Mathematical Modeling of Boundary Conditions for Laser-Molecule Time-Dependent Schrödinger Equations and Some Aspects of Their Numerical Computation—One-Dimensional Case

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Received 3 August 2007; accepted 10 December 2007
Published online in Wiley InterScience (www.interscience.wiley.com).
DOI 10.1002/num.20334

This article deals with boundary conditions for time-dependent Schrödinger equations for molecules excited by intense and ultrashort electric fields. On the basis of Volkov wavefunctions, we propose an original boundary condition design that allows to reduce spurious reflections at the domain boundary and allows to take at least partially, plasma effects into account. © 2008 Wiley Periodicals, Inc. Numer Methods Partial Differential Eq 00: 000–000, 2008

Keywords: Schrödinger equation; lasers; transparent and artificial boundary conditions

I. INTRODUCTION

Molecule behavior excited by intense and ultrashort electric fields is modeled using a time-dependent Schrödinger equation (TDSE) coupled with a laser operator. The wavefunction, solution of this TDSE is usually approximated using a finite difference, finite element, finite volume scheme, or a spectral method. Even if these numerical schemes are often well adapted to this equation, some boundary condition difficulties arise due to the fact that the computation domain is finite but should be chosen very large. Indeed physically and numerically, the initial wavefunction ψ_0 (initial bound state) support is located in the "Schrödinger computational domain center." Then the laser pulse interacts with the molecule and delocalizes its associated wavefunction (electrons and nuclei) which support can become very large (discrete and continuum spectra, see Fig. 1). To overcome this well-known problem in numerical scattering theory, we have to find an adapted method to design boundary conditions. The usual and natural idea to circumvent this difficulty is

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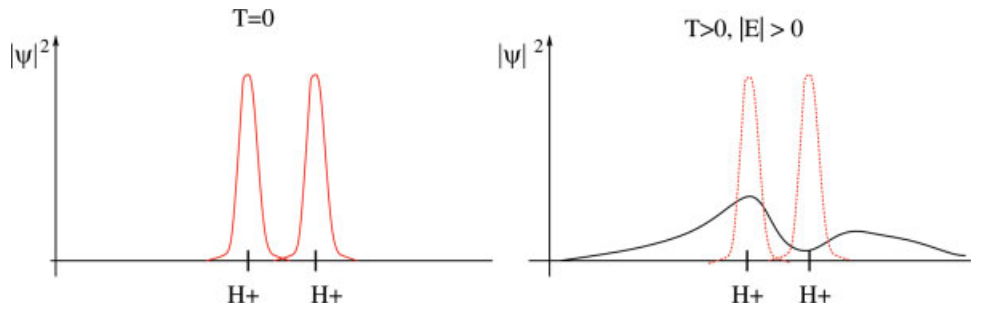

FIG. 1. Electronic wavefunction delocalization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to reduce the computational domain and to impose adapted boundary conditions. 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. Absorbing boundary conditions can also be used in order to absorb numerical spurious reflections. Even if this kind of methods allows effectively to reduce spurious reflections, there are often empirical (see for instance [1] in this framework), as some "parameters" have to be adapted for each numerical situation. Although the spurious reflections can be made to vanish, the wavefunction itself can also be partially or totally absorbed and its L^2-norm not preserved. 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 [1]). Ideally, we would like to impose boundary conditions such that the solution in the whole space restricted to a compact domain Ω (containing the initial data and Coulomb potential supports) is equal to the solution in Ω (that is without spurious reflections). Then outside this fictitious domain the wavefunction is accurately approximated and can be updated using for instance Volkov state propagator, or by another TDSE solver associated to other nuclei. In this article, we will make a non exhaustive overview of some possible boundary condition treatments for laser-molecule TDSE's, depending on the physical configuration: taking or not into account, plasma effects. In a first approach, if plasma effects are neglected, the electrons can "leave" the computational domain and then are "lost." In that sense the wavefunction can be absorbed with absorbing boundary conditions. In the opposite case, if the plasma effects are of interest in the considered physical problem, the boundary conditions have to be designed more precisely.

As the electron scattering is far more important than for nuclei (much heavier), we work with the Born-Oppenheimer approximation. In this article we will mainly consider a TDSE describing a H_2^+ molecule behavior excited by a laser field. Note, however, it is absolutely not restrictive and allows only to have a simple and explicit formula for the Coulomb potential. The TDSE can be written in atomic units [2] with $\mathbf{A} \in L^\infty(\mathbb{R}_+)^3$:

$$i\,\partial_t \psi(\mathbf{r},t) = \left[-\frac{1}{2}\triangle_{\mathbf{r}} + V_c(\mathbf{r},R_0) - \frac{i}{c}\mathbf{A}(t)\cdot\boldsymbol{\nabla}_{\mathbf{r}} + \frac{\|\mathbf{A}(t)\|^2}{2c^2}\right]\psi(\mathbf{r},t), \tag{1}$$

where ψ represents the molecular wavefunction, c is the velocity of light (equal to 137 is atomic units), and $\mathbf{A}(t)$ denotes the electric potential. As we work here under the dipole approximation, the electric and magnetic fields are supposed to be constant in space at the molecular scale, what is valid only if the electric field smallest internal wavelengths are much larger than the intermolecular distance (what can be not verified in the case of high-order harmonic generation, see [3]),

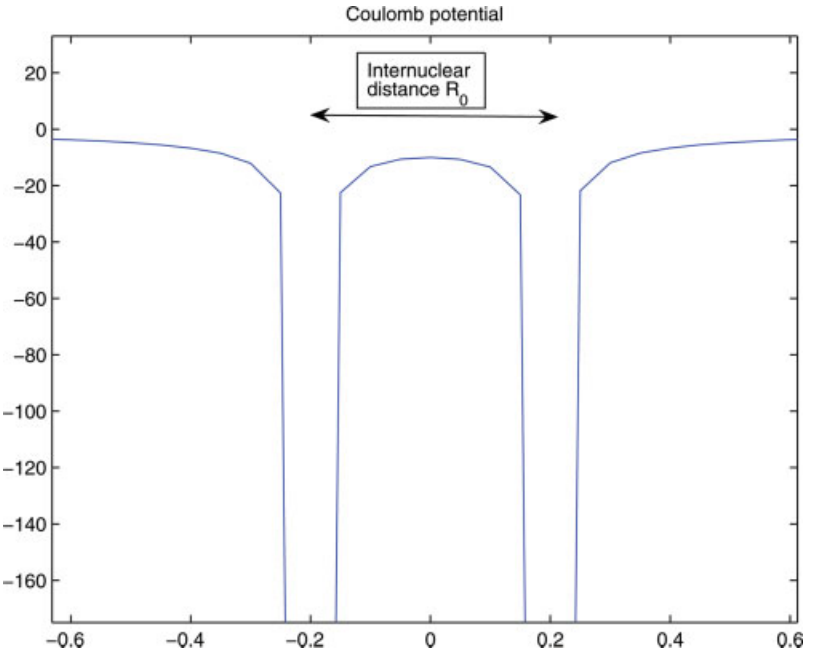

FIG. 2. Coulomb potential for H_2^+ molecules (internuclear distance is $R_0 = 0.4$ a.u. in this example).

see [4] for details on the model. Initially the electric potential is monochromatic, and then by laser-molecule interaction, the transmitted potential can have a very large harmonic spectrum. Electron-nuclei potential V_c (see Fig. 2) is given by

$$V_c(\mathbf{r}) = -\frac{1}{\sqrt{x^2 + (y - R_0/2)^2 + z^2}} - \frac{1}{\sqrt{x^2 + (y + R_0/2)^2 + z^2}}. \tag{2}$$

The electron position in the nuclei center of mass coordinates is denoted by $\mathbf{r} = (x, y, z)^T$. R_0 represents the internuclei distance supposed fixed because of the Born-Oppenheimer approximation.

Remark 1. The laser operator is an hyperbolic (convective) operator added to a constant operator in space (source term). At the boundary domain it is then possible to couple classical boundary conditions for hyperbolic equations of conservation laws (following the characteristics) with classical boundary conditions for laser-free TDSE (Neumann-Dirichlet for instance, see later). Indeed for the following equation on a smooth bounded domain Ω:

$$i\,\partial_t \psi(\mathbf{r}, t) = \left[-\frac{i}{c}\mathbf{A}(t) \cdot \nabla_{\mathbf{r}} + \frac{\|\mathbf{A}(t)\|^2}{2c^2} \right] \psi(\mathbf{r}, t),$$

the natural boundary conditions to make the problem well-posed are as follows. We denote $\mathbf{n}_\gamma$ the external normal of our computational domain Ω at a certain point $\gamma \in \partial\Omega$. We then impose a condition at γ if $\mathbf{A}(t) \cdot \mathbf{n}_\gamma < 0$ (incoming characteristics) and no condition if $\mathbf{A}(t) \cdot \mathbf{n}_\gamma > 0$ (out-coming characteristics), see Fig. 3. The case $\mathbf{A}(t) \cdot \mathbf{n}_\gamma = 0$ can be treated by an average

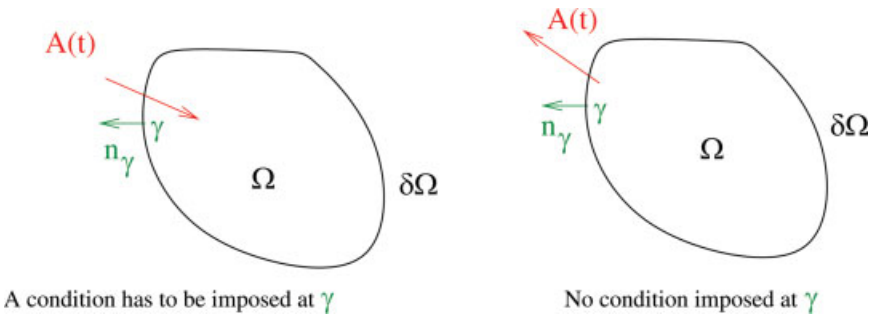

FIG. 3. Boundary conditions for the hyperbolic operator. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

process. Such a technique could be particularly interesting here since $\mathbf{A}(t)\cdot\nabla_{\mathbf{r}}$ and $\triangle_{\mathbf{r}}$ commute (that is $[\mathbf{A}(t)\cdot\nabla_{\mathbf{r}},\triangle_{\mathbf{r}}]=0$).

However, in this article, we propose to work in another gauge. The previous TDSE is given in the so-called *velocity gauge*. In the so-called *length gauge* we have

Proposition 1.1. *The TDSE* (1) *is equivalent to:*

$$i\,\partial_t\psi(\mathbf{r},t)=\left[-\frac{1}{2}\triangle_{\mathbf{r}}+V_c(\mathbf{r},R_0)+\mathbf{r}\cdot\mathbf{E}(t)\right]\psi(\mathbf{r},t), \tag{3}$$

with $\mathbf{E}=-\partial\mathbf{A}/c\partial t\in L^\infty(\mathbb{R}_+)^3$ *denoting the electric field.*

Proof. This result is very classical (see [5], [6]). It is sufficient to apply the unitary transformation

$$\psi\mapsto\psi\exp\left(-\frac{i}{2c^2}\int_0^t\|A\|^2(s)ds-\frac{i}{c}\mathbf{r}\cdot\mathbf{A}(t)\right), \tag{4}$$

in (1). ∎

In this article, the laser-molecule TDSE will be studied in the length gauge.

