^\infty}) \overline{\psi^\varepsilon} \right] \frac{\nabla_y \psi^\varepsilon}{2} + \nabla R \left[ (1 + \|\chi(r, R)\|_{L^\infty}) \overline{\psi^\varepsilon} \right] \frac{\nabla_R \psi^\varepsilon}{m_p}. \]
We easily obtain by derivation and Cauchy-Schwartz
\[ \frac{d}{dt} \int_{\mathbb{R}^4} (1 + \|\chi(r, R)\|_{L^\infty}) |\psi^\varepsilon|^2 \leq \frac{1}{2} \int_{\mathbb{R}^4} \|\chi(r, R)\|_{L^\infty} |\psi^\varepsilon|^2 + \frac{|\nabla_y \psi^\varepsilon|^2}{2} + \frac{|\nabla_R \psi^\varepsilon|^2}{m_p}. \]
The same manner we multiply by \( \partial_t \tilde{\psi} \) we take the real part and we integrate over \( \mathbb{R}^4 \). That is

\[
0 = \int_{\mathbb{R}^4} \text{Re} \left( -\frac{\partial_t \tilde{\psi} \Delta_y \psi}{2} - \frac{\partial_t \tilde{\psi} \Delta_R \psi}{m_p} + V_c^e \psi \partial_t \tilde{\psi} + V_i^e \psi \partial_t \tilde{\psi} + E \psi \partial_t \tilde{\psi} \right). 
\]

Then

\[
\frac{1}{2} \int_{\mathbb{R}^4} \partial_t \left( \frac{\nabla_y \psi \psi}{2} \right) + \partial_t \left( \frac{\nabla R \psi \psi}{m_p} \right) = \frac{1}{2} \int_{\mathbb{R}^4} (V_c^e + V_i^e + E) \partial_t |\psi|^2 \\
= \frac{1}{2} \int_{\mathbb{R}^4} (V_c^e + V_i^e + E) |\psi|^2 - \frac{1}{2} \int_{\mathbb{R}^4} \partial_t |\psi|^2.
\]

Then trivially there exists a constant \( C_2 \)

\[
\int_{\mathbb{R}^4} \partial_t E |\psi|^2 \leq C_2 \left\| \frac{\partial_t E}{1 + \|(r, R)^T\|_2} \right\|_{L^\infty} |\psi|^2_{H^1}.
\]

We then obtain the following estimate:

\[
\frac{d}{dt} \int_{\mathbb{R}^4} \frac{\nabla_y \psi \psi}{2} + \frac{\nabla R \psi \psi}{m_p} + \int_{\mathbb{R}^4} (1 + \|(r, R)^T\|_2) |\psi|^2,
\]

and because of (20) and (21) we have:

\[
\frac{d}{dt} E_{m_p}^e(t) = \frac{d}{dt} \int_{\mathbb{R}^4} \left( V_c^e + V_i^e + E \right) |\psi|^2 + C_2 \left\| \frac{\partial_t E}{1 + \|(r, R)^T\|_2} \right\|_{L^\infty} |E_{m_p}^e(t)|.
\]

As \( \psi \in H_1 \) and because of (20), there exists a positive constant \( C_3 \) such that:

\[
\frac{d}{dt} E_{m_p}^e(t) \leq \int_{\mathbb{R}^4} \left( V_c^e + V_i^e + E(0) \right) |\psi|^2 + C_3 \left[ 1 + \left\| \frac{\partial_t E}{1 + \|(r, R)^T\|_2} \right\|_{L^\infty} \right] E_{m_p}^e(s) ds + E_{m_p}^e(0).
\]

By integration we have

\[
E_{m_p}^e(t) \leq \int_{\mathbb{R}^4} \left( V_c^e + V_i^e + E(0) \right) |\psi|^2 + \int_{\mathbb{R}^4} \left( V_c^e + V_i^e + E(t) \right) |\psi|^2 + C_3 \int_0^t \left[ 1 + \left\| \frac{\partial_t E}{1 + \|(r, R)^T\|_2} \right\|_{L^\infty} \right] E_{m_p}^e(s) ds + E_{m_p}^e(0).
\]

