Time-dependent generalized pseudospectral method for accurate treatment of multiphoton processes of diatomic molecules in intense laser fields

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A B S T R A C T

We present a numerical method based on the generalized pseudospectral discretization in prolate spheroidal coordinates and split-operator time propagation. The method has been applied for the study of multiphoton processes of H 2 + and N 2 diatomic molecules in intense laser fields. It proves very accurate while using only moderate computer resources.

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1. Introduction

The pseudospectral (or collocation) approximation [1] assumes that the approximate function \( f_N(x) \) coincides with the exact function \( f(x) \) on the set of \( N \) collocation points \( \{x_j\} \):

\[
f(x) \cong f_N(x), \quad f_N(x_j) = f(x_j), \quad j = 1, \ldots, N. \tag{1}
\]

The approximate function \( f_N(x) \) can be expanded on the basis of the cardinal functions \( g_j(x) \):

\[
f_N(x) = \sum_{j=1}^{N} f(x_j) g_j(x), \tag{2}
\]

the expansion coefficients being the values of \( f(x) \) at the collocation points. The cardinal functions are equal to unity at one of the points \( x_j \) and vanish at other collocation points:

\[
g_j(x_i) = \delta_{ij}. \tag{3}
\]

The simplest scheme of the pseudospectral (PS) method makes use of the roots of orthogonal polynomials (with the Legendre polynomials used most frequently) as collocation points. All multiplication operators are represented by diagonal matrices; differential operators are represented by full matrices but the matrix elements have simple analytical expressions. The PS methods have a close relation to the discrete variable representation (DVR) [2] which uses basis set expansions and calculation of the matrix elements by Gaussian quadrature. It was shown [3] that representations through the expansion coefficients and the function values at quadrature points are equivalent. Historically, PS methods had applications in fluid dynamics [4] while DVR was mainly used in chemical physics problems involving nuclear motion [5]. The PS method was generalized [6] to facilitate its application to studies of the electronic structure of atoms and molecules. The generalized pseudospectral (GPS) method [6] features algebraic mapping of the coordinates, symmetrization of the eigenvalue problem, and complex scaling for treatment of the resonance states.

2. GPS discretization for two-center systems

For two-center quantum systems, like diatomic molecules, the electronic motion is naturally treated using the prolate spheroidal coordinates \( \xi, \eta, \) and \( \varphi \) [7]. In prolate spheroidal coordinates, the kinetic energy operator reads as (atomic units are used throughout the paper):

\[
-\frac{1}{2} \nabla^2 = -\frac{1}{2\alpha^2(\xi^2 - \eta^2)} \left[ \frac{\partial}{\partial \xi} (\xi^2 - 1) \frac{\partial}{\partial \xi} \right. \nonumber
\]

\[
\left. + \frac{\partial}{\partial \eta} (1 - \eta^2) \frac{\partial}{\partial \eta} + \frac{\varphi^2 - \eta^2}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2}{\partial \varphi^2} \right]. \tag{4}
\]

\( \alpha \) being the half internuclear separation. If the molecule is not subject to external fields, the projection \( m \) of the electronic angular
momentum onto the molecular axis is conserved, and the corresponding wave function can be expressed as follows:

$$\psi(\xi, \eta, \varphi) = \psi_m(\xi, \eta) \exp(\im \varphi).$$

Then the coordinate \(\varphi\) is eliminated, and one arrives at a 2D problem for the wave function \(\psi_m(\xi, \eta)\). We apply the GPS Gauss-Radau discretization scheme for \(\xi\) and Gauss-Legendre scheme for \(\eta\) using the following mapping transformations:

$$\xi(x) = 1 + R_1 \frac{1 + x}{a(1 + x + \frac{2R_1}{R_2-a})}, \quad \eta(y) = y$$

where \(R_1\) is the mapping parameter and \(R_2\) is the end point in the \(\xi\) domain. Upon discretization, the kinetic energy matrix elements have simple expressions [8] which are, however, different for even and odd \(m\), respectively. This happens because the exact wave functions have factors \((\xi^2 - 1)^m/\sqrt{2(1 - \eta^2)^m/2}\) which are non-analytical at the nuclei for odd \(m\). Straightforward numerical differentiation of non-analytical functions leads to significant loss of accuracy. A workaround results in different kinetic energy matrices for even and odd \(m\) [8]. Using these matrices with only 72 grid points for \(\xi\) and 24 grid points for \(\eta\), we were able to obtain the energies of the first several bound states of \(H_2^+\) with very high accuracy; the computation time did not exceed a few minutes. Table 1 shows the first 12 fully converged eigen-energies with 28 accurate digits.