The article is organized as follows. In Section II, we propose a theoretical study of the boundary condition problem for laser-molecule TDSE's in strong fields. In particular, we propose some original boundary conditions to reduce spurious reflexions at the domain boundary and an attempt to take plasma effects into account in Section III. More precisely, some ideas are proposed to transmit electrons from molecules to others. Some numerical tests are proposed to validate the presented techniques. We conclude the article by some remarks and issues.

II. THEORETICAL ASPECTS

We then study the TDSE boundary condition problem when the particle is excited by an intense and ultrashort electric field. The numerical benchmarks we propose in this section are not necessarily realistic but allow us to understand and to validate the main ideas of the proposed methods.

We suppose, in this article, that the TDSE is solved using a Crank-Nicolson scheme coupled with a spatial 3-point scheme to approximate the Laplace operator. The main advantage of such an approach is that it allows to conserve the ℓ^2-norm (and then is stable) of the discrete wavefunction at least on an infinite domain. However working on a finite domain and using nontrivial boundary conditions, a stability study should be provided. Note finally, that mainly, all the following analysis can be useful to any real space method (finite element or finite volume schemes for instance).

A. One-Dimensional Boundary Conditions Without Plasma Effects (Free Electrons)

Let us consider the reference equation

$$\begin{cases} i\partial_t u(y,t) + \frac{1}{2}\partial^2_{yy} u(y,t) - V_c(y)\cdot u(y,t) - yE(t)\cdot u(y,t) = 0, \\ u(y,0) = u_0(y), \quad u_0 \in H^1(\mathbb{R}). \end{cases}$$

We want to impose at the boundaries of a domain Ω, some conditions allowing us to absorb the wavefunction at the boundary without spurious reflection. As is well-known, Dirichlet or Neumann boundary conditions create large spurious reflecting waves interacting with the physical wavefunction. To avoid this, we can for instance use an absorbing buffer. In the bounded domain $\Omega = [y_{-\Gamma}, y_\Gamma]$, let ε be a small positive real number and V_0 a positive real number. For a large enough domain ($y_{-\Gamma}$, y_Γ, depending on the laser pulse intensity and duration) and for y in $[y_{-\Gamma}, y_{-\Gamma} + \varepsilon]$ and y in $[y_\Gamma - \varepsilon, y_\Gamma]$ the wavefunction is multiplied for instance respectively by $e^{-V_0(y-y_{-\Gamma}-\varepsilon)^2}$ and by $e^{-V_0(y-y_\Gamma+\varepsilon)^2}$ or more generally any decreasing function $f_\varepsilon(y)$, from 1 to 0. We will denote by v the solution of the previous TDSE in the domain Ω with absorbing boundary conditions. That is[1] for all t:

$$v(y,t) \leftarrow v(y,t) \times e^{-V_0(y-y_{-\Gamma}-\varepsilon)^2}, \quad \text{if } y \in [y_{-\Gamma}, y_{-\Gamma} + \varepsilon],$$

$$v(y,t) \leftarrow v(y,t) \times e^{-V_0(y-y_\Gamma+\varepsilon)^2}, \quad \text{if } y \in [y_\Gamma - \varepsilon, y_\Gamma].$$

The effect is then an absorption, avoiding or at least reducing spurious reflections. Naturally at time t, the ionization I_ε, will be given by:

$$I^2_\varepsilon(t) = 1 - \|v(t,\cdot)\|^2_2 = 1 - \int_{]y_{-\Gamma}+\varepsilon, y_\Gamma - \varepsilon[} |v(y,t)|^2 dy - \int_{[y_{-\Gamma}, y_{-\Gamma}+\varepsilon]} |v(y,t) \times e^{-V_0(y-y_{-\Gamma}-\varepsilon)^2}|^2 dy$$
$$- \int_{[y_\Gamma - \varepsilon, y_\Gamma]} |v(y,t) \times e^{-V_0(y-y_\Gamma+\varepsilon)^2}|^2 dy \qquad (5)$$

and plasma effects are then partially or totally lost since free electrons are absorbed.

Numerical Example. We show in the following example how efficient are these conditions. We compare them with Dirichlet boundary conditions. The benchmark is the following. The initial data is given by $u(y,0) = u_0(y) = e^{8iy}e^{-y^2}$, $\Omega = [-5,5]$ and the laser field is given by $E_0 \sin(\omega t) \times \exp(-\alpha(t - t_f/2)^2)$ where $E_0 = 0.05$, $\omega = 20$, $\alpha = 5 \times 10^{-4}$, and $t_f = 10$. The Coulomb potential is set to zero. The time step Δt is 0.02 and the space step Δy is equal to 0.025. We compare the solution obtained at time 0.47 with absorbing and Dirichlet boundary conditions. Moreover we compute, in function of time, the ℓ^2-norm error between the solution of reference

[1] $A \leftarrow B$ means A is replaced by B.

(computed on a very large domain) and those obtained with Dirichlet and absorbing boundary conditions that is $(t, \|u(\cdot,t) - v(\cdot,t)\|_{\ell^2})$. As expected the wavefunction reflections are well absorbed whereas the Dirichlet computation gives an almost total reflection of the wavefunction (see Fig. 4). The stability of the scheme is trivially guaranteed in that case.

We can obviously improve this result adapting empirically the parameters V_0 and ε depending on the domain size and the laser intensity. See for instance [1] for a full description of this kind of boundary conditions. The extension to higher dimensions is obvious as it only consists of adding absorbers at all boundaries of the domain.

B. One-dimensional boundary conditions taking plasma effects into account

We would like now to take plasma effects into account, that is to propagate free electrons created by ionization. Indeed, some important phenomena as filamentation [7] are due to plasmas: with a sufficiently intense and high frequency, a Gaussian beam, propagating in a dense medium, is focused (Kerr effect) and then defocused by the plasma created by free electron. The so-called created intense filaments can be propagated over very large distances. To observe numerically this phenomenon it is then not possible to absorb a part of the electron wavefunctions using absorbers, since electrons leaving the Schrödinger computational domains are precisely responsible for the plasma creation. It is then necessary to propose some boundary conditions such that:

- no spurious backward reflections occur at the domain boundaries interacting with the physical wavefunction inside the "Schrödinger computational domain" (what absorbers allow).
- the part of the wavefunction leaving the "Schrödinger computational domain" can be stored and be re-used in a way that we will describe in the sequel (what *a priori* absorbers do not allow).

In the first step, we will try to build some adapted boundary conditions allowing to guarantee the two previous conditions. This kind of boundary conditions are usually called *transparent* boundary conditions or *artificial* boundary conditions if they are not "exact." Then, we will explain how it will be possible to manage the wavefunction part leaving a TDSE computational domain.

Transparent Boundary Conditions. Let us first consider the following simplified model *without electric field*:

$$\begin{cases} i\,\partial_t u(y,t) + \frac{1}{2}\partial^2_{yy} u(y,t) - V_c(y)\cdot u(y,t) = 0, \\ u(y,0) = u_0(y), \quad u_0 \in H^1(\mathbb{R}). \end{cases}$$

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

$$\begin{cases} i\,\partial_t v(y,t) + \frac{1}{2}\partial^2_{yy} v(y,t) - V_c(y)\cdot v(y,t) = 0, \quad y \in \Omega, \\ \mathcal{B}(y,\partial_y,\partial_t) v(y,t) = 0, \quad y \in \Gamma, \\ v(y,0) = u_0(y), y \in \Gamma, \quad u_0 \in H^1(\mathbb{R}). \end{cases}$$

such that

$$u_{|\Omega\times[0,T]} = v. \tag{6}$$

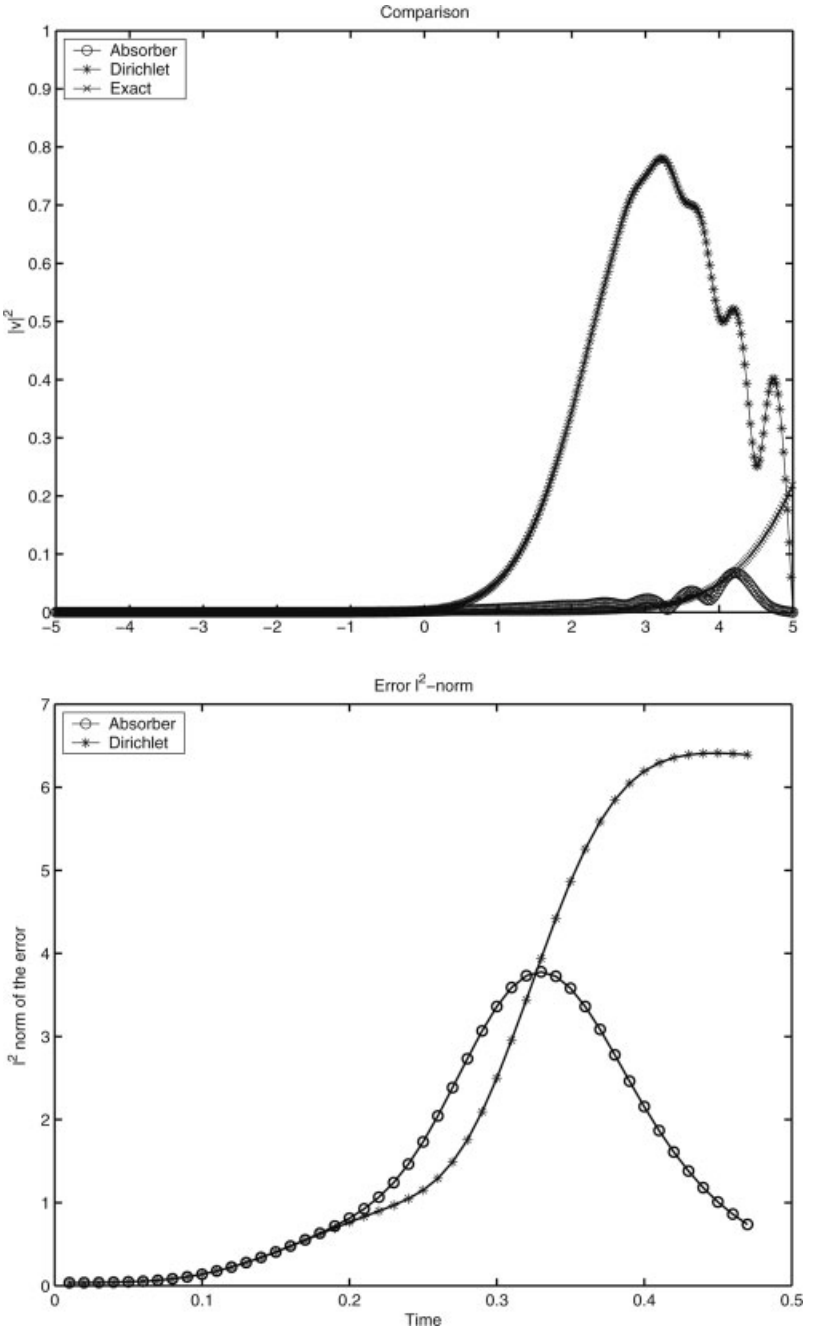

FIG. 4. Comparison between the solutions with Dirichlet boundary conditions and absorbing boundary conditions. ℓ^2-norm error between the solution of reference and Dirichlet and absorbing solutions in function of time.