As

\[
\int_{\mathbb{R}^4} (V_c^e + V_i^e) |\psi|^2 \leq \int_{\mathbb{R}^4} (V_c + V_i) |\psi|^2 \leq \left( \int_{\mathbb{R}^4} (V_c + V_i)^2 |\psi|^2 \right)^{1/2} \left( \int_{\mathbb{R}^4} |\psi|^2 \right)^{1/2}.
\]

By definition of \( V_i \) and \( V_c \) and applying an Hardy inequality, there exists a positive constant \( C_4 \) such that:

\[
\int_{\mathbb{R}^4} |\psi|^2 (V_c + V_i)^2 \leq 2 \int_{\mathbb{R}^4} |\psi|^2 (V_c^2 + V_i^2) \leq 8 \int_{\mathbb{R}^4} \left| \nabla_y \psi \right|^2 + \left| \nabla R \psi \right|^2 \leq D \| \nabla x, R \psi \|_{L^2}.
\]
So that, by the classical equality $\|\psi_0\|^2_{L^2} = \|\psi^\tau\|^2_{L^2}$,

$$\int_{\mathbb{R}^4} (V_\epsilon^\tau + V_i^\tau) |\psi|^2 \leq \frac{C_4}{2} \|\nabla_{\mathbf{r}, \mathbf{r}} \psi^\tau\|_{L^2(\mathbb{R}^4)} + \frac{C_4}{2} \|\psi_0\|_{L^2(\mathbb{R}^4)}.$$  \hspace{1cm} (22)

Now as $E \in L^\infty(0,T)$ and $\chi \in C^2_0(\mathbb{R}^4)$

$$\int_{\mathbb{R}^4} \mathcal{E}(t)|\psi|^2 \leq \frac{\mathcal{E}}{(1 + \|\mathbf{r}, \mathbf{r}\|^2_{L^2_{\infty}(0,T;\mathbb{R}^4)})} \|\psi\|^2_{H^1}.$$  \hspace{1cm} (23)

and because of (18):

$$E_{\mu_p}(0) \leq M_p \|\psi_0\|^2_{H^1 \cap H^1},$$

and by definition of $V_\epsilon$ and $V_i$ there exists a positive constant $C_5$ such that

$$\int_{\mathbb{R}^4} (V_\epsilon^\tau + V_i^\tau + \mathcal{E}(0)) |\psi|^2 \leq C_5 \|\psi_0\|^2_{H^1 \cap H^1}.$$ \hspace{1cm} (24)

So that (5), (22), (23), (24) lead to the existence of two positive constants $C_6$ and $C_7$ such that

$$\|\psi^\tau(t)\|^2_{H^1 \cap H^1} \leq C_6 \|\psi_0\|^2_{H^1 \cap H^1} + C_7 \int_0^t \left[ 1 + \frac{\partial_t \mathcal{E}}{(1 + \|\mathbf{r}, \mathbf{r}\|^2_{L^2_{\infty}(0,T;\mathbb{R}^4)})} \|\psi^\tau(s)\|^2_{H^1 \cap H^1} \right] ds$$

We then apply the Grönwall inequality that leads to the existence of a positive constant $C_\tau$ such that:

$$\|\psi^\tau(t)\|^2_{H^1 \cap H^1} \leq C_\tau \exp \left( \int_0^t \left[ 1 + \frac{\partial_t \mathcal{E}}{(1 + \|\mathbf{r}, \mathbf{r}\|^2_{L^2_{\infty}(0,T;\mathbb{R}^4)})} \|\psi^\tau(s)\|^2_{H^1 \cap H^1} \right] ds \right) \|\psi_0\|^2_{H^1 \cap H^1}$$

Now as $\partial_t E \in L^1(0,T)$, there exists a constant $C$ such that (19) occurs. The uniqueness is based on the same arguments than [11] again using a Grönwall inequality. \hspace{1cm} □

References