For diatomic molecules in laser fields, \(m\) is not conserved unless the orientation of the molecular axis is parallel to the polarization of the field. Then we have a full 3D problem where the states with even and odd \(m\) are coupled to each other. Using different kinetic energy matrices for even and odd \(m\) becomes inconvenient. We can circumvent the problem with the help of the special mapping transformations [9] for \(\xi\):

$$\xi(x) = 1 + R_1 \frac{(1+x)^2}{a(1-x+\frac{4R_1}{R_2-a})},$$

and \(\eta\):

$$\eta(y) = -\cos \left( \frac{\pi}{2}(1+y) \right).$$

Table 1

<table>
<thead>
<tr>
<th>State</th>
<th>Energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1\sigma_g)</td>
<td>(-1.102634144949461508968945)</td>
</tr>
<tr>
<td>(1\sigma_u)</td>
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</tr>
<tr>
<td>(1\pi_g)</td>
<td>(-0.4287711895856436313960911)</td>
</tr>
<tr>
<td>(2\sigma_g)</td>
<td>(-0.3608648753395033589695712)</td>
</tr>
<tr>
<td>(2\sigma_u)</td>
<td>(-0.25541316508484561472502361)</td>
</tr>
<tr>
<td>(3\sigma_g)</td>
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</tr>
<tr>
<td>(1\pi_u)</td>
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</tr>
<tr>
<td>(1\delta_u)</td>
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<tr>
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</tr>
<tr>
<td>(3\delta_u)</td>
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</tr>
<tr>
<td>(3\pi_g)</td>
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</tr>
<tr>
<td>(5\pi_g)</td>
<td>(-0.1307918776521809748361441234)</td>
</tr>
</tbody>
</table>

Interaction of the electron with the laser field in the dipole approximation is described by the potential

$$V(\xi, \eta, \varphi, t) = a F(t)(\xi \eta \cos \beta + \sqrt{(\xi^2 - 1)(1 - \eta^2) \cos \varphi \sin \beta}).$$

where \(\beta\) is the angle between the polarization vector of the laser field and the molecular axis, and \(F(t)\) is the electric field strength of the laser field. In our calculations, we use the laser pulse with the sine-squared envelope:

$$F(t) = F_0 \sin^2 \frac{\pi t}{T} \sin \omega_0 t$$

with the carrier frequency \(\omega_0 = 0.05696\) a.u. (wavelength 800 nm) and pulse duration \(T = 20\) optical cycles; \(F_0\) is determined by the peak intensity of the pulse.

In Fig. 1 we show the multiphoton ionization probability of the first excited \(1\sigma_u\) electronic state of \(H_2^+\) at the internuclear separation 2 a.u., for the peak intensity of the laser pulse \(2 \times 10^{14}\) W/cm². For the \(1\sigma_u\) state, this is a very strong field, and the ionization probability almost reaches 90% at the parallel orientation. The orientation dependence pattern is highly anisotropic, with the ionization probability less than 6% at the perpendicular orientation. This is well explained by the interference of the contributions to the ionization signal which come from the vicinity of each nucleus. For the antisymmetric \(1\sigma_g\) state, this interference is always destructive at the orientation angle \(\beta = 90^\circ\).
5. High-order harmonic generation of $N_2$

In multielectron diatomic molecules, we study multiphoton processes in the framework of the time-dependent density functional theory. The details of the method have been published elsewhere [9,11]. Here we present the results of the calculations of the orientation-dependent high-order harmonic generation (HHG) of $N_2$ molecule. The laser pulse parameters are the same as used in the $H_2^+$ study, except the peak intensity is $1 \times 10^{14}$ W/cm$^2$. Fig. 2 shows the HHG spectrum (energy emitted in the harmonic radiation during the interaction with the laser field) for the three orientation angles: $0^\circ$, $40^\circ$, and $90^\circ$. In the central part of the spectrum, the strongest HHG signal is observed at the parallel orientation; the signal becomes less intense at $\beta = 40^\circ$ and reaches its minimum at the perpendicular orientation. This is consistent with the orientation dependence of the ionization signal [11] and can be explained by the symmetry of the highest-occupied molecular orbital (HOMO). For $N_2$, the HOMO is $3\sigma_g$ with the electron density concentrated along the molecular axis, which favors harmonic generation at the parallel orientation. We should note, however, that our calculations take into account the contributions not only from HOMO but also from inner electron shells.

6. Conclusion

We have presented the time-dependent GPS method in prolate spheroidal coordinates for accurate and efficient treatment of multiphoton processes in diatomic molecules. This method naturally accounts for the symmetry of diatomic molecules and provides adequate description of Coulomb singularities due to non-uniform distribution of the grid points. The GPS method delivers high accuracy while using moderate computer resources; it is easy to implement since no calculation of potential matrix elements is required, and kinetic energy matrices have simple analytical expressions. Making use of the split-operator technique in the energy representation and spectral expansion of the propagator matrices with the control of high-energy contributions, the time-dependent GPS approach improves numerical stability of the computations. We have illustrated the method by calculations of the one-electron diatomic molecule $H_2^+$ and multielectron diatomic molecule $N_2$ in intense laser fields.

Acknowledgements

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