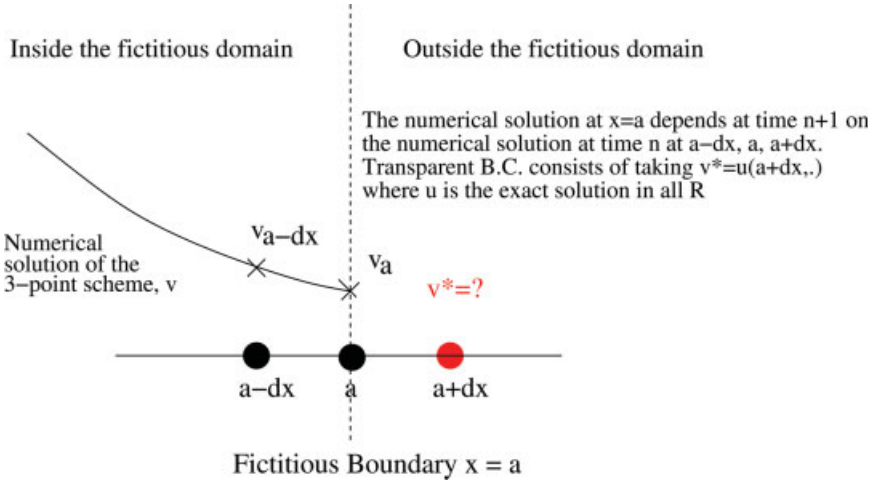

FIG. 5. Principle of the transparent boundary conditions for a 3-point scheme. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The main problem consists then of finding an adequate (pseudo-)differential boundary operator $\mathcal{B}$ on Γ such that (6) occurs, see Figs. 5 and 6. As is well-known these conditions, called Neumann-Dirichlet (or Dirichlet-Neumann), are nonlocal in time (and in space in higher dimension). Denoting by $\mathbf{n}$ the outward normal of Γ and $\partial_{\mathbf{n}}$ the trace operator on Γ we obtain:

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

This approach has been very well described in particular in [8], and some results can be found in [9, 10] or [11]. We also refer to [12] for the first discretization of nonlocal transparent boundary conditions for TDSE's. As unfortunately these conditions are nonlocal in time, many attempts

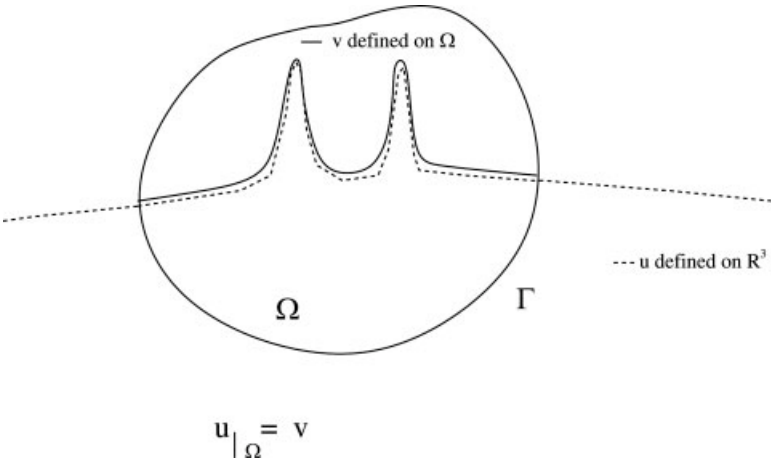

FIG. 6. Transparent boundary conditions.

have been devoted to find efficient numerical approximations of these conditions. At each iteration we can for instance decompose the convolution product as the sum of a local part and historical part at previous times, as proposed in [13]. Thus at time t^{n+1}:

$$v(y_\Gamma, t^{n+1}) = -e^{i\pi/4}\sqrt{2}\int_0^{t^{n+1}} \frac{\partial_y v(y_\Gamma,\tau)}{\sqrt{\pi(t^{n+1}-\tau)}}d\tau,$$

is decomposed into

$$v(y_\Gamma, t^{n+1}) = -e^{i\pi/4}\sqrt{2}\int_0^{t^{n}} \frac{\partial_y v(y_\Gamma,\tau)}{\sqrt{\pi(t^{n+1}-\tau)}}d\tau - e^{i\pi/4}\sqrt{2}\int_{t^n}^{t^{n+1}} \frac{\partial_y v(y_\Gamma,\tau)}{\sqrt{\pi(t^{n+1}-\tau)}}d\tau.$$

It is then possible to treat accurately each integral (see again [13]).

Coupling with the Laser. For excited molecules, the equation we consider here simply writes:

$$i\,\partial_t v(y,t) = \left(-\frac{1}{2}\partial^2_{yy} + V_c(y) + yE(t)\right) v(y,t). \tag{7}$$

It is important to note that the term $V_c(y) + yE(t)$ has not a compact support, so that it is no more possible to solve "easily" the free potential Schrödinger equation outside a fictitious domain using the same approach than above. Indeed, outside a given domain containing the support of the Coulomb potential, the equation is:

$$i\,\partial_t v(y,t) = \left(-\frac{1}{2}\partial^2_{yy} + yE(t)\right) v(y,t).$$

Using as above a Laplace transform in time would lead to a convolution product between Laplace transforms of E and v. We then propose not to solve exactly this equation but rather to give an approximate (artificial) condition based on a splitting approach. Given the solution on the boundaries at time t^n we look for it at time t^{n+1} splitting the Eq. (7) at the boundaries into:

$$\begin{cases} i\,\partial_t v(y,t) = yE(t)v(y,t), \quad y\in\Gamma, \quad t\in[t^n, t^{n+1/2}], \\ i\,\partial_t v(y,t) = \left(-\frac{1}{2}\partial^2_{yy} + V_c(y)\right) v(y,t), \quad y\in\Gamma, \quad t\in[t^{n+1/2}, t^{n+1}]. \end{cases} \tag{8}$$

The first equation provides the following solution:

$$v\left(y_\Gamma, t^{n+1/2}\right) = e^{-iy_\Gamma \int_{t^n}^{t^{n+1}} E(s)ds} v(y_\Gamma, t^n).$$

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

$$v(y_\Gamma, t^{n+1}) = -e^{i\pi/4}\sqrt{2}\int_0^{t^{n+1}} \frac{\partial_y v(y_\Gamma,\tau)}{\sqrt{\pi(t^{n+1}-\tau)}}d\tau.$$

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

$$v(y_\Gamma, t^{n+1}) = -e^{i\pi/4}\sqrt{2}\int_0^{t^{n}} \frac{\partial_y v(y_\Gamma,\tau)}{\sqrt{\pi(t^{n+1}-\tau)}}d\tau - e^{i\pi/4}\sqrt{2}\int_{t^n}^{t^{n+1}} \frac{\partial_y v(y_\Gamma,\tau)}{\sqrt{\pi(t^{n+1}-\tau)}}d\tau.$$

The historical part depends on v at time t^n and is then known at time t^{n+1}. For the local part, $v(y_\Gamma, t^{n+1/2})$ is used to compute $v(y_\Gamma, t^{n+1})$. More precisely and following for instance the approximations proposed by Greengard in [13], the historical part is approximated by:

$$-e^{i\pi/4}\sqrt{2}\int_0^{t^n}\frac{\partial_y v(y_\Gamma,\tau)}{\sqrt{\pi(t^{n+1}-\tau)}} \sim -e^{i\pi/4}\sum_{j=1}^{M} w_j c_j(n),$$

where $(c_j(n))_j$ and $(w_j)_j$ are some sequences described in [13]. The local part is then approximated by Gauss-Legendre quadrature:

$$-e^{i\pi/4}\sqrt{2}\int_{t^n}^{t^{n+1}}\frac{\partial_y v(y_\Gamma,\tau)}{\sqrt{\pi(t^{n+1}-\tau)}}d\tau \sim -e^{i\pi/4}\sqrt{\frac{2\Delta t^{n+1}}{\pi}}\left(\alpha v_{y,\Gamma}^{n+1/2}+(2-\alpha)v_{y,\Gamma}^{n}\right),\quad 0\le\alpha\le 2.$$

With such an approach we then have the following boundary conditions. If J denotes the last cell index: $J\Delta y = y_\Gamma \in \Gamma$,

$$\begin{cases} v_J^{n+1} = -e^{i\pi/4}\left(\sum_{j=1}^{N_c} w_j c_j(n) + \sqrt{\frac{2\Delta t^{n+1}}{\pi}}\right. \\ \qquad\left.\times\left(\alpha\frac{v_J^{n+1/2}-v_{J-1}^{n+1/2}}{\Delta y}e^{-iy_\Gamma\int_{t^n}^{t^{n+1}}E(s)ds}+(2-\alpha)\frac{v_J^n-v_{J-1}^n}{\Delta y}\right)\right), \\ c_j(n+1) = e^{s_j^2\Delta t^n}c_j(n)+\frac{\Delta t^n}{2}\left(e^{-s_j^2\Delta t^{n+1}}\frac{v_J^n-v_{J-1}^n}{\Delta y}+e^{-s_j^2(\Delta t^n+\Delta t^{n+1})}\frac{v_J^{n+1}-v_{J-1}^{n+1}}{\Delta y}\right). \end{cases}$$

With then,

$$v_J^{n+1/2} = e^{-iy_\Gamma\int_{t^n}^{t^{n+1}}E(s)ds}v_J^n,\quad v_{J-1}^{n+1/2} = e^{-iy_\Gamma\int_{t^n}^{t^{n+1}}E(s)ds}v_{J-1}^n.$$

The strength of this approach is that it allows first a fast and precise computation and it avoids data storage at the boundaries at all previous computational times, what would be an issue in high dimension (even for planar surfaces). Note that by induction, the historical part depends also on the laser pulse. A symmetric approach is proposed at $-y_\Gamma$. These two discrete equations at $-J$ and J close the Crank-Nicolson system. Then as the Hermitian structure of the sparse matrix is lost, a GMRES method is used to solve the linear system leading potentially to numerical difficulties due to a bad conditioning of this system (see [14] in another framework). The strong assumption made above has then consisted of searching for a numerical boundary condition of the type:

$$\int_0^t \partial_y v(y,\tau)/\sqrt{\pi(t-\tau)}d\tau, \tag{9}$$

that is, as if there was no laser. Even if the laser pulse is in fact taken into account by the historical-local process explained earlier, the presented splitting is then not totally satisfactory. Note also that it is straightforward to adapt the technique presented earlier in the velocity gauge. Other approaches are for instance presented in [11] or [15].

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

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

The fictitious domain is $\Omega = [-5, 5]$ and contains the initial data support. The space grid τ contains 1000 cells with a space step equal to 0.05. We impose the Neumann-Dirichlet boundary conditions coupled with the laser as described earlier, 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. We consider a two-cycle laser pulse with a field intensity equal to 0.05 and a time duration of 0.47.

