Numerical method for dynamic imaging of nonlinear polyatomic molecules

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Abstract. We present electron and nuclear dynamic imaging of a polyatomic molecule in an ultrashort intense laser pulse. A numerical solution of the time-dependent Schrödinger equation is described to study the non-perturbative nonlinear dynamic of a nonlinear polyatomic molecule in interaction with ultrashort intense laser pulse. In a quantum description of the molecular system, beyond the Born-Oppenheimer approximation, we investigate the full influence of the nuclear motion on the photoionization and harmonic generation processes.

1. Introduction
Quantum dynamic imaging of molecules is currently studied with the help of the recent advances in laser technology [1]. To perform dynamic imaging of molecules one has to take into account the different time scale in the motion of the particles within a molecule. Nuclei evolve on the time scale of the femtosecond ($1 \, fs = 10^{-15}\, s$). For instance, by applying a femtosecond laser pulse of a few optical cycles, in the near infrared spectral region, the ultrafast vibrational wavepacket dynamics in the dissociative ionization of $H_2$ molecule has been probed [2]. On the other hand, electrons evolve on the time scale of the attosecond ($1 \, as = 10^{-18}\, s$). Since only a decate, such ultrashort laser pulses are produced from the nonlinear interaction of matter with light through the process of high-order harmonics generation (HHG) in atoms [3] or molecules [4]. In this process an atom or a molecule is ionized by a femtosecond infrared laser pulse. The photoelectron is subsequently accelerated by the laser field. As the electric field changes phase within an optical cycle, the photoelectron changes its direction and recollide with the parent ion [3]. Alternatively, the electron may recollide with the neighbors at higher energies than recollision with the parent ion [4],[5]. It emits energy (photon) that it has accumulated under the laser field in the form of high-order harmonics of the carrier-wave frequency. To such high frequencies correspond ultrashort pulses of duration of few attoseconds, which can be used to image the electron dynamics in atoms and molecules [6].

Numerical simulations are playing an important role in the understanding of laser-matter interaction, in particular in quantum molecular dynamic imaging. The exact description of molecular dynamics should include the correlated electron-nuclei motion and electron-electron motion. Large-scale numerical solutions of the multidimensional time-dependent Schrödinger equation (TDSE) is used in this paper to simulate the nonlinear nonperturbative interaction of a nonlinear polyatomic molecule with ultrashort laser pulses on time scales of nuclear and electron motion. These simulations are possible, thanks to the constant advances of highly parallel computational resources.
2. Numerical method

We study the one electron molecular system $H_3^{++}$ in a nonlinear (triangular) configuration in a two-dimension plane. The nuclear coordinates are defined with Jacobi coordinates, $r$, being the relative coordinate between two lower nuclei (forming the basis of the triangle), and $R$, the relative coordinate between the upper nucleus and the center of mass of the two lower nuclei as shown in Fig. 1. The angle between these two Jacobi coordinates is fixed to $\theta = 90^\circ$ to ensure a $C_{2v}$ symmetry, i.e. an isosceles triangle. The nuclear coordinates are related to cartesian coordinates as follow: $x_{N_1} = 0, y_{N_1} = \frac{2}{3}R, x_{N_2} = -\frac{1}{2}r, y_{N_2} = -\frac{1}{2}R, x_{N_3} = \frac{1}{2}r, y_{N_3} = -\frac{1}{2}R$. The electron coordinates are defined with polar coordinates $\phi$ and $\rho$, with correspondence to cartesian coordinates as $\rho = \sqrt{x^2 + y^2}$ and $\phi = \arccos(x_e/\rho) [7]$.

The complete equation of motion of the molecule is prescribed by the time-dependent Schrödinger equation (TDSE) (in atomic units, $\hbar = m_e = 1$) beyond the Born-Oppenheimer approximation,

$$i\hbar \frac{\partial}{\partial t} \Psi(\rho, \phi, r, R, t) = \left( T_e + T_N + V(\rho, \phi, r, R, t) \right) \Psi(\rho, \phi, r, R, t),$$

(1)

with the kinetic energy operators

$$T_e = -\frac{1}{2\mu_e} \left[ \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right],$$

(2)

$$T_N = -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} - \frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2},$$

(3)

and the total potential

$$V(\rho, \phi, r, R, t) = V_{eN}(\rho, \phi, r, R) + V_{NN}(r, R) + V_{int}(\rho, \phi, t),$$