The "Neumann-Dirichlet numerical (Fig. 7) solution" is then far less reflected (even if a little reflection exists) than 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. A more tricky approach to make decrease reflections consists of making a better approximation of the historical part. To do this, it is necessary to approximate this historical integral using the solution at the boundary at all previous times (t^n, t^{n-1}, t^{n-2}, etc). This then would lead to the approach of Antoine and Besse in [9], where the authors are able to reduce drastically the spurious reflections for field free Hamiltonians and at the same time ensuring stability. The price to pay is, however, to store the solution at the boundary at all time, what can be problematic in higher dimensions.

However, as this approach is not totally satisfactory (see Fig. 7), in particular due to the non-justified assumption (9), we propose rather to introduce in the next section another approach based on the Volkov wavefunction. Note that, as proved in [9] in particular, a Dirichlet-Neumann approach would certainly be more efficient numerically than the Neumann-Dirichlet one. In particular, because of the time derivative of the time integral these conditions are certainly less restrictive. Unfortunately in both case the issue described earlier (nonlocal in time conditions) leads to prefer another approach for laser-molecule TDSE's.

Volkov Wavefunction Approach Without Coulomb Potential. The idea is here to use the Volkov wavefunction in order to introduce nonreflecting boundary conditions without loss of information. Remind that the Volkov wavefunction is the TDSE exact solution with electric field but without Coulomb potential. This can also be seen as the electron TDSE solution (with Coulomb potential), but far from the nuclei where their attraction is negligible. That is, we solve analytically for $E \in L^\infty(\mathbb{R}_+)$:

$$\begin{cases} i\partial_t u(y,t) + \frac{1}{2}\partial_{yy} u(y,t) - yE(t)u(y,t) = 0, \quad t \geq 0, \quad y \in \mathbb{R}, \\ u(y,0) = u_0(y) \in H^1(\mathbb{R}). \end{cases} \tag{10}$$

Proposition 2.1. *The exact solution of* (10) *is given by the so-called Volkov wavefunction defined by*:

$$u(y,t) = \frac{1-i}{2\sqrt{\pi t}} \exp\left(-iy\int_0^t E(s)ds - \frac{i}{2}\int_0^t \left(\int_0^s E(\tau)d\tau\right)^2 ds\right)$$
$$\times \int_{\mathbb{R}} u_0(y') \exp\left(\frac{i\left(y - \int_0^t \left(\int_0^s E(\tau)d\tau\right)ds - y'\right)^2}{2t}\right) dy', \quad y \in \mathbb{R}, \quad t \geq 0, \tag{11}$$

Proof. This is an old result. Apply the Fourier transform in space and solve the induced PDE. ∎

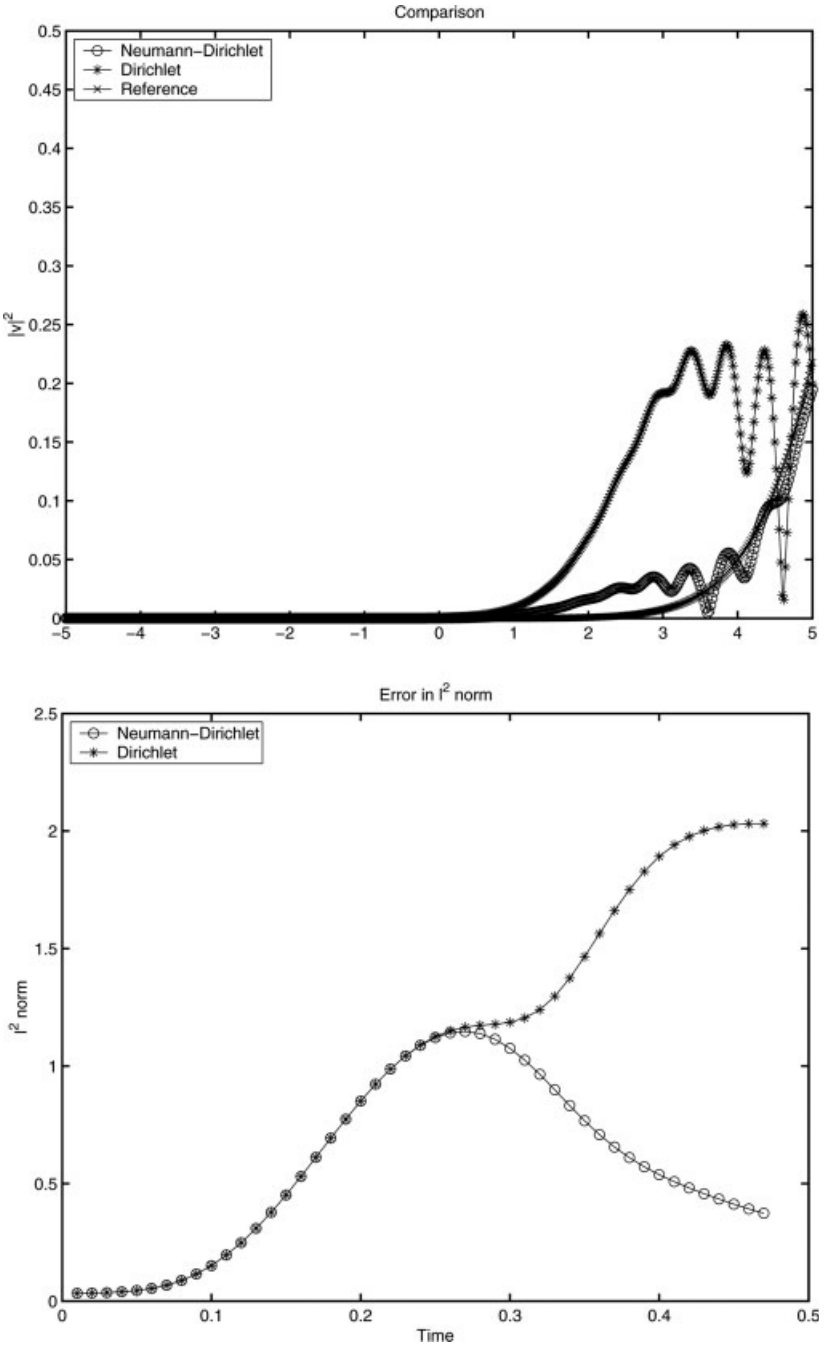

FIG. 7. Comparison between the reference solution and the numerical solutions obtained with Dirichlet and Neumann-Dirichlet boundary condition.

Although this solution is nonlocal in space, the convolution product is in fact an integral over the initial wavefunction support which is very small compared to the computational domain. Using this formula, we are then able to build some nonreflecting boundary conditions when the *Coulomb potential is negligible* everywhere. If we denote by $y_{-\Gamma}^{-} = y_{-\Gamma} - \Delta y$ and $y_{\Gamma}^{+} = y_{\Gamma} + \Delta y$, we have at time t:

$$
\begin{aligned}
v\left(y_{-\Gamma}^{-}, t\right) &= \frac{1-i}{2\sqrt{\pi t}} \exp\left(-i y_{\Gamma}^{-} \int_0^t E(s)ds - \frac{i}{2}\int_0^t \left(\int_0^s E(\tau)d\tau\right)^2 ds\right) \\
&\quad \times \int_{\mathbb{R}} v_0(y') \exp\left(\frac{i\left(y_{\Gamma}^{-} - \int_0^t \left(\int_0^s E(\tau)d\tau\right) ds - y'\right)^2}{2t}\right) dy', \\
v\left(y_{\Gamma}^{+}, t\right) &= \frac{1-i}{2\sqrt{\pi t}} \exp\left(-i y_{\Gamma}^{+} \int_0^t E(s)ds - \frac{i}{2}\int_0^t \left(\int_0^s E(\tau)d\tau\right)^2 ds\right) \\
&\quad \times \int_{\mathbb{R}} v_0(y') \exp\left(\frac{i\left(y_{\Gamma}^{+} - \int_0^t \left(\int_0^s E(\tau)d\tau\right) ds - y'\right)^2}{2t}\right) dy'.
\end{aligned}
$$

To approximate the solution at $y_{-\Gamma}$ and y_{Γ} and to close the Crank-Nicolson system, we naturally set:

$$
\begin{cases}
\left(\partial_{yy}^2 v\right)(y_{-\Gamma}, t^n) \sim \frac{v\left(y_{-\Gamma}^{-}, t^n\right) - 2v(y_{-\Gamma}, t^n) + v(y_{-\Gamma} + \Delta y, t^n)}{\Delta y^2}, \\
\left(\partial_{yy}^2 v\right)(y_{\Gamma}, t^n) \sim \frac{v\left(y_{\Gamma}^{+}, t^n\right) - 2v(y_{\Gamma}, t^n) + v(y_{\Gamma} - \Delta y, t^n)}{\Delta y^2}, \\
\left(\partial_{yy}^2 v\right)(y_{-\Gamma}, t^{n+1}) \sim \frac{v\left(y_{-\Gamma}^{-}, t^{n+1}\right) - 2v(y_{-\Gamma}, t^{n+1}) + v(y_{-\Gamma} + \Delta y, t^{n+1})}{\Delta y^2}, \\
\left(\partial_{yy}^2 v\right)(y_{\Gamma}, t^{n+1}) \sim \frac{v\left(y_{\Gamma}^{+}, t^{n+1}\right) - 2v(y_{\Gamma}, t^{n+1}) + v(y_{\Gamma} - \Delta y, t^{n+1})}{\Delta y^2}.
\end{cases}
$$

We then solve:

$$
\mathbf{A} v^{n+1} = \mathbf{B}^n v^n + (F^n + F^{n+1}), \tag{12}
$$

$$
\mathbf{A} = \begin{pmatrix}
1 - i\frac{\Delta t}{2\Delta y^2} + i\frac{\Delta t V_c}{2} & i\frac{\Delta t}{4\Delta y^2} & 0 & \cdots & 0 & 0 \\
i\frac{\Delta t}{4\Delta y^2} & 1 - i\frac{\Delta t}{2\Delta y^2} + i\frac{\Delta t V_c}{2} & i\frac{\Delta t}{4\Delta y^2} & 0 & \cdots & 0 \\
0 & i\frac{\Delta t}{4\Delta y^2} & 1 - i\frac{\Delta t}{2\Delta y^2} + i\frac{\Delta t V_c}{2} & i\frac{\Delta t}{4\Delta y^2} & \cdots & 0 \\
0 & \cdots & \cdots & \cdots & \cdots & 0 \\
0 & \cdots & 0 & i\frac{\Delta t}{4\Delta y^2} & 1 - i\frac{\Delta t}{2\Delta y^2} + i\frac{\Delta t V_c}{2} & i\frac{\Delta t}{4\Delta y^2} \\
0 & 0 & \cdots & 0 & i\frac{\Delta t}{4\Delta y^2} & 1 - i\frac{\Delta t}{2\Delta y^2} + i\frac{\Delta t V_c}{2}
\end{pmatrix} \tag{13}
$$

with

$$
\mathbf{B}^n = \bar{\mathbf{A}} - i E(t^n) \Delta t \mathbf{Y}, \tag{14}
$$

and where $\mathbf{Y}$ is a diagonal matrix with a diagonal given by $(y_{-\Gamma}, \ldots, y_{\Gamma})^T$. And finally

$$
\begin{aligned}
F^n &= i\Delta t\left(v\left(y_{-\Gamma}^{-}, t^n\right), 0, \ldots, 0, v\left(y_{\Gamma}^{+}, t^n\right)\right)^T / 4\Delta y^2, \\
F^{n+1} &= i\Delta t\left(v\left(y_{-\Gamma}^{-}, t^{n+1}\right), 0, \ldots, 0, v\left(y_{\Gamma}^{+}, t^{n+1}\right)\right)^T / 4\Delta y^2.
\end{aligned} \tag{15}
$$

The expression of $\mathbf{A}$ in (13) is general and we obviously have $V_c = 0$ if the nuclear attraction is neglected. At this point, this approach seems close to [16], even if the authors use a slightly different numerical scheme. However they apply directly Volkov boundary conditions, although their Coulomb potential is not zero in the whole space, what is uncorrect, as these conditions are clearly nonlocal in space. This particular but crucial point will be discussed the next section.

Numerical Example. We now present a numerical example illustrating the good behavior of this approach, when the Coulomb potential is zero. The domain is given by $\Omega = [-3.5, 3.5]$. We impose at the boundary, the conditions described earlier. The laser field is given by $E(t) = I \sin(\omega t)$ with $I = 0.5$ (we consider a 9-cycle pulse), $\omega = 20$ and the final time is 0.3 with a time step equal to 10^{-3}. The spatial grid has 400 points and the initial data is given by $e^{8iy}e^{-y^2}$. We compare the numerical solution obtained with Dirichlet boundary conditions, Volkov-like boundary conditions, and a reference solution (see Fig. 8).

Extension to Cubic Domains. As discussed earlier, the treatment of the boundary conditions is crucial in 2D or 3D to limit the computational cost. In this paragraph we will suppose that the TDSE is simply given by:

$$i\,\partial_t v_{\mathbf{r}'}(\mathbf{r},t) = \left[-\frac{1}{2}\triangle_{\mathbf{r}} + \mathbf{r}\cdot\mathbf{E}_{\mathbf{r}'}(t)\right] v_{\mathbf{r}'}(\mathbf{r},t). \tag{16}$$

Next, we consider that the computational domain is a cubic box. The Crank-Nicolson scheme for the TDSE requires boundary conditions to be imposed at the cube faces. It is naturally trivial to extend the modified Volkov-like boundary conditions seen above, on infinite planar surfaces. Then the technique can be extended in a bounded domain, for instance on cubic boxes, but then is badly defined on edges and corners of such singular domains. Di Menza for instance, proposed in [11] a way to treat domain singularities (where specific conditions are imposed at corners, in 2D) but is not fully satisfactory and a genuinely multidimensional approach would certainly be more appropriate. In particular for the genuinely 2D case, where nonlocal pseudo-differential operators in space are approximate by local differential operators (then local numerically) we refer to [8], [10]. The extension in 3D is obviously possible in theory but would lead to very technical computations.

We denote by $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5$, and Γ_6 the six faces of the domain, located at $x = x_{\Gamma_1}$, $x = x_{\Gamma_2}$, $y = y_{\Gamma_3}$, $y = y_{\Gamma_4}$, $z = z_{\Gamma_5}$, and $z = z_{\Gamma_6}$. Then, the boundary conditions are a natural extension of the 1D case:

$$\begin{aligned} v(x,y,z,t) = \frac{1-i}{2\sqrt{\pi t}} \exp\Bigg(&-ix\int_0^t E_x(s)ds - iy\int_0^t E_y(s)ds \\ &-iz\int_0^t E_z(s)ds - \frac{i}{2}\int_0^t \left\| \int_0^s \mathbf{E}(\tau)d\tau \right\|^2 ds\Bigg) \\ &\times \int_{\mathbb{R}^3} v_0(x',y',z') \exp\left(\frac{i}{2t}\left[\left(x - \int_0^t \left(\int_0^s E_x(\tau)d\tau\right)ds - x'\right)^2\right.\right. \end{aligned}$$

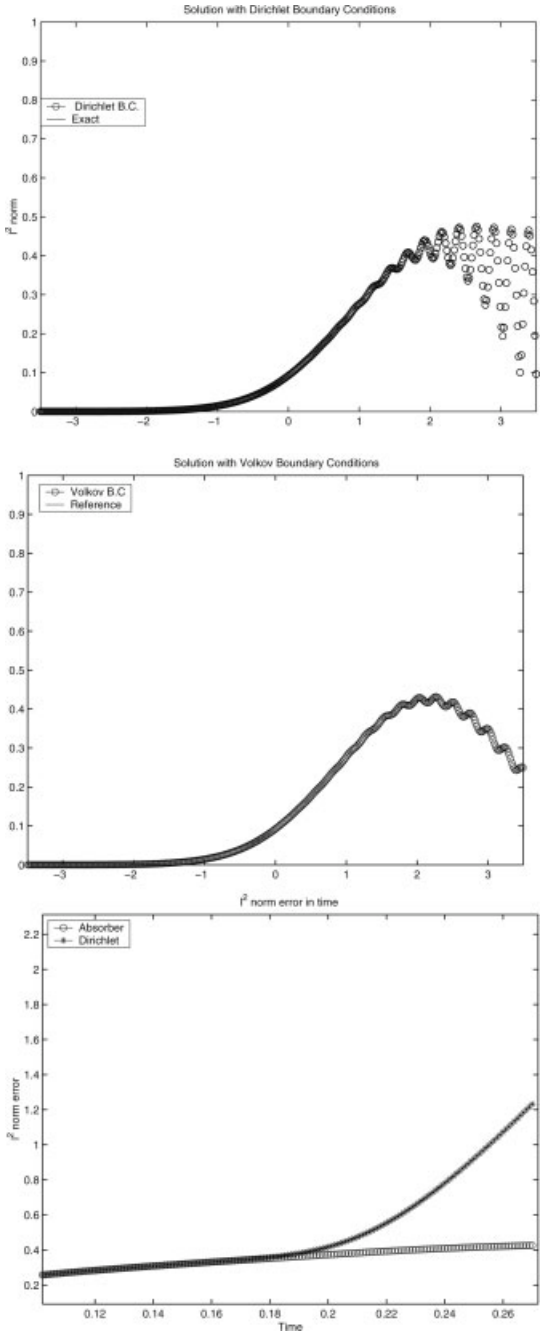

FIG. 8. Solutions obtained with Dirichlet B.C., Volkov-like B.C., and ℓ^2-norm error between reference solution and Dirichlet and Volkov solutions.

$$+\left(y-\int_0^t\left(\int_0^s E_y(\tau)d\tau\right)ds-y'\right)^2$$
$$+\left(z-\int_0^t\left(\int_0^s E_z(\tau)d\tau\right)ds-z'\right)^2\Bigg]\Bigg)dx'dy'dz',$$
$$(x,y,z)\in\Gamma_i,\quad i\in\{1,\cdots,6\},\quad t\geq 0.$$

Now, if we suppose that the laser is polarized in the direction y, and propagates in z', we can also simply extend the Neumann-Dirichlet conditions to planar surfaces, what finally gives:

$$\begin{cases}-\partial_{\mathbf{n}_{\Gamma_i}}v(x_{\Gamma_i},y,z,t)=e^{i\pi/4}\sqrt{2}\int_0^t\frac{\partial_x v(x_{\Gamma_i},y,z,\tau)}{\sqrt{\pi(t-\tau)}}d\tau,(x,y,z)\in\Gamma_i,i\in\{1,2\},t\geq 0,\\ \quad v(x,y_{\Gamma_i},z,t)=\frac{1-i}{2\sqrt{\pi t}}\exp\left(-iy_{\Gamma_i}\int_0^t E_{z'}(s)ds-\frac{i}{2}\int_0^t\left(\int_0^s E_{z'}(\tau)d\tau\right)^2ds\right)\int_{\mathbb{R}^3}v_0(x',y',z')\\ \qquad\qquad\times\exp\left(\frac{i\left((x-x')^2+\left(y_{\Gamma_i}-\int_0^t\left(\int_0^s E_{z'}(\tau)d\tau\right)ds-y'\right)^2+(z-z')^2\right)}{2t}\right)dx'dy'dz',\\ \qquad\qquad(x,y,z)\in\Gamma_i,\quad i\in\{3,4\},\quad t\geq 0,\\ -\partial_{\mathbf{n}_{\Gamma_i}}v(x,y,z_{\Gamma_i},t)=e^{i\pi/4}\sqrt{2}\int_0^t\frac{\partial_z v(x,y,z_{\Gamma_i},\tau)}{\sqrt{\pi(t-\tau)}}d\tau,\quad (x,y,z)\in\Gamma_i,\quad i\in\{5,6\},\quad t\geq 0.\end{cases}$$

This approximation is only valid if transverse effects are negligible. This is reasonable if the gas is not too dense. Indeed in this case, transverse components of $\mathbf{E}$ ($E_{x'}$, $E_{z'}$) are not strong enough for the electronic wavefunction to reach Γ_i ($i=1,2,5,6$).

Volkov State Propagator Approach Including Coulomb Potentials. As we can observed in Fig. 8, Volkov-like boundary conditions are particularly well adapted for laser-molecule interactions when the Coulomb potential is zero. We suppose now that the Coulomb potential support is included in a compact support, such that, as before V_c is zero for all $|y|>M$, with M large enough.

Remark 2. Let us first consider that the boundary conditions for instance in Γ with $|y_\Gamma^+|>M$ is:

$$\begin{aligned}v\left(y_\Gamma^+,t\right)=&\frac{1-i}{2\sqrt{\pi t}}\exp\left(-iy_\Gamma^+\int_0^t E(s)ds-\frac{i}{2}\int_0^t\left(\int_0^s E(\tau)d\tau\right)^2ds\right)\\ &\times\int_{\mathbb{R}}v_0(y')\exp\left(\frac{i\left(y_\Gamma^+-\int_0^t\left(\int_0^s E(\tau)d\tau\right)ds-y'\right)^2}{2t}\right)dy'.\end{aligned}\tag{17}$$

As the Coulomb potential is zero in Γ, it could seem natural to impose them as boundary conditions, unfortunately they are nonlocal in space.