(4)

where the electron-nuclei attraction, nuclear repulsion and interaction potentials are given respectively by

$$V_{eN}(\rho, \phi, R, r) = -\sum_{k=1}^{3} \frac{1}{\sqrt{\rho^2 + x_{N_k}(r)^2 + y_{N_k}(R)^2 - 2\rho(\cos \phi x_{N_k}(r) + \sin \phi y_{N_k}(R)) + c_{en}}}$$

(5)

$$V_{NN}(r, R) = \sum_{k,l=1,\ldots,3} \frac{1}{\sqrt{(x_{N_k}(r) - x_{N_l}(r))^2 + (y_{N_k}(R) - y_{N_l}(R))^2 + c_{NN}}}$$

(6)

$$V_{int}(\phi, \rho, t) = -\rho \cos(\phi - \theta) E(t).$$

(7)

The reduced masses in the kinetic operators $T_e$ and $T_N$, in Eqs. (2) and (3), are defined as

$$\mu_e = \frac{m_{N_1} + m_{N_2} + m_{N_3}}{1 + m_{N_1} + m_{N_2} + m_{N_3}}; \mu_r = \frac{m_{N_2}m_{N_3}}{m_{N_2} + m_{N_3}}; \mu_R = \frac{m_{N_1}(m_{N_2} + m_{N_3})}{m_{N_1} + m_{N_2} + m_{N_3}},$$

(8)

with $m_{N_i}, i = 1, \ldots, 3$ denoting the mass of the three nuclei.

In the attraction and repulsion potentials in Eqs (5) and (6), we use Coulomb softening parameters $c_{eN} = 0.35$ and $c_{NN} = 1$ which gives potentials for $H_3^{++}$ in good agreement with experimental geometries. The electric laser pulse in the interaction potential, Eq. (7), is linearly polarized along $(\cos \theta, \sin \theta)$ direction with electric strength $E(t) = \epsilon(t) \cos(\omega t + \varphi)$. Here, $\omega$ (a.u.) is the carrier-wave frequency which is linked to wavelength $\lambda$(nm) by $\omega = 2\pi c/\lambda$, $\varphi$ is the carrier-envelope phase and $\epsilon(t)$ is the laser pulse envelope of trapezoidal shape with two optical
cycles \((T = 2\pi/\omega)\) ramp on, two constant optical cycles at intensity \(E_0 = \sqrt{T}\), and two optical cycles ramp off, as depicted in Fig. 2.

In order to solve numerically the TDSE, Eq. (1), we adopt the second order split-operator method [8] for the temporal propagation of the wavefunction

\[
\Psi(t + \delta t) = e^{-iV(t+\delta t/2)\delta t/2} * e^{-iT_N \delta t/2} e^{-iT_e \delta t/2} e^{-iV(t+\delta t/2)\delta t/2} \Psi(t) + O(\delta t^3),
\]

where the exponential operator of the electron kinetic energy is approximated by the Crank-Nicholson method [9]

\[
e^{-iV(r,R,\phi) T_e} \Psi(t) = \frac{1 - i(\delta t/2)T_e}{1 + i(\delta t/2)T_e} \Psi(t) + O(\delta t^3),
\]

implied by the choice of spatial discretization of the wavefunction for the electron variable.

The wavefunction is periodic in the \(r, R\) and \(\phi\) directions where we apply an absorber at the \(r_{\text{max}}\) and \(R_{\text{max}}\) boundaries, so we choose momentum Fourier space via Fast Fourier Transform (FFT) for the approximation in these variables. Furthermore, as it is well known, the exponential of the Laplacian (kinetic energy \(T_N\) here) operator becomes a multiplication operator in the Fourier spectral space, so the Fourier representation of wavefunction in \(r\) and \(R\) is very efficient.

The finite difference (FD) method is chosen to discretize \(\rho\). The combined FD and Fourier series is applied to Eq. (11): The \(T_e\) operator is written in the Fourier space of \(\phi\), and the partial derivate operator for each Fourier coefficient of \(\phi\) is discretized with \(4^{th}\) order finite difference scheme. At origin, we profit from the symmetry (anti-symmetry) of these Fourier coefficient on \(\rho\) in order to avoid numerical boundary condition. More details can be found in [10].

The final algorithm requires FFT and diagonal band limited linear system solver. It is implemented by calling multithreads version subroutines of FFTW and OpenMP (multithreads) parallelized from Lapack linear solver.