It is not possible to apply (17) directly if there exists $|y|\leq M$ such that $V_c(y)\neq 0$. We then propose a very natural alternative which principle is as follows. Between t^n and t^{n+1} the solution of the equation

$$i\partial_t v=-\frac{1}{2}\partial_{yy}^2v+V_c(y)v+yE(t)v,\quad v(\cdot,t^n)=v^n,\tag{18}$$

can be approximated by the solution of (order 1 splitting):

$$\begin{cases}i\partial_t v(y,t)=\left(-\frac{1}{2}\partial_{yy}^2+yE(t)\right)v(y,t),\quad y\in\Gamma,\quad t\in[t^n,t^{n+1/2}],\\ i\partial_t v(y,t)=V_c(y)v(y,t),\quad y\in\Gamma,\quad t\in[t^{n+1/2},t^{n+1}].\end{cases}\tag{19}$$

Denoting by $\Delta t = t^{n+1} - t^n$, this naturally leads to impose at time t^{n+1} the following boundary conditions at $\pm\Gamma$:

$$
\begin{aligned}
v\big(y^-_{-\Gamma}, t^{n+1}\big) &= \frac{1-i}{2\sqrt{\pi\,\Delta t}} \exp\left(-i y^-_{\Gamma} \int_{t^n}^{t^{n+1}} E(s)ds - \frac{i}{2}\int_{t^n}^{t^{n+1}} \left(\int_0^s E(\tau)d\tau\right)^2 ds\right) \\
&\quad \times \int_{\mathbb{R}} v(y', t^n) \exp[-i\,V_c(y')\Delta t] \exp\left(\frac{i\left(y^-_{\Gamma} - \int_{t^n}^{t^{n+1}} \left(\int_0^s E(\tau)d\tau\right) ds - y'\right)^2}{2\Delta t}\right) dy', \\
v\big(y^+_{\Gamma}, t^{n+1}\big) &= \frac{1-i}{2\sqrt{\pi\,\Delta t}} \exp\left(-i y^+_{\Gamma} \int_{t^n}^{t^{n+1}} E(s)ds - \frac{i}{2}\int_{t^n}^{t^{n+1}} \left(\int_0^s E(\tau)d\tau\right)^2 ds\right) \\
&\quad \times \int_{\mathbb{R}} v(y', t^n) \exp[-i\,V_c(y')\Delta t] \exp\left(\frac{i\left(y^+_{\Gamma} - \int_{t^n}^{t^{n+1}} \left(\int_0^s E(\tau)d\tau\right) ds - y'\right)^2}{2\Delta t}\right) dy'.
\end{aligned}
\tag{20}
$$

This is an order 1 approximation of the exact solution (18), but it can easily be extended to order 2 by using a Strang splitting or beyond. The numerical system to solve is then (12), (15), and (18). We can deduce easily:

Proposition 2.2. *The continuous approximation* (20) *of the exact solution of* (18) *has the order of the chosen splitting method in* (19).

This time, the boundary conditions take Coulomb potential effects into account. Compared to the Neumann-Dirichlet approach the splitting used is now totally justified by the fact that the Volkov propagator is *local in time*.

However, these boundary conditions have potentially a major issue relatively to the time step. If Δt is small, the convolution product in (18) is highly oscillatory and then can be very hard to integrate numerically. A naive approach to circumvent this, is naturally to take a sufficiently large time step.

Numerical Example. The numerical test we present is as follows. The numerical domain is $[-5, 5]$ and we impose at $x = -5$ and $x = 5$ the boundary conditions (20). The initial data is the fundamental state v_0 such that λ_0 is the smallest eigenvalue of the field free Hamiltonian $-\partial^2_{yy}/2 + V_c$ with $V_c = -1/\sqrt{1 + (y - R_0/2)^2} - 1/\sqrt{1 + (y + R_0/2)^2}$ and $R_0 = 2$.

$$
\left[-\frac{1}{2}\partial^2_{yy} + V_c(y)\right] v_0(y) = \lambda_0 v_0(y).
$$

The grid has 200 points, and the time step is $\Delta t = 0.3$. The laser intensity is given by $E(t) = I \sin(\omega t) \exp(-\alpha(t - t_f/2)^2)$ with $\alpha = 5 \times 10^{-4}$, $t_f = 10$, $\omega = 0.057$, and $I = 0.5$. We show the numerical solution at times 2, 4, 8 and 9, Fig. 9.

Choosing a large time step approach is problematic, as the numerical error due to the splitting in (19) is polynomial in Δt. We then propose to approximate this integral using a Filon's quadrature (see [17], [18]). This quadrature is particularly well adapted for numerical integration of

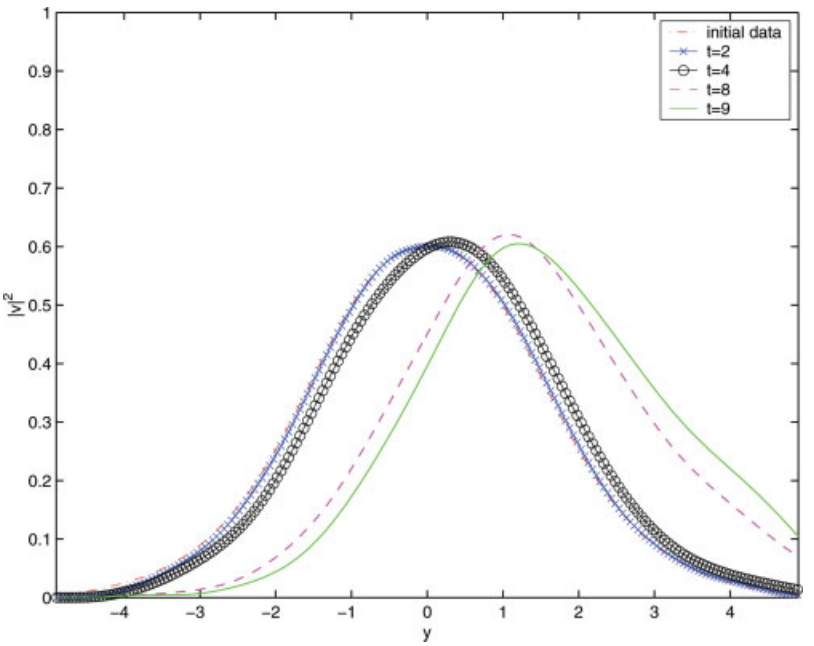

FIG. 9. Wavefunction for different times: $t = 0$, $t = 2$, $t = 4$, $t = 8$, $t = 9$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

highly oscillatory functions, that is in our case, when the time step is very small. More precisely the larger the frequency is, the better is the approximation. We propose to precise the method in our framework.

Filon's Approach: A Way to Efficiently Compute (18). Let us introduce some notations. We first define by f^n the following function coming from (18):

$$f^n(y) = v(y,t^n)\exp(-iV_c(y)\Delta t) \times \frac{1-i}{2\sqrt{\pi\Delta t}}\exp\left(-iy_\Gamma^- \int_{t^n}^{t^{n+1}} E(s)ds - \frac{i}{2}\int_{t^n}^{t^{n+1}}\left(\int_0^s E(\tau)d\tau\right)^2 ds\right). \quad (21)$$

We denote by a_-^n:

$$a_-^n = y_{-\Gamma}^- + \int_{t^n}^{t^{n+1}}\int_0^s E(\tau)d\tau ds.$$

We also denote by $\tilde{\omega}$ the inverted time step $1/\Delta t$. We finally need to numerically compute:

$$\int_{\mathbb{R}} f^n(y')\exp\left(\frac{i\tilde{\omega}}{2}(y'-a_-^n)^2\right)dy'. \quad (22)$$

To have an effective splitting in (19), it is necessary to choose a sufficiently small time step, that is a sufficiently large $\tilde{\omega}$. Precisely, the Filon's quadrature converges in $\mathcal{O}(\tilde{\omega}^{-3/2})$, so that the accuracy increases with the frequency. We give here some details for approximating this integral

using the Filon's quadrature. We denote by $\Omega_h = \{j\Delta y, j \in [j_{-\Gamma}, j_\Gamma]\}$ with $y_{-\Gamma} = j_{-\Gamma}\Delta y$ and $y_\Gamma = j_\Gamma \Delta y$. We denote by $j_{a_-^n}$, if it exists the integer such that $a_-^n \in \left[j_{a_-^n}\Delta y, (j_{a_-^n}+1)\Delta y\right]$. The integral (22) can then be rewritten

$$\sum_{j\in[j_{-\Gamma},j_\Gamma], j\neq j_{a_-^n}} \int_{j\Delta y}^{(j+1)\Delta y} f^n(y')\exp\left(\frac{i\tilde{\omega}}{2}(y'-a_-^n)^2\right)dy' + \int_{j_{a_-^n}\Delta y}^{(j_{a_-^n}+1)\Delta y} f^n(y')\exp\left(\frac{i\tilde{\omega}}{2}(y'-a_-^n)^2\right)dy'.$$

The reason why we split the integral is due to the fact that the behavior of oscillatory terms are totally different depending on the two situations, and then their respective approximation.

- For $j \neq j_{a_-^n}$ (see [17] for instance) and large enough $\tilde{\omega}$ we can naturally use the following approximation:

$$\begin{aligned}&\int_{j\Delta y}^{(j+1)\Delta y} f^n(y')\exp\left(\frac{i\tilde{\omega}}{2}(y'-a_-^n)^2\right)dy' \\ &\sim \frac{1}{i\tilde{\omega}}\left(f^n((j+1)\Delta y)\exp\left(\frac{i\tilde{\omega}}{2}((j+1)\Delta y - a_-^n)^2\right)/\big((j+1)\Delta y - a_-^n\big)\right. \\ &\left. - f^n(j\Delta y)\exp\left(\frac{i\tilde{\omega}}{2}\big(j\Delta y - a_-^n\big)^2\right)/\big(j\Delta y - a_-^n\big)\right) + \mathcal{O}(\tilde{\omega}^{-2}). \end{aligned} \tag{23}$$

- For $j \neq j_{a_-^n}$, such a simple approximation simple (23) is unfortunately not valid. It is then necessary to go further. Let us denote by $b_-^n = a_-^n - j_{a_-^n}\Delta y$ ($\in]0,1[$) and g^n the function defined by $g^n(y) = f^n(y\Delta y + j_{a_-^n}\Delta y)$. We then need to approximate the following integral:

$$\int_{j_{a_-^n}\Delta y}^{(j_{a_-^n}+1)\Delta y} f^n(y')\exp\left(\frac{i\tilde{\omega}}{2}\big(y'-a_-^n\big)^2\right)dy' = \int_0^{\Delta y}\exp\left(\frac{i\tilde{\omega}}{2}\big(y'-b_-^n\big)^2\right)g^n(y')dy'.$$

The Filon's quadrature is based on the approximation of the $\mu_k(\omega) = \int_0^{\Delta y} y^k \exp(i\omega(y - b_-^n)^2/2)dy$ (instead of $\int_0^{\Delta y} y^k dy$), for $k \in \mathbb{N}$.

Case 1. $\Delta y^2\tilde{\omega}$ **large enough.** Iserles in [17], [18] proves that for large enough $\tilde{\omega}$

$$\mu_k(\tilde{\omega}) \sim \sum_{j=0}^{r} v_j(\tilde{\omega})d_j^k\tilde{\omega}^{-\alpha_j} + \mathcal{O}(\tilde{\omega}^{-\beta}).$$

with $v_j \in L^\infty(\mathbb{R}^+)$ periodic functions, d_j nodes in $[0,\Delta y]$ and $0 < \alpha_j < \beta$ with β a real number depending on k and on the asymptotic expansion. We can easily prove by integration by parts that for $k \geq 1$:

$$\mu_{k+1}(\tilde{\omega}) - b_-^n\mu_k(\tilde{\omega}) + \frac{k}{i\tilde{\omega}}\mu_{k-1}(\tilde{\omega}) = \frac{\Delta y^k}{i\tilde{\omega}}\exp\left(i\tilde{\omega}\big(\Delta y - b_-^n\big)^2/2\right). \tag{24}$$

For $\tilde{\omega}$ large enough we can then neglect the last term of the L.H.S. We then deduce that:

$$\mu_{k+1}(\tilde{\omega}) \sim b_-^n \mu_k(\tilde{\omega}) + \frac{\Delta y^k}{i\tilde{\omega}} \exp\left(i\tilde{\omega}\left(\Delta y - b_-^n\right)^2/2\right) + \mathcal{O}(\tilde{\omega}^{-3/2}).$$

It is not necessary to approximate μ_0. Again we use the approach proposed in [18] where it is recalled that for large $|z|$ and $|\arg(z)| < 3\pi/4$,

$$\operatorname{erf}(z) \sim 1 - \frac{e^{-z^2}}{\sqrt{\pi} z}.$$

On the basis of this remark (details are skipped) we proved that provided that $\tilde{\omega}\Delta y^2$ is large enough:

$$\mu_0(\tilde{\omega}) \sim \sqrt{\frac{2i\pi}{\tilde{\omega}}} + \frac{1}{i\tilde{\omega}} \left(\frac{\exp\left(i\tilde{\omega}\left(\Delta y - b_-^n\right)^2/2\right)}{\Delta y - b_-^n} + \frac{\exp\left(i\tilde{\omega}\left(b_-^n\right)^2/2\right)}{b_-^n} \right) + \mathcal{O}(\tilde{\omega}^{-3/2}).$$

Now as

$$\sum_{l=0}^{m} b_l(\omega) c_l^k \sim \mu_k(\omega),$$

naturally appears a Vandermonde linear system that is solved to deduce the weights $b_l(\omega)$. In practice we take $m = 2$, $c_0 = 0$, $c_1 = b_-^n$, $c_2 = 1$. And $(b_l)_{l=0,1,2}$ are solutions of:

$$\begin{pmatrix} 1 & 1 & 1 \\ 0 & b_-^n & \Delta y \\ 0 & \left(b_-^n\right)^2 & \Delta y^2 \end{pmatrix} \begin{pmatrix} b_0 \\ b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} \mu_0 \\ \mu_1 \\ \mu_2 \end{pmatrix} \sim \begin{pmatrix} \sqrt{\frac{2i\pi}{\tilde{\omega}}} + \frac{1}{i\tilde{\omega}} \left(\frac{\exp\left(i\tilde{\omega}\left(\Delta y - b_-^n\right)^2/2\right)}{\Delta y - b_-^n} + \frac{\exp\left(i\tilde{\omega}\left(b_-^n\right)^2/2\right)}{b_-^n} \right) \\ b_-^n \mu_0 + \frac{1}{i\tilde{\omega}} \exp\left(i\tilde{\omega}\left(\Delta y - b_-^n\right)^2/2\right) \\ b_-^n \mu_1 + \frac{\Delta y}{i\tilde{\omega}} \exp\left(i\tilde{\omega}\left(\Delta y - b_-^n\right)^2/2\right) \end{pmatrix}.$$

We then conclude in approximating:

$$\int_{j_{a_-^n}\Delta y}^{(j_{a_-^n}+1)\Delta y} f^n(y') \exp\left(\frac{i\tilde{\omega}}{2}\left(y' - a_-^n\right)^2\right) dy' = \int_0^{\Delta y} \exp\left(\frac{i\tilde{\Delta} y^2 \tilde{\omega}}{2}\left(y' - b_-^n\right)^2\right) g^n(y') dy'$$

$$\sim \sum_{l=0}^{2} b_l(\tilde{\omega}) g^n(c_l). \quad (25)$$

Note however that if $\Delta y^2 \tilde{\omega}$ is not small enough, in particular compared to $b_-^n \in]0,1[$ (that can a priori be small) the last term of the L.H.S. of (24) cannot be neglected as we did. It is then necessary in that case to go beyond the above study.

Case 2. $\Delta y^2 \tilde{\omega}$ **small enough.** In that case the behavior of the function inside the integral is naturally totally different. Indeed it does not consist anymore of an highly oscillatory function, so that the use of Filon's quadrature is no more adapted. A simple Gauss-Legendre quadrature is then sufficient at least if we avoid the intermediate case $\tilde{\omega} = \mathcal{O}(1)$. For intermediate cases, in (24) the term $k\mu_{k-1}(\tilde{\omega})/\tilde{\omega}$ cannot a priori be simplified. However, following

the process presented in Case 1, the approximation of $\mathrm{erf}(z)$ is no more valid. Some aspects of this particular case can be found in [17], [18].

A symmetric approach is obviously applied at y_Γ^+. Finally (22) is approximated at each iteration using (23) and (25). Thus we obtain an accurate approximation of (21) then of (18). We then close the system (12). Note that these integrals have to be evaluated at each iteration. This corresponds to an order N complexity, when the complexity of the TDSE computation is of order $N^{3/2}$ (sparse badly conditioned linear system to solve). However it is important to note that

$$\int_{\mathbb{R}} f^n(y') \exp\left(\frac{i\tilde{\omega}}{2}\left(y' - a_-^n\right)^2\right) dy',$$

should in fact be computed on $\mathrm{Supp}(f^n)$ that is, at least for not too intense or ultrashort laser pulse, is a very localized set.

Remark 3. Another issue has to be studied. As is well-known transparent or artificial boundary conditions can produce unstable Crank-Nicolson schemes, even if the laser is null. For instance Arnold and Ehrhardt proposed a Crank-Nicolson scheme with T.B.C. conditionally stable. Later, Antoine and Besse improved this result [9], finding an adapted approximation of the Dirichlet-Neumann operator leading to an unconditionally stable Crank-Nicolson scheme. The study of the stability of the global scheme (and its extension in 2D and 3D), very technical will be presented in a forthcoming article.

C. Towards Plasma Effects

We now propose some ideas to take into account plasma effects due to free electrons coming from ionized molecules (for instance see [4] for physical details). In this goal we use the boundary conditions built above, verifying the two main points: nonreflection and no spurious absorption. Let us specify the data of the problem. The global domain is given by

$$\Omega = \cup_{i\in\{1,\cdots,\mathbb{N}\}}[y_{-\Gamma_i}, y_{\Gamma_i}] \text{ with } \omega_i = [y_{-\Gamma_i}, y_{\Gamma_i}]. \tag{26}$$

Initially a nonexcited molecule (ground state) is located at the center of each subdomain, Fig. 10. Nuclei are supposed to be fixed (Born-Oppenheimer) so that only the electron wavefunctions are of interest. The respective wavefunctions on $(\omega_i)_{i\in\{1,\ldots,N\}}$ associated to the molecules $(\mathcal{M}_i)_{i\in\{1,\ldots,N\}}$ are denoted by $(v_i)_{i\in\{1,\ldots,N\}}$ and are solutions of (here H_2^+-TDSE):

$$i\,\partial_t v_i = \left(-\frac{1}{2}\partial_{yy}^2 + V_c^{(i)}(y) + yE(t)\right) v_i, \quad y \in \omega_i. \tag{27}$$

As usual we suppose that the Coulomb potential is negligible in each domain far enough from the nuclei. The Coulomb potential associated to the $\mathcal{M}_i^{\text{th}}$ molecule is denoted by $V_c^{(i)}$. That is we introduce two sequences $(\varepsilon_i)_{i\{1,\ldots,N\}}$ and $(\ell_i)_{i\{1,\ldots,N\}}$ such that:

$$\left|V_c^{(i)}(y)\right| < \varepsilon_i, \text{ if } |y| \geq \ell_i, \quad \forall i \in \{1, \cdots, N\}. \tag{28}$$

Coefficients $(\ell_i)_i$ are obviously chosen such that $(\varepsilon_i)_i$ are sufficiently small. Then in each subdomain ω_i, for $|y| < \ell_i$, the wavefunction is computed using the quantum TDSE:

$$i\,\partial_t v_i = \left(-\frac{1}{2}\partial_{yy}^2 + V_c^{(i)}(y)\right) v_i + yE(t)v_i, \quad |y| < \ell_i.$$

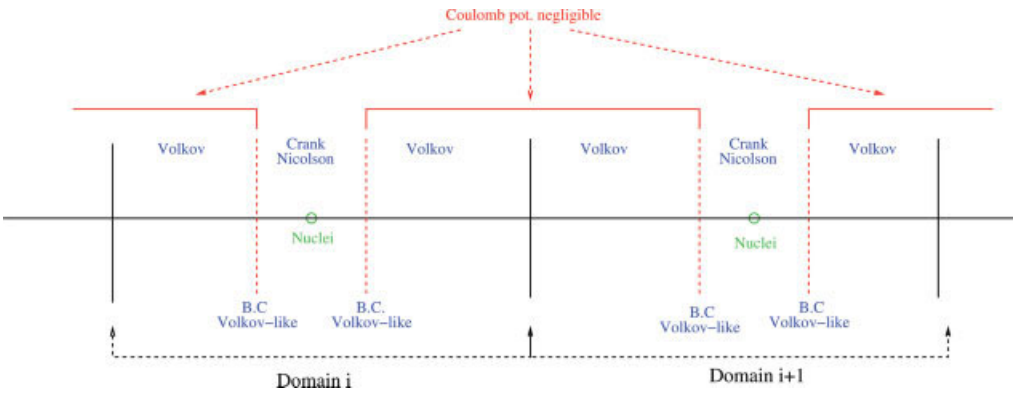

FIG. 10. Boundary conditions—Free electrons. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

We then impose at $|y| = \ell_i$, the boundary conditions defined in (18). Beyond $|y| > \ell_i$, the electrons are supposed to be free (not related anymore to a Coulomb potential) so that we apply a Volkov state propagator (see for instance [1]) which is an order N method and then much less costly numerically than a finite difference approach (order $\mathcal{O}(N^{3/2})$ due to preconditioned linear system solvers). In that situation we can prove that the quadratic norm of the wavefunction is conserved at order 2 in time under some assumptions. First we have to prove a classical result.

Lemma 2.1. *Let us introduce two positive times $t_0 \geq 0$ and $T > t_0$, and suppose that the electric field E is defined as a monochromatic wave $E(t) = -E_0 \cos(\omega t)$, where ω is the electric field frequency and E_0 its amplitude. We consider a free electron (no Coulomb potential) located initially at $y(t_0) = 0$ with zero velocity $\dot{y}(t_0) = 0$ and excited by E. Supposing that the electron motion is classically described, its position at time T is then given by:*

$$y(T) = \left(\frac{E_0}{\omega}\sin(\phi_0)\right)\frac{\phi_T - \phi_0}{\omega} + (\cos(\phi_0) - \cos(\phi_T))\frac{E_0}{\omega^2}. \tag{29}$$

Where $\phi_0 = \omega t_0$ and $\phi_T = \omega T$ are the initial and final electric field phases.

Proof. The proof is obvious as it only consists of the solution of the Newton's equation:

$$\begin{cases} \ddot{y}(t) = E(t), \\ y(t_0) = 0, \dot{y}(t_0) = 0. \end{cases}$$

The analytical solution at time T, of this system is given by (29). ∎

Here is an important result.

Proposition 2.3. *Let us consider (27) in each ω_i with $i \in \{1, \ldots, N\}$ with $V_c^{(i)}$ and $E(t)$ a monochromatic[2] electric field. We consider times $T > t_0$ such that for all $t \in [t_0, T]$, and denoting $\phi_t = \omega t$ and $\phi_0 = \omega t_0$, we have:*

$$\left|\left(\frac{E_0}{\omega}\sin(\phi_0)\right)\frac{\phi_t - \phi_0}{\omega} + (\cos(\phi_0) - \cos(\phi_t))\frac{E_0}{\omega^2}\right| \in \omega_i \tag{30}$$

[2]This assumption is not necessary but allows us to have an explicit condition.