3. Numerical results

3.1. Initial conditions and grid specifications

We apply the numerical method described above to the problem of electron and nuclear dynamics in the \(H_3^{++}\) molecular ion in interaction with an intense and ultrashort laser pulse. The initial molecular wavefunction is defined by \(\Psi(\rho, \phi, r, R, t = 0) = f(r, R) \Phi(\rho, \phi; r, R)\), where \(\Phi(\rho, \phi; r, R)\) is the electronic eigenfunction at fixed nuclear coordinates \(r\) and \(R\) obtained by imaginary-time propagation [11],[12]. \(f(r, R)\) is the initial proton function in terms of the nuclear coordinates centered at \(r = R = 2 \text{ a.u.}\) and describes a Franck-Condon transition from \(H_3^+\) to \(H_3^{++}\) at the equilibrium distance \(R_{eq}(H_3^+) = 2 \text{ a.u.}\) [13], [14], [15].

The electric laser pulse, linearly polarized along \(y\) axis, with the carrier-wave frequency \(\omega = 2\pi c/\lambda = 800 \text{ nm}\) = 0.057 a.u. of period \(T = 2\pi/\omega = 2.7 \text{ fs}\), carrier-envelope phase \(\varphi = 0\) and intensity \(I = E_0^2 = 2 \times 10^{14} \text{W/cm}^2(7.4 \times 10^{-2} \text{ a.u.})\), is depicted in Fig. 2. Recent experiments have shown that ionization probability is most favorable with a linearly polarized laser pulse oriented at \(0^\circ\) and \(90^\circ\), which justifies the choice of nuclear coordinates (with fixed angle \(\theta = 90^\circ\)) with the laser orientation along the \(R\) nuclear coordinate, \((y\) axis\), (see Fig. 1) [16].

The TDSE is solved numerically, with time step \(\delta t = 0.05 \text{ a.u.}\), and we use an electron grid of size \(\rho < \rho_{\text{max}} = 128 \text{ a.u.}\) with 512 points and \(0 < \phi < 2\pi\) with 128 points and a proton grid of size \(r < r_{\text{max}}\) and \(R < R_{\text{max}} = 19.2 \text{ a.u.}\) with 192 points in both \(r\) and \(R\) directions. For very short pulses, as considered here, it has been verified that the nuclear wavefunction is contained within the grid at all times, and that the electron grid size \(\rho_{\text{max}}\) is always longer than
the maximum free electron trajectory defined by \( \alpha = E/\omega^2 \) in a laser field of amplitude \( E \) and frequency \( \omega \). Thus, at \( I = 7.4 \times 10^{-2} \) a.u. and \( \omega = 0.057 \) a.u., \( \alpha = 23 \) a.u. \(<\rho_{\text{max}} \). Absorbing boundaries are used and we ensure that less than 20% of the population leaks to the absorbing boundaries during the propagation.

### 3.2. Observables

During the time propagation, we calculate the electron density,

\[
P_e(t) = \int_0^\infty dr \int_0^\infty dR |\Psi(\rho, \phi, r, R, t)|^2,
\]

and the nuclear density

\[
P_N(t) = \int_0^{\rho_{\text{max}}} d\rho \int_0^{2\pi} d\phi |\Psi(\rho, \phi, r, R, t)|^2 \rho.
\]

We are also interested in the laser induced electron dipole moment in the acceleration form [17],

\[
a(t) = \int d\rho \int d\phi \int dR \int dr \Psi^*(\rho, \phi, R, r, t) \left( \frac{\partial H}{\partial y_e} \right) \Psi(\rho, \phi, R, r, t) \rho
\]

\[
= \int d\rho \int d\phi \int dR \int dr \Psi^*(\rho, \phi, R, r, t) \left( -\nabla V_{\text{el}} + E(t) \right) \Psi(\rho, \phi, R, r, t) \rho.
\]

The Fourier transform of the dipole gives the molecular high-order harmonic generation (MHOHG) power spectrum,

\[
P(\omega) \propto |\int_0^{6T} a(t) \exp(-i\omega t) dt|^2.
\]