- *We suppose that in the subdomain* $\{y \in \omega_i, |y| \leq \ell_i\}$ *a Crank-Nicolson scheme in time with a spatial* 3*-point stencil to approximate the Laplace operator, is used to solve* (28)*. The time step is denoted by* Δt *and space step by* Δy*. We denote by* $v_i(y_j, t)$ *the numerical solution at* $j\Delta y$*,* $j \in \mathbb{Z}$*, and at time* t*.*
- *At* $|y| = \ell_i$*, we use the Volkov-like boundary conditions with an order-*2 *Strang splitting to solve* (18)*.*
- *In* $\{y \in \omega_i, |y| > \ell_i\}$*, the TDSE is solved using a Volkov state propagator* (see [1])*.*

Then, for all $t \in]t_0, T]$ *and for all* $i \in \{1, \ldots, N\}$*:*

$$\begin{aligned}\Delta y \sum_j |v_i(y_j, t)|^2 &= \Delta y \sum_j |v_i(y_j, t_0)|^2 + \mathcal{O}(\varepsilon_i) + \mathcal{O}((\Delta y)^2) + \mathcal{O}((\Delta t)^2) \\ &= 1 + \mathcal{O}(\varepsilon_i) + \mathcal{O}((\Delta y)^2) + \mathcal{O}((\Delta t)^2) \end{aligned} \tag{31}$$

We then have conservation of the wavefunction ℓ^2*-norm at order* 2 *in space and time, and* 1 *in* ε_i*.*

Remark 4.

- Assumption (30) allows us to guarantee that the electronic wavefunction support remains included in ω_i from times t_0 to T, as the Coulomb potential has an attractive effect on the electron.
- This result has to be compared for instance with (5), where much more information is lost.

Idea of the Proof 1. We suppose here that $\varepsilon_i = 0$ for all i. This is only a technical assumption that allows to simplify the proof but is really not restrictive. Initially we obviously have:

$$\Delta y \sum_j |v_i(y_j, t_0)|^2 = 1, \quad \forall i \in \{1, \ldots, N\}$$

that is a discrete version of:

$$\int_{\omega_i} |v_i(y, t_0)|^2 dy = 1.$$

We now denote by $v_i^{(\text{exact})}$ the exact solution of the TDSE in $\mathbb{R}$ restricted to ω_i for $\mathcal{M}_i$. In $\{y \in \omega_i, |y| < \ell_i\}$ the TDSE is numerically solved by a classical order 2 scheme, so that the error $\|v_i^{(\text{exact})} - v_i\|_{\ell^2(\{y \in \omega_i, |y| < \ell_i\})}$ is of order $\mathcal{O}((\Delta y)^2) + \mathcal{O}((\Delta t)^2)$. Inside $\{y \in \omega_i, |y| \geq \ell_i\}$ and especially at $|y| = \ell_i$, the error is at this same order. First because the Volkov operator used to solve the TDSE in $\{y \in \omega_i, |y| > \ell_i\}$ is exact, and then because the splitted operators used to solved the continuous approximate boundary condition is of order 2 in space and time. Then for all $t \in [t_0, T]$:

$$\|v_i^{(\text{exact})} - v_i\|_{\ell^2(\omega_i)} = \mathcal{O}((\Delta y)^2) + \mathcal{O}((\Delta t)^2).$$

Beyond the assumption $\varepsilon_i = 0$, the error would naturally (by definition of $(\varepsilon_i)_i$) be in $\mathcal{O}((\Delta t)^2) + \mathcal{O}((\Delta y)^2) + \mathcal{O}(\varepsilon_i)$. ■

Remark 5. In the model we have proposed in [4], [20] in a domain Ω (26), we suppose that each TDSE represents not one single molecule, but rather a large number of particles. Typically the number of particles $N_i(t)$ in each subdomain ω_i at time t is given by $\int_{\omega_i} n(y,t)dy$ where $n(y,t)$ represents the molecular density. In practice we choose n as piecewise constant function: $n(y,t) = \sum_{i=1}^{N} n_i(t)\mathbf{1}_{\omega_i}(y)$ so that $N_i(t) = \mathrm{vol}(\omega_i)n_i(t)$. The molecular density is defined in the model at time t by:

$$n_i(t) = n_0 \int_{\omega_i} |v_i(y,t)|^2 dy$$

where n_0 is a parameter and v_i the solution of (27). The wavefunction v_i introduced above is representative of all the particles inside ω_i, and is then not associated to one single molecule. At time $t = t_0$, we have:

$$\forall i \in \{1,\dots,N\}, \quad n_i(t_0) = n_0 \int_{\mathbb{R}} |v_i(t_0)|^2 dy.$$

And the total number of particles N_{part}, is given by:

$$N_{\mathrm{part}} = \sum_{i\in\{1,\dots,N\}} N_i(t_0) = \sum_{i\in\{1,\dots,N\}} n_i(t_0) \times \mathrm{vol}(\omega_i).$$

Corollary 2.1. *Working in the framework described above, under the assumptions of proposition* (2.3) *and supposing also that for all i in $\{1,\dots,N\}$, vol(ω_i) and ε_i are respectively equal to two positive constants V and ε, then at order two in space and time and order one in ε, the total number of particles in Ω is conserved.*

Proof. Using proposition (2.3), the proof is simply based on

$$\sum_{i}^{N} N_i(t) = \sum_{i=1}^{N} \mathrm{vol}(\omega_i) \times \int_{\omega_i} |v_i(t)|^2 dy = V \sum_{i=1}^{N} \int_{\omega_i} |v_i(t)|^2 dy.$$

Then we use the estimate (31). ∎

In fact it is possible to beyond what is presented here and to allow the transmission of free electrons from a domain to another (see the numerical example). When free electrons coming from domain ω_i enter in say ω_{i+1}, we then apply the TDSE solver for electrons in ω_{i+1}. This method allows us to consider electronic transfers between Schrödinger domains and then to avoid a loss of information due to ionization and absorption. This technique can only be applied to a large number of molecules (framework of remark (5)) and is no more valid for few particles where a nonlinear TDSE (Hartree-Fock, Thomas-Fermi, Khon-Sham, etc) would have been preferentially considered. Note, that recently, Persson *et al.* have also proposed in [19] a way to take plasma into account in the TDSE using a Drude model.

Numerical Example. To illustrate this idea let us consider the following problem. With the following data, $\omega = 20$, $E(t) = 0.5\sin(\omega t)$, $t_f = 0.3$, $\Delta t = 10^{-3}$, and for $\Omega = \omega_1 \cup \omega_2 = [-3.5, 3.5[\cup[3.5, 10]$ and $v_1(y,0) = e^{8iy}e^{-y^2}$, $v_2(y,0) = e^{12iy}e^{-y^2}$, we compute two independent TDSE's without Coulomb potential. That is for the wavefunctions v_1 and v_2 on two domains ω_1 and ω_2. At the boundary, we impose the conditions proposed earlier. In this numerical benchmark

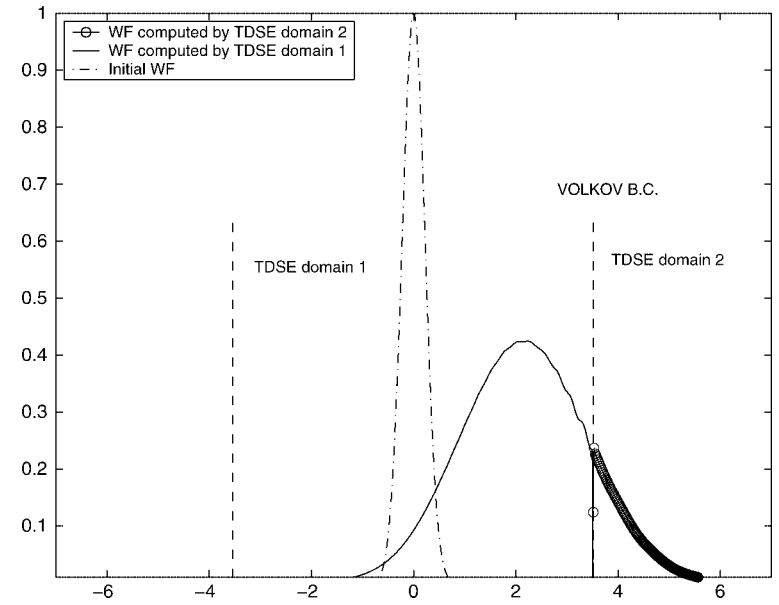

FIG. 11. Probability $|v|^2$ at the boundary between two computational domains.

we do not use a Volkov state propagator as the Coulomb potential free regions are fictitious to one single point, $y = 3.5$. When some electrons leave their computational domain say ω_1, to enter in ω_2 the process then consists of adding to v_2 the part of v_1 leaving ω_1. As we can see (Figs. 11 and 12), the electrons located initially in ω_1 have almost left it (now in ω_2). Similarly the electrons initially located in ω_2 have left Ω_i (now in the adjacent domain; virtually ω_3).

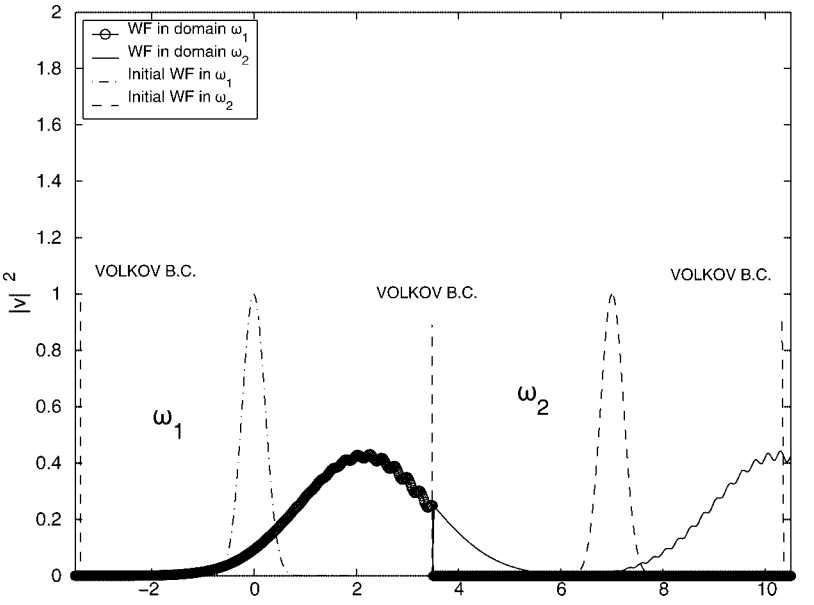

FIG. 12. Wavefunction transmission—two domains.

III. CONCLUSION

In this article we have proposed several approaches to treat the boundary condition problem for laser-molecule TDSE's. This analysis has allowed us to show that a simple absorbing boundary condition is not sufficient to take all physical phenomena into account (free electrons). Then a natural approach based on the Volkov wavefunction has been introduced. Emphasis has been placed on the numerical treatment of such boundary conditions as they require a particular attention. This approach with focus to plasma effects, will be used in order to simulate filaments (paper, in preparation) in a Maxwell-Schrödinger framework [4], [20].

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