### 3.3. Discussion

In this paper, we study the electron-nuclei correlation in the dissociating molecule \( H_3^{++} \). The electron and nuclear motion is clearly illustrated in Fig. 2 which describes the electron density as the molecule is dissociating under the electric laser pulse. Initially, the electron density is uniformly delocalized on the three protons, which form an equilateral triangle. Once the laser field is turned on, it oscillates at frequency \( \omega \) and period \( T = 2\pi/\omega \) and the electron density is pushed towards the upper proton when the field is negative (e.g. \( t = T, 2T, 3T, ... \)), and towards the two lower protons when the field is positive (e.g. \( t = 0.5T, 1.5T, 2.5T, ... \)). The electron, being a negative particle, moves in the opposite direction of the electric laser field. Moreover, after only few optical cycles, the electron density spreads out because the nuclei are moving apart, i.e. the molecule is dissociating. At \( t = 5T \), the electron density is delocalized on the three distinct protons, while at the end of the pulse, it is mainly localized on the upper proton, forming the product \( H + 2H^+ \). Also, as the nuclei move to larger distance due to nuclear repulsion, the field interaction becomes stronger compared to the Coulomb field and the molecule starts to ionize. The ionization probability is the most important at each peak of the laser pulse.

Once the molecule is ionized, there is a certain probability that the photoelectron recombines with the ion and emits high order harmonics. The MHOHG spectrum is shown in Fig. 3 where we compare the MHOHG generated from the case of the moving molecular ion with the case of the static molecular ion at fixed geometry \( R = r = 5 \) a.u.. From a time-frequency analysis (Gabor transform [18], not shown here) of the acceleration dipole, we observed that the main recollision event occurs at around four optical cycles (\( t = 4T \)). At this time, the molecular geometry is described by \( r = R = 5 \) a.u. (see Fig. 2). We observe similarities in the MHOHG spectra for the dynamic and static cases: there is a well-defined plateau, followed by a rapid
drop in the harmonic signal. This cutoff is predicted by the semi-classical electron recollision model \cite{3} and defines the maximum harmonic $N_{\text{max}}$ with energy $N_{\text{max}} = 3.17U_p + I_p = 43$, where the ponderomotive energy is $U_p = E_0^2/4\omega^2 = 0.4387$ a.u. and the ionization potential at $r = R = 5$ a.u. is $I_p = 1.029$ a.u.. The predicted value of $N_{\text{max}}$ is very close to the one calculated $N_{\text{max}} = 46$ \cite{19}. Even and odd harmonics are observed in both cases \cite{7}, due to the non-linearity of the molecule (absence of center of inversion) \cite{20}. The odd harmonics disappear at very high frequencies and the global amplitude of the harmonics profile is lower in the moving nuclear case due to the non-Born-Oppenheimer dynamics. This shows that electron dynamics is strongly influenced by the nuclear motion.

4. Conclusion
We have demonstrated with our multidimensional non-Born-Oppenheimer model the effect of nuclear motion on the electron dynamics for a nonlinear polyatomic molecule. This is illustrated in the MHOHG spectrum, which is a phenomenon of great importance in attosecond science \cite{6}. Work is in progress to extend this model and method to the stable two-electron molecular system $H^+_3$. To include nuclear and electron motion, this is at least a five body problem. With respect to memory resource, we have estimated about $60TB$ of fast accessible disk space necessary to perform calculations on relatively small grids $(n\rho = 512, n\phi = 128, nR = 192)$. Also, because of the very large number of spatial discretization points, one typical calculation may need $\approx 5$ days on a 12000 core parallel computer. With constant advances in computational resources, such intensive calculations will make possible the study of electron-electron correlation, influenced by the nuclear motion.

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Figure 1. Geometry of $H_3^{++}$ molecular ion in the $xy$ plane with the origin at the center of mass of the nuclei. Nuclear coordinates are labeled $r$, $R$ and $\theta$ (in black) and electron coordinates are labeled $\rho$ and $\phi$ (in blue).
Figure 2. Electric laser pulse, $E_y$, as a function of time. Snapshots of the electron density in the $xy$ plane. From left to right: upper panels $t = 0, T, 2T, 3T, 4T, 5T, 6T$; lower panels $t = 0.5T, 1.5T, 2.5T, 3.5T, 4.5T, 5.5T$, where $T = 2\pi/\omega$.

Figure 3. Molecular high-order harmonic (MHOHG) spectra of $H_3^{++}$ with moving nuclei (red curve) and fixed nuclei ($r = R = 5$ a.u.) (purple curve) at $I = 2 \times 10^{14}$ W/cm$^2$, $\omega = 0.057$ a.u. ($\lambda = 800$ nm), $T = 2.7$ fs.